

ELECTRICAL CONDUCTIVITY AND
PERMITTIVITY OF CERAMICS AND OTHER
COMPOSITES

By
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A thesis submitted to the Faculty of Science, University of the
Witwatersrand, Johannesburg, in fulfilment of the requirements for the
degree of Doctor of Philosophy.

Stellenbosch, 2005.

Declaration

I declare that this thesis is my own unaided work. It is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

(Signature of candidate)

_____ day of _____ 2005

Abstract

Determining the properties of composites and how these relate to those of the components and the microstructure is extremely useful as it enables the understanding of existing materials and the design of new materials with a variety of applications. However, the link between the ac conductivity data and the microstructure and composition of the composite is not a simple one. Simulations of binary composites are presented which show that from relatively simple component properties arise complex composite properties. Accurate identification of the components of composites, using characteristic frequencies, is demonstrated for simulated and actual experimental data.

The Maxwell-Wagner and Brick Layer Models, which are often applied beyond the range of their original derivation, are found to consistently fit the data of yttria-stabilized zirconia ceramics measured at various temperatures. The results from fitting single crystal and polycrystalline sample data indicate that accurate modeling of the properties of the polycrystalline samples requires more theoretical work on the conduction mechanisms in single crystals and the grains of the ceramics.

Data from a polyester-resin/silicon system is found to be best fitted using the Single Exponent Phenomenological Percolation Equation (SEPPE) with experimentally measured component properties as input. The percolation threshold obtained suggests a system where the insulator tends to coat the conductor. The results show that, with the actual component properties as input, the SEPPE can be used to qualitatively and semi-quantitatively model and fit composite ac conductivity data.

Analysis of the ac conductivity of liquid-phase-sintered silicon carbide ceramics showed that for this system, the features often observed in the impedance spectra are all due to a multi-component grain boundary/binder phase and not the SiC grains. This multi-component grain boundary phase can be fitted accurately to the Brick Layer Model, indicating a microstructure where an insulating component coats a more conducting component.

*Kuna amai na baba, Mike, Musafare, Tambudzai,
Loveness na Dorothy uye mudiwa wangu Gloria,
ndichitenda kuzvipira nekushingirira kwenyu.*

*To mom, dad, Mike, Musafare, Tambudzai,
Loveness, Dorothy and the love of my life, Gloria,
thanking you all for all the sacrifices you make.*

Acknowledgements

- I would like to thank Professor David S. McLachlan, my supervisor, for his patient guidance and constant support both on and off the job.
- Many thanks too to Mrs Eugenie McLachlan for her support and kind hospitality and for the many hours of private time she gave up, in order for this work to be completed.
- Many thanks to Dr. Louis Olumekor who facilitated the start of this part of the journey.
- Special thanks to Dr Timothy Armstrong formerly at the Pacific Northwest Laboratory and now at Oak Ridge National Laboratory, U.S.A who prepared and carried out initial analysis on the Yttria Stabilized Zirconia samples.
- Special thanks also to Mrs Antoinette Can who prepared and performed various analysis on the Liquid Phase Sintered Silicon Carbide samples.
- Special thanks too to Dr Mathias Herrmann of the Fraunhofer Institute for Ceramic Technologies and Sintered Materials, Dresden, Germany who provided samples of 6H Silicon Carbide Single Crystals as well as Solid State Sintered Silicon Carbide.
- Special thanks to the Advanced Materials and Processing Branch, NASA Langley Research Center (NASA-LaRC), Hampton VA., U.S.A. where some of the measurements were carried out, and to the National Institute of Aerospace (NIA), Hampton, VA., U.S.A. who facilitated my trip to NASA-LaRC.
- Throughout this research, various pieces of equipment had to be designed and made. My many thanks to the gentlemen of the University of the Witwatersrand's School of Physics' mechanical workshop, Misters John Augustine, Andrew Carpede, Gerry Germishuizen, Shawn Riekert, Curt January and Mervin Marvis. who on many an occasion took

a personal interest in getting my many job requests processed. Many thanks too to Mr Anthony Voorvelt of the School of Physics' electrical workshop.

- Many thanks go to my colleges and friends in the “Low Temperature” lab over the years.
- To my very dear friends Musafare Chitima, Michael Gora, Nicholas Makau, Cosmas Chiteme, Vela Mbele and George Amolo, a very big thank you to you, together we somehow helped each other see this thing through.
- My thanks go too to my parents and family without whom none of this could have happened. To my mother in law, Mrs Stevens, thank you for all your prayers. Along the way many took a special interest in seeing that it all got this far, I would like to say thank you to the Brien, Nielson, Sauti and Situma families, and to all my many friends in Zimbabwe, South Africa and some in far reaches of the globe who all provided me with encouragement and the strength to go on.
- Special thanks to my wife Gloria who, having joined this journey along the way, did so much to see it to the end. Thanks too to “Teddy” and “Eat Mor” for your silent but watchful vigil through the many nights spent in front of the computers.
- This thesis was typeset using MiKTeX L^AT_EX. Special thanks to the developers and contributors to the MiKTeX and other open source software projects.
- I would like to acknowledge financial assistance from the TW Khambule GOOT Fellowship at the University of the Witwatersrand.

Godfrey Sauti

Stellenbosch

2005

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List of Symbols and abbreviations

The following abbreviations are used to describe various models

BLM The Brick Layer Model

CC The Cole-Cole dielectric function

CTRW The Continuous Time Random Walk (model)

HN The Havriliak Negami dielectric function

JCDF The Justified Data-Curve Fitting approach

K-K Kramers-Kronig (relations)

LLS A dielectric function due to Leon, Lucia and Santamaria

MW The Maxwell-Wagner (model)

SEPPE Single Exponent Phenomenological Percolation Equation

TEPPE Two Exponent Phenomenological Percolation Equation

UDR Universal Dielectric Response (model)

UDR-BLM The BLM with the conductivity of the more conducting component substituted for by the relevant UDR expression

UDR-MW The Maxwell-Wagner equation with the conductivity of the more conducting component substituted for by the relevant UDR expression

UDR-SEPPE The SEPPE with the conductivity of the more conducting component substituted for by the relevant UDR expression

UDR-UDR-BLM The Brick Layer Model with the conductivity of the both components substituted for by the relevant UDR expressions

UDR-UDR-MW The Maxwell-Wagner equation with the conductivity of the both components substituted for by the relevant UDR expressions

Symbols used in representing the data

M^* The complex modulus

M' The real dielectric modulus

M'' The imaginary dielectric modulus

Z^* The complex impedance

Z' The (specific) real impedance (in this work calculated to be independent of the sample geometric factor)

Z'' The (specific) imaginary impedance

ϵ_p The characteristic dielectric constant ($=\sigma_{dc}/(\omega_p\epsilon_0)$).

$\epsilon_p^\dagger$ The characteristic dielectric constant of a grain boundary phase, normalized to the sample geometric factor

ϵ' The real (frequency dependent) dielectric constant

ϵ'' The (frequency dependent) dielectric loss

ϵ_∞ The high frequency value of the dielectric constant

ϵ^* The complex dielectric constant

ϵ_0 The vacuum permittivity

i $\sqrt{-1}$

θ_d The angle by which the center of a complex impedance (or modulus) plane arc is depressed below the axis.

σ_0 A pre-factor in the expression for the temperature dependence of the dc conductivity.

σ' The real (frequency dependent) conductivity.

σ_{dc} The dc conductivity (or contribution to the dc conductivity) extracted from complex impedance plane plots.

$\sigma_{dc}^\dagger$ The “dc” conductivity of a grain boundary phase, normalized to the sample geometric factor

σ^* The complex conductivity

ν (or f) Frequency

ω Angular frequency ($= 2\pi\nu$)

ν_0 A pre-factor in the expressions for the temperature dependence of the characteristic frequency

ν_p The characteristic frequency

ω_p The characteristic (angular) frequency ($2\pi\nu_p$).

The following abbreviations and symbols are used in the description of binary composites and their components.

ϵ_ℓ The dielectric constant of the less conducting component.

ϵ_h The dielectric constant of the more conducting component

ϕ Volume fraction of a high conductivity component

ϕ_c Critical volume fraction for percolation

σ_ℓ Conductivity of the less conducting component.

σ_h Conductivity of the more conducting component.

Miscellaneous symbols and abbreviations

3YSZ 3 mole % yttria-stabilized zirconia

5.7YSZ 5.7 mole % yttria-stabilized zirconia

8YSZ 8 mole % yttria-stabilized zirconia

9.5YSZ 9.5 mole % yttria-stabilized zirconia

12YSZ 12 mole % yttria-stabilized zirconia

AIC Akaike Information Criterion

CSZ Cubic Stabilized Zirconia

GPS Gas Pressure Sintered (liquid-phase-sintered silicon carbide)

HP Hot Pressed (liquid-phase-sintered silicon carbide)

HTHP Hot Treated Hot Pressed (liquid-phase-sintered silicon carbide)

IS Impedance Spectroscopy/Impedance Spectra

LPSSiC Liquid-phase-sintered silicon carbide

MSC Model Selection Criterion

PS0-PS36 Polyester-resin/silicon composites containing 0 to 36 volume %
silicon

TSZ Tetragonal Stabilized Zirconia

YSZ Yttria Stabilized Zirconia

Introduction

Composite materials of one form or the other are commonplace in nature (wood, bone, enamel...) and are also widely used in various technological applications (construction, medicine, aerospace...). Composites are therefore an important part of everyday life. *In a general sense composite materials are materials consisting of several phases which are strategically combined to achieve overall materials properties being at least, with respect to a certain application, superior to those of the individual constituents* [Fleig and Maier¹]. The term composite will be used here to define any system that has one or more components with some inhomogeneity in some property of interest on the micro (granular) scale and homogeneity on the macro (sample) scale.

Due the aforementioned prevalence of composites, determining their properties and how these relate to those of the components and the microstructure is extremely useful. This enables us not only in understand various natural materials but also to design materials with a variety of applications. The mechanical, thermal, electrical, optical and other properties of composites depend on the properties of their components and how these components are structured within the composite i.e. the microstructure of the composite. As emphasized in Nan², *Regardless of whether one is interested in measuring, developing or using a specific physical property of a heterogenous material there is a definite need for some understanding of microstructural effects*. Although some properties of composites may be obtained by simply averaging the properties of the pure components, the relation of other properties of the composites, such as the thermal or electrical conductivity, to those of the pure components presents a more complex problem, *one that has challenged the imagination of scientists and engineers for nearly a century* [Meredith and Tobias³].

The electrical properties of materials are of interest where it is intended to use these materials for electronic applications and in some cases, the desired properties are best obtained from composites. Further, electrical measurements can also be used as a tool for probing the properties of composites, including some whose intended applications are not necessarily electronic.

Direct current (dc) conductivity measurements probe the bulk properties of the materials. Dc conductivity measurements for “pure” materials, enable them to be classified into broad groups of insulators, semiconductors and conductors and enable some identification of materials. The temperature dependence of the conductivities of non-metallic materials enable the calculation of energy gaps/activation energies for the conduction processes in these materials.

On their own, dc conductivity measurements have a very limited ability to probe the properties of the components and microstructure of composites.

Alternating current (ac) conductivity measurements, often termed “impedance spectroscopy” or IS measurements add another dimension (frequency/time dependence) to the analysis and enable a more detailed probing of the composition and microstructure of composites.

The most common ac conductivity measurement technique, and the one utilized in the current work, is based on applying a single frequency voltage to the material and measuring the phase-shift and the amplitude or the real and imaginary parts of the resulting current at that frequency. Single commercial instruments, such as the one used in the current thesis, measure the impedance as a function of frequency in the range 10^{-4} to 10^7 Hz. Instruments are also available on the market that use different technologies to measure ac conductivity of materials up to microwave frequencies. Other ac conductivity measurement techniques include methods based on the simultaneous use of multiple frequencies, Fourier transforms from the time domain and the analysis of noise spectra [Raistrick⁴, Macdonald and Johnson⁵].

Focus in the current work is on the ac conductivity of **binary composites**. Ceramics, which consist of grains and inter-grain phases (grain boundaries and in some cases binder phases), will in this work also be classified as binary composites. It needs to be noted that in many cases the components of these binary composites may themselves be complex materials which can be

further subdivided into various constituents. For the purposes of simplifying the analysis, it will in most cases be assumed that each component can be characterized by a single average conductivity, even if this is the average of the component substructure.

The link between the data obtained from the ac conductivity measurement and the composition and microstructure of the composite is not a simple one. Various models have been suggested and are in use for the interpretation of the data, with varying degrees of success. Among the key methods for the analysis of ac conductivity data are equivalent circuits on the one hand and Effective Media Theories (EMT), the Brick Layer Model (BLM) and percolation theories on the other.

Details on the use of equivalent circuits to model and fit composite sample data, as well as examples of such fitting, can be found in Boukamp⁶, West et al.⁷, Macdonald⁸ and Rodgers⁹. While equivalent circuits are able to mimic any measured response, provided there is a large enough and varied number of components available in the circuit, they lack uniqueness i.e. several different circuits can be constructed which give the same response at *all* frequencies. This therefore makes it difficult to uniquely relate the components of any given circuit to the composition and microstructure of the material whose frequency response it emulates.

Effective Media Theories, the Brick Layer Model and percolation theories are based on particular microstructures. The models are derived from taking into account the structure of the composites and therefore should from the onset have uniqueness. They, especially the Maxwell-Wagner and the Brick Layer models, are however often applied beyond the range of their original derivation. It is often unclear whether or not the models are suitable to be used in the extended range and whether they can be used to consistently fit real experiment data, and in the design of composites. How well and consistently the Maxwell-Wagner EMT, the Brick Layer Model and percolation theories are able to fit experimental data will be investigated in this work. Effective media and percolation based theories for the properties of heterogenous materials are reviewed in detail in Meredith and Tobias³, Landauer¹⁰, Nan², McLachlan¹¹, McLachlan et al.¹² and Tuncer et al.¹³. Classical percolation theory is discussed in detail in Stauffer and Aharony¹⁴, while

its application to the electrical properties of composites are further discussed in the reviews by Kirkpatrick¹⁵, Clerc et al.¹⁶, Bergman and Stroud¹⁷ and Bunde and Dieterich¹⁸. The application of the Brick Layer Model to model and fit the ac conductivity of composite systems, its limitations and examples of fitting actual experimental data are given in Verkerk et al.¹⁹, Fleig and Maier²⁰ and Hwang et al.²¹.

One of the difficulties in assessing the efficacy of effective media (and other) theories in describing and fitting the properties of composite systems is the difficulty in constructing model systems, with known component properties and controlled microstructures. Often, the processing required to produce the composite leads to final component properties and microstructure which are not those originally planned for. There are also problems in ascertaining whether or not the various models correctly fit the experimental data, well enough for them to be confidently used for predicting the properties of new samples.

To try and understand the properties of the binary composites, as well as to establish whether or not the Maxwell-Wagner EMT, the Brick Layer Model and percolation theories are able to consistently fit the experimental results, a number of conditions had to be imposed when fitting the data. These will be described in detail in the chapters that follow. The emphasis in this work is on obtaining *consistent* fitting to a series of data. Individual best fit parameter values are difficult to verify as being either correct or incorrect. In part this is due to the very large range of physically meaningful values that some of these parameters, such as the conductivities, can take, which may stretch over several orders of magnitude.

The various ways of representing ac conductivity data, including impedance (IS) and modulus spectroscopy and how these are related are given in Chapter 1. A number of expressions for fitting the frequency as well as the temperature dependence of the conductivity are also given in this chapter, as are the Kramers-Kronig transforms used in data validation and for separating out relaxation and ohmic conduction losses.

The methods for preparation and/or sources of the samples studied in the current work are described in Chapter 2. Also in Chapter 2, the equipment for carrying out ac conductivity measurements at different temperatures is

briefly described. Various procedures for automated data manipulation are outlined, as is their implementation using *Mathematica*. These procedures include data validation using the Kramers-Kronig transforms, a procedure for separation and extracting information from impedance arcs, as well as procedures for simulating the properties of binary composites. Data fitting using various minimization algorithms, including the Levenberg-Marquardt algorithm, Differential Evolution, Simulated Annealing and the Nelder-Mead simplex, is also described, as is the use of the goodness of fit parameters, the Akaike Information Criterion (AIC) and the Model Selection Criterion (MSC), for choosing the best fitting models.

In order to be able to correctly model the properties of composite systems, the properties of the components have to be well characterized. Therefore, in Chapter 3, results of investigations carried out on the properties of yttria-stabilized zirconia (YSZ) single crystals, a component of the polycrystalline YSZ ceramics are presented and discussed. The aim of this work was to determine which was the best model to describe the electrical properties of several single crystals. The data from the single crystals could then be used to model the grains of the polycrystalline YSZ ceramics. The electrical properties of 3, 5.7, 9.5 and 12 mole percent YSZ single crystals were measured and analyzed.

In analyzing and modeling impedance spectra it is very useful, and sometimes essential, to be able to obtain some information about the electrical properties of the components, directly from the composite material's experimental data. The simulations discussed in Chapter 4 were used to investigate how identifiable the component properties are for a wide range of compositions and for the different effective media and percolation models.

The electrical properties of (polycrystalline) yttria-stabilized zirconia ceramics, the subject of Chapter 5, have been very widely studied [see Bauerle²², Verkerk et al.¹⁹, Badwal²³, Rühle et al.²⁴, Badwal and Drennan²⁵, Bonanos et al.²⁶, Abélard and Baumard²⁷, Pimenov et al.²⁸ and others]. This is largely due to the interest in the use of these ceramics in Solid Oxide Fuel Cells (SOFCs), oxygen sensors and in other technological applications. These materials may, to some degree, be considered a model system for study using impedance spectroscopy techniques, because of the clearly distinguishable grain and grain boundary contributions to the impedance spectra. Despite

these materials having been so widely studied, there remain great challenges in relating the microstructure to the electrical properties and this is still an active area of research in materials science. The current thesis further investigates the link between the microstructures and the electrical properties of a number of samples and aims at obtaining a *consistent* description of the experimental data.

The polyester-resin system, whose electrical properties are discussed in Chapter 6, was the only one in the current study whose composition could be directly controlled by the experimenter. This system is somewhat similar to the yttria-stabilized zirconia in that the more insulating component coats or tends to coat the more conducting component. In the YSZ, the insulating coating (the grain boundaries) persists up to very high volume fractions ($\phi \gtrsim 0.9$) of the more conducting (grain) component and the system appears to be genuinely an effective media system with a “percolation threshold” of essentially 1. On the other hand, grain to grain contacts in the polyester-resin/silicon composite can and do lead to a percolation threshold below 1. The percolation threshold was expected and seen to be higher than in most granular systems because the polyester-resin tends to coat the grains.

The polyester-resin/silicon system also has some similarities with the Liquid-Phase-Sintered Silicon Carbide (LPSSiC, discussed in Chapter 7) in that the ratio of the conductivities and the dielectric constants of the components are such that not all of them are clearly resolved in impedance spectra. The importance of using several different data representation formats and as many of the known electrical properties of the components as possible, to correctly identify the features in the impedance (and modulus) spectra for the composites, will be highlighted in both Chapters 6 and 7.

Silicon carbide ceramics are widely used as an abrasive, as a refractory, in heating elements and in voltage sensitive resistors (varistors). There are various forms of sintered polycrystalline silicon carbide, among which is liquid-phase-sintered silicon carbide, the subject of Chapter 7, produced by sintering silicon carbide powder and additives that form a binder phase. (Other processes for producing polycrystalline SiC include reaction bonding and solid state sintering).

To further understand the ac conductivity and IS of LPSSiC and their relation to the sintering conditions, additives and the microstructure, the properties of various samples were investigated. Using the analysis techniques developed from the study of the other composite and ceramic systems in the current thesis (YSZ and polyester-resin/silicon), the contributions to the usually observed arcs in the complex impedance plane (Cole-Cole or Nyquist) plots are identified as being *all* due to a complex multi-component grain boundary phase and *not* the silicon carbide, as previously reported [Schroeder et al.²⁹, Volz et al.³⁰ and others].

In Appendix A some results obtained using the arc separation procedure developed in this thesis, on actual experimental data, are presented and discussed.

Chapter 1

Theory

1.1 Introduction

In this chapter the various ways of representing and interpreting ac conductivity and Impedance Spectroscopy (IS) data are discussed. The microstructures represented by the Maxwell-Wagner, Brick Layer and Percolation theories are also described and the relevant expressions are given. A number of expressions for fitting the dispersive properties of the components of the composites are also described.

Also in the current chapter, expressions for fitting the temperature dependence of the conductivity of materials are briefly described. The Kramers-Kronig transforms, used in data validation and for separating out relaxation and ohmic conduction losses, are also presented.

1.2 Definition of terms and data presentation formats

The notation used in this work defines the complex conductivity as $\sigma^* = \sigma' - i\sigma''$, where $i = \sqrt{-1}$. This conductivity is related to the complex dielectric constant by $\sigma^* = i\omega\epsilon_0\epsilon^*$, where ω is the angular frequency and ϵ_0 is the vacuum permittivity. The complex dielectric constant is $\epsilon^* = \epsilon' - i\epsilon''$, where ϵ' and ϵ'' are the real dielectric constant and the dielectric loss respectively.

Table 1.1: Various representations of ac conductivity and IS data.

	Modulus (M^*)	Impedance (Z^*)	Admittance (Y^*)	Dielectric Constant (ϵ^*)
M^*	M^*	$(i\omega\epsilon_0 G)Z^*$	$(i\omega\epsilon_0 G)Y^{*-1}$	ϵ^{*-1}
Z^*	$(i\omega\epsilon_0 G)^{-1}M^*$	Z^*	Z^{*-1}	$(i\omega\epsilon_0 G)^{-1}\epsilon^{*-1}$
Y^*	$(i\omega\epsilon_0 G)M^{*-1}$	Z^{*-1}	Y^*	$(i\omega\epsilon_0 G)\epsilon^*$
ϵ^*	M^{*-1}	$(i\omega\epsilon_0 G)^{-1}Z^{*-1}$	$(i\omega\epsilon_0 G)Y^{*-1}$	ϵ^*

Various other representations of ac conductivity data are used in the literature and these are related as shown in Table 1.1. The term *immittance* will be used as bracketing any of the representations in Table 1.1. The sample geometric factor is $G = A/L$, where A is the sample area and L is the sample thickness. In this work, the representations most utilized will be the real dielectric constant (ϵ'), the real conductivity(σ'), the real and imaginary impedances (Z' and Z'') and the real and imaginary dielectric moduli (M' and M''). Where it is deemed necessary, the dielectric loss (ϵ'') will also be used, to highlight some particular features in the data. For the remainder of this work, Z' , Z'' and the term *impedance* will be used to describe the *specific impedance* i.e. the impedance independent of the sample geometric factor, which enables easy comparison of data from samples of different shapes and sizes.

To illustrate some of the above, the real dielectric constant and real conductivity as well as the real and imaginary impedances of a material consisting of a single component, in this case a single crystal of 9.5 mole % yttria-stabilized zirconia, are shown in Figure 1.1. This data encompasses the contribution of the crystal (at high frequency) as well as the contribution due to electrode effects at the lower frequencies, in this case $\log(\omega) < 3$. (Note that the electrodes are not considered as being a component of the material). Only one peak, due to the crystal, is observed in the imaginary impedance data. The position (frequency) of this peak will be shown to be a characteristic of the particular material and temperature at which the measurement is carried out.

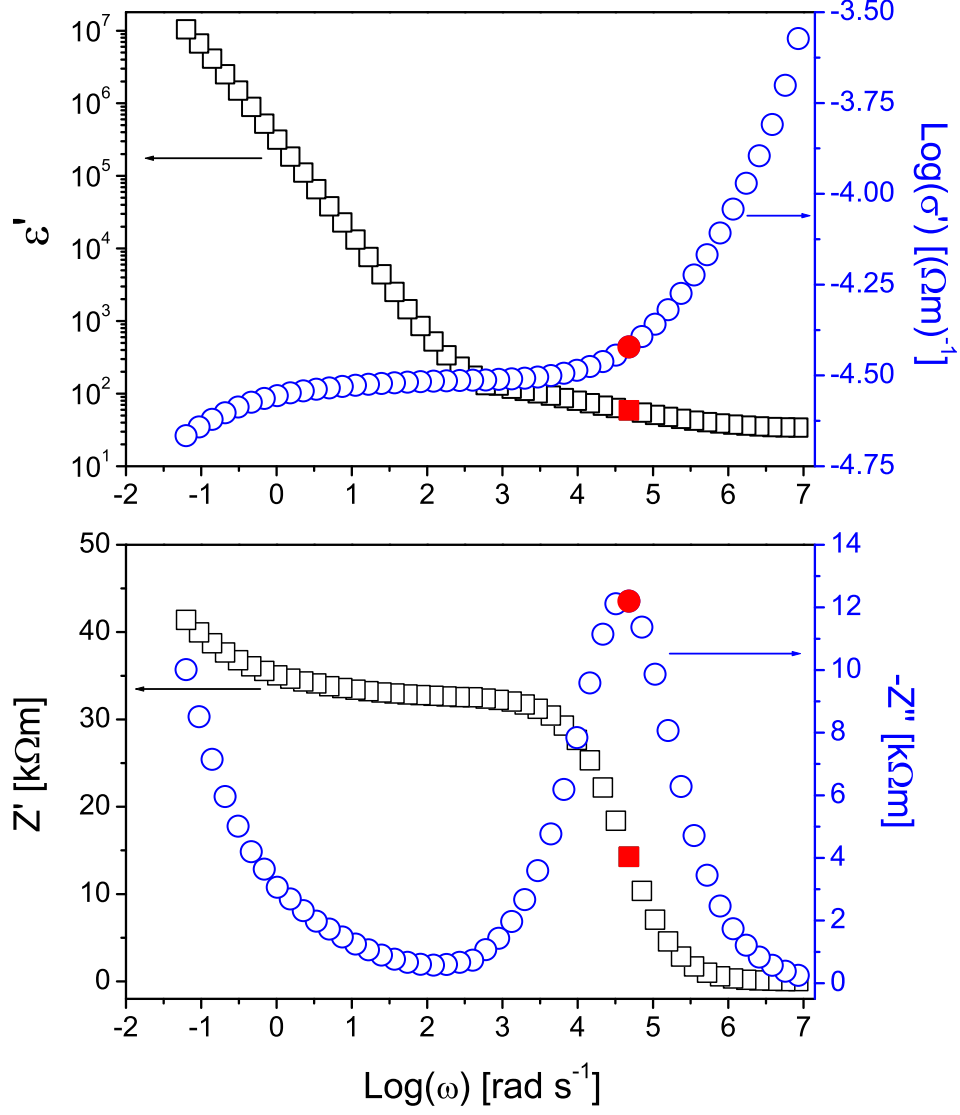


Figure 1.1: The frequency dependence of the real dielectric constant and the real conductivity (top) as well as the real and imaginary impedances (bottom) of a single component material, in this case a single crystal. Two processes contribute to the data, the crystal and electrode effects. The frequency point closest to the characteristic frequency of the material i.e the peak of the imaginary impedance curve, is marked. (This particular data is for a 9.5 mole % yttria-stabilized zirconia single crystal at 250 °C).

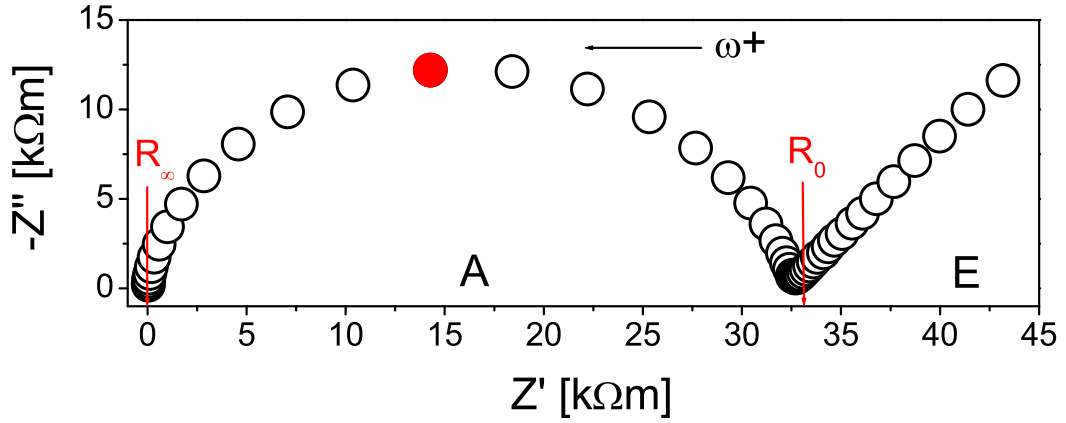


Figure 1.2: The complex impedance plane representation of the data for a single component material. Two arcs can be identified, the complete arc due to the crystal (*A*) and the incomplete arc (*E*), due to the electrode effects. Note that these arcs are depressed relative to true semicircles i.e. their centers lie below $-Z'' = 0$ (see Figure 1.3). (This particular data is for a 9.5 mole % yttria-stabilized zirconia single crystal at 250 °C).

A widely used representation of the real and imaginary data is the complex plane representation (also referred to, in the literature, as the Cole-Cole or Nyquist plot), Figure 1.2. In this figure, a plot of the real and imaginary impedances is shown but plots of the real and imaginary permittivities, conductivities or moduli are also widely used in certain fields. The two contributions to the sample properties, namely the crystal and the electrode effects, are better separated out in the complex impedance plane plot in Figure 1.2 than in the plots in Figure 1.1. These contributions give rise to the complete depressed arc *A* and the incomplete depressed arc *E* respectively. These arcs are depressed relative to perfect semicircles and have centers below $-Z'' = 0$. The sample dc resistance can be estimated from the intercepts of the arc *A* on the real axis. The resistance is $\approx R_0 - R_\infty$, where R_∞ should be, but is not always exactly, zero. The arc due to electrode effects does not contribute to the measured dc resistance.

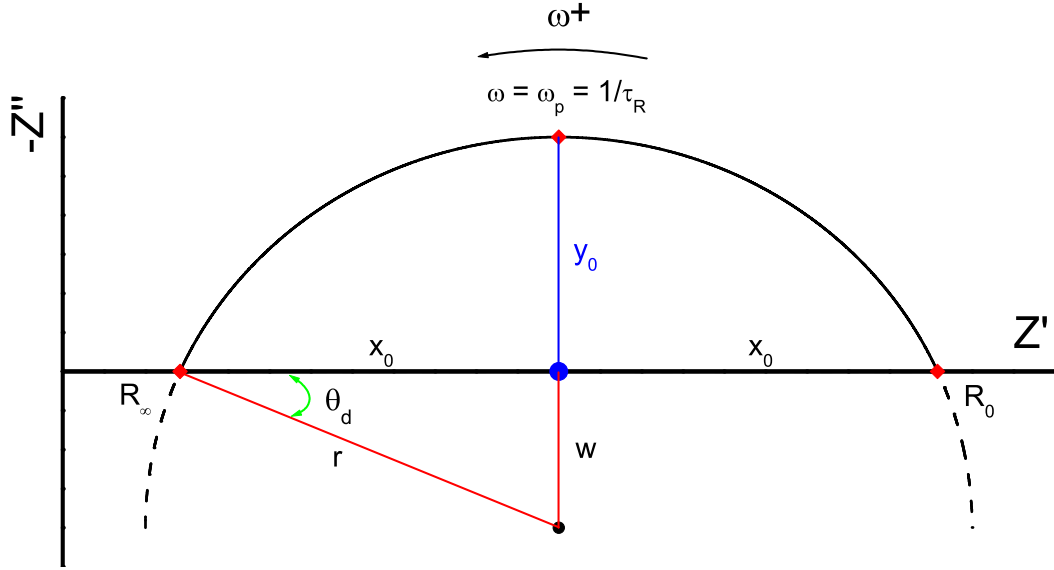


Figure 1.3: A complex impedance plane plot showing a depressed arc and the definitions of various quantities used in its analysis. (Figure adopted from Macdonald and Johnson⁵).

Figure 1.3 summarizes the various quantities used in the analysis of a single depressed arc. Key quantities to note are the intercepts R_∞ and R_0 from which the resistance $R = R_0 - R_\infty$ is obtained. The arc does not pass through the origin, either because there are other arcs appearing at higher frequencies and/or because $R_\infty > 0$ [Macdonald and Johnson⁵]. The frequency at which the arc reaches its peak is the characteristic frequency ω_p . This frequency is related with the relaxation time τ_R by $\omega_p = 1/\tau_R$.

The center of an experimental arc is frequently displaced below the real axis, because of the dispersive properties of the material. The relaxation time is then not single valued but is distributed continuously or discretely about around a mean, [Macdonald and Johnson⁵]. The angle $\theta_d (= \arctan[\frac{w}{x_0}])$, by which the semicircular arc is depressed below the real axis, is related to the width of the relaxation time distribution and as such is an important parameter. Note too that the (depressed) semicircle of a material with a single relaxation time (or narrow distribution of relaxation times) is symmetrical (or approximately symmetrical) about the line labeled y_0 [Macdonald and Johnson⁵].

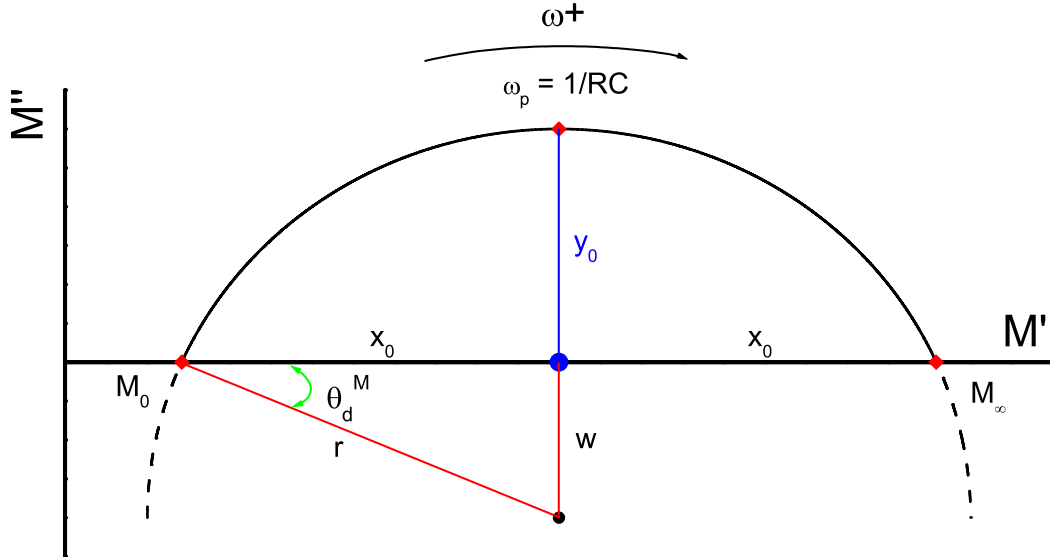


Figure 1.4: A complex modulus plane plot showing a depressed arc and the definitions of various quantities used in its analysis.

Another widely used representation of ac conductivity data [Sinclair and West³¹, Gerhardt³², Sinclair and West³³, Andres-Verges and West³⁴, McLachlan¹¹, Hodge et al.³⁵ and others], and which will also be used in the current work is the complex modulus, $M^* = M' + iM''$. In the current work, the complex modulus will be written in a form independent of the sample geometric factor and which can be obtained from the *specific* impedance (Z^*) using $M^* = i\omega\epsilon_0 Z^*$. Complex modulus plane plots (M' vs M'') give depressed semicircles similar to complex impedance plane plots. Figure 1.4 shows the quantities used to describe a complex modulus plane depressed semicircle. The diameter of the semicircle is inversely proportional to the sample capacitance (C) and therefore $C = \epsilon_0/(M_\infty - M_0)$, where M_∞ and M_0 are the high and low frequency intercepts to the real axis, in the complex modulus plane plot [Sinclair and West³¹, Andres-Verges and West³⁴]. The frequency of the modulus peak is $\omega_p = 1/RC$ where R is the resistance of the sample. As will be shown in the pages that follow, in some cases, modulus plots highlight features in the ac conductivity data that are not easily observable in the impedance representation.

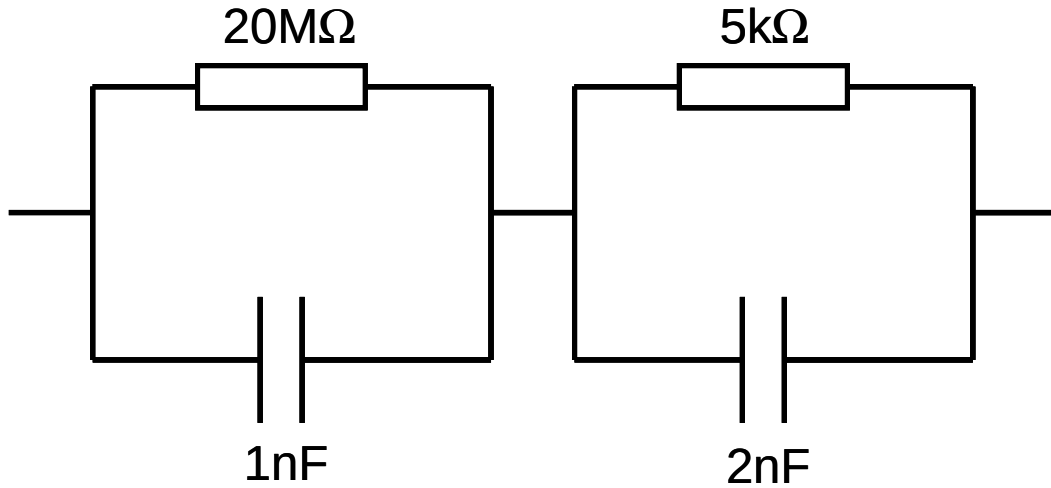


Figure 1.5: A simple circuit for illustrating the features highlighted by impedance and modulus representations of the data.

Figure 1.5 shows a simple circuit whose response is plotted in the complex impedance and modulus planes to show which features are highlighted by the two representations.

The complex impedance plane representation of the frequency response of the circuit is shown in Figure 1.6. While the circuit consists of two parallel resistor/capacitor (RC) elements in series, in this case, only one arc is observable in the complex impedance plane plot. This arc is due to the more resistive RC element. Figure 1.7 shows the complex modulus plane plot of the same data and here two arcs are observed.

The plot of Z'' and M'' vs $\log(\omega)$, in Figure 1.8, gives a clearer picture of the contributions to complex the impedance and modulus plane plots. The Z'' spectrum shows one peak while two are observed in the M'' spectrum. The single peak in the Z'' spectrum corresponds to the lower frequency peak in the M'' spectrum and these are both due to the more resistive RC element which dominates the overall impedance. The resistance associated with the high frequency M'' peak is too small for it to be easily detectable in the Z'' or complex impedance plane plot. The use of the two representations (impedance and modulus), enables the contributions of both the parallel RC elements of the circuit to be resolved and correctly identified. A similar analysis, in terms of M^* and Z^* can and will be used to resolve and correctly

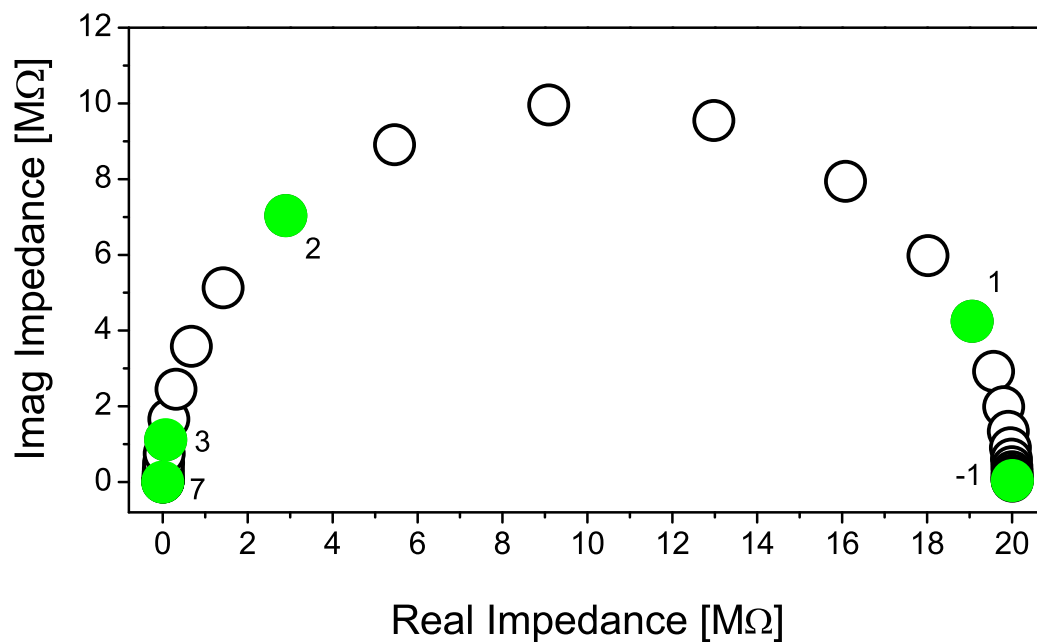


Figure 1.6: The complex impedance plane plot of the response of the circuit in Figure 1.5. Only one semicircle is resolved. Key values of $\log(\omega)$ are indicated.

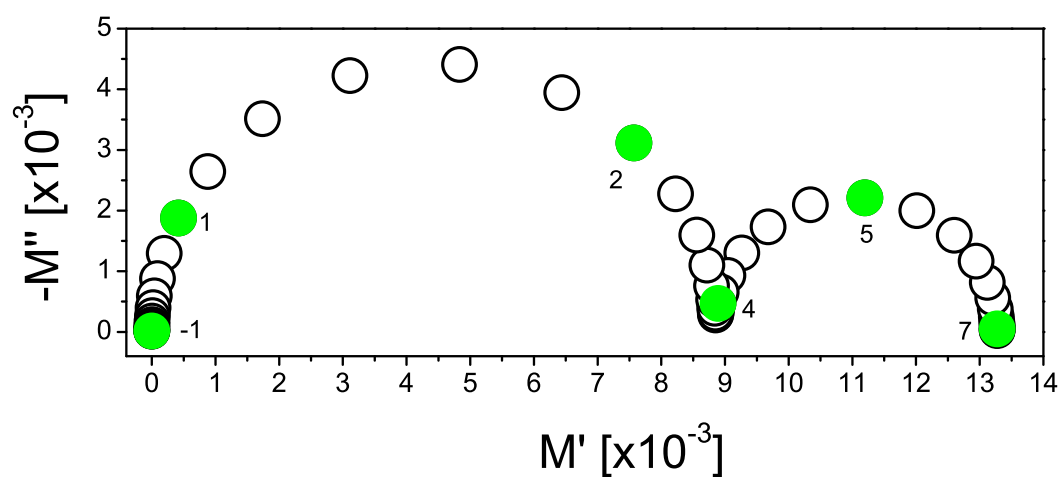


Figure 1.7: The complex modulus plane plot of the response of the circuit in Figure 1.5. Two distinct semicircles are observed. Key values of $\log(\omega)$ are indicated.

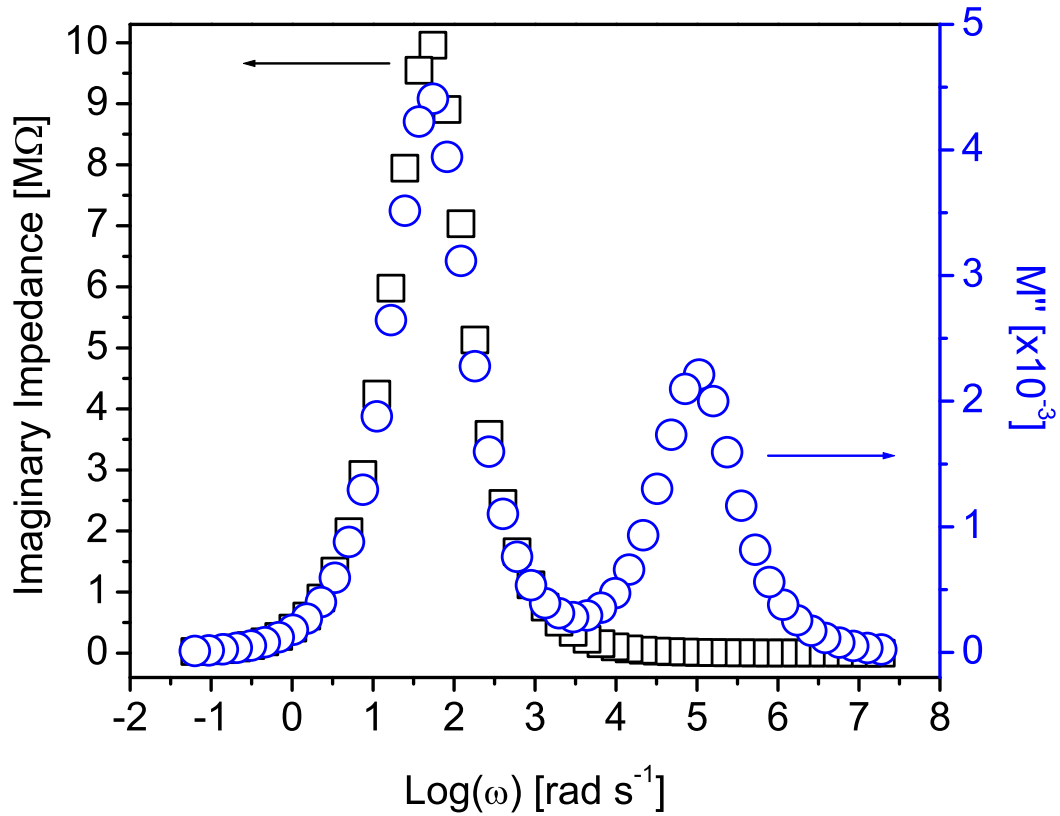


Figure 1.8: The frequency dependence of the imaginary impedance and modulus for the simple circuit in Figure 1.5. Only one peak, associated with the more resistive RC element, is observed in the Z'' , while the peaks due to both the elements can be seen in the M'' plot. The common position of the impedance and low frequency modulus peak shows they are associated with the same RC element. (Calculating the resistances and capacitances from the peak amplitudes further confirms the origin of the features in the plots. For ideal resistors and capacitors $Z''_{max} = (Z_0 - Z_\infty)/2$ and $M''_{max} = (M_\infty - M_0)/2$).

identify contributions, of the components, to composite sample impedance and modulus spectra.

The real conductivity and real dielectric constant as well as the real and imaginary impedances of a **binary composite** are shown in Figure 1.9. There are three contributions to the measured properties, the more conducting component, the less conducting component and electrode effects. Two peaks, attributed to the two components of the composite, are observed in the imaginary impedance plot. The frequency points nearest to the imaginary impedance peaks are marked in all the plots. Again the peak of the feature

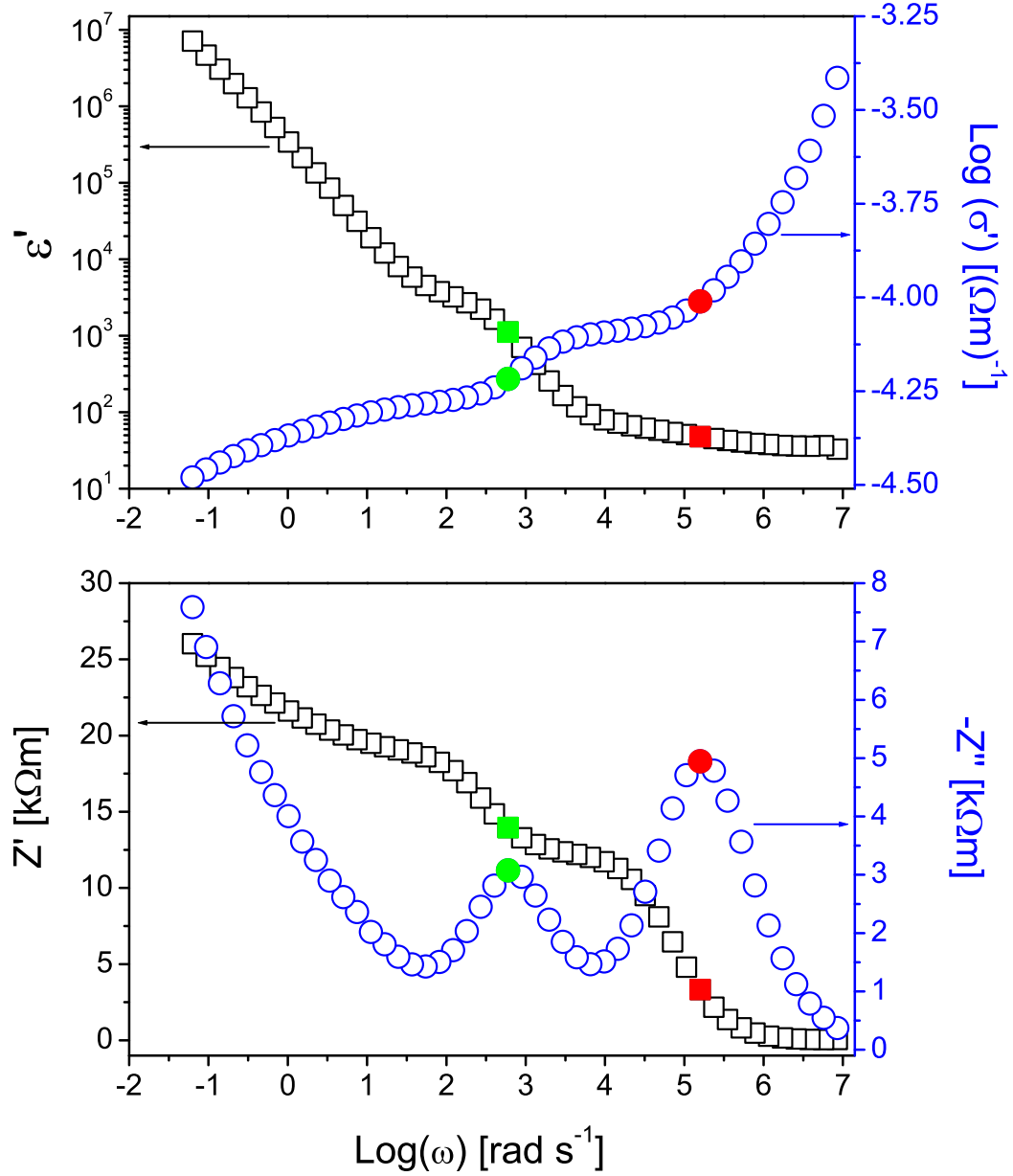


Figure 1.9: The frequency dependence of the real dielectric constant and the real conductivity as well as the real and imaginary impedances of a binary composite. There are three contributions to the measured properties, the more conducting component of the composite, the less conducting component and the electrode effects. The frequency points closest to the characteristic frequencies of the components of the composite, i.e. the positions of the peaks of the imaginary impedance curves, are marked. (This particular data is for a polycrystalline yttria stabilized zirconia sample, 8YSZ-D1, at 250 °C).

due to electrode effects lies at lower frequencies than those used in this work.

The three contributions to the measured impedance are better separated out in the complex impedance plane plot, Figure 1.10. They lead to the depressed arcs *A*, *B* and *E*. In a ceramic these would generally represent the grain, grain boundaries and electrode effects. The intercepts of the arcs on the real impedance axes give estimates of the contributions of the various components to the dc resistance. In the figure, $R_0 - R_\infty$ is the overall sample dc resistance made up of the contributions of the components *A* and *B*.

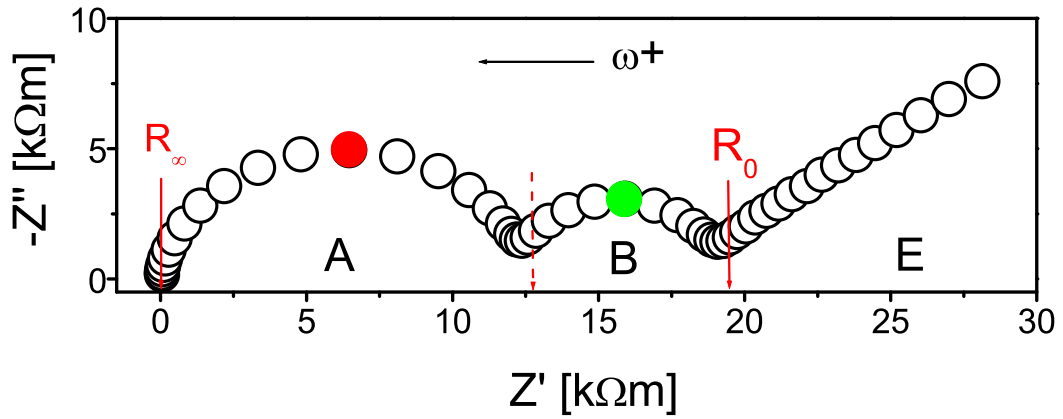


Figure 1.10: The complex impedance plane representation of the data for a binary composite. Three contributions can be distinguished which in ceramic materials would generally be attributed to the grains (*A*), grain boundaries (*B*) and electrode effects (*E*). All the arcs are depressed relative to perfect semicircles. The frequency points closest to the peaks of the complete arcs are indicated, as is the direction of increasing ω . (This particular data is for a polycrystalline yttria-stabilized zirconia sample, 8YSZ-D1, at 250 °C).

Impedance arcs are not always as clearly resolved as those shown in Figure 1.10, there are many cases where the characteristic frequencies of the components (marked in Figures 1.9 and 1.10) are close enough for the arcs to overlap.

1.3 Modeling composite data

The impedance data shown in Figure 1.9 and Figure 1.10 can be modeled using circuits giving a similar response at all frequencies. One of the simplest circuit arrangements leading to three arcs is a series connection of three parallel resistor/capacitor elements, Figure 1.11. The impedances of ideal resistors are $Z^* = R$ and $Z^* = 1/(i\omega C)$ for ideal capacitors.

Figure 1.12 shows the approximate contributions of the equivalent capacitances and resistances of the RC elements of the series circuit (Figure 1.11) to a composite's conductivity curve. At the very highest frequencies, the capacitance of component *A* dominates, then there is an intermediate plateau dominated by the resistance of that component. Below the frequencies of the first plateau, the capacitance of the second component (*B*) is dominant and at even lower frequencies there is a plateau due to the second component's resistance. At the lowest frequencies, the electrode effects (*E*) dominate.

This is the basis of **equivalent circuit** analysis of impedance spectra, with the circuit elements and their arrangements usually being more complex. In particular, the measured data is seen to give rise to depressed arcs as in the complex plane, as shown in Figures 1.2 and 1.10, a response not typical of simple capacitors and resistors. Therefore *constant phase elements* (CPEs) have to be added to the circuit when equivalent circuits are used to

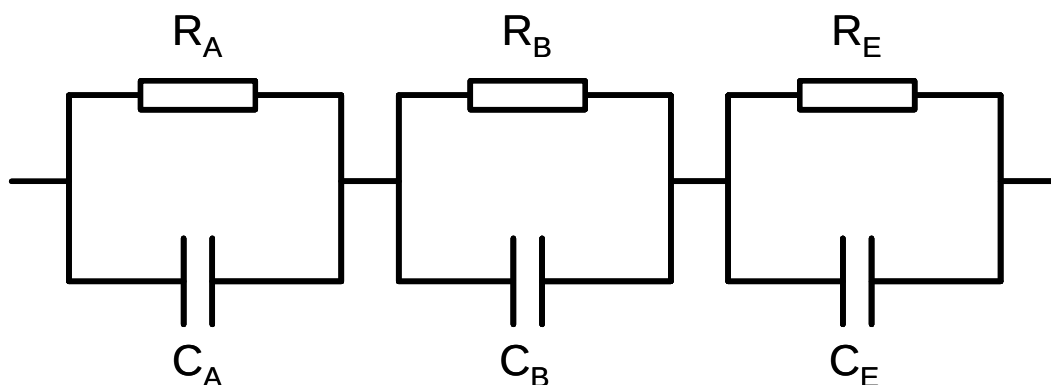


Figure 1.11: A simple circuit that produces a response similar to that in Figure 1.10.

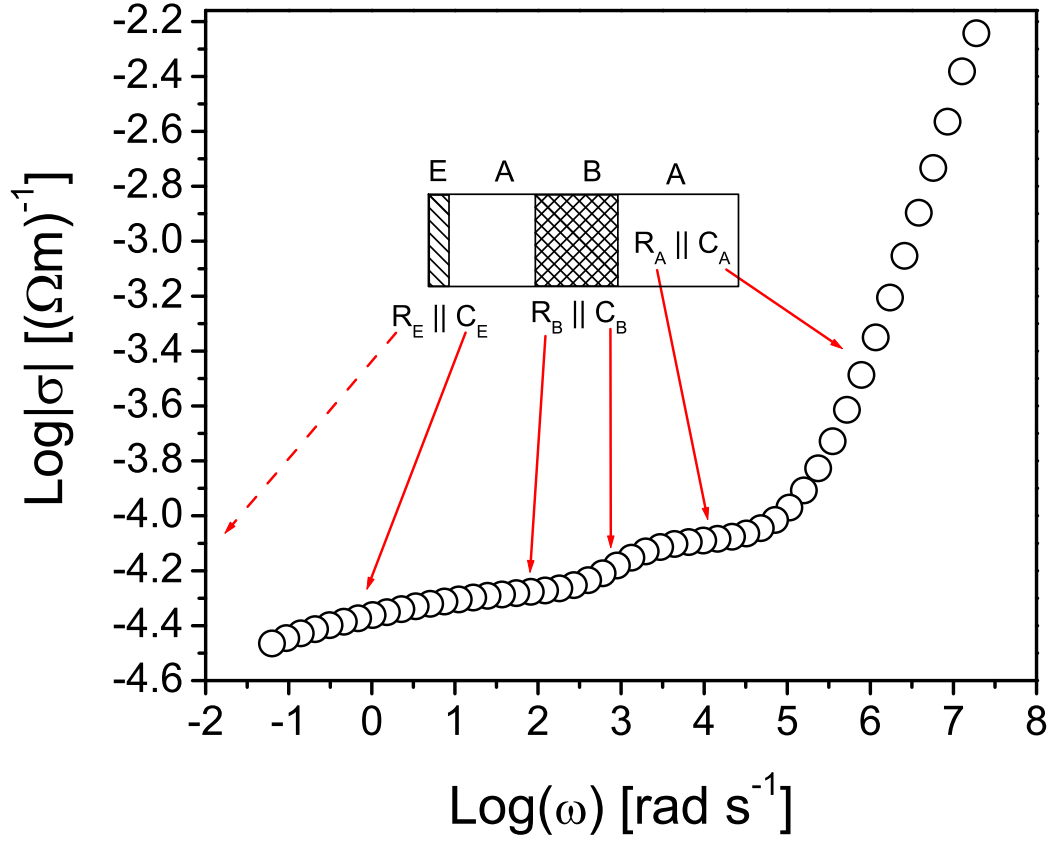


Figure 1.12: The frequency dependence of the contributions of the equivalent resistances (R_x) and capacitances (C_x) of the RC elements (A and B) as well as electrode effects (E) to the composite's absolute conductivity as modeled using the circuit in Figure 1.11. (Identification of components adopted from Waser and Hagenbeck³⁶. The particular data, obtained in the current work, is for a polycrystalline yttria-stabilized zirconia sample, 8YSZ-D1, at 250 °C).

fit and model data. The CPEs are usually, but not always, placed parallel with, or in place of, one or more of the capacitors in the circuit. While the individual resistances and capacitances are usually associated with particular constituents of the composite, the constant phase elements are often associated with some non-homogeneity of the system or a distribution (dispersion) of the value of some physical property of the system. Among other things, the CPEs have been associated with electrode roughness, inhomogeneous reaction rates on a surface, varying thickness or composition for coatings and non-uniform current distributions across sample surfaces [Rodgers³⁷ and the references therein]. However, for the composites measured in this work, it shall be shown that this effect is due to the bulk properties of the components. The impedance of the CPE is given by the phenomenological equation [Rodgers³⁷, Macdonald³⁸]

$$1/Z = Y = Q_0(i\omega)^n$$

where Q_0 is the admittance ($1/|Z|$) at $\omega = 1 \text{ rad/s}$ and $0 \leq n \leq 1$. When $n = 1$, this is the same equation as that of the impedance of a dispersionless capacitor. Q_0 and n may both be temperature dependent [Macdonald³⁸].

The circuit in Figure 1.11 is by no means unique, the same response can be obtained using different circuit arrangements and different resistor and capacitor values. In some cases it becomes unclear what the circuit elements represent and how they relate to the microstructure being studied. Examples of other configurations are the circuits shown in Figure 1.13 which, for appropriate values of the resistances and capacitances, give the same response as the circuit in Figure 1.11.

The lack of uniqueness of the equivalent circuits and that circuits are obtained which have elements that cannot be readily associated with the composition and microstructure of the composites are major disadvantages of the equivalent circuit approach.

With the advent of fast computers and better image processing techniques has arisen the use of finite element techniques which make use of large arrays

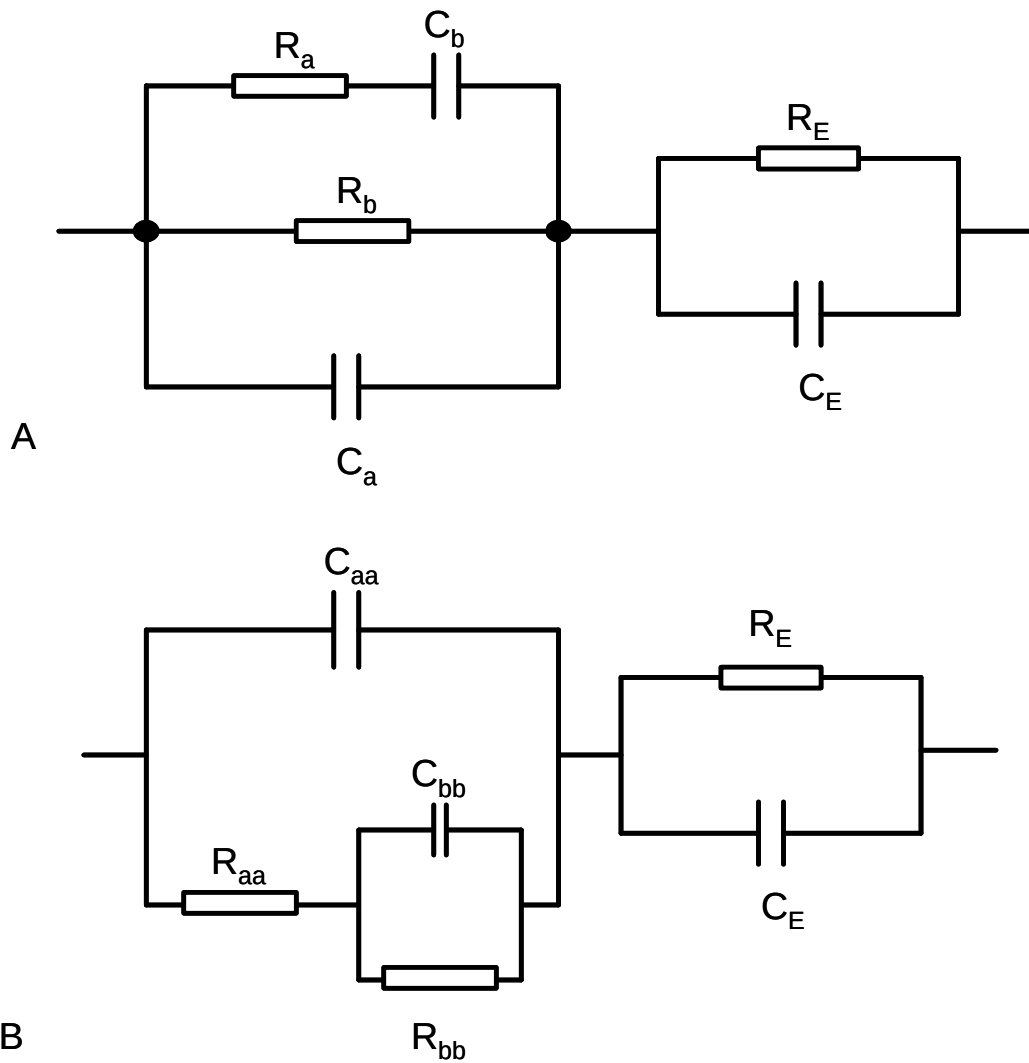


Figure 1.13: Other circuits that give the same response as the circuit in Figure 1.11, for appropriate values of the resistances and capacitances. These illustrate the lack uniqueness of the equivalent circuit approach.

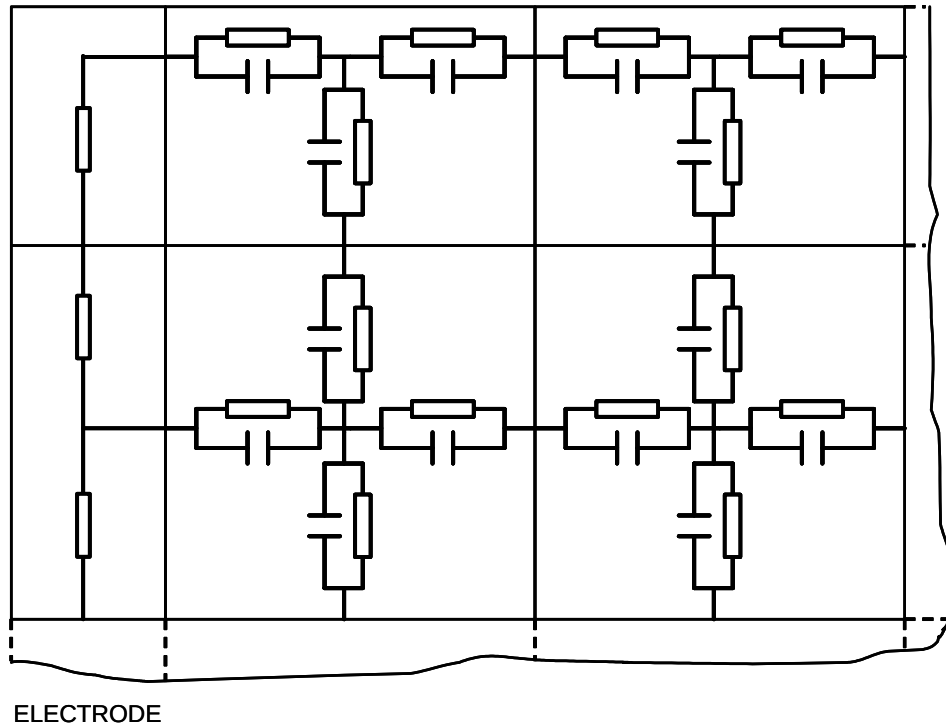


Figure 1.14: A section of an equivalent circuit consisting of components connected so as to match the microstructure in the composite as deduced from micrographs. (Figure adopted from Coverdale et al.³⁹).

of circuit elements to mimic the microstructure of the materials (as observed in micrographs) in the manner shown in Figure 1.14. The connections of the components are structured so as to match the composite microstructure observed in micrographs [Coverdale et al.³⁹]. This may lead to circuits that can be better associated with the microstructure and composition of the composites being studied. However, this approach may also suffer from some of the problems of the simpler equivalent circuit models namely the lack of uniqueness and the sometimes ad hoc nature in which circuit elements are chosen. The great complexity of the circuit networks obtained also means that the finite element approach requires enormous computing resources and therefore places some limitations to their general use. However, this area is a growing area of research as computers get faster.

A different approach to the modeling of Impedance Spectroscopy data is the use of **Effective Media**, **Brick Layer** and **Percolation Theories**. Each of these models corresponds to a particular class of microstructure and

often requires a single or only a few adjustable parameters, depending on the microstructure.

The microstructure upon which the widely used Maxwell-Wagner (MW) model, also known as the Maxwell-Garnet or Hashin-Shtrikman theory, is based is shown in Figure 1.15 [McLachlan et al.¹², McLachlan¹¹ and the references therein]. This microstructure consists of a large range of conducting spheres coated by a more insulating component with a constant ratio of the volume of the conducting component to that of the more insulating component. The microstructure generally leads to two arcs in complex impedance plane plots, when the impedances of the individual components are in a suitable range. Bonanos and Lilley⁴⁰ showed that the Maxwell-Wagner microstructure is equivalent to a series circuit of two parallel RC elements (i.e. Figure 1.11, excluding the element due to electrode effects), for suitable values of the resistances and capacitances. However, due to the nontrivial current distribution in real composites, the equivalence is only approximate. Inhomogeneous current distributions at grain boundaries and electrodes and their impact on the impedance of ceramics is further discussed in Fleig et al.⁴¹.

The reverse MW microstructure, where the conductor surrounds the insulator is also possible. It generally leads only to single arcs in the complex impedance plane as there is a continuous conducting path across the composite medium, which dominates the electrical properties. This extreme is not explored any further in the current work as no samples with this microstructure were studied experimentally.

For the Maxwell-Wagner microstructure, the complex conductivity of the binary composite σ_m is obtained from the relation [McLachlan¹¹ and the references therein]

$$\frac{\sigma_m - \sigma_\ell}{\sigma_m + 2\sigma_\ell} - \phi \frac{\sigma_h - \sigma_\ell}{\sigma_h + 2\sigma_\ell} = 0, \quad (1.1)$$

where σ_h is the complex conductivity of the more conducting component and σ_ℓ that of the less conducting (insulating) component. ϕ is the volume fraction of the more conducting component. This equation can also be written in terms of the complex permittivities ($\epsilon_0\epsilon^*$) or moduli (M^*). The conversions

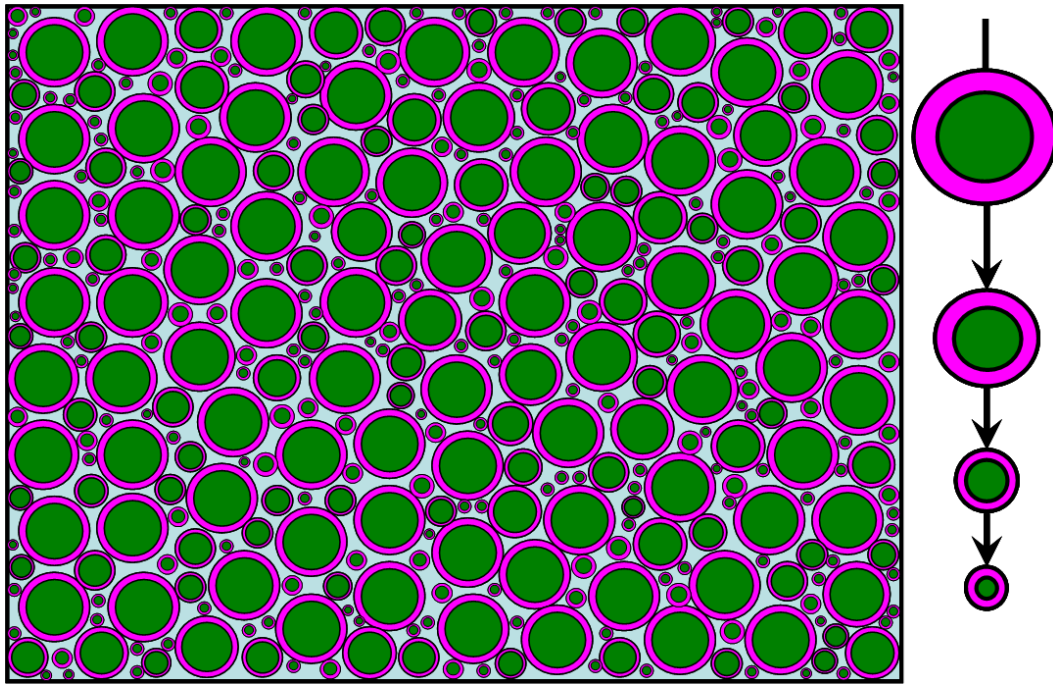


Figure 1.15: The Maxwell-Wagner microstructure consists of a large array of conducting spheres (green) surrounded by a less conducting component (magenta). In order that the volume is completely filled, there must be a large range of sphere sizes. The volume ratio of the interior to the exterior remains constant for all the coated spheres.

between the different representations are given in Table 1.1.

The microstructure represented by the Brick Layer Model (BLM) consists of conducting bricks surrounded by insulating mortar, Figure 1.16 [Verkerk et al.¹⁹]. Careful note must be made of the shapes and contribution of the end caps [Hwang et al.²¹]. An equivalent circuit to the BLM is shown in Figure 1.17. The impedance of the composite medium is given by

$$Z_m = (1/Z_h^\parallel + 1/(Z_\ell^\perp + Z_h))^{-1}, \quad (1.2)$$

where $Z_\ell^\parallel$ is the complex impedance of the square pipe, Z_h for the cubic brick and $Z_\ell^\perp$ for the end caps.

Using the definition of the impedance ($Z = 1/(\sigma G) = L/(\sigma A)$) and the component geometry, shown in Figure 1.16, the impedances of the composite and the various elements of the BLM microstructure can be written as

$$\begin{aligned} Z_m &= \frac{D + d}{\sigma_m(D + d)^2}, \\ Z_h &= \frac{D}{\sigma_h D^2}, \\ Z_\ell^\parallel &= \frac{D + d}{\sigma_\ell((D + d)^2 - D^2)} \end{aligned}$$

and

$$Z_\ell^\perp = \frac{d}{\sigma_\ell D^2}.$$

From Figure 1.16 it can also be seen that the conducting component volume fraction is

$$\phi = \frac{D^3}{(d + D)^3}.$$

By combining the expressions above, it can be shown that Equation (1.2) can be expressed in the form

$$\sigma_m = \frac{\sigma_\ell(\sigma_h + (\sigma_\ell - \sigma_h)\phi^{1/3}(\sigma_h - \sigma_\ell)\phi)}{\sigma_h + (\sigma_\ell - \sigma_h)\phi^{1/3}}, \quad (1.3)$$

from which the volume fraction of the conducting component (ϕ) can be readily obtained.

Neither the Maxwell-Wagner nor the Brick Layer model has a percolation threshold, the insulating coating or mortar persists till $\phi = 1$.

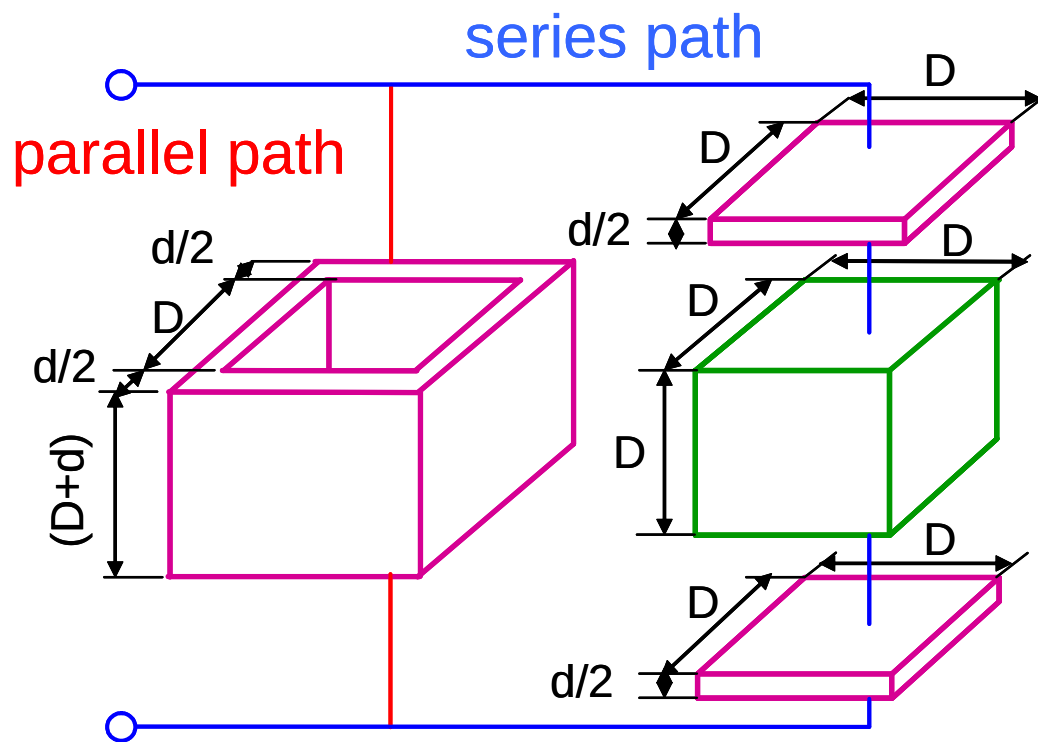


Figure 1.16: The microstructure for the Brick Layer Model. This microstructure is composed of conducting bricks (green) and insulating mortar (magenta). (Figure adopted from Hwang et al.²¹).

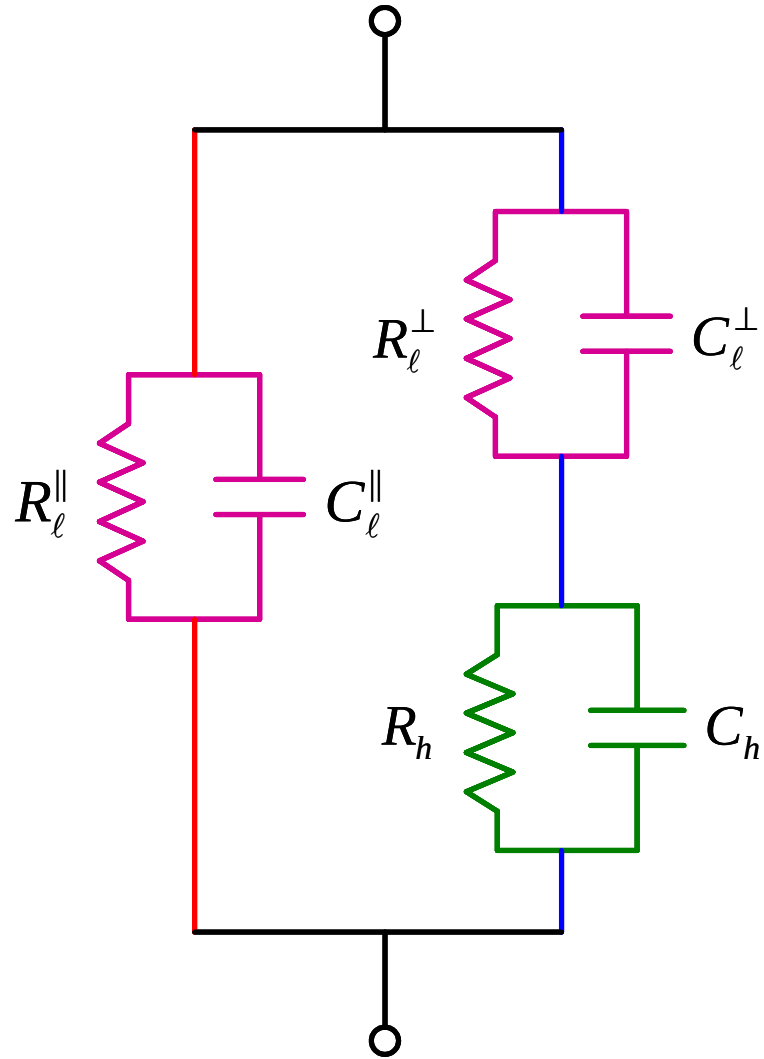


Figure 1.17: The circuit equivalent to the Brick Layer Model microstructure. The resistor, capacitor and connector colors correspond to the colors used to illustrate the different components of the BLM microstructure in Figure 1.16. (Figure adopted from Hwang et al.²¹).

A different class of theories for fitting and modeling the electrical properties of composites are the classical percolation theories and the Phenomenological Percolation Equations (PPEs), which are equivalent to classical percolation theory where they overlap. These are characterized by the presence of a percolation threshold (ϕ_c) where the conductivity and other properties of the composite change abruptly, sometimes by several orders of magnitude for very small changes in ϕ .

The normalized classical percolation equations are [McLachlan¹¹ and the references therein]

$$\sigma_m = \sigma_\ell(\phi_c^s/(\phi_c - \phi)^s), \quad \phi < \phi_c, \quad (1.4)$$

and

$$\sigma_m = \sigma_h((\phi - \phi_c)^t/(1 - \phi_c)^t), \quad \phi > \phi_c. \quad (1.5)$$

In the crossover region, where ϕ lies between $\phi_c - (\sigma_\ell/\sigma_h)^{1/(s+t)}$ and $\phi_c + (\sigma_\ell/\sigma_h)^{1/(s+t)}$,

$$\sigma_m \approx \sigma_\ell^{s/(s+t)} \sigma_h^{t/(s+t)}. \quad (1.6)$$

For ceramic systems, where percolation could occur via inter-grain contact, at a critical volume fraction (ϕ_c) close to 1, the microstructures described by percolation theory and the PPEs are shown in Figures 1.18 and 1.19.

The microstructures in Figures 1.18 and 1.19 represent one extreme. Various values of ϕ_c , spanning the range $0 < \phi_c < 1$ are feasible. For equal sized random spheres, the percolation threshold is 0.16 [Scher and Zallen⁴²]. Smaller values have been observed, for objects with large aspect ratios such as rod like structures. Values in the range of 0.001 have been recorded for some polymer-carbon nanotube composites [Sandler et al.⁴³, Ounaies et al.⁴⁴, McLachlan et al.⁴⁵]. It will later be shown that for systems where the insulator tends to coat the conductor, a relatively high value of ϕ_c is obtained.

The Single and Two Exponent Phenomenological Percolation Equations (SEPPE) and (TEPPE) are phenomenological equations which incorporate

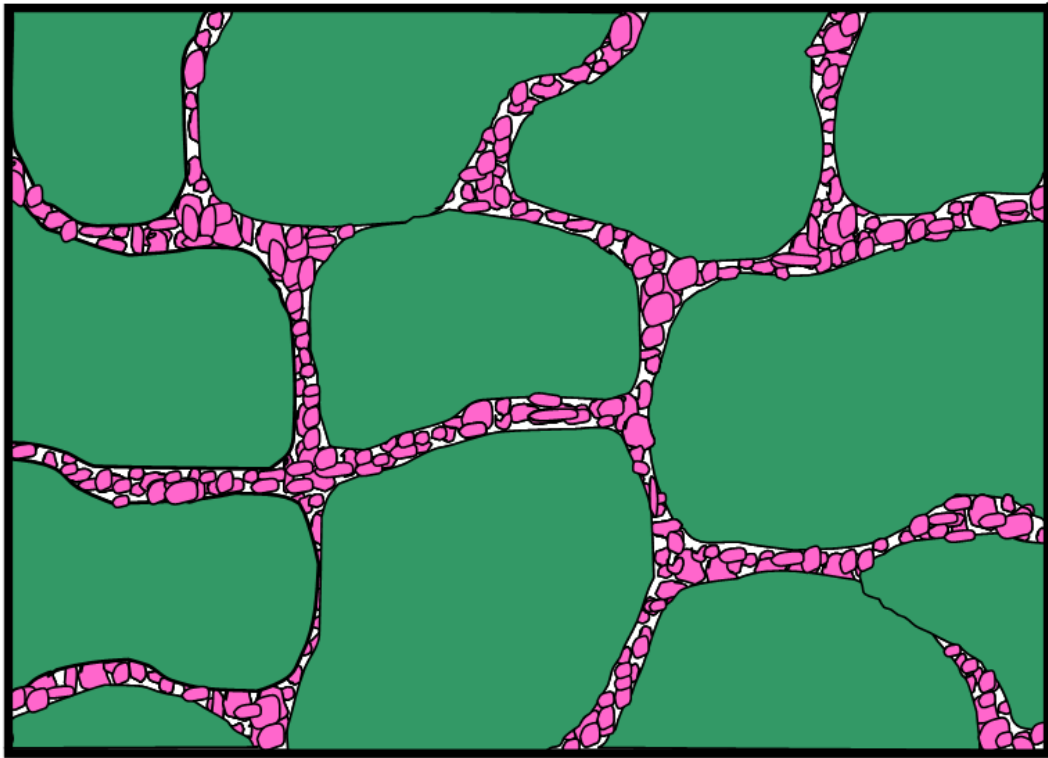


Figure 1.18: The microstructure for the Phenomenological Percolation Equations (SEPPE and TEPPE) below the percolation threshold. At this volume fraction of the conducting component (green) there is no continuous conducting path across the specimen.

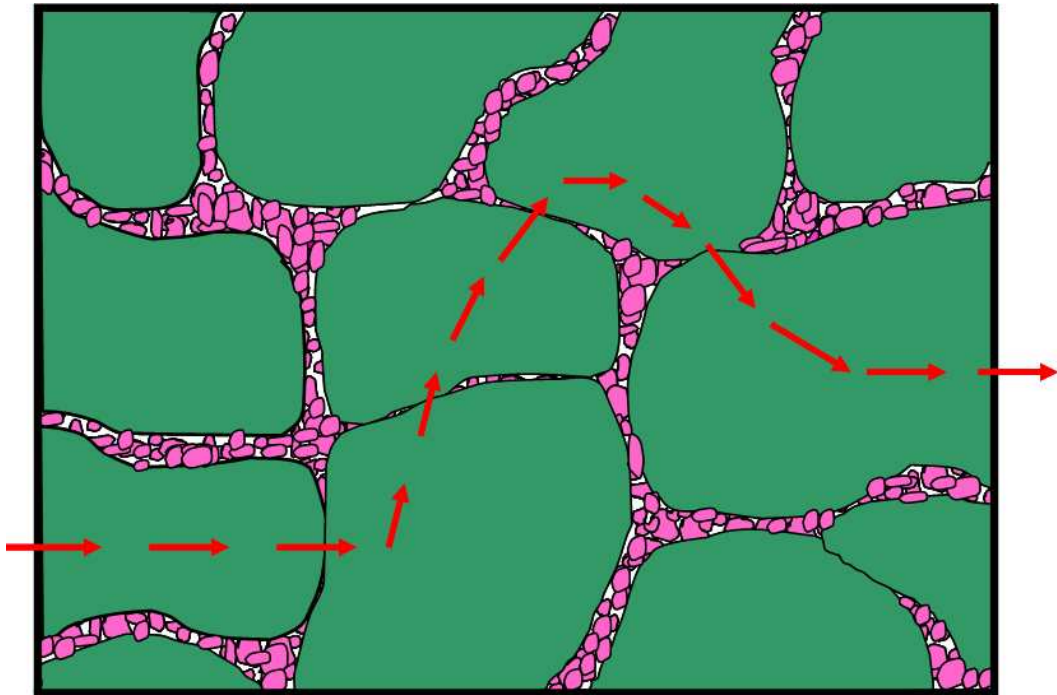


Figure 1.19: The microstructure for the Phenomenological Percolation Equations (SEPPE and TEPPE) above the percolation threshold, a continuous conducting path is established by direct contact between the more conducting grains (green).

classical percolation theory. The SEPPE was formally known as the General Effective Media (GEM) equation [McLachlan et al.^{12, 46}]. The SEPPE and TEPPE interpolate between the regions where the classical percolation equations, (1.4), (1.5) and (1.6) are valid.

The Single Exponent Phenomenological Percolation Equation is

$$(1 - \phi) \frac{\sigma_\ell^{1/t} - \sigma_m^{1/t}}{\sigma_\ell^{1/t} + A\sigma_m^{1/t}} + \phi \frac{\sigma_h^{1/t} - \sigma_m^{1/t}}{\sigma_h^{1/t} + A\sigma_m^{1/t}} = 0, \quad (1.7)$$

where t is an exponent and $A = \phi_c/(1 - \phi_c)$ [McLachlan et al.⁴⁶, McLachlan⁴⁷]. The SEPPE equation has been widely used to successfully fit dc conductivity data such as in McLachlan et al.⁴⁶, Xia et al.⁴⁸.

Equation (1.7) is solved in detail in Liu and Dougal⁴⁹. *Mathematica* gives as the physically correct solution,

$$\sigma_m = \left(\frac{\xi + \sqrt{\xi^2 + 4A\sigma_h^{1/t}\sigma_\ell^{1/t}}}{2A} \right)^t, \quad (1.8)$$

where $\xi = A\sigma_\ell^{1/t} + \phi(\sigma_h^{1/t} - \sigma_\ell^{1/t})(A + 1)$.

A more general and correct form of the phenomenological percolation equations is the two exponent equation, which has been applied successfully to a number of systems mostly for analysis the dc results or single frequency ac data for varying conducting component volume fractions [Wu and McLachlan^{50, 51}, McLachlan et al.⁵²]. The Two Exponent Phenomenological Percolation Equation is

$$(1 - \phi) \frac{\sigma_\ell^{1/s} - \sigma_m^{1/s}}{\sigma_\ell^{1/s} + A\sigma_m^{1/s}} + \phi \frac{\sigma_h^{1/t} - \sigma_m^{1/t}}{\sigma_h^{1/t} + A\sigma_m^{1/t}} = 0. \quad (1.9)$$

The PPEs are applicable for finite values of the conductivities of both the more conducting and the insulating component. On the other hand, strictly speaking, percolation theory only applies when either $\sigma_\ell = 0$ or $1/\sigma_\ell = 0$ which limits its applicability to real systems [McLachlan et al.⁴⁶]. The PPEs reduce to the appropriate percolation equations at these extremes and in the crossover region, Equation (1.6) is obtained. For the correct choice of s , t and ϕ_c , these equations also reduce to the Bruggeman symmetric and

Bruggeman asymmetric equations, [McLachlan et al.⁴⁶, McLachlan⁴⁷], which are also widely used to model composite systems but will not be used in this work as the microstructures they describe are dissimilar to those of the systems investigated.

Equation (1.9) is a transcendental equation, which cannot be solved analytically, for general values of the complex conductivities and the exponents s and t and therefore is extremely difficult to apply directly to frequency dependent ac impedance spectroscopy data as a function of the frequency.

A solution for ϕ can be obtained Equation (1.10) and used in analysis of dc data for varying σ_m , as done in [Wu and McLachlan^{50, 51}, Runyan et al.⁵³ and others]. The solution is

$$\phi = \frac{(\sigma_m^{1/s} - \sigma_\ell^{1/s})(\sigma_h^{1/t} + A\sigma_m^{1/t})}{(1 + A)(\sigma_h^{1/t} \sigma_m^{1/t} - \sigma_\ell^{1/s} \sigma_m^{1/t})}. \quad (1.10)$$

This form cannot be used to analyze complex conductivities and permitivities.

While the models described above are suitable for describing the ceramics and composites experimentally explored in the current work, various modifications need to be and have been made for the analysis of other systems.

Maier⁵⁴ discusses modifications to the Brick Layer model for materials with high interfacial conductivity and anisotropic grain boundary properties e.g. from highly conductive space charges. The validity and limits of the BLM for describing the properties of composites with highly resistive grain boundaries is discussed in Fleig and Maier²⁰.

The influence of non-ideal microstructures on the analysis of grain boundary impedances is discussed in Fleig⁵⁵. The non-ideal microstructures arise where the basic assumptions of the BLM (cubic grains, laterally homogenous grain boundaries, identical properties for all grain boundaries) are violated and are usually found in real ceramics. It is one of the conclusions of this work [Fleig⁵⁵] that deviations from the cubic grain size are acceptable for a BLM analysis as long as the grain size distribution is relatively narrow and spatially homogenous and as long as no pronounced anisotropy in the grain

shape distributions exists. It is also shown, using finite element methods, that grain boundary arc deviating from ideal semicircles do not only occur for distributions of relaxation times, but also for microstructures which differ from the BLM even if only a single grain boundary relaxation time is involved.

Kidner et al.⁵⁶ discuss the inadequacy of the Brick Layer and Maxwell-Wagner models in describing the properties of nano-grained electroceramics in which there are significant contributions from the grain boundaries. In this work, the authors propose the “Nested Cube Model (NCM).” The NCM has no percolation threshold, and is capable of describing impedance/dielectric behavior over the entire range of grain core volume fractions, from small values, where it agrees with Maxwell-Wagner model, to large values, where it agrees with the Brick Layer model. The NCM is also shown to have potential for describing multi-layer grain boundary structures and property gradients at grain boundaries (e.g. in space charge regions).

Properties of mixed conductors in which at least two different charge carriers are mobile (usually one is ionic and the other is an electronic defect) are discussed in Jamnik et al.⁵⁷ and Waser and Hagenbeck³⁶ and the references therein. Jamnik et al.⁵⁷ present an electrical network model for the impedance of these conductors.

1.4 Advanced models for the complex conductivities of the components

The “classical”, dispersionless, Debye dielectric function [Debye⁵⁸] cannot explain the complex conductivity of most materials, which are dispersive. Therefore, a number of expressions have been suggested, by various authors, to fit and model these dispersive properties. In order to be able to accurately model and fit the dispersive properties of the components of the composites in the current work, a number of models were considered and these are described in this section. With the possible exception of the model due to León,

Lucia, and Santamaria⁵⁹, which was developed by these authors specifically for yttria-stabilized zirconia, the other models have all been used to model and fit the dispersive properties of a wide range of materials with varying degrees of success and have a claim to some “universality”.

- The Cole-Cole dielectric response [Cole and Cole⁶⁰] can be represented as [Macdonald⁶¹]

$$\sigma(\omega) = \sigma_{dc}[1 + (i\omega\tau_0)^s] \quad 0 < s < 1. \quad (1.11)$$

This model reduces to the Debye relaxation (no dispersion) when $s = 1$.

- Jonscher introduced the “Universal Dielectric Response”, in Jonscher⁶², which characterized a wide range of dielectrics. He wrote

$$\sigma'(\omega) \propto \omega^s \quad s \leq 1,$$

for the conductivity arising from this universal response. In this work, Jonscher mainly discussed pure dielectrics in which the dc conductivity term $\sigma_{dc} = \sigma'(0)$ could be neglected.

However, in Jonscher⁶³ and in Jonscher⁶⁴, he proposed the expression

$$\sigma'(\omega) = \sigma_{dc}(T) + A(T)\omega^s,$$

an equivalent of which he had listed in Jonscher⁶⁵ as applicable to low conductivity materials. It is this expression, incorporating the dc conductivity term, which will be mainly used in the current work. To simplify the nomenclature, the term “Universal Dielectric Response” and abbreviations “UDR model” will be used hereinafter to refer to the expression that incorporates the dc conductivity term.

The equation for “Universal Dielectric Response” can be written as

$$\sigma^*(\omega) \propto (i\omega)^{s-1}, \quad (1.12)$$

where σ^* is the complex conductivity, giving the real conductivity and real dielectric constant [Pimenov et al.²⁸, Nowick et al.⁶⁶ and others]

$$\sigma'(\omega) = \sigma_{dc} + A\omega^s, \quad (1.13)$$

and

$$\epsilon'(\omega) = \epsilon_\infty + A\omega^{s-1} \tan\left[\frac{s\pi}{2}\right]/\epsilon_0. \quad (1.14)$$

A and s are temperature dependent parameters.

- For a large range of materials which exhibit disorder at the microscopic scale, Dyre⁶⁷ described a model based on the continuous time random walk for modeling and fitting their dispersive properties. One property that these systems have in common is that the data at various temperatures can be mapped onto a common “master curve” in a procedure known as scaling. When the sample data is scalable, the Continuous Time Random Walk (CTRW) based model (Equation (1.15)), is one of the models that can be considered for modeling and fitting the dispersion of the data. It has been successfully used to fit the data from a number of systems such as those given in Dyre⁶⁷ and Kremer⁶⁸.

The Continuous Time Random walk equation can be written as [Hodge et al.³⁵]

$$\sigma^*(\omega) = \sigma_{dc} \left(\frac{i\omega\tau}{\ln[1 + i\omega\tau]} \right) + i\omega\epsilon_0\epsilon_\infty, \quad (1.15)$$

where τ is the attempt frequency to overcome the largest barrier determining the dc conductivity.

Equation (1.15) gives

$$\sigma'(\omega) = \frac{\sigma_{dc}\omega\tau \arctan[\omega\tau]}{\arctan^2[\omega\tau] + \frac{1}{4} \ln^2[1 + \omega^2\tau^2]}, \quad (1.16)$$

and

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\sigma_{dc}\tau \ln[1 + \omega^2\tau^2]}{2\epsilon_0 \arctan^2[\omega\tau] + \frac{1}{2}\epsilon_0 \ln^2[1 + \omega^2\tau^2]}, \quad (1.17)$$

for the real conductivity and the real dielectric constant.

- A model for the properties of the yttria-stabilized zirconia based on correlated ion hopping in the stabilized zirconia crystal is described in León et al.⁵⁹. This model, hereinafter referred to as the “Leon-Lucia-Santamaria” or “LLS” model leads to Equation (1.18).

For Leon, Lucia and Santamaria's correlated ion hopping model,

$$\sigma^*(\omega) = \sigma_{dc} \left(1 + (i\omega \frac{\epsilon_\infty}{\sigma_{dc}})^s + \frac{i\omega \epsilon_\infty}{\sigma_{dc}} \right) \quad 0 < s < 1, \quad (1.18)$$

which gives

$$\sigma'(\omega) = \sigma_{dc} \left(1 + \left(\frac{\epsilon_0 \epsilon_\infty \omega}{\sigma_{dc}} \right)^s \cos\left[\frac{s\pi}{2}\right] \right), \quad (1.19)$$

and

$$\epsilon'(\omega) = \epsilon_\infty \left(1 + \left(\frac{\epsilon_0 \epsilon_\infty \omega}{\sigma_{dc}} \right)^{s-1} \sin\left[\frac{s\pi}{2}\right] \right). \quad (1.20)$$

for the real conductivity and real dielectric constant.

- Another model which are widely used to fit and model dielectric data is that due to Havriliak and Negami⁶⁹. The HN model can be extended to account for a number of relaxation processes in the material through additional terms in the sum in Equation (1.21). However, it has been pointed out by various authors, such as in Nigmatullin et al.⁷⁰, that the parameters appearing in the equations do not have any clear physical meaning.

The Havriliak-Negami function can be written as [Schaumburg⁷¹]

$$\epsilon^*(\omega) = \epsilon' - i\epsilon'' = -i \left(\frac{\sigma_{dc}}{\epsilon_0 \omega} \right)^s + \sum_{k=1}^3 \left[\frac{\Delta \epsilon_k}{(1 + (i\omega \tau_k)^{\alpha_k})^{\beta_k}} + \epsilon_{\infty k} \right], \quad (1.21)$$

where the α_k and β_k describe the symmetric and asymmetric broadening of the relaxation peaks [Schaumburg⁷¹, Hartmann et al.⁷²]. The HN expression includes the Debye and Cole-Cole (Equation (1.11)) functions.

- In their work, Nigmatullin et al.⁷⁰ propose the “Justified Data-Curve Fitting” (JDCF) approach based on complex permittivity functions containing two or more characteristic relaxation times as an alternative to the HN and other “imposed data-curve fitting” approach equations.

The JDCF approach gives

$$\epsilon(i\omega) = \epsilon_\infty + \frac{\epsilon(0) - \epsilon_\infty}{1 + R(i\omega)}, \quad (1.22)$$

where $\epsilon(0)$ is the static dielectric constant and the complex function $R(i\omega)$ is determined using the expressions:

$$R(i\omega) = (i\omega\tau_1)^{\nu_1} + (i\omega\tau_2)^{\nu_2},$$

for an equivalent circuit for $\epsilon(i\omega)$ containing two resistor capacitor elements connected in parallel and

$$R(i\omega) = [(i\omega\tau_1)^{-\nu_1} + (i\omega\tau_2)^{-\nu_2}]^{-1},$$

for an equivalent circuit for $\epsilon(i\omega)$ containing two resistor capacitor elements connected in series.

Neither the HN nor the JDCF approach was able to fit the data in the current work very well and therefore they will not be discussed any further. They have been included here to complete the set of models in the literature that were taken into consideration.

1.5 Temperature dependence

A number of expressions for determining and describing the temperature dependence of the conductivity (σ) and the characteristic frequency ($\nu = \omega/2\pi$) of materials, which are based on various different models, can be encompassed in the equation

$$\sigma_{dc}(or \ \nu_p) = \sigma_0(or \ \nu_0)T^n \exp[-B/T^q]. \quad (1.23)$$

By setting $q=1$, $n=0$ and $B = \frac{E_a}{k_B}$ in Equation (1.23), the Arrhenius expression for pure non-polar semiconductors is obtained. Highly ionic solids, where the large polaron mechanism operates, are described by setting $q=1$, $n=+1$ and $B = \frac{E_a}{k_B}$ in Equation (1.23) [Wang et al.⁷³]. For polar ionic solids

where the small polaron (hopping conduction) mechanism operates, $q=1$, $n=-1$ or $-\frac{3}{2}$, and $B = \frac{E_a}{k_B}$. A similar expression is obtained for conductivity in which there is motion of actual ions rather than polarons which are exclusively electronic in nature. For variable range hopping, $q = \frac{1}{4}$, $n = 0$ and $B = T_0^{1/4}$ [Mott and Davies⁷⁴, Helgren et al.⁷⁵]. σ_0 and ν_0 are pre-exponential factors while E_a , k_B and T_0 are the activation energy, Boltzmann constant and characteristic temperature respectively. Other values and combinations of q , n and B have been suggested, by other authors and are associated with various mechanisms. These will not be used in the current work.

1.6 Kramers-Kronig Relations

The Kramers-Kronig (K-K) relations, Equations 1.24 and 1.25, relate the real part of an immittance function ψ' to its the imaginary part, ψ'' . These relations can and are used in this work, both to validate experimental data (see Section 2.6.1) as well as for the analysis of the various relaxation and other processes contributing to the measured data, as described later in this section. In the first case, the immittance function utilized is the impedance (real and imaginary) while for the later case, the K-K transforms of the real and imaginary dielectric constants are considered

The K-K relations are,

$$\psi''(\omega_0) = -\frac{2\omega_0}{\pi} P \int_0^\infty \frac{\psi'(\omega) - 1}{\omega^2 - \omega_0^2} d\omega. \quad (1.24)$$

$$\psi'(\omega_0) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega \psi''(\omega)}{\omega^2 - \omega_0^2} d\omega. \quad (1.25)$$

P indicates the Cauchy principal value of the integral which must be used in order to deal with the singularity at $\omega = \omega_0$. The K-K relations, which are based on the principle of causality dictate that the real and imaginary part of any immittance function are interdependent provided that the following conditions are met [Macdonald and Urquidi-Macdonald⁷⁶, Boukamp⁷⁷]:

1. Causality: The response must be related to the excitation signal only.

2. Linearity: The perturbation/response of the system is described by a set of linear differential laws. Practically this condition requires that the immittance be independent of the magnitude of the perturbation. Inherently nonlinear responses, such as electrode effects, do not conform to the transforms, except when the excitation signal is very small.
3. Stability: The system may not change with time, nor continue to oscillate when the excitation signal is removed, which requires the system to be passive.
4. Finiteness: Immittance values must be finite for all values of ω , including $\omega \rightarrow 0$ and $\omega \rightarrow \infty$.

For practical application of the K-K transforms, the last condition is not critical.

To separate out relaxation and conduction processes, the following forms of the K-K relations are used [Steeman and van Turnhout⁷⁸],

$$\epsilon''(\omega_0) = \frac{\sigma_{dc}}{\epsilon_0 \omega_0} + \frac{2}{\pi} \int_0^\infty \epsilon'(\omega) \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega. \quad (1.26)$$

and

$$\epsilon'(\omega_0) = \epsilon_\infty + \frac{2}{\pi} \int_0^\infty \epsilon''(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega \quad (1.27)$$

Note that pure ohmic conduction does not contribute to the real dielectric constant, ϵ' . Therefore, the integral term in Equation (1.26) equals the relaxation loss, while the first term, $\frac{\sigma_{dc}}{\epsilon_0 \omega_0}$ pertains to the ohmic conduction losses. Thus, if the relaxation losses are obtained by transforming the real dielectric constant data using Equation (1.26), the ohmic conduction will be calculated by subtracting the polarization loss from the actual measured loss [Steeman and van Turnhout⁷⁸].

Chapter 2

Experimental Methods

2.1 Introduction

In this chapter the various experimental methods used in sample preparation, measurement and data analysis are described.

2.2 Sample preparation

A number of techniques were used to produce the samples analyzed in this study and these are described below. In the case of the yttria-stabilized zirconia (YSZ) and the liquid-phase-sintered silicon carbide (LPSSiC), the samples were obtained by the author ready made. Samples of the polyester-resin/silicon composite were produced by the author.

2.2.1 Yttria-Stabilized Zirconia Single Crystals

The grains of the polycrystalline YSZ ceramics are essentially tiny crystallites of YSZ. Therefore, in order for the electrical properties of these grains to be well characterized, single crystals of 3, 5.7 and 9.5 mole % YSZ grown by the skull method (an rf-heated crystal growth process) were obtained from Zirmat Corporation (Westford, MA 01886, U.S.A.). A single crystal of 12 mole % YSZ was obtained from Dr. Tim Armstrong at the Oak Ridge National Laboratory (Oak Ridge TN 37831-6186, U.S.A.). It was not possible to obtain

single crystals of 8 mole % YSZ on the market. The cubic stabilized zirconia crystals (9.5 and 12 mole % YSZ) were transparent, crack free and oriented in the (100) direction. The tetragonal stabilized zirconia crystals (3 and 5.7 mole % YSZ) were obtained as lumps of up to 100 grammes in the As-Grown condition. These lumps were opaque with various levels of cracking. Small crack free specimens approximately 1 mm thick and about 12 mm across at the widest point and with an irregular surface area, were cut from these lumps, for the electrical measurements.

2.2.2 Yttria-Stabilized Zirconia Ceramics

Samples of 8 and 3 mole % yttria-stabilized zirconia, 8YSZ and 3YSZ respectively, with varying grain sizes and in some cases with varying levels of silicon dioxide (SiO_2), as a deliberately introduced impurity, were sintered by Dr. Tim Armstrong then at the Pacific Northwest National Laboratory (Richland, WA99352, U.S.A.). Various grain sizes were obtained by varying the sintering conditions (time and temperature) as well as by using different starting powders. The samples were sintered from YSZ powders obtained from Tosoh Corporation and Daiichi Kigenso Kagaku Kogyo Co. Ltd (DKKK). The fused amorphous silicon dioxide powder, used as the deliberately introduced impurity, was obtained from Alfa AESAR. The samples were sintered in the form of 1 mm thick disks, approximately 23 mm in diameter.

A list of the polycrystalline YSZ samples studied and their preparation conditions, as supplied by Dr. Tim Armstrong, are given in Tables 2.1, 2.2

Table 2.1: The pure 8 mole % yttria-stabilized zirconia ceramic samples studied and the conditions under which they were sintered. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Powder Manufacturer	Sintering Temperature ($^{\circ}C$)	Sintering Time (Hrs)
8YSZ-D1	DKKK	1350	2
8YSZ-T1	Tosoh	1350	2
8YSZ-D2	DKKK	1600	10
8YSZ-T2	Tosoh	1600	10

Table 2.2: The pure 3 mole % yttria-stabilized zirconia ceramic samples studied and the conditions under which they were sintered. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Powder Manufacturer	Sintering Temperature (°C)	Sintering Time (Hrs)
3YSZ-T1A	Tosoh	1450	2
3YSZ-T1B	Tosoh	1450	2
3YSZ-T2A	Tosoh	1600	10
3YSZ-T2B	Tosoh	1600	10

Table 2.3: The 8 mole % yttria-stabilized zirconia samples containing silica and the conditions under which they were sintered. The YSZ powder was manufactured by Tosoh. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Silica Content (Weight %)	Silica Content (Volume %)	Sintering Temp. (°C)	Sintering Time (Hrs)
8YSZ-SiO ₂ -T1	0.1	0.3	1350	2
8YSZ-SiO ₂ -T2	0.5	1.2	1350	2
8YSZ-SiO ₂ -T3	1.0	2.7	1350	2
8YSZ-SiO ₂ -T4	5.0	12.4	1350	2
8YSZ-SiO ₂ -T5	10.0	23.0	1350	2

and 2.3. The sample names given in the tables will be used to refer to these samples in the remainder of this work. From time to time, they will also be referred to by their crystal structures, cubic stabilized zirconia (CSZ) for the cubic 8 mole % yttria-stabilized zirconia (and the 9.5 and 12 mole % single crystals) and tetragonal stabilized zirconia (TSZ) for the 3 mole % YSZ samples and the 5.7 mole % yttria-stabilized zirconia single crystal.

2.2.3 Polyester-resin/Silicon Composites

A series of composites consisting of polyester-resin and various volume fractions of high purity silicon powder (99.998%) obtained from GoodFellow Cambridge Limited (Huntingdon Cambridgeshire England) were prepared. The powder had an average particle size of 10 μm , measured, by the author, using a Malvern particle size analyzer. The Malvern instrument uses a light-scattering method to measure the powder particle sizes. The light source is a helium-neon laser ($\lambda \approx 0.63 \mu\text{m}$). The polyester-resin (Tradename Resin

Table 2.4: The polyester-resin/silicon samples prepared.

Sample Name	Proposed silicon volume %	Measured silicon weight %	Calculated silicon volume %
PS0	0	0	0
PS4	4	8.3	4.1
PS5	5	9.3	4.7
PS8	8	17.6	9.3
PS12	12	22.3	12.1
PS16	16	28.9	16.3
PS20	20	35.3	20.7
PS24	24	41.7	25.5
PS28	28	47.1	29.9
PS32	32	51.8	34.0
PS36	36	53.7	35.7

1935) was purchased in the unpolymerized form. A catalyst (Tradename Butanox M50), to speed up the polymerization process, was also purchased from the same source as the polyester-resin. Resin 1935, the catalyst and between 0 and ~ 40 volume % silicon were thoroughly mixed by stirring and the mixture was then left to set. The mixing was carried out until the onset of gelation of the polyester-resin (approximately 10 minutes). This prevented the silicon from settling. Care had to be taken during the stirring to minimize the formation air bubbles, and therefore the need for a very slow stirring speed in the highly viscous polyester-resin/silicon composite. The upper limit to the amount of silicon that could be loaded into the polyester-resin was that for which the polyester-resin could still bind together to make a stable compact, without external pressure. From optical micrographs of the composites obtained, in all cases, silicon particles were found to be completely surrounded by the polyester-resin. 10 mm thick disks, 22 mm in diameter were cast in teflon molds. The specimens were left in the molds for 36 hours to ensure that the polymerization process had continued to completion, as per the supplier's instructions. The compacts obtained were able to fully retain shape when removed from the molds. After removal from the molds, the specimens were left for a further seven days surrounded by silica gel to prevent any absorption of moisture. After the seven days the samples were then annealed,

in air at 160 °C, for 12 hours in a Carbolite type GLM11/3 muffle furnace. The above procedure ensured that the samples' electrical properties were stable at the temperature at which measurements were made. After annealing, the initial 10 mm thick disks were sliced into 3 mm thick specimens, for the measurements, using a Metal Research Ltd Type DS2 3-400 rev/min cutting machine with a Buehler diamond wafering blade (Buehler, Inc. Lake Bluff, IL 60044 U.S.A.). A list of the polyester-resin/silicon composites produced and the names used to refer to them, throughout the rest of this work, is given in Table 2.4.

2.2.4 Liquid-Phase-Sintered Silicon Carbide

Samples of liquid-phase sintered silicon carbide were prepared by Mrs Antoinette Can at the University of the Witwatersrand, Johannesburg, South Africa and at the Fraunhofer Institute for Ceramic Technologies and Sintered Materials, Dresden, D-01277, Germany. Commercially available powders of alpha-SiC (UF-15, H.C. Starck), Y_2O_3 (fine grade, H.C. Starck) and Al_2O_3 (AKP-50, Sumitomo) were used as the starting materials. Compositions with 10 weight% sintering additives consisting of varying mole ratios of yttria to alumina, ($Y_2O_3 : Al_2O_3 : 1 : 4$, $3 : 5$, $1 : 1$, $4 : 2$, $4 : 1$) and one case (LPSSiC-HPX) $Y_2O_3 : SiO_2$, were milled in a planetary ball mill for 2 hours, using triethylene glycol (Sigma-Aldrich; 0.5 weight %) and Triton X-100 (Sigma Aldrich; 3 weight %). The densification techniques chosen were hot pressing (HP) at 1925 °C for 30 minutes and gas pressure sintering (GPS) at 1925 °C for 60 minutes, at a final Argon gas pressure of 80 bars. Additional heat treatments were carried out on some hot pressed samples (HTHP) at 1925 °C for 8 hours in 80 bars argon. A list of the LPSSiC samples studied, the compositions of the sintering additives as well as the sample names used in the rest of this thesis is given in Table 2.5.

In addition to the above, single crystals of 6H silicon carbide, as well as solid-state-sintered silicon carbide samples, were obtained from Dr Mathias

Table 2.5: The liquid phase sintered silicon carbide samples studied, the conditions under which they were prepared and the sintering additives. * Does not contain alumina. The preparation techniques are described in the text. (Data courtesy of Mrs A. Can).

Sample Name	Preparation Technique	Sintering Additive Composition (mole ratio)
LPSSiC-HP1	HP	$3Y_2O_3 : 5Al_2O_3$
LPSSiC-HP2	HP	$4Y_2O_3 : 2Al_2O_3$
LPSSiC-HP3	HP	$1Y_2O_3 : 1Al_2O_3$
LPSSiC-HP4	HP	$4Y_2O_3 : 1Al_2O_3$
LPSSiC-HP5	HP	$1Y_2O_3 : 4Al_2O_3$
LPSSiC-HPX*	HP	$0.7Y_2O_3 : SiO_2$
LPSSiC-GPS1	GPS	$3Y_2O_3 : 5Al_2O_3$
LPSSiC-GPS2	GPS	$4Y_2O_3 : 2Al_2O_3$
LPSSiC-GPS3	GPS	$1Y_2O_3 : 1Al_2O_3$
LPSSiC-GPS5	GPS	$1Y_2O_3 : 4Al_2O_3$
LPSSiC-HTHP1	HP+HT	$3Y_2O_3 : 5Al_2O_3$
LPSSiC-HTHP2	HP+HT	$4Y_2O_3 : 2Al_2O_3$
LPSSiC-HTHP3	HP+HT	$1Y_2O_3 : 1Al_2O_3$
LPSSiC-HTHP5	HP+HT	$1Y_2O_3 : 4Al_2O_3$

Herrmann of the Fraunhofer Institute for Ceramic Technologies and Sintered Materials, Dresden, D-01277, Germany.

2.3 Non-Electrical sample characterization

To enable correlations to be made between the electrical properties and the composition and microstructure of the composite materials, a number of their other physical properties must be known. To obtain these physical properties, various methods of characterization were used and are described here.

2.3.1 Microscopy

The morphology of the yttria-stabilized zirconia and the liquid-phase sintered silicon carbide samples was obtained by studying the samples using scanning electron microscopy (SEM). This work was carried out by Dr. Tim Armstrong, in the U.S.A. and by Mrs. Antoinette Can, using a Philips Field

Emission Scanning Electron Microscope (FESEM), at the Element Six Laboratories in Springs, South Africa respectively. Sample grain sizes and, in the case of the LPSSiC, grain size distributions and contiguity values, were obtained from the scanning electron micrographs, using image analysis software obtained from Philips and other vendors. The determination of grain sizes from micrographs is further discussed in [Han and Kim^{79, 80}, Muirhead et al.⁸¹, Roebuck⁸² and the references therein]

The distribution of the silicon in the polyester-resin/silicon composites was analyzed using a Carl Zeiss AxioTech optical microscope (25HD G/180587) and the associated AxioTech 3.1 image capture software. Images were captured using a CCD camera attached to the microscope and controlled by AxioTech 3.1 software. Magnifications between 50X and 1000X were used. To prepare the specimens for optical microscopy, they were polished with 200 and 100 grit silicon carbide paper and finished off with a polishing cloth and 1 μm alumina paste (Leco Corporation Joseph, MI 49085 U.S.A.). The polishing was carried out on equipment obtained from Leco and Struers (Copenhagen, Denmark) . This procedure gave a shiny polished surface.

2.3.2 X-Ray Diffraction and Rietveld Analysis

To further investigate the properties of the constituent phases, the YSZ and LPSSiC ceramic samples were studied by X-Ray diffraction again by Dr. Armstrong, in the U.S.A. and Mrs. Can at the Fraunhofer Institute for Ceramic Technologies and Sintered Materials, Dresden, Germany (using an RD7 Seifert-FPM X-Ray Diffractometer and “Autoquan” software to do Rietveld calculations). This enabled the sample phases to be identified and, with use of Rietveld analysis for the LPSSiC, the relative amounts of the various SiC polytypes and the crystalline grain boundary phases could be obtained.

2.3.3 Other characterization

The densities of the samples were determined by the Archimedes principle as described in ASTM⁸³ standard C373-88.

Further studies of other LPSSiC properties, such as the hardness and toughness, were made by Mrs. Can and are reported in Can⁸⁴ and in publications in preparation.

2.4 Electrode preparation

Reliable and accurate electrical measurements require samples to have well bonded, low resistance electrodes. For this study, the sample material was sandwiched between a pair of electrodes bonded to its surface, so as to form a parallel plate capacitor (Figure 2.1). A number of errors can be introduced in the measurement due to poor contact between the electrodes and the sample surface. These may include the appearance of features that may be incorrectly interpreted as being due to the components of the sample material [Mason et al.⁸⁵, Schaumburg⁸⁶, Beltrán et al.⁸⁷].

To obtain well bonded electrodes, for the YSZ and LPSSiC samples, the sample surfaces, already polished to 1 μm , were first cleaned in acetone for approximately 15 minutes in an ultrasonic bath to remove any organic material, from handling. A layer of colloidal gold paint, as used in decorative ceramics, was then painted onto each clean sample surface using a fine artists' paint brush. The sample was then left in air for a few minutes (~ 10) to allow most of the solvent to evaporate. After 10 minutes or so, the surface was examined and it was possible to ascertain if there were any major flaws in the gold coating. If any flaws were detected, the surface was further painted over and again left to dry. Evaporation of the solvent was speeded up by placing the sample under a 60 Watt incandescent light bulb.

When a uniform painted surface had been obtained the coated sample was then placed in the Carbolite type GLM11/3 muffle furnace where it was heated to 750 °C at 600 °C/hr in air. The temperature was maintained at 750 °C for 10 minutes, to ensure that all the binder of the colloidal gold had burnt off, after which the samples were naturally cooled to room temperature. Estimates of the thickness of the coat, obtained from weighing the samples

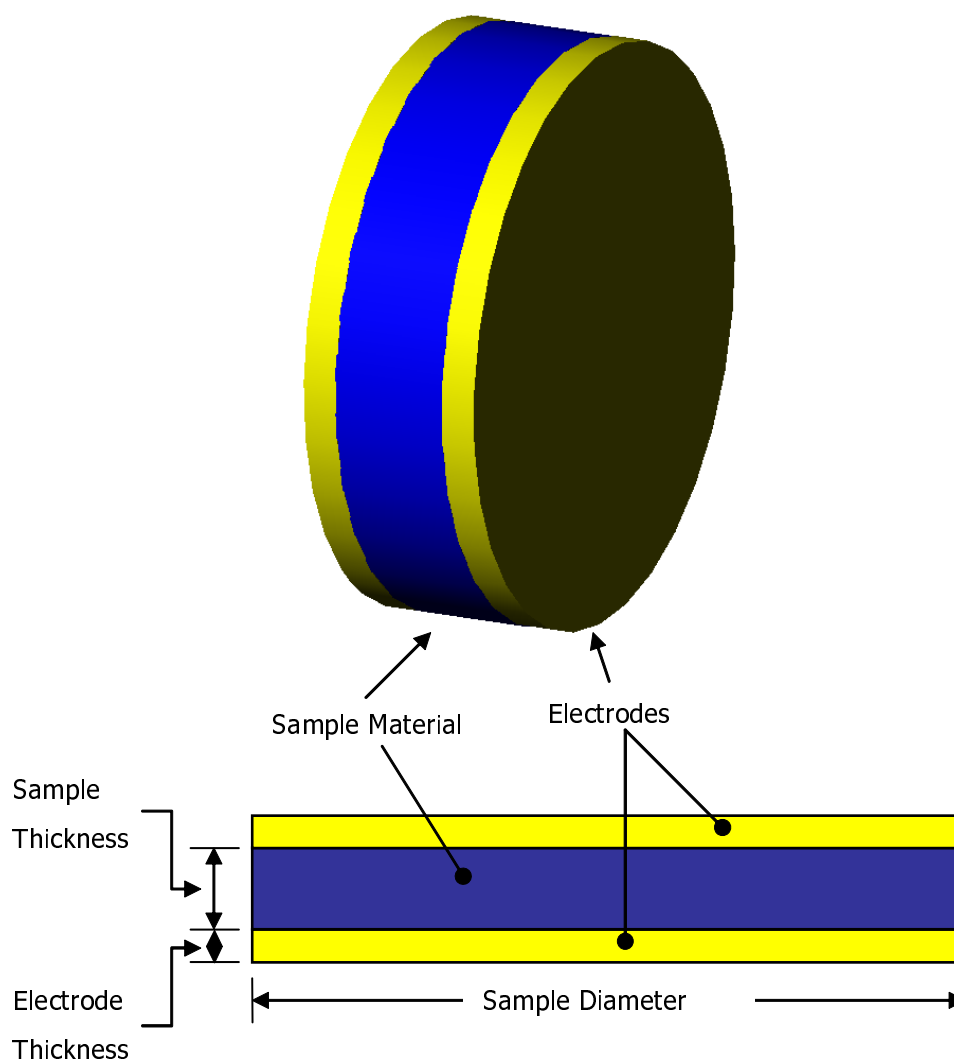


Figure 2.1: Samples for electrical measurements were prepared in the form of parallel plate capacitors. Wherever possible, samples of regular geometry, and in particular disk shaped samples, were used. However, in some cases, such as for the 3 and 5.7 mole % YSZ single crystals, it was not possible to obtain specimens with a regular geometry. The use of samples with irregular geometries often leads to the increase in the uncertainty of the measured sample geometric factor.

before and after applying electrodes, gave a figure of approximately 3000 Å. Coats of this thickness were found to be the most robust and to remain undamaged during the electrical measurements. If the coats were too thin they would easily be scratched off the surface and if they were too thick they flaked off the surface. In a few cases, such as for the polished 9.5 YSZ single crystal, which came with highly polished surfaces, the application of electrodes had to be attempted more than once as the electrodes initially partially peeled off the surface after annealing. In these cases, the earlier electrode was first gently polished off and the surface was again cleaned, as described above, before the application of the new electrode coating.

For the polyester-resin/silicon composites, where measurements were only carried out at temperatures less than 200 °C and where the samples could not be heated to the firing temperature required for the gold electrodes, silver electrodes, prepared at room temperature, were used. Colloidal silver (Electrodag 1415, Acheson Industries) was applied onto the sample surface using a soft brush. After fully curing and the stabilization heat treatment, the polyester-resin was found not to readily dissolve in the solvent in which the colloidal silver was suspended (amyl-acetate). In spite of this, the solvent was evaporated rapidly to ensure that there was as little contact time as possible with the sample surface, to minimize the chance of any of the polyester-resin dissolving and forming an insulating layer. This was done by speeding up the evaporation of the solvent as described above. After drying, the continuity of each electrode was tested by checking that the resistance between any two extreme points was less than 1 Ω on a Wavetek (DM28XT) resistance meter. Where electrodes did not meet this specification, they were polished off using 200 grit Silicon Carbide paper and reapplied. The samples, ready for measurement were stored, covered in silica gel, to minimize the absorption of moisture.

2.5 Dielectric and conductivity measurements

2.5.1 The oven and sample holder for electrical measurements

In order for electrical measurements to be made at high temperatures and in a suitable atmosphere, an appropriate oven and temperature controlled sample holder had to be designed and made.

Figure 2.2 shows the **oven** for carrying out electrical measurements in a suitable atmosphere. This oven was constructed double walled to minimize the transmission of heat between the inner chamber, 1, in Figure 2.2 and the outside environment. Most measurements of the composite materials' electrical properties were carried out at a vacuum of ~ 10 *milliTorr* obtained with an Edwards "2 stage 8" rotary vane pump (BOC Edwards, Sussex, United Kingdom). This vacuum, used so that the atmosphere (partial pressure of nitrogen and/or oxygen) dependence of the properties of the samples would not be a factor in the data analysis, was monitored by Balzers TPR 010 gauge heads connected to a Balzers PKG010 Pirani-Cold Cathode gauge.

Pumping down the inner chamber of the oven, into which the sample holder was placed, was done through port 2 in Figure 2.2. For thermal insulation, the space between the walls of the oven was pumped down to a rotary pump vacuum through the port 3. High vacuum valves were used to isolate the pumping line for the inner chamber and that for the space between the walls of the oven. This minimized the volume needing to be pumped down when it was not necessary that both vacuums be broken and it enabled different atmospheres to be maintained in the two spaces. Heating wire was wound onto the outside of the oven, 4 and together with a thermocouple enabled the temperature at the wall to be controlled. This helped to minimize the temperature gradient from the inner chamber outward and therefore made it easier to maintain a constant temperature at the sample stage. A layer of thermally insulating ceramic fibre was also placed over the wire on the outside wall of the oven. This fibre was in turn wrapped in shiny heavy

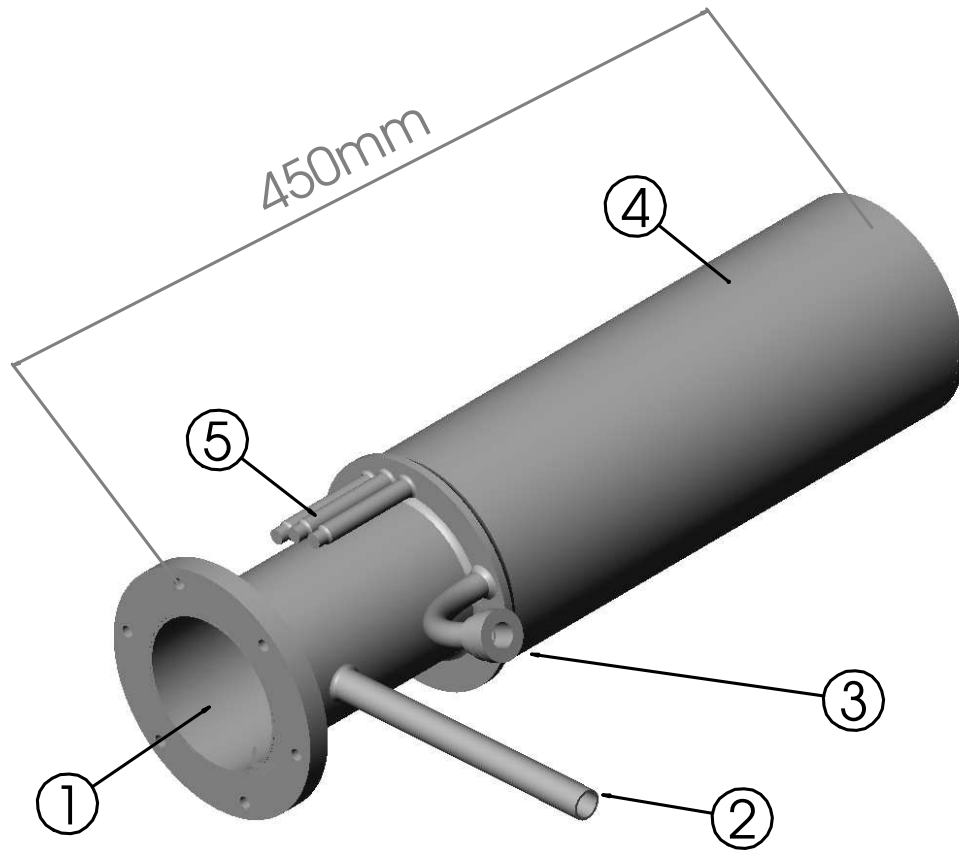


Figure 2.2: The oven of the high temperature measurement system. The various labeled components are describe in the text.

duty aluminium foil which helped minimize loss of heat by radiation. Extra ports, 5, were maintained for pumping cooling gas into the space between the walls of the oven.

A **sample holder**, suitable for measurements at high temperatures, Figure 2.3, was also designed and constructed. The sample stage and lower electrode consisted of a pair of copper plates, connected to the upper flange by a set of steel wires, acting as both structural supports and electrical contacts. A platinum sheet was screwed down onto the sample stage to form a clean primary contact point with the sample. Adequate clearance was left between the sample stage and the walls of the oven to prevent any electrical or thermal contact being made. As a further precautionary measure, alumina spacers were mounted onto the bottom plate of the stage, slightly protruding from it, to minimize thermal and electrical conduction between the sample

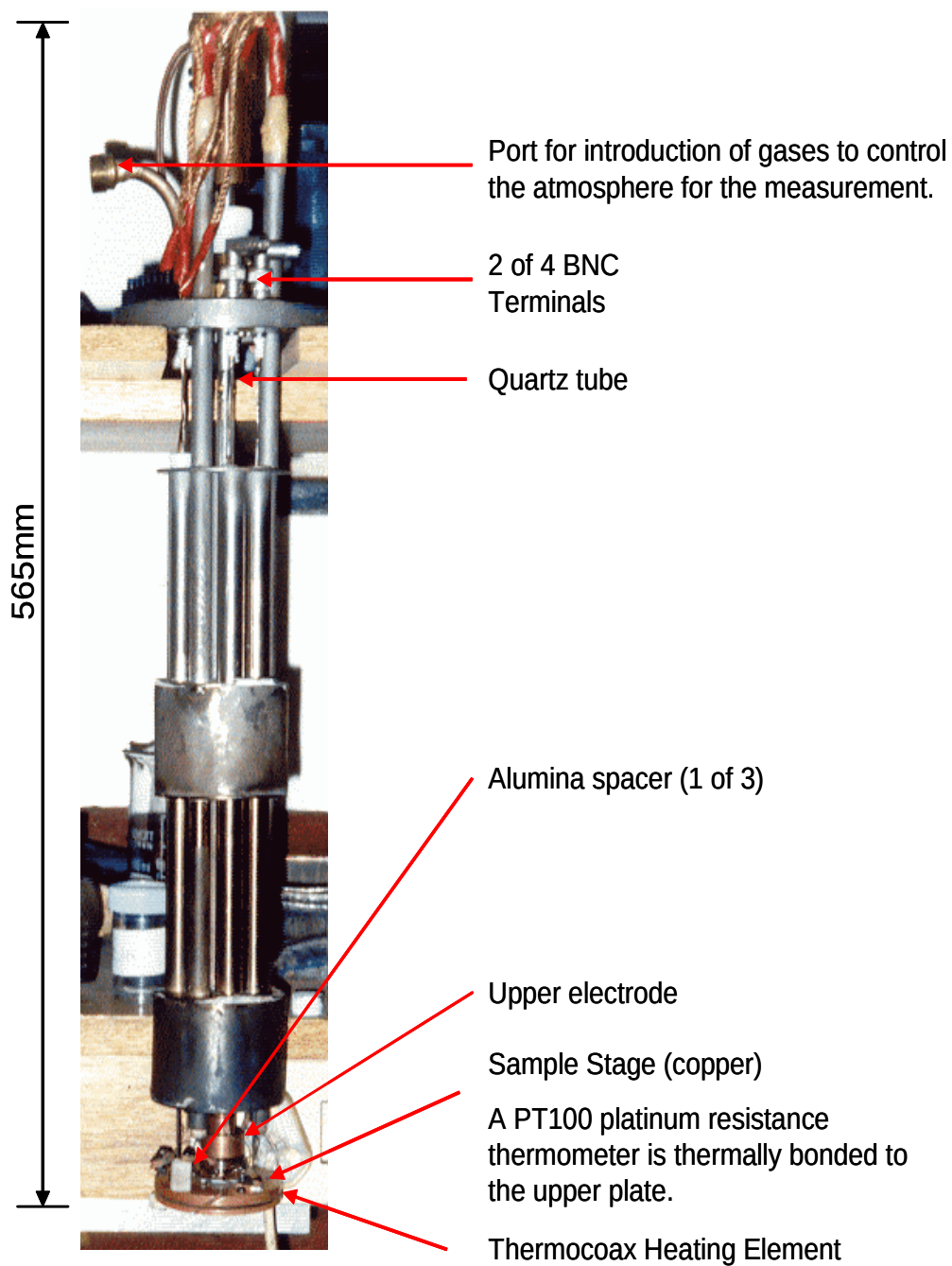


Figure 2.3: The sample holder designed and constructed for measurements at high temperatures.

stage and the inner oven wall, in the event of contact being made during the heating or cooling process.

Two meters of Thermocoax heating element (Thermocoax, France), was wound in-between the two copper plates forming the base and lower electrode. The resistance of this length of the Thermocoax was impedance matched for obtaining the maximum power output from the temperature control unit as per the manufacturers' instructions. Mounted upon the sample stage was a PT100 platinum resistance thermometer. Having the heating element and the thermometer in close proximity to the sample enabled maximum heating and temperature control to be obtained.

A copper upper electrode was kept firmly pressed onto the sample, via a spring, by a quartz tube upon which a constant load was applied through a sliding o-ring. The quartz tube ensured minimal electrical and thermal contact between the sample and the oven walls while the spring protected the fragile quartz from breakage due to the movement from the expansion and contraction of other parts of the unit.

Various gases, such as nitrogen, could be introduced into the measurement oven through a port at the top of the sample holder, when such an atmosphere was required. In this design, an oxidizing atmosphere could not be maintained for long periods at high temperatures because of the copper components of the sample holder which would be oxidized.

2.5.2 The measurement setup

Figure 2.4 shows the basic setup for a dielectric measurement. An ac excitation signal produced by the generator is applied to the sample and the complex voltage across the sample U^* and the current I^* as well as the phase shift between the current and the voltage are measured. The complex parallel capacitance of the sample C_p^* is then

$$C_p^* = -i \frac{I^*}{\omega U^*} - C_{edge},$$

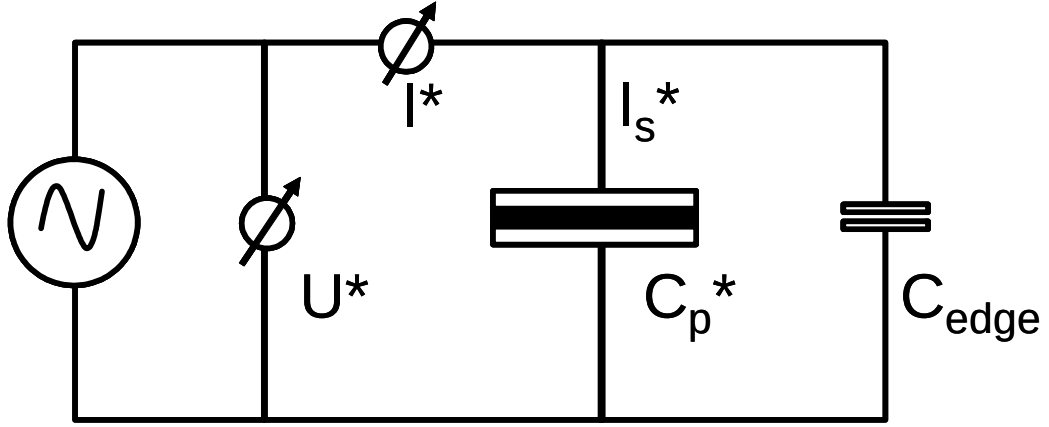


Figure 2.4: The general setup for a dielectric measurement. (Figure adopted from Schaumburg⁸⁶).

where C_{edge} denotes edge effects. Edge effects can be partly corrected for and this was done by the measurement software, as described in [Schaumburg⁸⁶ and Novocontrol⁸⁸].

The sample impedance is then

$$Z_s^* = -\frac{i}{\omega C_p^*}.$$

Other immittance data is calculated from the above using the functions in Table 1.1.

Greater detail on how the ac measurement is carried out, using the Novocontrol Broad Band Dielectric Converter (BDC) and Solartron SI1260 Impedance /Gain-Phase Analyzer as a generator and detector, is shown in Figure 2.5. The generator (Solartron SI1260) drives the sample with the voltage U_s which is directly measured with channel I (Ch I, in the figure) of a vector voltage analyzer (VVA; Solartron SI1260). The current I_s is measured with the VVA's channel II (Ch II) after it is transformed by a current to voltage converter. The VVA uses the same principal as lock-in amplifiers. Two internal harmonic reference signals, shifted by 90° in phase, are multiplied with the measured signal. After averaging over many periods, both signals correspond directly to the input signal's real and imaginary parts [Novocontrol⁹⁰ and Schaumburg⁸⁹].

A schematic of the experimental setup used for carrying out the ac and

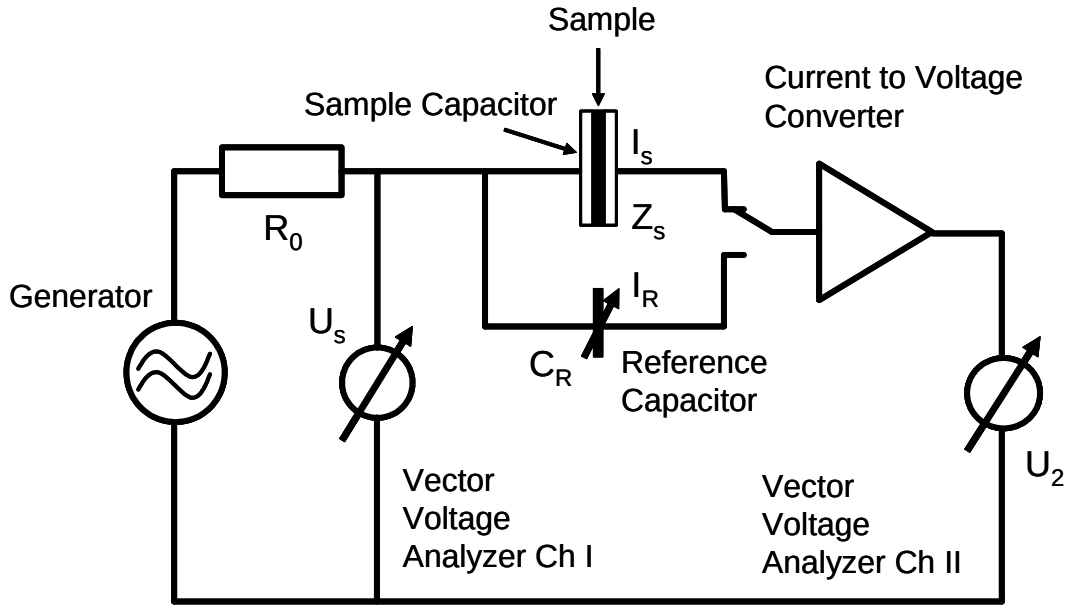


Figure 2.5: Detailed setup of a dielectric measurement using the Novocontrol BDC + Solartron SI1260. (Figure adopted from Schaumburg⁸⁹).

dc measurements in a suitable atmosphere and at controlled temperatures is shown in Figure 2.6. Either the Novocontrol Broadband Dielectric Converter (BDC) and/or the Solartron SI1260 were used for the ac conductivity measurements. The BDC + Solartron combination is a two probe arrangement with an impedance measurement range of 10Ω to $200 \text{ T}\Omega$ at frequencies ranging from $10 \mu\text{Hz}$ to 10 MHz and a $\tan(\delta)$ resolution $< 0.1 \text{ mrad}$ [Novocontrol⁹⁰]. The Solartron SI1260 on its own is configured for four probe measurements and has an impedance measurement range of $10 \text{ m}\Omega$ to $100 \text{ M}\Omega$ at frequencies ranging from $10 \mu\text{Hz}$ to 32 MHz and a $\tan(\delta)$ resolution $< 4 \text{ mrad}$ [Novocontrol⁹⁰]. The dielectric spectrometers (the BDC and Solartron SI1260) were connected to a controlling computer on an IEEE bus. The measurements were setup and run using WinDETA 3.4 software (Novocontrol GmbH, Hundsangen, Germany).

For most measurements, sample excitation voltages of 1.5 V for the BDC + Solartron combination and 0.7 V for the Solartron SI1260 on its own were used. In measurements where the voltage dependence of the sample properties was being investigated in detail, other excitation voltages were used and these will be indicated. No dc bias voltage was applied to the sample in any of

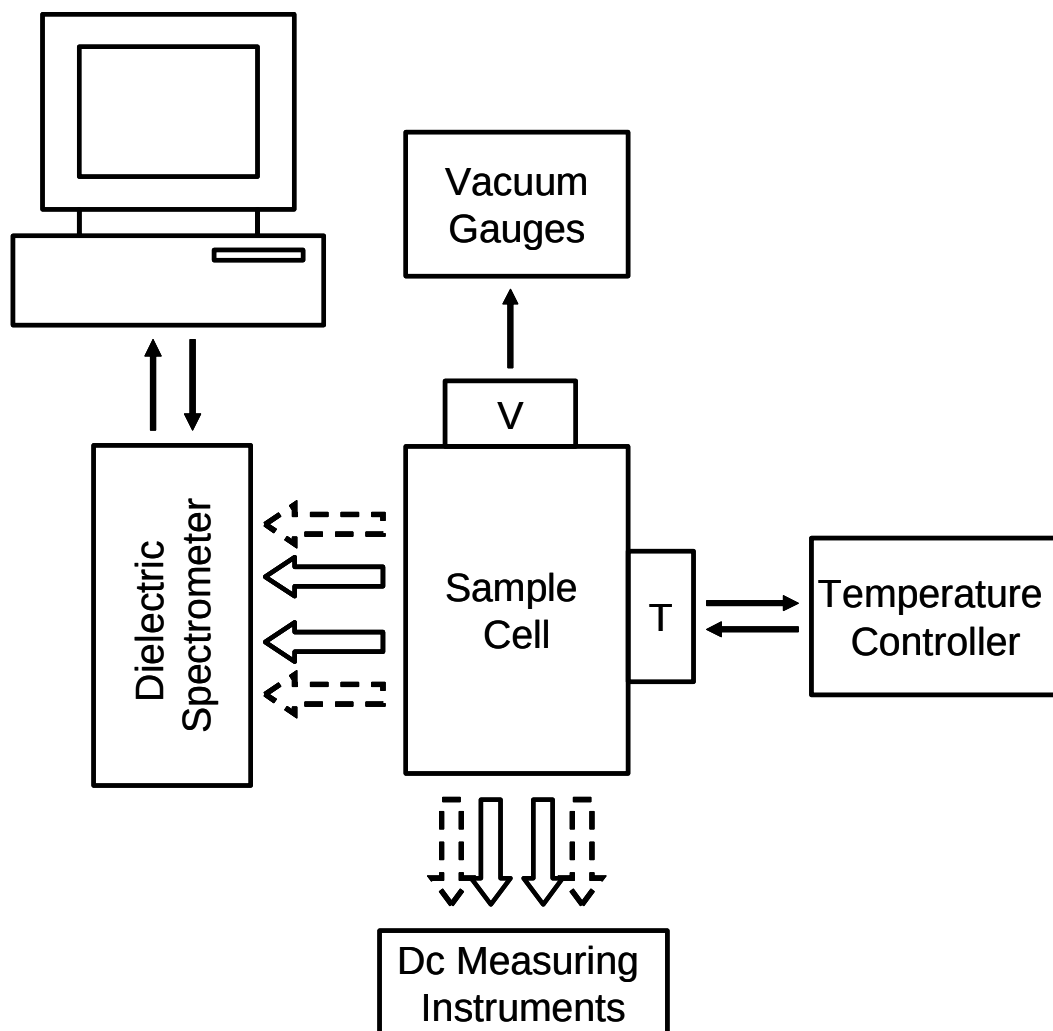


Figure 2.6: A schematic of the instrumentation setup for taking ac and dc measurements in a suitable atmosphere and at controlled temperatures. The broad arrows indicate measurement connections (2 or 4 probe), while the single arrows indicate both analogue and digital data flow between instruments. T are the primary temperature control hardware (thermometers and heating elements) mounted onto the sample holder and on the oven, while V are the vacuum control hardware (gauge heads, pumps) mounted onto various vacuum lines leading into and out of the oven. Note that vacuum gauges only monitor the state of the vacuum, there is no control signal to the pumps.

the measurements discussed in this work. Where the electrical properties of interest were in the optimum frequency and resistance range of both the BDC + Solartron and the Solartron 1260 on its own, both configurations were used for cross checking purposes. Mason et al.⁸⁵ and Dygas et al.⁹¹ assert that the comparison of the results obtained by two and four probe techniques is *crucial* for avoiding erroneous interpretation of impedance spectroscopy data.

Sample temperature was monitored and controlled to ± 0.5 °C by a LakeShore DRC93-CA controller (LakeShore Cryotronics Inc. Westerville, Ohio, U.S.A.). This controller received input from the PT100 platinum resistance thermometer mounted on the sample stage and drove the Thermocoax heating element, wound between the plates making up the stage, via a Hewlett Packard (HP 6274B) dc power supply (Hewlett Packard Berkeley Heights New Jersey U.S.A.) acting as a current amplifier. Edwards rotary vane pumps were used to maintain a vacuum of ~ 10 milliTorr which was necessary to protect the copper components in the sample holder from oxidation as well as for providing a suitable atmosphere for measuring sample electrical properties known to be atmosphere dependent. Dc measurements were also carried out in conjunction with the ac measurements. These were mainly for use in cross checking and validating the low frequency ac data. A Keithley 617 Electrometer (Keithley Instruments Inc, Cleveland, Ohio, U.S.A.) in V/I mode [Keithley⁹²] was used for measuring impedances greater than 1 M Ω and a combination of a LakeShore 120 Current Source and Prema 5000 Digital Multimeter (Prema, Mainz, Germany) was used for measuring resistances below this value. A Wavetek DM28XT multimeter ($\sim 0 \Omega - 2 G\Omega$; Wavetek Corporation, Instruments Division, San Diego, U.S.A.) and a Keithley 614 Electrometer ($1 \Omega - 200 G\Omega$) were also used in the appropriate resistance ranges.

The measurements on the silicon carbide samples at liquid nitrogen temperature were carried out by placing the sample in a long glass walled sample holder and then suspending this in a liquid nitrogen dewar.

Non-linear voltage dependence as well as some low temperature measurements on the liquid-phase-sintered and solid-state-sintered silicon carbide samples were carried out by the present author, on Novocool and Novotronic Systems at the *Advanced Materials and Processing Branch, NASA Langley Research Center (NASA-LaRC)*, Hampton VA., U.S.A.

2.6 Data manipulation and analysis procedures

Ac conductivity measurements generate a large amount of data which can be represented and analyzed in a variety of ways. For each sample there may be say 50 frequency points, at each temperature, where a measurement is carried out and typically 7 or more temperature points per sample. This poses a major challenge in order that all this data is analyzed in a systematic manner. To aid the process, a number of procedures were developed for automated data handling and implemented as *Mathematica* notebooks and packages. Some of these procedures utilized techniques that are, to the best of this author's knowledge, first described in this work.

2.6.1 Data validation using the Kramers Kronig Transforms

Before experimental data is fully analyzed, it is often useful if there is some way of validating it. This enables experimental errors to be detected and eliminated and avoids incorrect conclusions being drawn from erroneous data. One way of validating impedance spectroscopy data is through the Kramers-Kronig transforms (see Section 1.6).

In principle, the K-K transforms requires an infinite frequency range, which is not available in practice. However, numerical approximations can be made that enable the practical use of the relations. A numerical integration algorithm suggested by Brather⁹³, further developed by Steeman and van Turnhout⁷⁸ and implemented as a *Mathematica* notebook by Bange and Blischke⁹⁴ and altered by this author to automatically handle multiple data

files, was used in this work.

The forms of the K-K relations used for data validation are [Boukamp⁷⁷, Agarwal et al.⁹⁵]:

$$Z''(\omega_0) = -\frac{2\omega_0}{\pi} \int_0^\infty \frac{Z'(\omega) - Z'(\omega_0)}{\omega^2 - \omega_0^2} d\omega \quad (2.1)$$

and

$$Z'(\omega_0) = Z'_\infty + \frac{2}{\pi} \int_0^\infty \frac{\omega Z''(\omega) - \omega_0 Z''(\omega_0)}{\omega^2 - \omega_0^2} d\omega. \quad (2.2)$$

These expressions are obtained by substituting the impedances into the K-K equations for the general immittance function, Equations 1.24 and 1.25.

For data validation, imaginary impedance data was calculated from numerical integration of the experimentally measured real impedance data, using the *Mathematica* notebook described above. The calculated and experimental imaginary impedance data was then compared. For a valid measurement, the calculated data and the experimental data should be essentially the same, save for some minor discrepancies due to the approximations used in the numerical integration process.

2.6.2 Preparation of data for detailed fitting and the separation of impedance arcs

The steps described in this section were carried out before or after the data validation process (Section 2.6.1).

A systematic procedure for the initial manipulation of the data was developed. This procedure enabled data obtained as ASCII files from the WinDETA software controlling the measurement (see Section 2.5.2), to be converted into forms more suitable for displaying, interpretation and fitting. The version of the measurement control software used in this work, WinDETA 3.4, allowed for at most 8 columns of data at a time to be exported as ASCII files. Two of these were the independent variables, frequency and time and six dependent variables of the user's choice. The dependent variables exported by this author were the real dielectric constant and the dielectric loss, the real and imaginary conductivities and the real and imaginary impedances. Even

though variables other than the above could also have been obtained, it was decided to calculate these, as required at the point of use, using the standard relations in Table 1.1. Maintaining a compact set of data minimized the time consuming shuttling between the measurement control and data analysis computers, which sometimes leads to file mixups.

Note that the separation of arcs using the derivatives, $\tan(\delta)$, $1/\tan(\delta)$ and the imaginary impedance, $-Z''$, steps 4 to 7 in the procedure listed below will be further discussed later in this section.

The automated data manipulation procedure was applied as follows:

1. Initial data formatting operations. $\text{Log}[\omega]$ was evaluated from the cyclic frequency, f ($\omega = 2\pi f$). Conductivity values, given in $(\Omega\text{cm})^{-1}$ by WinDETA, were converted to SI units and the sample geometric factor independent specific impedances Z' and Z'' were calculated. At each frequency point, values of the real and imaginary modulus (M' and M'') as well as $\tan(\delta)$ and $1/\tan(\delta)$, used in arc separation, were calculated and two pairs of columns consisting of these values was added to the already existing data columns. The loss factor, $\tan(\delta)$ is defined as:

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} = -\frac{Z'}{Z''}.$$

2. Data selection. Unrealistic or obviously nonphysical values, particularly those occurring at the extremes of the available frequency range, where the measuring instruments were really operating at their limit, were removed.
3. Check for data consistency. After elimination of unrealistic data points, most sample data varies in a smooth manner, and with some degree of monotonicity (increasing or decreasing) as a function of the frequency. Checks were carried out to ensure that the data was varying as expected. If several points were not varying in the expected manner, they may have, after careful deliberation, been removed from the analysis.

4. Derivatives calculation. The first and second slopes of the imaginary vs real impedance, dZ''/dZ' and d^2Z''/dZ'^2 were numerically calculated. As described below, these derivatives were a key tool in accurately determining the regions of overlap between the impedance arcs and sometimes for indicating the start or finish of an arc for which there was insufficient data.
5. Determination of turning points. Maxima and minima in the imaginary impedance, the impedance derivatives, $\tan(\delta)$ and $1/\tan(\delta)$ data were determined.
6. Arc separation. The information on the turning points was used to determine the region in which the arcs overlap. Separate arcs were obtained by taking only the data on either side of the overlap region. The use of the turning points data, to determine the arc overlap regions, is further explained in the pages that follow.
7. Separated arc cleanup. The separated arcs from step 6 were further analyzed to check for any distortions indicative of contributions from neighboring overlapping arcs. These distortions, if found, were removed by a procedure to be described below.
8. Data storage. The separated arcs, with electrode arcs removed, as well as combined arcs in the frequency range covered by the clean separated arcs were stored for further analysis. The latter data represented the properties of the composite free of erroneous points.

The above procedure was implemented as a *Mathematica* notebook, together with the associated packages (sub-programs). These are all however too long and complex to be included in this thesis.

Other impedance data representation formats to enable the identification of contributions to the spectra have been suggested by various authors. Abrantes et al.^{96, 97, 98} describe and demonstrate the use of a representation

based on Z' vs (Z''/f) and the corresponding derivative $dZ'/d(Z''/f)$, where f is the frequency, in hertz.

In their work Ruiz-Morales et al.⁹⁹ describe an impedance data representation using the derivative of the tangent of the phase angle which allows discrimination between impedance processes within a factor of 2 in their relaxation frequencies for processes of similar strength. Further references to other procedures for resolving the contributions of the components to the impedance spectra of composites can also be obtained in this work.

Arc separation using the impedance derivatives, imaginary impedance, $\tan(\delta)$ and $1/\tan(\delta)$, is a procedure that enables the frequency regions where the contributions to the impedance spectrum are dominated by a single component to be identified. This procedure, which can be readily implemented by computer and used to obtain parameters for use in detailed fitting of the data is described below. No assumptions about the source of the contributions leading to the arcs, such as the circuit elements used in equivalent circuit based fitting programs like that used in Boukamp⁶, Santos and Domingues¹⁰⁰ and by other authors, are required here. At this stage, no particular physical model is chosen for the dispersive properties of the components of the composite, as is done in Pizzitutti and Bruni¹⁰¹. The data need not be described by an equivalent circuit or any other model at all, including those used in this work. Characteristic trends in impedance spectroscopy data and the mathematical properties of semicircles (and depressed semicircles) are utilized instead. Derivatives can be used to highlight features in the impedance, modulus or any other representation which gives arcs in the complex plane. For practical arc separation, the derivatives data must be used together with other representations to increase robustness and noise immunity as discussed below using the impedance derivatives. The procedure is very fast as it does not require least squares fitting, which often takes a lot of time and manipulation of starting parameters, for a good fit to be obtained. All computation steps are mostly simple data manipulation.

Separation of arcs using the first and second derivatives data as well as the

imaginary impedance and $\tan(\delta)$ data is based on finding regions (frequency or real impedance) for which all or some combination of the following is true:

1. The region is bordered by a maximum and minimum in the derivative, dZ''/dZ' .
2. The region contains a peak in the second derivative, d^2Z''/dZ'^2 .
3. The region features a peak or trough in $\tan(\delta)$ or $1/\tan(\delta)$.
4. The region features a trough in the imaginary impedance or at least does not contain any of the peaks in the imaginary impedance, $-Z''$.

In practice, not all of the above conditions are always met. For example large overlap of the arcs can lead to there being no clear troughs in the imaginary impedance data. Further, noise in the experimental data often makes it difficult to detect whether or not the conditions are met. Some stray points could be misinterpreted as being a peak. In cases where most of the above conditions are not met, the arc separation algorithm fails. This was found to occur in less than 10% of the data studied in this work. Usually, a combination of some of the conditions above is sufficient to clearly identify the arc overlap region and therefore to separate the arcs. Note that the procedure is based on finding turning points (local maxima or minima) in the data which can readily be picked out by a computer program. More complex features in the data such as shoulders, where there is a change in the magnitude but not sign of a slope are generally more difficult to directly pick out as this change can occur slowly. To increase the probability of obtaining clearly identified arc overlap regions, the different data representations (derivatives, $\tan(\delta)$, $1/\tan(\delta)$, imaginary impedance) are all used, because peaks (and troughs) occur in them at slightly different but related frequencies, giving a range of easily detectable indicators of the arc overlap regions.

The patterns in the data on which the separation process is based and which the program detects are further described below:

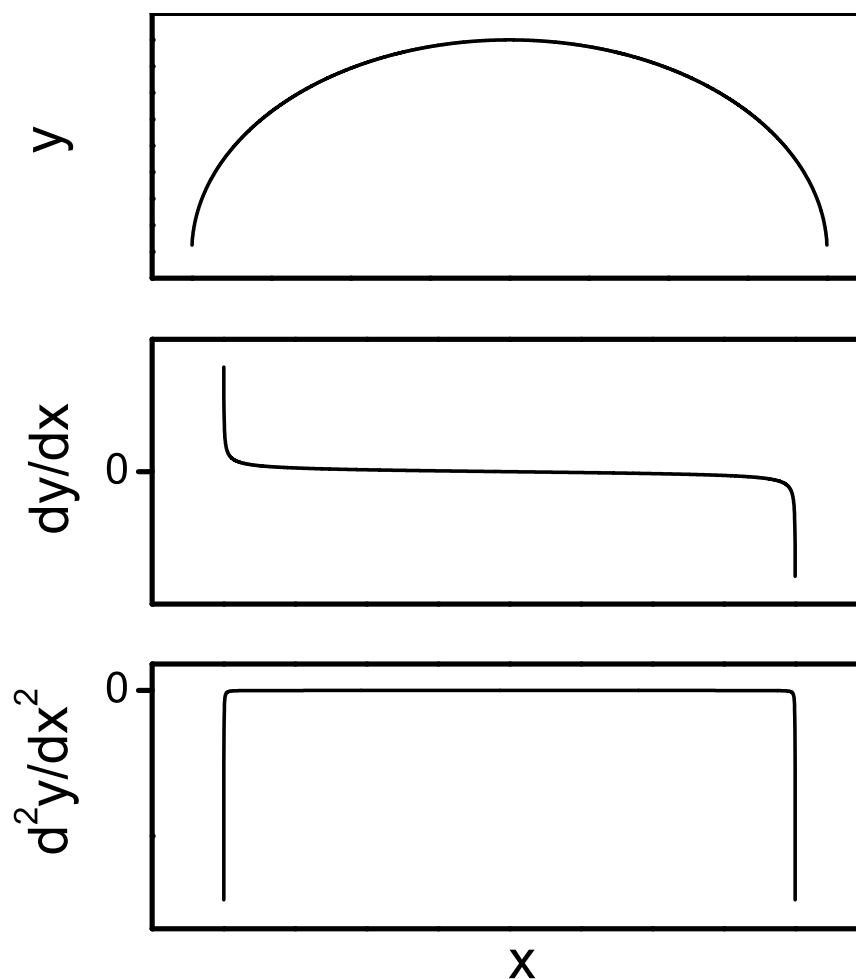


Figure 2.7: A semicircle (top) and the characteristic first and second derivatives (middle and bottom respectively). The particular shape of the derivatives, i.e. asymptotic at the ends and nearly flat in the middle is used in impedance arc separation as a means of identifying when an arc is or is not distorted by the presence of neighboring arcs.

- Figure 2.7 shows a semicircle and its first and second derivatives. Each of these derivatives has a characteristic shape. The first derivative has a positive asymptote, goes through zero and ends with a negative asymptote. The second derivative has negative asymptotes at either end, separated by a relatively flat region. Whenever there is an overlap of semicircles, the asymptotes in the derivatives of the individual semicircles are modified to local peaks and troughs, whose amplitude depends on the amount of overlap.

It is these characteristic shapes/patterns which are used in the current

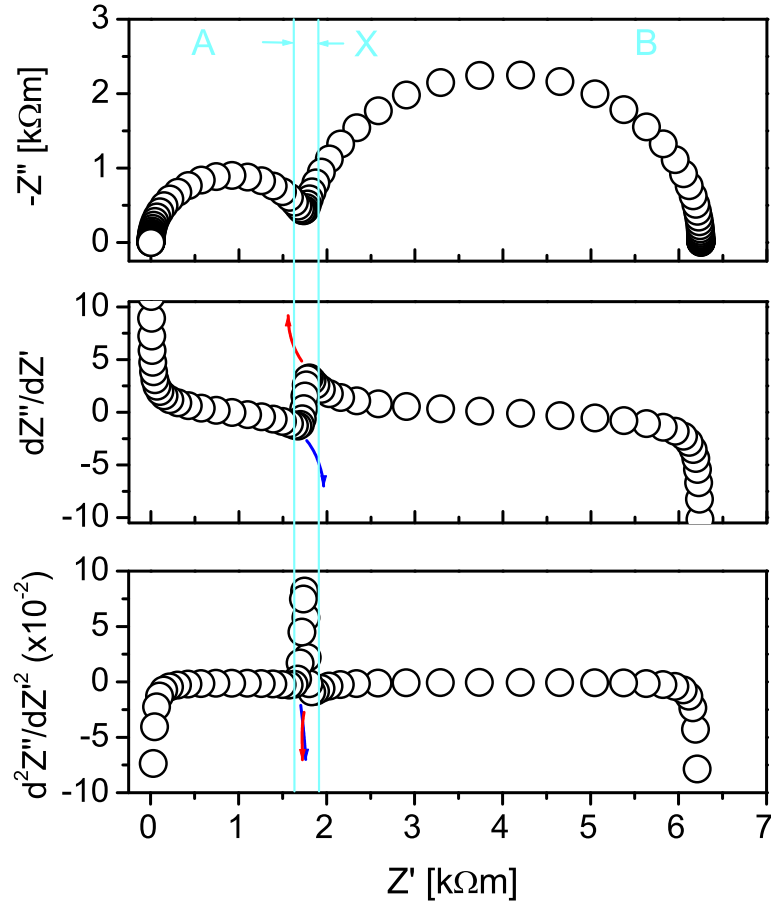


Figure 2.8: The complex impedance plane plot (top), the first derivative (middle) and the second derivative (bottom) of simulated composite data. In this case the arcs *A* and *B* only overlap slightly and therefore the turning points (maxima or minima in the slopes), forming the boundaries of the overlap region, *X*, are clearly observed. The arrows on the slopes indicate the direction of the asymptotes for the individual arcs, had these arcs not been overlapping. (see Figure 2.7).

procedure to identify the overlap region. Figure 2.8 shows arcs that overlap slightly and their characteristic first and second derivatives.

The derivatives are shown using an expanded frequency scale in the slope vs $\log(\omega)$ plot in Figure 2.9. The key points to note, in the figures, are the local maxima and minima of the first and second derivatives in the region labeled *X*, which corresponds to the overlap region in the complex impedance plane plot. In practice, *X* is defined to be a few points (user defined) outside the zone bounded by the maximum and minimum of the first derivative.

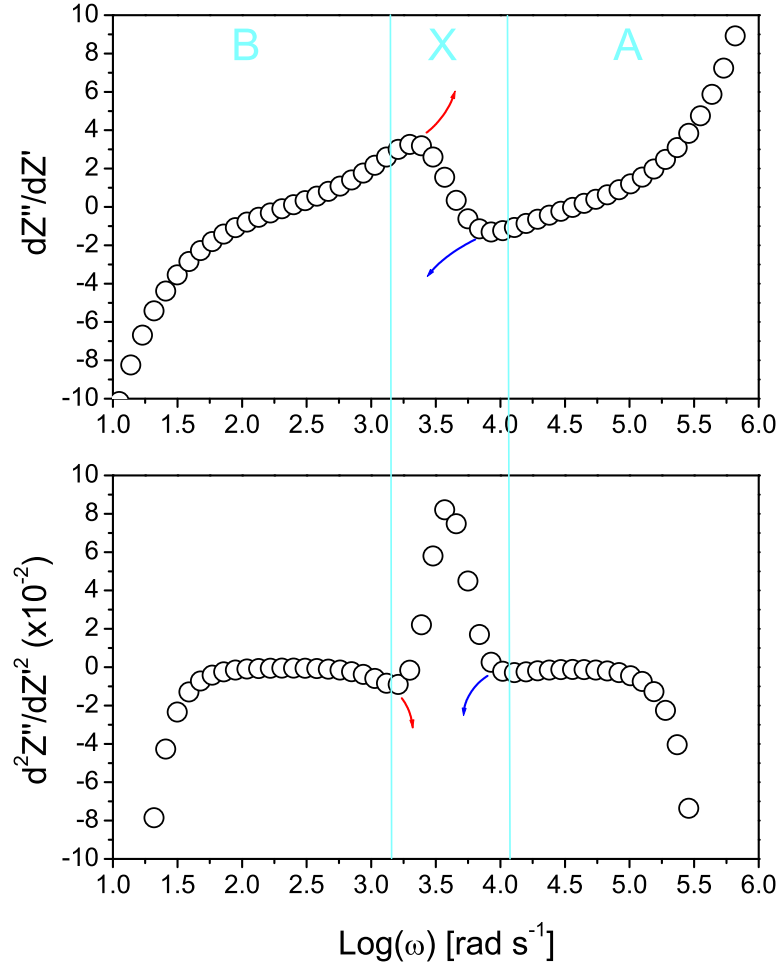


Figure 2.9: The first and second derivatives of simulated composite data featured in Figure 2.8, this time plotted as a function of $\log(\omega)$. This highlights the arc overlap region X . The points in this region do not belong exclusively to either arc A or B and therefore they are dropped from the individual arc data, in the arc separation process. Note though that they are still part of the combined data for the composite. The arrows on the slopes indicate the direction of the asymptotes of the individual arcs had these arcs not been overlapping. (see Figure 2.7).

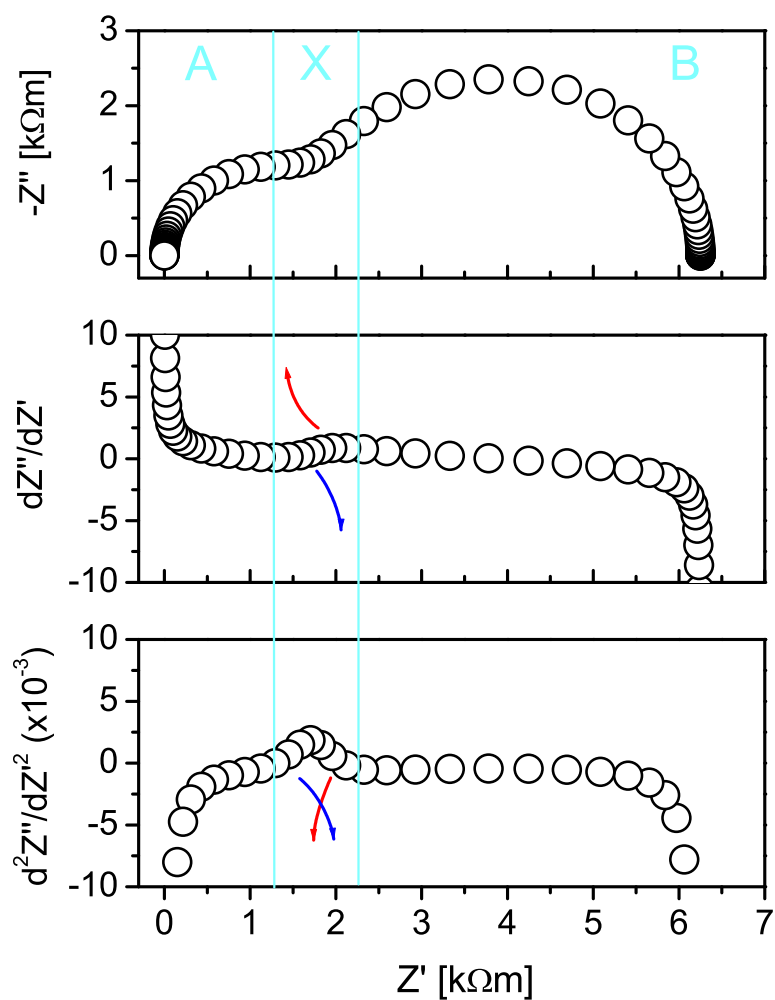


Figure 2.10: The complex impedance plane plot (top), first derivative (middle) and the second derivative of simulated composite data. In this example, there is greater overlap of the arcs than in the previous case and the turning points in the derivative data are not as sharp as in the previous example. However, there are still sharp enough to be readily picked out by a peak seeking routine.

Figure 2.10 shows arcs that overlap by a greater amount than those in the previous case and the characteristic derivatives. These derivatives are shown using an expanded frequency scale in the slope vs $\log(\omega)$ plot in Figure 2.11. The same key features seen when the arcs overlapped slightly are observed, but on a reduced scale. However, the extent of the overlap region can again be determined from the local maximum and minimum in the first derivative. The peak in the second derivative centered in this same region serves as part of the conformation to its being the overlap region.

The arc separation procedure is based on finding series of points in the actual experimental data whose structure corresponds to that of the region labeled *X* in Figures 2.8 to 2.11. When looked at in the slope vs $\log(\omega)$ plots, this requires that there is a maximum and a minimum in the first derivative bracketing a peak in the second derivative.

Unfortunately, the arc overlap regions cannot always be conclusively identified from the derivatives data alone. Often, noise in the experimental data, which is amplified when the derivatives are computed, may cause features that are not true turning points to be incorrectly identified as turning points and therefore potentially lead to the wrong identification of overlap regions. In practice, there are not always as many experimental points as those shown in the previous figures from which the overlap region can be identified. Therefore, a decision has to be made as to the minimum number of points that must match the pattern for the overlap region to be deemed identified. A balance needs to be struck between aggressive searching for overlap regions, which calls for the number of points needed to identify such a region to be small and conservative searching where more points are required and which leads to greater certainty that only genuine overlap regions are identified as such.

For example, a conservative search routine which calls for at least 5

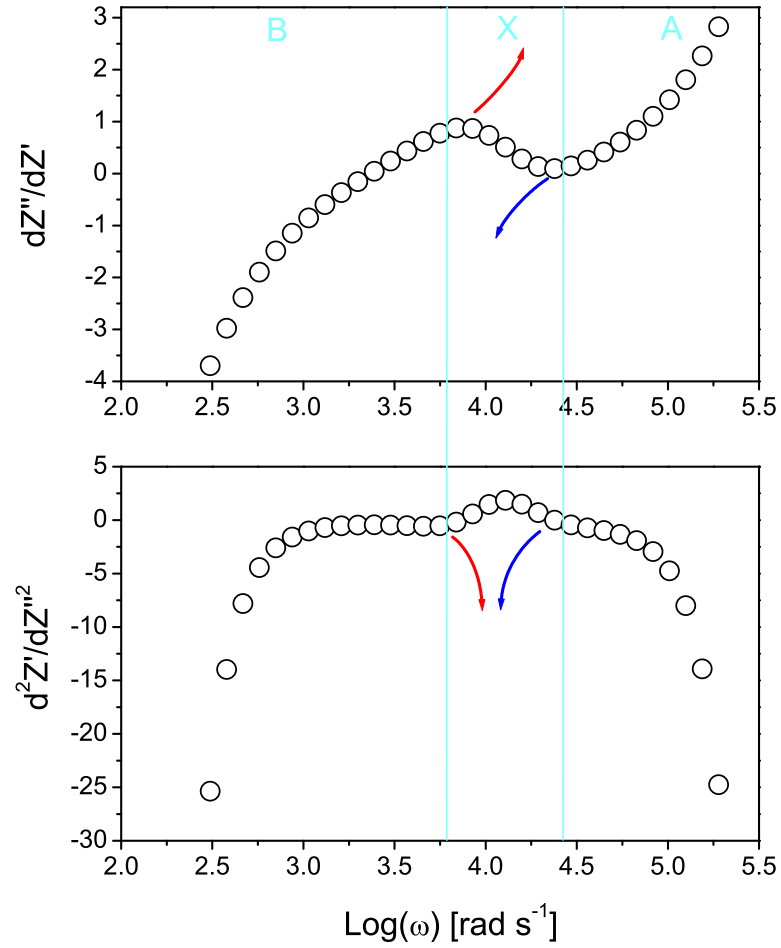


Figure 2.11: The first and second derivatives of the simulated composite data featured in Figure 2.10, this time plotted as a function of $\log(\omega)$. This highlights the arc overlap region X . The points in this region do not belong exclusively to either arc A or B and therefore they are dropped from the individual arc data, in the arc separation process. Note though that they are still part of the combined data for the composite.

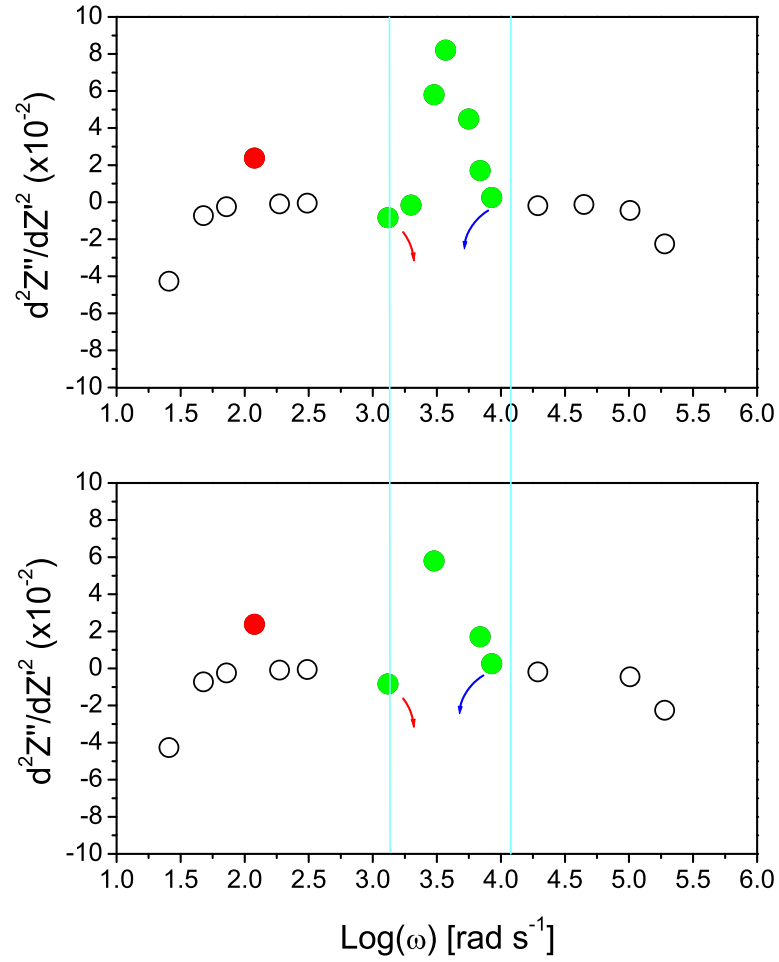


Figure 2.12: Two peaks are shown for which there is a different number of points by which they can be identified. A conservative routine would only find the one at the top and not that at the bottom and would not have any problems with the spurious point (red dot). On the other hand, an aggressive routine would find both the peaks but is also likely to identify the spurious point as being a peak.

points to clearly identify a peak would pick out the peak at the top of Figure 2.12 but not the one at the bottom. It would also not have any problem with the spurious data point shown in red in the figure. On the other hand, a more aggressive routine which requires only 3 points to identify a peak would locate the peaks in both the top and bottom plots in Figure 2.12 but would also likely indicate that the spurious point qualifies as a peak. The current routine uses an adjustable sensitivity for peak detection and ensures that the overall pattern in the data, including the positions and number of peaks identified, matches that expected for overlapping arcs. In the current analysis procedure the derivative turning points are stored as *potential* boundaries to the overlap regions and further analysis, based on the other data representations, ($\tan(\delta)$, $1/\tan(\delta)$ and imaginary impedance), is carried out to conclusively identify any of these as the correct boundaries of overlap regions.

- As shown in Figures 2.13 and 2.14, a feature such as a peak, trough or asymptote in the $\tan(\delta)$ or $1/\tan(\delta)$ plot corresponds to some feature of interest in the sample impedance plot, such as a peak (indicating the characteristic frequency of a contributing component) or an arc overlap region (see Figures 2.8 to 2.11). The peaks or troughs do not identify any clearly defined boundaries and therefore they cannot be used in themselves to map out overlap regions. However, they do give some indication of where the overlap regions are.

The following features of the $\tan(\delta)$ and $1/\tan(\delta)$ and imaginary impedance data, which are illustrated in Figures 2.13 and 2.14 are used in the arc separation process:

1. At the ends of arcs (individual or a series of overlapping), where $Z'' \rightarrow 0$ and sometimes $Z' \rightarrow 0$ (high frequency end), there is an asymptote in $\tan(\delta)$ or $1/\tan(\delta)$ (recall that $\tan(\delta) = -Z''/Z'$). This is observed in the regions labeled 1 and 4 in Figures 2.13 and

2.14 and therefore identifies these as the start and end positions of the arcs.

2. Where there are arcs overlapping, $Z'' \rightarrow 0$ for each of the arcs and therefore what would have been asymptotes in $\tan(\delta)$ are modified to peaks, due to the influence of both the overlapping arcs. This is the peak labeled 2 in the figures. In Figure 2.13, this peak coincides with a trough in $-Z''$ therefore confirming that it is indeed in the overlap region. Note also that this is the same region X identified earlier using the derivatives and which was linked to the overlap region in the complex impedance plane plot. Figure 2.14 shows that in the case where there is a great amount of overlap between the arcs, there is only a shoulder in $-Z''$, but there is still a clearly identifiable peak in $\tan(\delta)$, which can be readily detected by computer.
3. Peaks (troughs) in $1/\tan(\delta)$ ($\tan(\delta)$) also occur near the imaginary impedance peaks, where $-Z''$ becomes large for relatively small values of Z' . These peaks lie at frequencies close to those of the imaginary impedance peaks and are therefore readily associated with them rather than being mistaken as indicating overlap regions. The peaks (troughs) labeled 3 in Figures 2.13 and 2.14 are examples of $1/\tan(\delta)$ peaks that lie close to the imaginary impedance peaks.

While in the case of arcs that just overlap, the peaks and troughs in the imaginary impedance and the complex impedance plot appear distinct enough to be used by themselves to determine the key points of the arcs, this is not always the case with real experimental data, in which there are various degrees of overlap and noise in the data and therefore the need for the confirmations using different data representations.

In the **next step of the analysis**, part of the procedure, outlined above, is repeated on each of the separated arcs. The slopes of these arcs and the

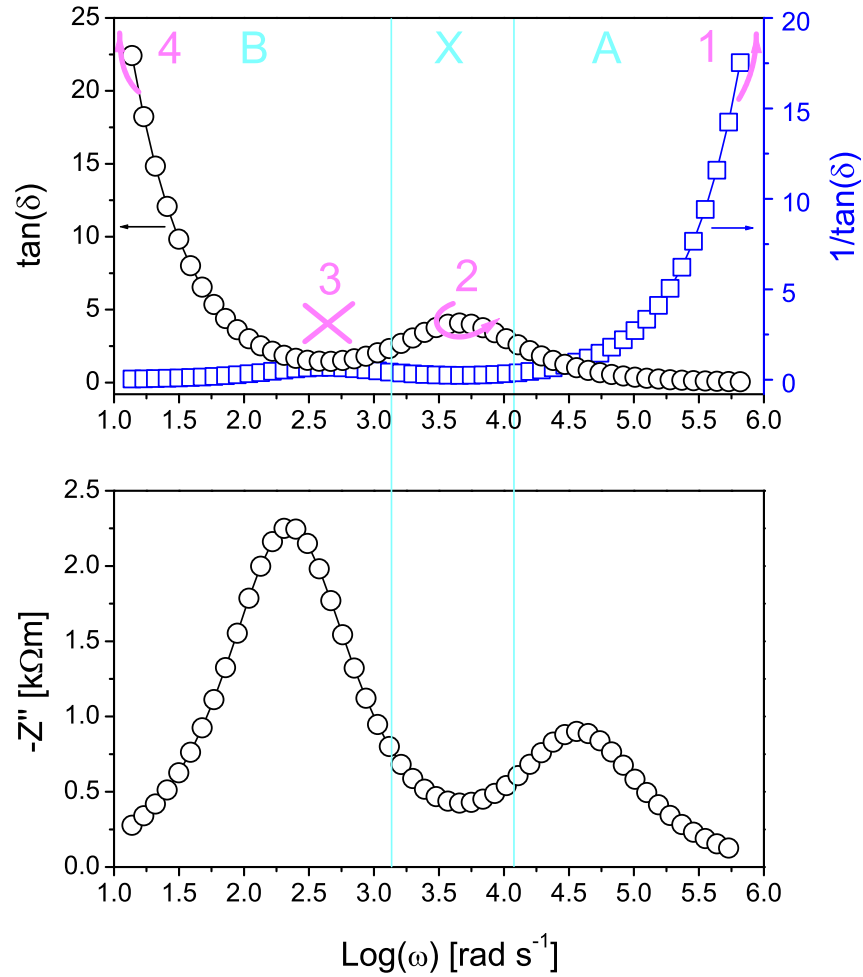


Figure 2.13: The key points in typical $\tan(\delta)$ and $1/\tan(\delta)$ curves (top) used in determining arc overlap points, and how they relate to key points in the imaginary impedance plot (bottom). The significance of the various labeled regions is explained in the text. The data featured here is the same as that of the simulations in Figures 2.8 and 2.9, for which the overlap region of the arcs can readily be determined from the imaginary impedance and other data. The range of frequency points displayed has been chosen to highlight the overlap region X. Note that $\tan(\delta)$ and $1/\tan(\delta)$ continue their rise, (see 1 and 4 in the figure), even at frequencies beyond those in the plot.

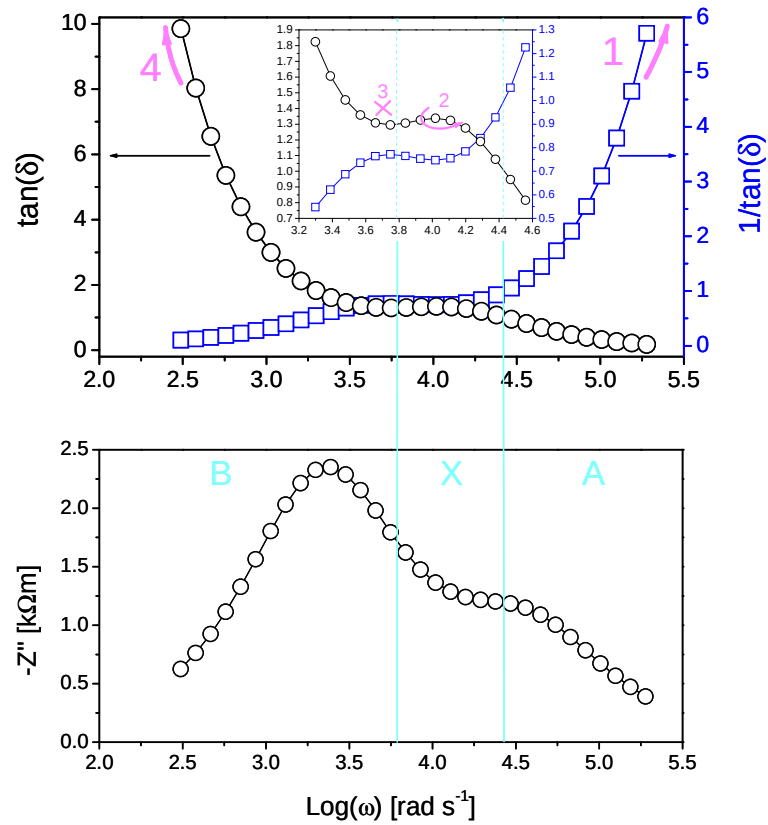


Figure 2.14: The key points in typical $\tan(\delta)$ and $1/\tan(\delta)$ curves (top) used in determining arc overlap points, and how they relate to key points in the imaginary impedance plot (bottom). The significance of the various labeled regions is explained in the text. The data featured here is the same as that of the simulations in Figures 2.10 and 2.11, for which there is greater overlap between the arcs. The range of frequency points displayed has been chosen to highlight the overlap region X. Note that $\tan(\delta)$ and $1/\tan(\delta)$ continue their rise, (see 1 and 4 in the figure), even at frequencies beyond those in the plot.

$\tan(\delta)$ and $1/\tan(\delta)$ values, particularly those near the ends of the arcs are compared to what would be expected for “perfect” individual semicircles (or depressed semicircles). Any points not consistent with the expected form of a “perfect” single arc are removed.

The above procedure is not always successful in separating out arcs, however, it was found to succeed in the majority of the cases ($> 90\%$) tested. Noisy derivative data was often the cause of the failures as it prevented turning points from being located or lead to multiple turning points being erroneously identified. Due to their length, examples of the arc separation process, for some actual experimental data, are given in Appendix A.

2.6.3 Analysis of impedance arcs and extraction of component parameters

It is vitally important to be able to obtain some useful information from the composite material’s ac conductivity data before fitting to any Effective Media or other models aimed at relating the composite properties to those of its components. If known, the information can be utilized in formulating parameter starting and boundaries values for any fitting, or to identify and describe the components of the composite. The information from the arcs is mainly in the form of obvious peaks and, sometimes more difficult to determine, arc-axis intercepts. Greater understanding and utilization of these could widely extend the use of ac measurement techniques in studying materials.

A number of the properties of the components of a composite can be obtained by analyzing the separated arcs. The characteristic frequency (i.e the frequency at the top of the arc in a complex impedance plane plot) is one such useful property that can be readily obtained from the data. This frequency can be more accurately determined from the $-Z''$ vs $\log(\omega)$ plots using the Lorentzian peak fitting function which, of the various peak fitting functions (Gaussian, Voigt e.t.c), was found to be the best for fitting experimental data. Single component (as opposed to composite) impedance arcs are symmetrical depressed semi-circles in the complex plane. The center of

symmetry corresponds to the characteristic frequency of the component. The contribution to the total sample dc resistance (recall that in this work specific resistances are being used) of each of these components can be estimated from its the intercepts of the arcs on the real impedance axis. Therefore, to complete arcs and estimate arc-axis intercepts a technique of data reflection across the symmetry axis was developed. This aids the visualization of the data by effectively doubling the number of available data points and gives *virtual* points at impedance values that are not experimentally accessible. Only the impedance data (Z' and Z'') can be obtained by this technique. It is not possible to convert backwards to the other properties such as the dielectric constant, dielectric loss or conductivities at specific frequencies.

The procedure used for the extraction of information from single component arcs was as follows:

1. Find the peak in the imaginary impedance vs $\log(\omega)$ data and fit it to the Lorentz function to accurately determine the characteristic frequency ω_p .

The amplitude version of the Lorentz peak function (mathematically equivalent to the area version) is,

$$Z'' = Z_0'' + (Z_{max}'' - Z_0'') \frac{w^2}{4(\log(\omega) - \log(\omega_p))^2 + w^2},$$

where the amplitude of the peak is $(Z_{max}'' - Z_0'')$, w is the full width at half maximum and ω_p is the center frequency.

2. If there are points on both sides of the characteristic frequency (i.e. the characteristic frequency is well defined), reflect the data points both ways across the characteristic frequency line. As mentioned above, this doubles the number of data points for plotting and aids the visualization of the data.
3. Fit the data for a particular component to a depressed semicircle function of the form,

$$r^2 = (x - x_0)^2 + (y - y_0)^2,$$

where (x_0, y_0) , which lies directly under ω_p , is the center of the depressed semicircle. The axis intercepts when $y = 0$, which give the resistances (or specific resistances in the current work), R_∞ and R_0 , are calculated using the best fit parameter values. The contribution to the dc resistance of the particular component is then $R_{dc} = R_0 - R_\infty$, where R_0 and R_∞ are the low and high frequency intercepts for that component. The dc conductivity, the depression angle (of the arc relative to a true semicircle, see Section 1.2) and the characteristic dielectric constant are also calculated.

4. The and peak frequency and the dc conductivity, calculated from the (specific) resistance, can then be used to characterize the material. If there are measurements at various temperatures, the temperature dependence of the characteristic frequencies and the dc conductivities can be investigated. The measured values of ω_p and σ_{dc} can also be used as starting and/or limiting parameter values in other fitting procedures.

Figures 2.15 and 2.16 show a typical run of the *Mathematica* program developed for this work, applying the procedure outlined above to obtain the characteristic frequency and contributions to the sample dc resistance from the two arcs (grain and grain boundary) of a single polycrystalline YSZ sample. Note that in this case, R_0 for the high frequency arc and R_∞ for the low frequency arc overlap and the arcs are what would have been for single components.

2.6.4 Simulations of composites

How the dispersive properties of the components affect the properties of the composites was investigated using a number of simulations of composite data. The simulations were also used to compare the results from the various Effective Media and percolation models. The simulations were also intended for investigating which of the properties of the components of the composites could still be resolved from the data for the composites, as well as how

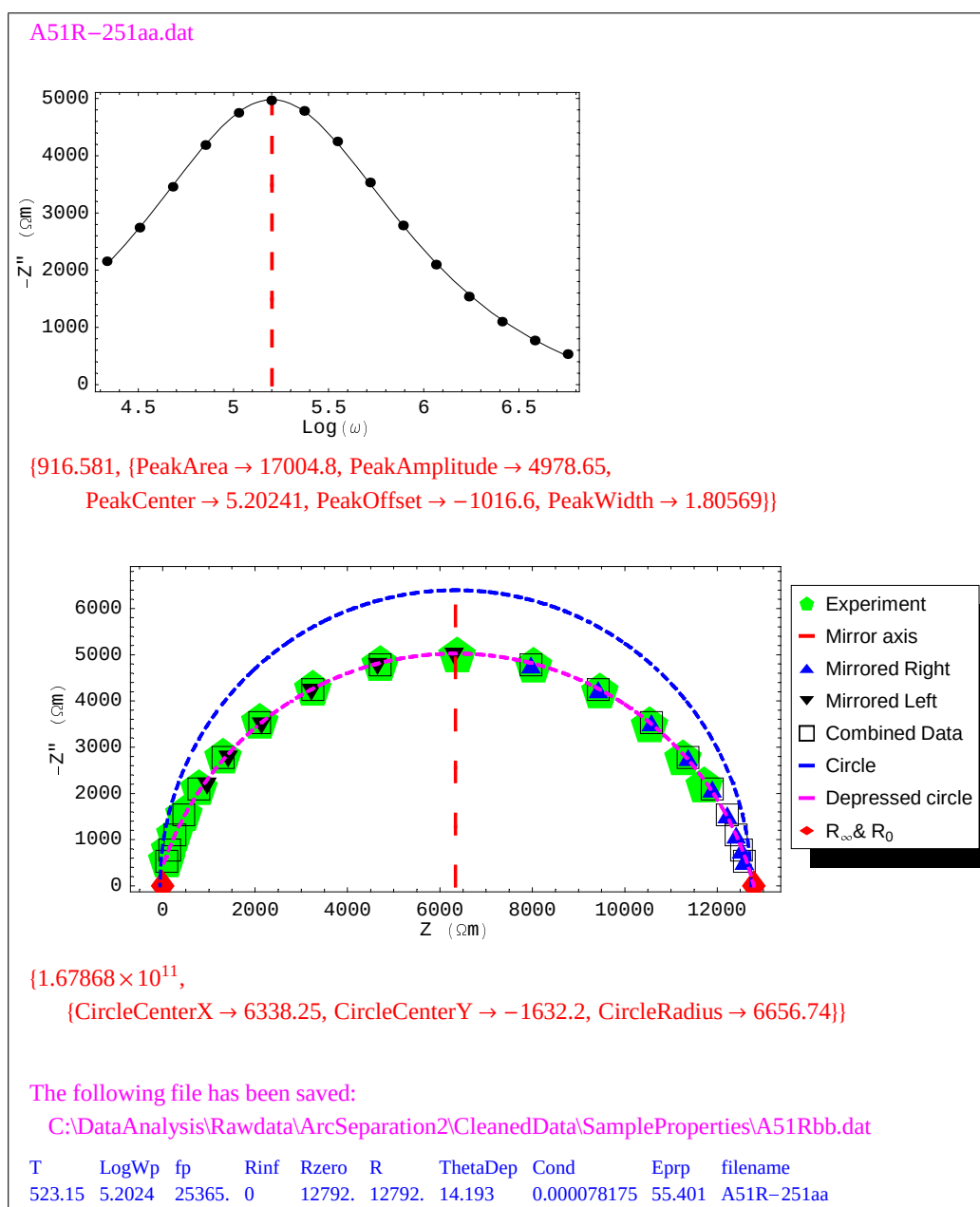


Figure 2.15: Typical fitting to obtain the characteristic frequency (top) and estimate the contribution of the first arc to the sample dc resistance (bottom). The characteristic frequency is obtained by fitting to the Lorentzian function. Estimation of the arc-axes intercepts is aided by effectively doubling the data points through reflection of the experimental points both ways about the characteristic frequency. The data is then fitted to a depressed semi-circle function. Note that in this case where there are a number of experimental points on both sides of the reflection axes, the reflected data and the experimental data are consistent. ThetaDep is the depression angle of the arc (θ_d), in degrees. (This particular data is from a polycrystalline sample, 8YSZ-D1 at 250 °C).

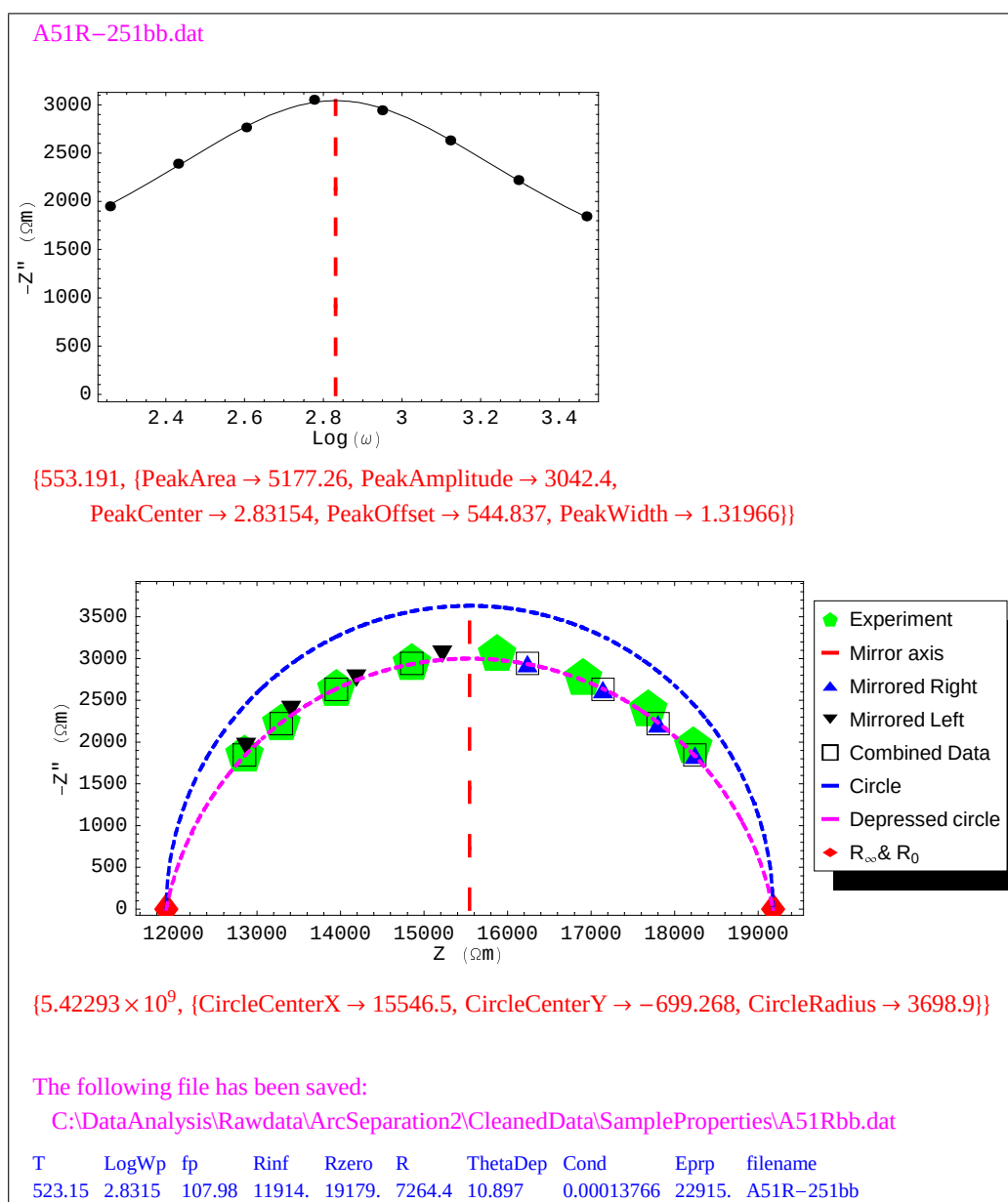


Figure 2.16: Typical fitting to obtain the characteristic frequency and estimate the contribution of the second arc to the sample dc resistance. Note that there are fewer points in this arc than in the first arc, Figure 2.15 and therefore there is likely to be greater uncertainty in the computed values, particularly the resistances. ThetaDep is the depression angle of the arc (θ_d), in degrees. (This particular data is from a polycrystalline sample, 8YSZ-D1 at 250 °C).

accurately they could be resolved. The simulations were calculated using the Maxwell-Wagner equation, the Brick Layer Model (BLM) and the Single Exponent Phenomenological Equation (SEPPE). The procedure used, implemented as a *Mathematica* notebook and related packages, allowed for the following options and features:

- Frequency dependent and/or independent component properties.
- Component properties could be entered as fixed parameters for one of several models Section 1.4, which would then be used to calculate the data points, or as actual data (fixed points), such as obtained from a single crystal.
- Component parameters could also be determined by first fitting some experimental data either for a component as a single crystal or the data from a composite sample, in the frequency region where that component is dominant.
- Component properties and those of the composites generated by the simulation were displayed in the same plots to enable easy visualization of correlations.
- Automatic generation of parameter values, for input into the models for the dispersive properties of the components, as well as the models for the electrical properties of the composite, was also possible. The automatic generation of parameters, in user defined ranges, enabled a large range of realistic combinations to be studied. Note that not all of the possible permutations and combinations of components' dispersive properties and ϕ generated were experimentally realizable.

The results from the above simulations are presented and discussed in detail in Chapter 4.

2.6.5 Fitting of the experimental composite data to the Effective Media Theories

One of the more difficult topics in all of data analysis in the physical sciences is fitting data to nonlinear models. Often such fits require large computational resources and great skill, patience, and intuition on the part of the analyst....In addition, computational methods of nonlinear fitting is still a current research topic in computer science [WRI¹⁰²].

Fitting data to the Effective Media and percolation models is a problem of Complex Nonlinear Least Squares fitting (CNLS) for which in general it is impossible to be certain of having obtained the global best solution. Thus, one of the main difficulties in ascertaining the usefulness of the models in the analysis of experimental data is the ability to consistently obtain good fits, for a “good” set of starting parameters. (Note that while a “best fit” is always obtained, for a given set of starting parameters and fitting procedures, some “best fits” are not particularly good and it can easily be seen, in graphs for example, that the fit poorly reproduces the data being fitted). If the global best fit could be guaranteed at each attempt at fitting, then it could readily be decided, using various criteria, whether or not the models are adequate to describe the data. Without the guarantee of finding the global best fit, failure of the fitting process may indicate that the effective media models are not adequate to represent the data or it may also just be a failing of the particular optimization methods used to find the best fit (i.e. there may have been a much better solution which was not found).

Busetti¹⁰³ notes; *Any efficient optimization algorithm must use at least two techniques to find a global maximum (minimum): exploration to investigate new and unknown areas in the search space, and exploitation to make use of knowledge found at points previously visited to help find better points. These two requirements are contradictory, and a good search algorithm must find a tradeoff between the two.*

In order to try and fit the effective media models in the best possible way

a procedure using four different minimization techniques was adopted in the current work. The sum of squares function that has to be minimized in most CNLS fitting, also known as the objective or merit function, and referred to hereinafter as χ^2 is

$$\chi^2 = \sum_{i=1}^n w_i (Y_{obs_i} - Y_{calc_i})^2,$$

where Y_{obs} are the observed (experimental) data, Y_{calc} the calculated data, n is the number of data points and w are weights chosen by the user.

As noted in Macdonald⁸; *The choice of weighting to use in CNLS fitting is usually very important and may even be crucial to the achievement of a good fit.*

Therefore, in addition to equal weighting, two other weighting methods were supported, *Weighting by $1/Y^2$ (relative weighting)* and *weighting by $1/Y$.*

The weighting method used most often is weighting by $1/Y^2$. This method minimizes the sum-of-squares of the relative distances of the data from the curve. It is the appropriate method when it is expected that the average distance of the points from the curve will be higher when Y is higher, but the relative distance (distance divided by Y) to be a constant. In this common situation, minimizing the sum-of-squares is inappropriate because points with high Y values will have a large influence on the sum-of-squares value while points with smaller Y values will have little influence. Minimizing the sum of the square of the relative distances restores equal weighting to all points. This case applies for dielectric data where, for example, the real dielectric constants at low frequency become very large such that this region then dominates the χ^2 value. For $1/Y^2$ weighting, the modified sum of squares function is [Motulsky¹⁰⁴]

$$\chi^2 = \sum_{i=1}^n \left(\frac{Y_{obs} - Y_{calc}}{Y_{obs}} \right)^2 = \sum_{i=1}^n \frac{1}{Y_{obs}^2} (Y_{obs} - Y_{calc})^2$$

Another weighting method is weighting by $1/Y$ which is a compromise between minimizing the actual distance squared and minimizing the relative

distance squared. One situation where $1/Y$ weighting is appropriate is when the Y values follow a Poisson distribution which would be the case for example when Y values are radioactive counts. For $1/Y$ weighting, the modified sum of squares function is [Motulsky¹⁰⁴]

$$\chi^2 = \sum_{i=1}^n \left(\frac{Y_{obs} - Y_{calc}}{\sqrt{Y_{obs}}} \right)^2 = \sum_{i=1}^n \frac{1}{\sqrt{Y_{obs}^2}} (Y_{obs} - Y_{calc})^2.$$

Only relative $(1/Y^2)$ weighting was used to obtain the results presented in this work.

The four methods chosen for minimizing the sum of squares (χ^2) were the standard Levenberg-Marquardt (LM) method [Lourakis¹⁰⁵, Press et al.¹⁰⁶], Simulated Annealing (SA) [Kirkpatrick et al.¹⁰⁷, San¹⁰⁸, Press et al.¹⁰⁹, Wolfram¹¹⁰], the Nelder-Mead Method (NM) [Nelder and Mead¹¹¹, Press et al.¹¹², Wolfram¹¹⁰, Mathews and Fink¹¹³, Abecasis¹¹⁴] and Differential Evolution (DE) [Storn and Price^{115, 116}, Wolfram¹¹⁰, Ahlers et al.¹¹⁷]. DE is a form of genetic algorithms (GAs). Note that Simulated Annealing, Differential Evolution and the Nelder-Mead Method are meta-heuristics, with a number of adjustable *minimizer specific options (MSOs)*, which determine their convergence properties. These methods were chosen, from those available in *Mathematica 5*, to give as broad a combination of robustness and speed as is possible. Descriptions of these methods can be found in the references.

It has been noted in the literature that while some algorithms are good (quick and accurate) at local searching for the minimum namely the LM and NM methods, these perform relatively poorly at global searches. On the other hand, global search methods, such as SA and DE are efficient at localizing the best areas for further searching, while they are relatively slow at converging and not as accurate at pinning down the minimum. Combinations of these global and local search techniques have been suggested for obtaining robust tools for function optimization [Chelouah and Siarry¹¹⁸, Hart¹¹⁹ and others].

To optimize on the different strengths of the various minimization methods, the procedure used in this work consisted of two stages. In the first stage, the global search methods, (SA) and (DE) were used to find promising regions

of the parameter space worthy of further exploration. In the second stage, local search methods (LM) and (NM) were used to explore the promising regions found in the first stage.

The procedure is summarized as follows:

- First stage
 1. A number of random points are generated in the available parameter space (a point, in the parameter space, consists of a complete set of parameter values). The number of random points was set to depend on the number of parameters in the problem.
 2. A number of minimization routines are then utilized to try to improve upon each starting point in turn. The minimizers are run several times with a number of the aforementioned minimizer specific options (MSOs), in the program, being changed in each run. At this stage, the best output is expected from the global search techniques but the local search minimizers, which are fast, are also given a short run (a few iterations) at each point, just in case the minimum lies nearby. The number of iterations was chosen so as to strike a balance between thorough searching and increased computation time). Each “best fit” is added to the list of all “best fits” from the initial search. A penalty is imposed on any fits with parameter values outside the prescribed range.
 3. The list of “best fits,” one for each original random point, is sorted according to the χ^2 value. The very best of these “best fits” is included in a second list of the fits to be further improved.
 4. The remainder of the fits whose χ^2 value lies within a certain range (specified as a few standard deviations) of the best of the “best fits” are then sorted according to how different their parameter values are. This difference is calculated using the n-dimensional generalization of the Pythagoras theorem, where n is the number

of parameters. The most different of the fits as obtained above are also added to the list of fits worthy of further exploration. The aim here is to ensure that the local searches explore as broad a region of the promising parameter space as possible. Choosing only the best fits, based on the χ^2 value, for the local searches, in most cases results in secondary searches in essentially the same region of the parameter space. (The problem of how to choose points worthy of further exploitation and some more sophisticated techniques for determining these are discussed in Hart¹¹⁹. Some of these techniques may be incorporated into later versions of the software initially developed for the analysis of impedance spectroscopy data in the current work).

- Second Stage

1. Taking each of the points in the list of points worthy of further exploration, the local search minimizers are used to optimize the objective function
2. For each point, the minimizers are run a few times with MSOs being altered at each run. Each minimum obtained is stored and ranked.
3. At each stage, a penalty function is imposed on the fit if the parameters stray outside the permissible boundaries. The Boole integral (also known as Iverson's convention) defined as $Boole[True] \rightarrow 1$ and $Boole[False] \rightarrow 0$ applied on inequalities of the parameters values

$$\chi'^2 = \chi^2 + \sum C(1 - Boole[a(i)_l \leq a(i) \leq a(i)_u])$$

was used as the penalty function. C is the penalty constant, typically chosen to be several orders of magnitude greater than the maximum expected legitimate value of χ^2 (a value of 10^{40} was

used). The values $a(i)_l$ and $a(i)_u$ are the lower and upper bounds respectively for the parameters $a(i)$.

The detailed flow chart for the data fitting process is given in Figures 2.17 and 2.18. Key points to note are:

- The option for fitting multiple files in the first few steps of Figure 2.17. This is used, for example, if there is data from one sample, measured at various temperatures. In this case there should be some common parameters such as the volume fraction, if no major structural or compositional changes are taking place in the material, due to the temperature changes. Some restrictions can also be made on the parameters, going from one data set to the next, based on their temperature dependence if this are known. The large data matrices generated for this process may however slow down of the convergence of the merit function substantially and the minimization can easily take up to several days on a fast personal computer.
- An alternative, and much faster, way of ensuring that the values of parameters common to all data sets are kept within a specified range is also provided while the data sets are fitted one by one. This is done by adjusting the parameter boundaries from each data set fitting to the next, to take into account the values already obtained. The constraints are “tightened” according to the relationship between the data sets already fitted and that currently being fitted as well as, for example, the temperature dependence of the parameters. For example if the best fit for data measured at a lower temperature than that of the current fit has already been computed, the calculated conductivity for that data would now be the lower bound for the new conductivity, if a positive temperature dependence has been entered for the sample conductivity. *Negative*, *Zero* and *Unknown* are also supported for the temperature (or other factor) dependence. An example of the “parameter-constraints tightening,” process is shown in the program dialogue in Figure 2.19.

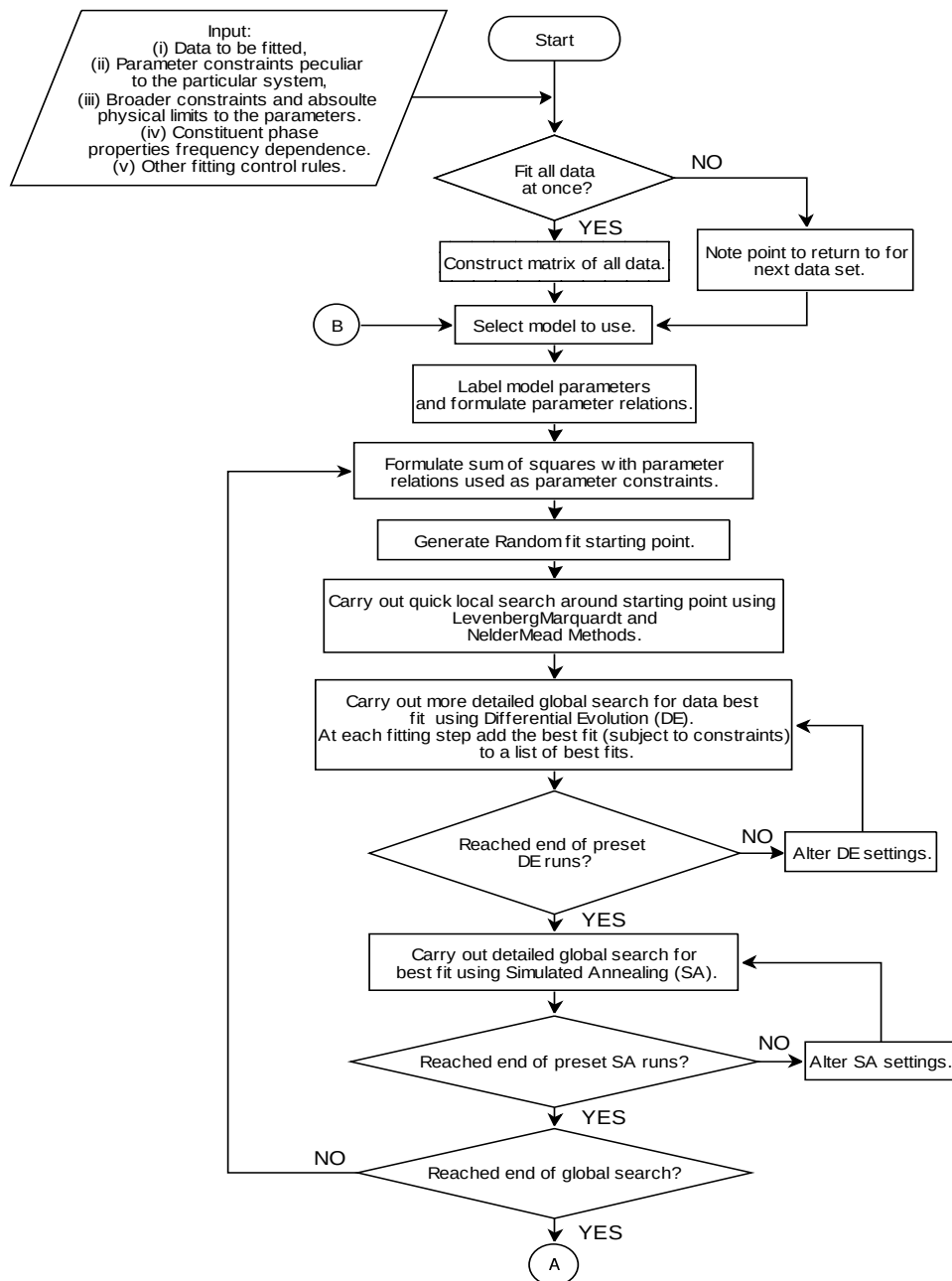


Figure 2.17: Part one of the flow chart describing the fitting routine implemented as a *Mathematica* program and used for fitting data in the current work.

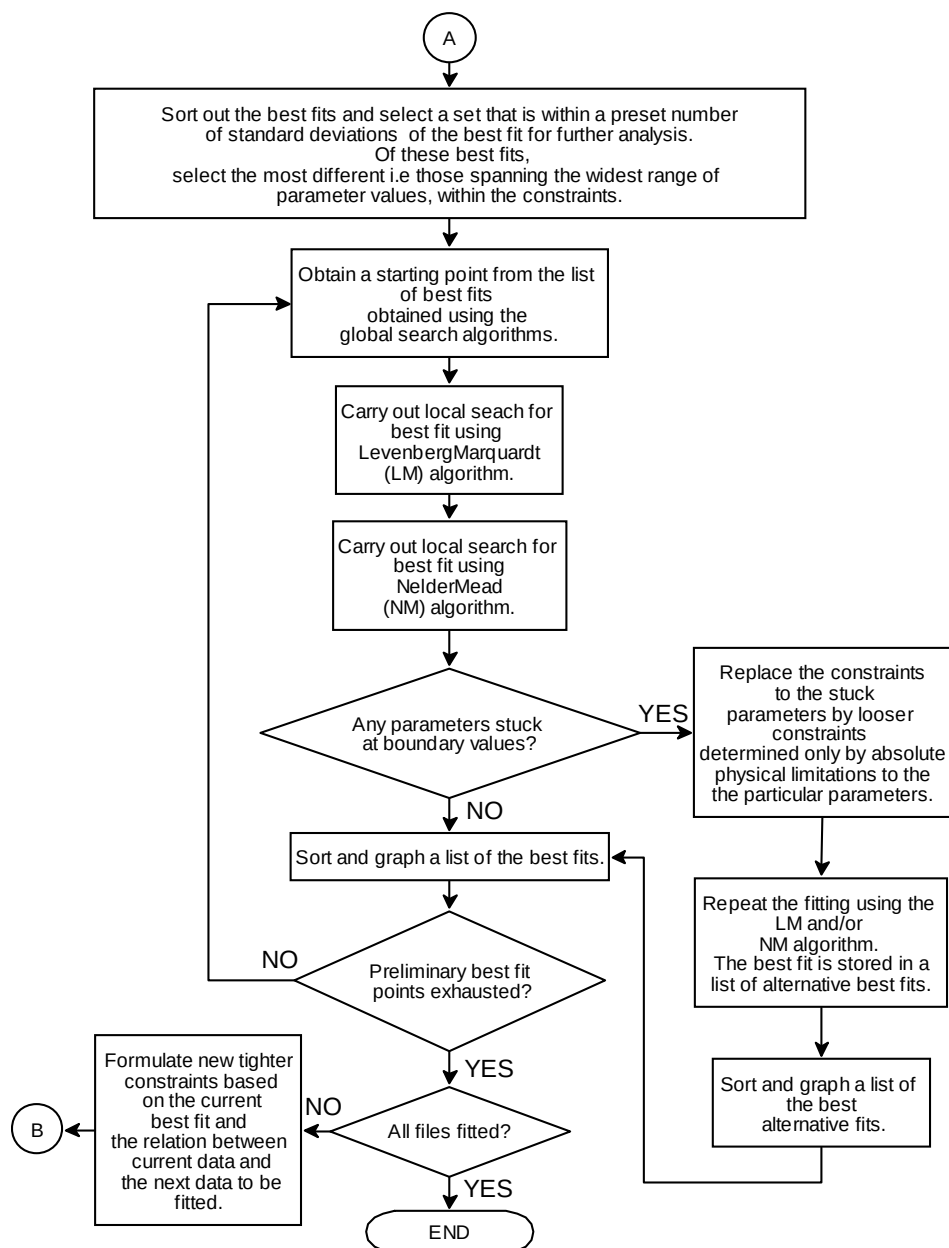


Figure 2.18: Part two of the flow chart describing the fitting routine implemented as a *Mathematica* program and used for fitting data in the current work.

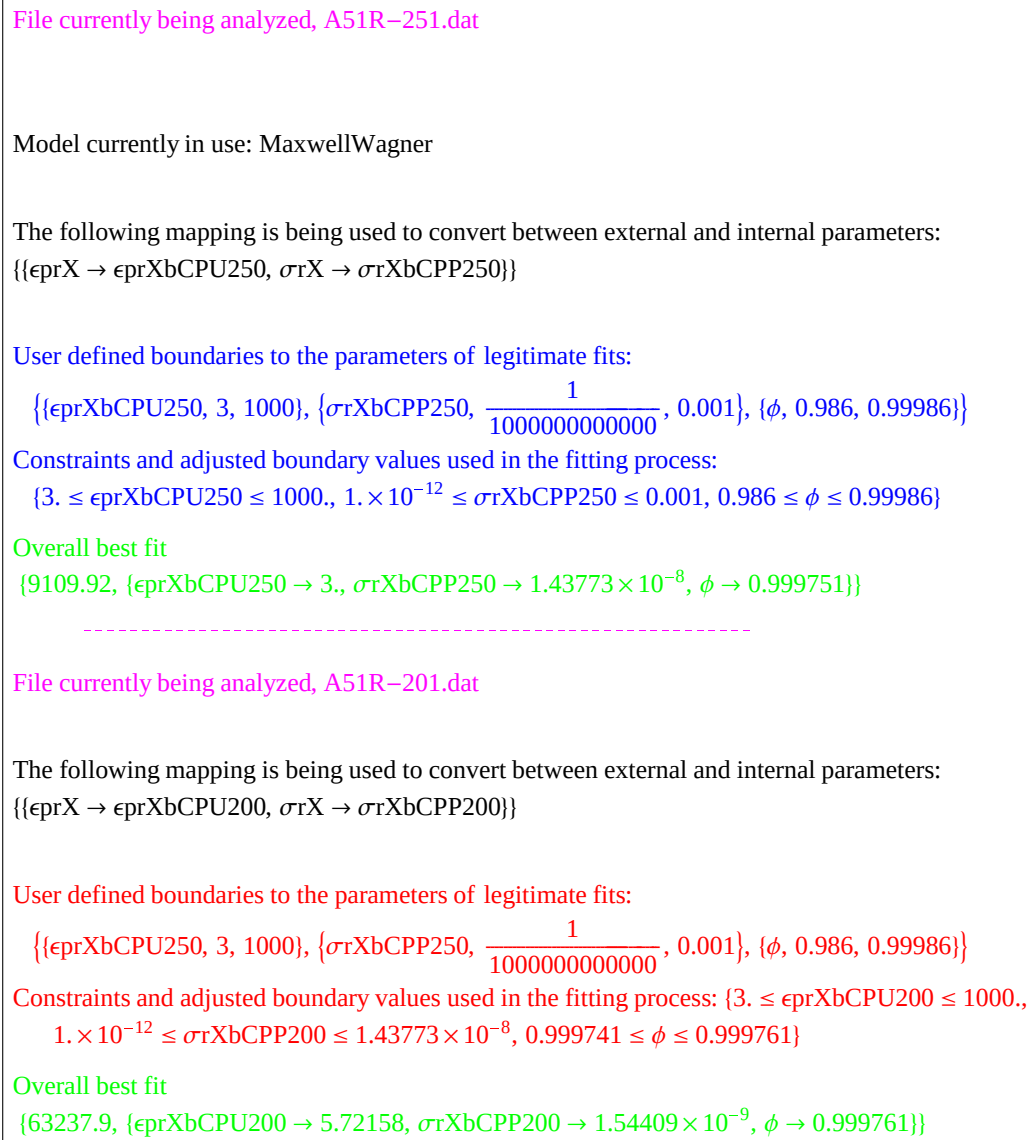


Figure 2.19: Program dialogue showing an example of constraining of parameters in subsequent fits based on the current best fit. In the example, the temperature dependence of the real dielectric constant $\epsilon_{pr}X$ (of the “bad Conductivity Phase” (bCP)) has been input as having an *Unknown* temperature dependence (U) and therefore this is mapped to two unrelated parameters for the two temperatures, $\epsilon_{pr}XbCPU250$ and $\epsilon_{pr}XbCPU200$) The conductivity parameter σ_{rX} has been input as having a *Positive* temperature dependence (P) and is therefore mapped to the internal variables $\sigma_{rXbCPP250}$ and $\sigma_{rXbCPP200}$, for the two temperatures. The variables that are not clearly independent of the temperature are mapped to internal variables which include the measurement temperature, so they can be sorted and the relation operators ($<$, $>$, $\leq$, $\geq$) can be applied. The values from the overall best fit for the first set of data are used to readjust the constraints and boundary values for the second fitting. The volume fraction ϕ is independent of the temperature (*Zero* dependence) and therefore does not need to mapped to individual values for the different temperatures.

In the Figure 2.19, the first fit is for a data set at 250 °C and the second at 200 °C, the order of the fitting being defined by an internal algorithm which tries to work out which data set has the better data (more points e.t.c).

- Another item to note in the flow charts (bottom half of Figure 2.18) are the alternate best fits that are also computed. Sometimes the straying of parameters from the defined search zone is indicative of the best mathematical solution (based on χ^2) actually lying outside the search region defined by the user. To account for this possibility, alternative solutions, whose parameter values are freed from the user imposed restrictions are kept and further developed in a stream separate from the “main” fitting stream. These “unrestricted” fits are not totally free as they are penalized if their parameter values lie outside the range of physically meaningful values. Note that they are only free from user imposed limitations. The modified penalty function for the alternate best fits is:

$$\chi'^2 = \chi^2 + \sum C(1 - \text{Boole}[a(i)_{l-abs} \leq a(i) \leq a(i)_{u-abs}]),$$

where $a(i)_{l-abs}$ and $a(i)_{u-abs}$ are the physical limits to the parameters. For example, the volume fraction ϕ cannot lie outside the range $0 \leq \phi \leq 1$ for any physically meaningful best fit. If the χ^2 value of the alternative best fit is lower than that of the best fit that meets the user imposed restrictions, the results of the best fit with parameters free are also presented at the end of the optimization for comparison, by the operator, with the best solution that lies within the parameter restrictions. It is envisaged that if the “unrestricted” best fits are significantly better than those that meet the restrictions, then the user seriously needs to think about the validity of the restrictions. The validity of the model to which the data is being fitted in describing the properties of the particular system is also brought into question, if choosing the (better) “unrestricted” fit parameters leads to results that are inconsistent with

other known properties of the material.

To compare the performances of the various models, some of which had different numbers of parameters a modification of the Akaike Information Criterion (AIC) [Akaike¹²⁰], called the Model Selection Criterion (MSC) was used. The AIC is defined by the formula

$$AIC = n * \ln\left(\sum_{i=1}^n w_i [Y_{obs_i} - Y_{calc_i}]^2\right) + 2p,$$

where n is the number of data points, p the number of parameters and the Y_{obs_i} and Y_{calc_i} are the observed and calculated values respectively. The w_i are weighting factors. The AIC attempts to represent the information content of a given set of parameter estimates by relating the coefficient of determination to the number of parameters (the number of degrees of freedom) that are required to obtain the fit. The most appropriate model gives the smallest value of the AIC. When comparing models with different numbers of parameters, this criterion places the burden on the model with more parameters to produce a better coefficient of determination and quantifies the required improvement [MicroMath¹²¹]. The MSC,

$$MSC = \ln\left(\frac{\sum_{i=1}^n w_i [Y_{obs_i} - \bar{Y}_{obs_i}]^2}{\sum_{i=1}^n w_i [Y_{obs_i} - Y_{calc_i}]^2}\right) - \frac{2p}{n},$$

gives the same rankings as the AIC but is normalized so that it is independent of the scaling of the data points. Also, whereas the most appropriate model gives the lowest value of the AIC, it gives the largest value of the MSC.

The program gives as output the best fit parameter values, graphs of the experimental and the calculated data, in various representations (σ vs $\log(\omega)$, complex impedance plane e.t.c), as well as the Model Selection Criterion (MSC) values. For each selected option, the final decision on whether the best fitting results obtained are a satisfactory representation of the experimental data rests with the operator.

Chapter 3

Component Properties: Yttria-Stabilized Zirconia Single Crystals

3.1 Introduction

As has already been stated, in order to be able to correctly model the properties of composite systems, the properties of the components have to be well characterized. Therefore, investigations were carried out on the properties of yttria-stabilized zirconia (YSZ) single crystals. The aim of this work was to obtain the best fitting model to describe the electrical properties of several single crystals and this model could then be used to model the grains of the polycrystalline YSZ ceramics. The ac conductivity of single crystals of 3, 5.7, 9.5 and 12 mole percent YSZ was measured and analyzed. The following models, described in Section 1.4 were considered to fit the properties of the single crystals: The Cole-Cole (CC) model, Equation (1.11), the Universal Dielectric Response model (UDR), Equation (1.12), the Continuous Time Random Walk (CTRW) model, Equation (1.15) and the Leon-Lucia-Santamaria (LLS) model, Equation (1.18). The results of the fitting are presented and discussed later in this chapter.

3.2 Results and Discussion

3.2.1 Impedance data validation

As a first step to analyzing ac conductivity data, it must be proven to be valid and consistent as described in Section 2.6.1. The validity of the experimental single crystal data was checked using the Kramers-Kronig relations, Equations 2.1 and 2.2. Figure 3.1 shows typical transforms of the real impedance to imaginary impedance, for 9.5 and 12 YSZ crystals. In this figure, Z'' *calculated* from a transform of the *experimental* Z' data using Equation (2.1) is compared with the *experimental* Z'' data. It can be seen in the figure that there are no major differences between the experimental data and that obtained from the transform.

As pointed out in Section 1.6, inherently non-linear processes such as electrode effects do not satisfy the K-K relations, when the excitation voltage is large. This is clearly illustrated in Figure 3.2. In the frequency region where the crystal is dominant there are only small differences between the calculated and the experimental values, which can be attributed to the errors arising from approximating the K-K transform by numerical integration over a finite frequency range. However, at frequencies dominated by electrode effects ($\log(\omega) \leq 3$), the difference between the calculated and the experimental values rises sharply, illustrating that electrode effects are non-linear.

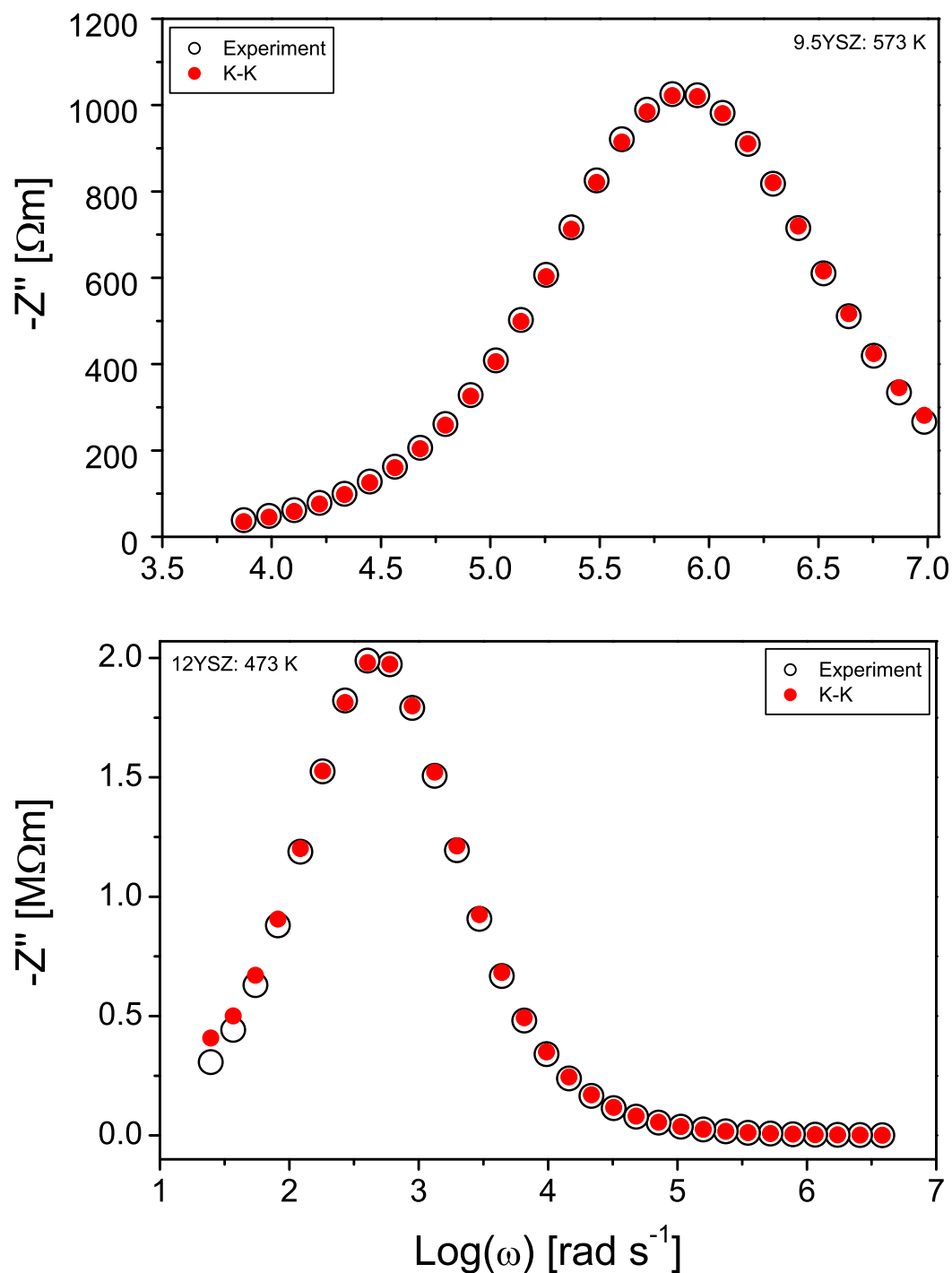


Figure 3.1: Validation of single crystal impedance data using Kramers-Kronig transforms. The calculated and experimental imaginary impedance data are seen to be in close agreement for a 9.5YSZ crystal at 300 °C (top) and for a 12YSZ crystal at 200 °C (bottom).

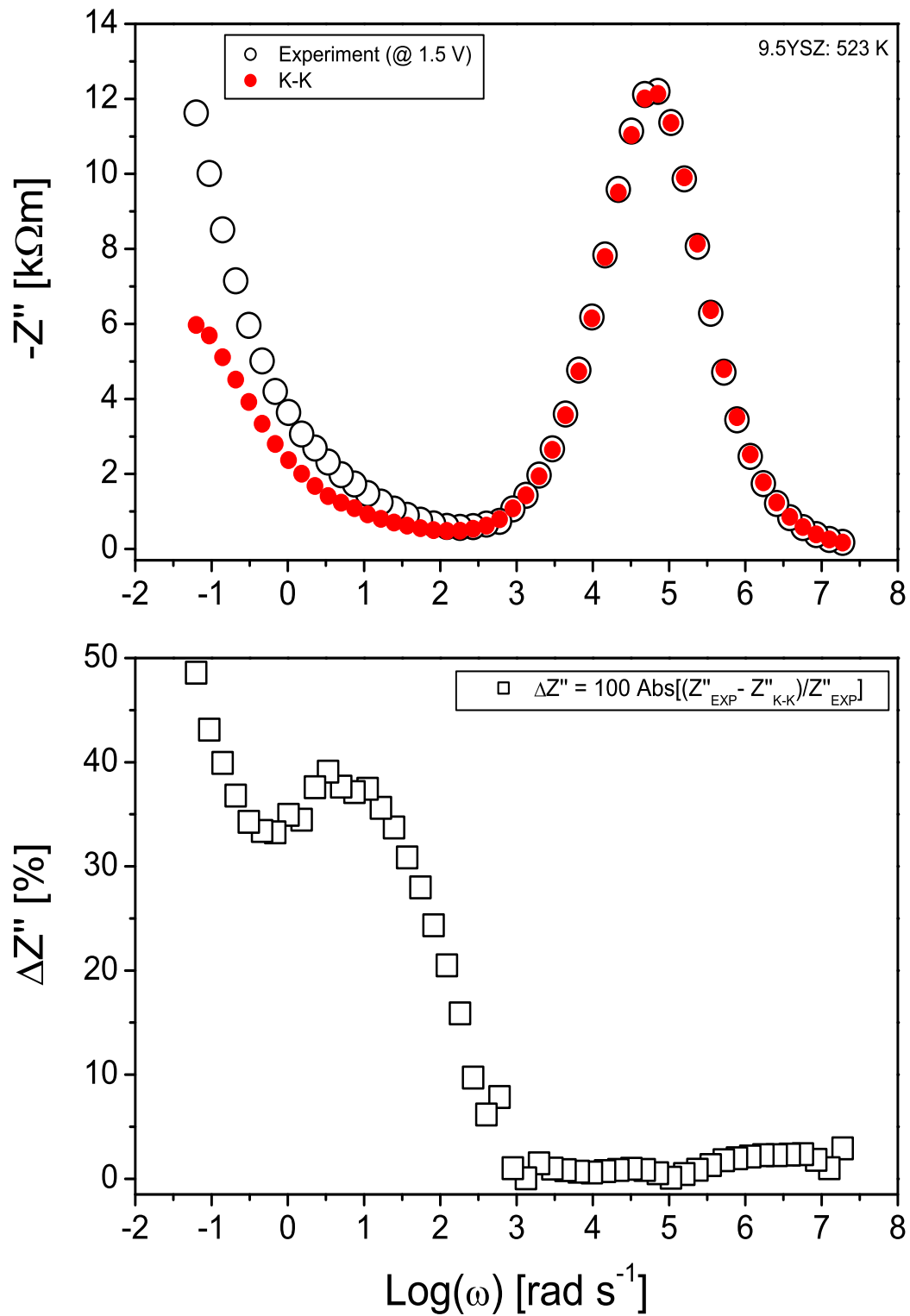


Figure 3.2: K-K transform showing the non-linearity of the electrode effects. The difference between the experimental and transformed data increases markedly at low frequencies ($\text{log}(\omega) < 3$) where electrode effects, which are non-linear and therefore do not conform to the K-K relations, dominate. (The particular data is from a 9.5YSZ crystal at 250 °C. The excitation voltage for the measurement is 1.5 V).

3.2.2 The frequency dependence of the electrical properties of YSZ single crystals

The frequency dependence of the real dielectric constant and the real conductivity of the 9.5YSZ single crystal, between 100 °C and 330 °C, is shown in Figures 3.3 and 3.4. In Figure 3.3, the experimental data at all frequencies is shown, while in Figure 3.4 the data at frequencies dominated by electrode effects (as seen in complex impedance plane plots) has been removed (using the procedure described in Section 2.6.2). In both the figures, the dielectric constant and the conductivity are seen to be strongly frequency and temperature dependent. Blocking effects at the electrodes cause the large increase in the dielectric constant at low frequencies which can be seen in Figure 3.3.

For the crystal, excluding electrode effects (Figure 3.4), the real dielectric constant (top) rises from a high frequency value of ~ 28 to over 100 at low frequencies. The dielectric constant at low frequencies continues to rise at all accessible frequencies and no plateau is observed. However, at high temperatures (≥ 573 K), there appears to be a kink in the data, in the frequency region $5 \leq \log(\omega) \leq 6$, indicating possible changes in the underlying relaxation mechanisms. No corresponding kink can be seen in the conductivity data (Figure 3.4, bottom). The conductivity follows Jonscher-type power law behavior [Jonscher^{62, 63, 64}] (i.e $\sigma \propto \omega^s$) at high frequency and levels off at low frequencies. The flat region, due to the dc conductivity, rises with increase in temperature and at the highest temperatures becomes a dominant feature in the accessible frequency range.

Figure 3.5 shows the frequency dependence of the imaginary impedance and normalized imaginary impedance at various temperatures (the normalization is achieved by dividing by the highest point for each data set). The magnitude of the imaginary impedance Figure 3.5 (top) decreases with increasing temperature, while the peak frequency increases with increasing temperature. The increase in the peak frequency is seen more clearly in the normalized impedance plot, Figure 3.5 (bottom). The peak frequency, ω_p , is related to

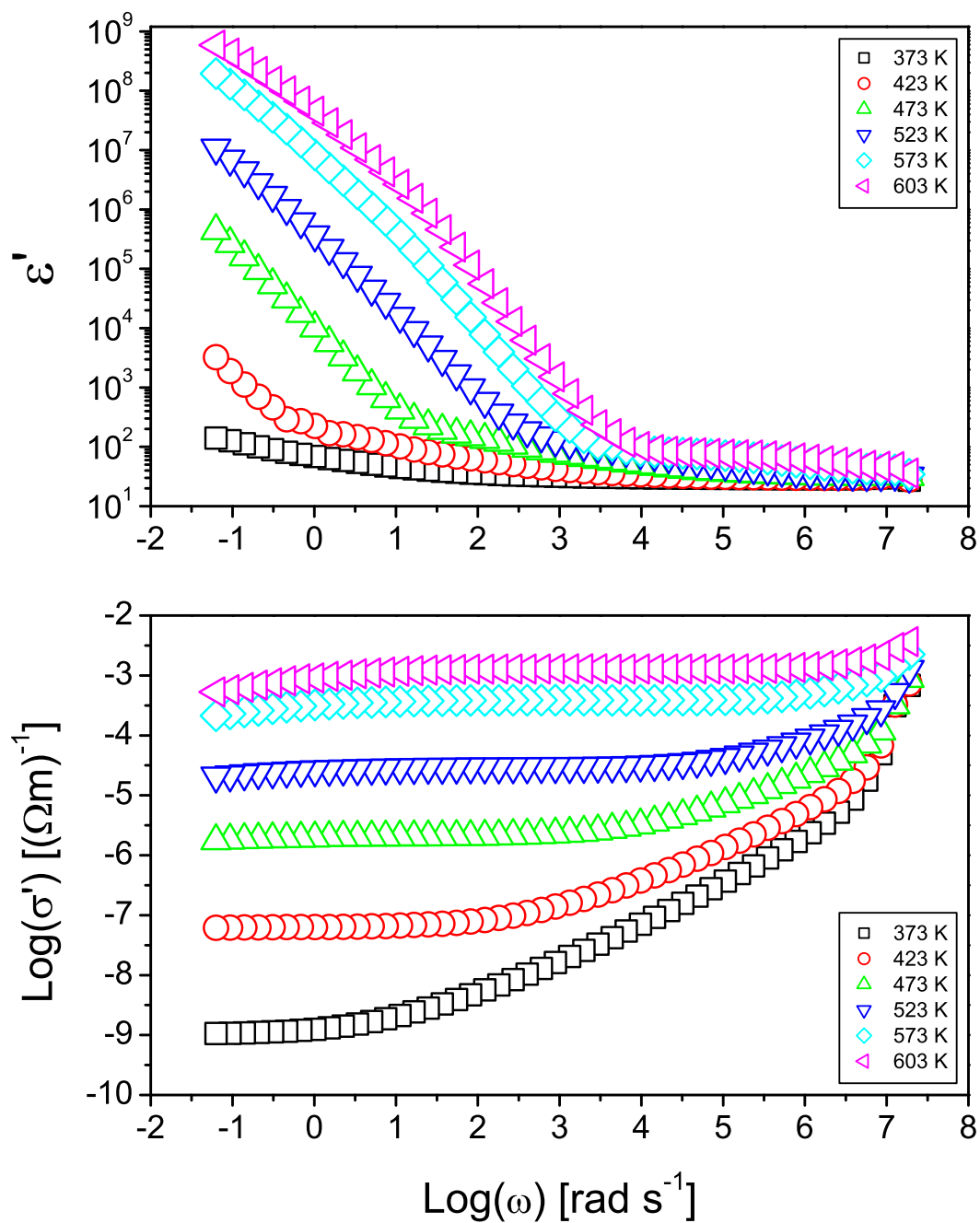


Figure 3.3: The frequency dependence of the real dielectric constant (top) and the real conductivity (bottom) of a single crystal of 9.5 mole % YSZ at various temperatures (including the data at frequencies where electrode effects dominate).

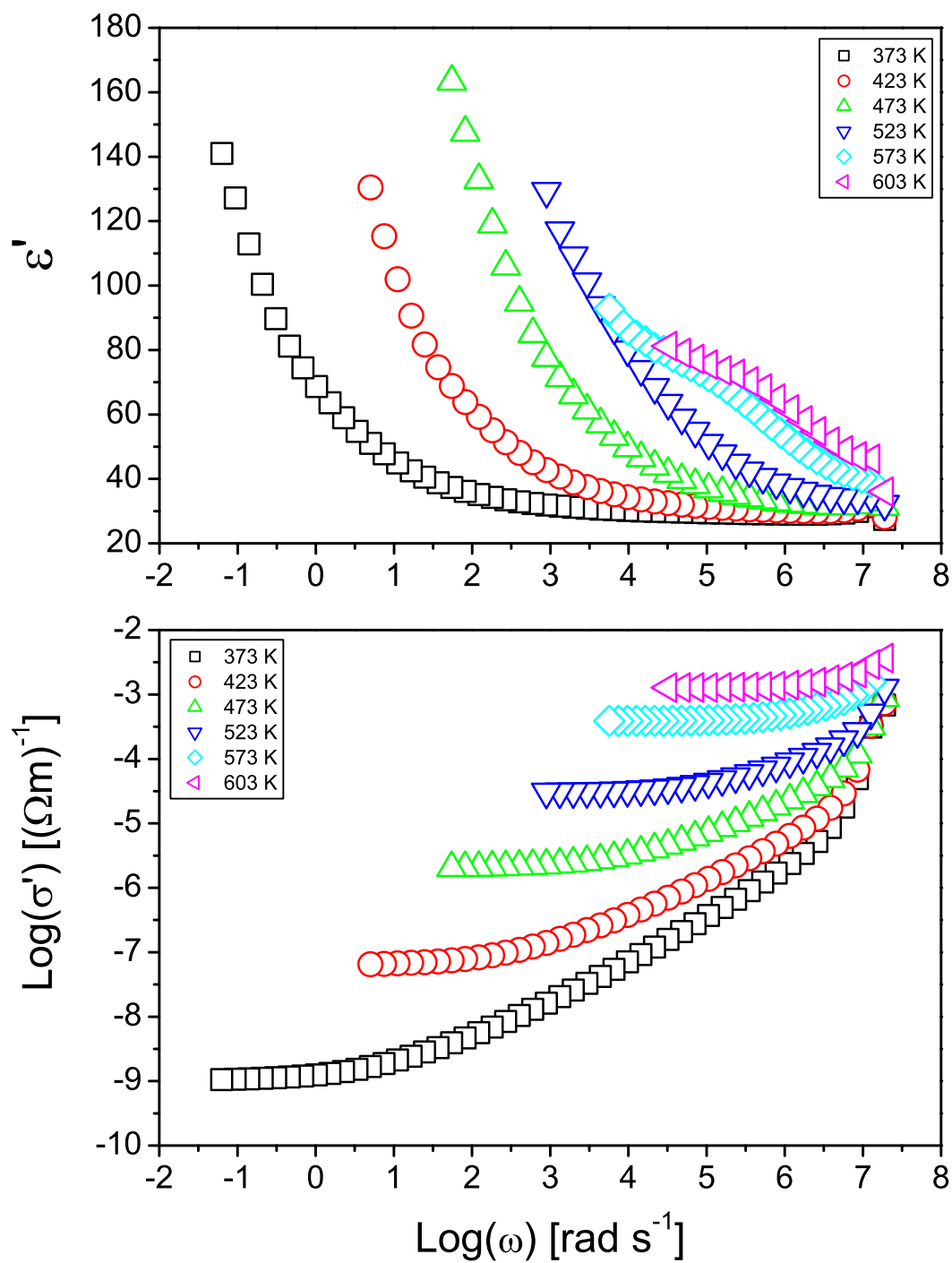


Figure 3.4: The frequency dependence of the real dielectric constant (top) and the real conductivity (bottom) of a single crystal of 9.5 mole % YSZ at various temperatures (excluding the data at frequencies where electrode effects dominate).

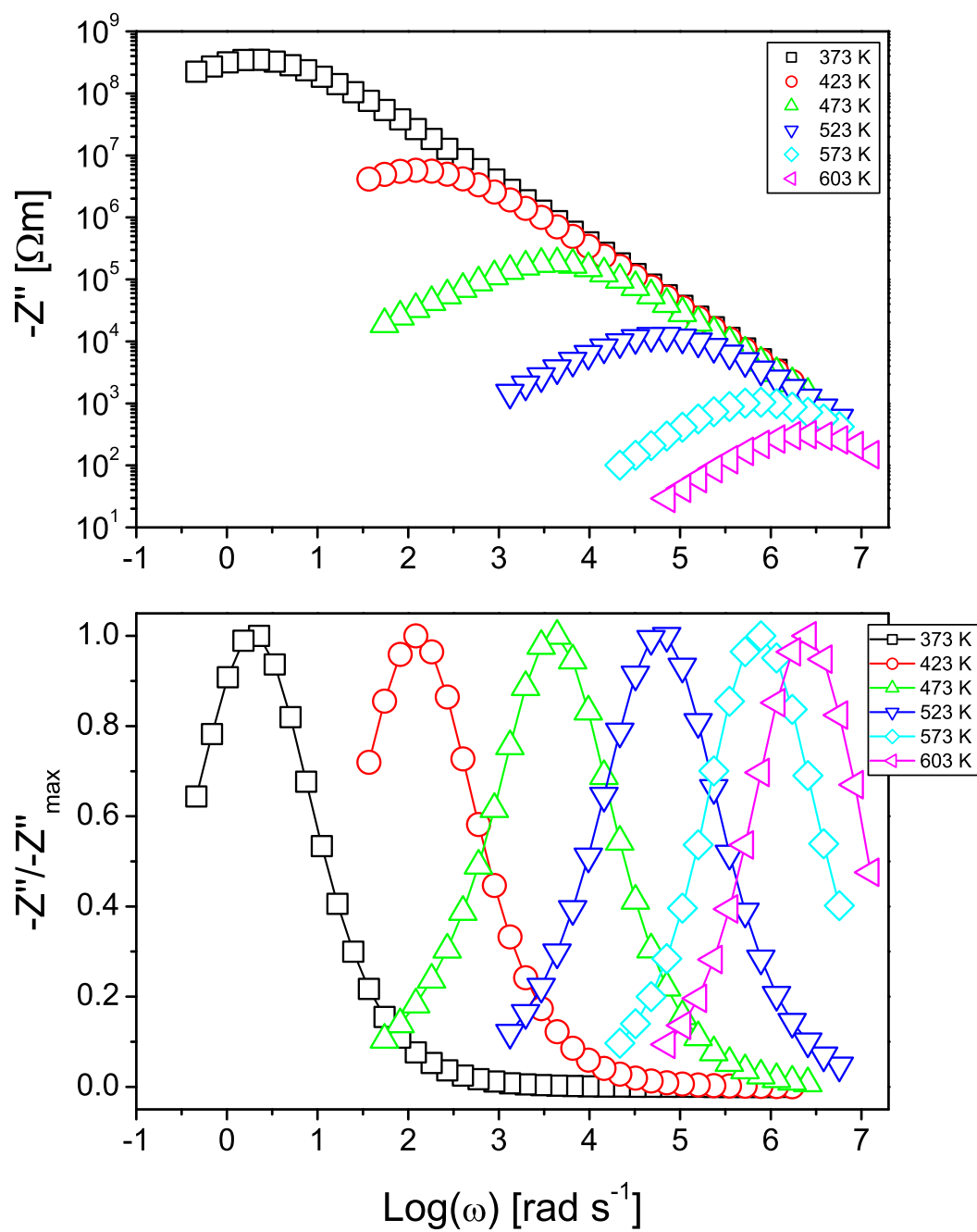


Figure 3.5: The frequency dependence of the imaginary impedance (top) and normalized imaginary impedance (bottom) of a 9.5 mole % YSZ single crystal at various temperatures. The peak frequency is seen to rise with increase in the temperature. The lines in the normalized impedance plot are a guide to the eye.

the dc conductivity σ_{dc} and the dielectric constant ϵ_p by the equation,

$$\omega_p = \frac{\sigma_{dc}}{\epsilon_p \epsilon_0}, \quad (3.1)$$

and is a characteristic feature of the material at the particular temperature. Hence it shall, hereinafter, be referred to as the *characteristic frequency*. The *characteristic frequency* is associated with the characteristic time constant (τ_R) for the relaxation process,

$$\tau_R = \frac{1}{\omega_p} = \frac{\epsilon_p \epsilon_0}{\sigma_{dc}}, \quad (3.2)$$

Note that the characteristic frequency (time constant) may also depend on the atmosphere in which the measurement is made and on other factors which affect σ_{dc} and/or ϵ_p .

Similar results and trends to those shown in the figures and discussed above for the 9.5YSZ single crystal were also observed for the 3, 5.7 and 12 mole % YSZ crystals. It was expected and it will be shown, in Chapter 5, that the electrical properties of the grains of the polycrystalline YSZ samples show similar frequency dependence to those of the single crystals.

Figures 3.6 and 3.7 show the frequency dependence of the imaginary impedances and normalized imaginary impedances, at 100 and 250 °C, of YSZ single crystals **with different amounts of yttria**. It can be seen in the figures that at a given temperature the impedance increases with increase in the yttria content and the peak frequency decreases. The characteristic frequencies of the tetragonal stabilized zirconia crystals (3 and 5.7 mole % YSZ) are very close at both temperatures (they were also found to be close at all other temperatures investigated). For the cubic stabilized zirconia crystals (9.5 and 12 mole % YSZ), the characteristic frequencies are notably different from each other at both (and all other) temperatures.

The complex impedance plane representation of the raw data for the 9.5 mole % YSZ crystal at 250 °C is shown in Figure 3.8. One complete depressed semicircle, due to the crystal, and an incomplete arc, due to the electrode effects, are observed. For *all* the crystals studied only one depressed semicircle

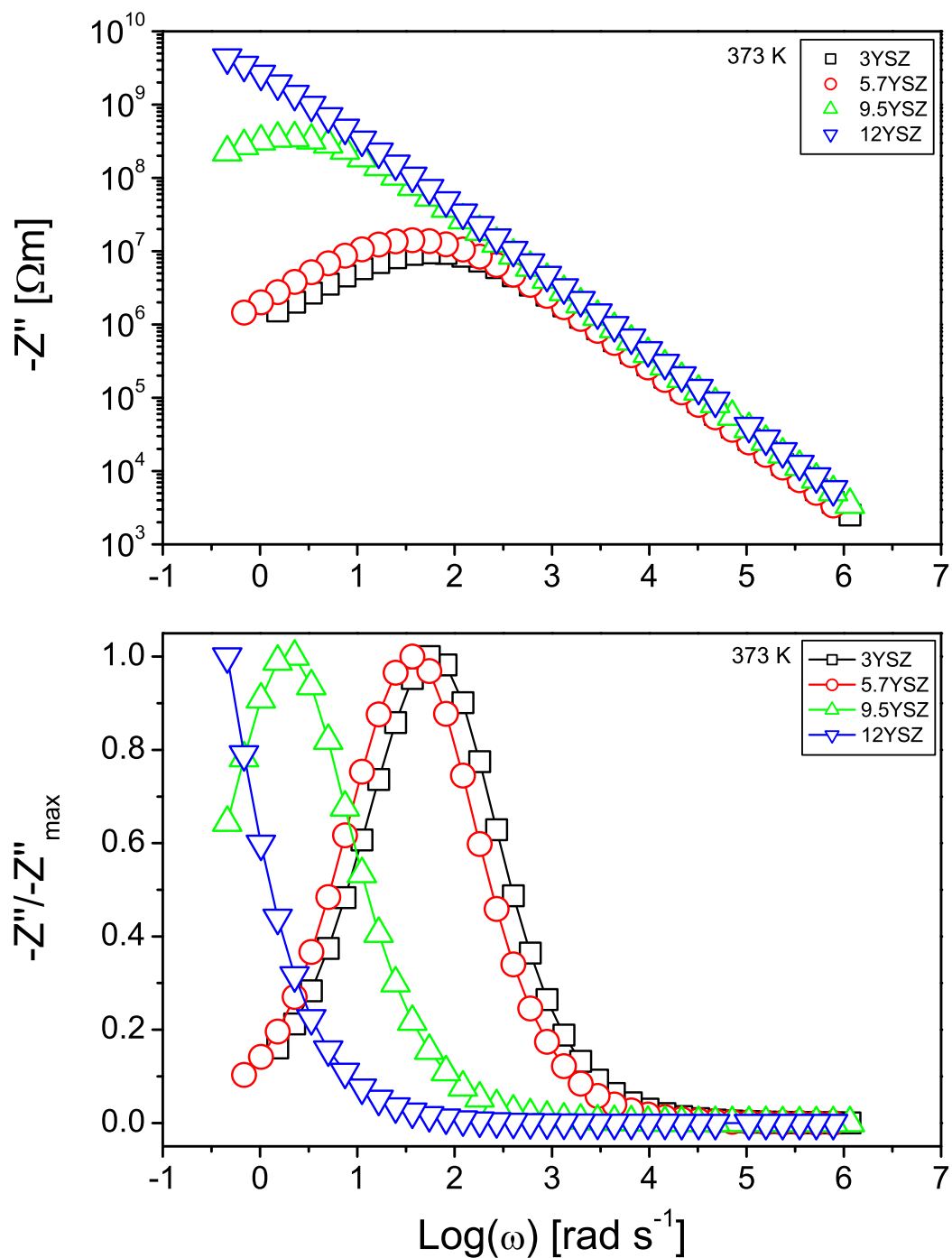


Figure 3.6: The frequency dependence of the imaginary impedance (top) and normalized imaginary impedance (bottom) of the various yttria-stabilized zirconia single crystals at 100 °C. The characteristic frequency is seen to depend on the yttria content and decreases as the amount of yttria increases. The lines in the normalized impedance plot are a guide to the eye.

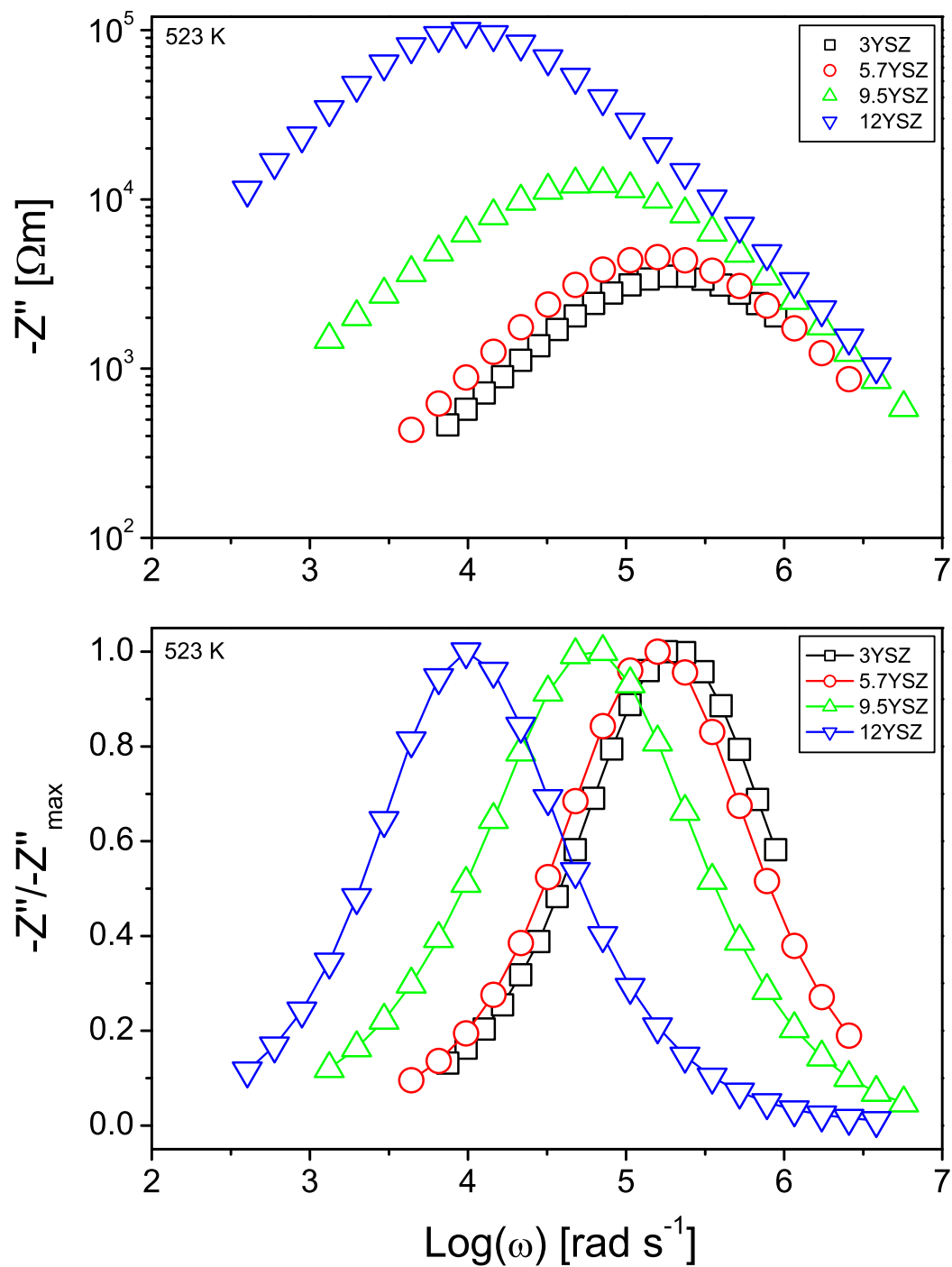


Figure 3.7: The frequency dependence of the imaginary impedance (top) and normalized imaginary impedance (bottom) of various yttria-stabilized zirconia single crystals at 250 °C. For each yttria content, the characteristic frequency is higher than that at 100 °C, (Figure 3.6) but again the same trend, where this frequency decreases with increasing Yttria content, is observed. The lines in the normalized impedance plot are a guide to the eye.

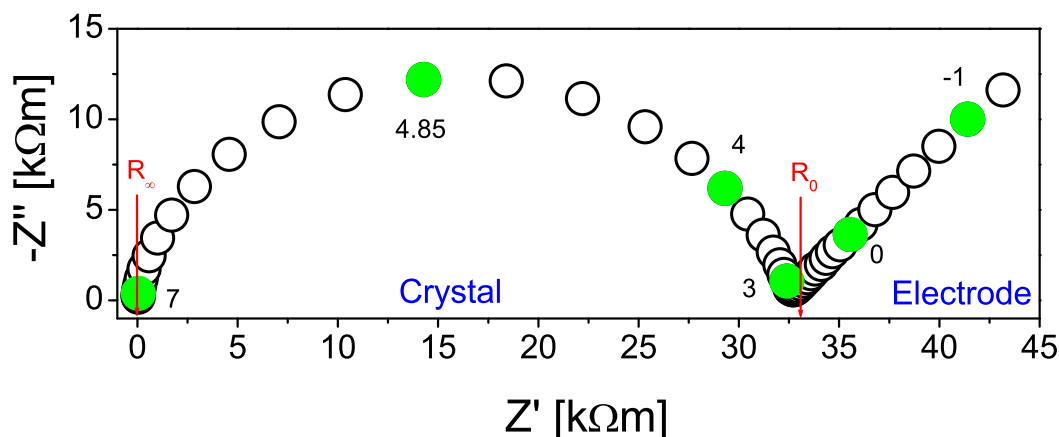


Figure 3.8: Typical complex impedance plane plot of the data from a single crystal. Note that the data includes that at low frequencies where electrode effects are dominant. The bulk gives rise to the complete depressed arc while electrode effects give rise to the incomplete arc. Shown in the figure is the data from a 9.5 mole % YSZ crystal at 250 °C. R_∞ and R_0 are the high and low frequency intercepts on the real axis from which the dc resistance and conductivity are determined. Key values of $\log(\omega)$ are indicated.

was observed in the complex impedance plane (excluding the partial arc due electrode effects). This confirms that the crystals are single component (as opposed to composite) materials. In spite of this, the ac conductivity of the crystals is very complex.

3.2.3 The temperature dependence of the properties of Yttria-Stabilized Zirconia single crystals

The temperature dependence of the “dc” conductivity, extracted from the complex impedance plane plots (which, for simplicity, will be referred to as the dc conductivity), and the peak frequencies of all the crystals studied is best described by the expressions

$$\sigma_{dc}T = \sigma_0 \exp\left[-\frac{E_{a-\sigma}}{k_B}T\right] \quad (3.3)$$

and

$$\nu_p T = \nu_0 \exp\left[-\frac{E_{a-\nu}}{k_B}T\right], \quad (3.4)$$

where $E_{a-\sigma}$ and $E_{a-\nu}$ are the activation energies for the conductivities and the peak frequencies respectively.

Equations (3.3) and (3.4) are obtained by setting $B = \frac{E_a}{k_B}$, $p=1$, $n=-1$ in Equation (1.23) and are associated with the ionic conduction (see Section 1.5).

Figure 3.9 shows the temperature dependence of the dc conductivity (plotted as $\ln(\sigma_{dc}T)$ vs $1000/T$) and the characteristic frequency (plotted as $\log(\omega_p)$ vs $1000/T$) of the tetragonal stabilized zirconia crystals (3 and 5.7 mole % YSZ; top and bottom respectively). Figure 3.10 shows the same for the cubic stabilized zirconia crystals (9.5 and 12 mole % YSZ; top and bottom respectively). Note the linear temperature dependence of the dc conductivities and the characteristic frequencies, which are best fitted using Equations (3.3) and (3.4).

Table 3.1: Activation energies of the dc conductivities and the characteristic frequencies of the YSZ single crystals. σ_0 and ν_0 are the pre-factors in Equations (3.3) and (3.4) respectively.

Composition (mole %)	Property	σ_0/ν_0 (Ωm) ⁻¹ K/HzK	Activation energy (eV)
3	Conductivity	$(59 \pm 8) \times 10^6$	0.94 ± 0.01
3	Peak Frequency	$(30 \pm 2) \times 10^{15}$	0.96 ± 0.01
5.7	Conductivity	$(61 \pm 6) \times 10^6$	0.95 ± 0.01
5.7	Peak Frequency	$(26 \pm 3) \times 10^{15}$	0.97 ± 0.01
9.5	Conductivity	$(12 \pm 4) \times 10^9$	1.23 ± 0.04
9.5	Peak Frequency	$(4 \pm 1) \times 10^{18}$	1.23 ± 0.04
12	Conductivity	$(23 \pm 9) \times 10^9$	1.35 ± 0.07
12	Peak Frequency	$(7 \pm 2) \times 10^{18}$	1.34 ± 0.04

The best fit parameters to Equations (3.3) and (3.4) for the conductivity and the characteristic frequency and the activation energies corresponding to these parameters are given in Table 3.1. It can be seen in the table that the separately obtained activation energies for the conductivities and the characteristic frequencies are similar, indicating that they are governed by the same processes in the material. The activation energies increase with increasing yttria content.

Figure 3.11 shows the temperature dependence of the dielectric constants and the depression angles of the YSZ crystals. No model could be found in

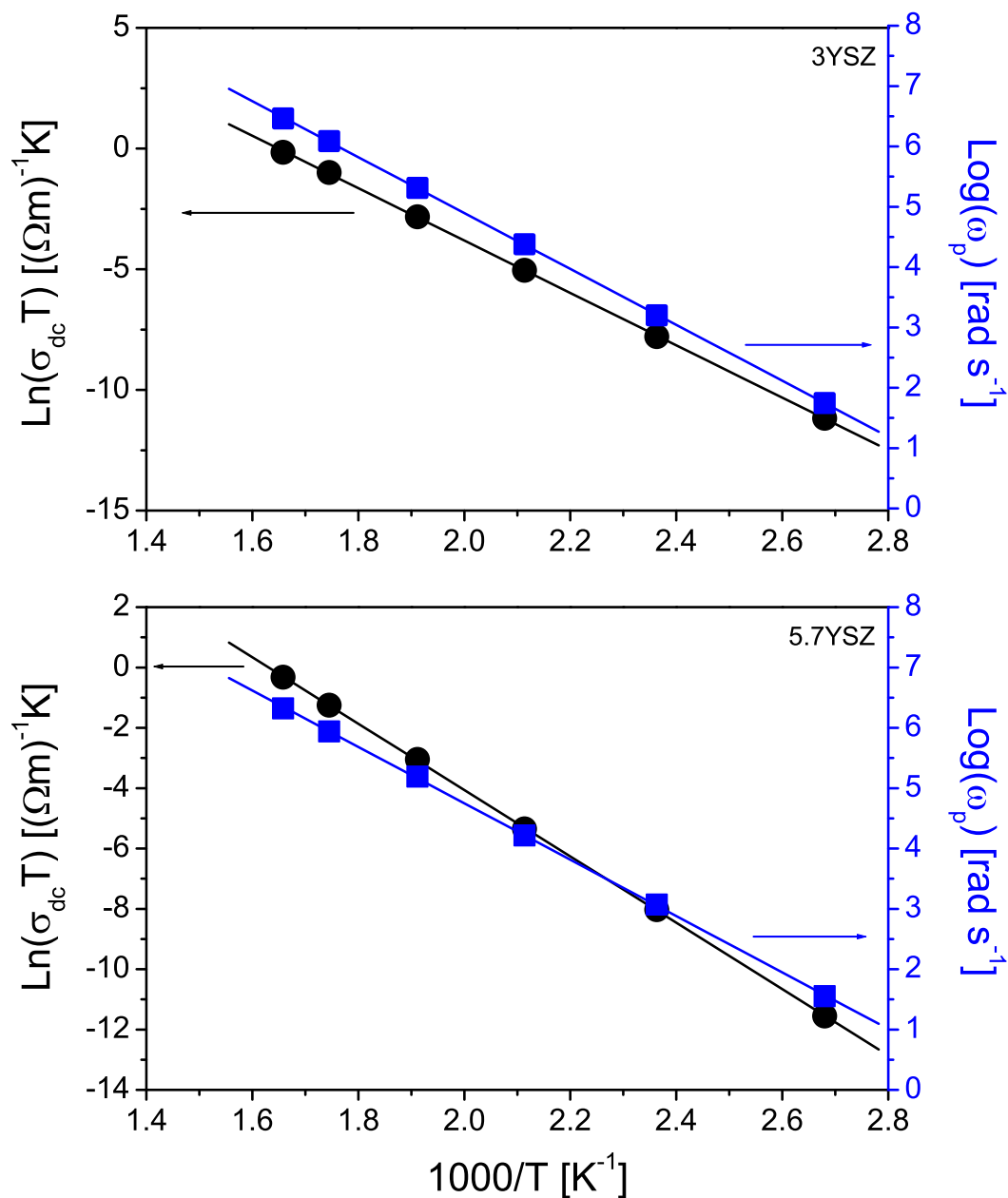


Figure 3.9: The temperature dependence of the dc conductivities extracted from complex impedance plane plots and the characteristic frequencies of the 3 (top) and 5.7 (bottom) mole % YSZ single crystals in the temperature range 100 to 400 °C. The lines are linear fits to the data.

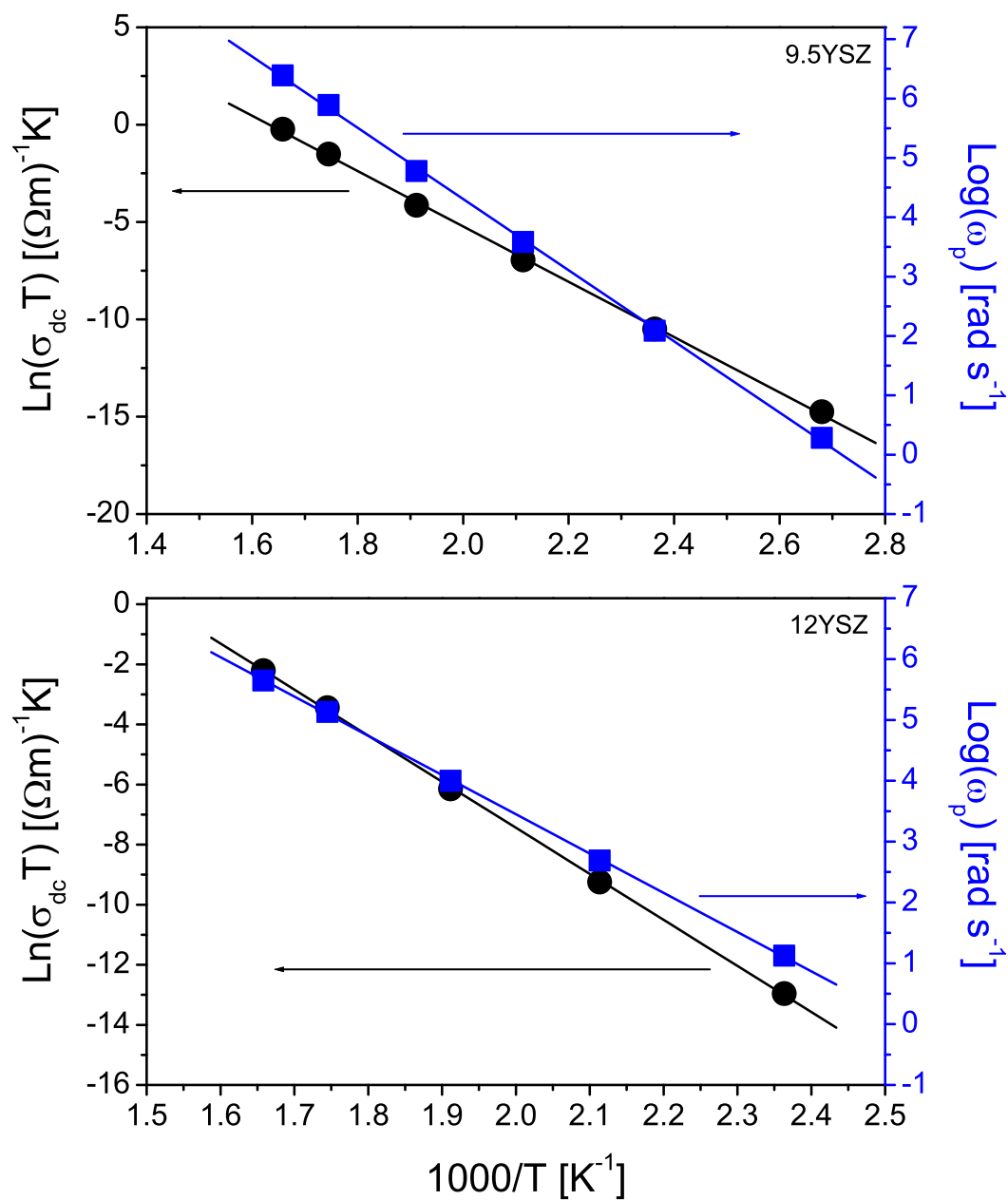


Figure 3.10: The temperature dependence of the dc conductivities extracted from complex impedance plane plots and the characteristic frequencies of the 9.5 (top) and 12 (bottom) mole % YSZ single crystals in the temperature range 100 to 400 °C. The lines are liner fits to the data.

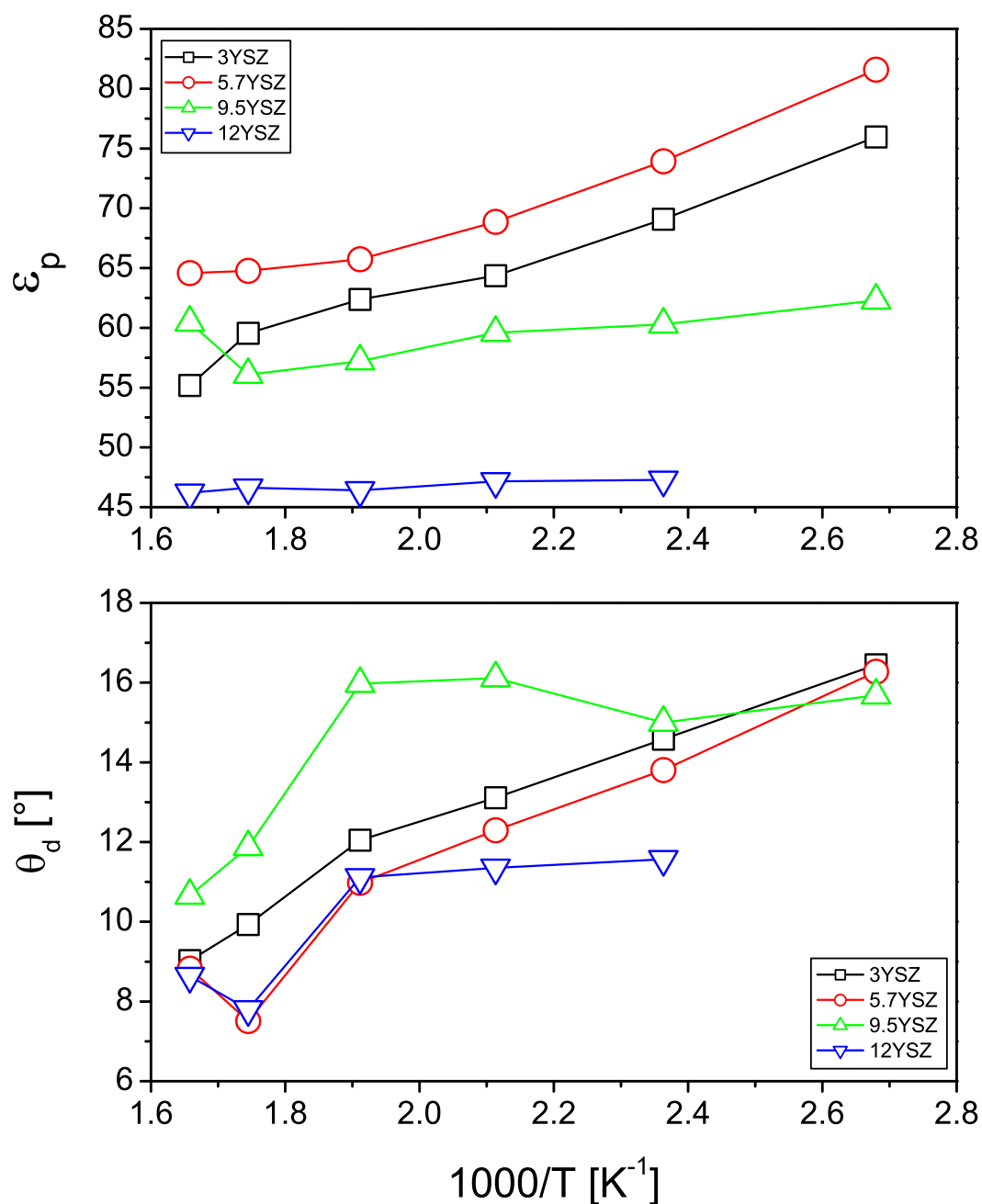


Figure 3.11: The temperature dependence of the dielectric constants (top) and the depression angles (bottom) of the YSZ crystals in the temperature range 100 to 400 °C. The dielectric constant generally decreases with increasing temperature, in the temperature range of the measurements. The depression angles are for the most part above 10 °, possibly indicating a large scatter in the relaxation times of the underlying processes. The lines are a guide to the eye.

the literature for the temperature dependence of the characteristic dielectric constants shown in Figure 3.11 (top). However, they appear to generally decrease with increasing temperature. The depression angles of the arcs, shown in Figure 3.11 (bottom), which are parameters sensitive to the heterogeneity of the material [Santos et al.¹²²], are rather surprisingly large ($> 10^\circ$) for most of the samples. This usually indicates a relatively large scatter in the relaxation times of the underlying processes [Verkerk et al.¹⁹, Macdonald and Johnson⁵].

3.2.4 Fitting the dispersive properties of the Yttria-Stabilized Zirconia single crystals

A number of models were considered for fitting the ac conductivity of the yttria-stabilized zirconia single crystals and for use in modeling the properties of the grains in zirconia ceramics. Consistency demands that both the real and imaginary parts (permittivities or equivalently conductivities) come from the same model.

The models considered to fit the properties of the single crystals were the Cole-Cole (CC) model, Equation (1.11), the Universal Dielectric Response model (UDR), Equation (1.12), the Continuous Time Random Walk (CTRW) model, Equation (1.15) and the Leon-Lucia-Santamaria (LLS) model, Equation (1.18). The CTRW model was considered because the properties of the single crystal, in particular the conductivity, can be mapped to a common “master curve.” This is a feature of a wide range of disordered systems, some of whose properties have been successfully fitted using the CTRW model [as is shown in Dyre and Schröder¹²³]. Figures 3.12 and 3.13 show that this scaling property is also observed in the experimental results for the YSZ single crystals. The mapping required to obtain the “master curve” can be seen in the axes labels in the figures. (Note that the real dielectric constant does not scale as well as the conductivity).

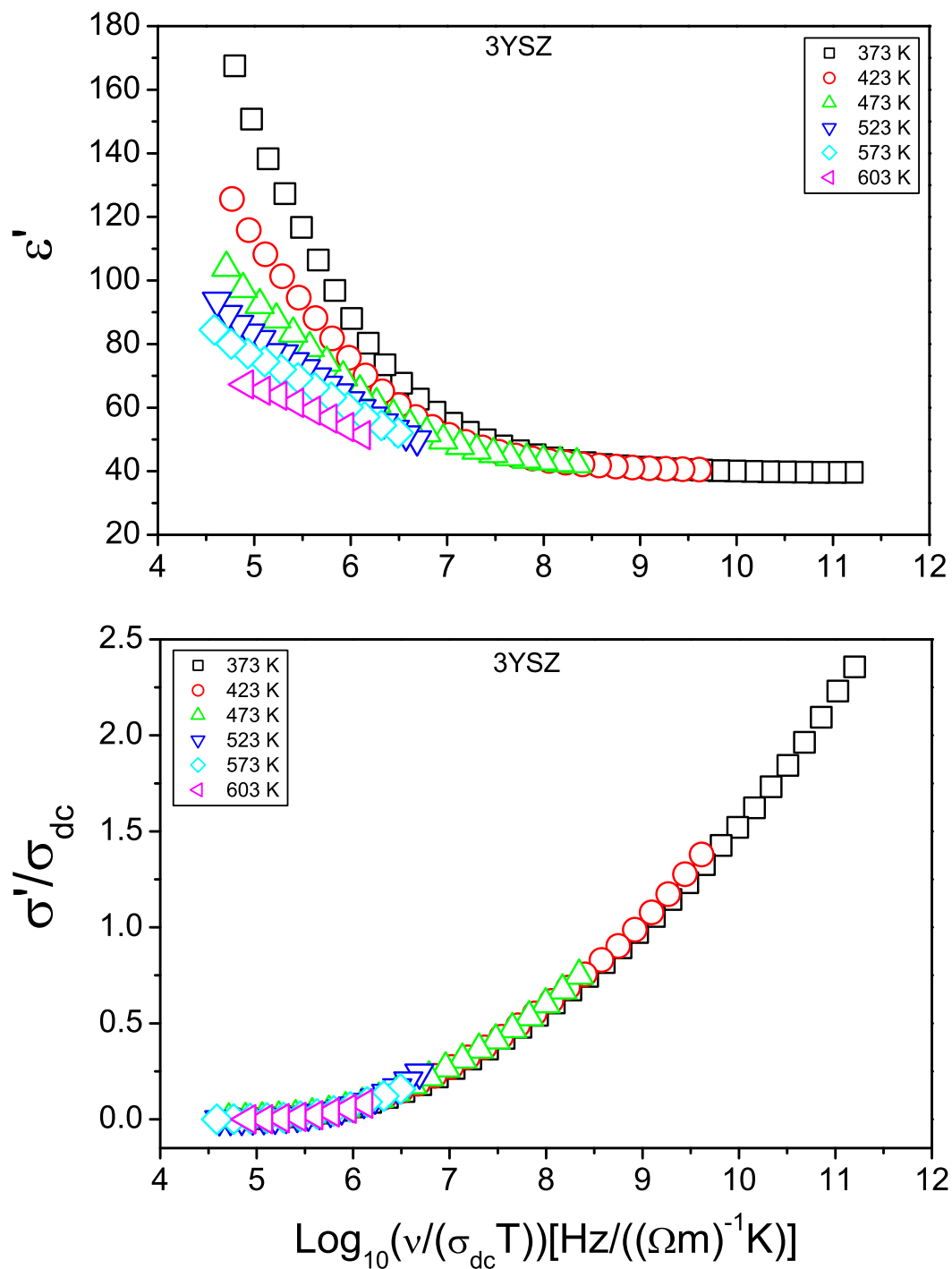


Figure 3.12: Scaling of the real dielectric constant and the real conductivity of a 3 mole % YSZ crystal. The mapping used to obtain the common curve is indicated by the axes labels. ($\nu = \omega/2\pi$ is the cyclic frequency). Note that the dielectric constant does not scale as well as the conductivity.

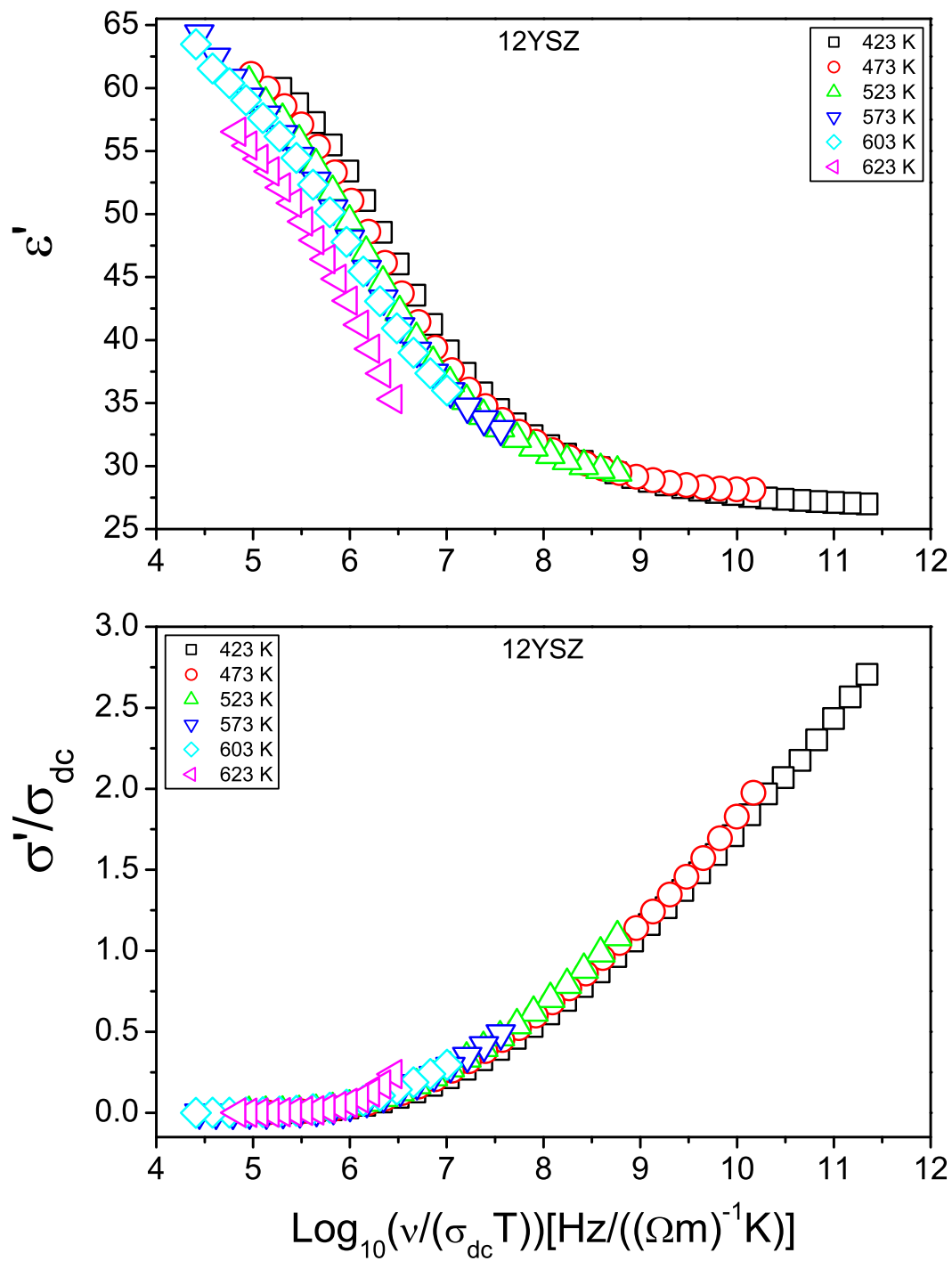


Figure 3.13: Scaling of the real dielectric constant and the real conductivity of a 12 mole % YSZ crystal. The mapping used to obtain the common curve is indicated by the axes labels. ($\nu = \omega/2\pi$ is the cyclic frequency). Again note that the dielectric constant does not scale as well as the conductivity.

The original data was fitted to the four models listed above and the best fitting model was determined, based on the Model Selection Criterion (see Section 2.6.5) and visual observation of the plots of the experimental data and the best fits.

Figures 3.14 and 3.15 show the experimental data and the best fit curves obtained from fitting the data from the 9.5YSZ crystal at 100, 200 and 300 °C to the various models.

It can be seen in Figure 3.14 that the CC and CTRW functions do not fit the experimental data from the 9.5YSZ crystal particularly well. While the shape of the plot for the CC function (Figure 3.14, left) at 100 and 200 °C is similar to that of the experimental data, there is a frequency mismatch, i.e. the calculated values at particular frequencies are markedly different from the experimental values at the same frequencies. At 300 °C, the curve for the calculated data is very different from that of the experimental data. It can also be seen quite clearly in Figure 3.14 (right) that the CTRW does not fit the data at all well and that there are notable differences between the measured and calculated values, especially of the dielectric constant. The best fit parameters to both the CC and CTRW models are given in Table 3.2.

Figure 3.15 shows that the UDR and LLS models fit the 9.5YSZ crystal data reasonably well at most temperatures. There are however some discrepancies at higher temperatures, such as at 300 °C, Figure 3.15 (bottom). The parameters for the best fits are given in Table 3.3.

Table 3.4 gives the values for the Model Selection Criterion (MSC) obtained from fitting the 9.5YSZ single crystal data. Recall that the most appropriate model gives the highest value of the MSC. From the MSC values and the plots presented earlier, it can be seen that the CTRW and CC models do not fit the 9.5YSZ crystal data as well as the LLS and UDR models. Similar results were obtained for the other single crystals. Therefore, the CC and CTRW models were dropped from the list of models suitable for fitting the data for the YSZ crystals. The LLS model is the best for fitting the data when equal weighting is applied while with relative weighting the UDR model fits the data best.

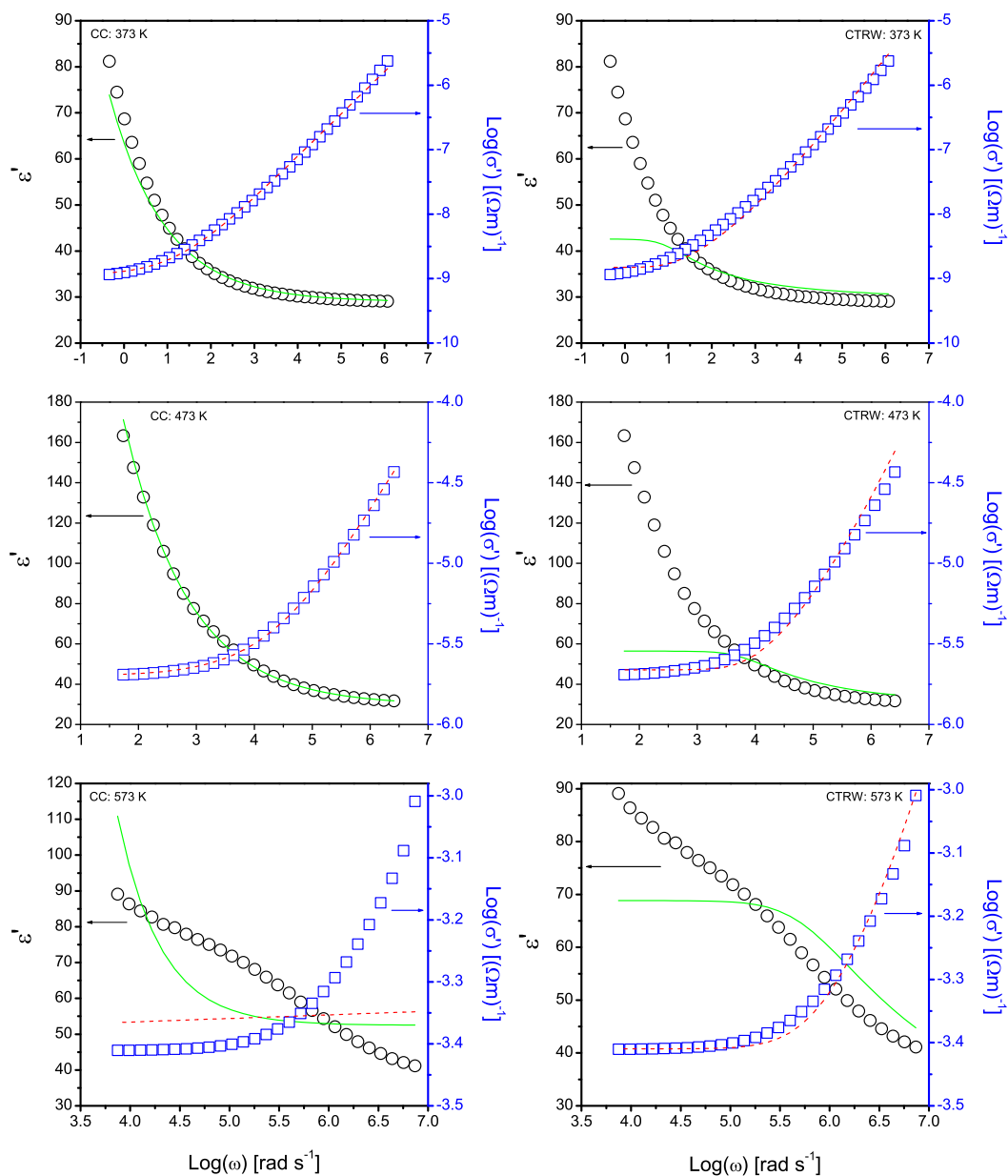


Figure 3.14: Fitting of the frequency dependent dielectric constant and conductivity of the 9.5YSZ crystal at 100 °C (top), 200 °C (middle) and 300 °C (bottom) using the CC and CTRW models (left and right respectively). ○ and □ are the experimental data and the lines are the best fits to the models. Equal weighting was used for the data points. Note that the CC model appears to fit the data reasonably well at 100 and 200 °C. However it can clearly be seen at low frequencies in the dielectric constant curves that the model and the experiment values are different. By 300 °C, the calculated and experimental values are very different for both the models and this difference is more clearly observed in the dielectric constants plots. The best fit parameters are given in Table 3.2.

Table 3.2: The parameters for the Cole-Cole and CTRW models' best fits to the 9.5YSZ crystal data, shown in Figure 3.14. *Value settles at whatever is set as the lower bound for the fitting, i.e. no stable solution found.

Temp. (°C)	Parameter	CC	CTRW
100	$\sigma_{dc} (\Omega m)^{-1}$	$(1.0161 \pm 0.0078) \times 10^{-9}$	$(1.164 \pm 0.024) \times 10^{-9}$
	s	0.6277 ± 0.0059	-
	ϵ_{∞}	28.784 ± 0.062	17.90 ± 0.99
	τ (sec)	0.2486 ± 0.0061	0.774 ± 0.072
200	$\sigma_{dc} (\Omega m)^{-1}$	$(2.00 \pm 0.88) \times 10^{-6}$	$(2.0492 \pm 0.0011) \times 10^{-4}$
	s	0.614 ± 0.003	-
	ϵ_{∞}	29.47 ± 0.81	$24 \pm ?^*$
	τ (sec)	$(1.0366 \pm 0.0043) \times 10^{-4}$	$(6.17 \pm 0.50) \times 10^{-4}$
300	$\sigma_{dc} (\Omega m)^{-1}$	$(3.89 \pm 0.60) \times 10^{-4}$	$(3.89 \pm 0.81) \times 10^{-4}$
	s	0.88 ± 0.26	-
	ϵ_{∞}	16 ± 12	$16 \pm ?^*$
	τ	$9 \times 10^{-7} (\pm 10)$	$(2.605 \pm 0.053) \times 10^{-6}$

Table 3.3: The parameters for the UDR and LLS models' best fits to the 9.5YSZ crystal data, shown in Figure 3.15. *Value settles at whatever is set as the lower bound for the fitting, i.e. no stable solution found.

Temp. (°C)	Parameter	UDR	LLS
100	$\sigma_{dc} (\Omega m)^{-1}$	$(1.0161 \pm 0.0078) \times 10^{-9}$	$(1.0163 \pm 0.0057) \times 10^{-9}$
	s	0.6277 ± 0.0059	0.6291 ± 0.0060
	ϵ_{∞}	28.784 ± 0.062	28.72 ± 0.12
	A	$(2.341 \pm 0.068) \times 10^{-10}$	-
200	$\sigma_{dc} (\Omega m)^{-1}$	$(1.9952 \pm 0.0017) \times 10^{-6}$	$(1.99606 \pm 0.00086) \times 10^{-6}$
	s	0.6401 ± 0.0047	0.6463 ± 0.0014
	ϵ_{∞}	28.20 ± 0.28	27.535 ± 0.076
	A	$(3.25 \pm 0.14) \times 10^{-9}$	-
300	$\sigma_{dc} (\Omega m)^{-1}$	$(3.88 \pm 0.16) \times 10^{-4}$	$(3.87 \pm 0.81) \times 10^{-4}$
	s	0.91 ± 0.36	0.8187 ± 0.0031
	ϵ_{∞}	16 ± 18	26.25 ± 0.20
	A	$(2 \pm 1) \times 10^{-10}$	-

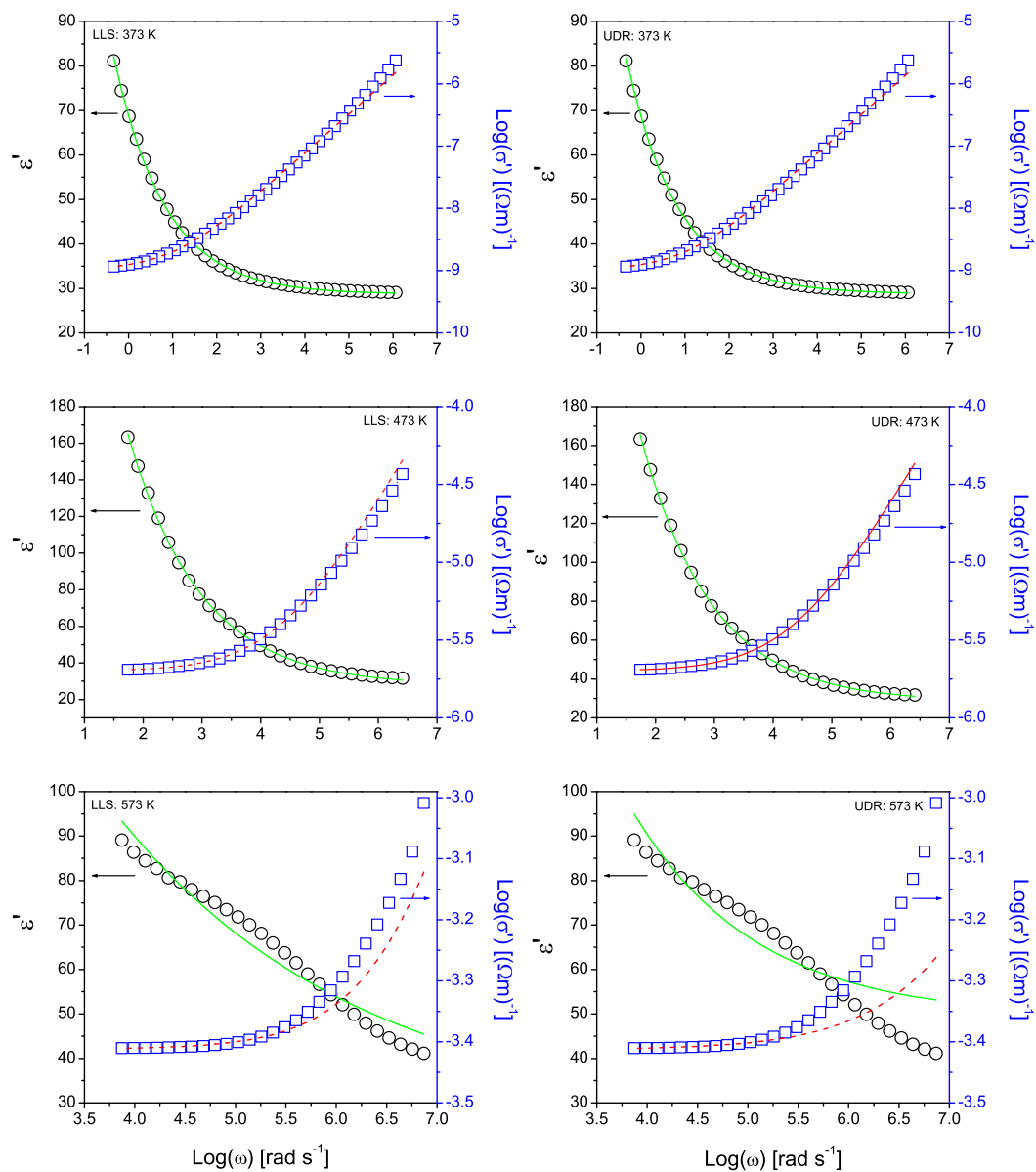


Figure 3.15: Fitting of the dispersive properties of a 9.5YSZ crystal at 100 °C (top) and 300 °C (bottom) the LLS and the UDR models (left and right respectively). $\circ$ and $\square$ are the experimental data and the lines are the best fits to the models. Equal weighting was used for the data points. Note that at low temperatures, including 100 °C the LLS and UDR models give similar results. The LLS model performs better than the UDR model at the highest temperatures. The parameters for the best fits are given in Table 3.3.

Table 3.4: Values of the Model Selection Criterion for selection of the best fitting model for the frequency dependence of the real dielectric constants and conductivities of the 9.5YSZ crystal.

Model	9.5YSZ, Equal Weighting	9.5YSZ, Relative ($1/Y^2$) Weighting
LLS	11.78	15.25
UDR	10.17	15.52
CC	9.79	14.11
CTRW	8.36	13.13

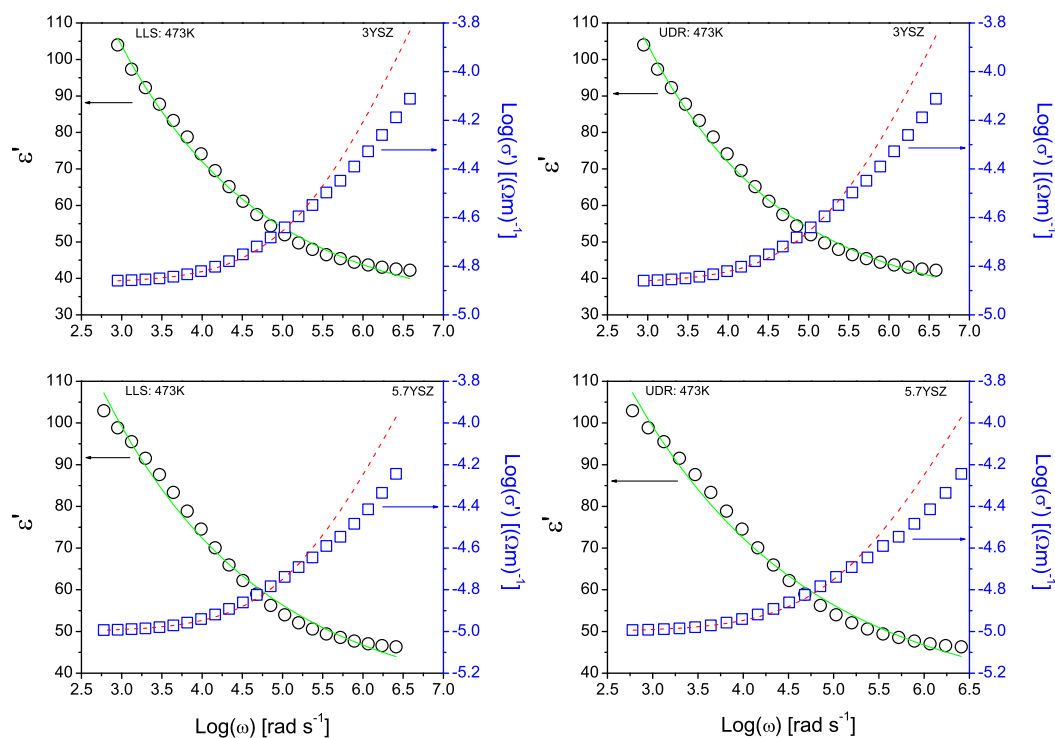


Figure 3.16: The experimental frequency dependent real dielectric constants ($\circ$) and conductivities ($\square$) of the two tetragonal stabilized zirconia single crystals (top and bottom) at 200 °C and the best fits to the LLS and UDR models (lines, left and right respectively). Neither of the two models fits the experimental data very accurately at this temperature.

The results obtained from fitting the data from the various crystals to the LLS and UDR models are now presented.

Figure 3.16 shows the results of fitting the experimental data from the two **tetragonal stabilized zirconia** single crystals using the LLS and UDR models. From the plots, it is quite difficult to pick between the models, as they produce curves that are almost identical. The values of the best fit parameters at various temperatures are shown in Figures 3.17 and 3.18 for the

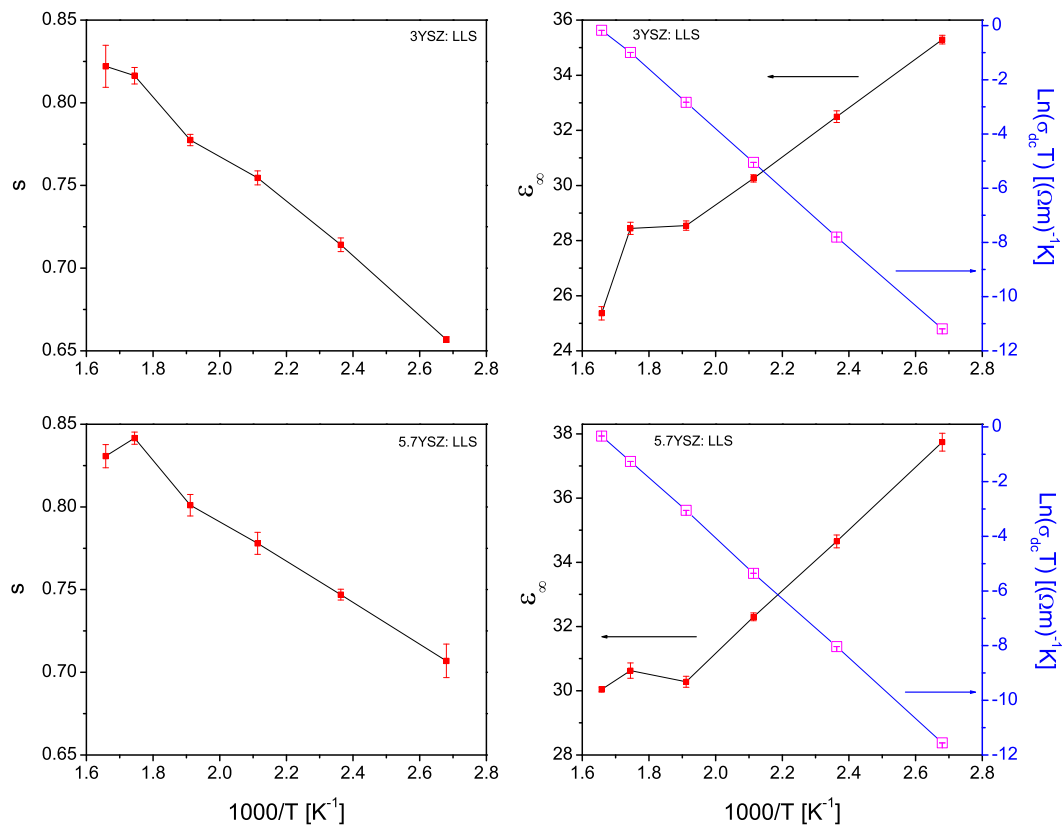


Figure 3.17: The temperature dependence of the best fit parameters to the LLS equation for the tetragonal stabilized zirconia single crystals.

LLS and UDR models respectively. It can be seen in Figure 3.17 that for the LLS, the value of the exponent s rises with increasing in temperature, while $\ln(\sigma_{dc}T) \propto 1/T$ as would be expected from Equation (3.3). The calculated value for the high frequency dielectric constant (ϵ_∞) decreases slowly with increasing temperature. Figure 3.18 shows that for the UDR model, the exponent s and the high frequency dielectric constant (ϵ_∞), appear more or less independent of the temperature. The log of the pre-factor, A , also appears not to be strongly dependent on the temperature. Again, $\ln(\sigma_{dc}T) \propto 1/T$ as would be expected.

The results obtained from fitting the data from the two **cubic stabilized zirconia** single crystals at 200 °C are shown in Figure 3.19. Both the models fit the data from the 9.5YSZ crystal, particularly well. However, there is a feature in the dielectric constant of the 12YSZ crystal at $\log(\omega) \approx 2$ which

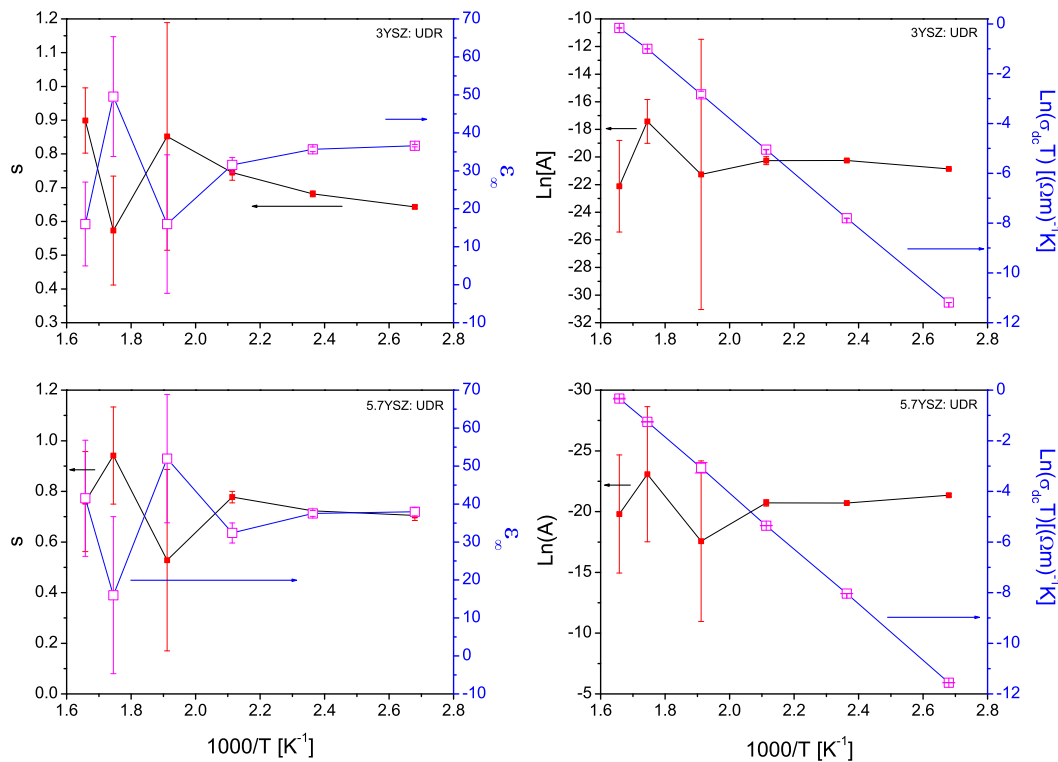


Figure 3.18: The temperature dependence of the best fit parameters to the UDR equation for the tetragonal stabilized zirconia single crystals.

cannot be fitted accurately by either of the two models, which give a dielectric constant whose slope increases monotonically with decreasing frequency. None of the other models considered could properly fit this feature well, while at the same time giving correct results for the conductivity.

The best fit parameters at various temperatures are shown in Figures 3.20 and 3.21 for the LLS and UDR models respectively. Generally, trends similar to those for the TSZ crystals are seen. However, the value of 16 at 300 °C from the UDR model is likely to be incorrect as it does not match the general trend in the data.

Table 3.5 gives the values for the Model Selection Criterion (MSC) obtained from fitting the data from *all* the YSZ single crystals. Note that the table includes the MSC values for the CC and CTRW models. Again it is seen that the LLS model is the best for fitting the data when equal weighting is applied. With relative weighting, the UDR model fits the data best. The LLS and UDR models will therefore both be used to fit the electrical properties of the grains of the polycrystalline YSZ samples.

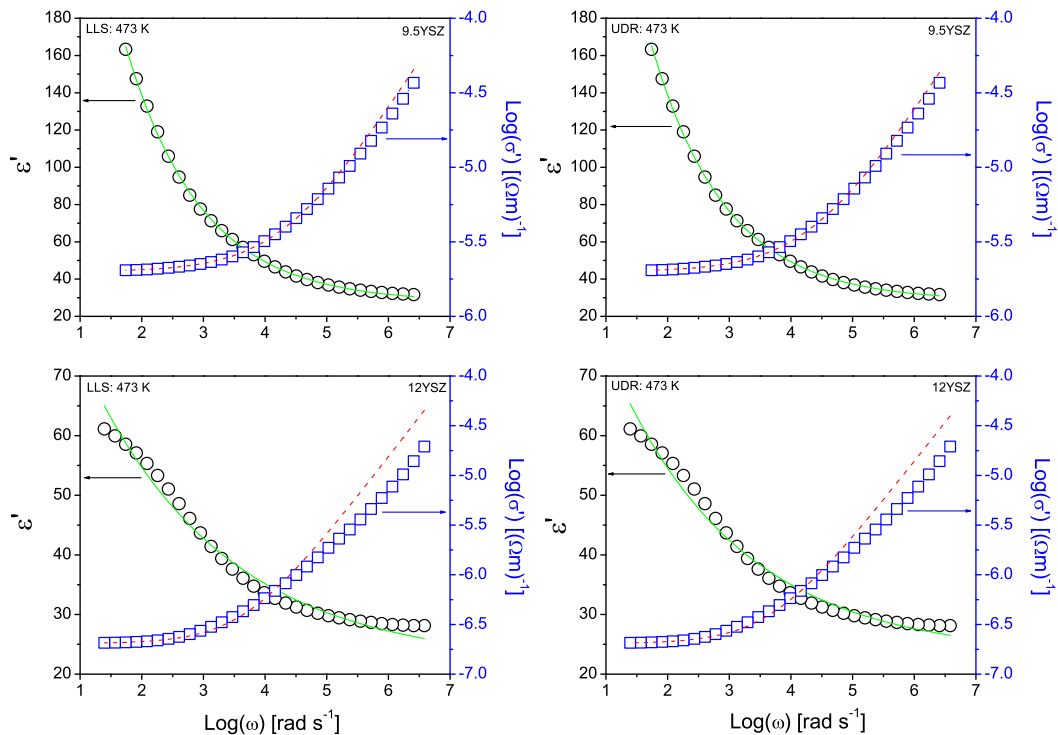


Figure 3.19: The experimental frequency dependent real dielectric constants ($\circ$) and conductivities ($\square$) of the two cubic stabilized zirconia crystals (top and bottom) at 200 °C and the best fits to the LLS and UDR models (lines, left and right respectively).

The validity of the best fit parameters values for the two models that fit the data well can be checked by comparing them with measured values, where these are available. A parameter that can be readily compared with measured values is the high frequency dielectric constant, ϵ_{∞} . The high frequency dielectric constant of pure and yttria stabilized zirconia is dependent on the crystal structure and level of yttria doping. Values ranging from 18 to the high 30's are quoted in the literature. Some of these values are summarized in Table 3.6. Other results, which could not be tabulated in Table 3.6, are as follows: Smith and Davis¹²⁶ report values of 33.4 at 300 K and 32.0 at 77 K, for an unspecified composition YSZ sample, measured using a method described in that work and the references therein as the dielectric rod resonator method (DRRM). A value of 25.7 for the high frequency dielectric constant of a 12YSZ single crystal, calculated from the constant level of infrared reflectivity, is reported in Abelard and Baumard¹²⁷ and the references therein.

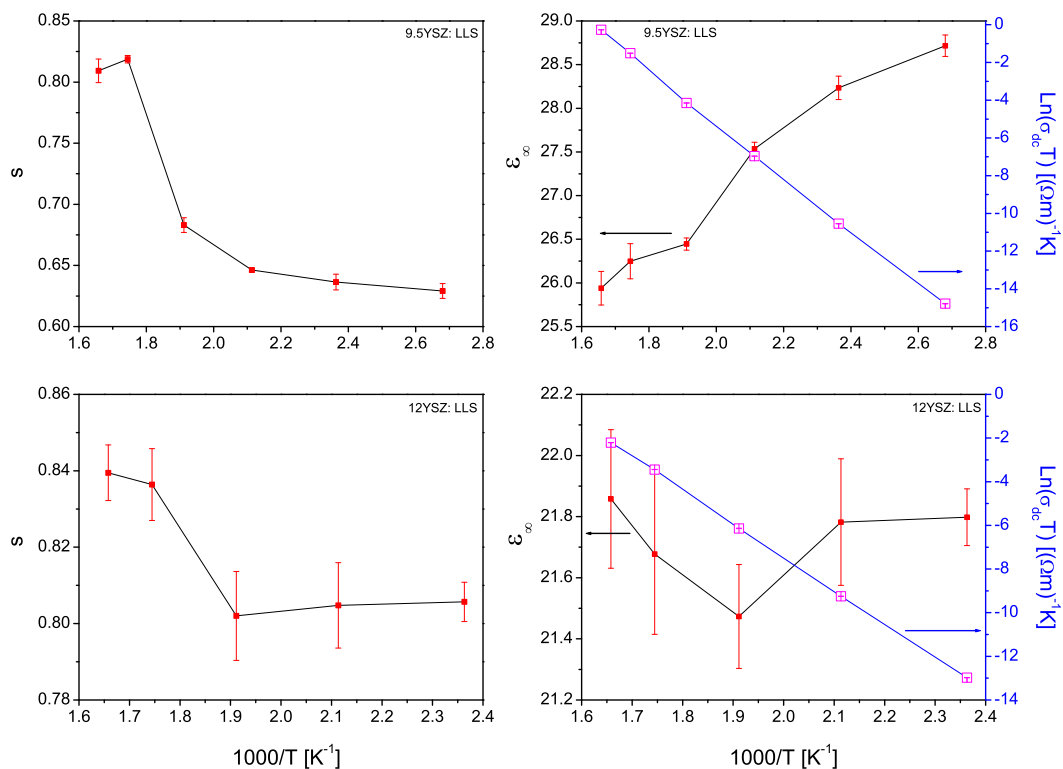


Figure 3.20: The temperature dependence of the best fit parameters to the LLS equation for the cubic stabilized zirconia single crystals.

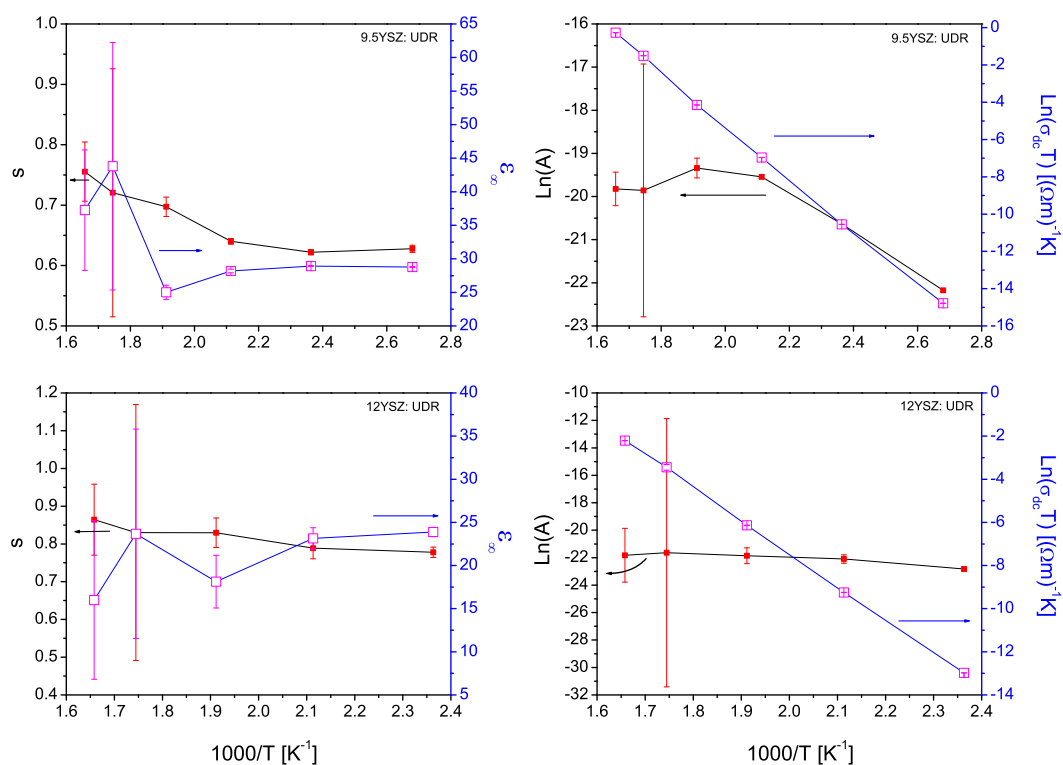


Figure 3.21: The temperature dependence of the best fit parameters to the UDR equation for the cubic stabilized zirconia single crystals.

Table 3.5: Values of the Model Selection Criterion for selection of the best fitting model for the frequency dependence of the real dielectric constants and conductivities of *all* the YSZ crystals.

Model	All Crystals, Equal Weighting	All Crystals, Relative Weighting
LLS	10.85	13.28
UDR	10.15	14.78
CC	9.14	13.64
CTRW	8.05	12.35

Table 3.6: Some of the values for the high frequency dielectric constant of YSZ found in the literature.

Yttria content (mole %)	Structure	Temp.	Freq.	Dielectric Constant	Source
0	Monoclinic and Polycrystalline	300 K	10 GHz	17.9	[Lanagan et al. ¹²⁴]
2	Monoclinic and Tetragonal	300 K	10 GHz	34.5	[Lanagan et al. ¹²⁴]
3	Tetragonal	77 K	1 GHz	31.73	[Hosking et al. ¹²⁵]
3	Tetragonal	300 K	1 GHz	32.99	[Hosking et al. ¹²⁵]
9	Single crystal cubic	300 K	10 GHz	27.2	[Lanagan et al. ¹²⁴]

With the exception of a value of 16 obtained from the UDR model for 5.7 and 12 mole % crystals at 300 °C, the best fit values obtained from the LLS and the UDR models are consistent with the values measured by other authors.

Figure 3.22 (top) shows the **measured** real dielectric constant and dielectric loss, for the 12YSZ crystal at 200 °C. Figure 3.22 (bottom) shows the **measured** imaginary impedance and the dielectric loss **calculated** from the K-K transform of the measured real dielectric constant, also for the 12YSZ crystal at 200 °C. As discussed in Section 1.6, the K-K transform allows relaxation losses, which in the measured data are masked by the dominant ohmic conduction losses, to be clearly observed. The calculated dielectric loss data in Figure 3.22 (bottom) indicates that there is a single dominant polar relaxation process in the crystal. It can also be seen that the peak frequency

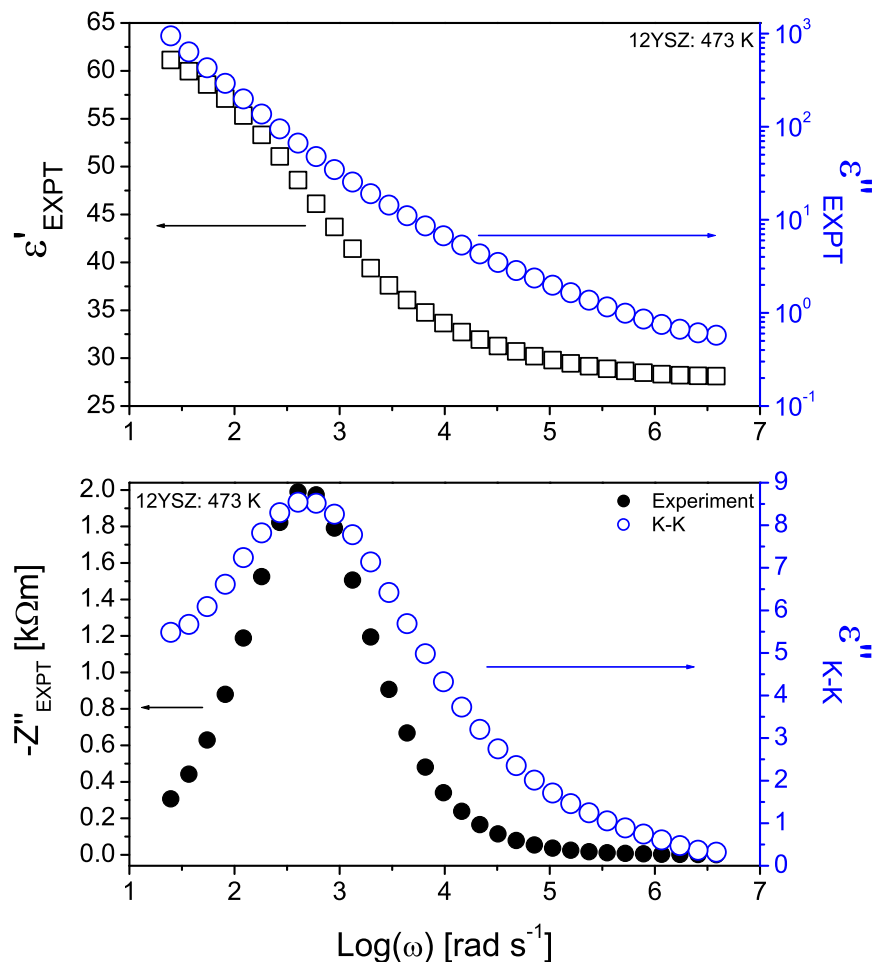


Figure 3.22: The top figure shows the measured dielectric constant and dielectric loss of the 12YSZ single crystal at 200 °C. The bottom figure shows the measured imaginary impedance and the dielectric loss calculated from a K-K transform of the measured dielectric constant. All are plotted as functions of $\log(\omega)$.

of the polar relaxation process is the same as that of the measured $-Z''$. This suggests that, in spite of the dominance of the ohmic conduction losses in the measured data, the underlying relaxation process determines the characteristic frequency of the crystal. Only a single relaxation loss peak (incomplete at some temperatures) is observed for all the crystals and at all temperatures investigated (again note that electrode effects are excluded from this analysis).

Even though it only has a small influence on the magnitude of the measured dielectric loss, the polar relaxation process has a notable influence on

the measured real dielectric constant, seen by the change in slope of the ϵ' curve in Figure 3.22 (top), at the same frequency as the peak of both the measured Z'' and the calculated ϵ'' . The failures, particularly at higher temperatures, of the UDR and LLS models, may arise from their not being able to fit this relaxation process accurately. Recall that, for consistency, the models must *simultaneously* accurately fit both the real and imaginary parts of the data.

3.3 Conclusions

From the single crystal data, it is seen that the conductivity of yttria-stabilized zirconia is very strongly frequency and temperature dependent. The CTRW and CC models do not fit the data particularly well at most frequencies and temperatures. The LLS model has been found to be the best for fitting the experimental data when equal weighting is used. It is also observed that while this expression gives the best fit to the data, in some cases, especially at higher temperatures, it does not always describe the crystal data very well and the “best fits” obtained are not particularly good. The UDR model also fits the data reasonably well and when relative weighting is used, it produces better fit statistics than the LLS model. The work on the single crystals has not established either the UDR or LLS model as being the superior in all situations and therefore, when fitting polycrystalline sample data, both models will be used and the results for the best fit to both models will be presented. More theoretical work is needed on models to fit the ac conductivity of single crystal yttria-stabilized zirconia and other similar systems. The models currently available in the literature do not fit the experimental data over a wide enough frequency and temperature range. Various authors are still discussing some fundamental aspects of the transport properties in YSZ [Monty¹²⁸ and the references therein]. The uncertainty in the modeling of the electrical properties of the single crystals will certainly lead to errors and inconsistencies in the modeling and fitting of composites and ceramics data,

in which crystalline grains are a component as the fitting of the total ceramic data *cannot* be better than that of the component data. However, it will later be shown that these are not too serious and that reasonable fitting of experimental polycrystalline ceramic data is usually obtained.

Chapter 4

Simulations of the electrical properties of binary composites

4.1 Introduction

In analyzing and modeling impedance spectra it is very useful to be able to obtain some information about the electrical properties of the components, directly from the composite material's experimental data. The simulations discussed in this chapter are used to investigate how identifiable the component properties are for a wide range of compositions and for the different effective media and percolation models. In particular, the dependence of the characteristic frequencies and the contributions of the components to the dc conductivity on the component properties and the composition are investigated. Other areas in physics and chemistry (x-ray spectroscopy, optics) make wide use of "signature line" data bases, to identify materials from spectra, without the need for sophisticated fitting each time. While this may not be entirely applicable to the ac conductivity, there may still be some scope for some limited and rapid identification of component materials, when their properties lie in the right range to give identifiable features. This would complement and not replace detailed fitting of the composite properties to the various models and help ensure correct analysis of the data.

4.2 Results and discussion

4.2.1 Composites where the properties of only one of the components are dispersive.

The ac conductivity and impedances of simulated composites, where the properties of only one of the components are dispersive, are compared with the properties of the components.

For the simulations in this section, the parameters used in the LLS model (Equation (1.18)) for the dispersive properties of the more conducting (grain) component are $\sigma_{dc} = 2.004 \times 10^{-6}(\Omega m)^{-1}$, $\epsilon_{\infty} = 27.481$, $s = 0.651$. Realistic values for these parameters were obtained from the best fit for a 9.5 mole % YSZ single crystal at 200 °C. The less conducting component (grain boundary or matrix) is modeled with a dispersionless real dielectric constant $\epsilon_{\ell} = 12$ and conductivity $\sigma_{\ell} = 1 \times 10^{-8}(\Omega m)^{-1}$.

Figure 4.1 shows the frequency dependence of the real dielectric constants and the real conductivities of the components ($\phi = 0$ and $\phi = 1$) and of a simulated composite ($\phi = 0.99$) calculated using the Maxwell-Wagner model (Equation (1.1)). It can be seen in the figure that relatively simple component properties lead to complex composite properties. Note the characteristic shapes of the dielectric constant and conductivity curves for a high ϕ binary composite. The rise in the composite dielectric constant from its high frequency value is in two stages separated by a shoulder at intermediate frequencies. This shoulder is not seen in the single component data. The conductivity is characterized by a power law drop ($\sigma' \propto \omega^s$) at high frequencies, a shoulder at intermediate frequencies and a broad flat region at the lowest frequencies (see also Section 1.2). To simplify the analysis, electrode effects have been omitted from these simulations. It can also clearly be seen that the composite data at high frequency closely follows that of the more conducting component and therefore, at least in some range of high volume fractions, the

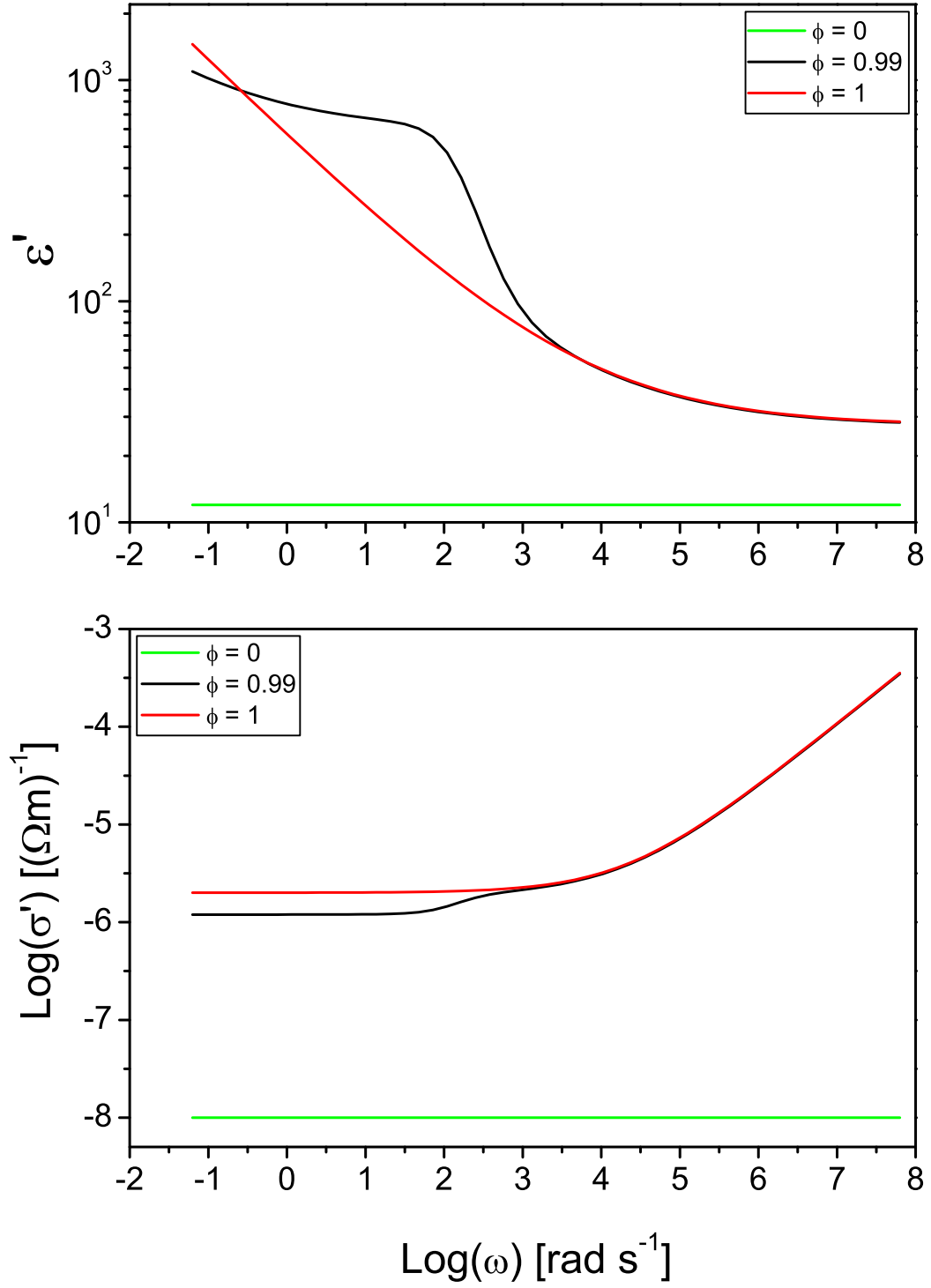


Figure 4.1: The frequency dependence of the real dielectric constant (top) and the real conductivity (bottom) of a composite simulated using the Maxwell-Wagner equation with $\phi = 0.99$ and those of its components ($\phi = 0$ and $\phi = 1$). The other simulation parameters are $\sigma_{dc} = 2.004 \times 10^{-6}(\Omega\text{m})^{-1}$, $\epsilon_{\infty} = 27.481$ and $s = 0.651$, for the more conducting component, whose properties were calculated using the LLS model and $\epsilon_{\ell} = 12$, $\sigma_{\ell} = 1 \times 10^{-8}(\Omega\text{m})^{-1}$ for the dispersionless properties of the less conducting component.

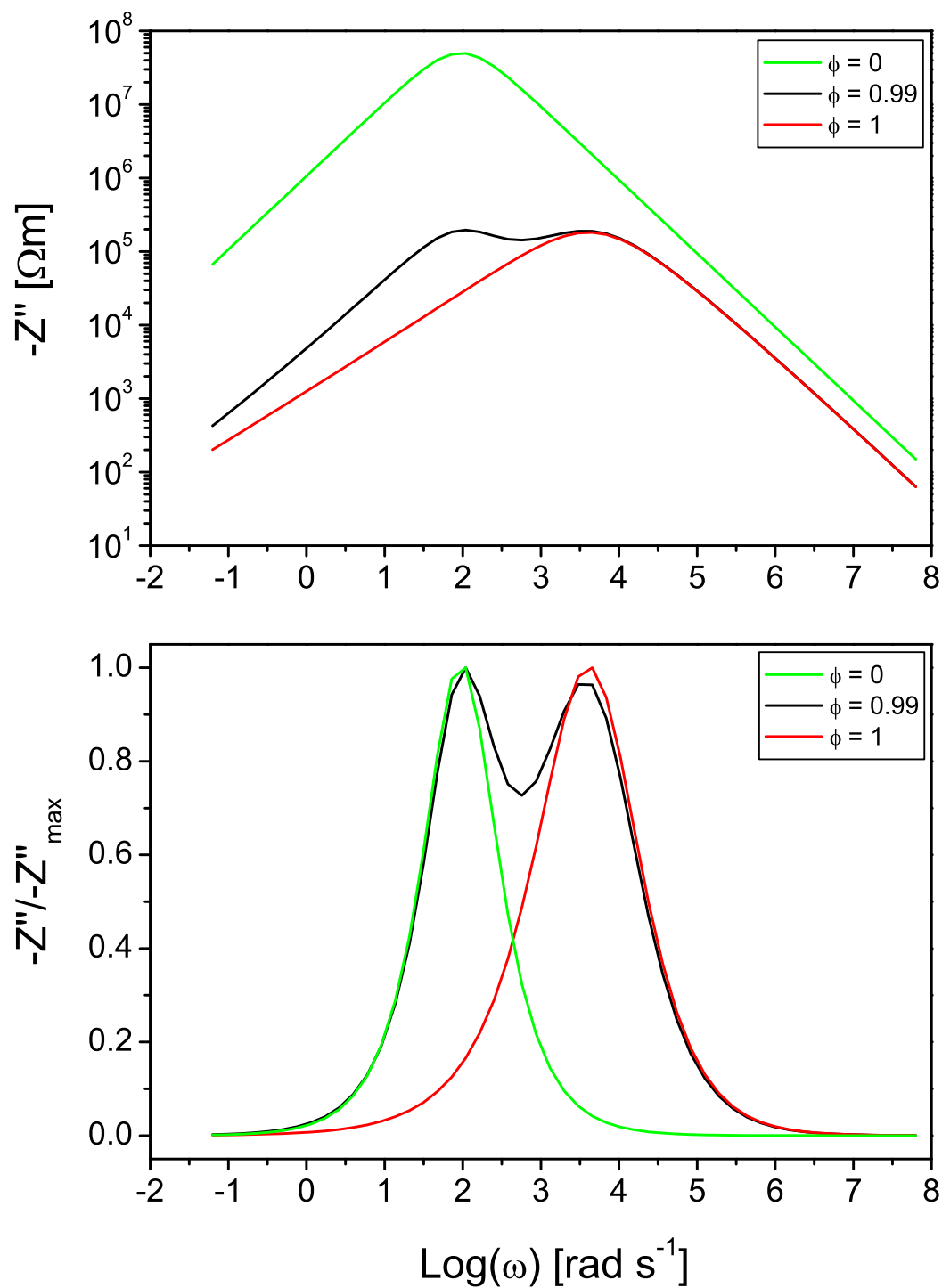


Figure 4.2: The frequency dependence of the imaginary impedance and the normalized imaginary impedance of a composite simulated using the Maxwell-Wagner equation with $\phi = 0.99$ and those of its components. The other simulation parameters are given in Figure 4.1 and in the text.

high frequency portion of the composite data can be taken as closely representing the more conducting component. This may and is exploited later in the fitting of experimental composite data, with the more conducting component properties being estimated by fitting the data at high frequency. Not much information about the properties of the less conducting component can be readily extracted from the dielectric constant and conductivity plots, without sophisticated fitting and some knowledge about the microstructure of the composite. However, the imaginary impedance plots and in particular the normalized plot, Figure 4.2, show that the contributions of the components can be readily identified by their characteristic frequencies. The impedance peaks of the composite lie in essentially the same positions as those of the pure components and therefore, in principle, it is possible to identify the components of the composite. However, it should be noted that these peak frequencies depend on both the dc conductivity (σ_{dc}) and permittivity ($\epsilon_0\epsilon_r$) of the material,

$$\omega_{peak} = \frac{\sigma_{dc}(T)}{\epsilon_0\epsilon_r(T)}.$$

Both σ_{dc} and (ϵ_r) are temperature dependent and they may also depend on the gaseous atmosphere under which the measurement is made. This makes the identification of the component contributions reliant on there being data on the components' properties obtained under approximately the same conditions as those for the measurement of the composite properties.

Figure 4.3 shows the frequency dependence of the real dielectric constants and the real conductivities of simulated composites with **varying conducting component volume fractions** (ϕ). At a conductor volume fraction $\phi = 0.90$, the high frequency properties of the composite are markedly different from those of the higher volume fraction composites and therefore those of the more conducting component. At even lower conductor volume fractions this difference increases. The figures indicate that there is a limit to the volume fractions where the component properties can be reasonably accurately obtained from the properties of the composite, when using the Maxwell-Wagner theory (this applies for the other models as well).

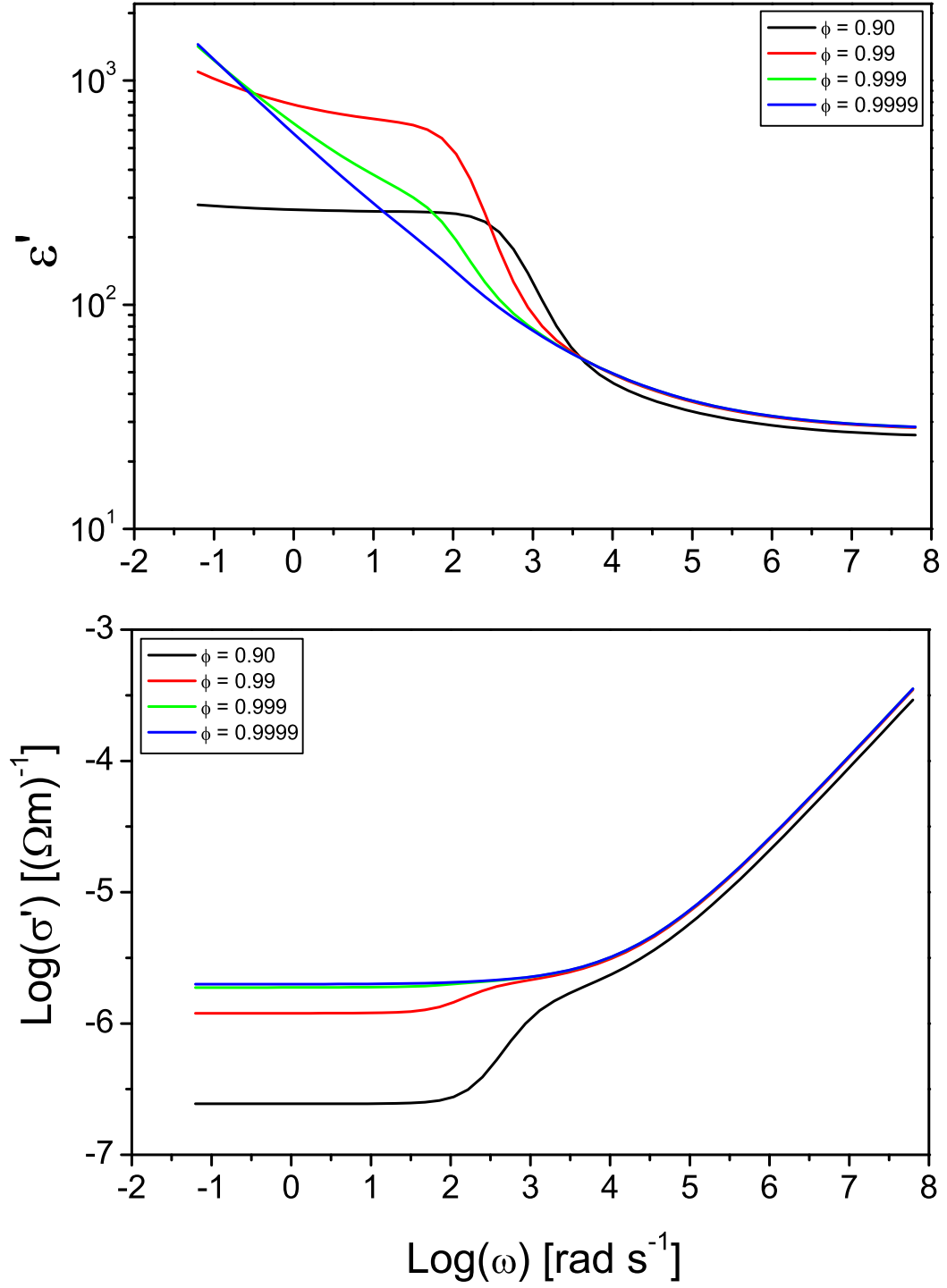


Figure 4.3: The frequency dependence of the real dielectric constants and the real conductivities of composites simulated using the Maxwell-Wagner model, with varying conducting component volume fractions. The other simulation parameters are $\sigma_{dc} = 2.004 \times 10^{-6} (\Omega m)^{-1}$, $\epsilon_{\infty} = 27.481$ and $s = 0.651$, for the more conducting component, whose properties were calculated using the LLS model and $\epsilon_{\ell} = 12$, $\sigma_{\ell} = 1 \times 10^{-8} (\Omega m)^{-1}$ for the dispersionless properties of the less conducting component.

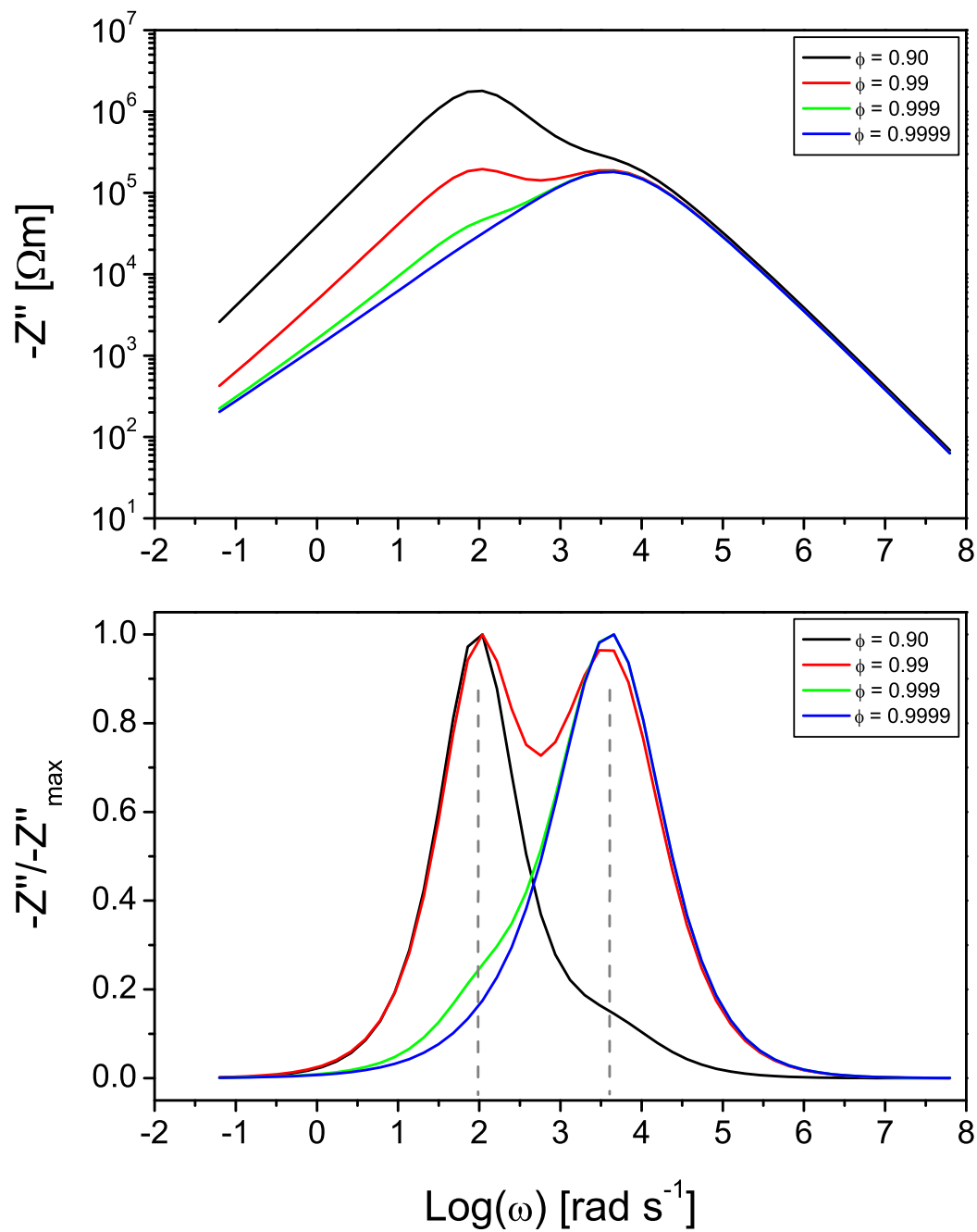


Figure 4.4: The frequency dependence of the imaginary impedance and normalized imaginary impedance of composite simulated using the Maxwell-Wagner model, with varying conducting component volume fractions. The dashed lines indicate the characteristic frequencies of the components. The other simulation parameters are given in Figure 4.3 and in the text.

The imaginary impedances and the characteristic frequencies (positions of the peaks in the imaginary impedance curves) of the composites simulated with varying ϕ are seen in Figure 4.4. Note that the $\phi = 0.90$ and $\phi = 0.9999$ simulations only give shoulders near the peak frequency of the component dominant at high and low frequencies respectively. For the various volume fractions, the identifiable peak frequencies are only slightly perturbed and it is still possible to identify the contributions of each component of the composite. At a volume fraction $\phi = 0.90$ the just observable high frequency shoulder still lies at essentially the same frequency as the other high frequency peaks and can therefore still be associated with them and hence with the more conducting component. Similarly, at $\phi = 0.999$ the low frequency shoulder lies at the same frequency as the well resolved low frequency peaks and is therefore associated with the less conducting component. At $\phi = 0.9999$ the low frequency shoulder can barely be observed.

The complex impedance plane plots of the data simulated using the Maxwell-Wagner model with varying conducting component volume fractions are shown in Figures 4.5 and 4.6. The figures also show plots of the data simulated using the Brick Layer Model which, at this value of ϕ , are essentially similar to those of the Maxwell-Wagner model, even though the two models are based on diametrically opposed microstructures (see Section 1.3). The agreement between the two models is better at $\phi = 0.99$ which is well within the dilute limit while there are small deviations at $\phi = 0.90$ which is at the extreme end of the dilute limit ($(1 - \phi_d) \approx 0.1$) [Meredith and Tobias³]. The simulations for the SEPPE ($\phi < \phi_c$), which differ quite markedly from the Maxwell-Wagner equation and BLM simulations are also shown. Note that the microstructure described by the SEPPE in which the conductor is randomly dispersed in the insulating matrix is different from that of the Maxwell-Wagner and Brick Layer models, where the insulator completely coats the conductor. This therefore leads to the differences in the simulations calculated using the SEPPE and those obtained using the Maxwell-Wagner and Brick Layer models. Further SEPPE simulations are discussed below.

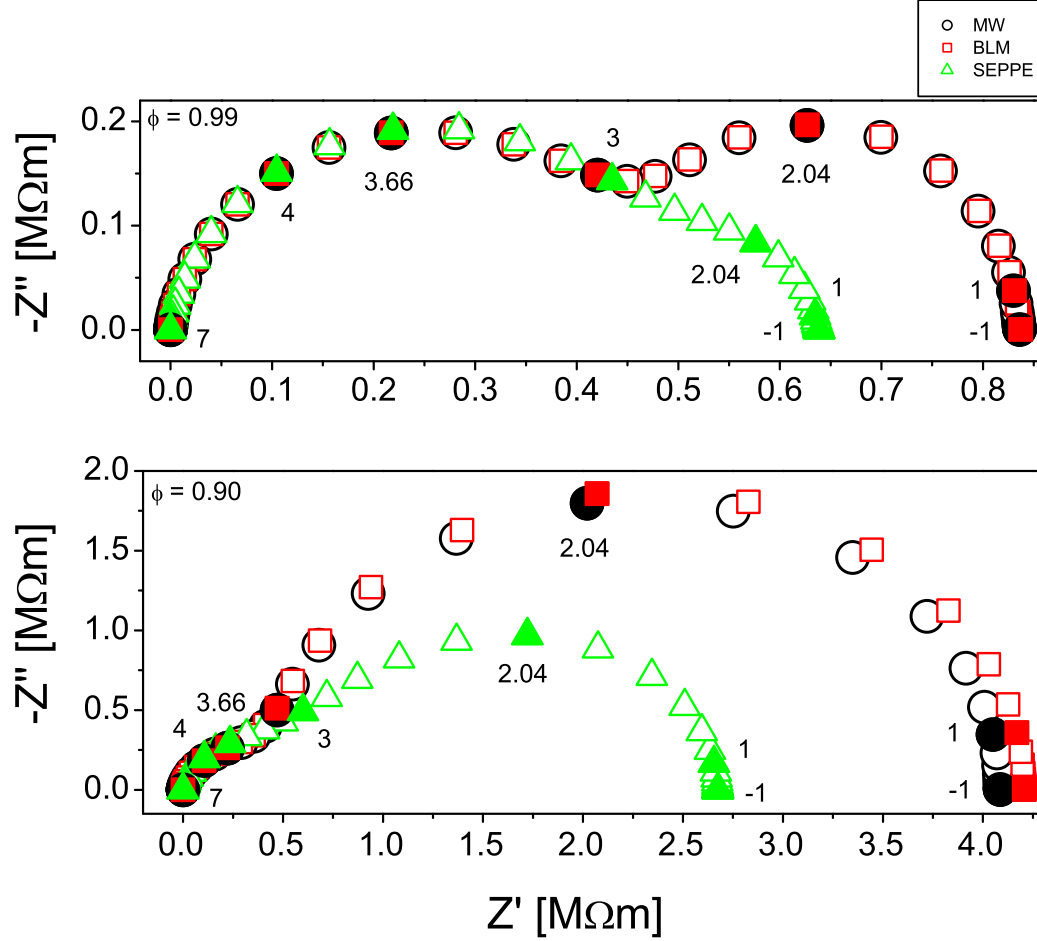


Figure 4.5: The complex impedance plane plots of the data for Maxwell Wagner equation, BLM and SEPPE simulations of binary composites with $\phi = 0.99$ (top) and 0.90 (bottom). The other simulation parameters are $\sigma_{dc} = 2.004 \times 10^{-6}(\Omega m)^{-1}$, $\epsilon_{\infty} = 27.481$ and $s = 0.651$, for the more conducting component, whose properties were calculated using the LLS model and $\epsilon_{\ell} = 12$, $\sigma_{\ell} = 1 \times 10^{-8}(\Omega m)^{-1}$ for the dispersionless properties of the less conducting component. The SEPPE simulation has the additional parameters $\phi_c = 0.999998$ and $t = 2.0$. Key values of $\log(\omega)$ are indicated.

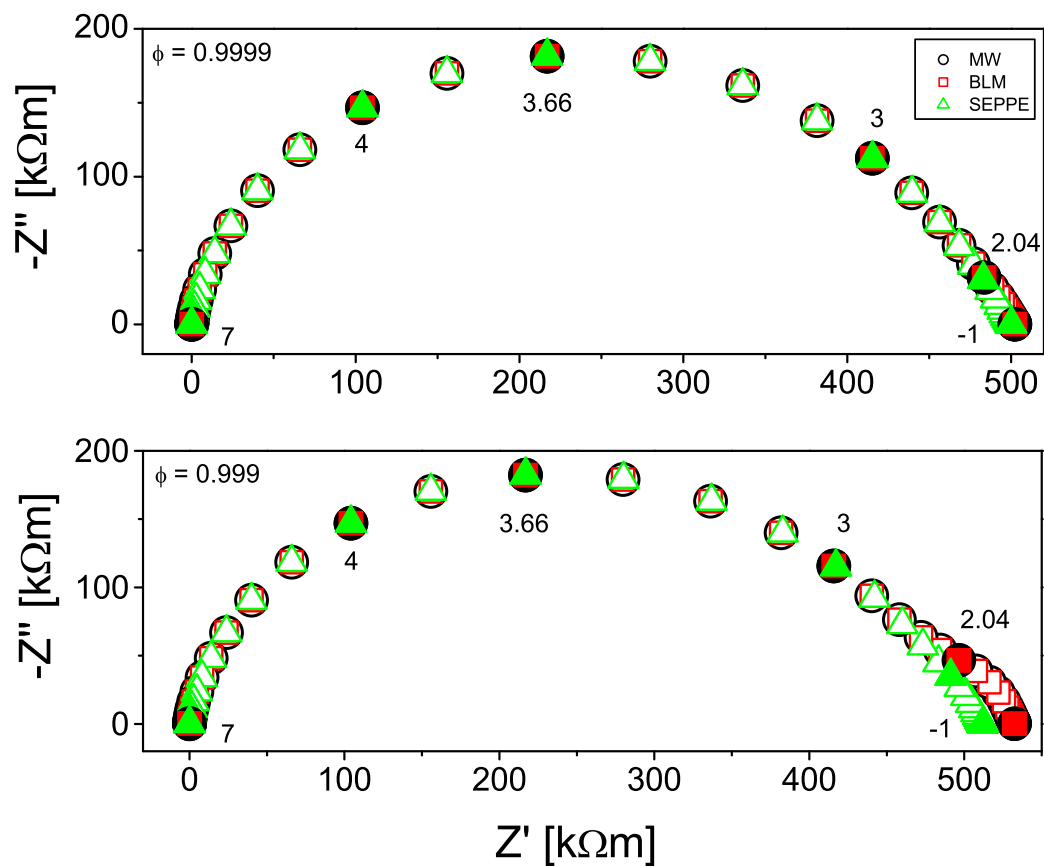


Figure 4.6: The complex impedance plane plots of the data for binary composites simulated using the Maxwell Wagner model, BLM and SEPPE with $\phi = 0.9999$ (top) and 0.999 (bottom). The other simulation parameters are given in Figure 4.5 and in the text. Key values of $\log(\omega)$ are indicated.

The SEPPE uses two extra parameters t and ϕ_c , in addition to the component properties and the conductor volume fraction (ϕ). The effect of varying the values of t and ϕ_c , on the electrical properties of the simulated composites, were investigated and are presented below.

The frequency dependence of the imaginary impedances and normalized imaginary impedances for a number of simulations using the SEPPE, with **varying values of t** , is shown in Figure 4.7. The components can still be identified from the characteristic frequencies, even though these are perturbed in the composite. The complex impedance plane plot, Figure 4.8, also clearly shows that the different values of t lead to impedance spectra which differ significantly. In particular, changes in t have a very noticeable influence on the lower frequency (less conducting component) contribution. At low values of t , the contribution of the less conducting component is very prominent but this contribution diminishes as t increases. The sample dc resistance (intercepts on the real impedance axes) changes by $\sim 100\%$ as t varies from 1.2 to 2.8. The different values of t correspond to different current paths. Values of t between 1.2 and 1.4 are usually observed in two dimensional systems where the current, confined in a plane, *must* flow around the insulating component leading to the prominent features due to this component, which can be seen in the figures. Values between 1.6 and 2.8 are often observed in three dimensional systems where the current can flow around the insulating components in three dimensions giving a greater possibility of connected conducting paths. Therefore, the features due to the less conducting component become less prominent with increasing t . It must again be emphasized that the above features are for the same component properties and the same conducting component and critical volume fractions (ϕ and ϕ_c).

The effects of changing the critical volume fraction (ϕ_c) for fixed component properties, conductor volume fraction (ϕ) and the exponent t are seen in Figures 4.9 and 4.10. If $\phi_c - \phi < 0$ i.e. $\phi > \phi_c$ then only one arc is observed, with the characteristic frequency of the more conducting component, as virtually all the current passes through this component. As $\phi_c - \phi$ increases,

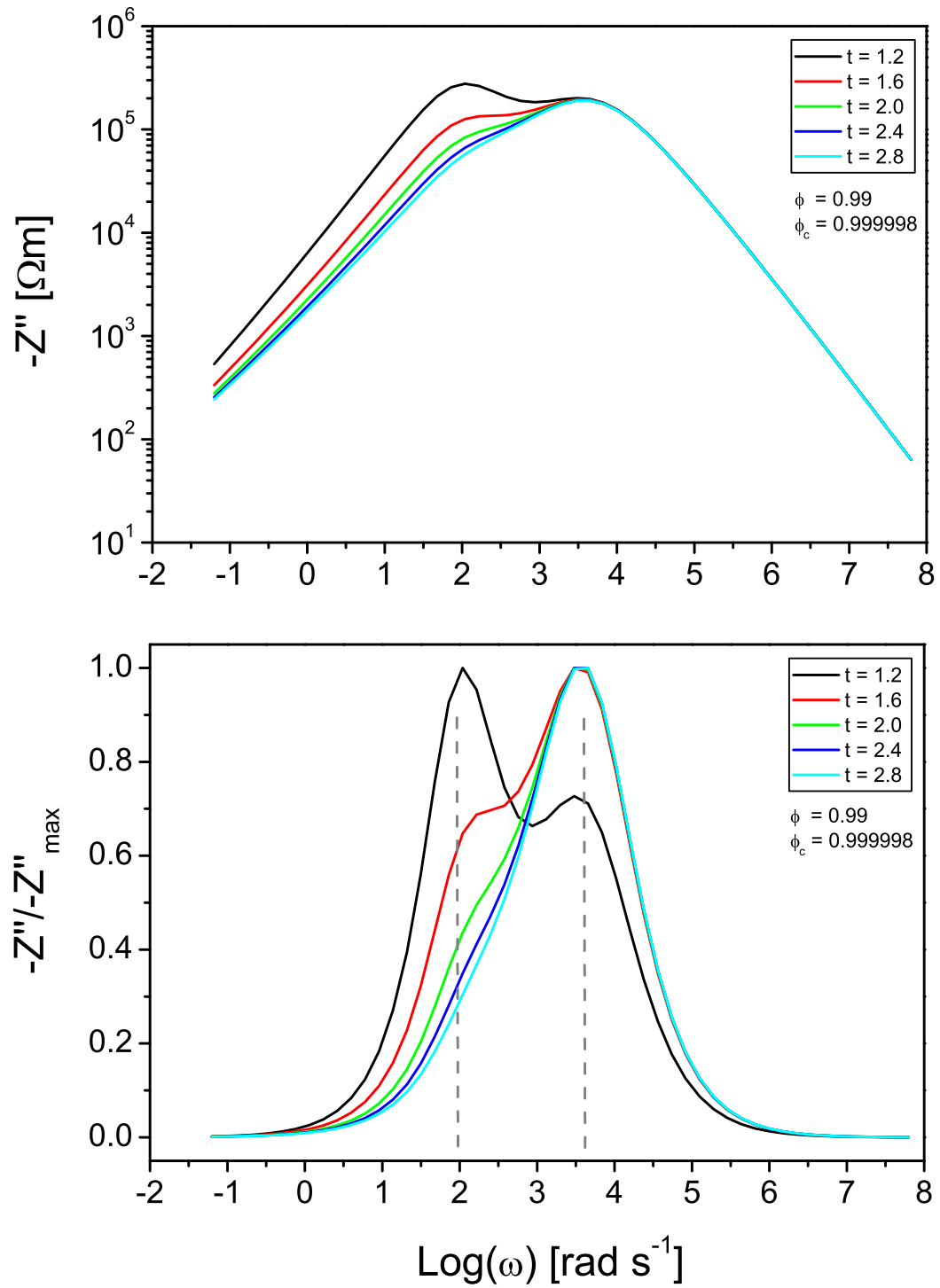


Figure 4.7: The frequency dependence of the imaginary impedances and normalized imaginary impedances of binary composites simulated using the SEPPE, with varying values of the exponent t and fixed values of $\phi = 0.99$ and $\phi_c = 0.999998$. The other simulation parameters, whose values were also fixed, are $\sigma_{dc} = 2.004 \times 10^{-6}(\Omega m)^{-1}$, $\epsilon_\infty = 27.481$ and $s = 0.651$, for the more conducting component, whose properties were calculated using the LLS model and $\epsilon_\ell = 12$, $\sigma_\ell = 1 \times 10^{-8}(\Omega m)^{-1}$ for the dispersionless properties of the less conducting component.

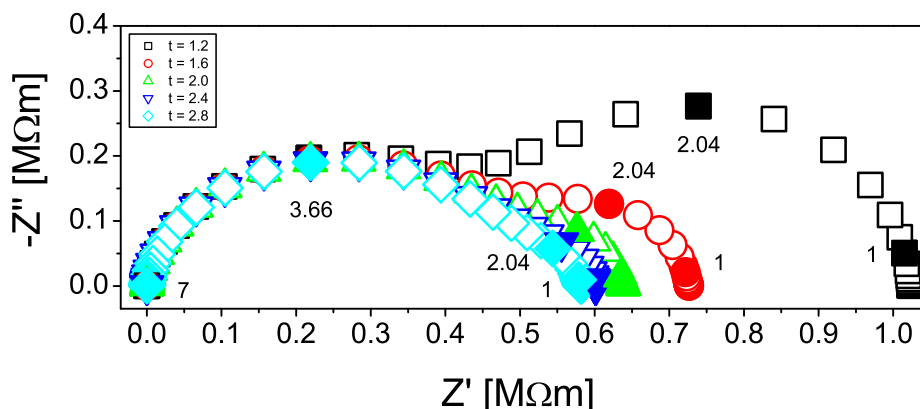


Figure 4.8: The complex impedance plane plot of the data for composites simulated using the SEPPE, with varying values of the exponent t and fixed values of $\phi = 0.99$ and $\phi_c = 0.999998$. The other simulation parameters, whose values were also fixed, are given in Figure 4.7 and in the text. Key values of $\log(\omega)$ are indicated.

the contribution due to the less conducting component becomes more prominent. The higher $\phi_c - \phi$ is, the more prominent is the contribution of the less conducting component. The impedance curves of the simulated composites converge as $\phi_c \rightarrow 1$ (high $\phi_c - \phi$).

4.2.2 Composites where the more conducting component has an (anomalously) large real dielectric constant

Experimentally, a number of systems have been found where one or both of the components have dielectric constants that are extremely high ($\gg 10^3$). To investigate this class of composites, a number of simulations using the Maxwell-Wagner equation, BLM and SEPPE were computed. For simplicity, the simulated properties of both the components are non-dispersive and described by the parameters $\sigma_h = 2.0 \times 10^{-8}$, $\epsilon_h = 10000$, for the “more conducting” component and $\sigma_\ell = 1.8 \times 10^{-8}$, $\epsilon_\ell = 4$ for the “less conducting” component. For the SEPPE simulation, $\phi_c = 0.58$ and $t = 2$. While the same trends in the results were obtained for other component properties

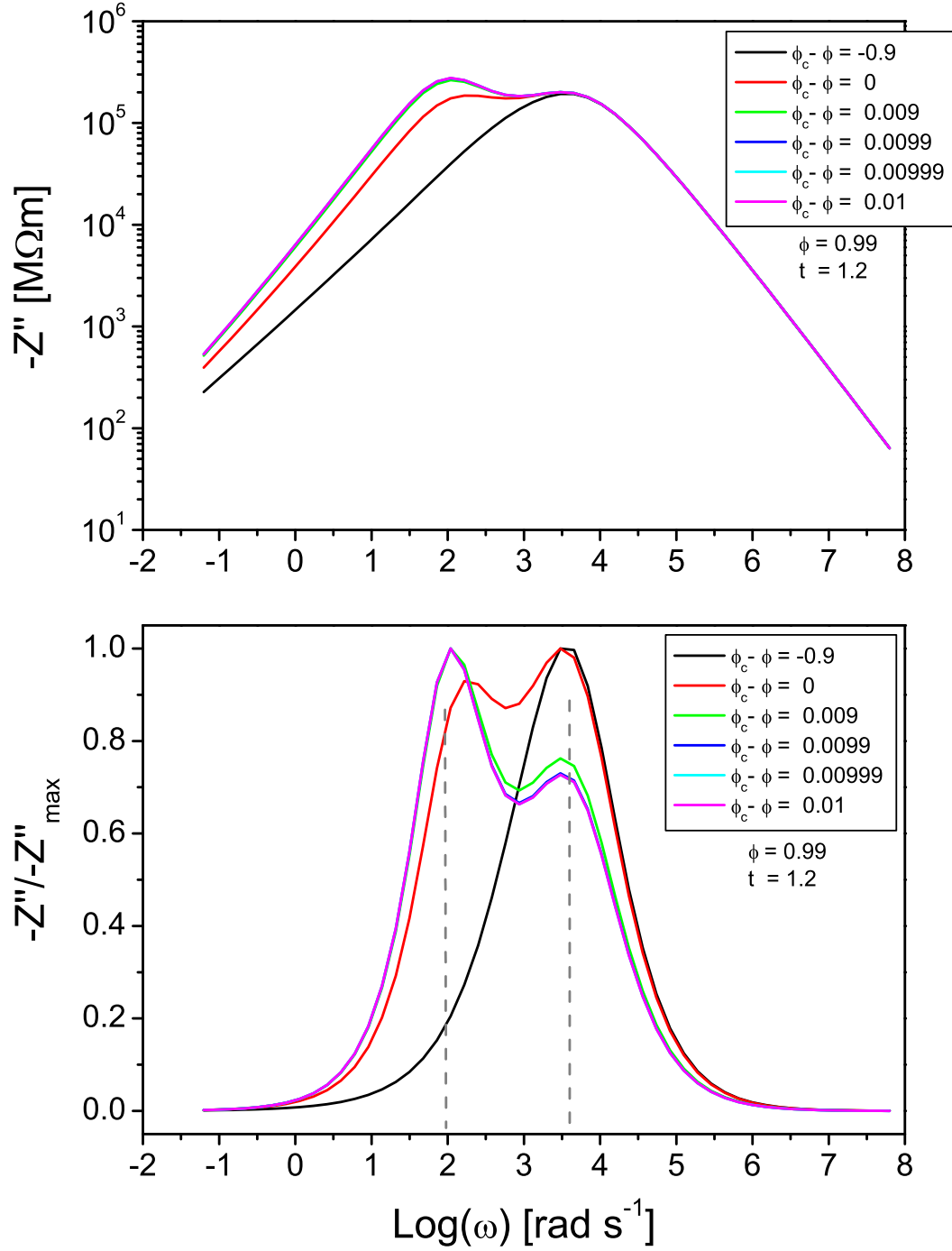


Figure 4.9: The frequency dependence of the imaginary impedances and normalized imaginary impedances of binary composites simulated using the SEPPE, with varying values of ϕ_c and fixed values of $\phi = 0.99$ and $t = 1.2$. The other simulation parameters, whose values were also fixed, are $\sigma_{dc} = 2.004 \times 10^{-6}(\Omega m)^{-1}$, $\epsilon_{\infty} = 27.481$ and $s = 0.651$, for the more conducting component, whose properties were calculated using the LLS model and $\epsilon_{\ell} = 12$, $\sigma_{\ell} = 1 \times 10^{-8}(\Omega m)^{-1}$ for the dispersionless properties of the less conducting component.

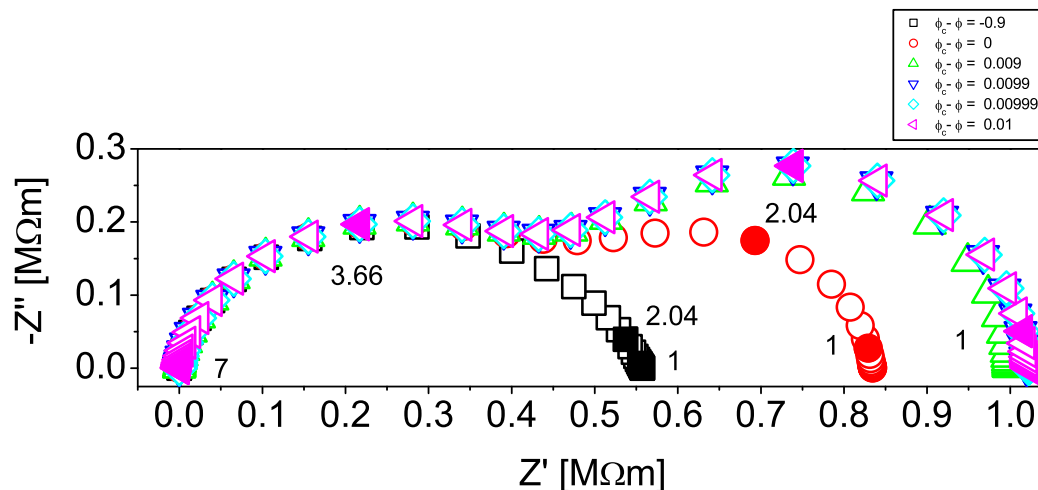


Figure 4.10: Complex impedance plane plots for composites simulated using the SEPPE and variable ϕ_c and fixed values of $\phi = 0.99$ and $t = 1.2$. The other simulation parameters, whose values were also fixed, are given in Figure 4.9. Key values of $\log(\omega)$ are indicated.

and conducting component volume fractions, the conductivity ratio and ϕ range presented here were chosen so that they are similar to those of the polyester-resin/silicon composites discussed in Chapter 6.

The frequency dependence of the real dielectric constants and the real conductivities of composites where one component has an anomalously high dielectric constant, is shown in Figure 4.11 for $\phi = 0.24$, which is representative for all the composites simulated. For all the models, the composite dielectric constant (Figure 4.11, top) lies between those of the components while the conductivity (Figure 4.11, bottom) is higher than that of both the components at all but the lowest frequencies. Figures 4.12, 4.13 and 4.14 show, for increasing conducting component volume fractions, the imaginary impedances and the normalized imaginary impedances for simulations computed using the different models. An important observation to be made is that the order of the peaks is reversed relative to that in the previous simulations i.e. the peak that can be identified as being associated with the “more conducting” component ($\phi = 1$) is at the lower frequencies. While this result is to be expected, since the characteristic frequency is $\omega_p = \frac{\sigma_{dc}}{\epsilon_0 \epsilon_p}$, it does have some implications on the interpretation of experimental data. In

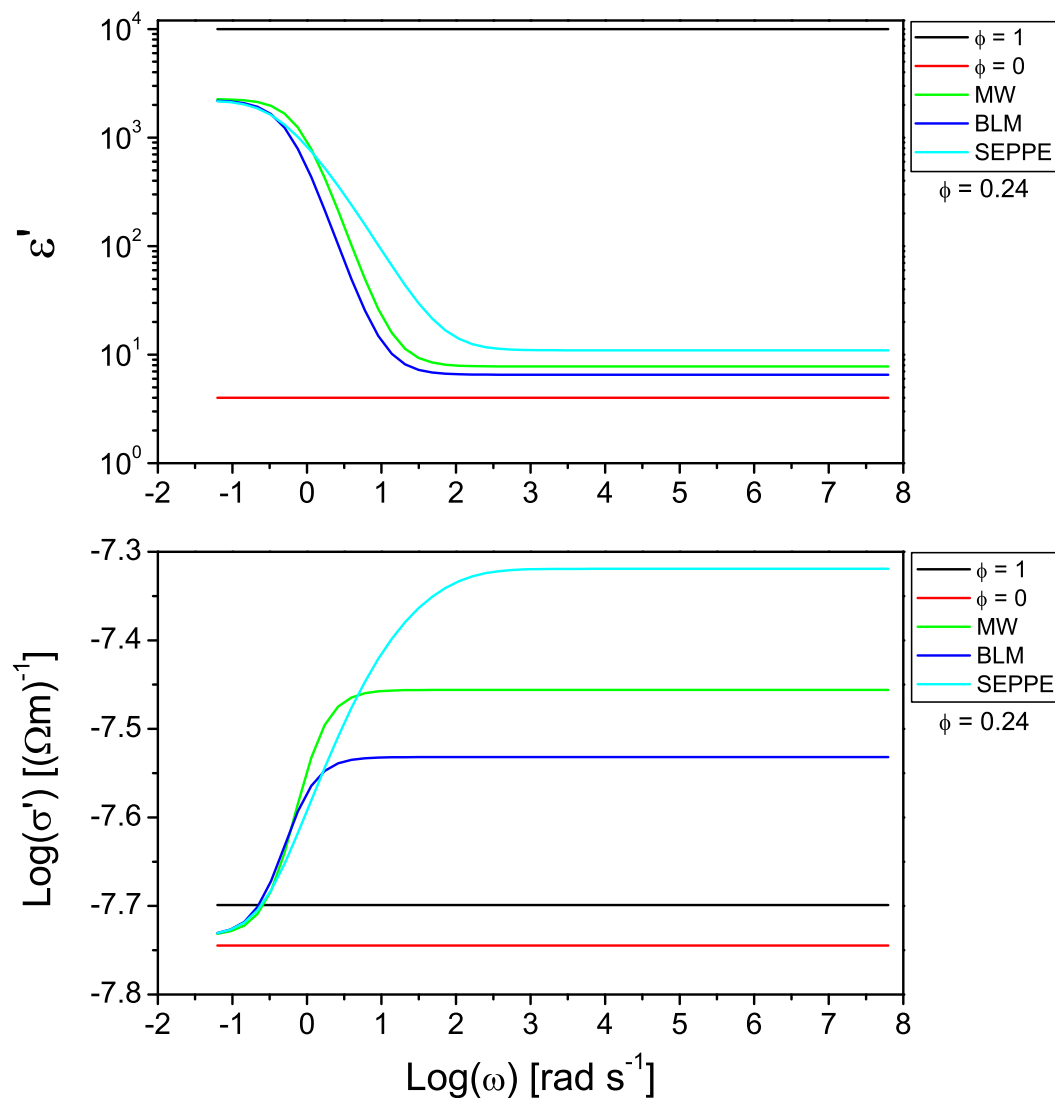


Figure 4.11: Typical dielectric constant and conductivity curves, for simulated composites where the “more conducting” component has an anomalously high dielectric constant, plotted as functions of $\log(\omega)$. The dielectric constants of the simulated composites lie between those of the components, at all frequencies, while the conductivities are higher than that of either component, at all but the lowest frequencies. For the simulated composites, $\phi = 0.24$ and the other parameters are $\sigma_h = 2.0 \times 10^{-8}$, $\epsilon_h = 10000$, $\sigma_\ell = 1.8 \times 10^{-8}$, $\epsilon_\ell = 4$. For the SEPPE simulation, $\phi_c = 0.58$ and $t = 2$.

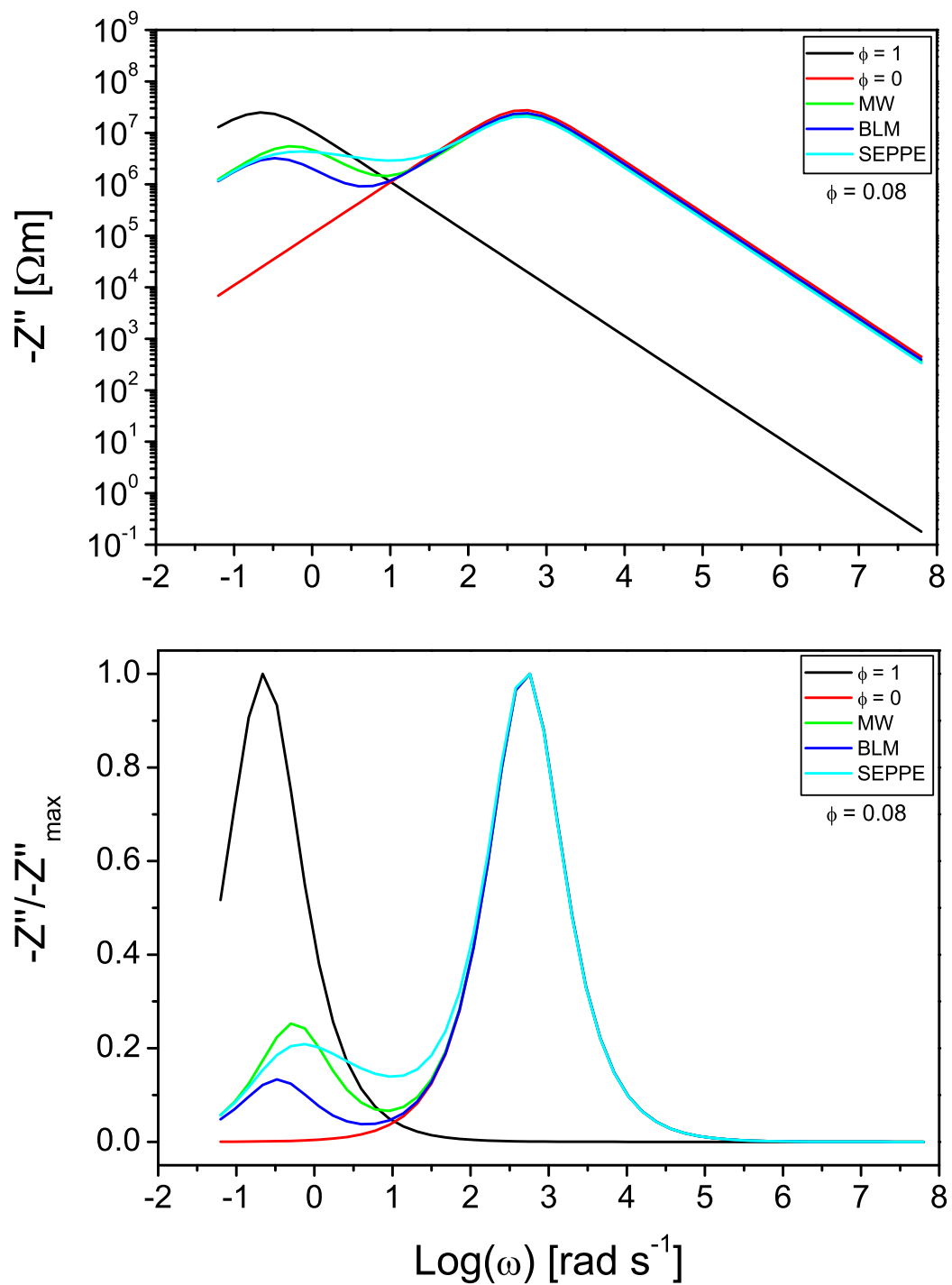


Figure 4.12: The frequency dependence of the imaginary impedances and normalized imaginary impedances of simulated composites, where the “more conducting” has a very large real dielectric constant. Note the relative positions of the peaks, that of the more conducting component ($\phi = 1$) is at the lower frequencies. For the simulated composites, $\phi = 0.08$ and the other parameters are given in Figure 4.11 and in the text.

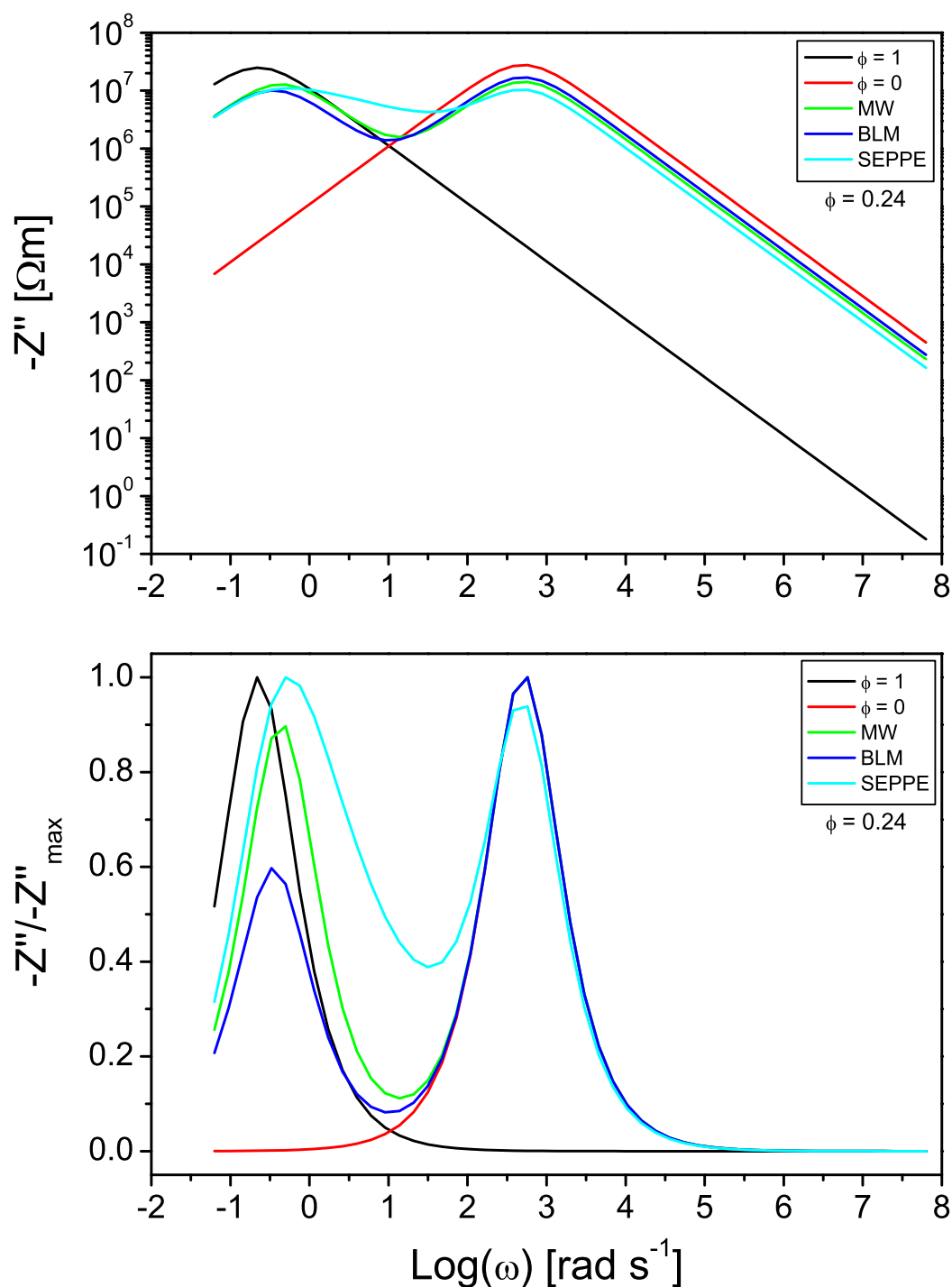


Figure 4.13: The frequency dependence of the imaginary impedances and normalized imaginary impedances of simulated composites, where the “more conducting” has a very large real dielectric constant. Note the relative positions of the peaks, that of the more conducting component ($\phi = 1$) is at the lower frequencies. For the simulated composites, $\phi = 0.24$ and the other parameters are given in Figure 4.11 and in the text.

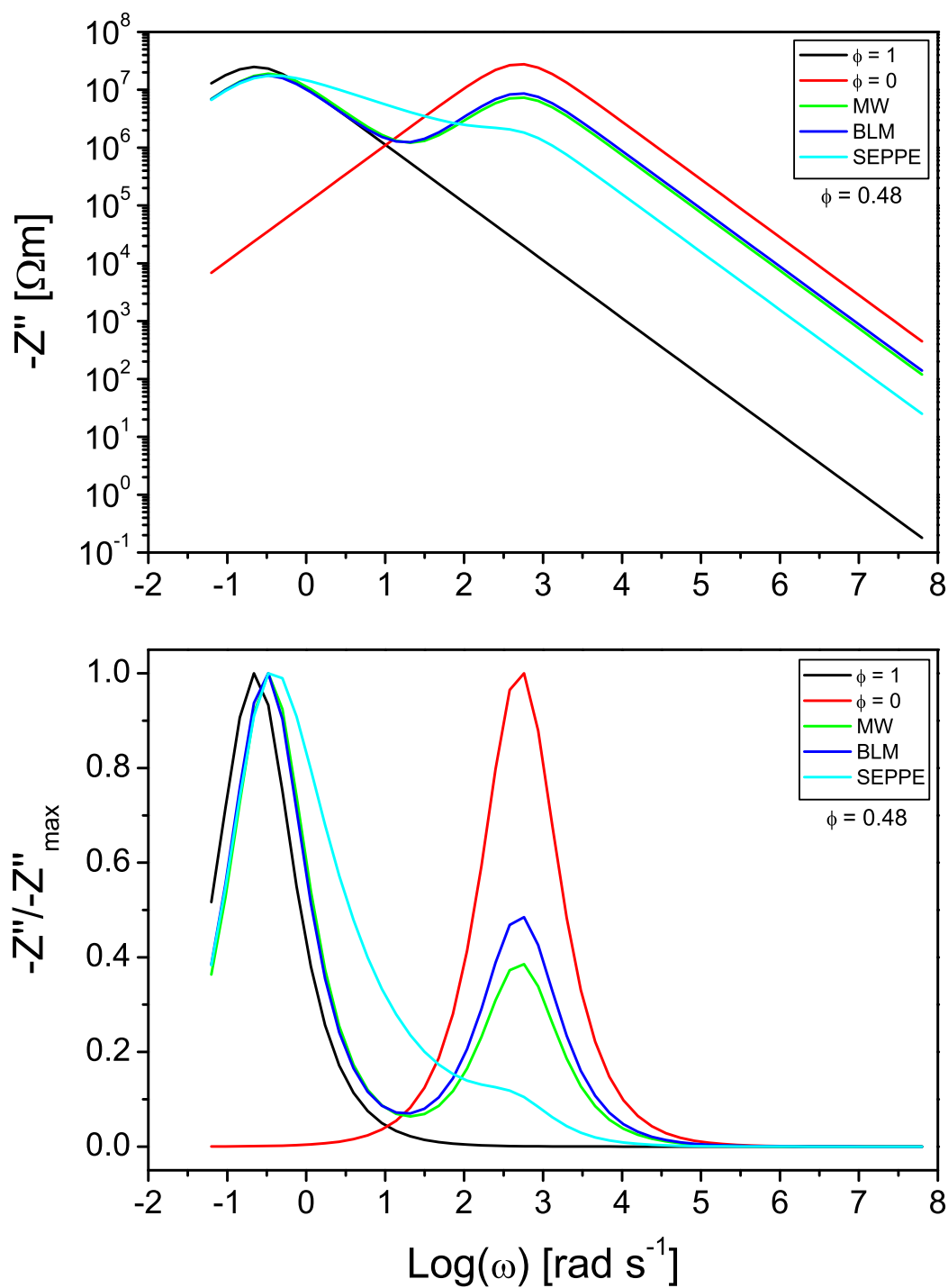


Figure 4.14: The frequency dependence of the imaginary impedances and normalized imaginary impedances of simulated composites, where the “more conducting” has a very large real dielectric constant. Note the relative positions of the peaks, that of the more conducting component ($\phi = 1$) is at the lower frequencies. For the simulated composites, $\phi = 0.48$ and the other parameters are given in Figure 4.11 and in the text.

general, the characteristic frequency (dielectric constant and dc conductivity) of at least one of the components *must* be known before any identification of the contributions can be made. Each peak in the composite imaginary impedance plot still lies at about the same frequency as that of the pure component and therefore again it is possible to readily identify the contributing component, if the component data is available. However, it should also be noted that the low frequency peaks are perturbed quite significantly in the range $0.08 \leq \phi \leq 0.5$ presented here, for all three models (the peaks are less perturbed at higher values of ϕ).

The complex impedance plane plots in Figure 4.15 also show that for this range of ϕ values ($\phi < 1$), the Maxwell-Wagner, the Brick Layer models and the SEPPE ($\phi < \phi_c$) all produce curves that are clearly distinct from each other. However, the total resistances of the simulated composites are the same for all three models at all the conducting component volume fractions simulated.

4.2.3 Composites where the properties of both the components are dispersive

To complete the investigation of the direct effect of the component properties on the properties of the composites, simulations of composites in which both components have dispersive properties were calculated. The properties of the components were presumed to be described by the Universal Dielectric Response (Equation (1.12)), which has been successfully used to model and fit data from a wide range of materials (a wider range than for the LLS model). The parameters of the more conducting component are $A = 1 \times 10^{-8}$, $s = 0.6$, $\sigma_{dc} = 1 \times 10^{-5}(\Omega m)^{-1}$ and $\epsilon_{\infty} = 24$. For the less conducting component, $A = 1 \times 10^{-8}$, $s = 0.8$, $\sigma_{dc} = 1 \times 10^{-7}(\Omega m)^{-1}$ and $\epsilon_{\infty} = 4$. The conducting component volume fraction, $\phi = 0.95$. For the SEPPE simulations, $\phi_c = 0.999998$ and $t = 2$.

Figures 4.16, 4.17 and 4.18 show the properties of simulated composites

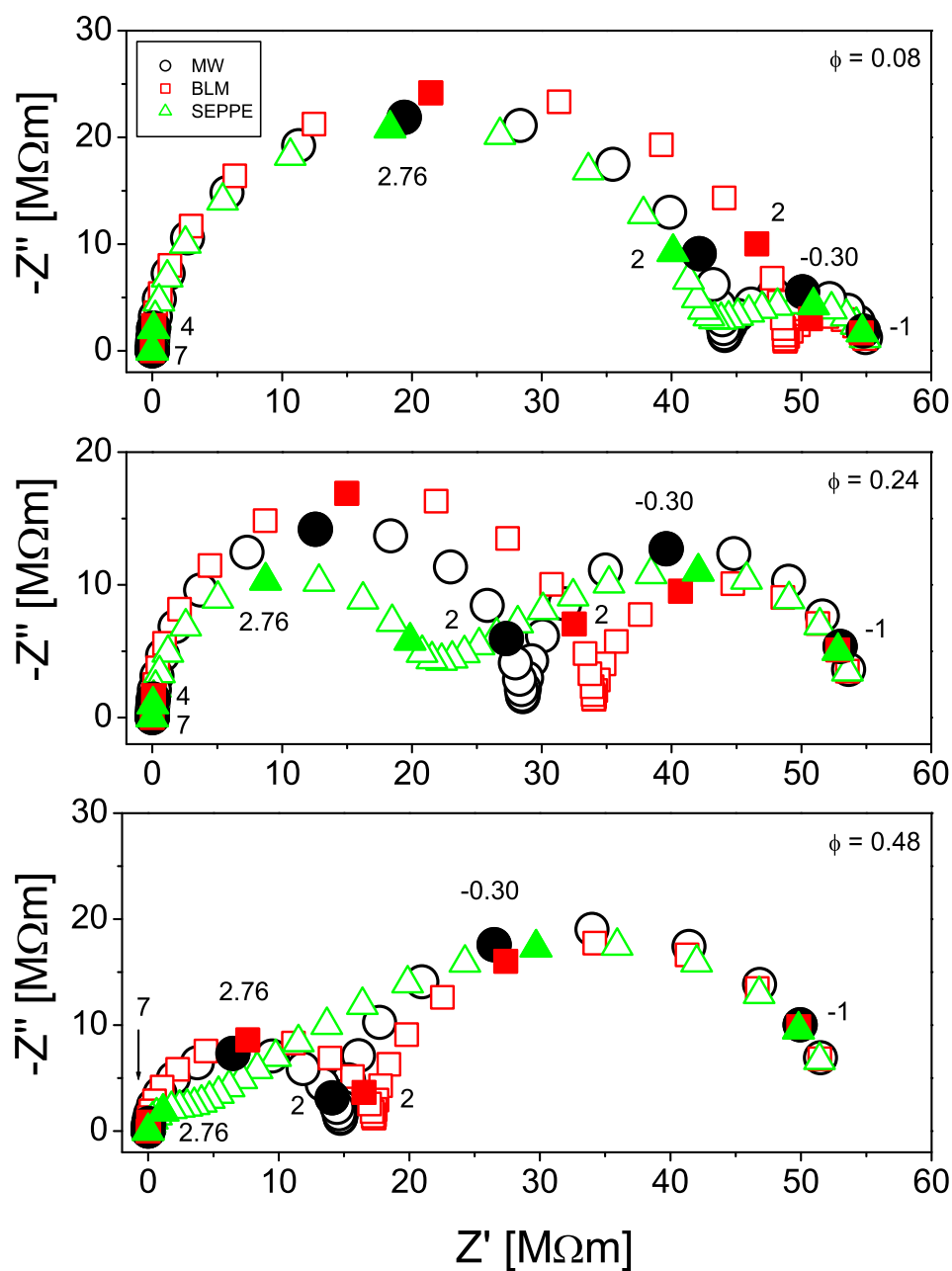


Figure 4.15: Complex impedance plane plots of simulations of a medium where the “more conducting” component has a very large real dielectric constant. The volume fractions for each simulation are given in each plot. The other parameters are given in Figure 4.11 and in the text. Key values of $\log(\omega)$ are indicated.

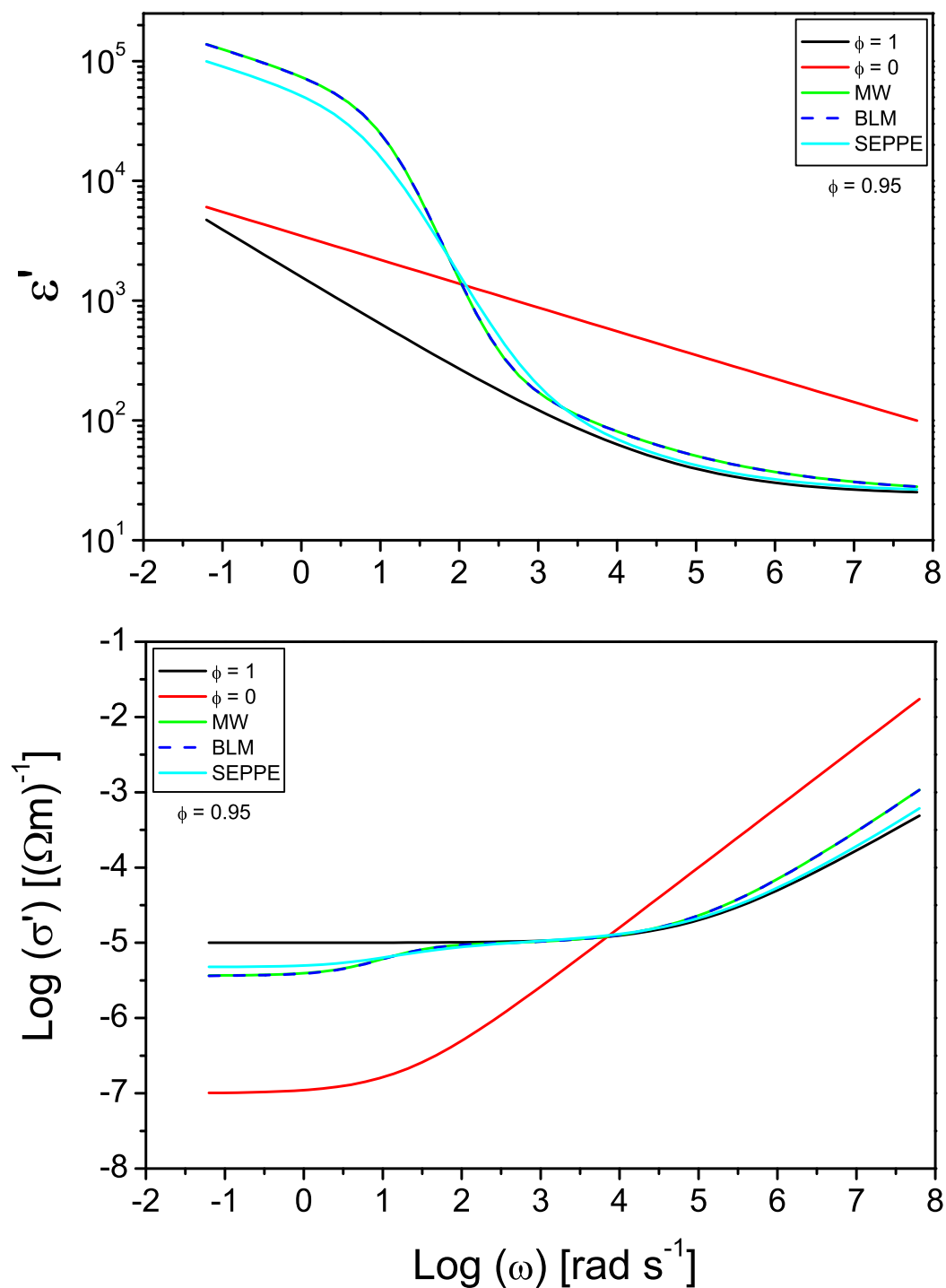


Figure 4.16: The frequency dependence of the real dielectric constant and the real conductivity of a simulated composite and its components, where the properties of both the components are dispersive. The dispersive properties of both the components were modeled using the UDR model. For the more conducting component, $A = 1 \times 10^{-8}$, $s = 0.6$, $\sigma_{dc} = 1 \times 10^{-5}(\Omega m)^{-1}$ and $\epsilon_{\infty} = 24$. For the less conducting component, $A = 1 \times 10^{-8}$, $s = 0.8$, $\sigma_{dc} = 1 \times 10^{-7}(\Omega m)^{-1}$ and $\epsilon_{\infty} = 4$. $\phi_c = 0.999998$ and $t = 2$ for the SEPPE simulation. Note the superposition of the Maxwell-Wagner and Brick Layer model curves.

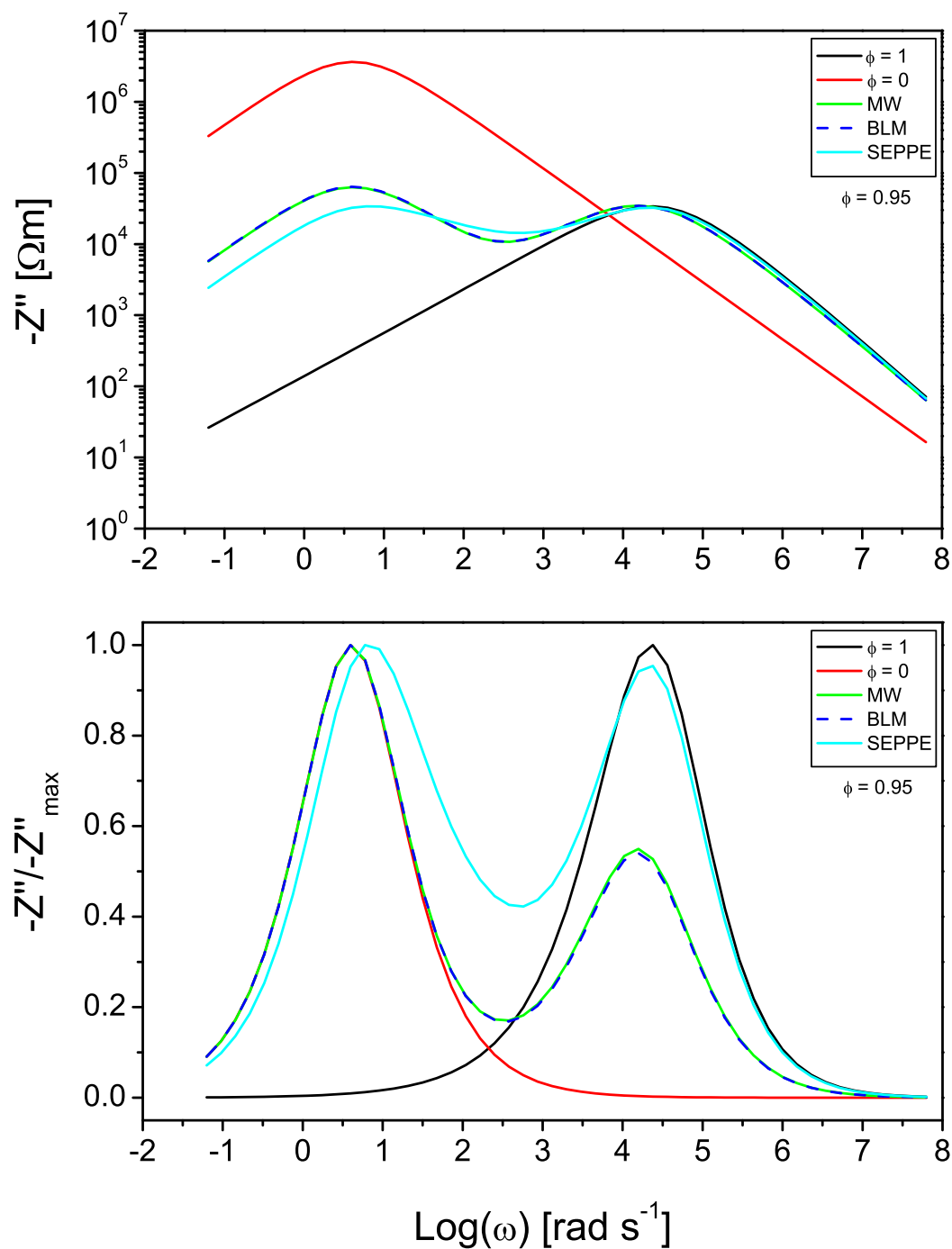


Figure 4.17: The frequency dependence of the imaginary impedances and normalized imaginary impedances of a simulated composite and its components, where the properties of both the components are dispersive. The dispersive properties of both the components were modeled using the UDR model. The parameters for the simulations are given in Figure 4.16 and in the text.

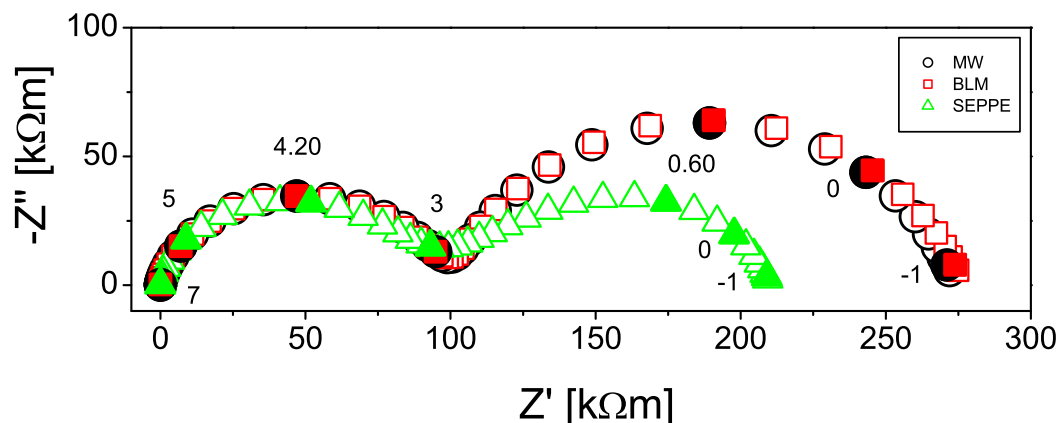


Figure 4.18: The complex impedance plane plot of data for a simulated composite where the properties of both the components are dispersive. The dispersive properties of both the components were modeled using the UDR model (Equation (1.12)). The parameters for the simulations are given in Figure 4.16 and in the text. Key values of $\log(\omega)$ are indicated.

and compare them to those of the components. Again, the contributions of the components can be identified in the imaginary impedance plot, though the peaks in the composite plots, and in particular those at high frequencies, are displaced from the component peaks. The complex impedance plane representation of the data is shown in Figure 4.18. At $\phi = 0.95$, the Maxwell-Wagner and Brick Layer models produce similar results while those of the SEPPE are notably different

4.3 Conclusions

4.3.1 Simulated composite properties

- The Maxwell-Wagner and Brick Layer models give similar results at high values of the volume fraction ($\phi > 0.9$), where the SEPPE gives composite properties that are markedly different except in the trivial case of ϕ very close to 1.
- For the SEPPE, with a set of fixed component properties and the conducting component volume fraction ϕ , varying the exponent t , ($\phi < \phi_c$)

and/or the critical volume fraction ϕ_c greatly alters the simulated composites' ac conductivity properties as well as the dc resistances (extracted from complex impedance plane plots).

- The features at the high frequencies in the various impedance spectroscopy plots (such as peaks in imaginary impedance plots or the arcs at low impedance in the complex impedance plane plots) are not always those due to the more conducting component. The frequencies at which the various components of the composite are dominant depends on both their conductivities and dielectric constants. Therefore, the order of the features may be reversed (from the “normal”, conducting component features at high frequency, order). This occurs for example when the more conducting component has an anomalously high dielectric constant.
- At high volume fractions ($\phi \gtrsim 0.9$), the Maxwell-Wagner model and BLM give similar results even if the properties of both the components are dispersive. Again the SEPPE gives different results to the other models which, as explained earlier, are due to the very different microstructure that it describes.
- Simulation shows that for the Maxwell-Wagner model, the BLM and the SEPPE there is a perturbation of the characteristic frequencies associated with the features in the binary composites from those of the pure components. For the composites simulated, this effect was strongest for the component dominant at low frequencies. Therefore if variation in seen ω_p seen in experimental data it is probably due to that component being in a binary composite.

4.3.2 Identifying components from the composite data

- It is possible to identify the contributions of the components in the composite impedance spectrum based on the characteristic frequencies

which are readily obtained from the positions of the peaks in $-Z''$ vs $\log(\text{frequency})$ plots. This was demonstrated for composites simulated using models representing different microstructures and for dispersive and non-dispersive component properties. However, note that the peak frequencies are not single valued, as the peaks are slightly displaced in the composites. In practice, the identification of the components contribution to the composite properties requires that data of the component properties measured under the same conditions as those under which the composite properties are measured be available. The characteristic frequency is dependent on both the conductivity and the dielectric constant, both of which are temperature dependent and therefore is itself temperature dependent.

- In cases, such as that discussed in Section 4.2.2, where the conducting component has an anomalous dielectric constant and the positions of key feature in the IS plots are reversed. However, the characteristic frequency is still a convenient tool for identifying the contributions due to the components.

Chapter 5

Polycrystalline Yttria-Stabilized Zirconia

5.1 Introduction

As mentioned in the introduction to this thesis, the electrical properties of yttria-stabilized zirconia have been very widely studied [see Bauerle²², Verkerk et al.¹⁹, Badwal²³, Rühle et al.²⁴, Badwal and Drennan²⁵, Bonanos et al.²⁶, Abélard and Baumard²⁷, Pimenov et al.²⁸ and others], largely due to the interest in the use of these ceramics in Solid Oxide Fuel Cells (SOFCs), oxygen sensors and in other technological applications. YSZ may, to some degree, be considered a model system for study using impedance spectroscopy techniques, because of the clearly distinguishable grain and grain boundary contributions to the impedance spectra. To further investigate the link between the microstructure and the electrical properties, a number of samples, prepared as described in Section 2.2.2, were studied in the current work. The sections that follow describe the microstructure and compositions of these samples, as well as the frequency and temperature dependence of the electrical properties of the YSZ grains and the grain boundaries (as distinguished in complex impedance plane plots). The complex conductivity data from the measurements was fitted to the Maxwell-Wagner model (Equation (1.1)) and in some cases to the Brick Layer Model (BLM) (Equation (1.3)) and the

Single Exponent Phenomenological Percolation Equation (SEPPE) (Equation (1.7)). Recall from Chapter 4 that for high values of the conducting component volume fraction (ϕ), such as in these ceramics, the Maxwell-Wagner and Brick Layer models give essentially the same results.

5.2 Results and Discussion

5.2.1 Composition and Microstructure

Figure 5.1 shows Scanning Electron Microscopy (SEM) micrographs of 8 mole % (cubic) yttria-stabilized zirconia samples sintered at 1350 °C for 2 hours (1350/2) and at 1600 °C for 10 hours (1600/10), from powder manufactured by Daiichi Kigenso Kagaku Kogyo (DKKK). It can clearly be seen, in the micrographs, that these samples have vastly different grain sizes. The combination of the higher sintering temperature and longer sintering time leads to marked, and rather anomalous, grain growth in the 1600/10 material. X-ray spectra of the samples, Figure 5.2, show that despite the differences in the grain sizes, the samples have the same crystal structure and composition. This is as would be expected.

The microstructure of the samples sintered from powder manufactured by Tosoh are shown in Figure 5.3. While the sample sintered at the higher temperature and for the longer time has the larger grains, these grains are not as large as those of the sample sintered under the same conditions from the powder manufactured by DKKK.

The x-ray spectra in Figure 5.4 confirm that all the samples sintered from the powder manufactured by Tosoh have a similar composition and crystal structure. Further more, the peaks observed are the same for the samples sintered using the powders from the two different manufacturers. Any impurities that may be in the powders are likely to produce non-crystalline (glassy) phases in the sintered ceramic and therefore would be difficult to detect in the x-ray spectra even though they could influence the grain growth

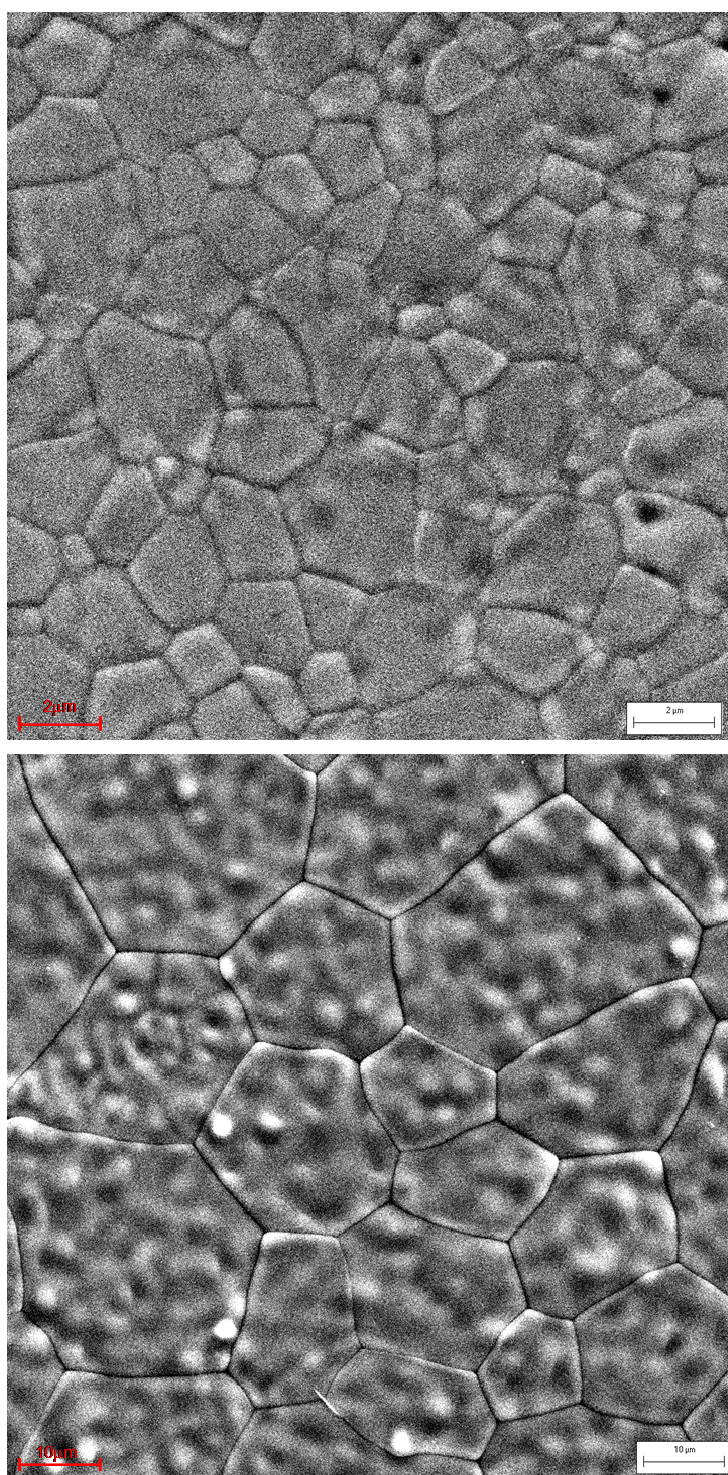


Figure 5.1: Scanning electron micrographs of the pure 8YSZ samples sintered from powder manufactured by DKKK. These samples are 8YSZ-D1 sintered at 1350 °C for 2 hours (top) and 8YSZ-D2 sintered at 1600 °C for 10 hours (bottom). Note the large difference in the grain sizes of these samples. (Micrographs courtesy of Dr. Tim Armstrong).

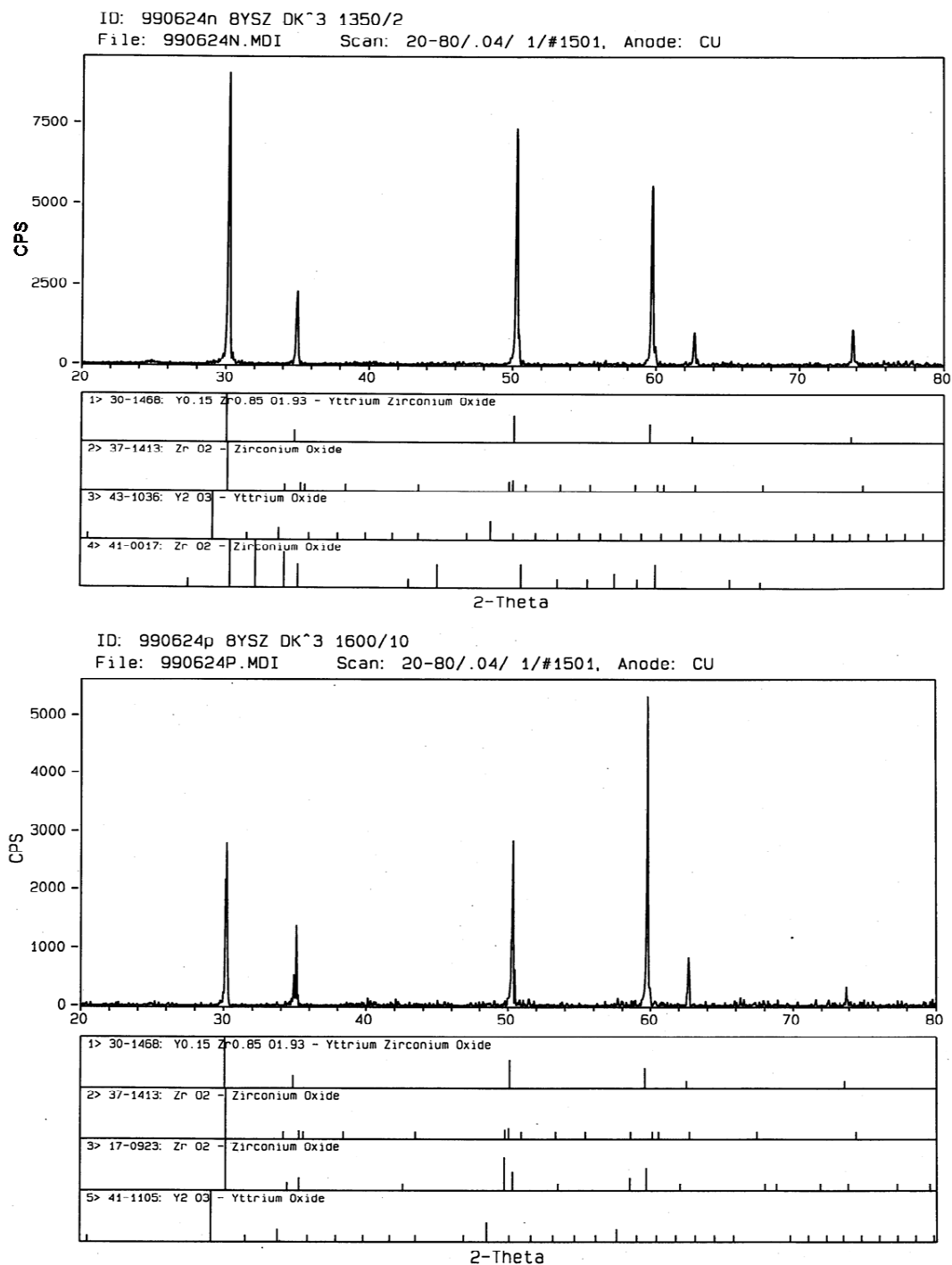


Figure 5.2: X-ray spectra of the pure 8YSZ samples sintered from powder manufactured by DKKK. These samples are 8YSZ-D1 sintered at 1350 °C for 2 hours (top) and 8YSZ-D2 sintered at 1600 °C for 10 hours (bottom). (Spectra courtesy of Dr. Tim Armstrong).

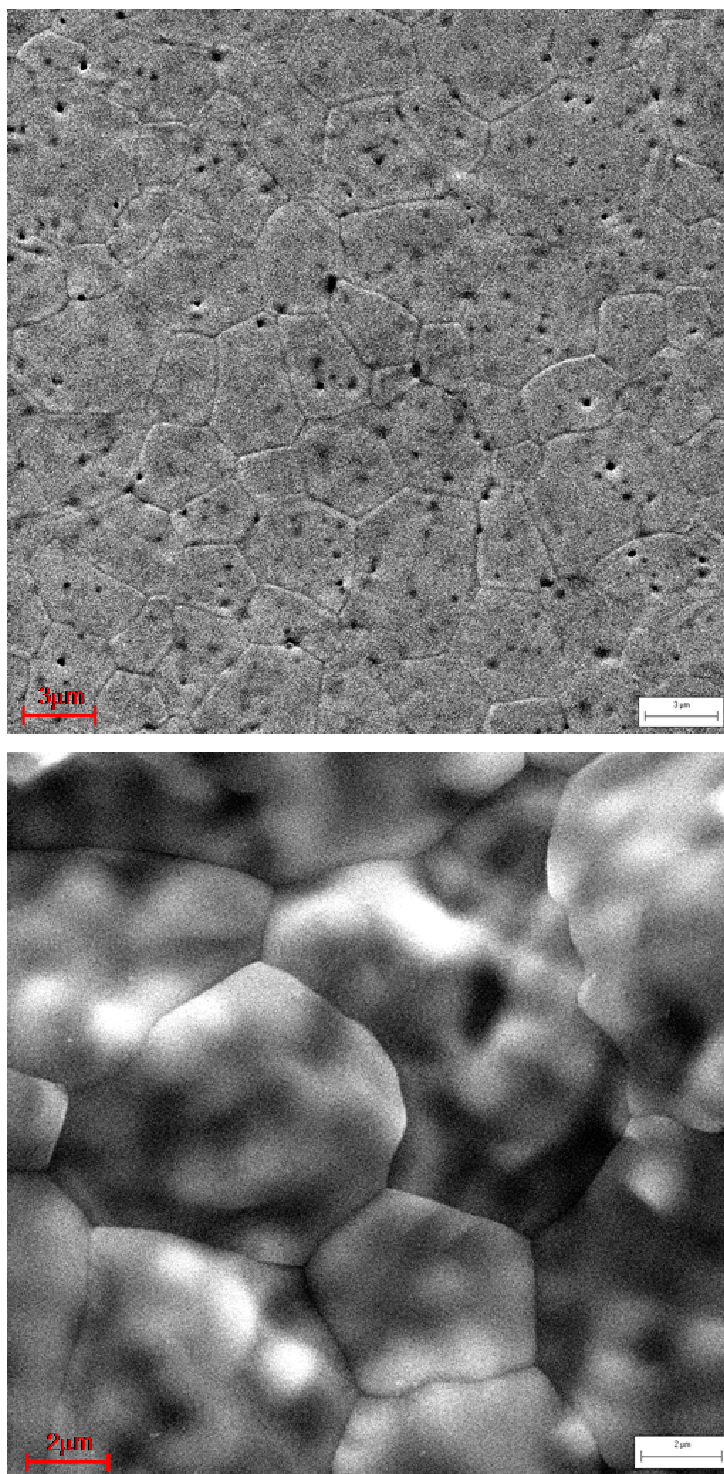


Figure 5.3: Scanning electron micrographs of the pure 8YSZ samples sintered from powder manufactured by Tosoh. These samples are 8YSZ-T1 sintered at 1350 °C for 2 hours (top) and 8YSZ-T2 sintered at 1600 °C for 10 hours (bottom). The difference in the grain sizes is not as marked as that of the samples featured in Figure 5.1. (Micrographs courtesy of Dr. Tim Armstrong).

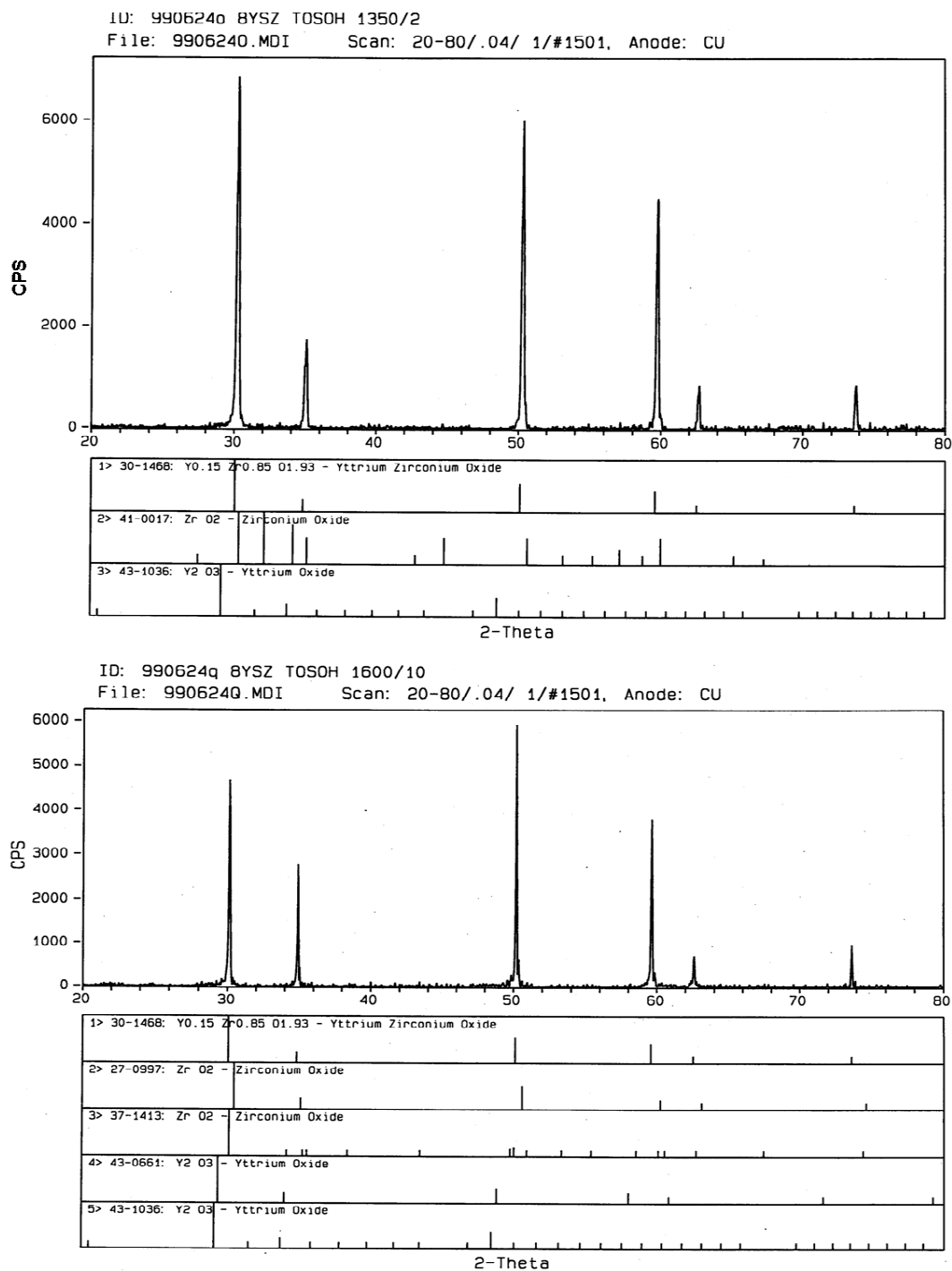


Figure 5.4: X-ray spectra of YSZ samples sintered from powder manufactured by Tosoh. These samples are 8YSZ-T1 sintered at 1350 °C for 2 hours (top) and 8YSZ-T2 sintered at 1600 °C for 10 hours (bottom). (Spectra courtesy of Dr. Tim Armstrong).

and/or the electrical properties of the ceramics.

The differences in the size of the grains between the large grained DKKK 1600/10 (8YSZ-D2) and Tosoh 1600/10 (8YSZ-T2) samples cannot simply be attributed to differences in the sizes of the particles of the initial powders alone because at 1350/2, the Tosoh powder produces samples with a larger grain size than that of the samples sintered at 1350/2 from powder manufactured by DKKK. The mechanism responsible for the rapid grain growth in the DKKK 1600/10 is as yet not understood. A summary of the grain sizes and densities of the 8YSZ samples is given in Table 5.1. There is no porosity visible in the SEM micrographs and this is confirmed by the measured sample density being $\sim 100\%$ of the theoretical density.

From the SEM micrographs, in Figure 5.5, it can be seen that the microstructures of the samples containing 0.1 and 0.5 wt% silica are similar. It can also be seen that these samples contain some porosity, which was not seen for the samples sintered from pure YSZ. This implies that the presence of the silica is having an influence on the sintering process, inhibiting full densification of the ceramic.

The SEM micrographs of the samples with 2.7 and 12.4 volume % silica are shown in Figure 5.6. It can be seen in these micrographs that the amount of porosity increases with increasing silica content. No silica peaks are observed in the x-ray spectra for the samples containing the impurity. Figure 5.7 shows the spectra for the samples with 2.7 and 12.4 volume % silica, where only the peaks associated with the YSZ are observed. This confirms that there is no

Table 5.1: The density and average grain sizes of 8YSZ samples studied. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Powder Manufacturer	Sintering Temp./Time ($^{\circ}\text{C}/\text{hrs}$)	Density (%ThD)	Av. Grain Size (μm)
8YSZ-D1	DKKK	1350/2	100	1.79 ± 0.34
8YSZ-D2	DKKK	1600/10	100	19.15 ± 3.50
8YSZ-T1	Tosoh	1350/2	100	3.24 ± 0.54
8YSZ-T2	Tosoh	1600/10	100	5.92 ± 1.45

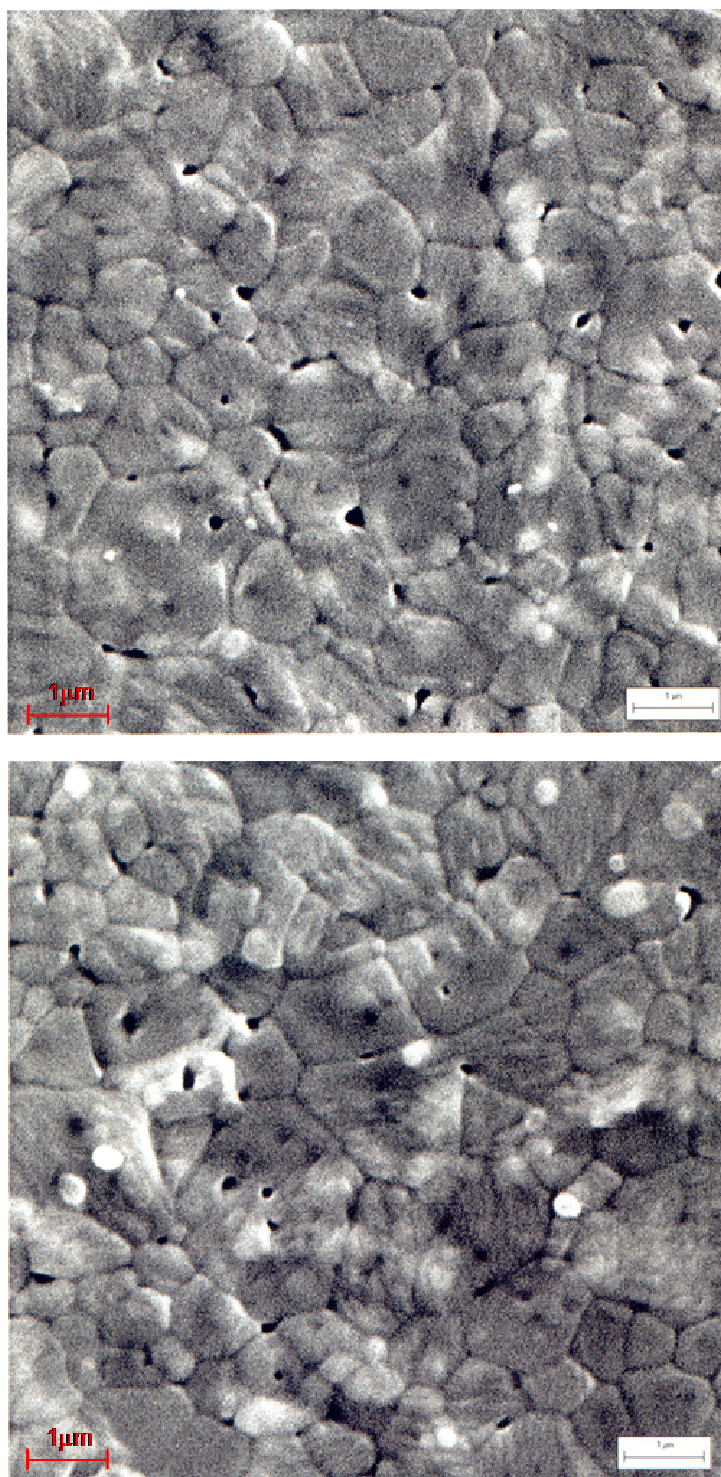


Figure 5.5: Scanning electron micrographs of YSZ samples containing low levels of silica. These are the sample containing 0.3 volume % silica (8YSZ-SiO₂-T1; top) and that containing 1.2 volume % silica (8YSZ-SiO₂-T2; bottom). The samples have nearly identical grain sizes. (Micrographs courtesy of Dr. Tim Armstrong).

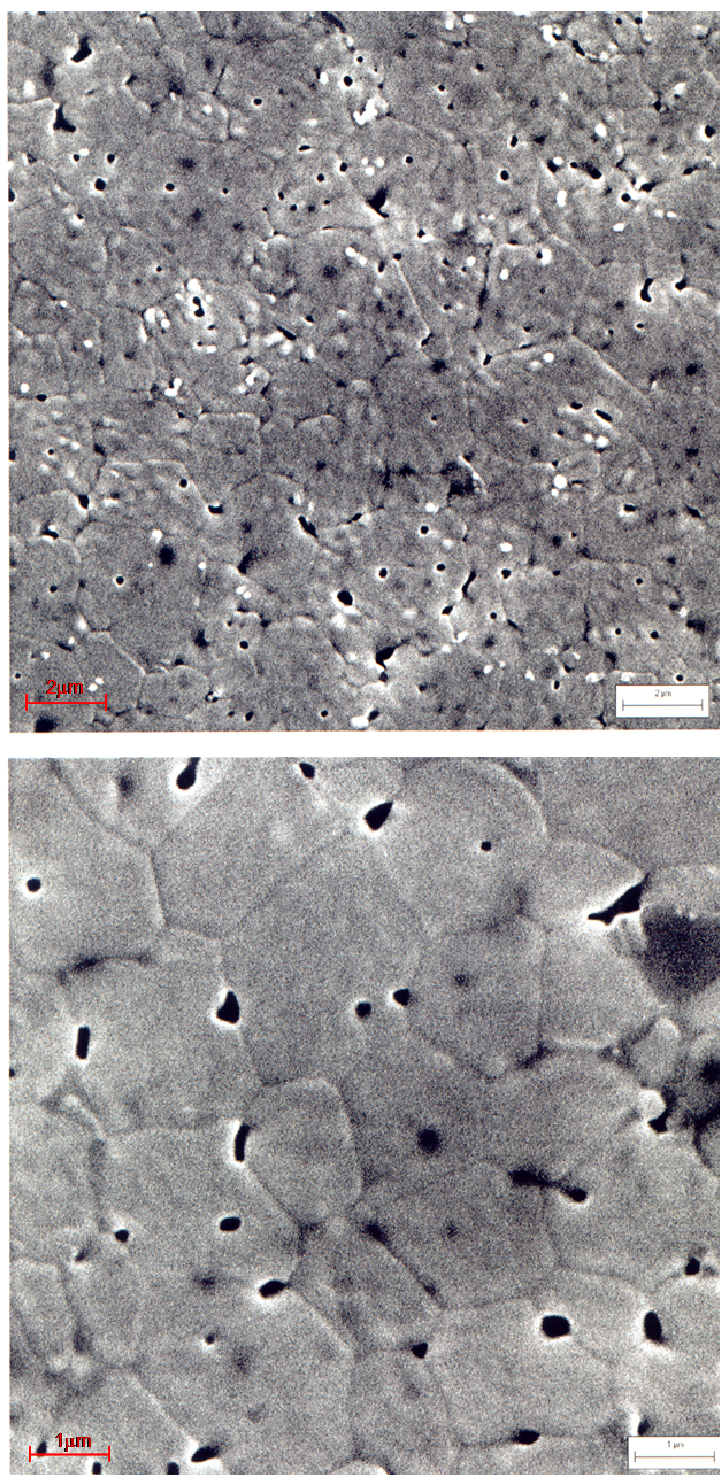


Figure 5.6: Scanning electron micrographs of the samples containing intermediate levels of silica. These are the sample containing 2.7 volume % silica (8YSZ-SiO₂-T3; top) and that containing 12.4 volume % silica (8YSZ-SiO₂-T4; bottom). The porosity increases from one sample to the next, as the silica content is increased. (Micrographs courtesy of Dr. Tim Armstrong).

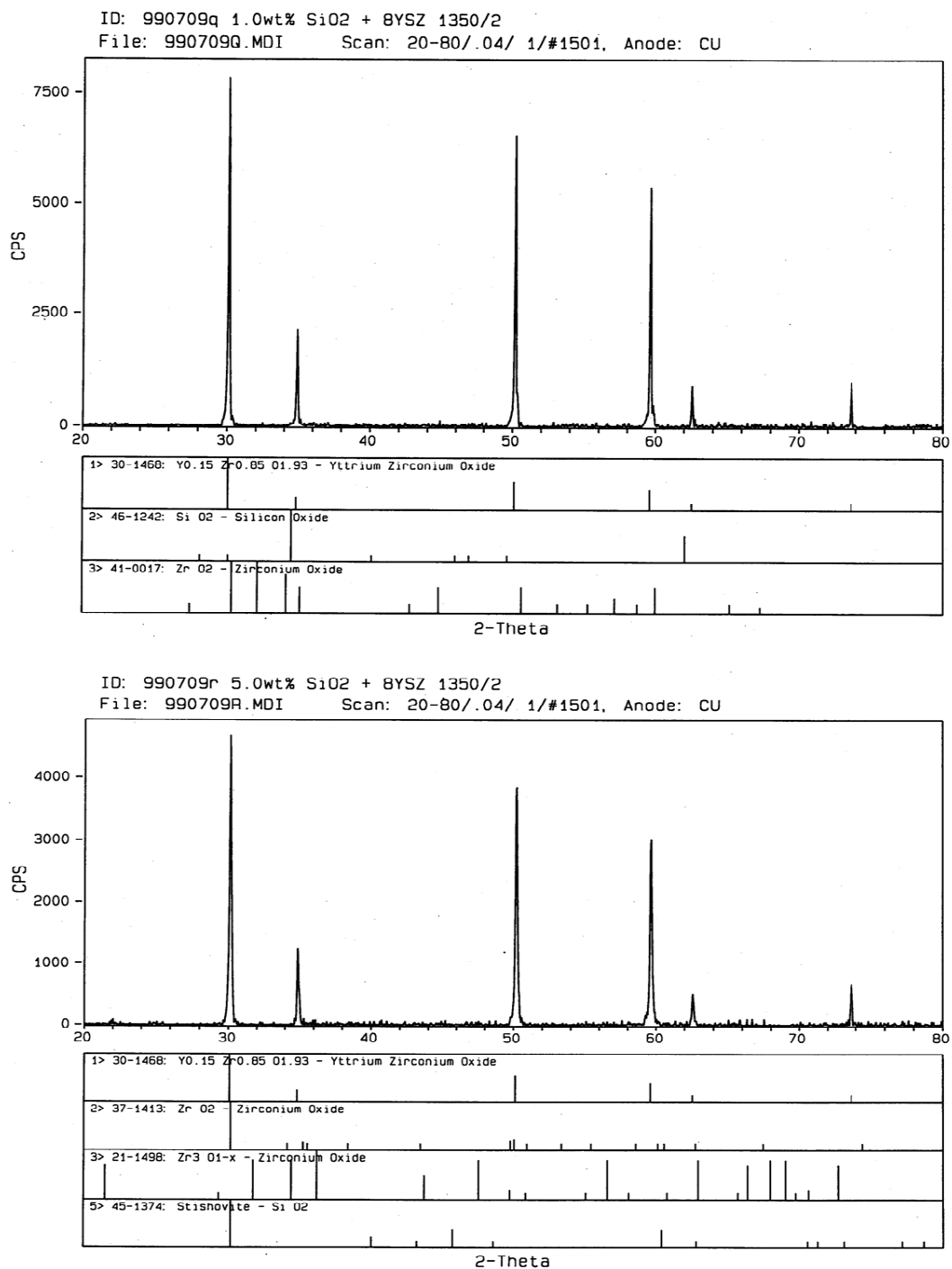


Figure 5.7: X-ray spectra of YSZ samples containing silica. These samples are the sample containing 2.7 volume % silica (8YSZ-SiO₂-T3; top) and that containing 12.4 volume % silica (8YSZ-SiO₂-T4; bottom). (Spectra courtesy of Dr. Tim Armstrong).

crystalline silica in the materials.

Figure 5.8 shows that the sample with the highest silica content, 23 volume %, also has the highest amount of porosity. This leads to this sample having the lowest density.

Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis in Gremillard et al.¹²⁹, on 3YSZ, suggests that the adjacent grain boundaries do not consist of a continuous glassy phase and contain no silica at all but that instead the silica accumulates in the triple junctions. Their observations are somewhat in contradiction to those of Gödickemeier et al.¹³⁰ who, also working with 3YSZ, report having observed glassy films between 0.5 and 2nm thick and no “clean” grain boundaries in all the silica containing samples that they investigated, some of which had other impurities in addition to the silica. While pure silica will not melt at the sintering temperatures used in this work, if the silica were to combine with other impurities such as alumina (Al_2O_3), yttria (Y_2O_3) or alkali metals such as sodium and potassium, then this would lower its liquidus temperature [Appel and Bonanos¹³¹].

It can be expected that the location of the silica within the ceramic will influence the effect that this silica has on the measured grain boundary electrical properties. The conductivity and dielectric properties of silica are different from those of YSZ and therefore if it is present in the grain boundaries their properties should be different from those of “clean” boundaries. If, instead, the silica is isolated in the triple points between the grains then it will have

Table 5.2: The density and average grain sizes of the 8YSZ+SiO₂ samples studied. Note the decrease in the density with increasing silica content. All samples were sintered at 1350 °C for 2 hrs. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Powder Manufacturer	Silica Content (Volume %)	Density (%ThD)	Av. Grain Size (μm)
8YSZ-SiO ₂ -T1	Tosoh	0.3	98	0.88 ± 0.11
8YSZ-SiO ₂ -T2	Tosoh	1.2	97	1.02 ± 0.12
8YSZ-SiO ₂ -T3	Tosoh	2.7	95	2.53 ± 0.47
8YSZ-SiO ₂ -T4	Tosoh	12.4	92	1.39 ± 0.18
8YSZ-SiO ₂ -T5	Tosoh	23.0	90	2.72 ± 0.56

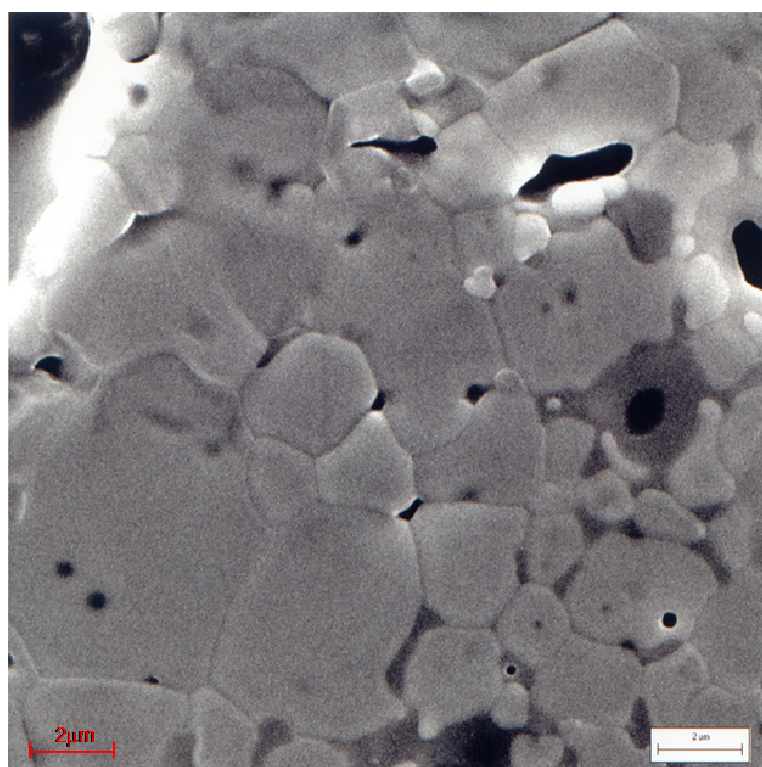


Figure 5.8: Scanning electron micrograph of a sample containing 23 volume % silica, 8YSZ-SiO₂-T5. This sample has the highest level of porosity and therefore the lowest density. (Micrograph courtesy of Dr. Tim Armstrong).

little effect on the critical conducting paths (see Figure 1.19) and therefore the measured grain boundary conductivity. This will be discussed in the sections that follow. The average grain sizes and densities of the YSZ samples containing silica are summarized in Table 5.2.

Figure 5.9 shows x-ray spectra of the samples 3YSZ-T1A and 3YSZ-T2A. These samples have a different crystal structure to that of the cubic (8YSZ*) samples discussed in the preceding pages and this leads to the differences between the x-ray spectra in Figures 5.2 to 5.7 and those in Figure 5.9. 3YSZ has a tetragonal crystal structure. This leads to the extra peaks that are observed in the spectra in Figure 5.9.

Table 5.3: The density and average grain sizes of 3YSZ samples studied. (Data courtesy of Dr. Tim Armstrong).

Sample Name	Powder Manufacturer	Sintering Temp./Time ($^{\circ}\text{C}/\text{hrs}$)	Density (%ThD)	Av. Grain Size (μm)
3YSZ-T1A	Tosoh	1350/2	99	0.51 ± 0.07
3YSZ-T1B	Tosoh	1350/2	99	0.51 ± 0.07
3YSZ-T2A	Tosoh	1600/10	99	1.15 ± 0.23
3YSZ-T2B	Tosoh	1600/10	99	1.15 ± 0.23

The grain sizes and the densities of the 3YSZ samples are summarized in Table 5.3.

Gibson et al.¹³² report that at densities between 95% and 100%, the bulk and grain-boundary conductivity of YSZ samples remain unchanged. With the exception of the 8YSZ samples containing 12 and 23 weight % silica, the densities of the samples investigated in the current work are above 95% of the theoretical density and therefore the density is not expected to be a major factor when explaining the differences in the electrical properties of various samples.

The link between the microstructure and composition of the YSZ samples and their electrical properties will be discussed in the sections that follow.

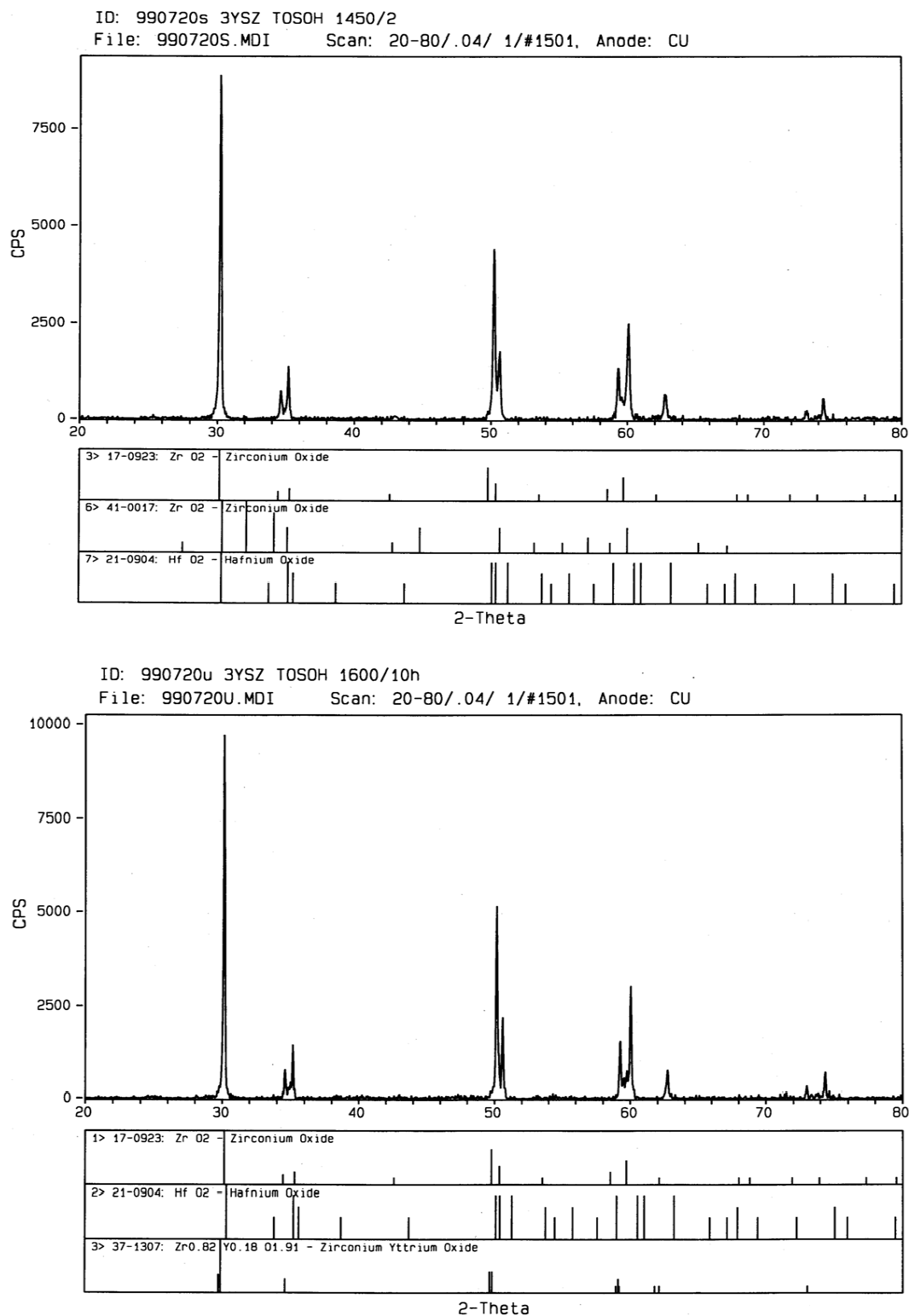


Figure 5.9: X-ray spectra of the tetragonal stabilized zirconia samples 3YSZ-T1A (top) and 3YSZ-T2A (bottom). The crystal structure of these samples (tetragonal) is different from that of the cubic 8YSZ* samples described earlier in this section. This difference in crystal structure leads to the difference in the peaks in the spectra above to those of the cubic stabilized zirconia samples in the earlier figures. (Spectra courtesy of Dr. Tim Armstrong).

5.2.2 Impedance data validation

As previously highlighted, the first step to analyzing ac conductivity data must be proving it to be valid and consistent, as described in Section 2.6.1. Kramers-Kronig transforms were used to verify the validity of the experimental data which will be presented and discussed later in this chapter. Figure 5.10 shows two sets of experimental imaginary impedance data and the imaginary impedance data calculated from the K-K transform of the experimental real impedance data. Within the accuracy of the numerical integration techniques, the experimental and the calculated data are in agreement. Note that there are small discrepancies at the lowest frequencies which can be attributed to errors due to the finite range of frequencies in the experiment (recall that, in principle, K-K transforms require an infinite frequency range, which is not obtainable in practice). Results similar to those shown in Figure 5.10 are obtained for other samples and at other temperatures, therefore confirming the validity of the experimental data.

As described in Section 2.6.1, the K-K conditions are not met by inherently non-linear responses, such as electrode effects, when the excitation signal is relatively large. Figure 5.11 clearly illustrates this phenomenon. While the data attributed to the grains and the grain boundaries of the ceramic conforms to the transforms, there are large errors at the lowest frequencies, where the electrode effects dominate. Similar results were observed for a single crystal and its electrodes (see Section 3.2.1).

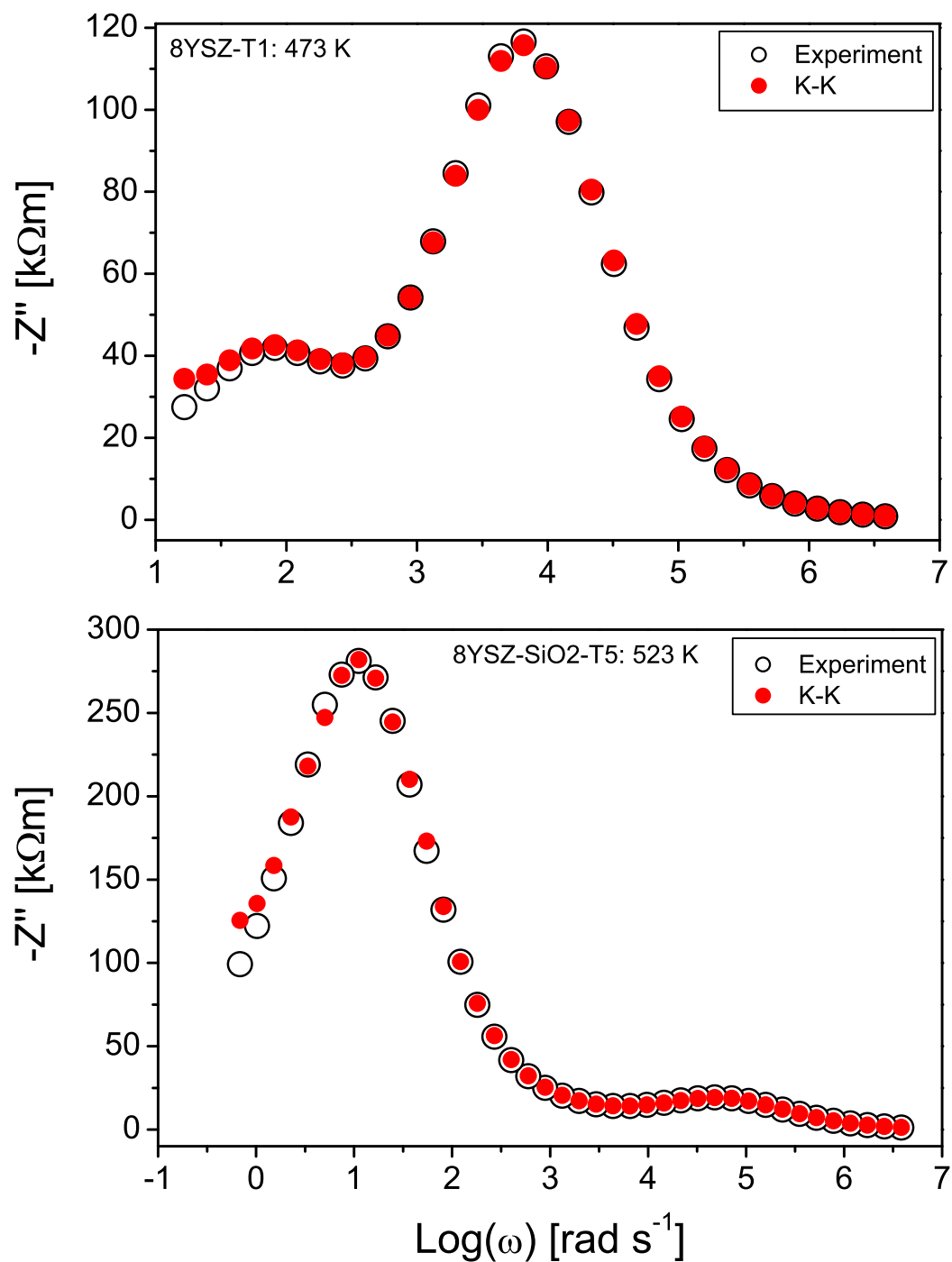


Figure 5.10: Validation of polycrystalline YSZ impedance data using Kramers-Kronig transforms. The calculated and experimental data are seen to be in close agreement for pure CSZ sample 8YSZ-T1, at 200 °C (top) and the CSZ sample with 23 volume % silica, 8YSZ-SiO₂-T5 at 250 °C (bottom).

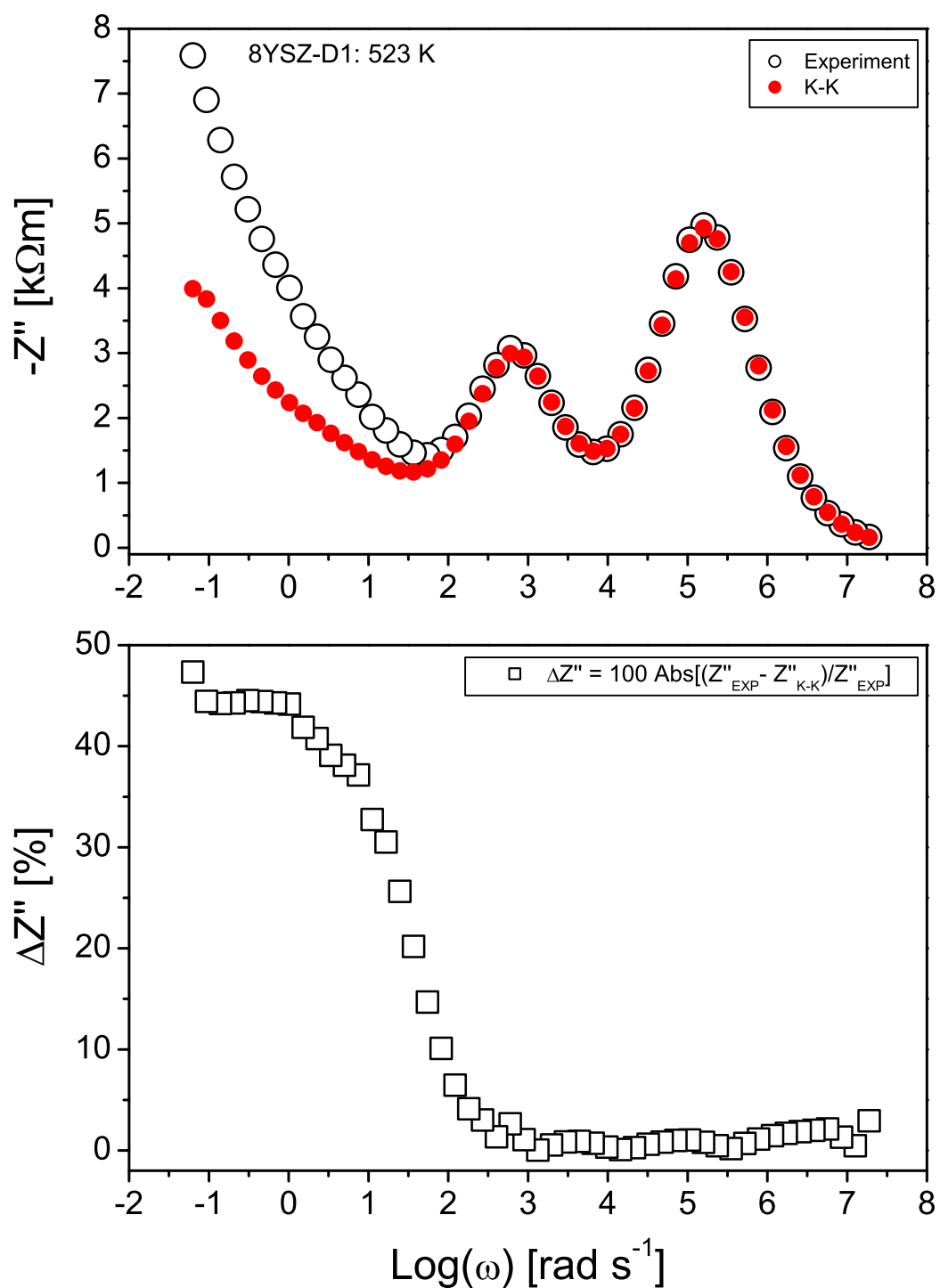


Figure 5.11: The Kramers-Kronig transform of data that includes electrode effects (top). Note the large differences between the calculated and experimental data in the frequency region ($\log(\omega) \lesssim 2$) where electrode effects, which are non-linear, dominate (bottom). (This data is from the CSZ sample 8YSZ-D1 at 250 °C and the excitation voltage for the measurement is 1.5 V).

5.2.3 The frequency dependence of the electrical properties of polycrystalline YSZ

The frequency dependence of the real dielectric constants and the real conductivities of several 8 mole % (cubic) YSZ samples with and without added impurities, is shown in Figure 5.12, for measurements at 100 °C. The real dielectric constants rise from their high frequency values in the 20's to several 1000's at low frequencies. For each sample, the conductivity shows Jonscher-type power law behavior (i.e $\sigma \propto \omega^s$) as it drops from the high frequency value through a shoulder at intermediate to low frequencies and just starts to drop off again at the lowest frequencies. The dropping off of the conductivity at the lowest frequencies indicates that there are at least two contributions to the sample properties at this temperature. (The contributions are better resolved in the imaginary impedance and the complex impedance plane plots in Figures 5.13 and 5.14).

Figure 5.13 shows that the component dominant at high frequencies, and for which there is a complete arc in the complex impedance plane plot, is common to all the samples and the characteristic frequencies are nearly identical (with the possible exception of the sample with a very high silica content (23 volume %, 8YSZ-SiO₂-T5)). Therefore, it can be concluded that this is due to the same component in all the samples and as its features are very similar this suggests that it is the YSZ crystallites (the grains in the ceramic), which are common to all the samples. The complex impedance plane plot Figure 5.14 clearly shows the two contributions to the sample impedance. These are attributed to the YSZ grains at high frequencies and the grain boundaries at low frequencies. The identification of the grain boundary contribution is further discussed below based on measurements at higher temperatures.

Figure 5.15 shows the real dielectric constants and the real conductivities at 250 °C. The shapes of these curves, which are characteristic of two component materials, are markedly different from those for single crystals (Chapter 3). Again the real dielectric constant initially rises from its high

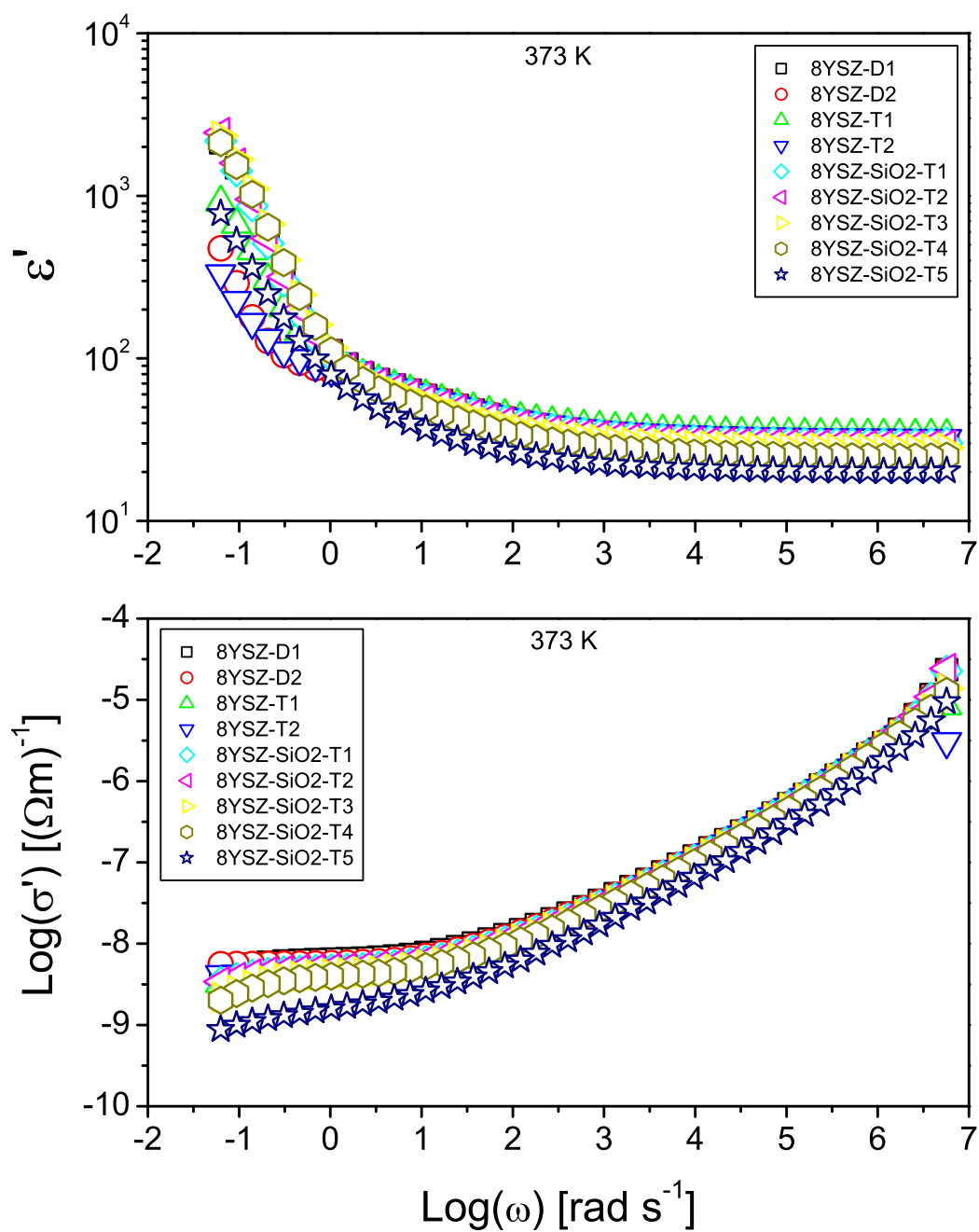


Figure 5.12: The frequency dependence of the real dielectric constant and the real conductivity of several cubic stabilized zirconia samples at 100 °C.

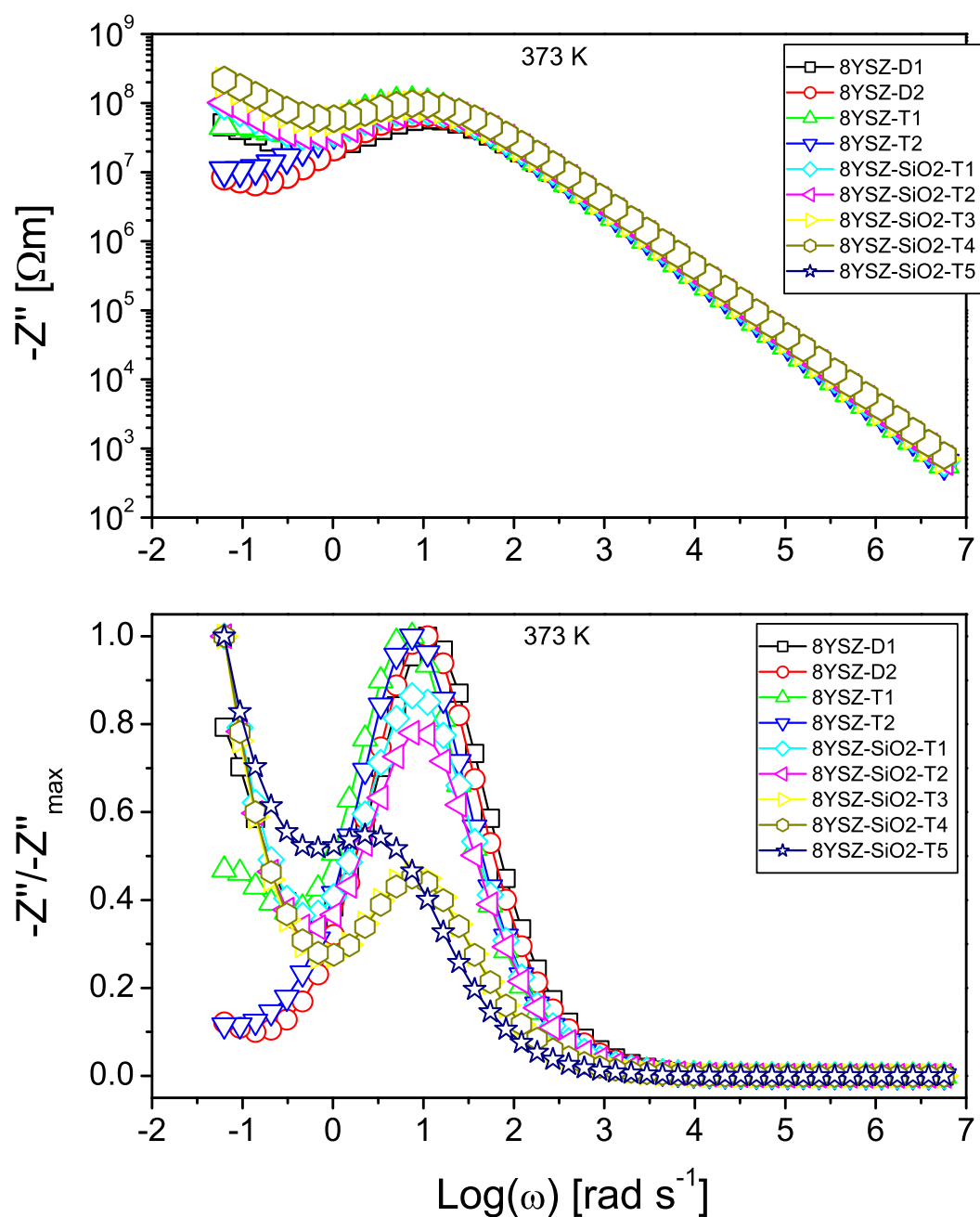


Figure 5.13: The frequency dependence of the imaginary impedances and normalized imaginary impedances of several cubic stabilized zirconia samples at 100 °C. The grains of the samples have similar characteristic frequencies. The characteristic frequencies of the grain boundaries are still below the measurable range.

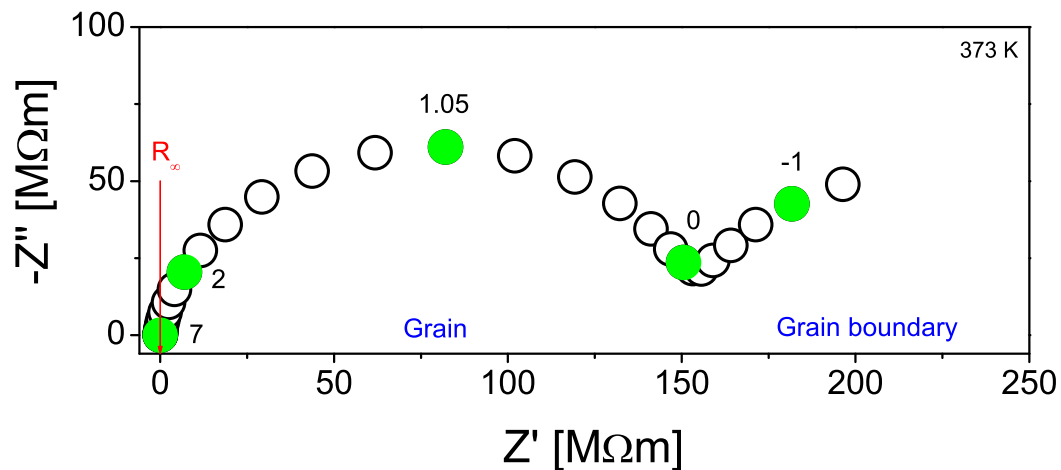


Figure 5.14: The complex impedance plane plot of the “raw” data for a polycrystalline CSZ sample at 100 °C showing arcs due to the grains and part of the arc due to the grain boundaries. The rest of the grain boundary arc and the arc due to electrode effects is at frequencies below the lower measurement limit. The dc impedance is equivalent to the impedance of the grains + the grain boundaries which is about 275 $M\Omega m$ for this sample. Key values of $\log(\omega)$ are indicated. This particular data is from the sample 8YSZ-D1.

frequency value in a similar manner to that of the single crystals. However, a feature not present in the single crystal data, characterized by a notable change in the slope between at $\log(\omega)$ values between 2 and 3, is observed. At this scale, this effect, which at this temperature is present in the curves for all the samples, is not readily observed in those of the samples that do not contain silica. The conductivity data also differs from that of the single crystals. After the initial power law drop at the highest frequencies (region labeled 1, in Figure 5.15), there is a shoulder at intermediate frequencies (region 2) followed by another drop (region 3) to a flat plateau at low frequencies (region 4). At the very lowest frequencies (region 5), the conductivity data again starts to decrease. The imaginary impedance data plotted in Figure 5.16 confirms that there are three contributions giving rise to three distinct features. The first peak is at essentially the same frequency ($\log(\omega) \approx 5$) for all the samples, except that with the highest silica content (8YSZ-SiO₂-T5), indicating a common origin. There is a somewhat wider spread in the position of the second peak, but even there, the frequencies lie in a narrow range

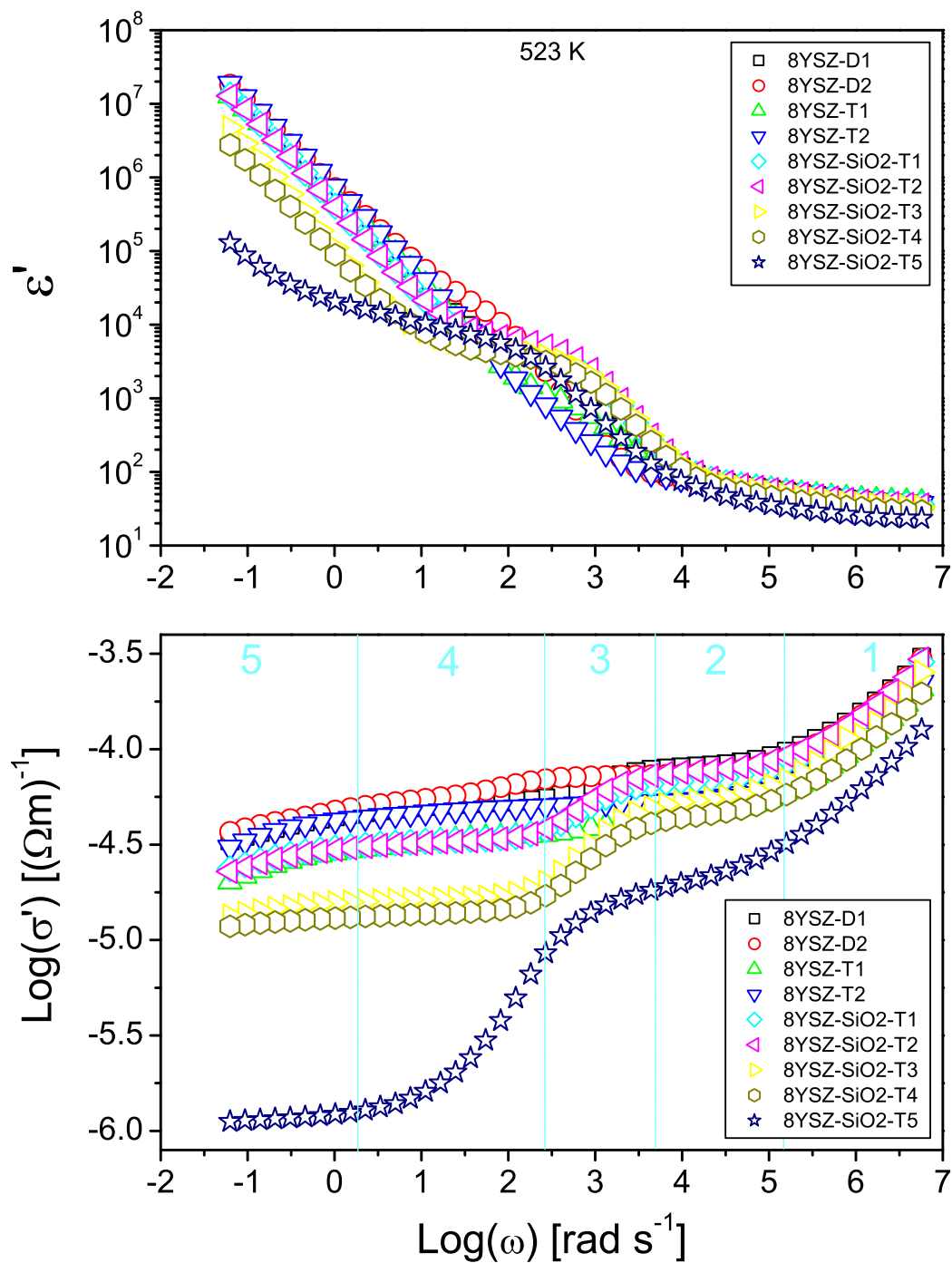


Figure 5.15: The frequency dependence of the real dielectric constants (top) and the real conductivities (bottom) of several cubic stabilized zirconia samples at 250 °C. Included is the data at frequencies dominated by electrode effects. The various sections of the conductivity curve are described in the text.

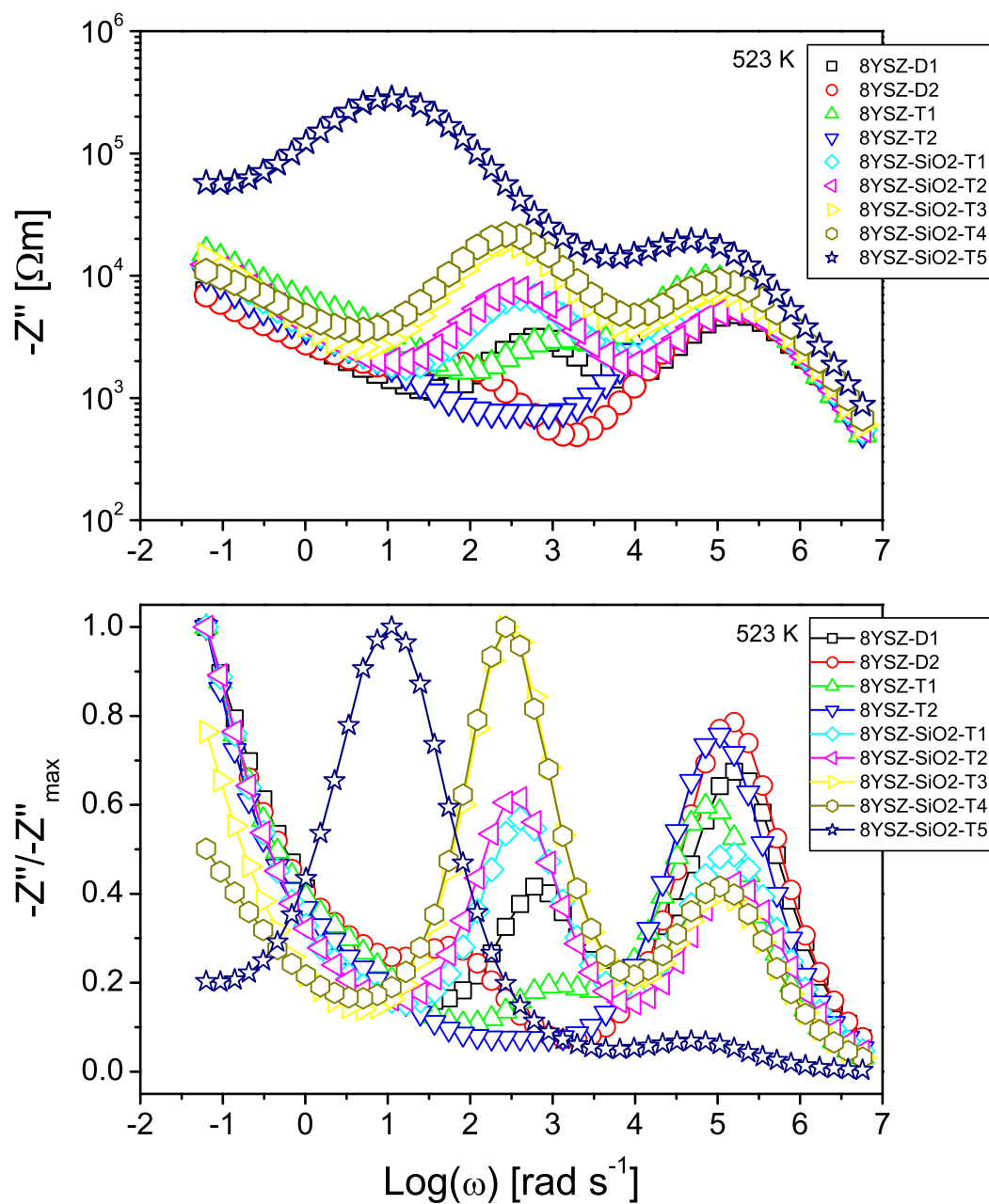


Figure 5.16: The frequency dependence of the imaginary impedances (top) and the normalized imaginary impedances (bottom) of several cubic stabilized zirconia samples at 250 °C. Included is the data at frequencies dominated by electrode effects.

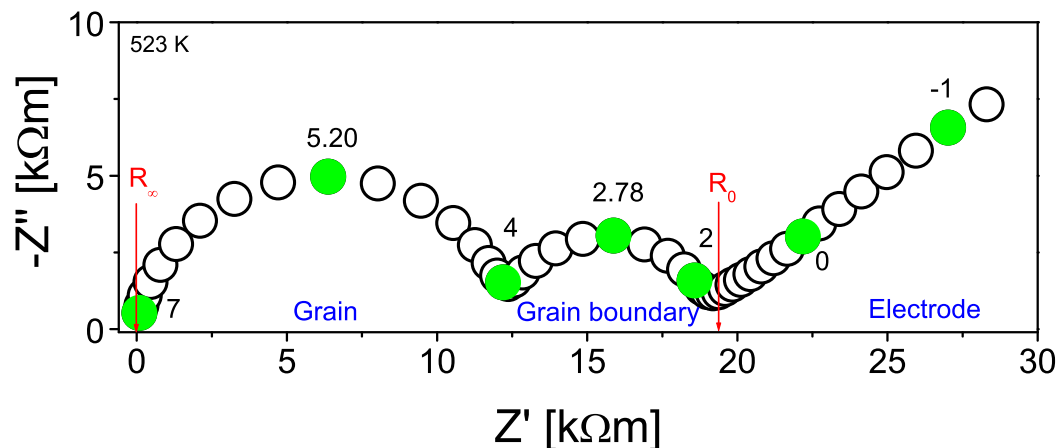


Figure 5.17: The complex impedance plane plot of the “raw” data for a polycrystalline CSZ sample showing arcs due to the grains, grain boundaries and electrode effects. The total impedance of the samples is the sum of the impedance of the grains and that of the grain boundaries. Key values of $\log(\omega)$ are indicated. This particular data is from the sample 8YSZ-D1 at 250 °C.

(again with the exception of 8YSZ-SiO₂-T5). It therefore follows that this second feature must also be present and be of a similar nature in nearly all the samples. It is associated with the grain boundaries, which are dislocation networks between the YSZ crystallites, a second phase consisting of impurities or combinations of these. The physical origins of the grain-boundary impedance in stabilized zirconia are discussed in Guo¹³³, Lee and Kim¹³⁴ and the references therein. The third, incomplete, feature in Figure 5.16 is due to electrode effects. Figure 5.17 shows the complex impedance plane representation of the data for a typical polycrystalline YSZ sample at this temperature. The three contributions to the sample impedance due to the grains, grain boundaries and electrode effects give rise to three depressed semicircles, one of which is incomplete. Between 100 °C and 250 °C, the sample impedance drops by about 4 orders of magnitude.

Similar trends to those described above for the cubic zirconia samples are also seen in the data from the tetragonal stabilized zirconia (3 mole % YSZ) samples, 3YSZ-T1A and 3YSZ-T2A, Figures 5.18 to 5.21. Figures 5.18 and 5.20 show that at high frequencies the dielectric constants and the

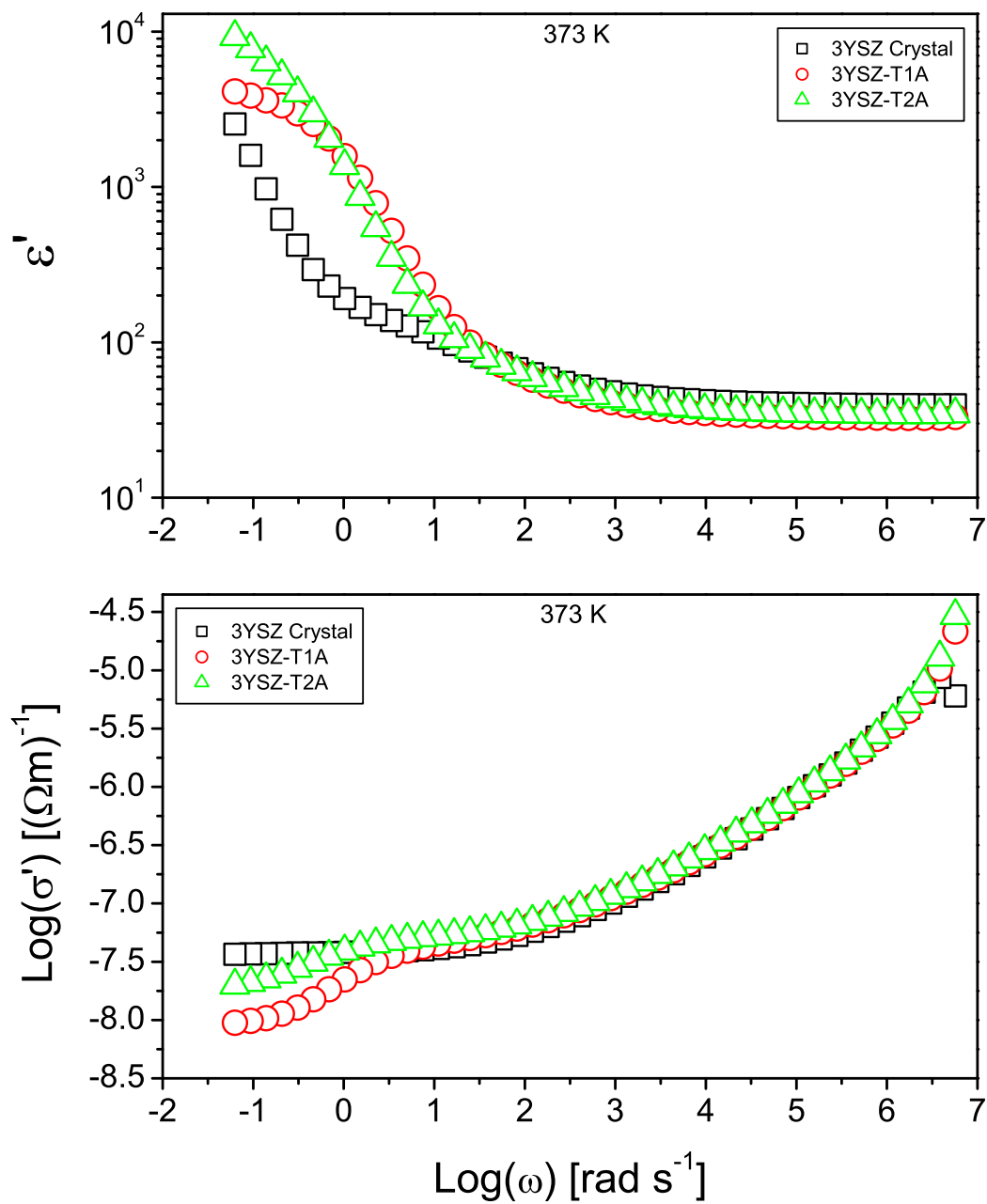


Figure 5.18: The frequency dependence of the real dielectric constants (top) and the real conductivities (bottom) of a tetragonal stabilized zirconia single crystal and several polycrystalline samples at 100 °C.

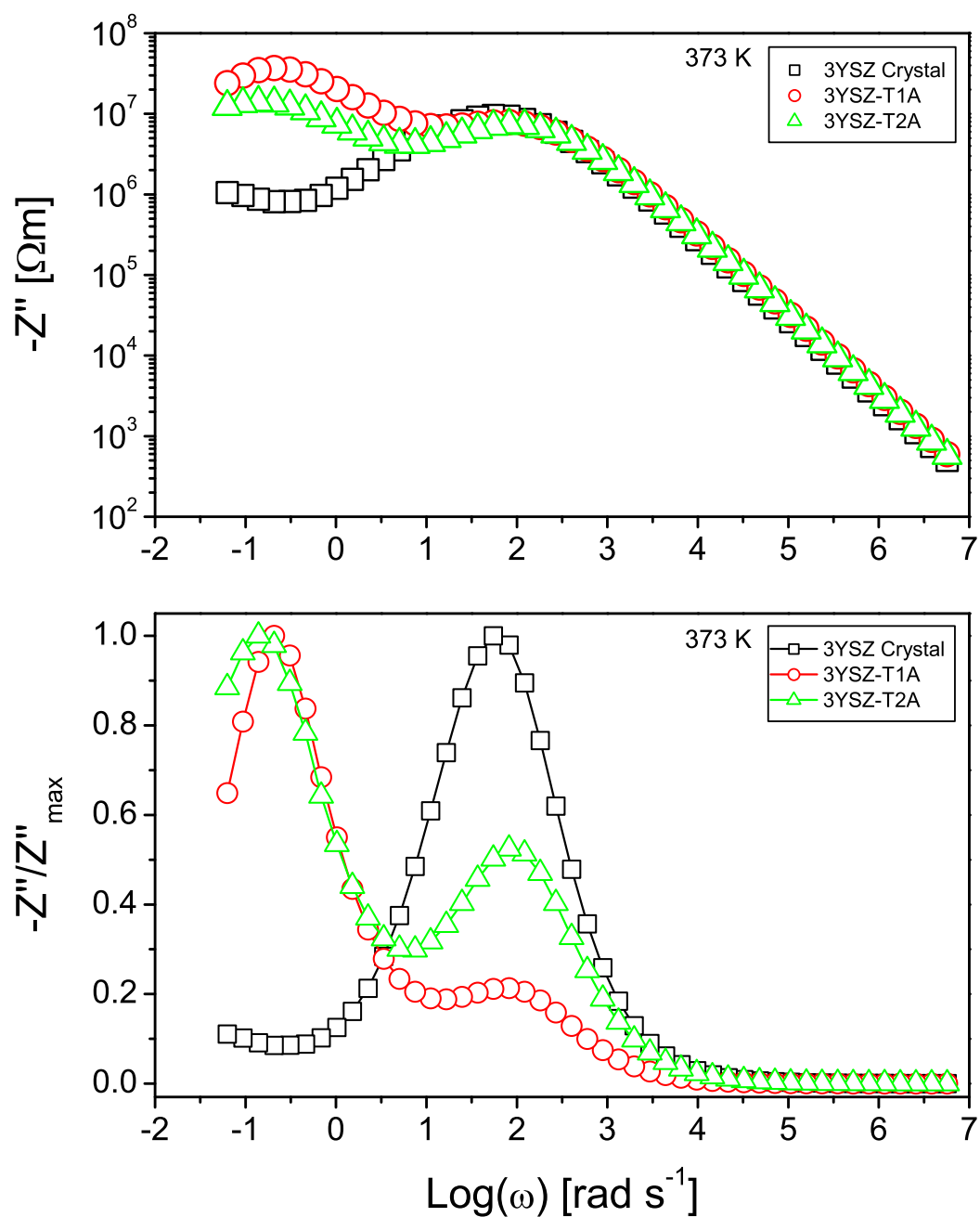


Figure 5.19: The frequency dependence of the imaginary impedances (top) and normalized imaginary impedances (bottom) of a 3YSZ single crystal and several polycrystalline 3 mole % YSZ samples at 100 °C. Note that the characteristic frequency of the single crystal is almost the same as that of the component of the ceramic dominant at high frequencies (the grains).

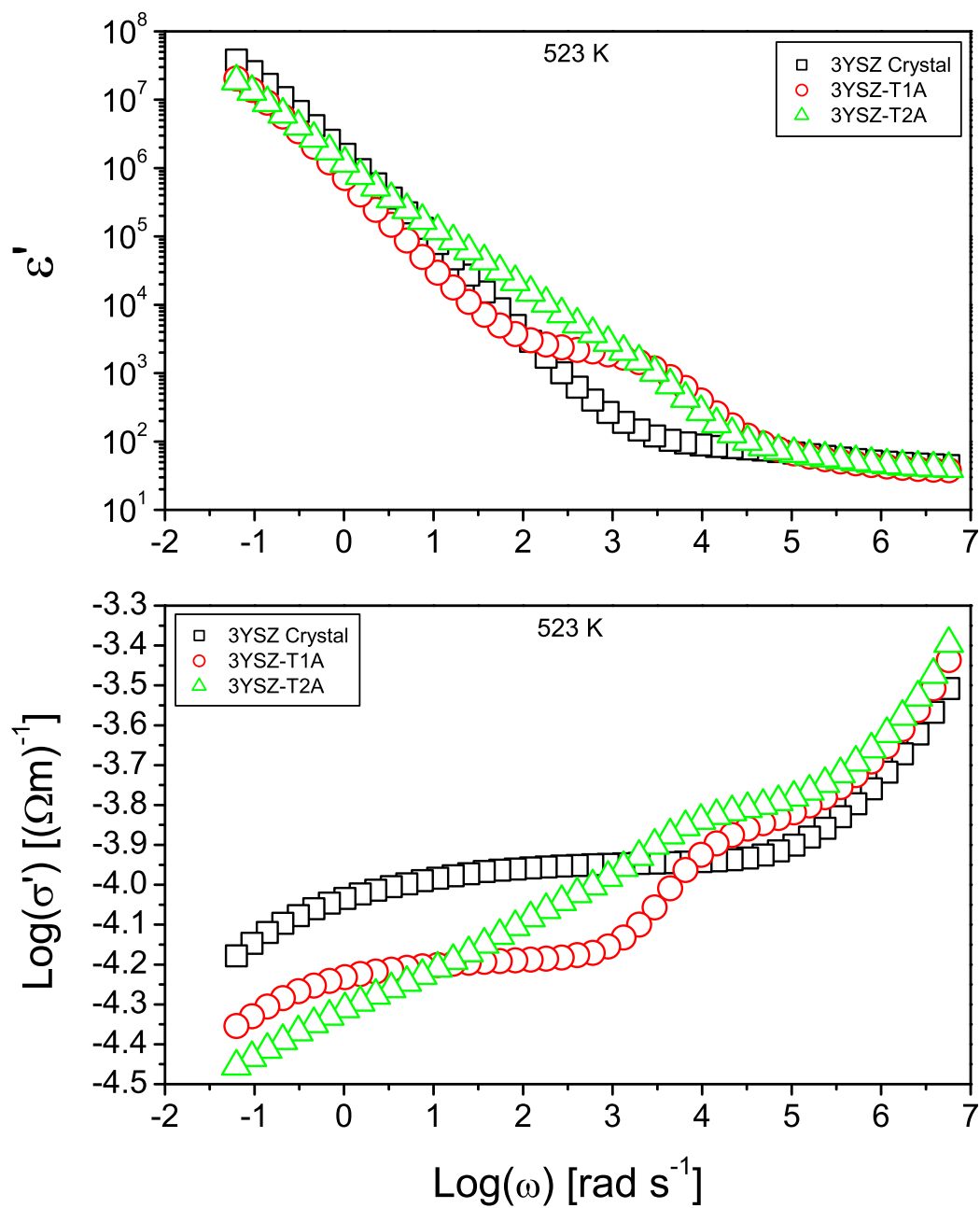


Figure 5.20: The frequency dependence of the real dielectric constants (top) and the real conductivities (bottom) of a tetragonal stabilized zirconia single crystal and several polycrystalline samples at 250 °C. Included the data at frequencies where electrode effects are dominant.

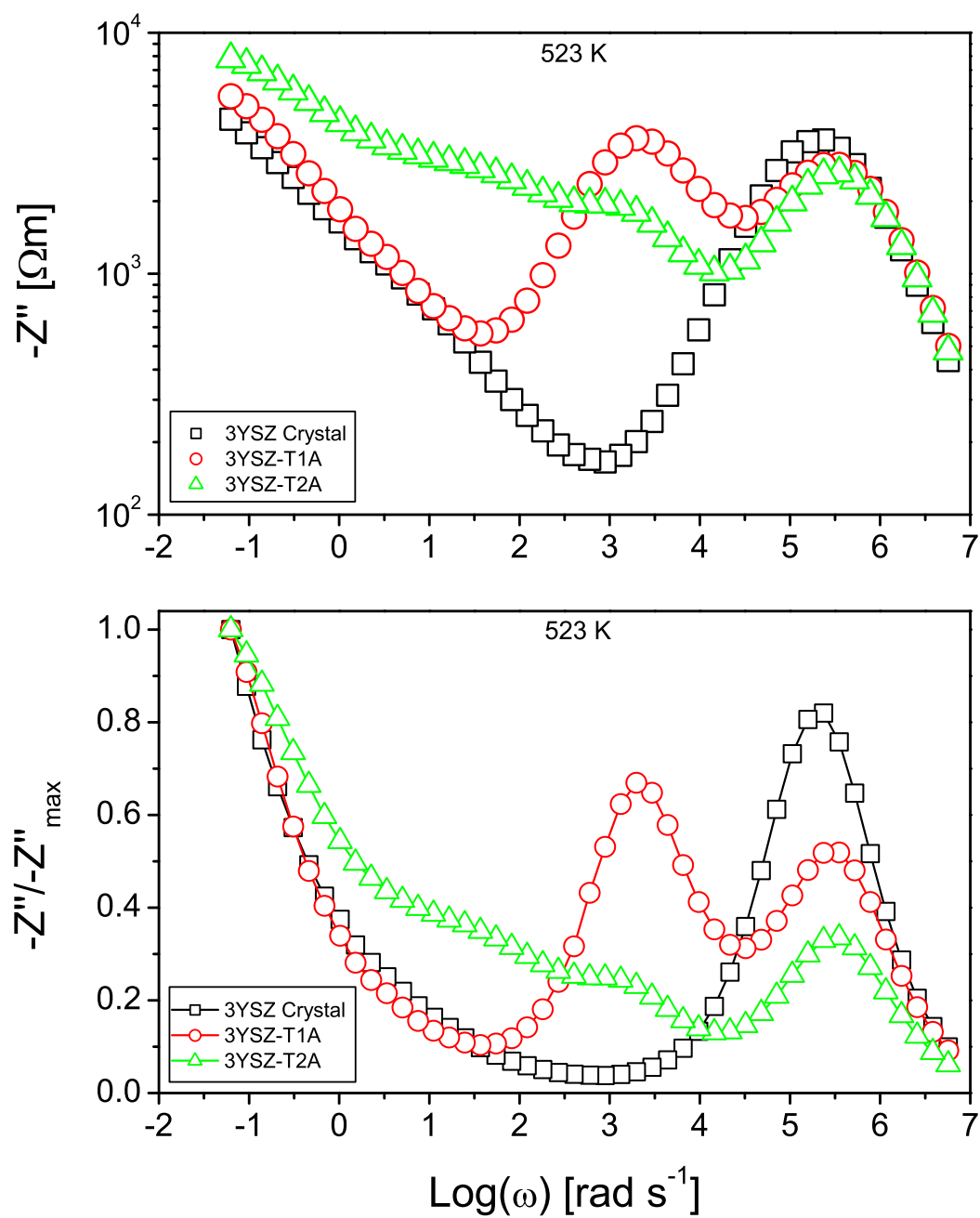


Figure 5.21: The frequency dependence of the imaginary impedances and normalized impedances of a 3YSZ single crystal and polycrystalline 3 mole % YSZ at 250 °C. Note the long “tail” at low frequencies, due to electrode effects.

conductivities of the polycrystalline samples are similar to those of the 3YSZ single crystal. It can also be seen in Figures 5.19 and 5.21 that the peak frequency of the 3YSZ single crystal lies in the same region as that of the peak at high frequencies, in the polycrystalline sample data. This further confirms the conclusion that this contribution is due to the YSZ crystallites, the grains in the polycrystalline material. Note however that the crystal peak frequency is not exactly the same as that of the grains, as there is a slight perturbation, which in part may be due to experimental errors in the positions of the peaks. In addition, as has been shown in the simulations in Chapter 4, the peaks in the plots for composite data are usually not in exactly the same positions as those for the components.

5.2.4 The temperature, grain size and silica content dependence of the electrical properties of polycrystalline yttria-stabilized zirconia

The temperature dependence of the “dc” conductivity, extracted from complex impedance plane plots (which, for simplicity, will be referred to as the dc conductivity) and peak frequencies of all the YSZ samples studied is best described by an ionic conductivity mechanism (see Section 1.5). Recall from Section 3.2.3 that for ionic conductivity, Equation (1.23) becomes,

$$\sigma_{dc}T = \sigma_0 \exp\left[-\frac{E_{a-\sigma}}{k_B}T\right] \quad (5.1)$$

and

$$\nu_p T = \nu_0 \exp\left[-\frac{E_{a-\nu}}{k_B}T\right], \quad (5.2)$$

where $E_{a-\sigma}$ and $E_{a-\nu}$ are the activation energies for the conductivities and the peak frequencies respectively.

The temperature dependence of the electrical properties of the grains and the grain boundaries of the polycrystalline YSZ samples was also studied. Figure 5.22 shows that the temperature dependence of characteristic frequencies, (plotted as $\text{Log}(\omega_p)$ vs $1000/T$) and the dc conductivities (plotted as

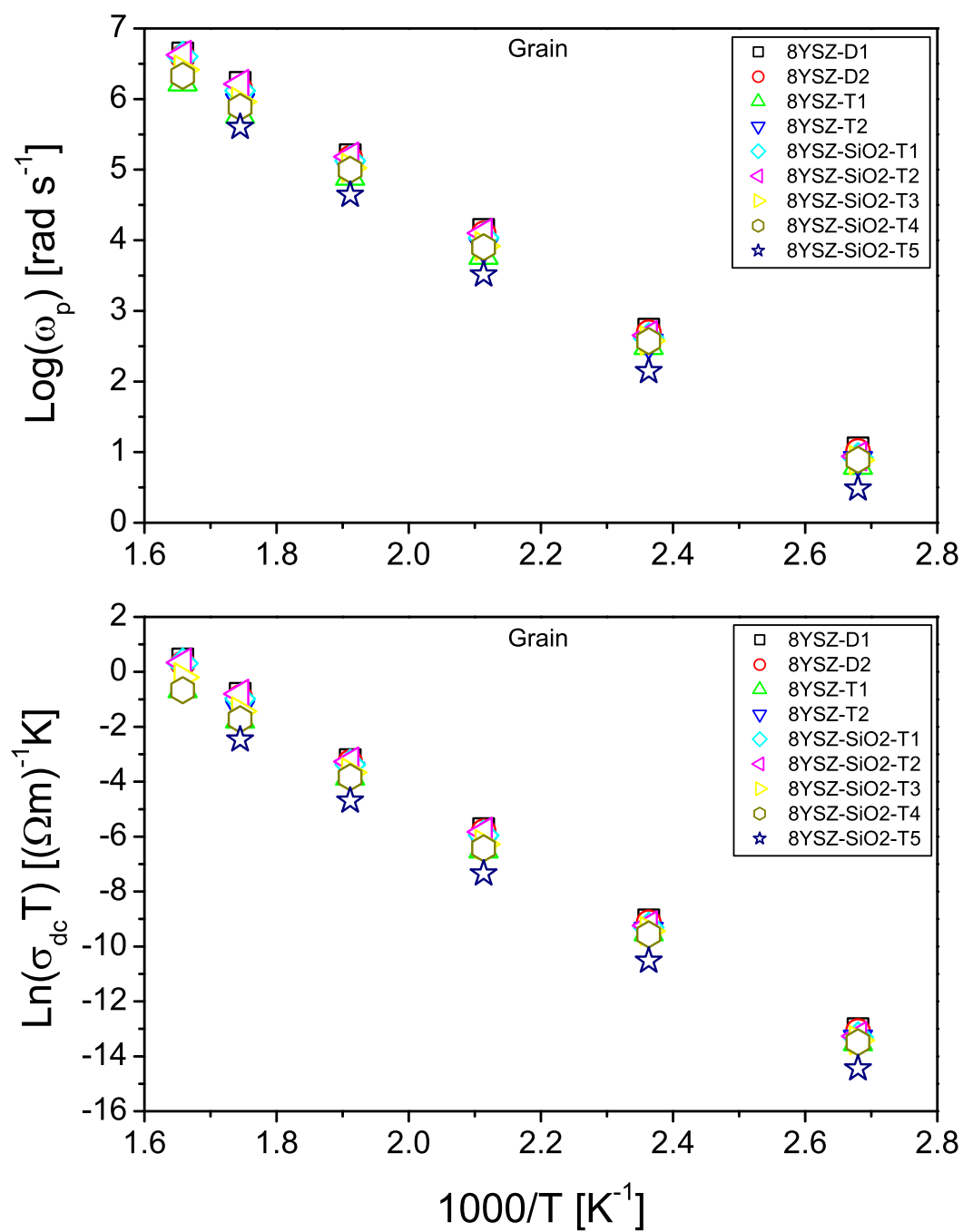


Figure 5.22: The temperature dependence of the characteristic frequencies (top) and “dc” conductivities (bottom) of the grains of various polycrystalline CSZ samples.

$\ln(\sigma_{dc}T)$ vs $1000/T$), of the grains of the various CSZ samples are essentially the same. There are only small changes in magnitude observable, due to the increasing silica content. This is to be expected as silica is almost insoluble in YSZ [Appel and Bonanos¹³¹] and therefore should not affect the bulk properties significantly. The silica is likely to accumulate in the grain boundaries and triple points as discussed below. At 23 volume percent silica (sample 8YSZ-SiO₂-T5) however, there appears to be enough silica to have a significant influence on the properties of the ceramic grains causing changes in the magnitude but not the slope. Note however that the effect of the silica on the grain properties may not be as a result of doping but may instead be due to other mechanisms such as changing of the yttrium distribution in the ceramic [Gremillard et al.¹²⁹].

The temperature dependence of the characteristic dielectric constants and the depression angles of the grains of the CSZ samples is shown in Figure 5.23. While there are no models to describe the temperature dependence of the dielectric constants the curves for most of the samples are tightly grouped, indicating similar behavior. The dielectric constants of the two samples with the highest silica content are notably different from those of the rest of the samples. The depression angles of the sample containing the highest silica content are the only ones which are noticeably higher than those of the rest of the samples, at all temperatures. The depression angles of the high frequency (grain) semicircles are mostly greater than 10° and similar to those of the YSZ single crystals (see Section 3.2.3).

The effects of the grain size on the grain dc conductivity (plotted as $\ln(\sigma_{dc}T)$ at 250 °C) are shown in Figure 5.24 (top) while Figure 5.24 (bottom) shows the effect of the sample silica content on the characteristic frequency and the dc conductivity (again plotted as $\ln(\sigma_{dc}T)$ at 250 °C) of these grains. The different grain sizes do not have a very large influence on the grain conductivity, which remains within a narrow range for the grain sizes investigated, including the sample with the very large grains. Figure 5.24 (bottom) shows that the silica only has really marked effects at very high levels, 23

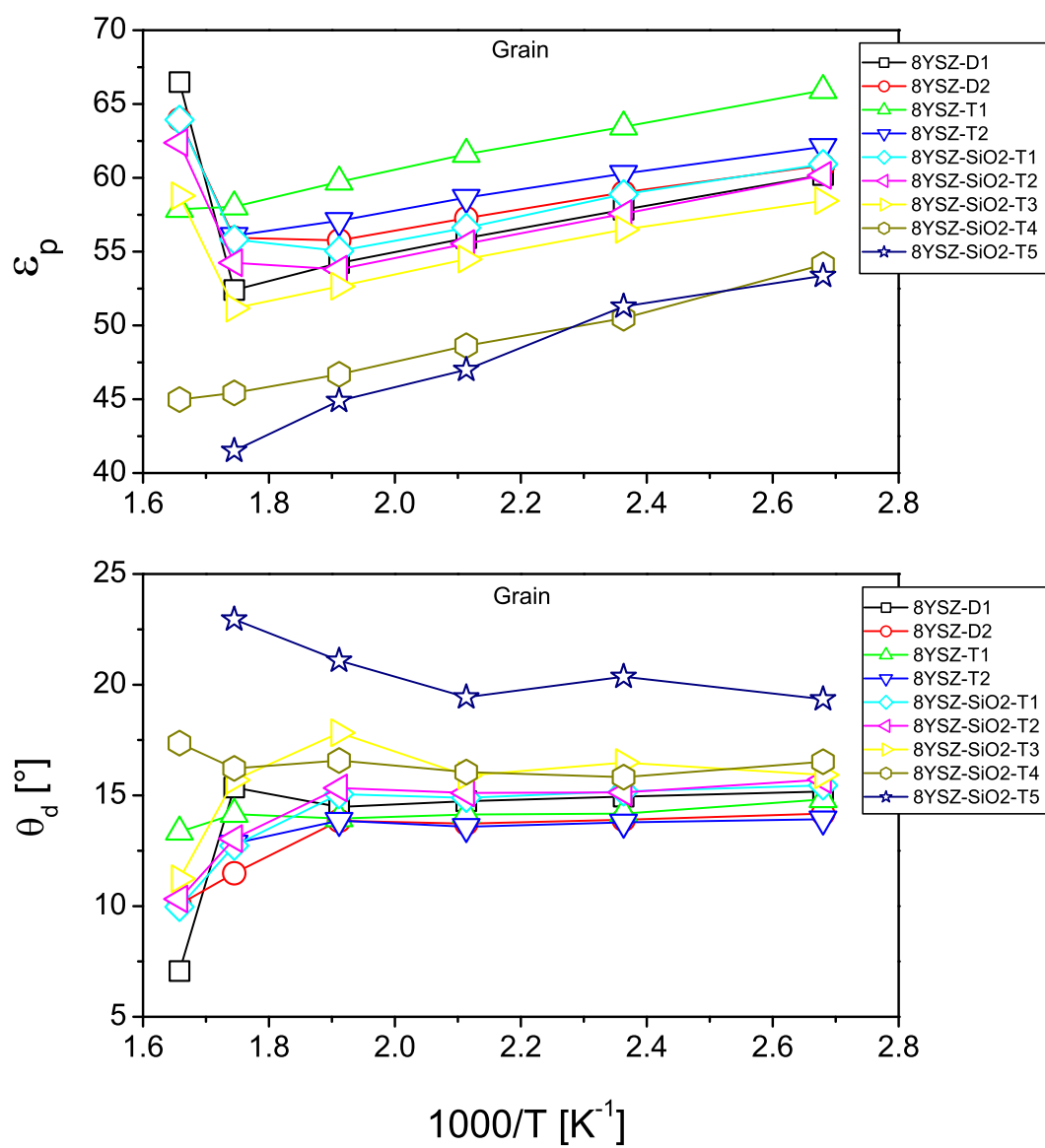


Figure 5.23: The temperature dependence of the characteristic dielectric constants (top) and the depression angles (bottom) of the grains of various polycrystalline CSZ samples. Note the linear scale on the y-axis.

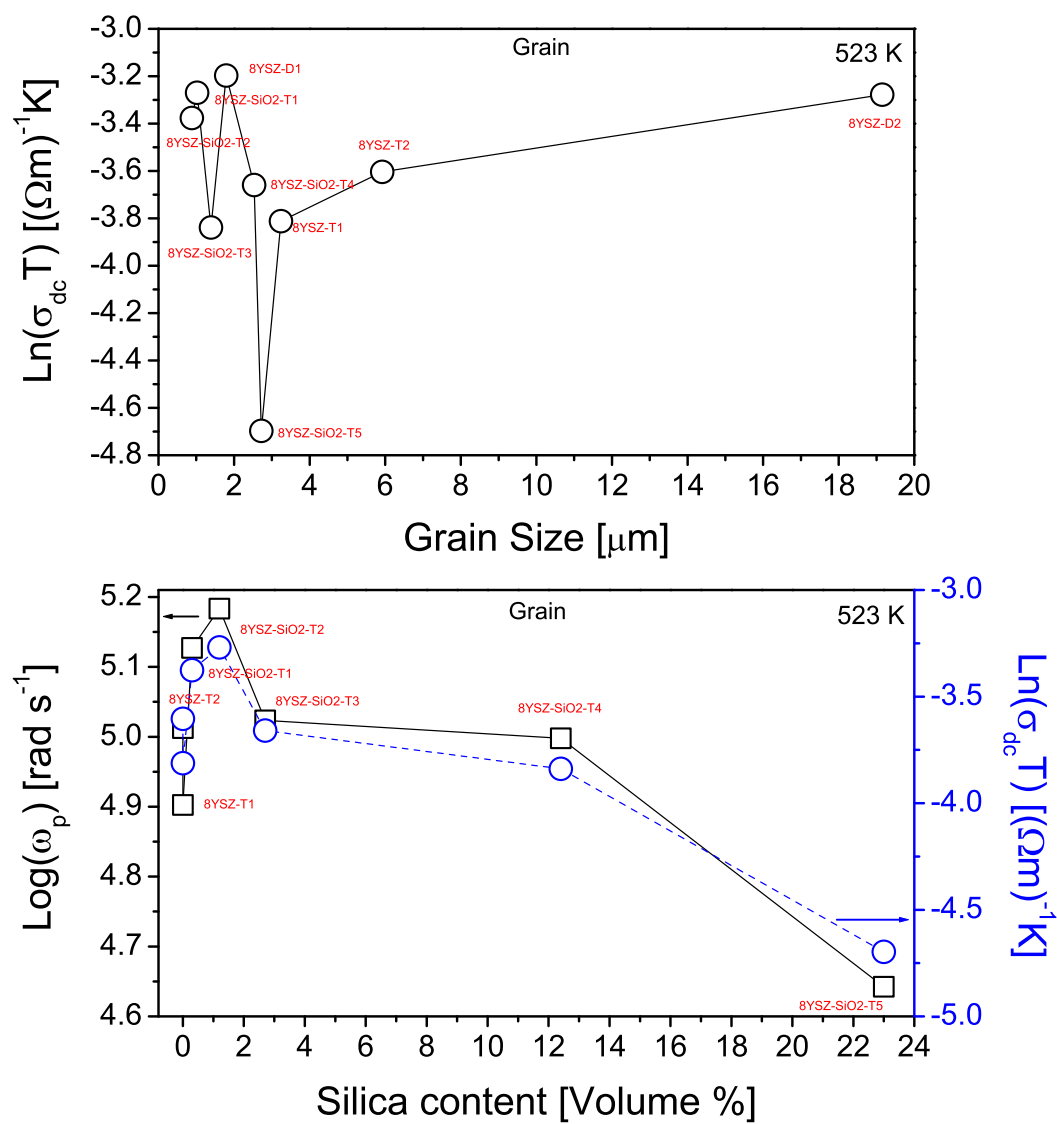


Figure 5.24: The effect of the grain size on the grain conductivity and that of the sample silica content on the characteristic frequencies and conductivities of the grains of various polycrystalline CSZ samples at 250 °C.

volume % in this case. Up to 12 volume % silica, the properties of the grains are similar to those of samples with little or no silica.

The characteristic frequencies and the dc conductivities of the grain boundaries, as a function of $1/T$, show a wider spread than those of the grains, as can be seen in Figures 5.25 and 5.27. However, the temperature dependence ($\propto 1/T$) is similar to that of the grains. Note that, as is done by several authors, such as in Verkerk et al.¹⁹, Bowen et al.¹³⁵ and others, the conductivities ($\sigma_{dc}^\dagger$) plotted in Figure 5.25 are the “effective” conductivities of the grain boundaries, i.e the grain boundary conductivities normalized to the sample geometric factor (G).

As both Z' and Z'' are in Ωm in the current work, the resistance values read from the intercepts are in Ωm and normalized to the sample geometric factor. Therefore, in the current notation

$$\sigma_{dc}^\dagger = 1/R,$$

where in this case R is the “specific resistance” (Ωm) of the grain boundary (normalized to the sample geometric factor and not to the dimensions of the grain boundaries). Note that where the impedances (Z' and Z'') are not normalized to the sample geometric factor,

$$\sigma_{dc}^\dagger = 1/(R^*G),$$

where R^* is the dc resistance extracted from the complex impedance plane plot, in ohms.

The specific conductivity of the grain boundaries (normalized to the dimensions of the grain boundaries) is related to their “effective” dc conductivity by [Verkerk et al.¹⁹]

$$\sigma_{gb}^{sp} = \sigma_{dc}^\dagger \delta_{gb}/d_g,$$

where d_g is the average grain size and δ_{gb} is the grain boundary thickness.

The term “dc conductivity” when used in connection to the grain boundaries will still be used to refer to the “effective” dc conductivity ($\sigma_{dc}^\dagger$).

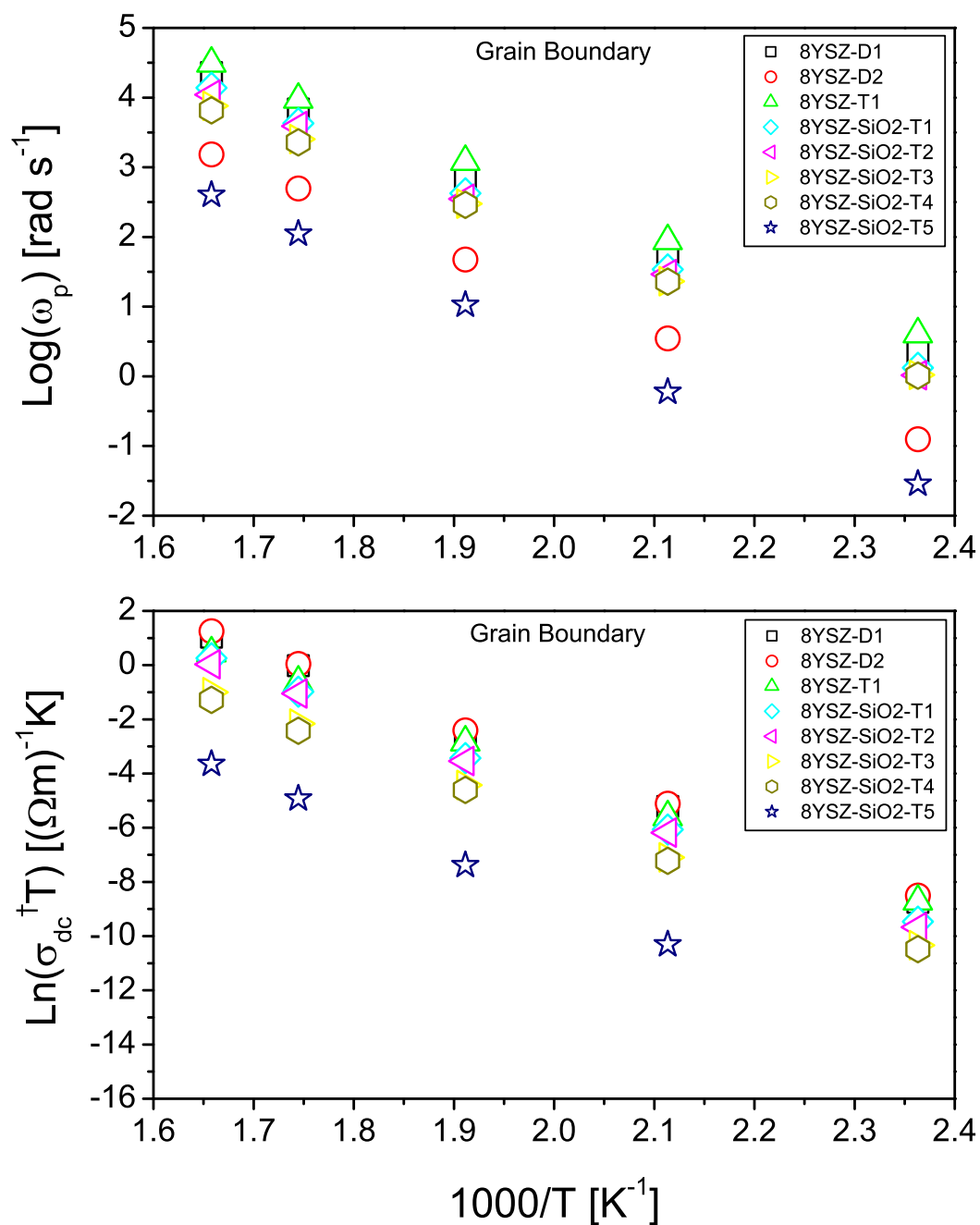


Figure 5.25: The temperature dependence of the characteristic frequencies (top) and the “dc” conductivities (bottom) of the grain boundaries of various polycrystalline CSZ samples.

The resistance per area (specific resistance) can be approximated as [Guo¹³³, Lee et al.¹³⁶]

$$\rho_{dc}^{\dagger} d_g,$$

where $\rho_{dc}^{\dagger} = 1/\sigma_{dc}^{\dagger}$ is the “effective” resistivity. It follows that the specific conductance is approximately

$$\sigma_{dc}^{\dagger}/d_g.$$

The temperature dependence of the grain boundary specific conductances (plotted as $\ln(\sigma_{dc}^{\dagger}/d_g \cdot T)$), for the various samples, is shown in Figure 5.26 (top). The specific conductances are again tightly grouped highlighting the fact that the electrical properties of the grain boundaries in these ceramic materials are similar. Note that there are some slight differences between this grouping of the specific conductances and that of the conductivities in Figure 5.25, indicating some small effects due to the different grain sizes and silica contents of the samples. Figure 5.26 (bottom) shows the dependence of the specific conductances, at 250 °C and plotted as $\ln(\sigma_{dc}^{\dagger}/d_g \cdot T)$ on the grain size. The conductances of all the samples except for the one with the highest silica content again lie in a narrow range.

Figure 5.27 (top) shows that the magnitude of the characteristic frequency and the conductivity of the grain boundaries decreases with increasing silica content but there is no sudden big decrease in the conductivity, except for the sample with the highest silica content. The changes in the characteristic frequency follow those of the conductivity, which indicates that the dielectric constant of the grain boundaries is changing slowly with the increasing silica content. Figure 5.27 (bottom) shows two distinct drops in the specific conductance at 250 °C (again plotted as $\ln(\sigma_{dc}^{\dagger}/d_g \cdot T)$), one between the samples 8YSZ-SiO₂-T2 and 8YSZ-SiO₂-T3 and another between the samples 8YSZ-SiO₂-T4 and 8YSZ-SiO₂-T5. Figure 5.28 shows the total (grain + grain boundaries) conductivities of the samples containing various amounts of silica. It can be seen that the conductivities monotonically decrease with increasing silica content.

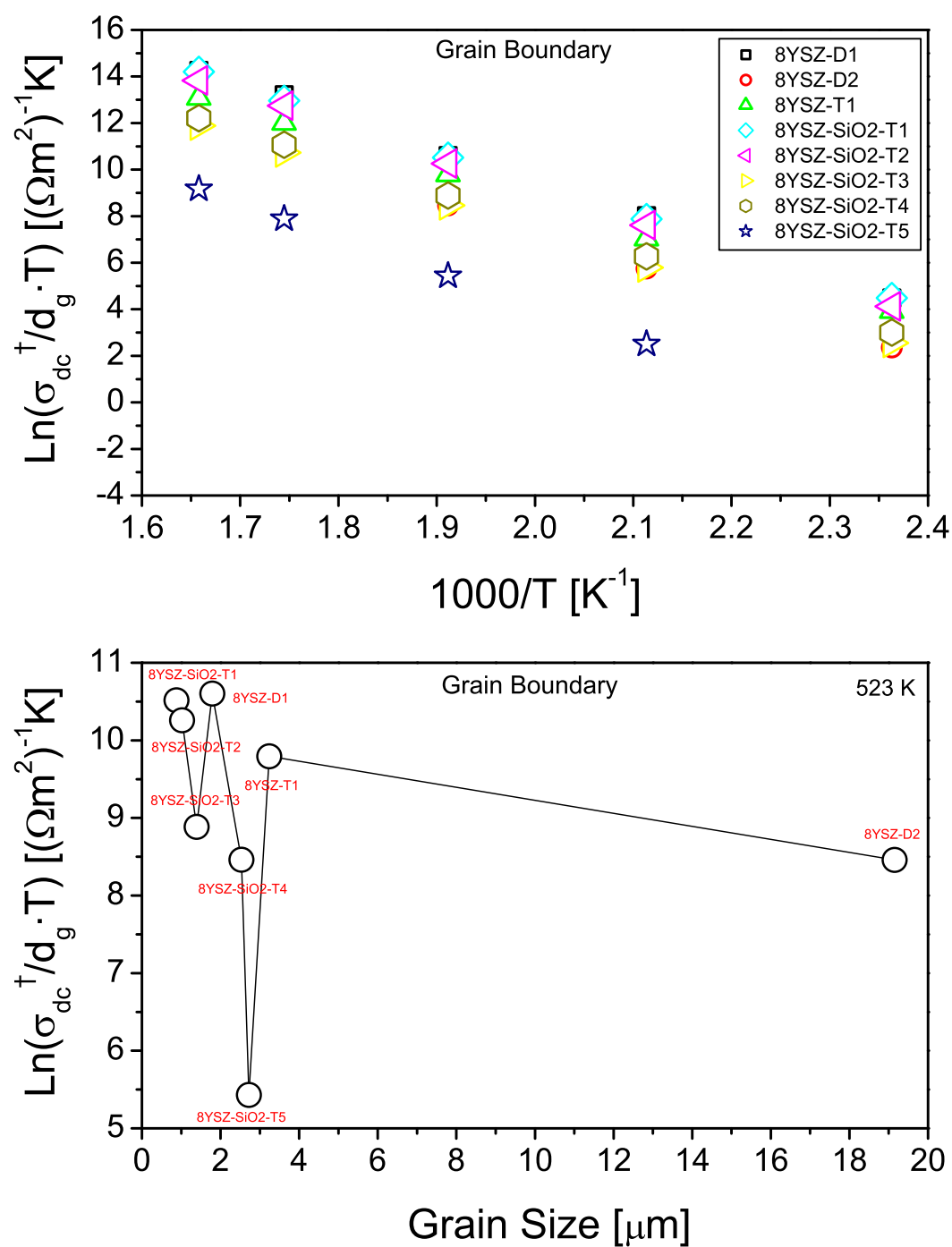


Figure 5.26: The temperature (top) and grain size (bottom) dependence of the specific conductance of the grain boundaries of various cubic stabilized zirconia samples. The grain size dependence is analyzed at 250 °C

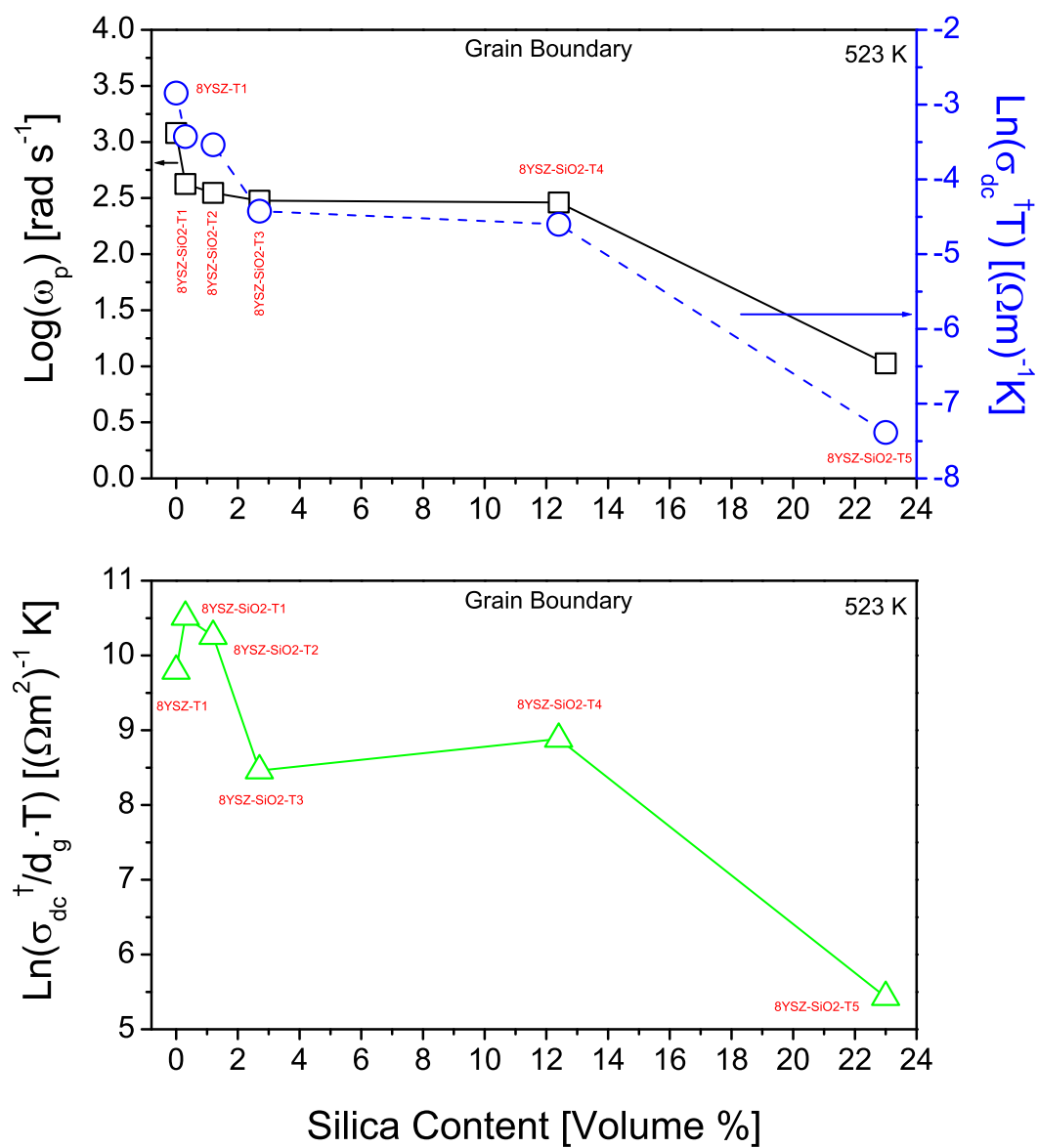


Figure 5.27: The effects of the silica content on the grain boundary characteristic frequencies and conductivities (top) and on the specific conductances (bottom) at 250 °C.

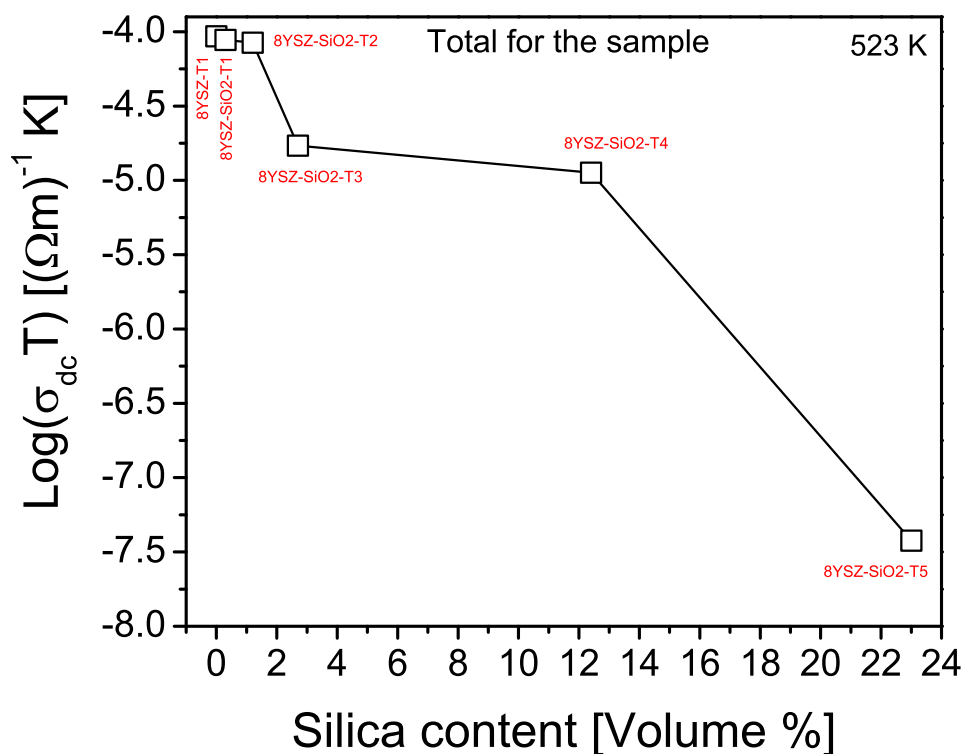


Figure 5.28: The effects of the silica content on the total conductivities of the samples at 250 °C.

The results discussed above and the characteristic frequencies shown earlier suggest that while the silica may modify the properties of some grain boundaries, there are still continuous paths through the grains and “clean” grain boundaries through which most of the current flows. At lower silica contents, most of the silica probably accumulates in the triple junctions as observed using Transmission Electron Microscopy and energy-dispersive X-ray (EDX) analysis in Gremillard et al.¹²⁹ and does not affect the critical conducting paths (see Figure 1.19). As previously mentioned, these authors observed no silica at all in the grain boundaries of their samples. The monotonic decrease in the total sample conductivity with increasing silica content (Figure 5.28) and the non-monotonic trend in the specific conductance of the grain boundaries (Figure 5.27) supports a conclusion that the silica initially accumulates in the triple points, thereby influencing the overall sample conductivity while having minimal influence on the critical conducting paths.

At very high silica content (> 12 volume %), there may be some silica entering into the grain boundaries, which possibly explains the significant decrease in the conductivity of the 23 volume % silica sample. However, this is has not been conclusively established.

The temperature dependence of the grain boundary “effective” dielectric constants ($\epsilon_p^\dagger$), and the depression angles is shown in Figure 5.29. While no model has been found for the temperature dependence of the “effective” dielectric constants, they are nearly constant in the temperature range studied. Recalling that $\omega_p = \frac{\sigma_{dc}}{\epsilon_p}$, constant or nearly constant values of the “effective” dielectric constant lead to the almost identical activation energies of the peak frequencies and the conductivities. The “effective” dielectric constant of the sample with the largest grain size (8YSZ-D2) is noticeably different from that of the other samples, a behavior that could be directly linked to its large grain size.

The depression angles Figure 5.29 (bottom) lie in two groupings, low values ($\lesssim 10^\circ$) for most of the samples and high values ($\gtrsim 20^\circ$) for the samples with the largest amount of SiO_2 (8YSZ-SiO₂-T5), the largest grains (8YSZ-D2) and surprisingly the sample 8YSZ-T1. Note though that of the samples studied, this sample has the third largest grain size and the trend in the depression angles may be linked to both the grain size and the silica content. No grain boundary arc was observed in a complex impedance plane plot of the data for the sample with the second largest grain size (8YSZ-T2).

The temperature dependence of the characteristic frequencies and the dc conductivities of the tetragonal stabilized zirconia samples is shown in Figure 5.30. It can be seen, in the figure, that the grains of the tetragonal stabilized zirconia samples sintered under different conditions (temperature and time, 1350/2 and 1600/10) have similar properties, which are close to those of the 3YSZ single crystal. The temperature dependence of the dielectric constants and the depression angles is shown in Figure 5.31 where again, it can be seen that the properties of the grains are similar for the different ceramic samples and those of the single crystal.

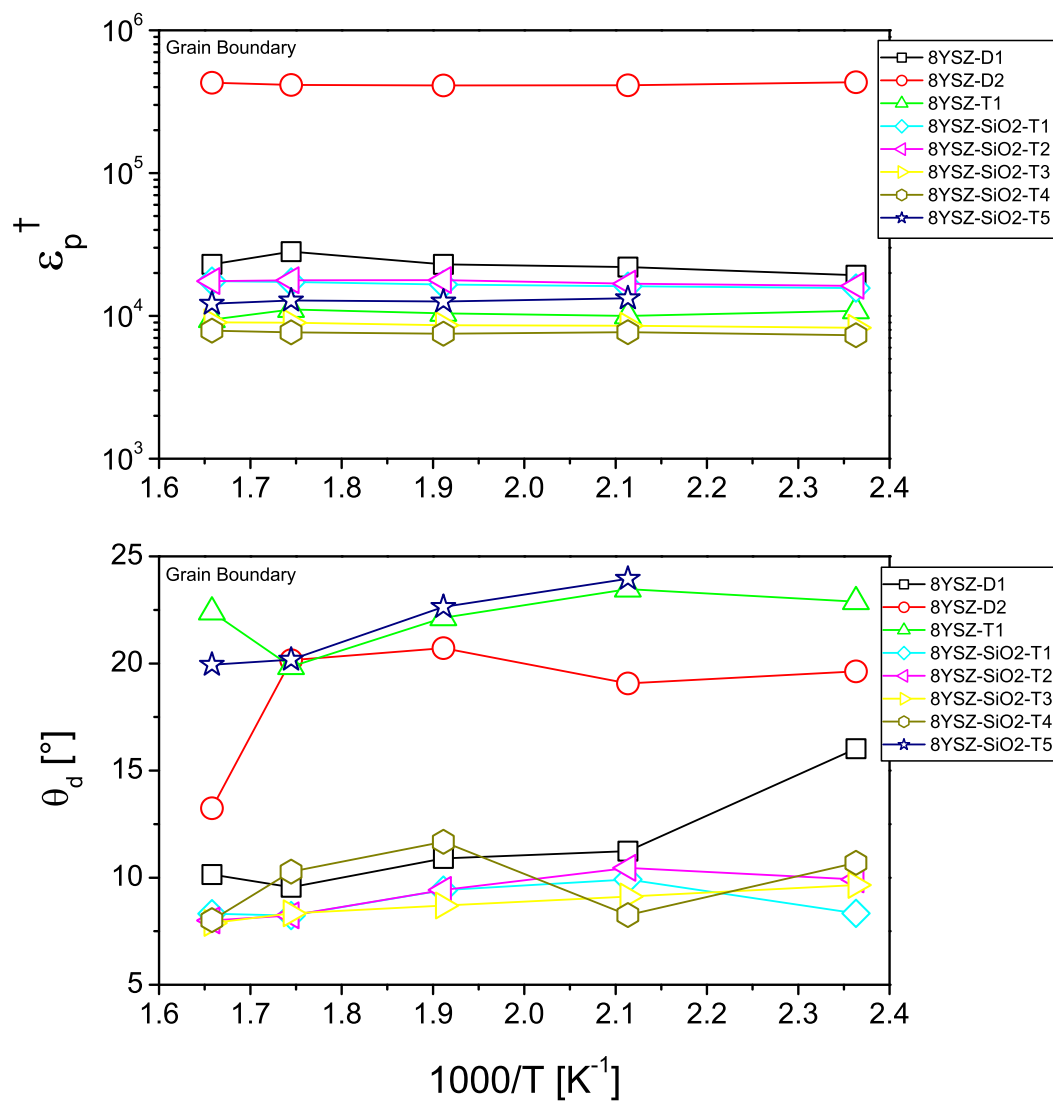


Figure 5.29: The temperature dependence of the real dielectric constants (top) and the depression angles (bottom) of the grain boundaries of various polycrystalline CSZ samples. Note the linear scale on the y-axis for the depression angles.

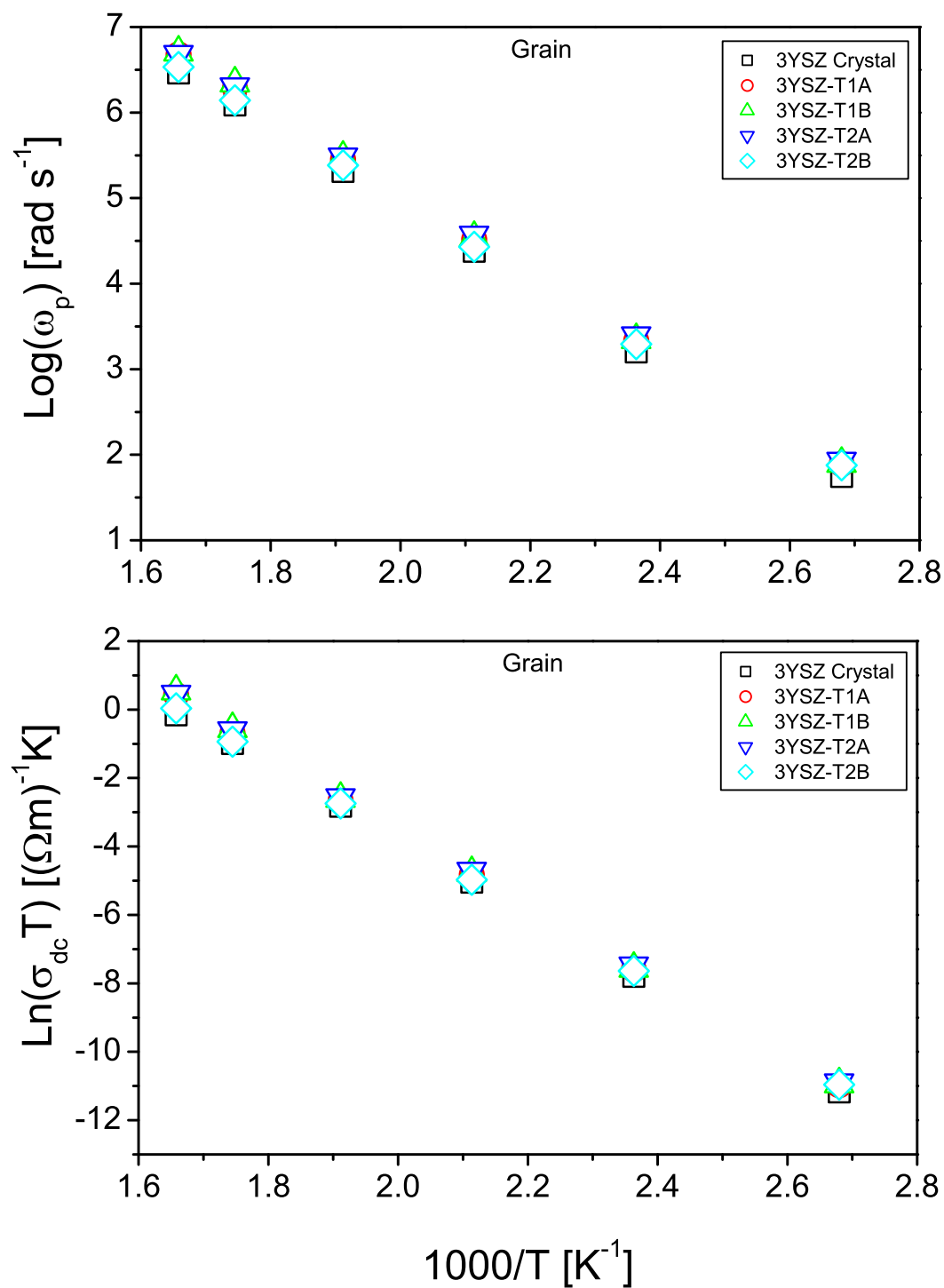


Figure 5.30: The temperature dependence of the characteristic frequencies (top) and the dc conductivities (bottom) of a 3YSZ single crystal and of the grains of various polycrystalline 3YSZ ceramics.

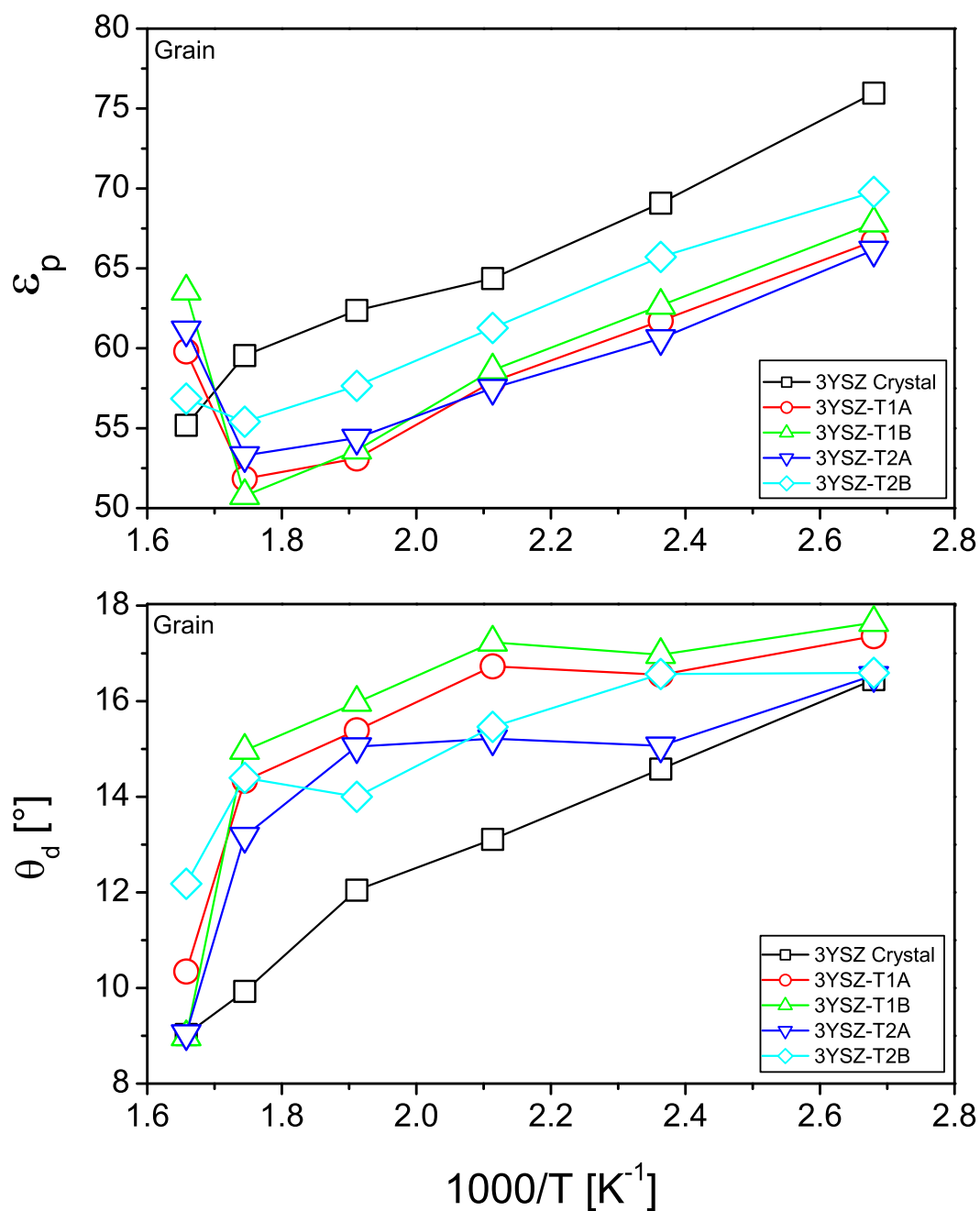


Figure 5.31: The temperature dependence of the dielectric constants (top) and depression angles (bottom) of a 3YSZ single crystal as well as those of the grains of polycrystalline 3YSZ ceramics. Note the linear scale on the y-axis.

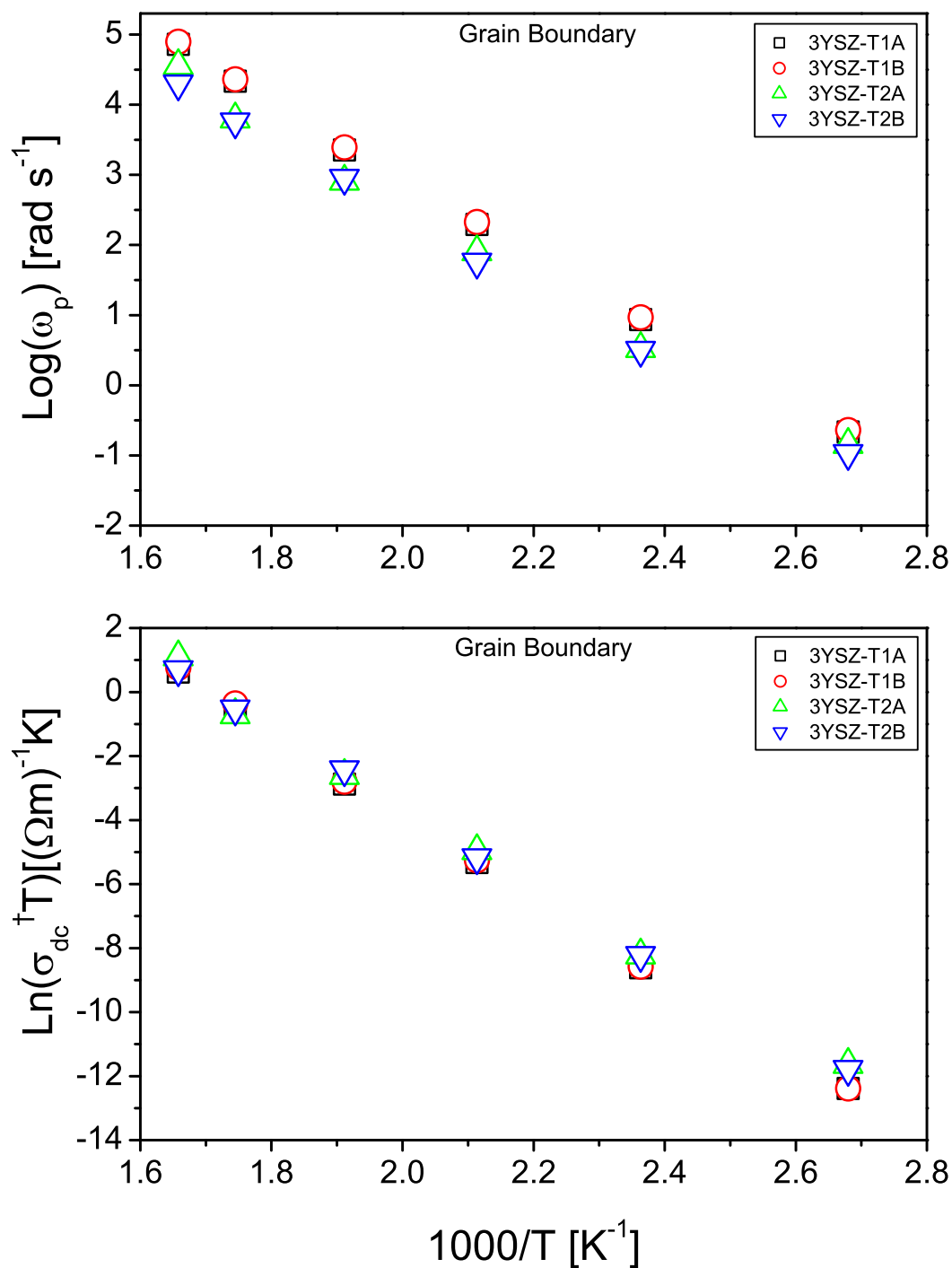


Figure 5.32: The temperature dependence of the characteristic frequencies (top) and the dc conductivities (bottom) of the grain boundaries of various polycrystalline 3YSZ ceramics.

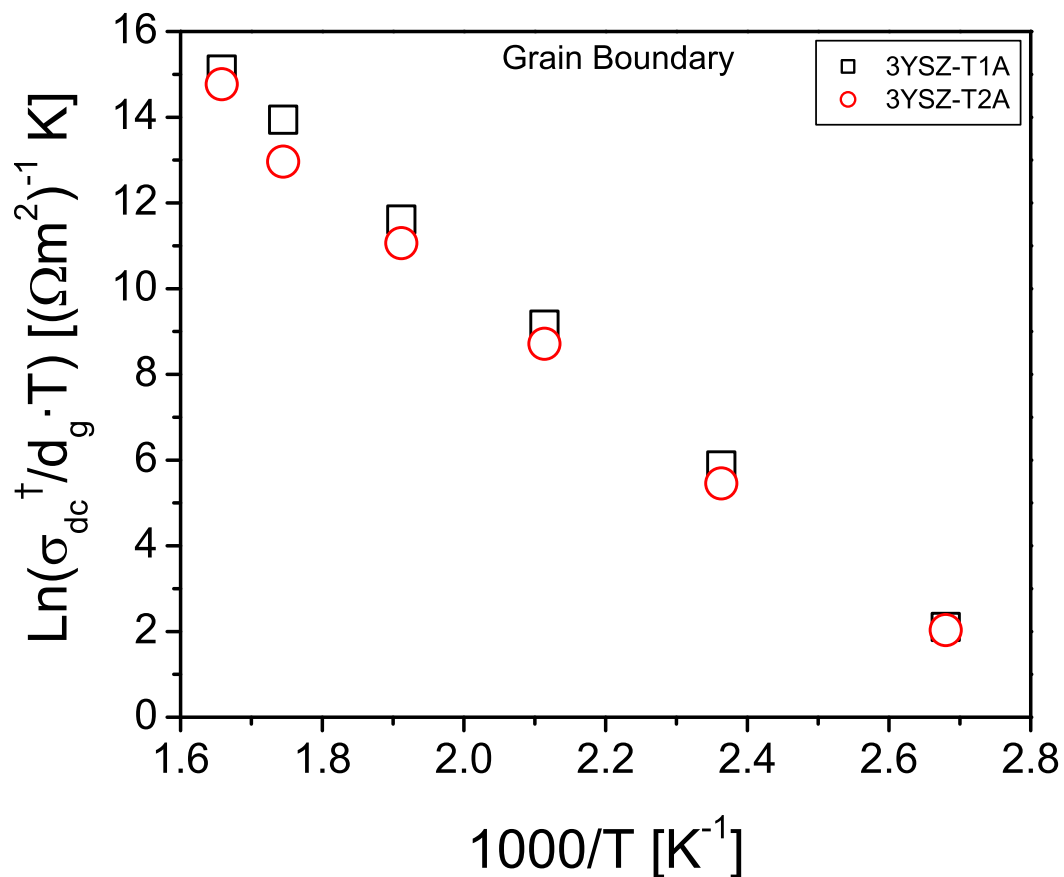


Figure 5.33: The temperature dependence of the specific conductances (plotted as $\text{Ln}(\sigma_{dc}^{\dagger}/d_g \cdot T)$) of two 3YSZ sample sintered under different conditions.

Figure 5.32 shows the temperature dependence of the characteristic frequencies (plotted as $\text{Log}(\omega_p)$ vs $1000/T$) and the dc conductivities (plotted as $\text{Ln}(\sigma_{dc}T)$ vs $1000/T$), of the grain boundaries of the polycrystalline 3 mole % YSZ samples. On the scale of the figures, only small differences, in the magnitude, are seen between the properties, at the same temperature, of the grain boundaries of the polycrystalline samples sintered under different conditions. There is no discernible difference in the slopes of the data from the different samples. The conductivities, Figure 5.32 (bottom), and the specific conductances, Figure 5.33, are similar for the different samples, at the same temperature. It can be seen in Figure 5.34 (top) that the small differences in the characteristic frequencies, seen in Figure 5.32, are driven by the grain boundary “effective” dielectric constants which are notably different.

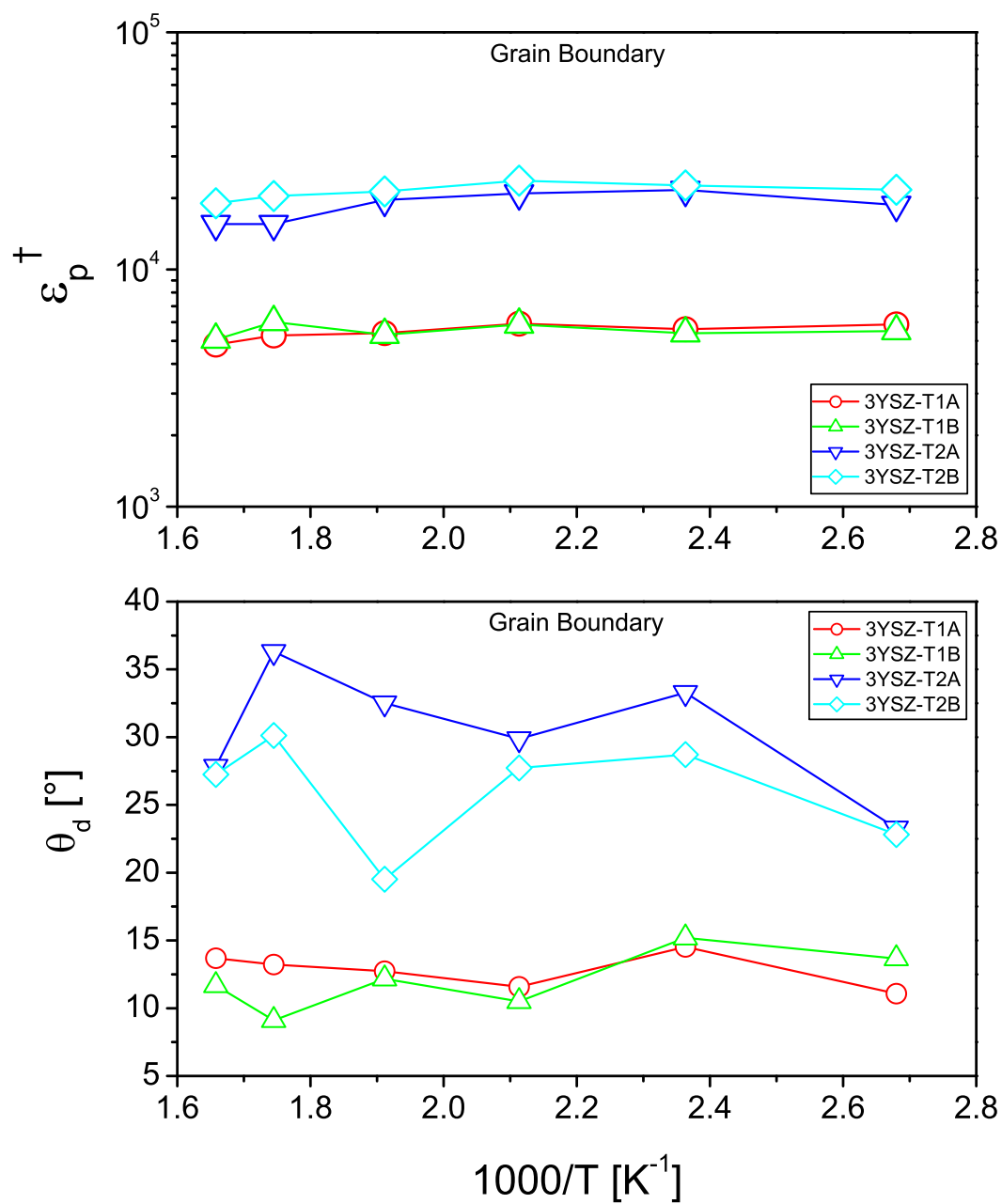


Figure 5.34: The temperature dependence of the real dielectric constants (top) and the depression angles (bottom) of the grain boundaries of various 3YSZ ceramic samples. Note the log scale (top) and linear scale (bottom) on the y-axis.

The depression angles, Figure 5.34 (bottom) are also different for the samples sintered under the different conditions. There appears to be a correlation between the “effective” dielectric constants and the depression angles.

Table 5.4: Activation energies (AE) of the dc conductivity (Cond) and the characteristic frequency (Freq) in polycrystalline 8 mole % yttria-stabilized zirconia (Cubic). σ_0 and ν_0 are the pre-factors in Equations (5.1) and (5.2) respectively.

Sample Name	Prop.	Grain		Grain Boundary	
		σ_0/ν_0 $(\Omega m)^{-1} K / Hz K$	AE (eV)	σ_0/ν_0 $(\Omega m)^{-1} K / Hz K$	AE (eV)
8YSZ-D1	Cond	$(4 \pm 1) \times 10^9$	1.13 ± 0.04	$(3 \pm 1) \times 10^{10}$	1.20 ± 0.06
	Freq	$(13 \pm 3) \times 10^{17}$	1.13 ± 0.03	$(11 \pm 4) \times 10^{15}$	1.17 ± 0.05
8YSZ-D2	Cond	$(31 \pm 8) \times 10^8$	1.13 ± 0.03	$(31 \pm 9) \times 10^9$	1.19 ± 0.04
	Freq	$(10 \pm 2) \times 10^{17}$	1.13 ± 0.02	$(14 \pm 3) \times 10^{14}$	1.19 ± 0.03
8YSZ-T1	Cond	$(59 \pm 8) \times 10^7$	1.08 ± 0.01	$(4 \pm 1) \times 10^9$	1.13 ± 0.04
	Freq	$(23 \pm 3) \times 10^{16}$	1.09 ± 0.01	$(8 \pm 2) \times 10^{15}$	1.13 ± 0.03
8YSZ-T2	Cond	$(12 \pm 3) \times 10^8$	1.10 ± 0.03	—	—
	Freq	$(5 \pm 1) \times 10^{17}$	1.11 ± 0.03	—	—

Tables 5.4, 5.5 and 5.6 summarize the temperature dependence of the properties of the YSZ ceramics. The characteristic frequencies and dc conductivities have similar activation energies, indicating that they are due to the same processes in the material. As can be seen in the tables, there is also a small but notable difference between the activation energies for the processes in the crystalline grains and those in the amorphous grain boundaries. There are also notable differences between the activation energies for the processes in the cubic stabilized zirconia and the tetragonal stabilized zirconia.

Table 5.5: Activation energies (AE) of the dc conductivity and characteristic frequency in polycrystalline 3 mole % yttria-stabilized zirconia (Tetragonal). σ_0 and ν_0 are the pre-factors in Equations (5.1) and (5.2) respectively.

Sample Name	Prop.	Grain		Grain Boundary	
		σ_0/ν_0 $(\Omega m)^{-1} K/H z K$	AE (eV)	σ_0/ν_0 $(\Omega m)^{-1} K/H z K$	AE (eV)
3YSZ-T1A	Cond	$(13 \pm 3) \times 10^7$	0.96 ± 0.03	$(25 \pm 8) \times 10^8$	1.10 ± 0.04
	Freq	$(6 \pm 1) \times 10^{16}$	0.97 ± 0.02	$(11 \pm 4) \times 10^{15}$	1.11 ± 0.04
3YSZ-T1B	Cond	$(17 \pm 5) \times 10^7$	0.96 ± 0.04	$(4 \pm 1) \times 10^9$	1.11 ± 0.04
	Freq	$(7 \pm 2) \times 10^{16}$	0.98 ± 0.02	$(13 \pm 4) \times 10^{15}$	1.11 ± 0.04
3YSZ-T2A	Cond	$(13 \pm 3) \times 10^7$	0.95 ± 0.02	$(12 \pm 5) \times 10^8$	1.05 ± 0.09
	Freq	$(54 \pm 7) \times 10^{15}$	0.97 ± 0.01	$(19 \pm 9) \times 10^{14}$	1.07 ± 0.11
3YSZ-T2B	Cond	$(56 \pm 8) \times 10^6$	0.93 ± 0.01	$(12 \pm 4) \times 10^8$	1.06 ± 0.05
	Freq	$(27 \pm 4) \times 10^{15}$	0.95 ± 0.01	$(13 \pm 5) \times 10^{14}$	1.07 ± 0.06

Table 5.6: Activation energies (AE) of the dc conductivity and characteristic frequency in polycrystalline 8 mole % yttria-stabilized zirconia with silica. σ_0 and ν_0 are the pre-factors in Equations (5.1) and (5.2) respectively.

Sample Name	Prop.	Grain		Grain Boundary	
		σ_0/ν_0 $(\Omega m)^{-1} K/H z K$	AE (eV)	σ_0/ν_0 $(\Omega m)^{-1} K/H z K$	AE (eV)
8YSZ-SiO2-T1	Cond	$(4 \pm 1) \times 10^9$	1.15 ± 0.04	$(10 \pm 3) \times 10^9$	1.18 ± 0.04
	Freq	$(14 \pm 3) \times 10^{17}$	1.15 ± 0.03	$(8 \pm 2) \times 10^{15}$	1.17 ± 0.04
8YSZ-SiO2-T2	Cond	$(5 \pm 1) \times 10^9$	1.15 ± 0.03	$(9 \pm 3) \times 10^9$	1.19 ± 0.04
	Freq	$(18 \pm 4) \times 10^{17}$	1.15 ± 0.03	$(7 \pm 2) \times 10^{15}$	1.18 ± 0.04
8YSZ-SiO2-T3	Cond	$(14 \pm 3) \times 10^8$	1.11 ± 0.02	$(12 \pm 2) \times 10^8$	1.14 ± 0.02
	Freq	$(52 \pm 8) \times 10^{16}$	1.12 ± 0.02	$(20 \pm 3) \times 10^{14}$	1.13 ± 0.02
8YSZ-SiO2-T4	Cond	$(58 \pm 5) \times 10^7$	1.08 ± 0.01	$(67 \pm 3) \times 10^7$	1.12 ± 0.00
	Freq	$(32 \pm 3) \times 10^{16}$	1.10 ± 0.01	$(135 \pm 8) \times 10^{13}$	1.12 ± 0.01
8YSZ-SiO2-T5	Cond	$(5 \pm 1) \times 10^8$	1.11 ± 0.03	$(9 \pm 1) \times 10^8$	1.26 ± 0.02
	Freq	$(34 \pm 9) \times 10^{16}$	1.13 ± 0.03	$(5 \pm 2) \times 10^{14}$	1.22 ± 0.08

5.2.5 Microstructure and the modeling of the electrical properties

As mentioned in the introduction to the chapter, while YSZ has been widely studied there remains a great challenge in relating the microstructure to the electrical properties. In particular there are problems in ascertaining whether or not various models correctly fit the experimental sample data well enough for these models to be confidently used for predicting the properties of new samples.

To try and understand the properties of the ceramics, as well as to establish whether or not the Maxwell-Wagner model, BLM and SEPPE are able to consistently fit the data, a number of conditions were imposed in the fitting of the data and these will be described starting below. As discussed in the introduction to the thesis, the emphasis here is on obtaining *consistent* fitting to a series of data. Individual best fit parameter values, such as a grain boundary conductivity of $10^{-6} (\Omega m)^{-1}$, for example, are difficult to verify as being either correct or incorrect. In part this is due to the very large range of physically meaningful values that the conductivity can take, which stretch over several orders of magnitude.

In the current work, the properties of the grains were fitted to both the UDR and LLS models, as the work on the single crystals did not conclusively prove which of these two was the better model to use to fit the properties of the ceramic grains (Chapter 3). The best fitting results for the composite obtained using both the models were then compared and in the majority of cases (not presented here), the UDR model gave better results. Based on this work on the polycrystalline samples, the UDR model was then taken as the most appropriate model to use for fitting the properties of the grains and all results presented in this chapter have the grain properties fitted to the UDR model.

The composite sample data was fitted to a model that combined, in one

expression, the equation for the UDR model for the grains and the Maxwell-Wagner equation, BLM or SEPPE. The models obtained thus will be referred to as the UDR-MW model, UDR-BLM and UDR-SEPPE respectively. The data was fitted as described in Section 2.6.5.

With the exception of the results presented and discussed in Section 5.2.9, the properties of the less conducting (grain boundary) component were assumed to be dispersionless, an assumption which appears to work well for many samples.

In the fitting, the primary search region for values of the conductor volume fraction (ϕ) was the range corresponding to physical grain boundary thicknesses of between 0.5 and 6 nm as reported in the literature, from transmission electron microscopy (TEM) and high resolution TEM (HRTEM) studies of similar materials [Badwal and Drennan²⁵, Waser and Hagenbeck³⁶ and others]. However, solutions outside this range, which could indicate electrical grain boundary thicknesses greatly different from the physical thickness or inconsistencies in the models used to fit the data were also explored as part of the set of “alternative best fits,” (see Section 2.6.5). For the set of polycrystalline YSZ samples studied, none of the “alternative best fits” were found to be significantly better than the best solutions that satisfied the imposed parameter restrictions.

5.2.6 Fitting to the UDR-MW equation, the UDR-BLM and the UDR-SEPPE

The dielectric constant and conductivity from the best fit to the experimental data for the sample 8YSZ-D1 obtained using the UDR-MW equation and the UDR-BLM are shown in Figure 5.35. The complex impedance plane representations of the experimental data and the calculated values are shown in Figure 5.36. Both the models appear to fit the data well at this volume fraction ($\phi \approx 0.999$). As already mentioned and demonstrated in Chapter 4, the Maxwell-Wagner model and the BLM produce essentially the same results

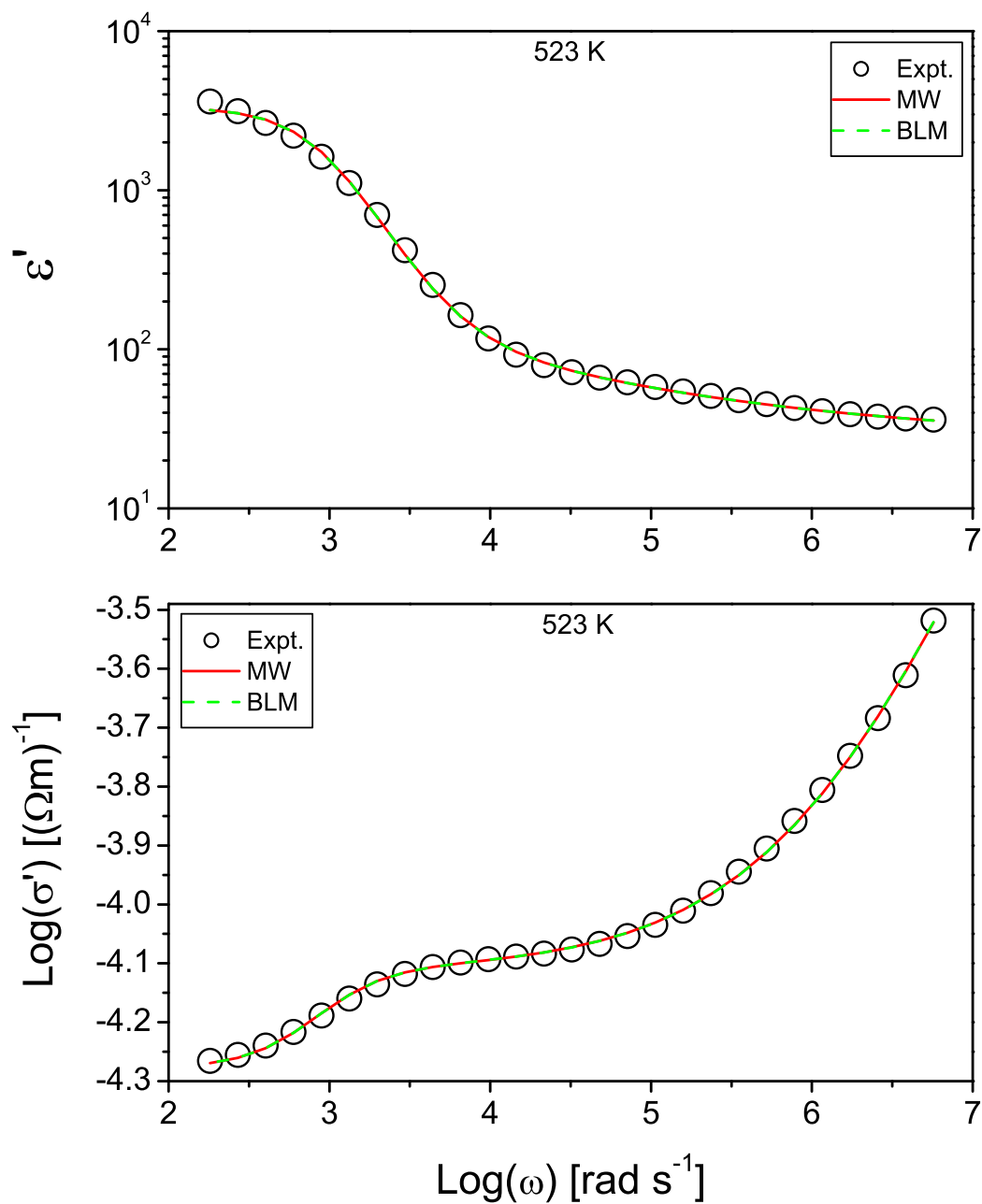


Figure 5.35: The frequency dependence of the dielectric constant and the conductivity of 8YSZ-D1 at 250 °C fitted to the UDR-MW equation and the UDR-BLM. The best fitting parameters are given in Figure 5.36.

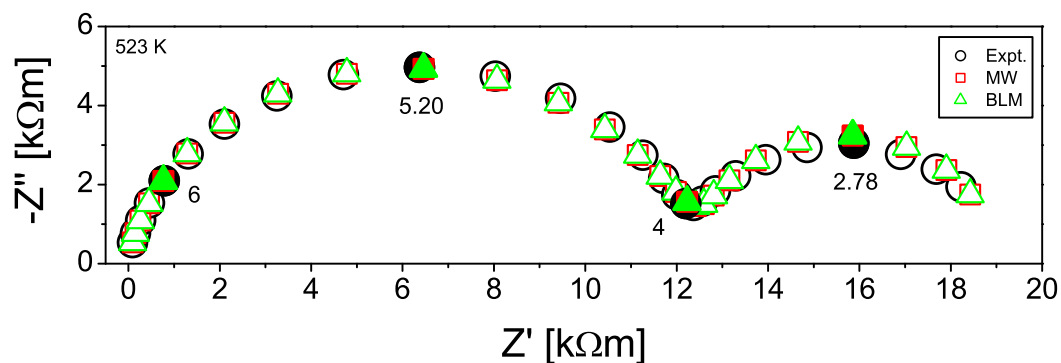


Figure 5.36: Complex impedance plane plot of data for the sample 8YSZ-D1 at 250 °C fitted to the UDR-MW and the UDR-BLM models. The best fit parameters, for both the models, are $A = 6.3 \pm 0.1 \times 10^{-9}$, $\sigma_{dc} = 7.81 \pm 0.01 \times 10^{-5} (\Omega m)^{-1}$, $s = 0.673 \pm 0.002$ and $\epsilon_{\infty} = 27.9 \pm 0.1$ for the dispersive properties of the more conducting component, which were fitted to the UDR model. For the less conducting component, whose properties were taken to be dispersionless, $\epsilon_{\ell} = 8 \pm 3$ and $\sigma_{\ell} = 4 \pm 1 \times 10^{-8} (\Omega m)^{-1}$. The conducting component volume fraction, $\phi = 0.9992 \pm 0.0004$, again for both models. Key values of $\log(\omega)$ are indicated.

at high values of ϕ such as for these samples. This is again confirmed in the fitting of this experimental data. The UDR-MW model and the UDR-BLM return the same value for the model selection criterion ($MSC \approx 40$), which again indicates that they fit the data equally well.

As already discussed in Chapter 4, the microstructures described by the SEPPE and those of the Maxwell-Wagner model and the BLM are quite different. It is therefore to be expected that for these samples with a core (grain) shell (grain boundary) microstructure, the Maxwell-Wagner model and the BLM fit the experimental data better than the SEPPE, which, for $\phi_c \approx 1$ represents the microstructures shown in Figures 1.18 and 1.19. It was therefore, generally more difficult to obtain a good fit to the data using the SEPPE. While the best fit values to the parameters of the UDR-MW model and UDR-BLM, could be reached from various starting values (giving some confidence that these were indeed the global best fitting solutions), all attempts at fitting using the UDR-SEPPE lead to local solutions, always close to the starting values and there was no convergence to what could be considered a global best fitting solution.

Since the Maxwell-Wagner and Brick Layer models give essentially the same results, only the fitting results obtained using the Maxwell-Wagner model will be presented and discussed in the remainder of this chapter.

5.2.7 Consistent fitting of data from the same sample, measured at different temperatures

One major assessment of how well a model really fits the properties of the sample can be made by investigating whether or not that model is able to consistently model a series of data, where there are some common properties. This also has implications on whether or not the model can be used to predict the properties of new samples, or the same sample under different conditions.

Data obtained at different temperatures, from the same sample, constitutes one series of data which the model must fit consistently. Some restrictions can be imposed on the best fitting parameter values and it is investigated whether or not “good” fits are obtained which satisfy the given restrictions.

In the current fitting, the following restrictions were imposed on the parameter values:

- The conducting component volume fraction, ϕ , must be the same at all temperatures, as it is not expected that these ceramic materials are undergoing any major structural or compositional changes at the temperatures of the measurements.
- The values of ϕ obtained must correspond to grain boundary thicknesses that are consistent with the range of values found in the literature. Alternative fits where this condition was somewhat relaxed were also investigated as there is still some uncertainty as to the extent of the *electrically active* region of the grain boundaries.
- Conductivities, including σ_{dc} in the UDR model used to model the properties of the more conducting component, are taken to have a positive

temperature dependence i.e. $\sigma_{T2} > \sigma_{T1}$ if $T2 > T1$, which is consistent with the results presented in temperature dependence studies in Chapter 3 as well as earlier in the current chapter.

- The temperature dependence of the dielectric constant of the less conducting component is unknown, as is the temperature dependence of the parameters A , s and ϵ_∞ in the UDR model, used for the properties of the more conducting component. Therefore, values for these parameters are calculated at each temperature.

In addition, for satisfactory fits, which are consistent at all temperatures, the following temperature dependence was also expected (and observed) for the best fit parameters:

- $\ln(\sigma T) \propto 1/T$ for both the conductivity of the more insulating component and the conductivity term in the UDR model for the more conducting component.
- $\ln(\omega_p) \propto 1/T$ for the peak frequencies calculated from the best fit conductivities and dielectric constants.

Figures 5.37 to 5.40 show the best fits to the UDR-MW model for the **sample 8YSZ-D1** at various temperatures. It can be seen in the figures that the model fits the data reasonably well at all temperatures. Of some concern though is the distribution of the residuals (shown in the inserts), which is not entirely random. This implies that there are some underlying fundamental differences between the models and the data. As already seen in Chapter 3, the UDR model does not always fit the data well at all temperatures and frequencies and this could be one cause of the differences between the experimental data and the composite properties calculated using the combined UDR-Maxwell Wagner model.

The value of the conducting component volume fraction, $\phi = 0.9991 \pm 0.002$ corresponds to a grain boundary thickness of $\sim 0.5 \text{ nm}$, for 8YSZ-D1

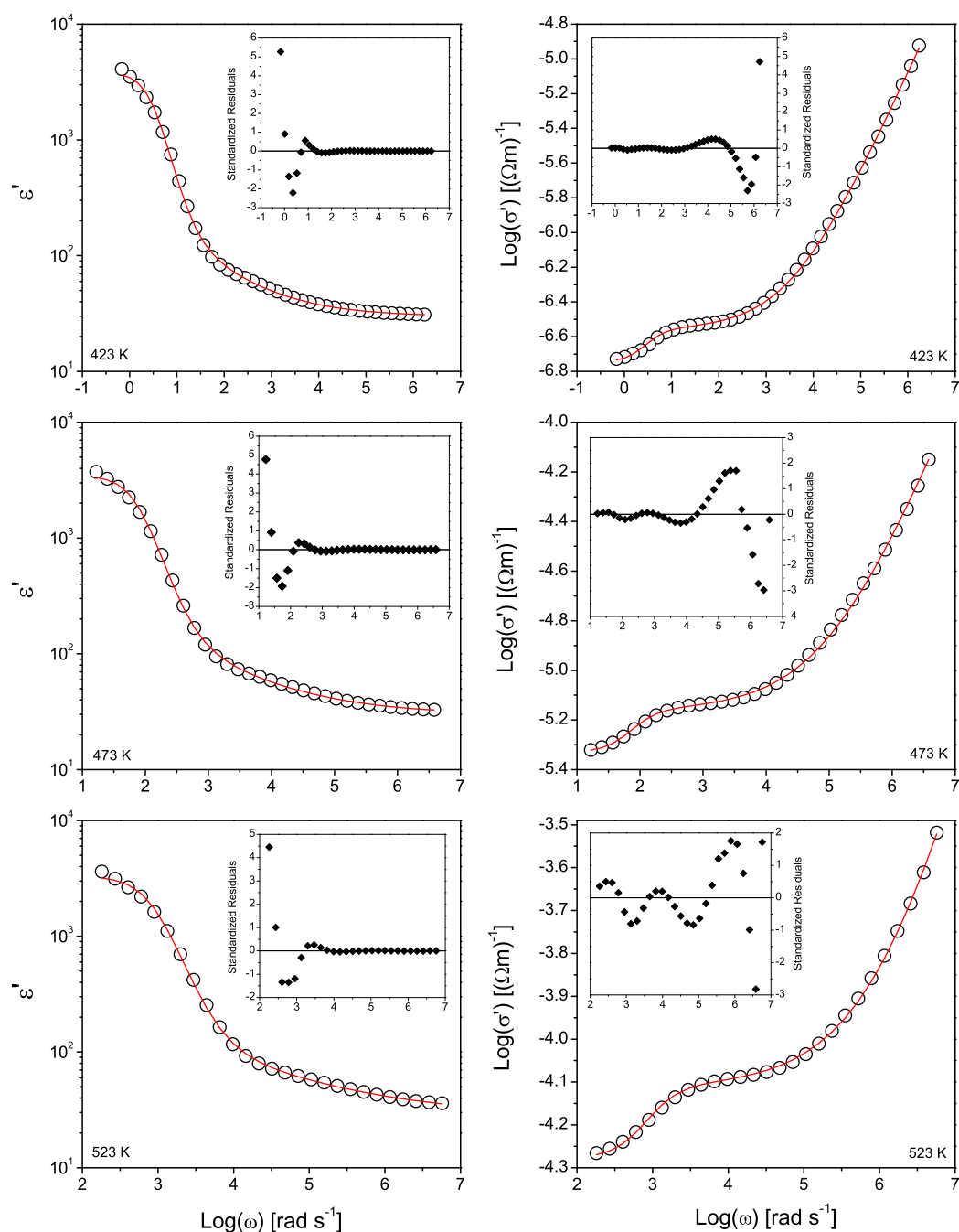


Figure 5.37: The frequency dependence of the real dielectric constant and the real conductivity of the sample 8YSZ-D1 ($\circ$) at 150, 200 and 250 $^{\circ}\text{C}$ and the best fits to the UDR-MW model (lines). All the data obtained in the temperature range 150 to 330 $^{\circ}\text{C}$ was fitted to a common volume fraction (ϕ) and the restriction $\sigma_{T2} > \sigma_{T1}$ if $T2 > T1$ was imposed on the conductivity parameters. The temperature dependence of the real dielectric constant and the parameters of the UDR model, s and A was taken to be unknown, at each temperature. For the best fit, $\phi = 0.9991 \pm 0.0020$. The rest of the best fitting parameter values are given in Figure 5.41.

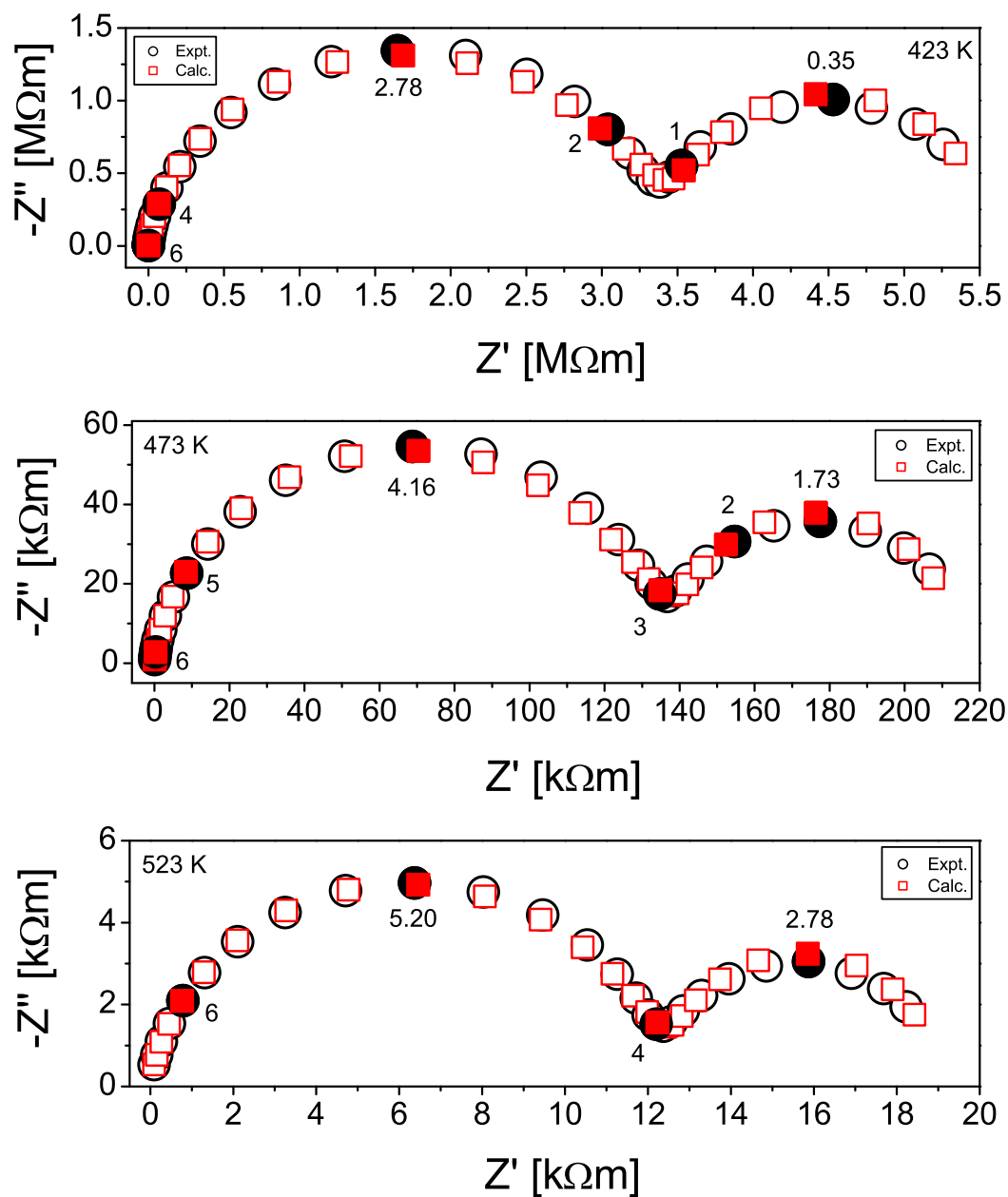


Figure 5.38: Complex impedance plane plots of the experimental data and the best fits to the UDR-MW model for the sample 8YSZ-D1 at 150, 200 and 250 °C. The best fits were obtained with common values for the volume fractions and values for the conductivities, consistent with a positive temperature dependence. For the best fit, $\phi = 0.9991 \pm 0.0020$. The rest of the best fitting parameter values are given in Figure 5.41. Key values of $\log(\omega)$ are indicated.

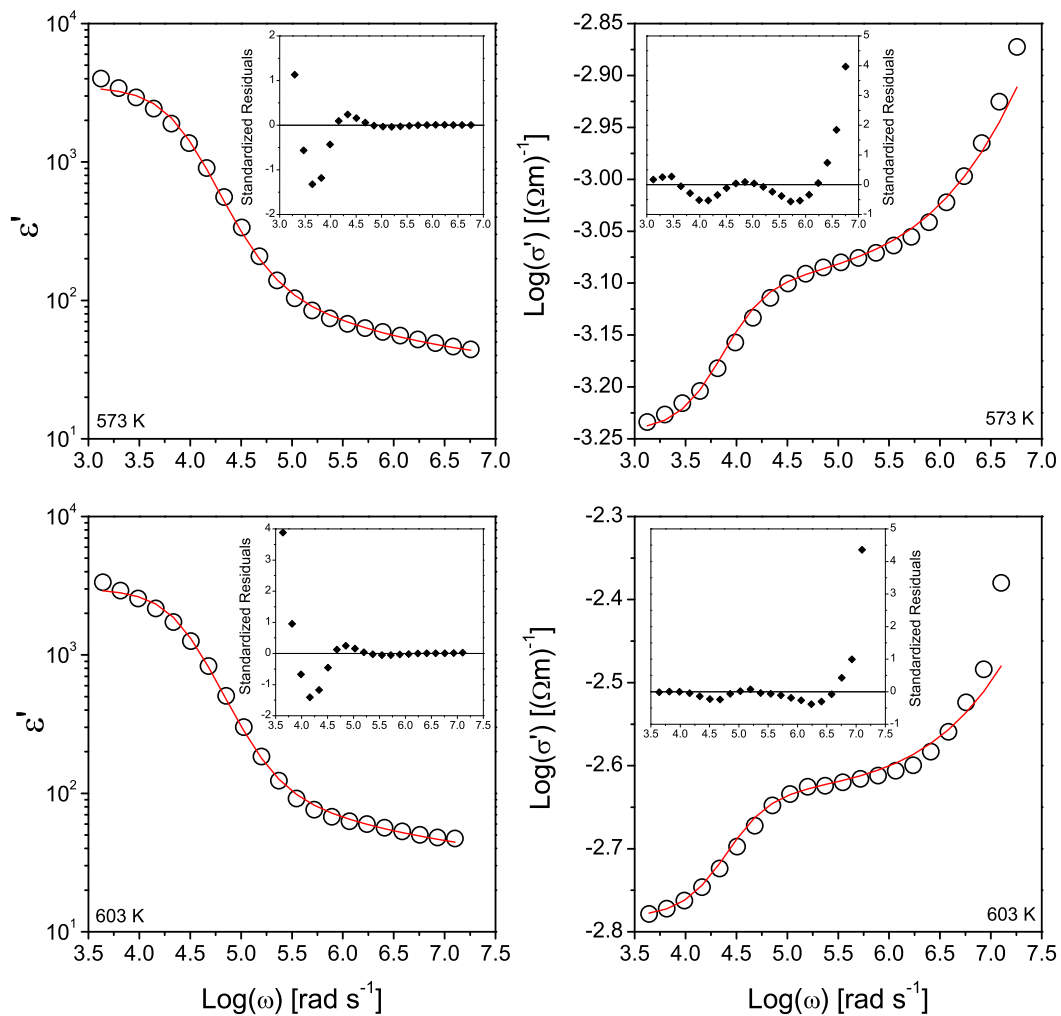


Figure 5.39: The frequency dependence of the real dielectric constants and the real conductivities of the sample 8YSZ-D1 ($\circ$) at 300 and 330 °C and the best fits to the UDR-MW model (lines). Details of the fitting are given in the text and in Figure 5.37. For the best fit, $\phi = 0.9991 \pm 0.0020$. The rest of the best fitting parameter values are given in Figure 5.41.

with an average grain size of $1.79 \mu\text{m}$. The estimate of 0.5 nm is obtained by assuming the shape of the grains is cubic. This thickness is at the extreme lower end of the values found in the literature. There is a strong correlation between the volume fraction and the dielectric constant parameters of the less conducting component such that similar fit statistics (equally good fits) are obtained for best fits with higher dielectric constants and lower conductor volume fractions and vice versa. This can be understood by considering that

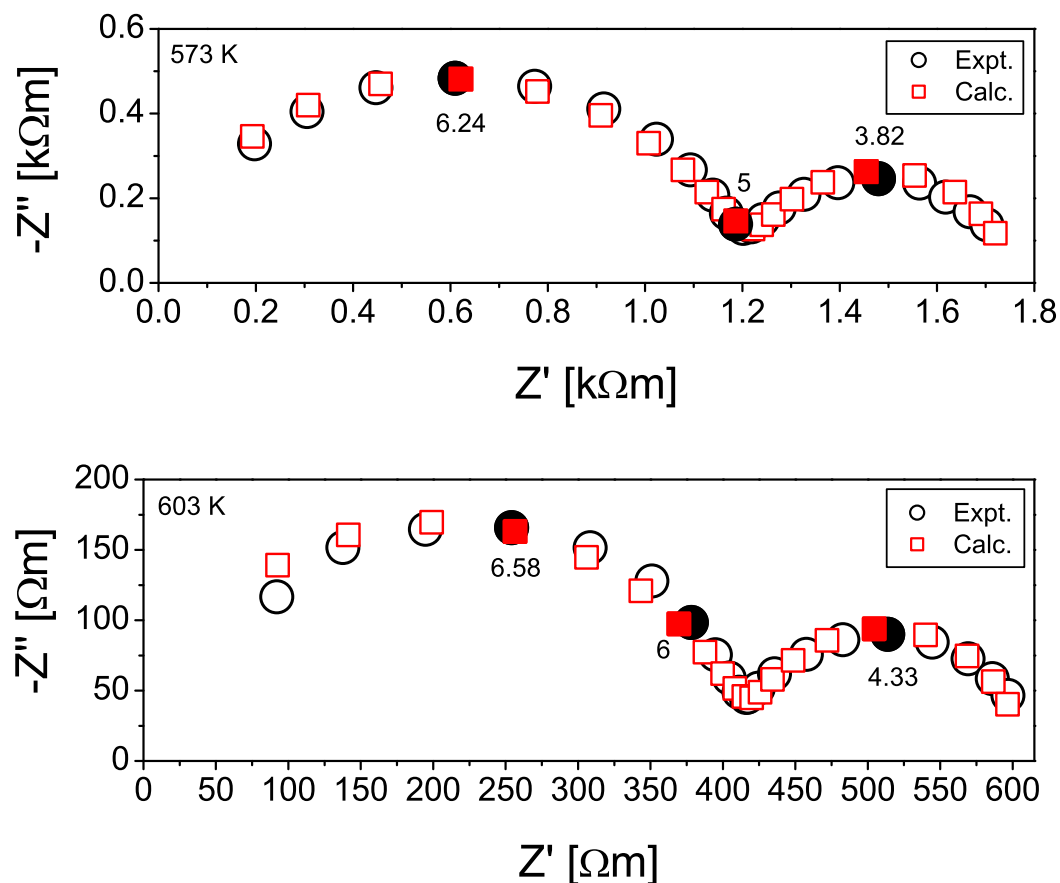


Figure 5.40: Complex impedance plane plots of the experimental data and the best fits to the UDR-MW model for the sample 8YSZ-D1 at 300 and 330 °C. The best fits were obtained with common values for the volume fractions and values for the conductivities, consistent with a positive temperature dependence. For the best fit, $\phi = 0.9991 \pm 0.0020$. The rest of the best fitting parameter values are given in Figure 5.41. Key values of $\log(\omega)$ are indicated.

the grain boundary capacitance is $C_{gb} = \epsilon_0 \epsilon_{gb} \frac{d_g}{\delta_{gb}}$, where ϵ_{gb} is the grain boundary dielectric constant, d_g the average grain size and δ_{gb} the grain boundary thickness. ϕ increases with increase in the ratio $\frac{d_g}{\delta_{gb}}$. Therefore, to fit a particular grain boundary capacitance, either ϵ_{gb} or $\frac{d_g}{\delta_{gb}}$, which is related to ϕ , can be adjusted. For a fixed capacitance C_{gb} , decreasing ϵ_{gb} can be compensated for by increasing $\frac{d_g}{\delta_{gb}}$ (or ϕ) while a large ϵ_{gb} is matched by a small $\frac{d_g}{\delta_{gb}}$ (or ϕ). Without more knowledge about the exact nature of the dielectric properties of the grain boundaries and their extent, it is difficult to pick the best combination of ϕ and ϵ_ℓ with high accuracy. The relatively large uncertainty in the value of ϕ is related to the correlation between ϕ and ϵ_ℓ .

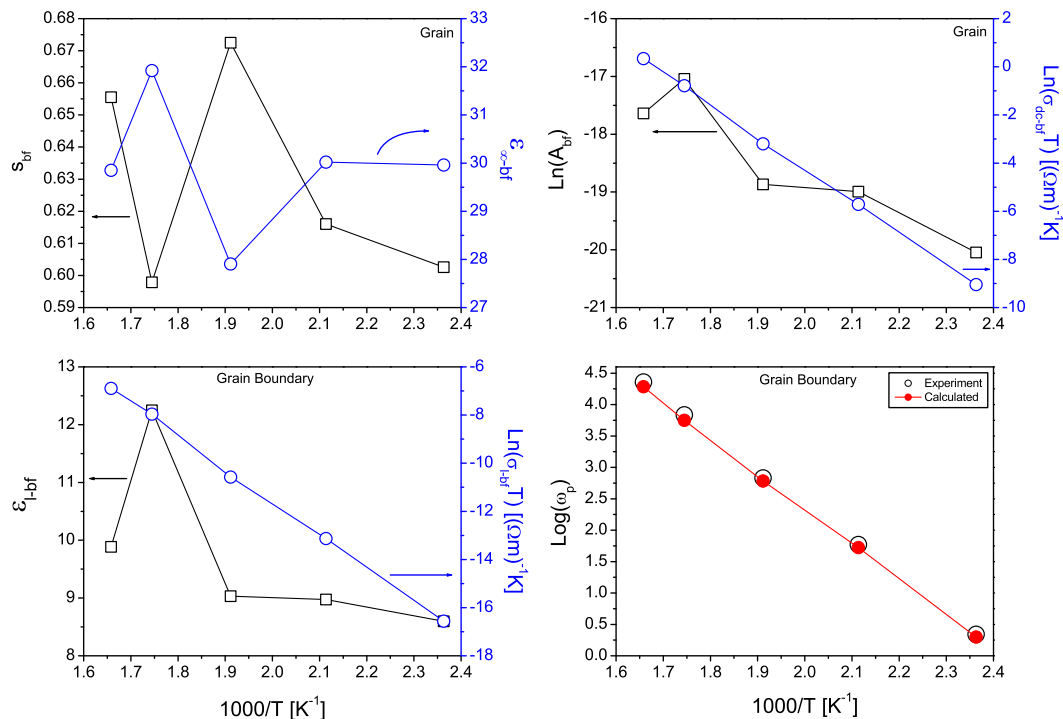


Figure 5.41: The best fit parameters to the UDR-MW model for the grain (top) and the grain boundary properties (bottom) for the sample 8YSZ-D1 at various temperatures. $\phi = 0.9991 \pm 0.0020$. The calculated and experimental characteristic frequencies for the conduction processes in the grain boundaries are shown in the bottom right hand figure.

Figure 5.41 shows the temperature dependence of the remainder of the parameters of the best fits to the experimental data. There is no clear trend in temperature dependence of the dielectric constants $\epsilon_{\infty-bf}$ for the grains, modeled using the UDR model, and ϵ_{l-bf} for the dispersionless grain boundaries, even though the values lie in a narrow range. There is also no clear trend in the value s and A for the UDR model. $\text{Ln}(\sigma_{0-bf}T)$ for the UDR model and $\text{ln}(\sigma_{l-bf}T)$ for the grain boundaries are found to be proportional to $1/T$ as expected, as is $\log(\omega_p)$ for the grain boundaries, indicating that the fitting results are consistent. Further, the characteristic frequencies calculated from the best fit parameters are found to be similar to the experimental values at all temperatures (bottom right of Figure 5.41).

Figures 5.42 to 5.44 show a consistent set of best fitting results obtained for the CSZ sample **8YSZ-T1** at different temperatures. Again the UDR-MW model appears to fit all the data well at all temperatures (some not

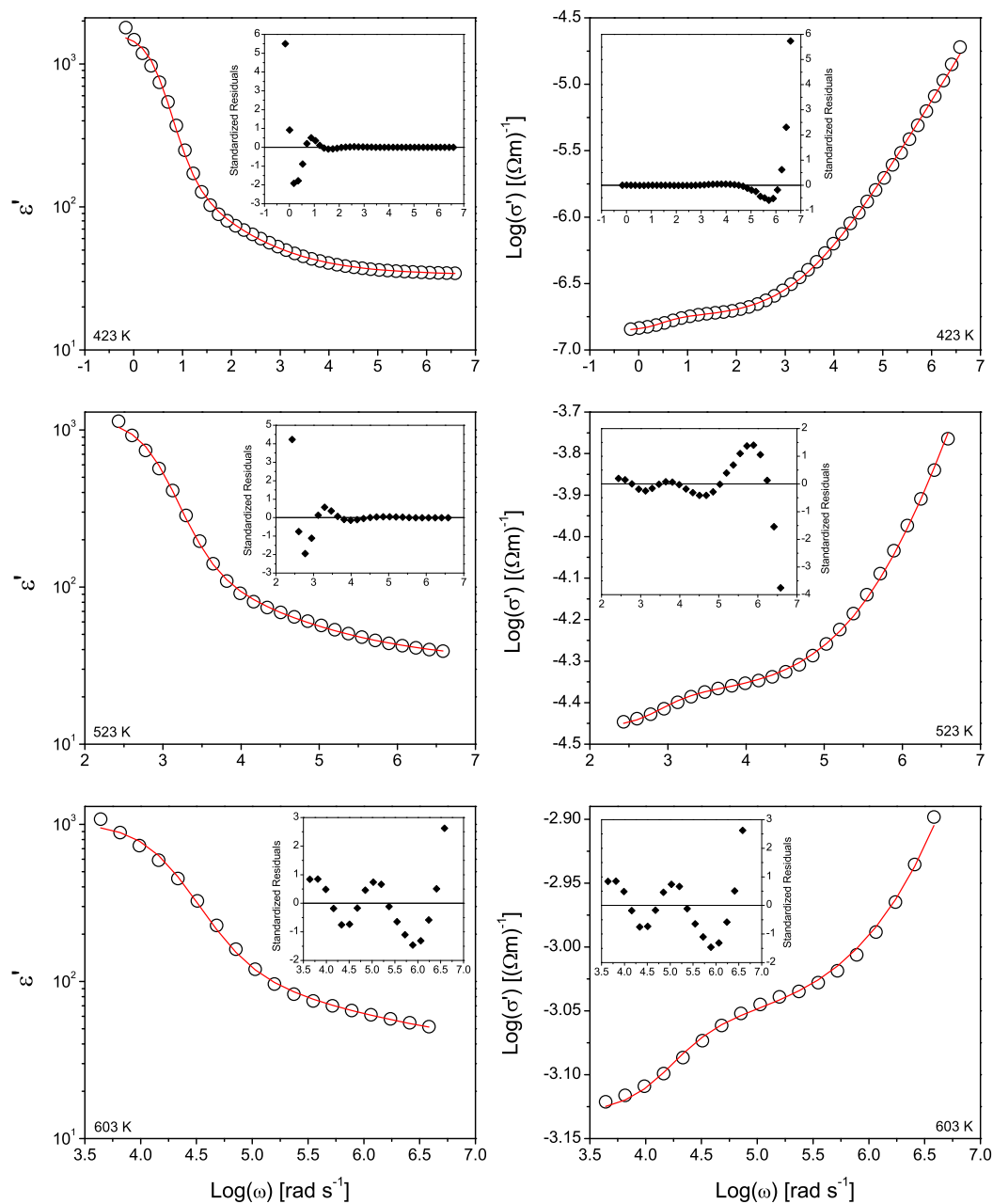


Figure 5.42: The frequency dependence of the real dielectric constants and the real conductivities of the sample 8YSZ-T1 (○) at 150, 250 and 330 °C and the best fits to the UDR-MW model (lines). All the data obtained in the temperature range 150 °C to 330 °C were fitted to a common volume fraction (ϕ) and the restriction $\sigma_{T2} > \sigma_{T1}$ if $T2 > T1$ was imposed on the conductivity. The temperature dependence of the real dielectric constant and the parameters of the UDR model, s and A was taken to be unknown. For the best fit, $\phi = 0.998 \pm 0.004$. The rest of the best fitting parameter values are given in Figure 5.44.

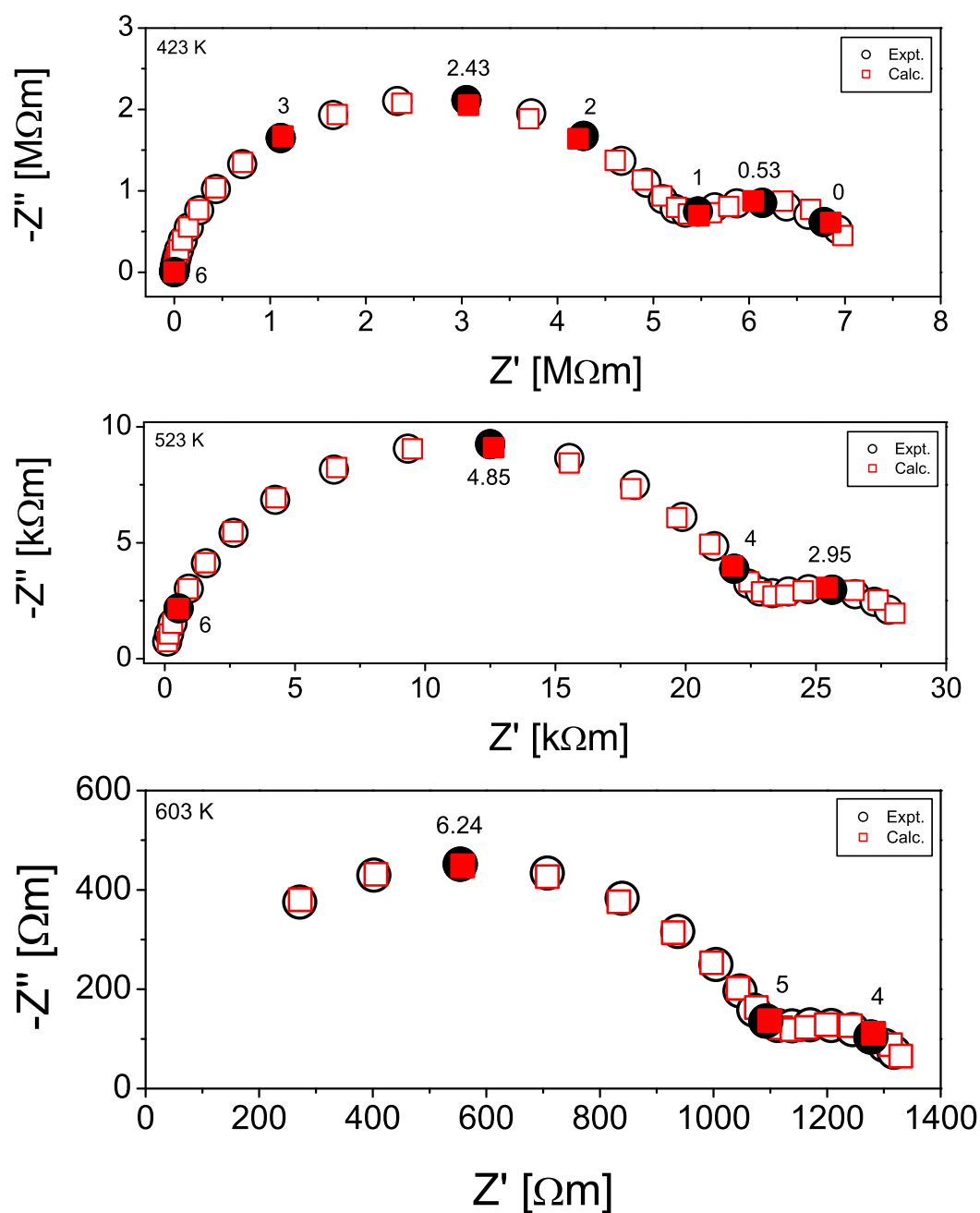


Figure 5.43: Complex impedance plane plots of the experimental data and the best fits to the UDR-MW model for the sample 8YSZ-T1 at 150, 250 and 330 °C. For the best fit, $\phi = 0.998 \pm 0.004$. The rest of the best fitting parameter values are given in Figure 5.44. Key values of $\log(\omega)$ are indicated.

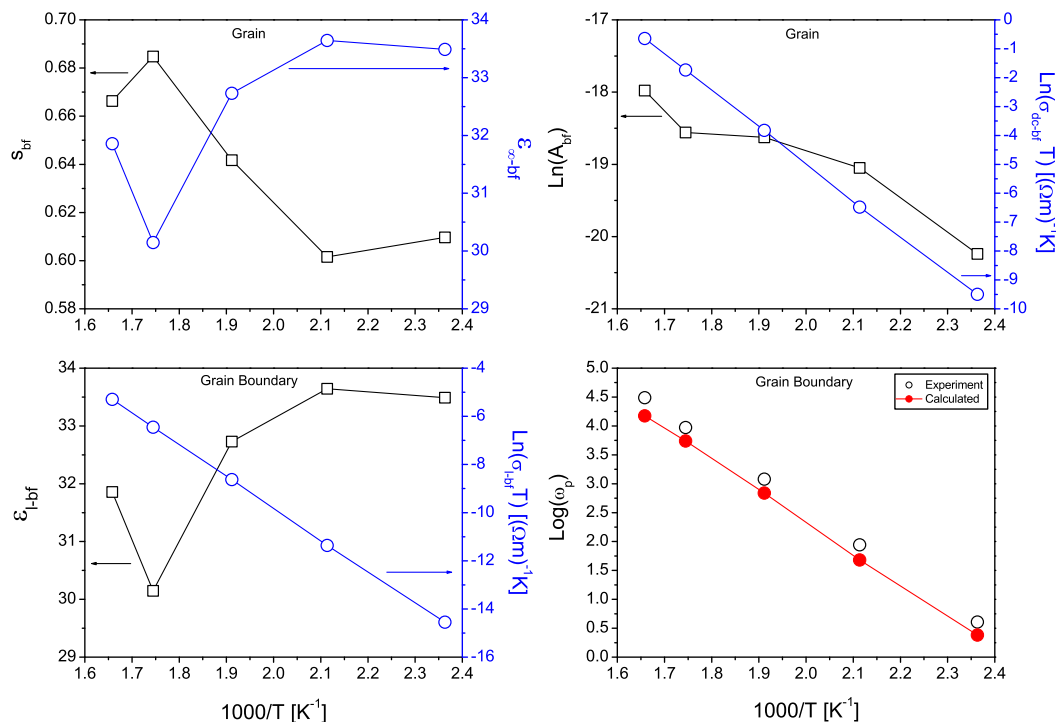


Figure 5.44: The best fit parameters to the UDR-MW model for the grain (top) and the grain boundary (bottom) properties for the sample 8YSZ-T1 at various temperatures. $\phi = 0.998 \pm 0.004$. The calculated and experimental characteristic frequencies for the conduction processes in the grain boundaries are shown in the bottom right hand figure.

shown in the figures). The best fit parameters are given in Figure 5.44. There are consistent temperature dependence for the conductivities and the characteristic frequencies. The other parameters all lie within a physically plausible range. For this sample, with an average grain size of $3.24 \mu\text{m}$, $\phi = 0.998 \pm 0.004$ corresponds to a grain boundary thickness in the region of 2 nm . Again note the relatively large uncertainty in the value of ϕ , which is related to the correlation between ϕ and ϵ_{ℓ} . The best fitting parameters for the properties of the grains (σ_{dc} , A , s and ϵ_{∞}) of the sample 8YSZ-T1 lie in the same range as those of 8YSZ-D1 (Figures 5.41 and 5.44). There are some notable differences in the best fit parameters for the grain boundaries and in particular ϵ_{ℓ} , which lies in the range $8.5 \leq \epsilon_{\ell} \leq 12.5$ for 8YSZ-D1 and $30 \leq \epsilon_{\ell} \leq 34$ for 8YSZ-T1. An explanation of these differences, requires more direct information on the structure of the *electrically active* region of the grain boundaries and a greater understanding of the correlation between

ϕ and ϵ_ℓ for the grain boundaries.

Figures 5.45 and 5.46 show some of the experimental and best fit curves obtained from fitting the data of the *sample with the largest grains, 8YSZ-D2*. Note the relatively large value of ϕ corresponding to a grain boundary thickness in the region of 0.5 nm. The rest of the parameters are plotted in Figure 5.47. The UDR-MW model appears to fit the data well, except at 300 °C, where an unlikely value of $\epsilon_\infty = 16$ is obtained. As seen in Chapter 3, this is primarily due to the UDR model not fitting the data very accurately at high temperatures.

From Figures 5.37 to 5.47, the UDR-MW model appears to fit the electrical properties of a number of samples consistently over the measured temperature range. The grain boundary thicknesses obtained from the best fitting values of ϕ generally lie at the extreme lower end of the values in the literature, though it must again be noted that ϕ and ϵ_ℓ are strongly correlated and therefore different values of ϕ are obtained for different values of ϵ_ℓ . The values of the rest of the parameters lie within a physically plausible range and the temperature dependence of the calculated conductivities and characteristic frequencies is as expected. This again indicates that the model fits the data consistently.

5.2.8 Fitting to the UDR-MW model with temperature independent dielectric constants

The results in the previous section and the similar activation energies for the conductivities and characteristic frequencies (Sections 3.2.3 and 5.2.4) suggest that both the high frequency dielectric constant in the UDR model (ϵ_∞) and the dielectric constant of the less conducting component (ϵ_ℓ) may be temperature independent or approximately so. This was further investigated by fitting the data for the sample 8YSZ-D1 with common values for both the dielectric constants at all the temperatures. Note that this means that there are now two less temperature dependent parameters. The experimental data

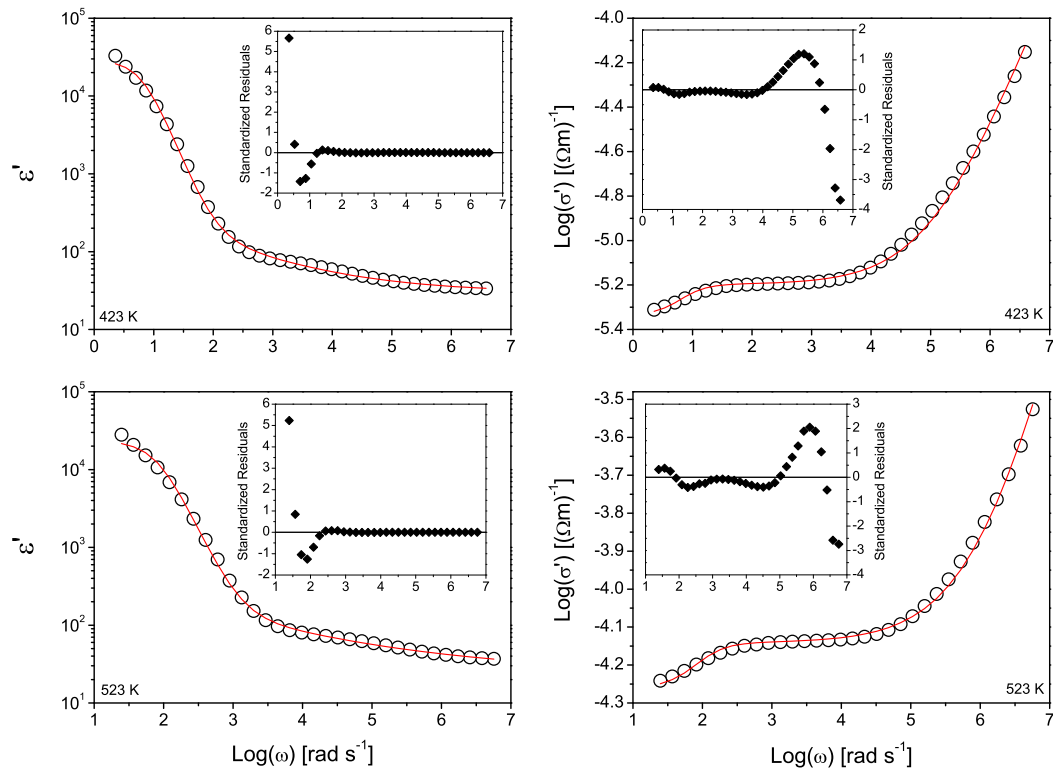


Figure 5.45: The frequency dependence of the real dielectric constants and the real conductivities of the sample 8YSZ-D2 ($\circ$) at 200 and 250 °C and the best fits to the UDR-MW model (lines). All the data obtained in the temperature range 150 to 330 °C was fitted to a common volume fraction (ϕ) and the restriction $\sigma_{T2} > \sigma_{T1}$ if $T2 > T1$ was imposed on the conductivity. The temperature dependence of the real dielectric constant and the parameters of the UDR model, s and A was taken to be unknown. For the best fits, $\phi = 0.99992 \pm 0.00040$. The rest of the best fitting parameter values are given in Figure 5.47.

and best fitting curves are shown in Figures 5.48 to 5.51. Up to 250 °C, the model and experimental values are in close agreement, Figures 5.48 and 5.49. However, above 250 °C (Figures 5.50 and 5.51), the model does not fit the experimental data very well. It can be seen in these figures that at 300 and 330 °C the calculated and experimental values are not the same. Note also the strong positive bias in the conductivity residuals at 300 °C (Figure 5.50, top right) suggesting some systematic differences between the model and the experimental results.

The best fit parameters obtained from fitting with restricted dielectric constants are shown in Figure 5.52. It can be seen in the figure that imposing

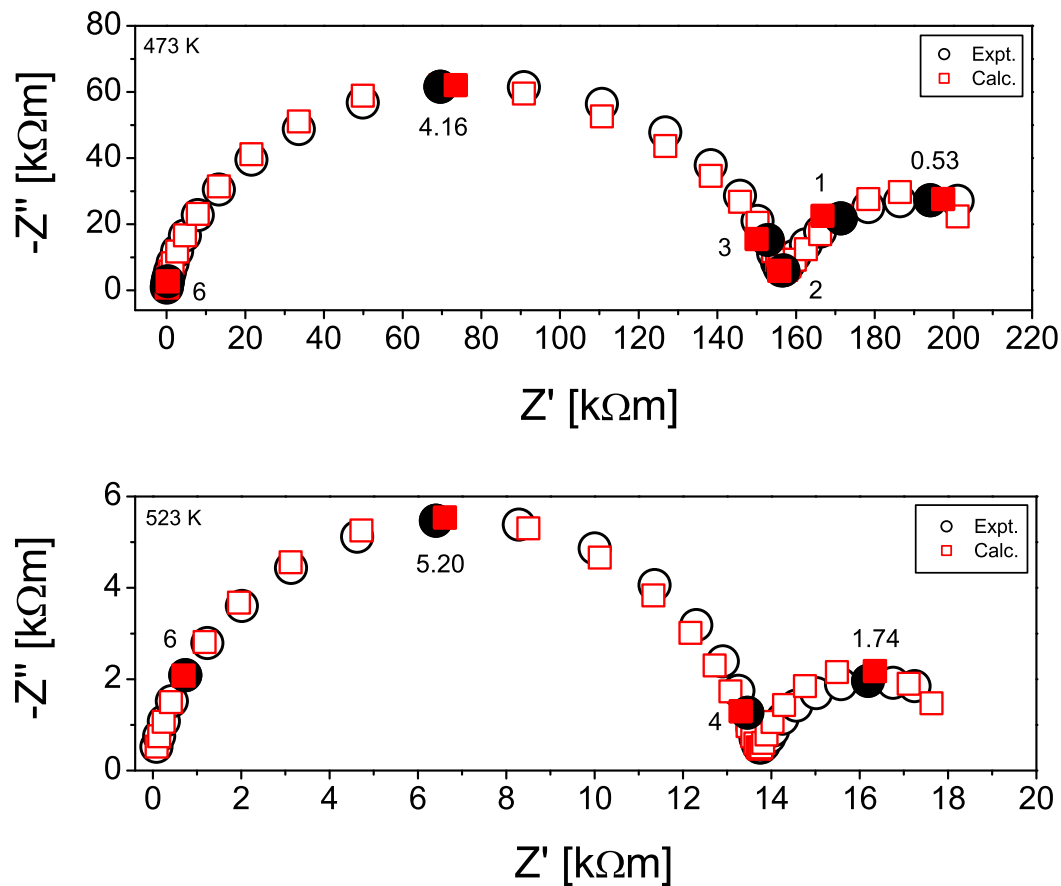


Figure 5.46: Complex impedance plane plots of the experimental data and the best fits to the UDR-MW model for the sample 8YSZ-D2 at 200 and 250 °C. For the best fit, $\phi = 0.99992 \pm 0.00040$. The rest of the best fitting parameter values are given in Figure 5.47.

the added restriction on the dielectric constants also has an effect on s and A which now exhibit a strictly monotonic trend.

Due to the inconsistent and poor high temperature results, fitting the data with temperature independent dielectric constants will not be explored any further.

5.2.9 Fitting to the Maxwell-Wagner model with dispersive grain and grain boundary conductivities

In all the fitting described thus far, it has been assumed that the properties of the less conducting component are dispersionless, and reasonably good fits to

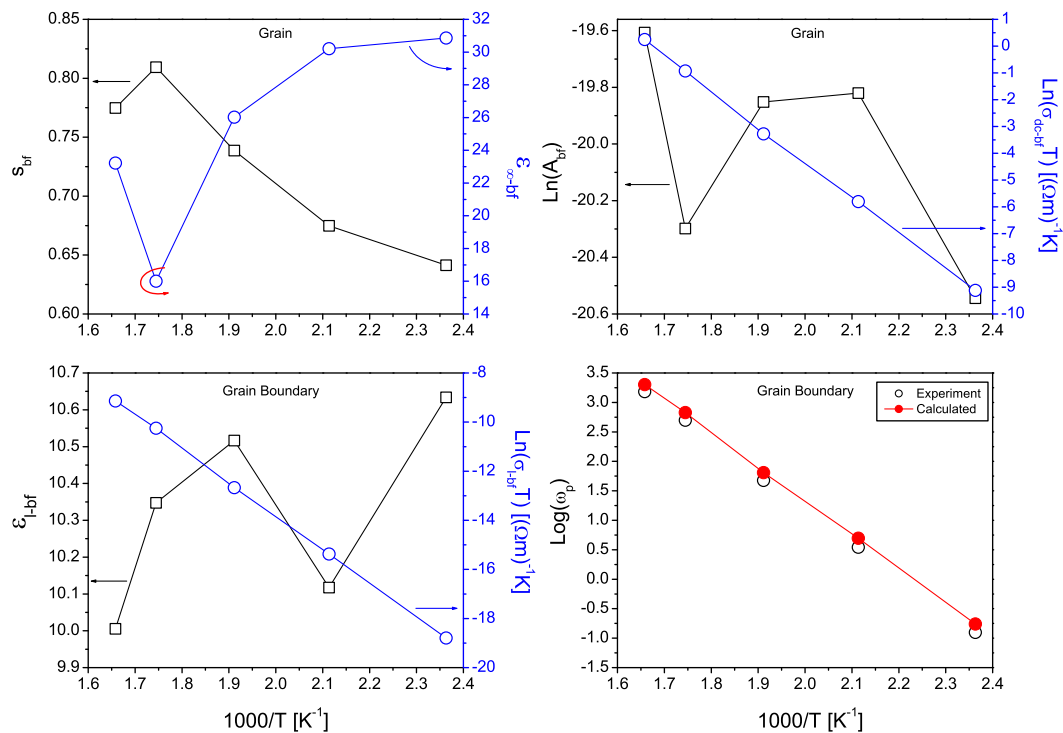


Figure 5.47: The best fit parameters to the UDR-MW model for the grain (top) and the grain boundary (bottom) properties for the sample 8YSZ-D2 at various temperatures. $\phi = 0.99992 \pm 0.00040$.

the experimental data have been obtained. However, in reality it is not likely to be so. This section explores fitting of the data with a dispersive function, the UDR model, for the properties of both the grains and the grain boundaries (with different parameter values). The parameters for the UDR model are obtained by directly fitting the composite data into what will be termed the “UDR-UDR-MW” expression. The data from samples containing silica as well as that of the 3YSZ samples showed the strongest discrepancies when fitted using a dispersionless expression for the grain boundary properties.

Figure 5.53 (top) shows that the data for the sample containing a low level of silica can be fitted reasonably accurately by assuming the grain boundary properties are dispersionless. This is confirmed in the complex impedance plane plot Figure 5.54 (top). For the sample with the highest silica content however the model with dispersionless grain boundary properties does not fit the data very well Figure 5.53 (middle) and Figure 5.54 (bottom).

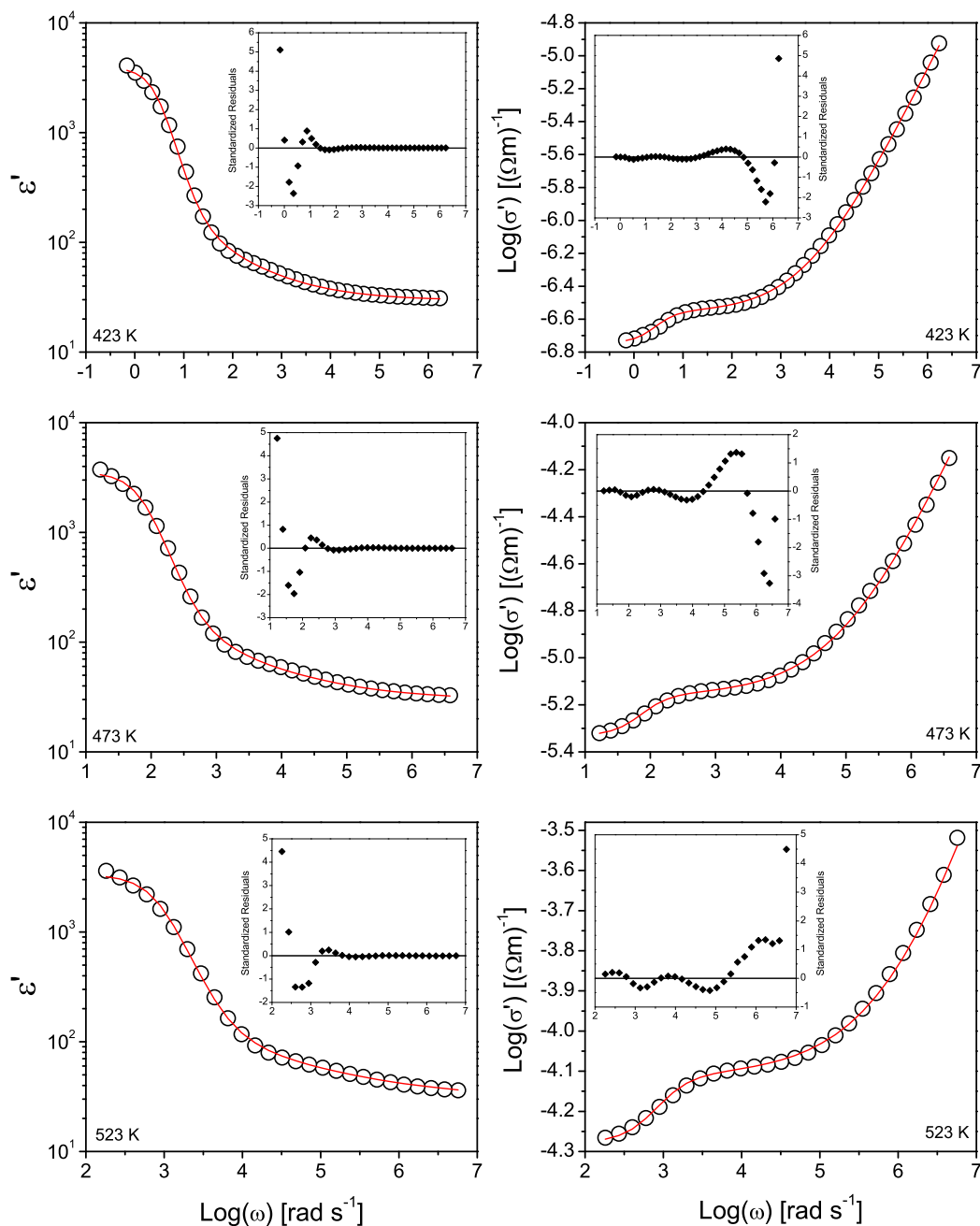


Figure 5.48: The frequency dependence of the real dielectric constants and the real conductivities of the sample 8YSZ-D1 (○) at 150, 200 and 250 °C and the best fits to the UDR-MW model with temperature independent dielectric constants. As previously done, the data for all samples in the temperature range 150 to 330 °C was fitted to a common volume fraction (ϕ) and the restriction $\sigma_{T2} > \sigma_{T1}$ if $T2 > T1$ was imposed on the conductivity parameters. In addition, the dielectric constants were kept the same for the different temperatures. The temperature dependence of the parameters of the UDR model, s and A was taken to be unknown. For the best fit, $\phi = 0.9983 \pm 0.0020$, $\epsilon_{\infty} = 29.6 \pm 0.6$ and $\epsilon_{\ell} = 17(\pm 60\%)$. The rest of the best fitting parameter values are given in Figure 5.52.

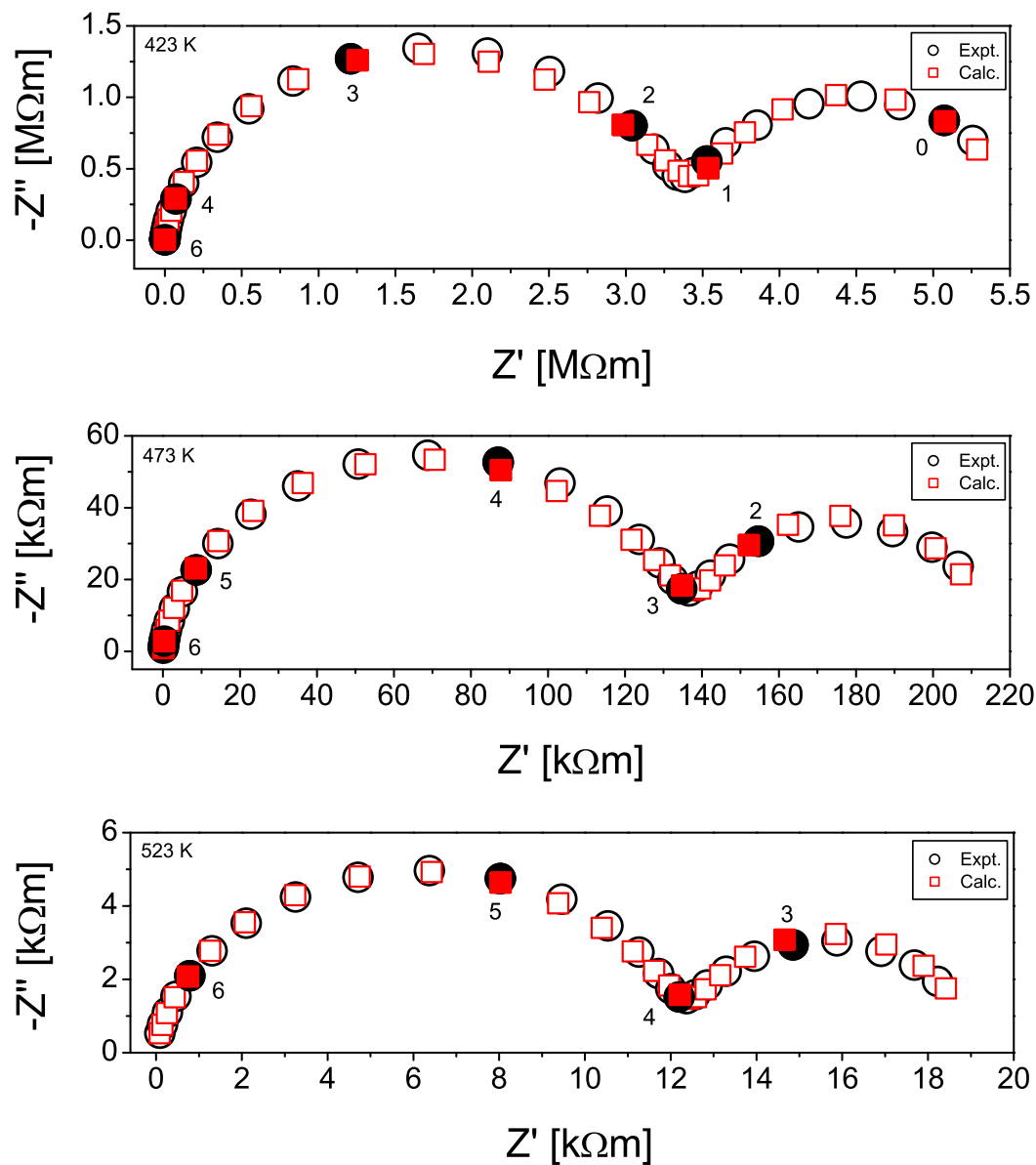


Figure 5.49: Complex impedance plane plots of the best fits to the UDR-MW model, with temperature independent dielectric constants for the sample 8YSZ-D1 at 150, 200 and 250 °C. For the best fit, $\phi = 0.9983 \pm 0.0020$, $\epsilon_{\infty} = 29.6 \pm 0.6$ and $\epsilon_{\ell} = 17(\pm 60\%)$. The rest of the best fitting parameter values are given in Figure 5.52. Key values of $\log(\omega)$ are indicated.

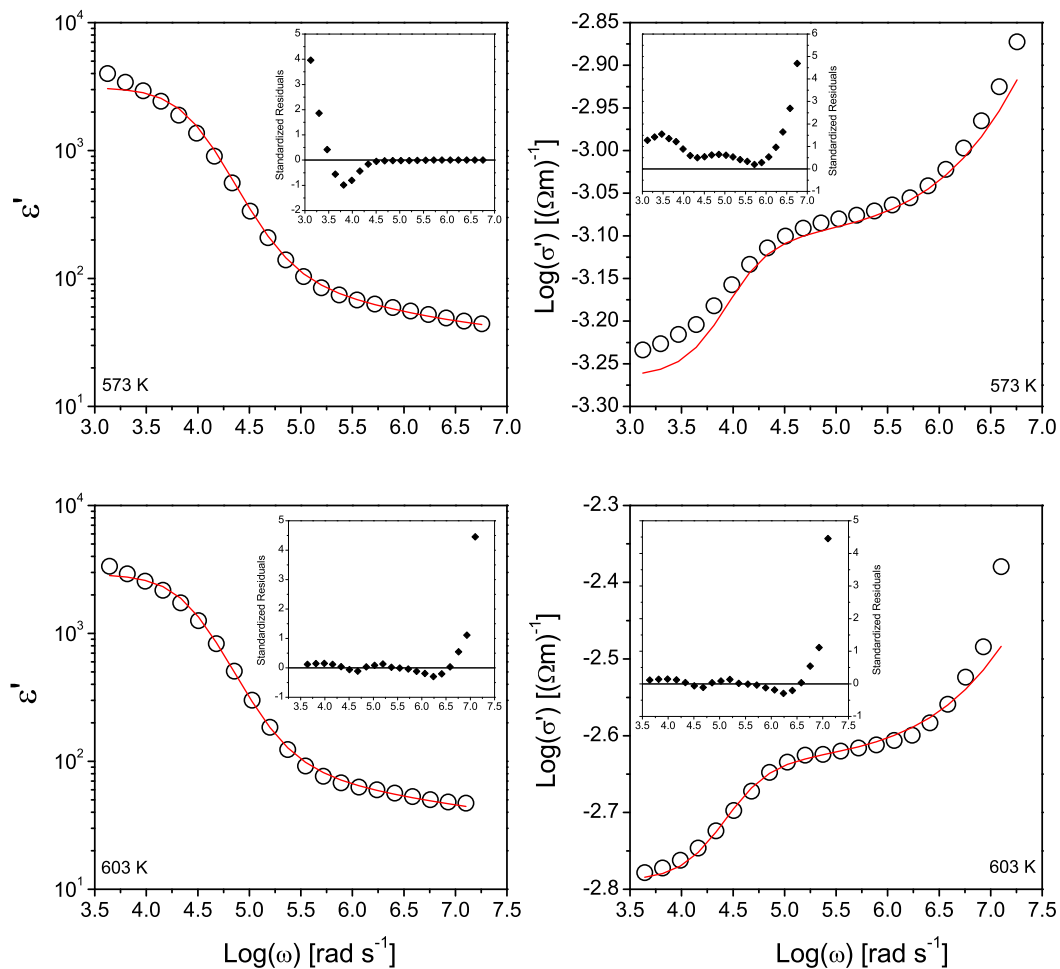


Figure 5.50: The frequency dependence of the real dielectric constants and the real conductivities of the sample 8YSZ-D1 ($\circ$) at 300 and 330 °C and the best fits to the UDR-MW model (lines), with temperature independent dielectric constants. For the best fit, $\phi = 0.9983 \pm 0.0020$, $\epsilon_{\infty} = 29.6 \pm 0.6$ and $\epsilon_{\ell} = 17(\pm 60\%)$. The rest of the best fitting parameter values are given in Figure 5.52.

At 23 volume % impurities, the assumption that the grain boundary properties are not dispersive clearly appears to be no longer valid. Fitting the data to the UDR-UDR-MW model produces better results Figure 5.53 (bottom) and Figure 5.54 (bottom).

For the sample 8YSZ-SiO₂-T1 (0.3 volume % silica), the best fit parameters to the UDR-MW model are:

$$\sigma_{dc} = 6.56 \times 10^{-5} (\Omega m)^{-1}, A = 8.47 \times 10^{-9}, s = 0.65, \epsilon_{\infty} = 27, \sigma_{\ell} = 3.55 \times 10^{-7} (\Omega m)^{-1}, \epsilon_{\ell} = 105, \phi = 0.985.$$

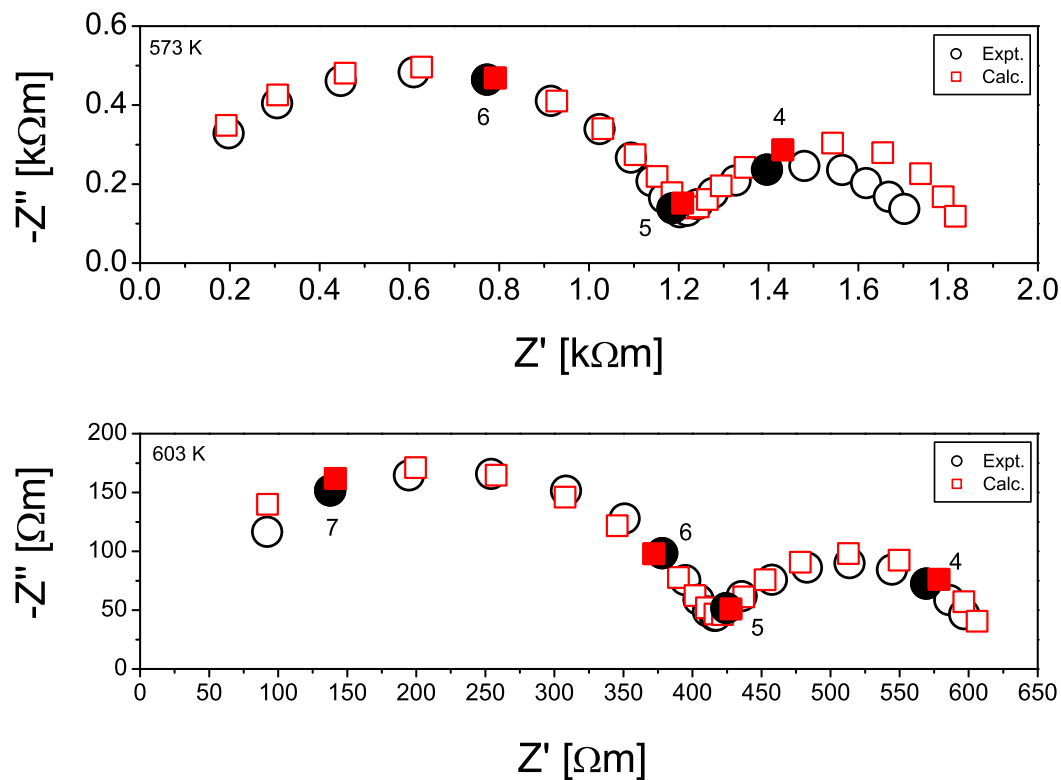


Figure 5.51: Complex impedance plane plots of the experimental data and the best fits to the UDR-MW model, with temperature independent dielectric constants for the sample 8YSZ-D1 at 300 and 330 °C. The conductivities were taken to have a positive temperature dependence. For the best fit, $\phi = 0.9983 \pm 0.0020$, $\epsilon_{\infty} = 29.6 \pm 0.6$ and $\epsilon_{\ell} = 17(\pm 60!)$. The rest of the best fitting parameter values are given in Figure 5.52. Key values of $\log(\omega)$ are indicated.

The parameters to the UDR-MW and the UDR-UDR-MW model for the sample 8YSZ-SiO₂-T5 (23 volume % silica) are:

UDR-MW: $\sigma_{dc} = 1.46 \times 10^{-5} (\Omega m)^{-1}$, $A = 4.44 \times 10^{-8}$, $s = 0.51$, $\epsilon_{\infty} = 2$, $\sigma_{\ell} = 4.33 \times 10^{-8} (\Omega m)^{-1}$, $\epsilon_{\ell} = 320$, $\phi = 0.918$. Note that the value for ϕ is inconsistent with a 23 volume % silica content. A very poor fit is obtained when ϕ is fixed at 0.77.

UDR-UDR-MW: $A_{gb} = 8.43 \times 10^{-9}$, $A_g = 3.42 \times 10^{-8}$, $\sigma_{dc-gb} = 1.07 \times 10^{-7} (\Omega m)^{-1}$, $\sigma_{dc-g} = 2.03 \times 10^{-5} (\Omega m)^{-1}$, $s_{gb} = 0.72$, $s_g = 0.41$, $\epsilon_{\infty-g} = 2.00$, $\epsilon_{\infty-gb} = 99$ and $\phi = 0.77$ (fixed).

An alternative best fit was obtained which is statistically better than that above and has the following values for the parameters: $A_{gb} = 1.63 \times 10^{-10}$,

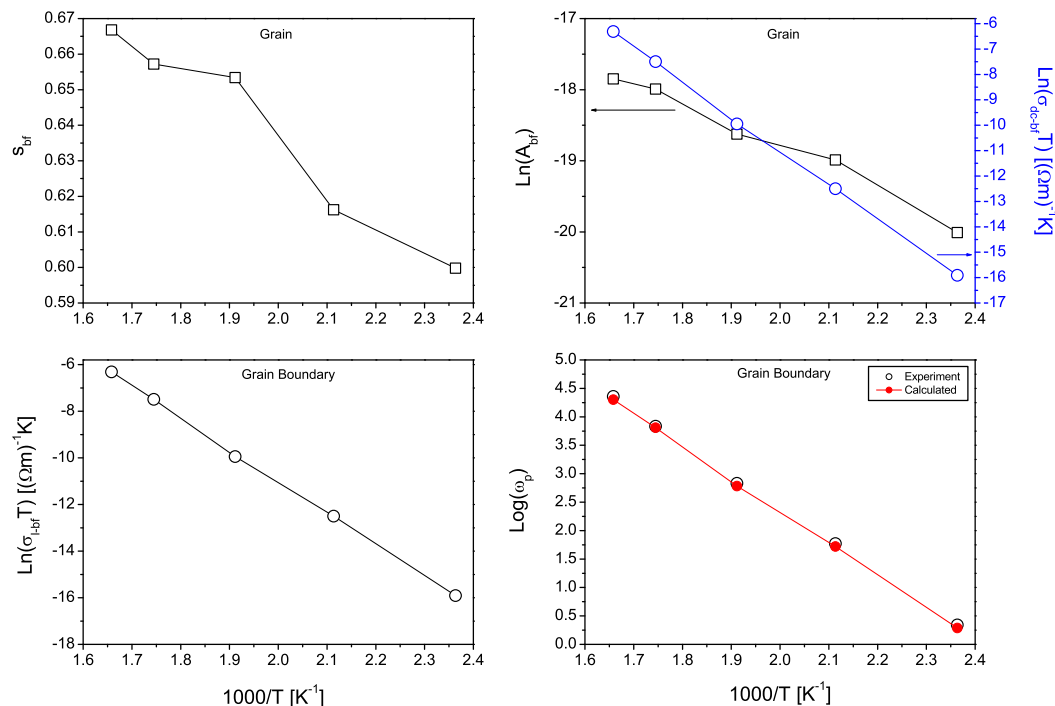


Figure 5.52: The best fitting parameters to the UDR-MW model, with temperature independent dielectric constants, for the grain (top) and the grain boundary (bottom) properties of the sample 8YSZ-D1 at various temperatures. For the best fit, $\phi = 0.9983 \pm 0.0020$, $\epsilon_{\infty} = 29.6 \pm 0.6$ and $\epsilon_{\ell} = 17(\pm 60!)$.

$A_g = 2.69 \times 10^{-8}$, $\sigma_{dc-gb} = 1.96 \times 10^{-9} (\Omega m)^{-1}$, $\sigma_{dc-g} = 1.68 \times 10^{-5} (\Omega m)^{-1}$, $s_{gb} = 0.68$, $s_g = 0.53$, $\epsilon_{\infty-gb} = 5.78$, $\epsilon_{\infty-g} = 20.59$ and $\phi = 0.995$. However note that $\phi = 0.995$ is inconsistent with the material having 23 volume % silica.

Fitting with dispersive grain boundary properties for the pure CSZ, samples with “clean” grain boundaries, did not significantly improve the results but took up an increased amount of computer processing time, due to the large number of parameters.

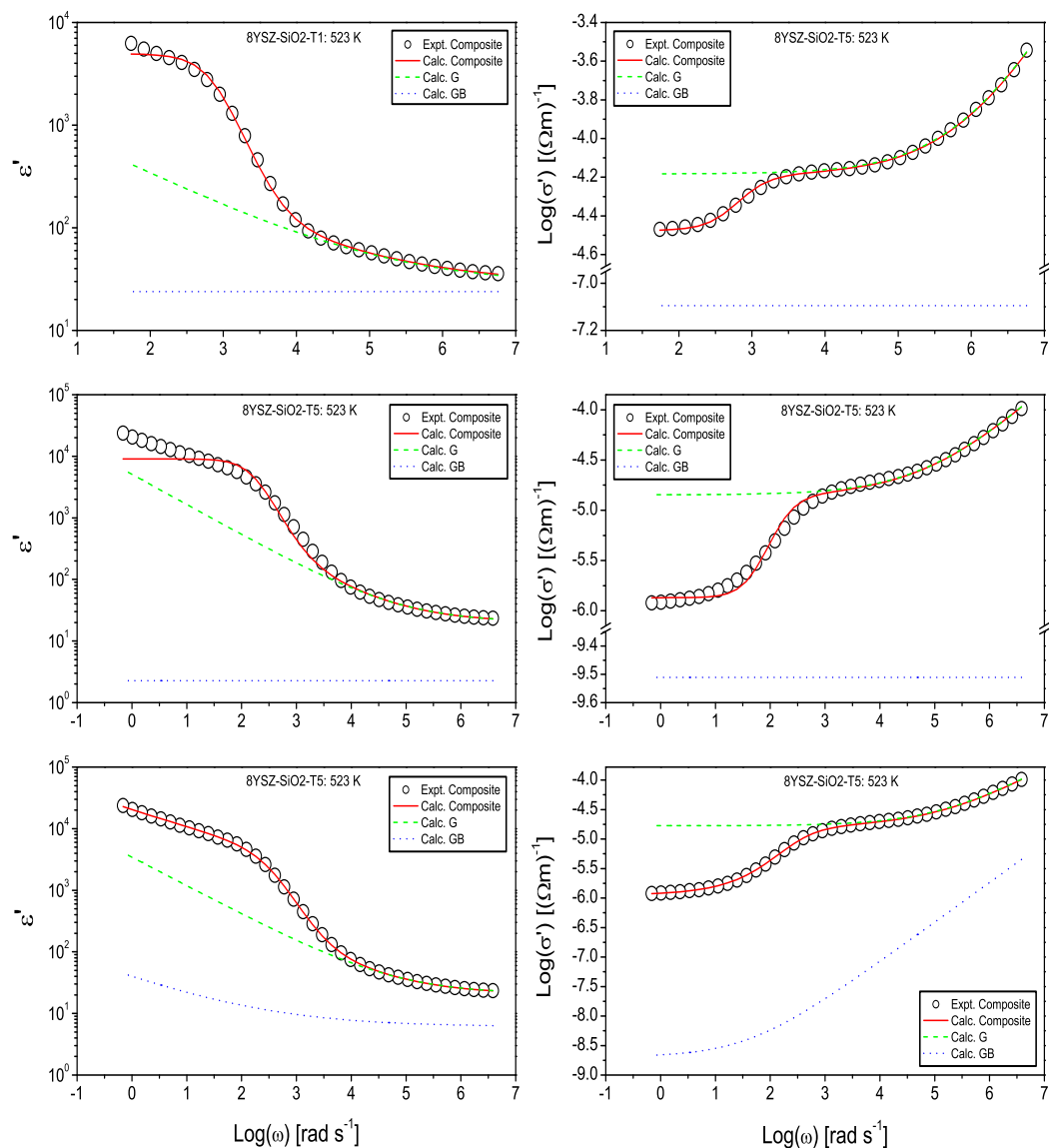


Figure 5.53: The dielectric constants (left) and conductivities (right) obtained from experiment and the best fitting curves to the Maxwell-Wagner model with dispersionless (top and middle) and dispersive (bottom) grain boundary properties for the experimental data of the samples 8YSZ-SiO₂-T1 (top) and 8YSZ-SiO₂-T5 (middle and bottom). The best fitting parameter values are given in the text.

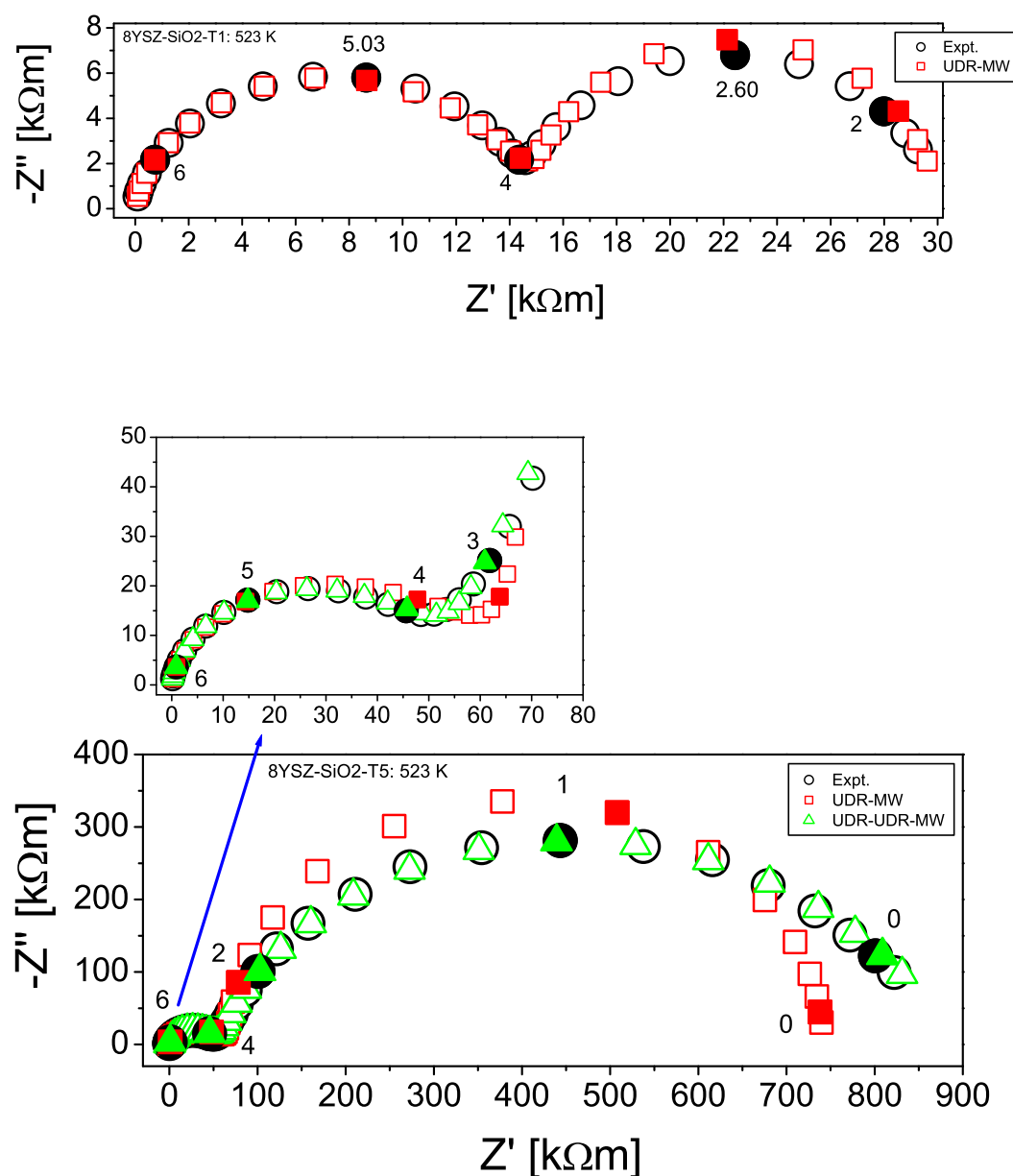


Figure 5.54: The complex impedance plane representation of experimental data and calculated values obtained from fitted to the Maxwell-Wagner model with dispersionless (UDR-MW) and dispersive (UDR-UDR-MW) grain boundary conductivities for the samples 8YSZ-SiO₂-T1 (top) and 8YSZ-SiO₂-T5 (bottom). The best fitting parameter values are given in the text. Key values of $\log(\omega)$ are indicated.

5.2.10 Fitting polycrystalline 3YSZ data with starting grain parameters obtained from fitting single crystal data

Ideally, when fitting composite data using the properties of the components, obtained separately from the composite fitting, these properties should be known in the entire frequency range where the composite (ceramic) properties are measured. However, electrode effects for example limit the frequency range where useful data on the component properties can be obtained. The UDR model was used to extrapolate 3YSZ single crystal data to low frequencies, dominated by electrode effects in the single crystal data, in the fitting of polycrystalline 3YSZ data. This extrapolation can only be done reasonably accurately at relatively low temperatures (100 and 150 °C, in this case, as the UDR model does not model the crystal data very well at higher temperatures (see Chapter 3)). The frequency range in which electrode effects are dominant also increases with increasing temperature thereby limiting the frequency range where accurate data for the single crystal properties can be obtained. Unlike for the cubic zirconia sample results presented earlier, where assuming that the properties of the grain boundaries were dispersionless gave good fitting results, for the polycrystalline TSZ samples the UDR model has to be used in order to obtain satisfactory results.

The experimental and calculated dielectric constants and conductivities for the TSZ sample 3YSZ-T2 at 100 and 150 °C are shown in Figure 5.55, while the complex impedance plane representation of the data is shown in Figure 5.56. The fitted dispersive properties of the grains and those of the grain boundaries are also plotted in Figure 5.55. The parameters for the best fit are given in the caption in Figure 5.55. It can be seen in the figures that the UDR-UDR-MW model, with single crystal best fit parameters as starting values, fits the data well.

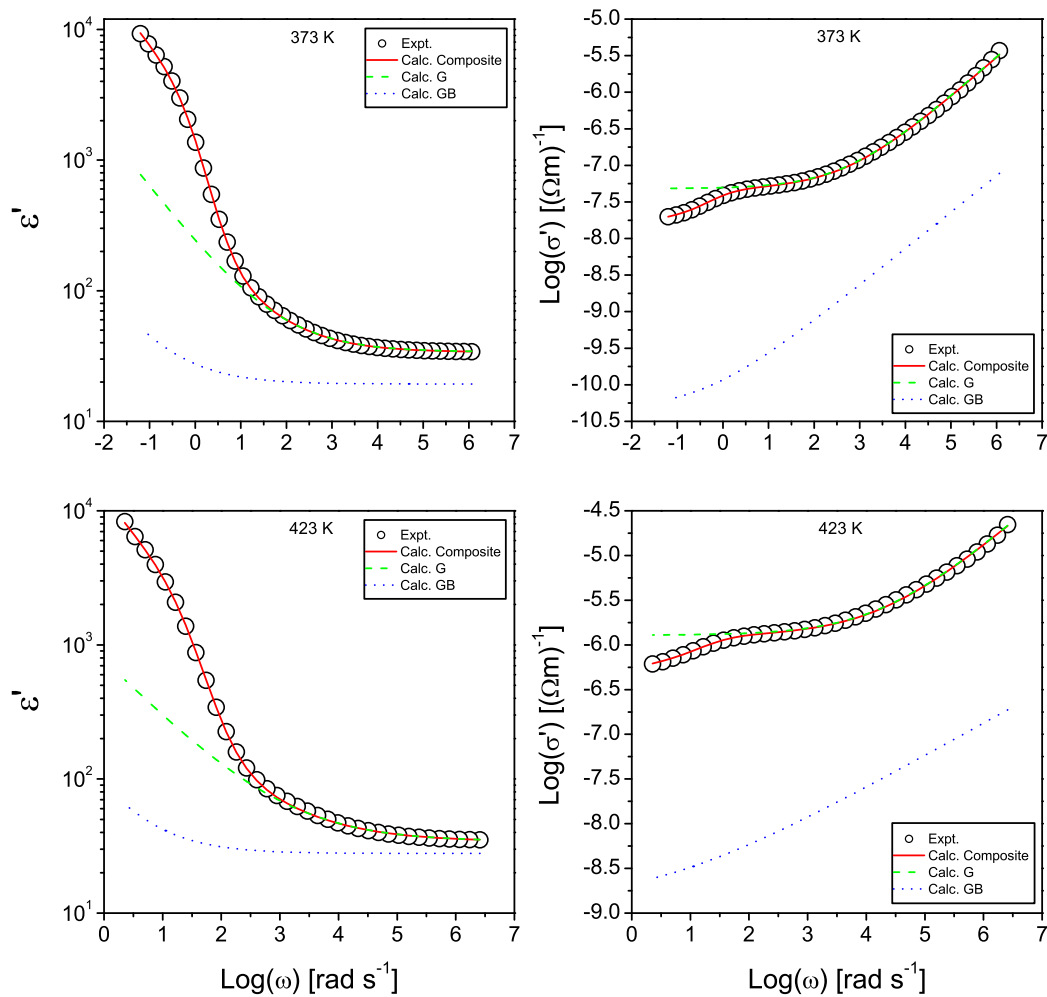


Figure 5.55: The experimental dielectric constant and conductivity, at 100 °C (top) and 150 °C (bottom) and results (Calc. Composite) obtained from fitting the data with the grain properties calculated from the parameters obtained from fitting single crystal data separately, as starting parameters. The dispersive properties of the grains and the grain boundaries, calculated from the best fit parameters, are also plotted. For the grains, the parameters in the UDR model needed to extrapolate to lower frequencies are $\sigma_{dc} = (5 \pm 2) \times 10^{-8} (\Omega m)^{-1}$, $A = (1.72 \pm 0.40) \times 10^{-9}$, $s = 0.54 \pm 0.02$, $\epsilon_{\infty} = 34 \pm 6$ at 100 °C and $\sigma_{dc} = 1.3 \pm 0.5 \times 10^{-6} (\Omega m)^{-1}$, $A = (5 \pm 1) \times 10^{-9}$, $s = 0.557 \pm 0.002$, $\epsilon_{\infty} = 34 \pm 6$ at 150 °C. The best fit parameters for the dispersive properties of the grain boundary obtained from using the UDR-UDR-MW model are $\sigma_{dc} = (4.7 \pm 0.3) \times 10^{-11} (\Omega m)^{-1}$, $A = (7.2 \pm 0.5) \times 10^{-11}$, $s = 0.5 \pm 0.2$, $\epsilon_{\infty} = 19 \pm 10$ at 100 °C and $\sigma_{dc} = (1.3 \pm 4) \times 10^{-9} (\Omega m)^{-1}$, $A = (5.5 \pm 0.2) \times 10^{-10}$, $s = 0.5 \pm 0.3$, $\epsilon_{\infty} = 22 \pm 10$ at 150 °C. The grain volume fraction, $\phi = 0.994 \pm 0.004$.

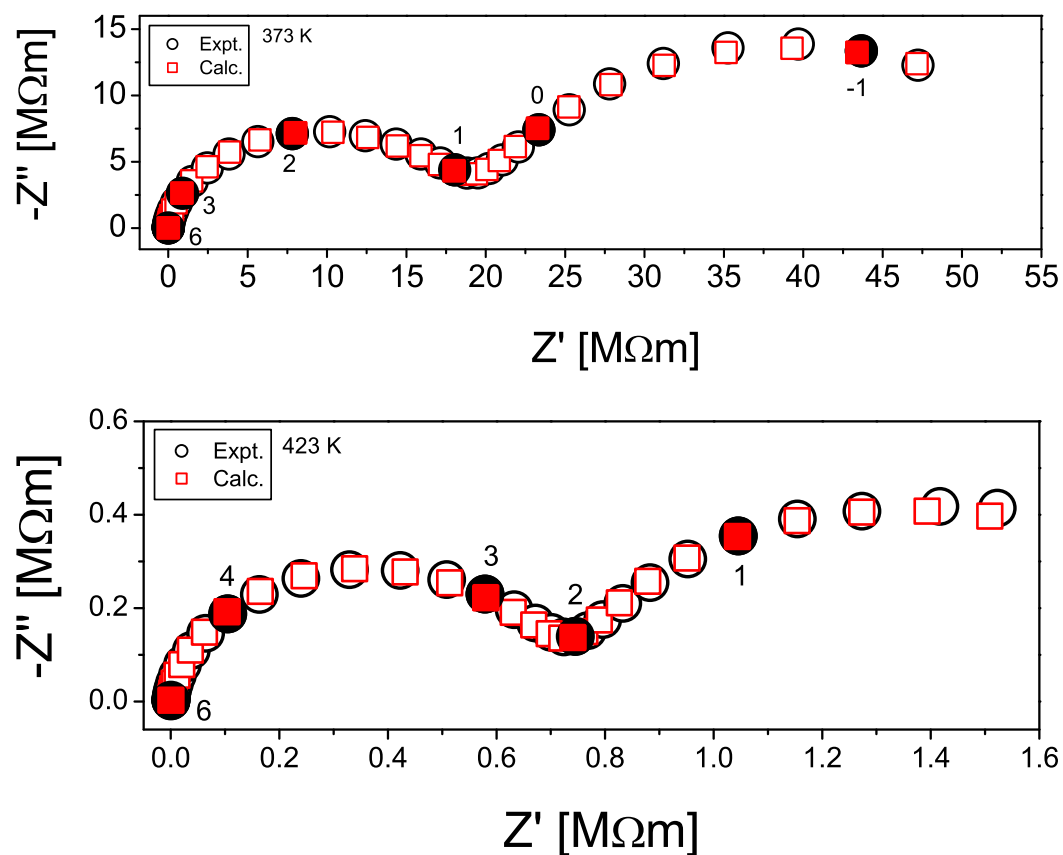


Figure 5.56: The complex impedance plane plot of the experimental data, for the sample 3YSZ-T2, and the best fitting results where the grain properties were calculated from the parameters obtained from separately fitting single crystal data. The best fitting parameters are given in Figure 5.55. Key values of $\log(\omega)$ are indicated.

5.3 Conclusions

In this chapter, the microstructure, composition and electrical properties of several polycrystalline YSZ samples have been described. The frequency dependence of the electrical properties of the samples confirm that the YSZ can be considered as a binary composite with the grains and grain boundaries as the two components. It was also observed that activation energies for the conduction processes (grain and grain boundary) in 8 mole % YSZ (cubic) are higher than those in the 3 mole % YSZ (tetragonal) samples. The temperature dependence of the characteristic frequencies and the conductivities of both the grains and the grain boundaries are best described by the ionic

conductivity mechanism. No model could be found to fit the dielectric constants which vary erratically. The frequency and temperature dependence of the properties of the grains of the polycrystalline sample were found to be similar with those of the single crystals of the same or similar composition (Chapter 3). The silica added to the samples as a deliberately introduced impurity was found to have little influence on the properties of the grains, except possibly at 23 volume %. However, at intermediate and high quantities, it had an observable effect on the properties of the grain boundaries. The results support the hypothesis that the silica mainly accumulates first at triple points and then at higher quantities the rest of the grain boundaries.

The following was observed for the UDR-MW model used to fit the experimental data. Similar conclusions apply to the UDR-BLM.

- The model appears to fit the data satisfactorily and consistently over a range of temperatures. However, the non-random distribution of fit residuals suggests that in reality the UDR-MW and UDR-UDR-MW models only approximately describes the yttria-stabilized zirconia properties.
- Some of the parameter values obtained from the best fits have a temperature dependence which is irregular making it impossible to accurately predict the properties of other composites, at all temperatures, using these models
- Forcing common values for the dielectric constants ϵ_{∞} and ϵ_{ℓ} imposes a monotonic temperature dependence on the values of (A and s) but appears to introduce systematic errors, in the fitting, seen by a positive bias in the residuals.
- In some, but not all cases, it is necessary to model the properties of the grain boundaries with a dispersive function in order to obtain satisfactory fitting results for the ceramic.

Chapter 6

Polyester-resin/Silicon Composites

6.1 Introduction

A number of polyester-resin/silicon composites were prepared as described in Section 2.2.3. The ac conductivity of these composites, which had varying volume fractions of silicon was then investigated. Of the composite systems investigated in the current work, the polyester-resin system was the only one where the composition could be directly controlled by the experimenter. The investigation of the electrical properties was mainly carried out at 150 °C, where both the silicon and polyester-resin conductivities were in a range where their properties could be resolved in impedance and/or modulus plots. At lower temperatures, the polyester-resin was very highly insulating, while higher temperatures caused permanent changes in the polyester-resin properties and ultimately led to the polyester-resin's decomposition. Samples of the pure polyester-resin were also prepared and their ac conductivity was measured, for use as fixed input when fitting the composite data.

The importance of using several different data representation formats and as many of the known electrical properties of the components as possible, to correctly identify the features in the impedance (and modulus) spectra of composites, will be highlighted.

6.2 Results and Discussion

6.2.1 Composition and Microstructure

Figure 6.1 shows optical micrographs of a polyester-resin/silicon composite containing 16 volume % silicon at two different magnifications. The specimens for microscopy were cut and polished as described in Section 2.2.3. It can be seen, in both micrographs, that the particles of silicon are randomly dispersed in the polyester-resin matrix. At 16 volume %, the silicon grains are quite far apart.

Figure 6.2 shows the regions immediately surrounding silicon grains, at higher magnification. The presence of the silicon particles causes some disruption of the polymer matrix.

Figure 6.3 shows micrographs of a composite sample containing 36 volume % silicon. Again the silicon is seen to be randomly dispersed within the polyester-resin matrix. At 36 volume %, the silicon particles, in 2-dimensions, are now much more closely packed, and there is a possibility of silicon-silicon contacts being formed in 3-dimensions.

A summary of the polyester-resin/silicon samples investigated in the current work, their silicon content (volume %) and the sample names that will be used to refer to them is given in Table 6.1.

6.2.2 Impedance data validation

As a first step to analyzing ac conductivity data, it must be proven to be valid and consistent as described in Section 2.6.1. Kramers-Kronig transforms are used here to verify the validity of the some of the experimental data, which will be presented and discussed in more detail later in this chapter. Figure 6.4 shows the experimental and calculated imaginary impedance ($-Z''$), for the pure polyester-resin (PS0) and for a sample containing 4.7 volume % silicon (PS5).

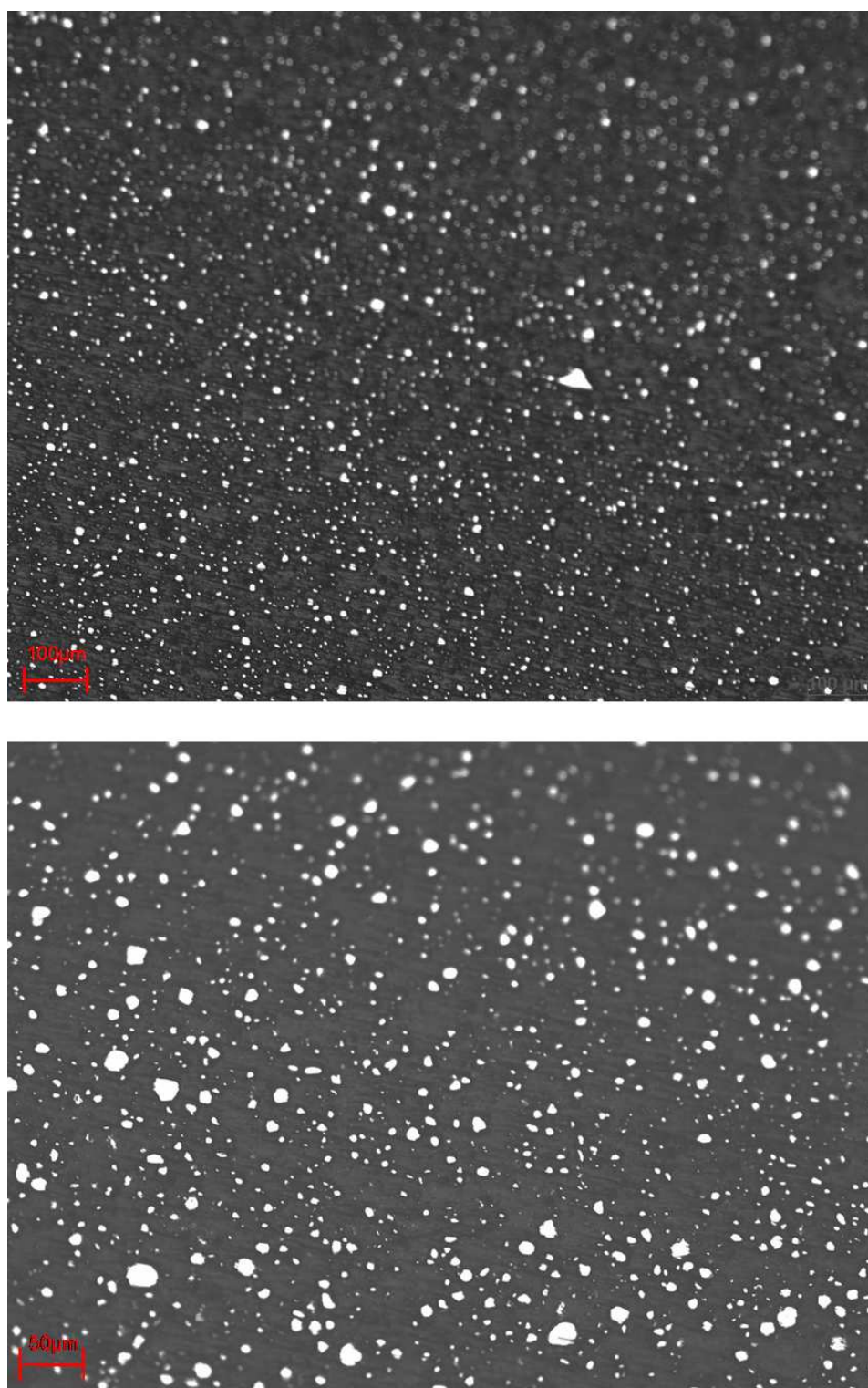


Figure 6.1: Optical micrographs of a polyester-resin/silicon composite containing 16 volume % silicon, at low magnification (top) and higher magnification (bottom). It can be seen in both the micrographs that the silicon particles are randomly distributed within the polymer matrix.

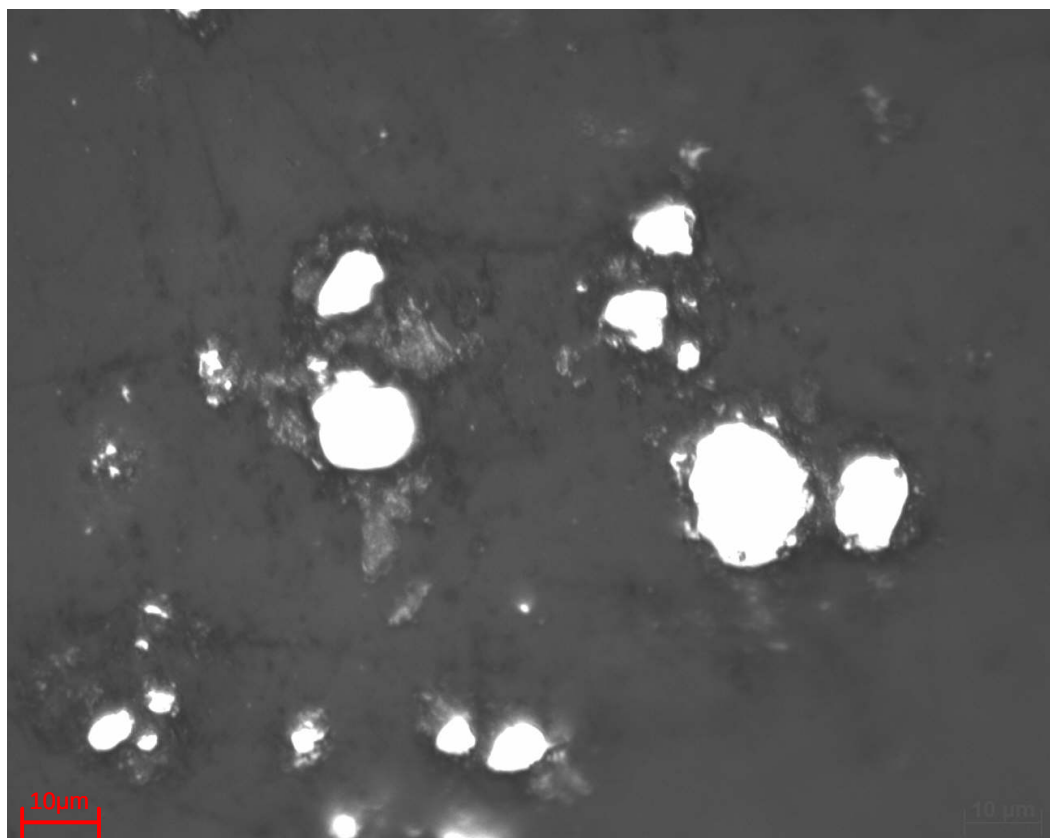


Figure 6.2: High magnification optical micrograph of a polyester-resin/silicon composite showing the region immediately surrounding silicon grains.

Table 6.1: The polyester-resin/silicon samples prepared.

Sample Name	Calculated silicon content (volume %)
PS0	0
PS4	4.1
PS5	4.7
PS8	9.3
PS12	12.1
PS16	16.3
PS20	20.7
PS24	25.5
PS28	29.9
PS32	34.0
PS36	35.7

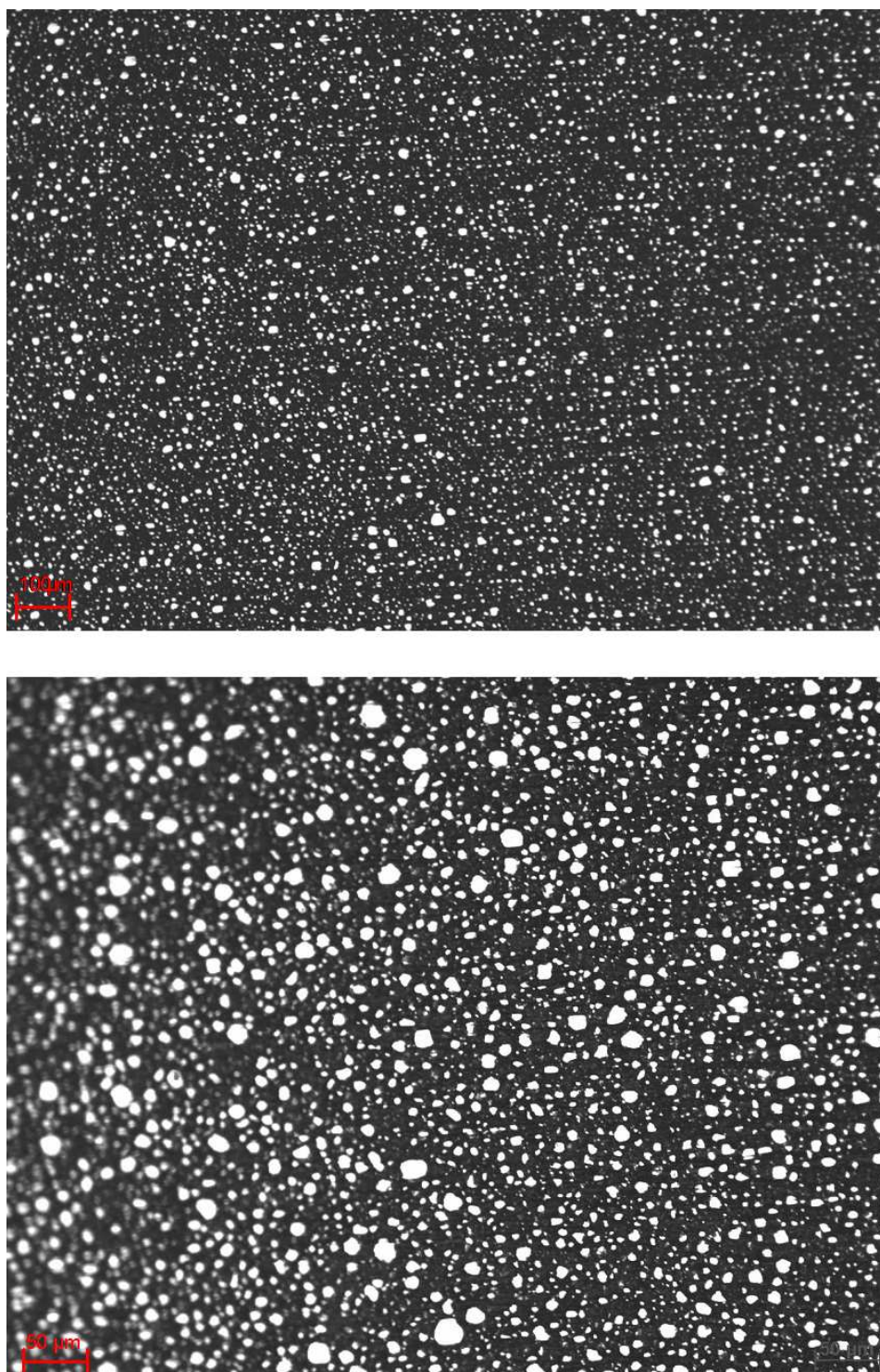


Figure 6.3: Optical micrographs of a 36% polyester-resin/silicon sample at low magnification (top) and at higher magnification (bottom). Again it can be seen that the silicon particles are randomly distributed within the polyester-resin matrix. At 36 volume % silicon, the particles are now much closer together than they were at 16 volume % silicon

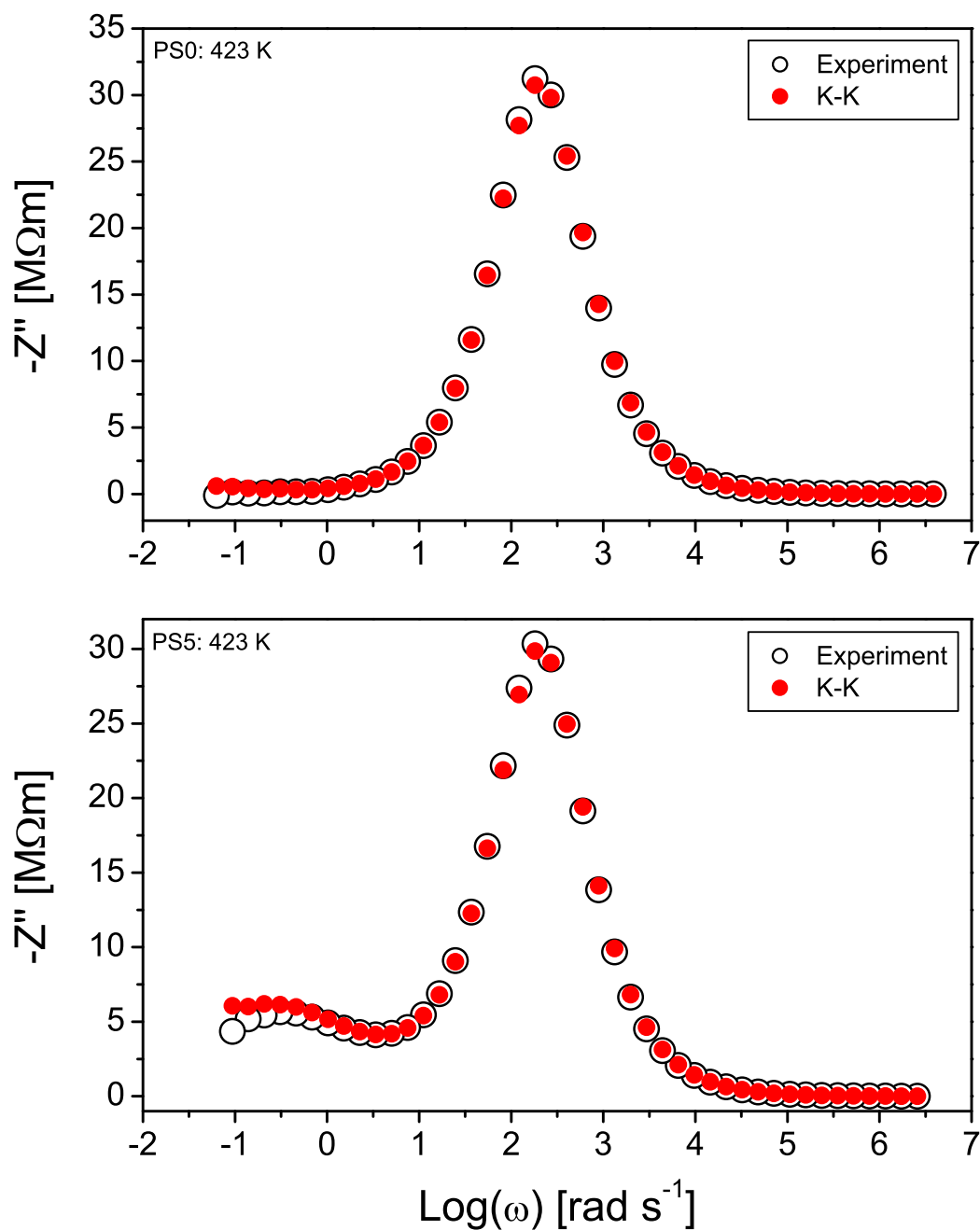


Figure 6.4: Comparison of the experimental imaginary impedance data with that obtained from the K-K transform of the experimental real impedance data for the pure polyester-resin (PS0) and the composite sample containing 4.7 volume % silicon (PS5). For the pure polyester-resin, the experimental and the calculated data are in good agreement at all frequencies while there appear to be some differences between the experimental and the calculated data at low frequencies ($\text{Log}(\omega) \leq 1$) for the 4.7 % sample.

For the pure polyester-resin, Figure 6.4 (top), the experimental and calculated data are seen to be in good agreement at all frequencies and therefore confirming the validity of the experimental data. The data at high frequencies for the composite sample, Figure 6.4 (bottom) also conforms to the K-K transforms. There are some differences between the experimental and the calculated data at low frequencies for the sample PS5. This could indicate a non-linear response in the composite, which does not satisfy the K-K relations. Recall though that due to the limited frequency range over which the K-K transforms are calculated, in practice, the high and low frequency ends are regions of increased uncertainty. Therefore, it cannot be firmly concluded from this data alone that the low frequency feature is due to an inherently non-linear response such as electrode effects.

Figure 6.5 shows the experimental and the calculated data for the 20.7 (PS20) and 35.7 (PS36) volume % silicon samples. Again there is a very strong but inconclusive suggestion of non-linear effects at low frequencies. Again note that this finding is considered inconclusive as the notable differences between the experimental and the calculated data are for the last few frequency points, where the numerical integration is least accurate (contrast this with the data for the electrode effects for the single crystal, Figure 3.2, and the polycrystalline yttria-stabilized zirconia sample, Figure 5.11, where there was a wide range of frequencies where the experimental and the calculated data were not in agreement, and it could be clearly (and correctly) concluded that the problem with the low frequency data was due to electrode effects).

From the results of the K-K transforms, it can be concluded that the pure polyester data and the data at high frequency for the composites is valid and due to the material. There is some doubt about the source of the discrepancies at low frequencies but it will be shown later that they are most probably due to electrode effects. The results of further analysis, to identify and measure the properties of the components dominating the various features in the impedance spectra, will now be presented and discussed.

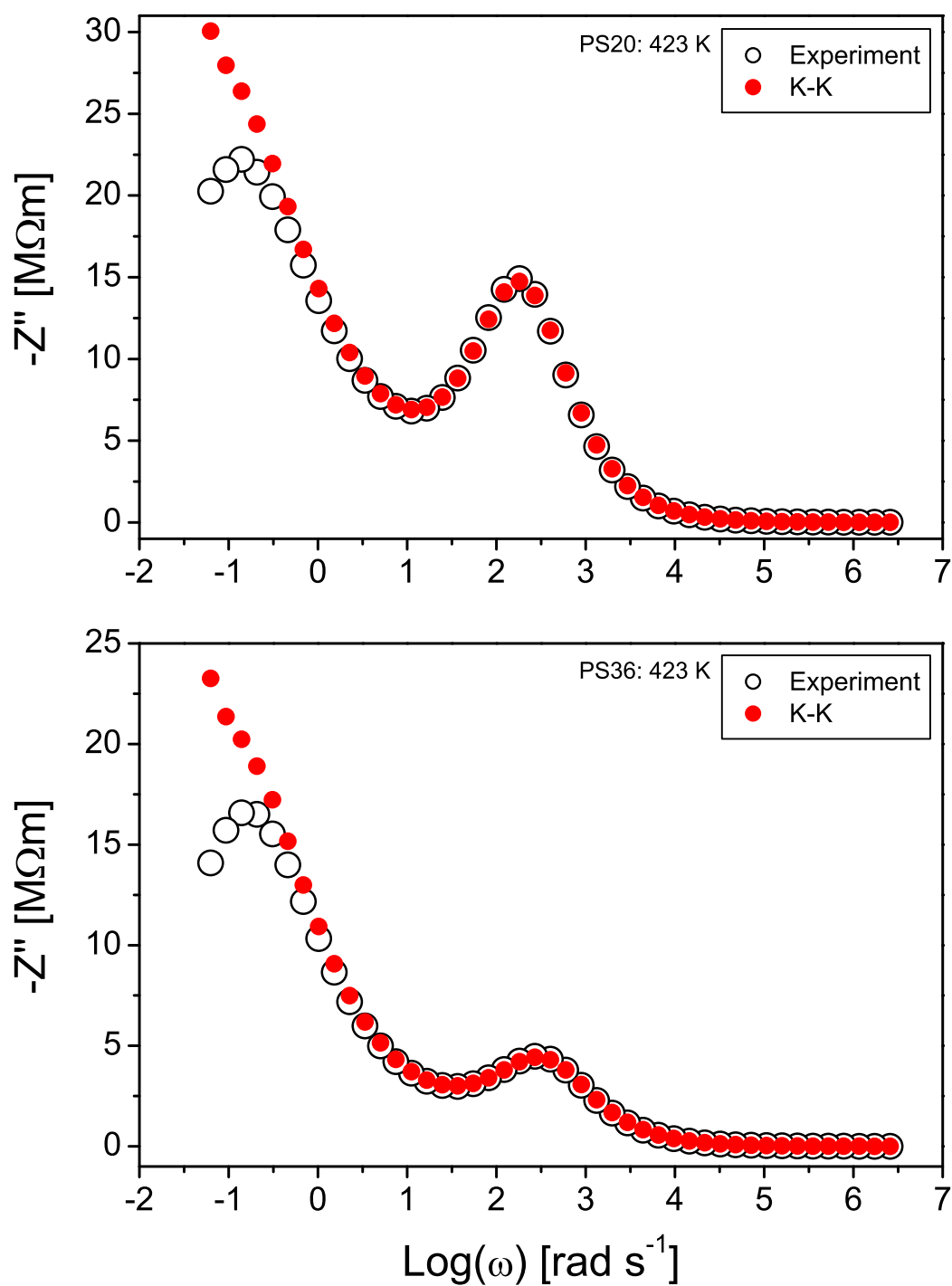


Figure 6.5: Comparison of the experimental imaginary impedance data with that obtained from the K-K transform of the experimental real impedance data for the composite samples containing 20.7 (PS20) and 35.7 (PS36) volume % silicon. Again there is a strong suggestion of some non-linear effects at low frequencies ($\text{log}(\omega) \leq 1$), which do not satisfy the K-K conditions.

6.2.3 The frequency dependence of the electrical properties of polyester-resin/silicon composites

The real dielectric constants and the real conductivities of various polyester-resin/silicon composites (at all measured frequencies) are shown in Figure 6.6. For clarity, the data from some of the samples investigated has been omitted from these plots. The omitted data shows the same trends as are observed in the data presented. It will later be shown that all the samples studied are below the percolation threshold, ϕ_c .

No notable change is observed in the dielectric constant of the pure polyester-resin on the log scale, Figure 6.6 (top), even at the lowest frequencies. For each sample of the samples containing silicon, the dielectric constant rises from a high frequency value ~ 8 , through a shoulder at intermediate frequencies to a low frequency value greater than 10^3 . It can also be seen that the dielectric constant at each frequency point increases as the volume fraction of the more conducting component (silicon) increases. The rapid rise in the dielectric constant observed at the lowest frequencies, in the data for the composite samples, is similar to that usually attributed to electrode effects (see also Figures 3.3 and 3.4).

It can be seen in Figure 6.6 (bottom) that the conductivity of the pure polyester-resin follows a Jonscher type power law drop ($\sigma \propto \omega^s$) at high frequency and then levels off to a flat region at low frequencies. For the samples containing silicon, a partial shoulder, which becomes more pronounced with increasing silicon content, can just be seen at the highest frequencies ($\log(\omega) > 6$). The significance of this shoulder will become apparent in the sections that follow. From the high frequency partial shoulder, the data follows a power law drop to a broader shoulder at intermediate frequencies. It then starts to drop off slowly at the lowest frequencies ($\log(\omega) < 0$).

Figure 6.7 shows the real dielectric constant and the **dielectric loss** of the pure polyester-resin. It can be seen in Figure 6.7 (top) that the dielectric constant rises from some high frequency value which cannot be estimated from

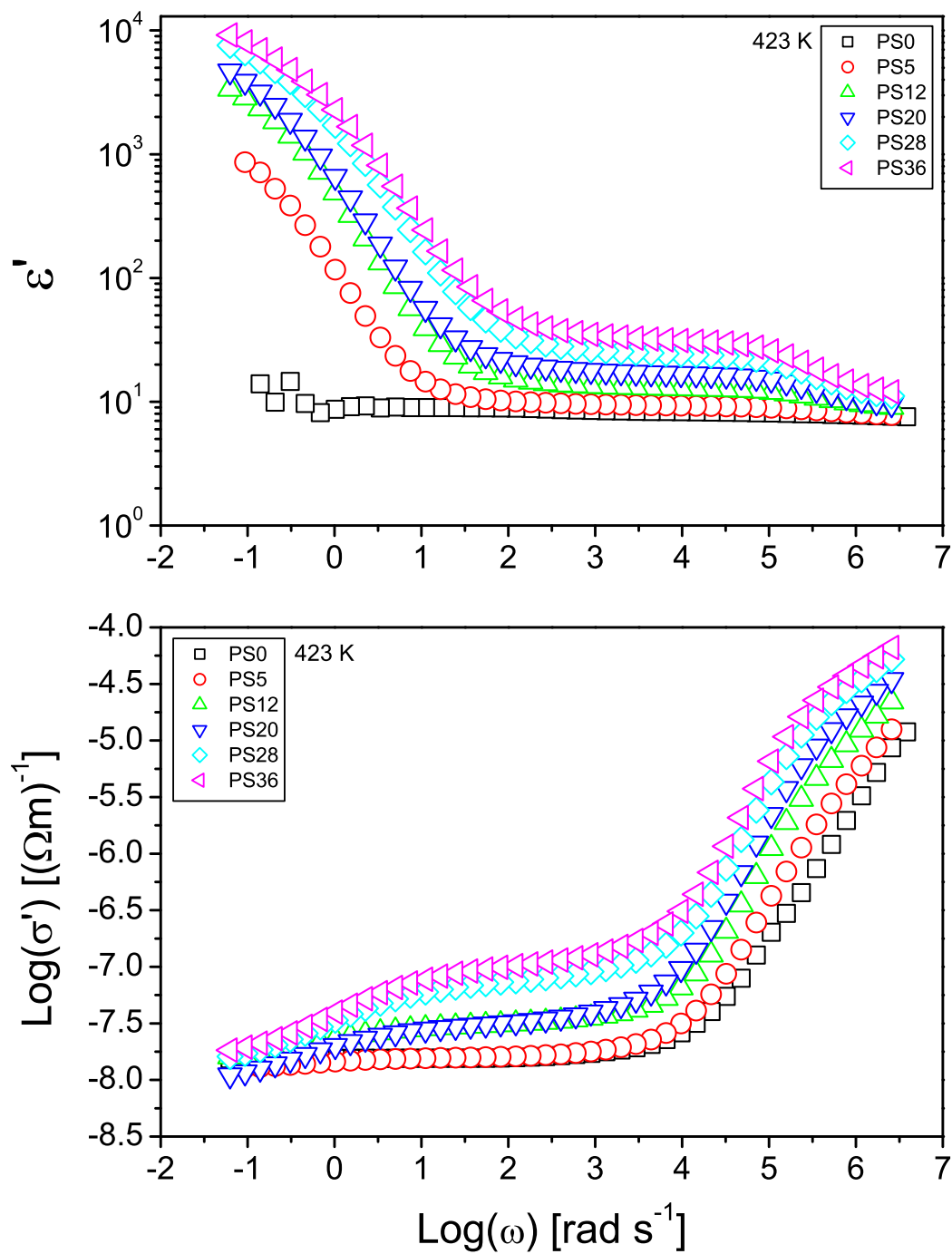


Figure 6.6: The frequency dependence of the real dielectric constants and the real conductivities of some polyester-resin/silicon composites at 150 °C. It can be seen that for the samples containing silicon, the dielectric constant rises by several orders of magnitude at low frequencies, a feature not observed in the data for the pure polyester-resin.

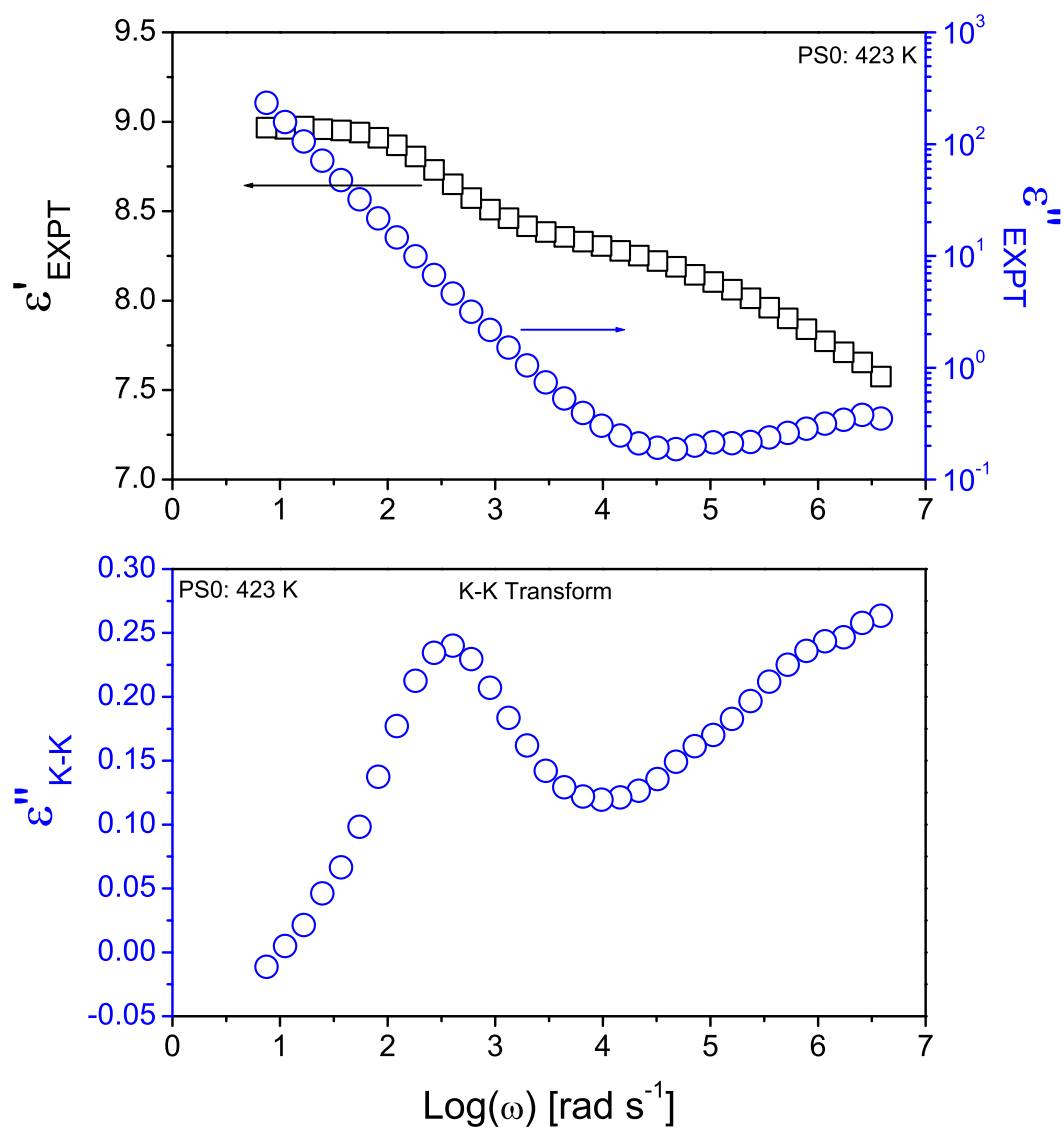


Figure 6.7: The measured dielectric constant and the dielectric loss of the pure polyester-resin at 150 °C (top) and the dielectric loss obtained from a numerical Kramers-Kronig transform of the measured dielectric constant (bottom), all plotted as functions of $\log(\omega)$. The transformed dielectric loss shows two peaks, indicating two polar relaxations in the resin.

the data in the available frequency range, through a weak shoulder at intermediate frequencies to a low frequency plateau ~ 9 . The measured dielectric loss data (also in Figure 6.7, top) shows a partial peak at high frequencies, indicating some relaxation process in the material with $\log(\omega_p) \geq 7$. Below $\log(\omega) \approx 4.5$, ϵ'' rises monotonically. The measured data does not show any clearly observable feature in the frequency region $2.0 \leq \log(\omega) \leq 3.5$, corresponding to the weak shoulder in the real dielectric constant data. The dielectric loss calculated from the K-K transform of the real dielectric constant is shown in Figure 6.7 (bottom). As discussed in Section 1.6, the K-K transform removes the normally dominant ohmic conduction losses. Figure 6.7 (bottom) clearly shows a peak at frequencies corresponding to the region of rapid change in the dielectric constant ($\log(\omega) \approx 2.5$), and a partial peak at higher frequencies. This clearly indicates that there are at least two polar relaxation processes in the polyester-resin, probably due to different components of the resin. (contrast this with the yttria-stabilized zirconia single crystals, where only a single relaxation process was observed, see end of Section 3.2.4). The nature of the components of the polyester-resin is not discussed any further in the current work.

The frequency dependence of the imaginary impedances and the normalized imaginary impedances of some of the polyester-resin/silicon composites is shown in Figure 6.8. It can be seen in Figure 6.8 (top) that above $\log(\omega) = 1$, the imaginary impedance decreases monotonically with increasing silicon content. This trend is to be expected, as the silicon is the more conducting component. For the peak at lower frequencies ($\log(\omega) < 1$), there is a non-monotonic trend in $-Z''$ with increasing silicon content. Recall that the low frequency peak did not satisfy the K-K transforms (Section 6.2.2). It can also be seen, particularly in the normalized impedance plot in Figure 6.8 (bottom), that the characteristic frequency of the component dominant at high frequencies in the composite is essentially the same as that of the pure polyester-resin (PS0) at this temperature. In results at other temperatures (not presented here), it was also seen that the characteristic frequency of

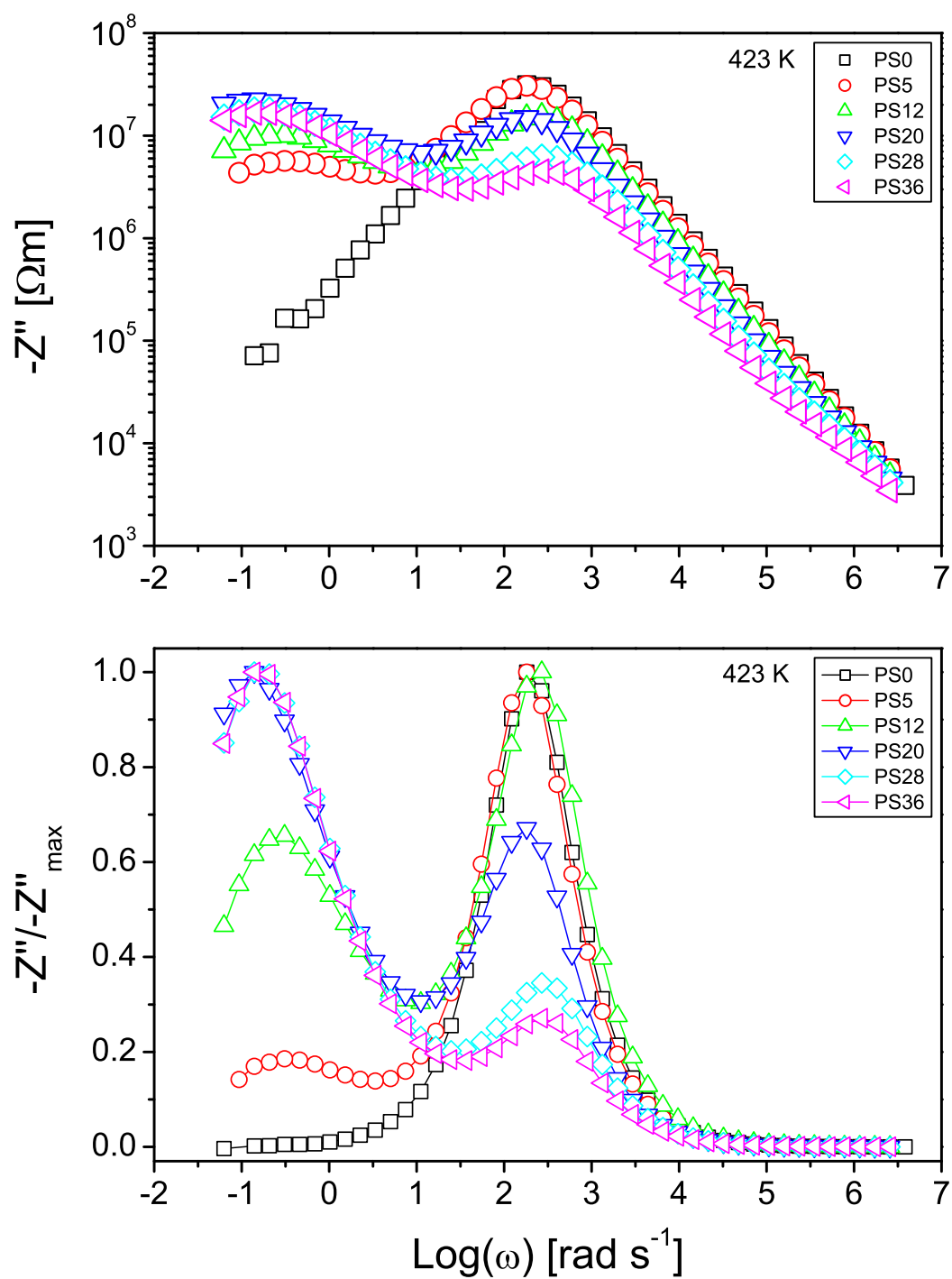


Figure 6.8: The frequency dependence of the imaginary impedance and the normalized imaginary impedance of various polyester-resin/silicon composites at 150 °C. The silicon volume fractions are given in Table 6.1.

the component at high frequencies in the imaginary impedance data for all the composites, is the same as that of the pure polyester-resin at that temperature. This confirms that this dominant component is the polyester-resin, irrespective of the silicon content.

It is usually expected in impedance spectroscopy results, that the component dominant at high frequencies is the more conducting component. It has already been shown in Section 4.2.2 of the current work that if the more conducting component has an anomalously high dielectric constant, then the positions of the imaginary impedance peaks may be reversed. This would allow the peak observed at low frequencies in the imaginary impedance plot, which appears to be at more or less the same frequency for the different samples ($\log(\omega) \approx -0.7$), to be that due to the silicon, if its “effective” dielectric constant is very large. However, there are a number of inconsistencies that would result from drawing the conclusion that the peak at low frequencies is due to the silicon itself.

1. As already seen, the component dominant at low frequency possibly does not satisfy the K-K relations.
2. A measurement on the same silicon powder as used in the composites, compressed at room temperature ($\sim 26^\circ\text{C}$), gave a value 1.8 for $\log(\omega_p)$. This is already higher than that of the component of the composite dominant at low frequencies, measured at 150°C . For semiconductors, $\log(\omega_p)$ usually increases rather than decreases with increasing temperature. Single crystal silicon, or better still silicon with a similar morphology and doping as that in the composites, such as perhaps porous silicon, could not be obtained, for measurements of the ac conductivity under the same conditions as for the composites.
3. “Dc” conductivities extracted from the complex impedance plane plots of the data (presented further below), obtained using the low frequency intercepts of the second arcs as one end of the arcs (i.e. assuming that the data at all frequencies is valid and due to the composite material)

give points that show no particular pattern with increasing silicon content.

The inconsistencies strongly support a conclusion that the low frequency data is not due to the composite material but is instead due to electrode effects.

It will be conclusively shown below, using the impedance *and* the modulus representation of the data, that the contribution of the silicon is at high frequencies and therefore that the low frequency peak ($\log(\omega) \approx 0.7$) is *not* due to the silicon.

Figure 6.9 shows the frequency dependence of the imaginary impedance and the imaginary modulus of the pure polyester-resin (PS0) and the composite sample PS5. For the pure polyester-resin, Figure 6.9 (top), only one peak is seen in the imaginary impedance plot. In the modulus plot, there is a dominant peak at essentially the same frequency as that of the imaginary impedance peak, and a partial peak at high frequencies, related to the secondary relaxation process seen in Figure 6.7. It will be seen, in the figures that follow, that in the composites the high frequency peak is either enhanced or dominated by the silicon. Figure 6.9 (bottom) shows the imaginary impedance and modulus data for the sample PS5. One dominant peak at $\log(\omega) \approx 2.3$ and a smaller low frequency satellite peak can now be seen in the imaginary impedance. The imaginary dielectric modulus data shows a dominant peak at $\log(\omega) \approx 2.3$ and a flat peak at high frequencies. The high frequency peak is much more pronounced than the partial peak in the pure polyester-resin data (Figure 6.9, top). By comparing Figure 6.9 (bottom) with Figures 6.8 and 6.9, it can be seen that the central peak, where the low frequency imaginary modulus peak and the high frequency imaginary impedance peak coincide, is due to the primary relaxation process in the polyester-resin. The flat peak seen at low frequencies in the impedance data indicates a component more insulating than the polyester-resin or electrode effects. The flat peak seen at high frequencies in the dielectric modulus data indicates a component more conducting than the polyester-resin.

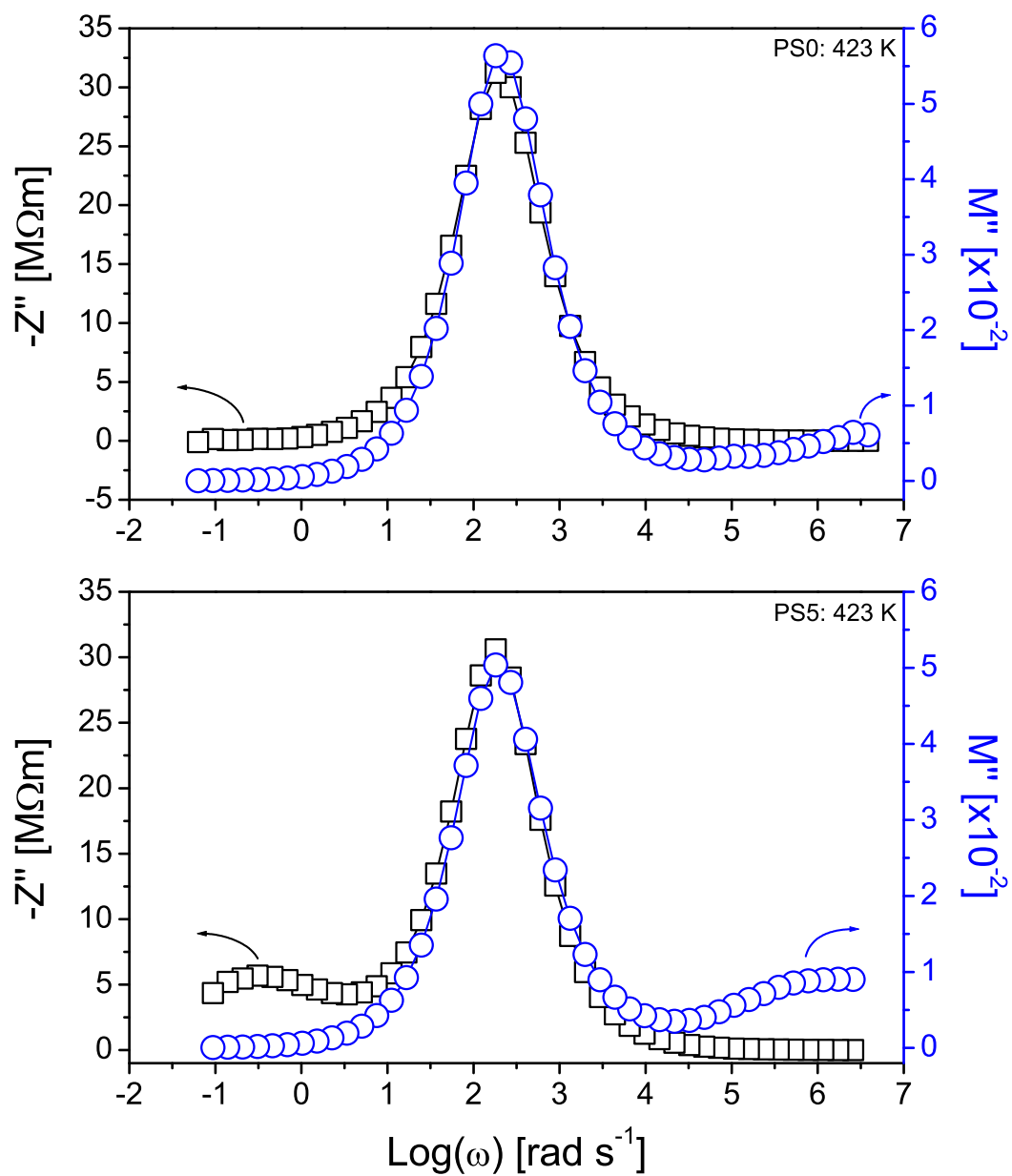


Figure 6.9: The frequency dependence of the imaginary impedance and the imaginary modulus of the pure polyester-resin and of the composite sample containing 4.7 volume % silicon (PS5).

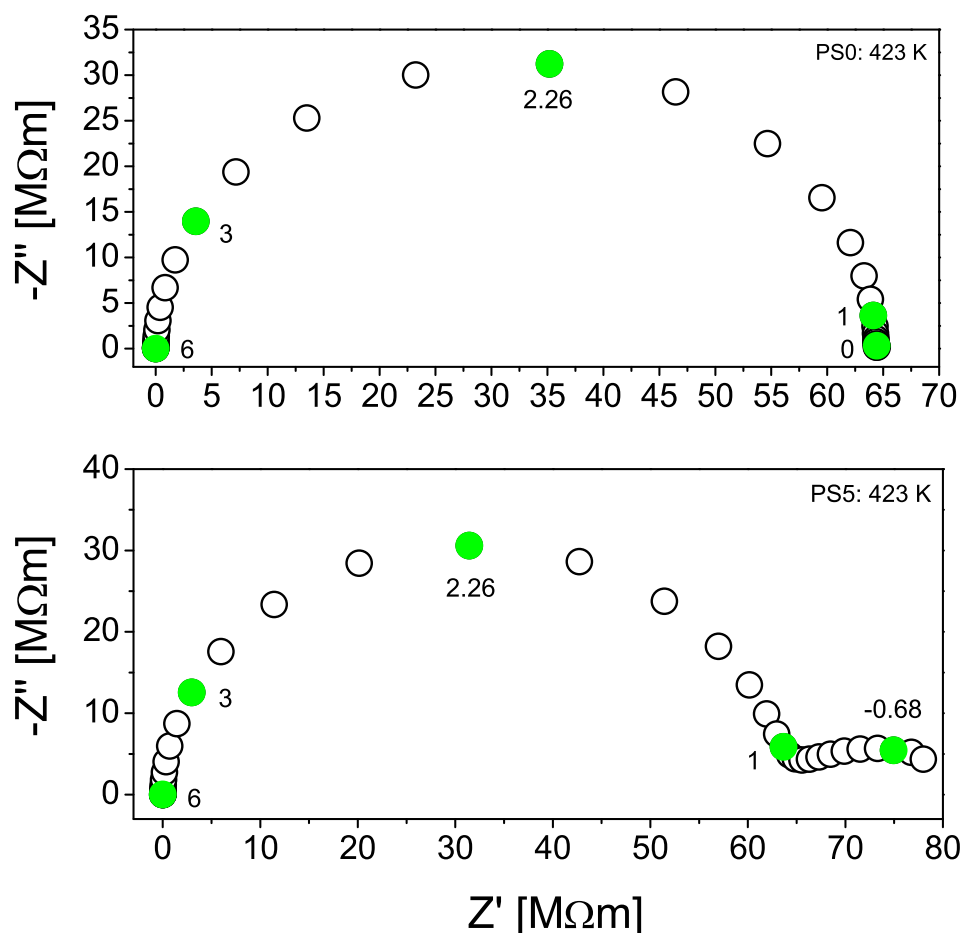


Figure 6.10: Complex impedance plane plots of the data for the pure polyester-resin sample (PS0) showing only one arc and that for the 4.7 volume % silicon sample (PS5) showing two arcs. Key values of $\log(\omega)$ are indicated in the plots. Note that there is no high frequency $\log(\omega) \geq 4$ arc in the complex impedance plane plot, corresponding to that in the complex modulus plane plots (Figure 6.11).

The complex *impedance* plane plots of the data for PS0 and PS5 are shown in Figure 6.10. Only one arc, due to the polyester-resin is observed for the pure polyester-resin, while two arcs are observed for PS5, one of which it has already been suggested is due to electrode effects.

Figure 6.11 shows the complex *modulus* plane plots of the data for the samples PS0 and PS5. The plot of the data for PS0, Figure 6.11 (top) shows one dominant arc and a small feature at high frequencies due to the secondary relaxation process in the polyester-resin, already seen in Figure 6.7. One complete arc and a partial arc at high frequency are observed in the plot

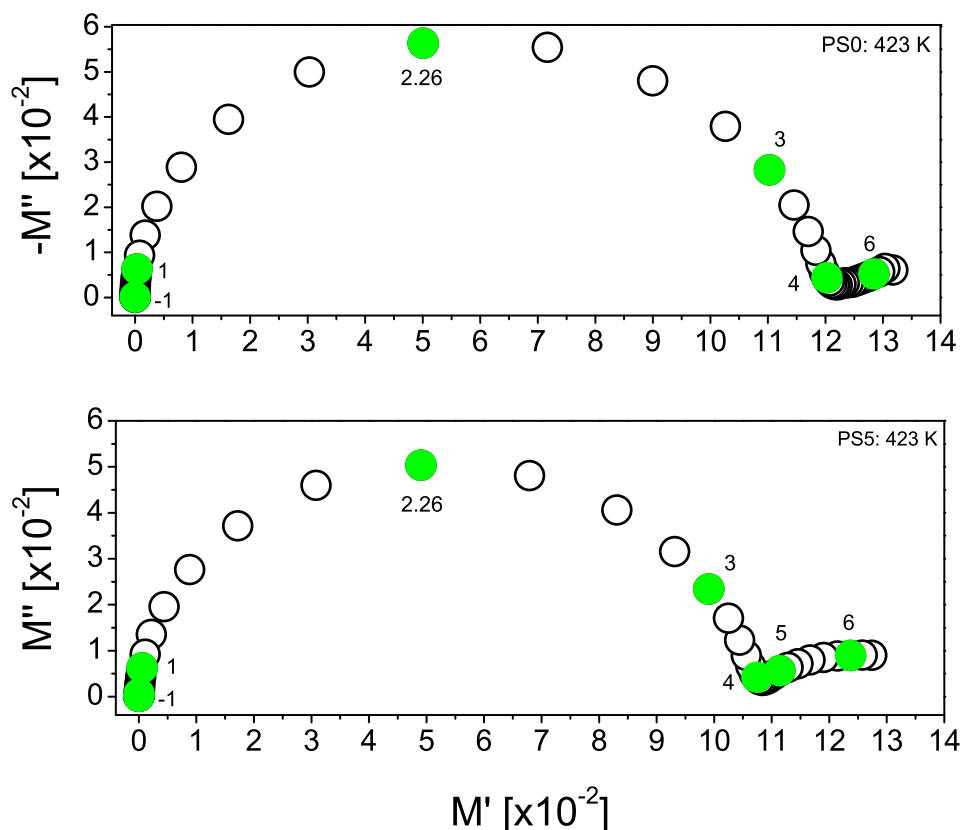


Figure 6.11: Complex modulus plane plots of the data for the pure polyester-resin (PS0) and that for the 4.7 volume % silicon sample (PS5). The partial arc that is observed in the pure polyester-resin modulus plot at high frequencies is enhanced (or dominated) by the silicon, in the modulus plot for the composite sample. Key values of $\log(\omega)$ are indicated in the plots. Note that there is no low frequency ($\log(\omega) \leq 1$) arc in the complex modulus plane plot, corresponding to the low frequency arc in the complex impedance plane plot (Figure 6.10).

of the data for the composite sample PS5 (Figure 6.11, bottom). The arc at high frequencies may be the result of the silicon enhancing the secondary relaxation process in the polyester-resin or due to the silicon itself. It will be shown later that it is most likely to be due to the silicon itself.

The frequency dependence of the imaginary impedance and modulus of the polyester-resin/silicon composites PS20 and PS36 is shown in Figure 6.12. Again it can be deduced from these plots that there are three contributions to the measured electrical properties of the composites, the polyester-resin, giving the peak in both the impedance and modulus which is at the center

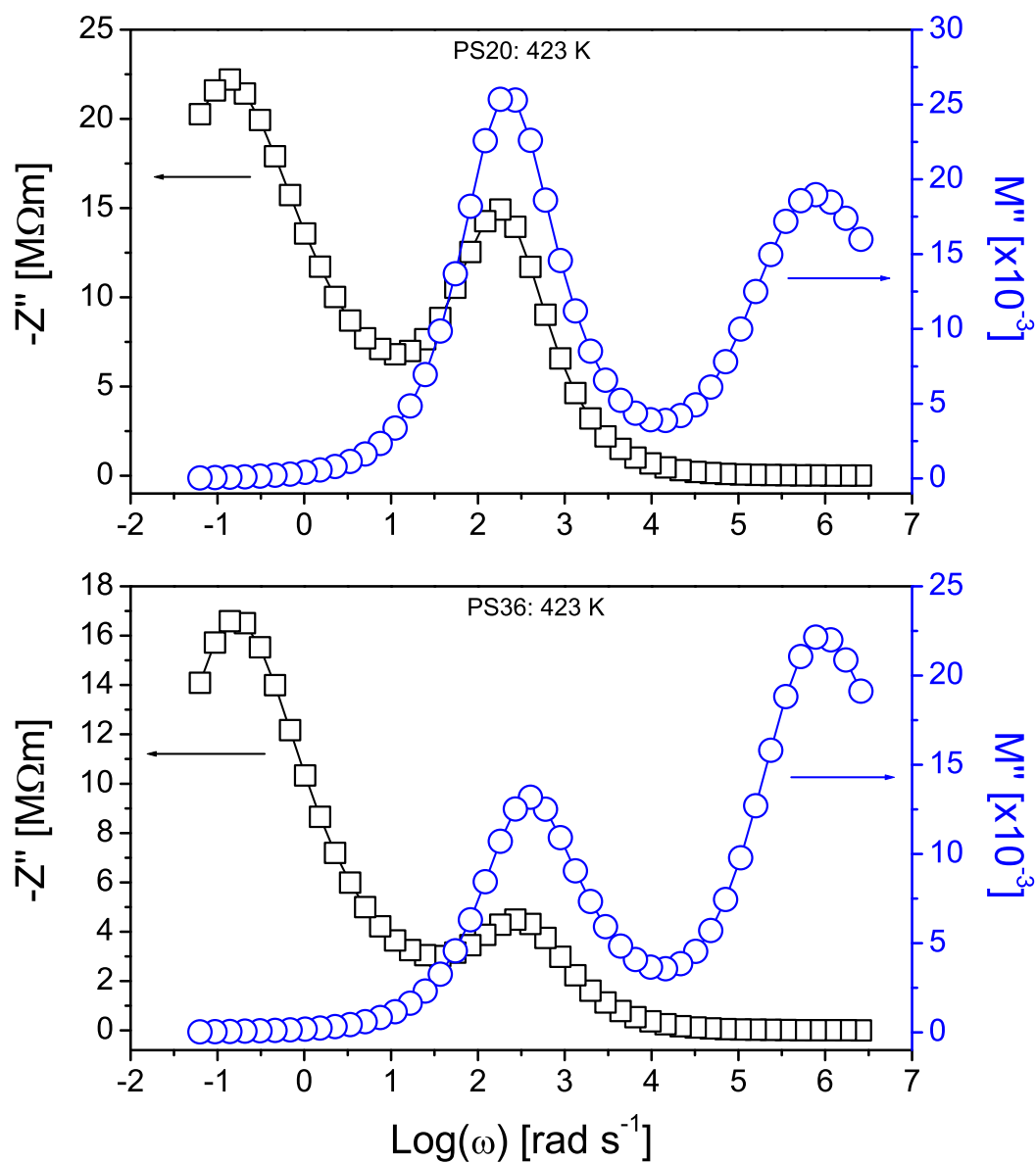


Figure 6.12: The frequency dependence of the imaginary impedance and imaginary modulus of the samples containing 20.7 (PS20) and 35.7 (PS36) volume % silicon. Note that the high frequency peak in the modulus plot is greatly enhanced or dominated by the silicon.

($\log(\omega) \approx 2.3$), a low resistivity component giving the peak high frequencies in the modulus and electrode effects giving the low frequency impedance peak.

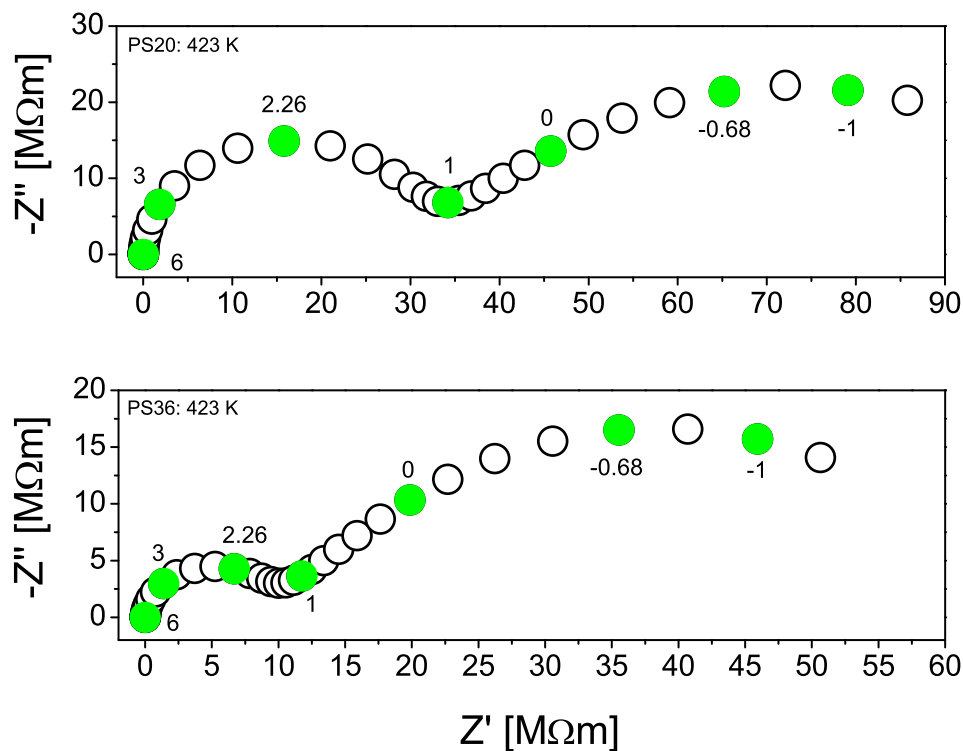


Figure 6.13: Complex impedance plane plots of the data for the 20.7 (PS20) and 35.7 (PS36) volume % silicon samples. Key values of $\log(\omega)$ are indicated in the plots.

The complex impedance and complex modulus plane representations of the data for the samples PS20 and PS36 are shown in Figures 6.13 and 6.14. Two arcs are clearly observed in each of the data representations. Again the arcs in the complex impedance plane plots (Figure 6.13), are attributed to the polyester-resin (high frequency) and electrode effects (low frequency) while those in the complex modulus plane plots (Figure 6.14) are attributed to the polyester-resin (low frequency) and the silicon enhanced secondary relaxation process in the polyester-resin or the silicon itself (high frequency).

Together with the results in the sections that follow, the results in the current section will be used to argue that the arc at high frequencies in the modulus data is primarily due to the presence of the silicon.

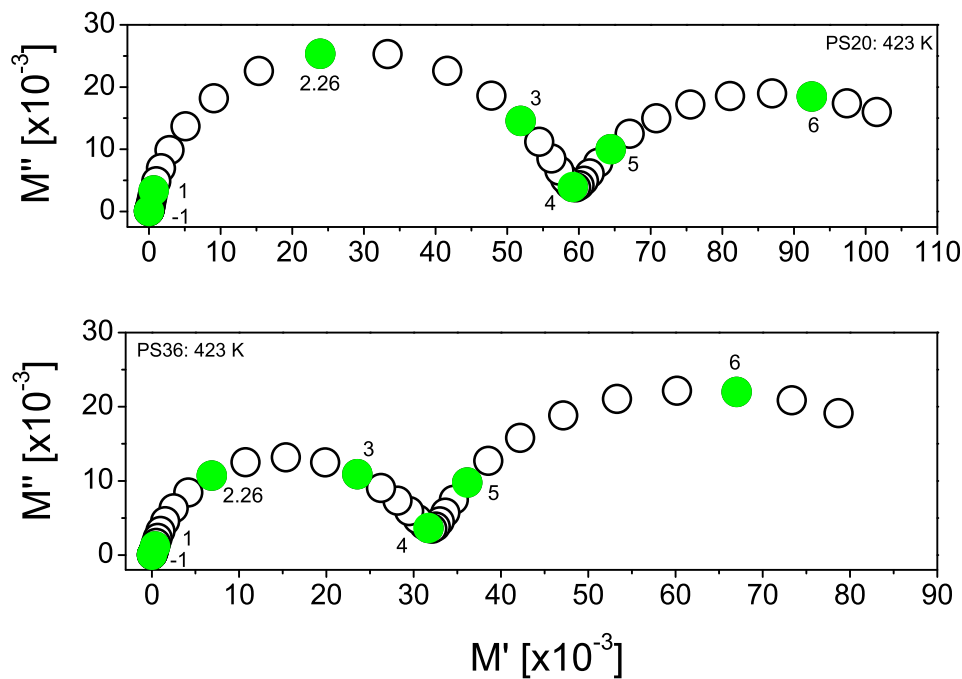


Figure 6.14: Complex modulus plane plots of the data for the 20.7 (PS20) and 35.7 (PS36) volume % silicon sample. Key values of $\log(\omega)$ are indicated in the plots.

6.2.4 The temperature dependence of the electrical properties of a polyester-resin/silicon composite

The temperature dependence of the conductivities and the characteristic frequencies of the components of the composite sample PS20, is shown in Figure 6.15. These results are representative for all the composites. Figure 6.15 (top) shows the temperature dependence of the characteristic frequencies, plotted as $\text{Log}(\omega_p)$ vs $1000/T$. Figure 6.15 (bottom) shows the dc conductivities extracted from complex impedance plane plots for the polyester-resin and, estimated from the modulus peaks (see Section 1.2), for the component dominating the modulus at high frequencies (silicon). The conductivities of both components are plotted as $\text{Ln}(\sigma_{dc})$ vs $1000/T$. (The details on the accurate determination of characteristic frequencies and the extraction of dc conductivities from complex impedance plane plots are given in Section 2.6).

It can be seen, in Figure 6.15, that both $\text{Log}(\omega_p)$ and $\text{Ln}(\sigma_{dc})$ are proportional to $1/T$. A $1/T$ dependence of $\text{Ln}(\sigma_{dc})$ is expected for silicon, a

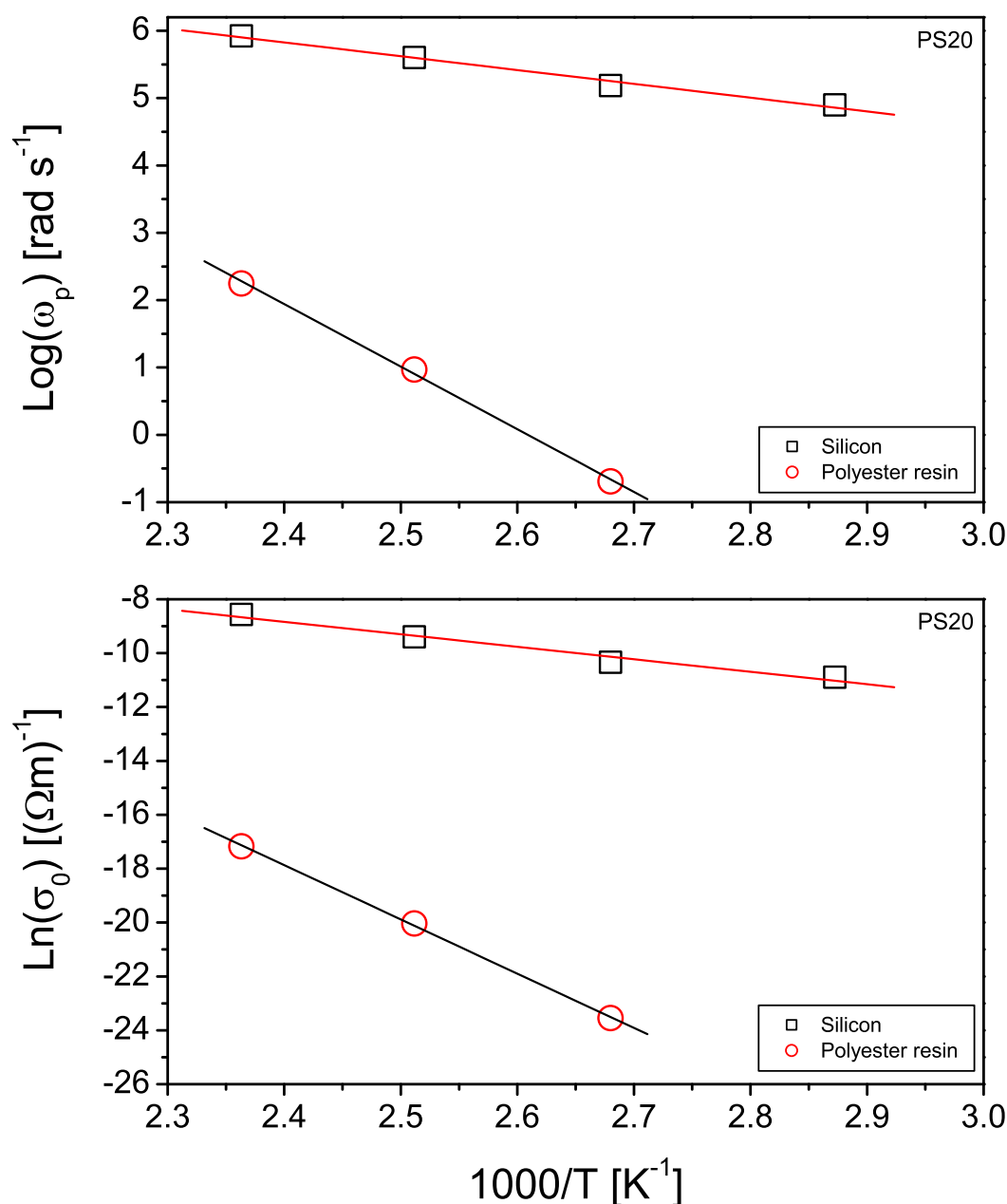


Figure 6.15: The temperature dependence of the characteristic frequencies and the dc conductivities of the components of the sample containing 20.7 volume % silicon (PS20), extracted from complex impedance plane plots for the less conducting component (polyester-resin) and estimated from the modulus peaks for the more conducting component (silicon). Note that the properties of the polyester-resin could not be accurately determined at $T \leq 95^\circ\text{C}$, as it gave an arc too incomplete to be used by the procedure described in Section 2.6 to estimate the characteristic frequency or contribution to the dc resistance.

semiconductor. Pure silicon, as used in electronics, has an energy gap of ~ 1.1 eV [Marder¹³⁷]. The excitation energy 0.41 ± 0.03 eV calculated from the data plotted in Figure 6.15 for the silicon is closer to the 0.46 and 0.50 eV obtained for porous silicon in Axelrod et al.¹³⁸ and in Ben-Chorin et al.¹³⁹. The morphology and perhaps doping of the porous silicon may be closer to the silicon in the composites than that of ultra-pure single crystals. The value obtained in the current work suggests impurity conduction in the nominally pure silicon. An excitation energy of 1.66 ± 0.03 eV is obtained for the conduction processes in the polyester-resin.

The $1/T$ temperature dependence of the conductivity and the value of the activation energy, for the component dominating the modulus at high frequency, is consistent with it being the silicon grains. Note that the closeness of the characteristic frequencies of the high frequency relaxation process in the polyester-resin and that of the silicon ($\text{Log}(\omega_p) \gtrsim 6$) means that they are both having an effect on the high frequency conductivity and therefore the respective conduction processes will contribute to the calculated activation energies. If the high frequency relaxation process in the polyester-resin is not enhanced by the silicon, then it will only make a very small contribution (see Figures 6.9 to 6.14).

6.2.5 Microstructure and the modeling of the electrical properties

It was not possible to obtain satisfactory and consistent fitting results for the ac conductivity data of the polyester-resin/silicon composites using the Maxwell-Wagner equation and the BLM, with the separately measured properties of the polyester-resin and the actual volume fractions of silicon used in making the samples as input data.

Satisfactory and consistent results could only be obtained by fitting the data to the SEPPE. Some of the results obtained from fitting the data are presented and discussed below. The following restrictions were imposed on

the fitting:

- As mentioned above, the properties of the polyester-resin and the silicon volume content were *fixed* at the separately measured values.
- The data from *all* the samples was fitted with common values for all the variable parameters. These are the exponent t , the percolation threshold ϕ_c and the conductivity of the more conducting component, the silicon.
- Since no straight forward model could be found for the ac conductivity of the silicon powder at 150 °C, it was assumed that its properties were dispersionless.

Figure 6.16 shows the dielectric constants and the conductivities of several polyester-resin/silicon composites and the best fits to the experimental data obtained using the SEPPE (with the separately measured electrical properties of the polyester-resin and the measured silicon volume fractions as fixed input and σ_h^* , ϕ_c and t as the variable parameters). With the exception of the sample with the highest silicon content, there is satisfactory agreement between the experimental and the calculated conductivities. At all but the lowest frequencies, there is also qualitative and semi-quantitative agreement between the measured and the experimental dielectric constants.

The discrepancies between the measured and the calculated values at low frequencies could be due to too simple a model for the dispersive properties of the silicon. Axelrod et al.¹³⁸ working with porous silicon use a combination of two UDR expression as well as two Havriliak-Negami functions to model the properties of the silicon alone. This was considered too complex to be incorporated in the current analysis. The results in Pan et al.¹⁴⁰ also show dispersive properties in porous silicon, particularly at low frequencies.

Figures 6.17 and 6.18 show the complex impedance and modulus plane plots of the experimental data for the samples featured in Figure 6.16 and the best fitting results obtained using the SEPPE. Again it can be seen that, with

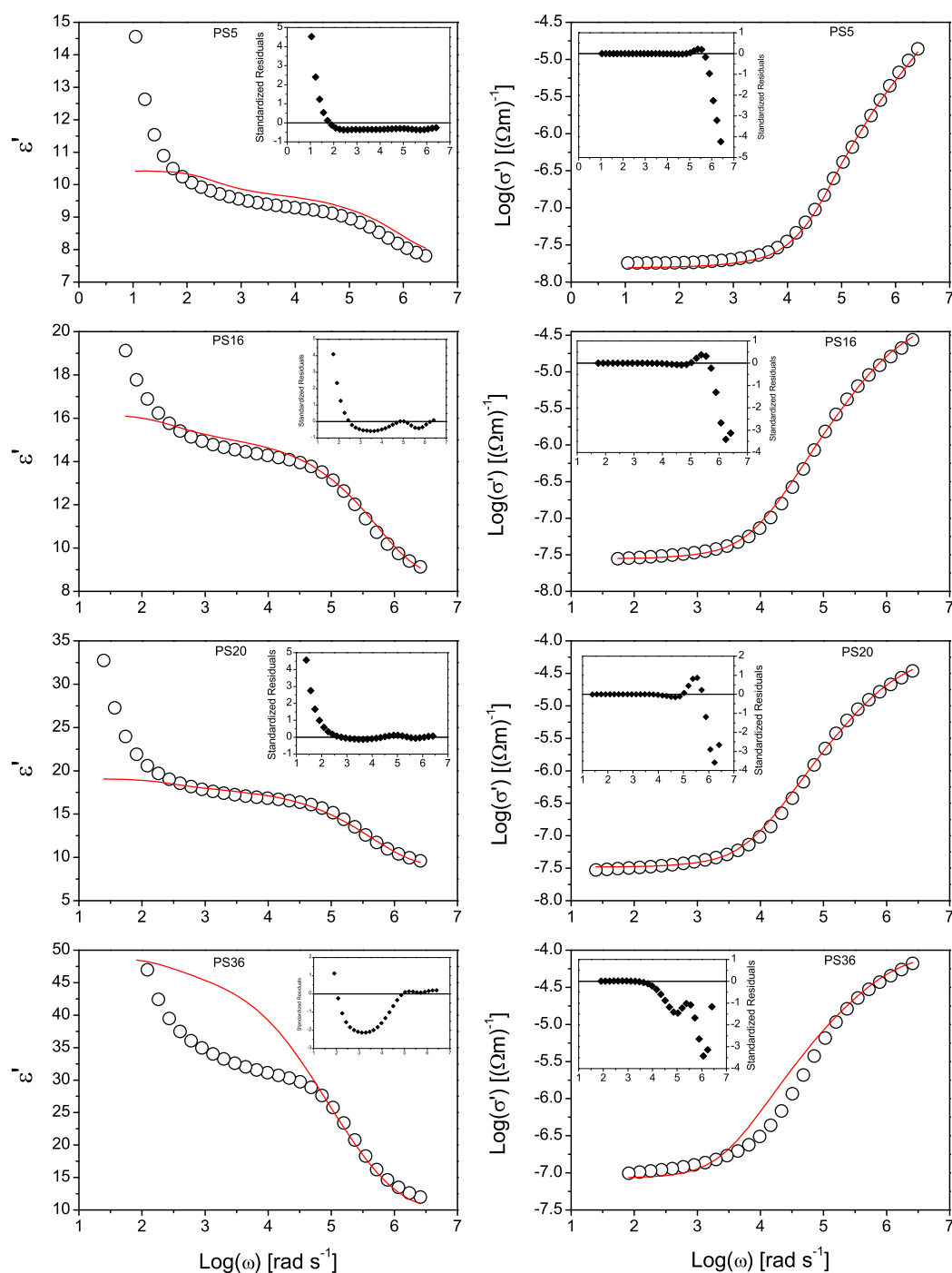


Figure 6.16: The experimental values (○) of the dielectric constant, $\epsilon'(\omega)$ (left) and the conductivity, $\sigma'(\omega)$ (right) of four polyester-resin/silicon composites and the results obtained from fitting the data to the SEPPE (lines). In the fitting of the experimental data, the conducting component volume fractions were fixed at the values used in the sample preparation (see Table 6.1) and the separately measured electrical properties of the polyester-resin were used as fixed input data. The rest of the parameters for the SEPPE fit are given in Figure 6.19.

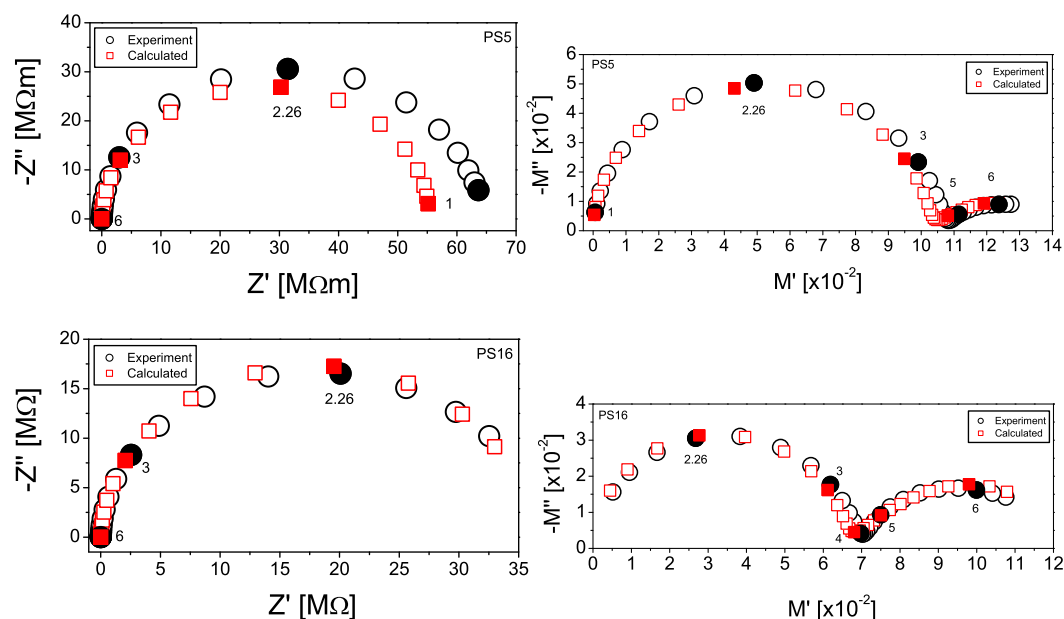


Figure 6.17: Complex impedance and complex modulus plane plots of the experimental data and the best fit to the SEPPE, for the samples PS5 and PS16. Key values of $\log(\omega)$ are indicated in the plots.

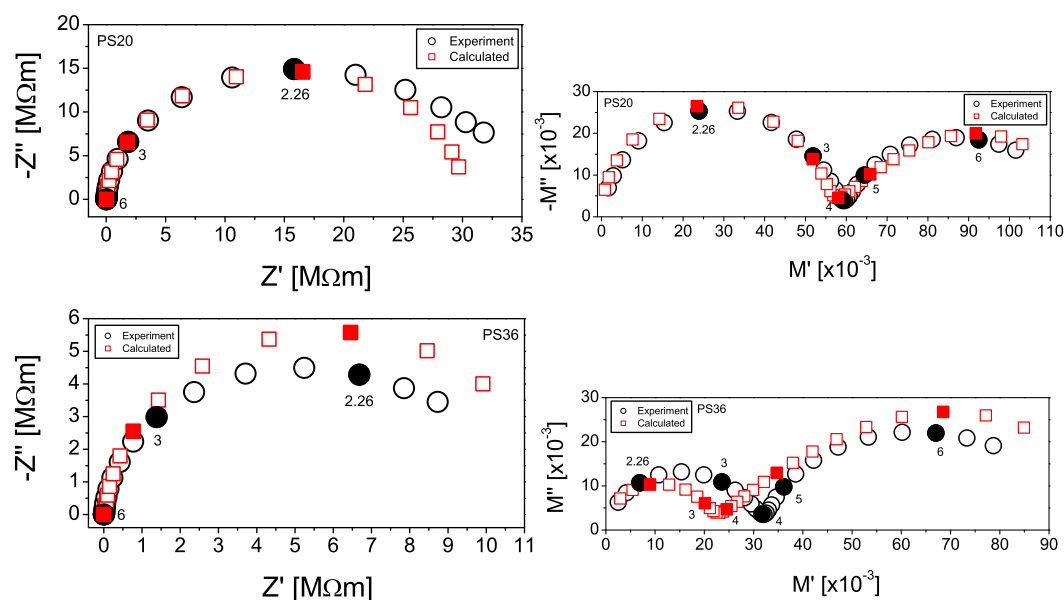


Figure 6.18: Complex impedance and complex modulus plane plots of the experimental data and the best fit to the SEPPE, for the samples PS20 and PS36. Key values of $\log(\omega)$ are indicated in the plots.

the possible exception of the sample with the highest silicon content, PS36, there is satisfactory agreement between the model and the experimental data. Even for sample PS36, there is qualitative agreement between the model and the data.

Figure 6.19 shows the dc conductivities extracted from complex impedance plane plots and the best fit curve obtained using the SEPPE, together with the parameters from fitting the ac conductivity data. The dc conductivity results are in good agreement with the theoretical values, confirming the self consistency of the results of fitting the ac data to the SEPPE. The parameters for the best fit to the ac data are also given in the figure.

Figure 6.20 shows the experimental dielectric loss (top) and that calculated using the SEPPE (bottom), with the parameters obtained from the fitting of the data described above. In the composites, there is a marked rise in the flat peak, seen at high frequencies, in the pure polyester-resin (PS0) data. This rise, which can clearly be seen in both the experimental and the theoretical results, is attributed to the increasing silicon content (increasing ϕ). Moreover, it can be seen that the SEPPE *consistently* models this feature. Figure 6.21 shows the experimental dielectric loss for the pure polyester-resin, and that for composites containing silicon (Si), germanium (Ge) and barium titanate ($BaTiO_3$). It can clearly be seen that while the addition of each of the conducting powders to the pure polyester-resin causes an increase in the dielectric loss, a clear peak at high frequencies is only observed for the samples containing silicon. This makes it unlikely that the peak is due to the enhancement of some component of the polyester-resin, such as that in the distorted region, immediately neighboring the powder particles (Figure 6.2). Such an enhancement would most likely have been observed from adding the other powders as well. This further supports the conclusion that the high frequency peak is due to the silicon itself.

The depression angle (θ_d) of the dominant arc (polyester-resin) increases approximately linearly with increasing conducting component volume fraction, Figure 6.22. To the author's knowledge there are no other experimental

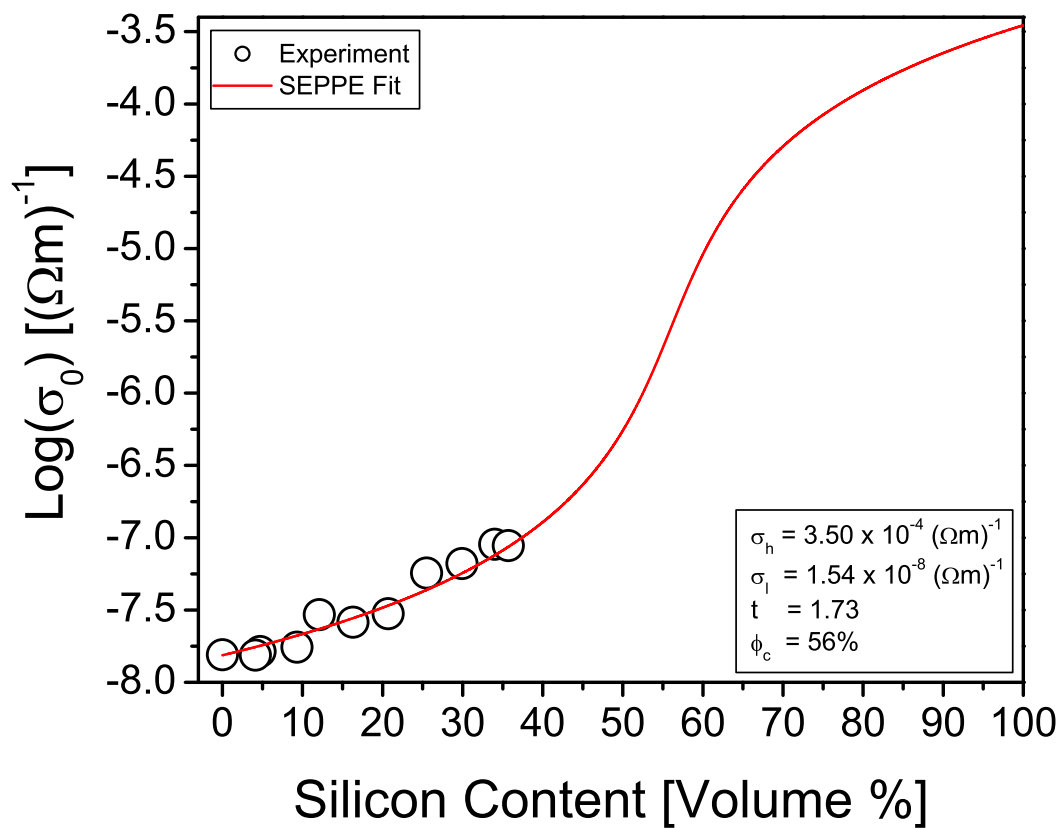


Figure 6.19: The dc conductivity extracted from the complex impedance plane plots and the best fit to the SEPPE. The parameters for the SEPPE fit were obtained from fitting the ac data. In addition to the parameter values given in the figure, for the best fit to the ac conductivity data, $\epsilon_\ell = 18$. Again note that no stable composites with $\phi > 0.40$ could be made, using the techniques described in Section 2.2.3.

or theoretical results indicating and explaining why it is so. Recall that θ_d is related to the width of the relaxation time distribution (Section 1.2 and the references given there).

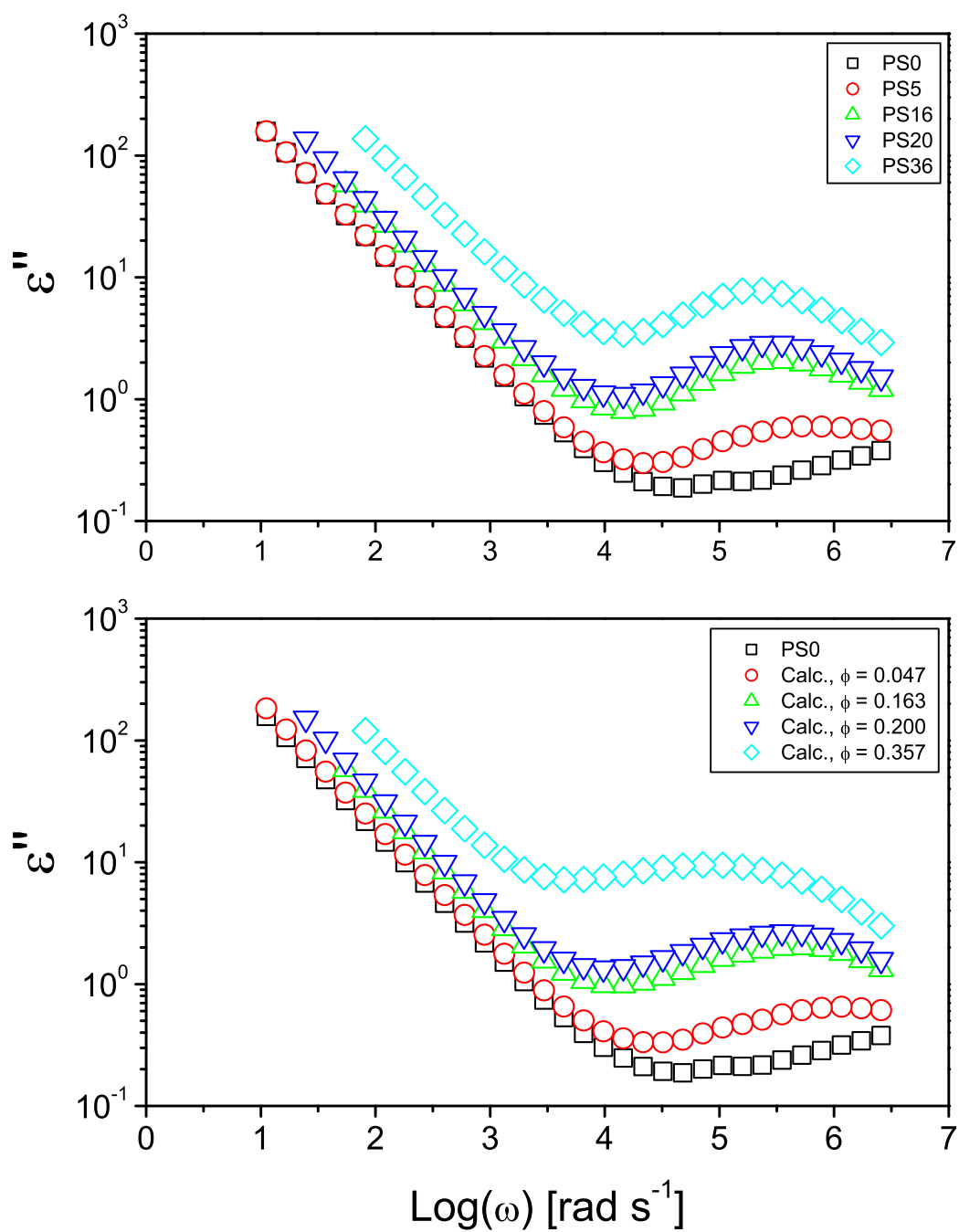


Figure 6.20: The frequency dependence of the measured dielectric loss and that calculated using the SEPPE, with the measured pure polyester resin properties and the same silicon volume fractions as used in the preparation the samples in the top figure, as input. The rest of the parameters for the SEPPE are given in Figure 6.19.

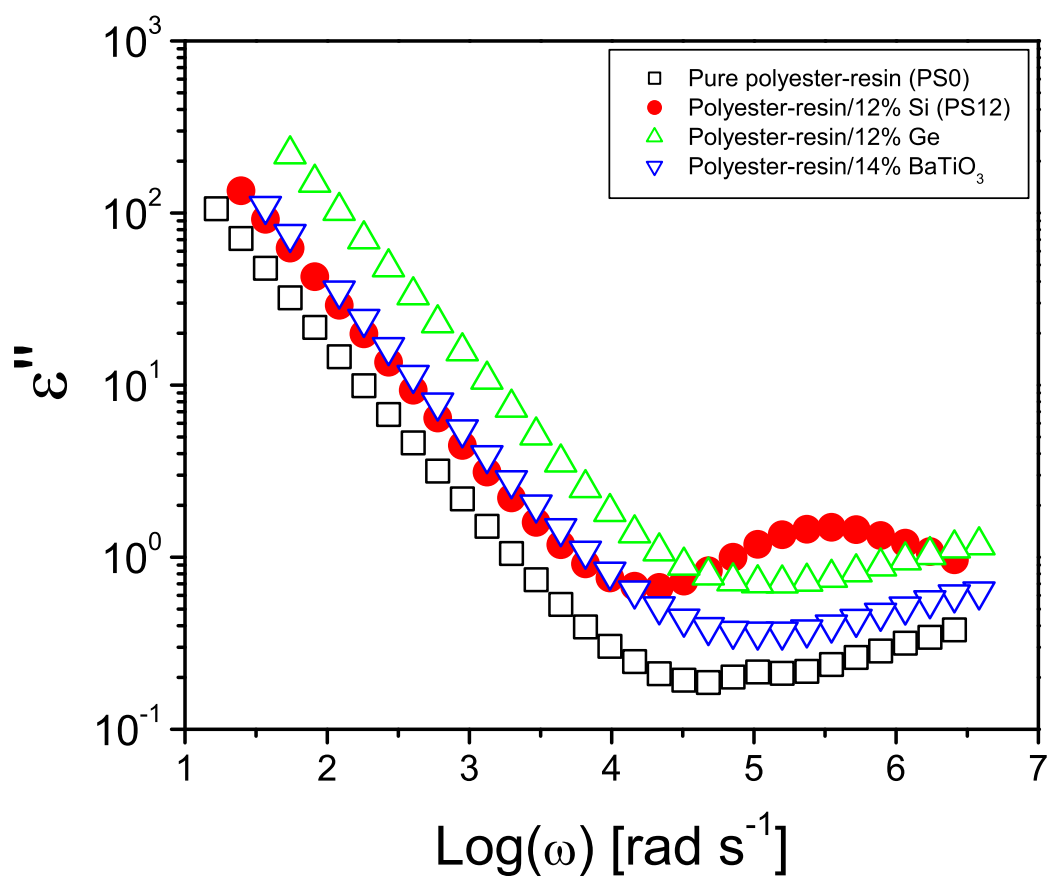


Figure 6.21: The frequency dependence of the dielectric loss of composites consisting of polyester-resin and three different conducting powders, silicon, germanium and barium titanate.

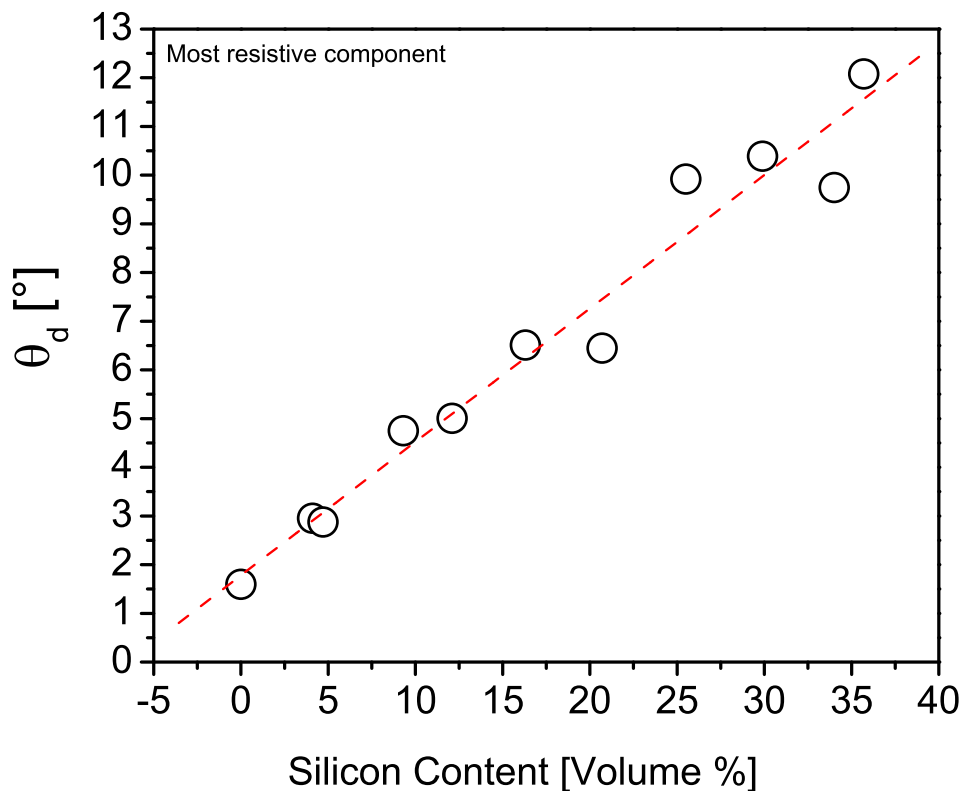


Figure 6.22: The dependence of the depression angle (θ_d) on the conducting component volume fraction. The line is a linear fit to the data.

6.3 Conclusions

In the current chapter, the importance of using various representations of the immittance spectroscopy (in this case impedance and modulus) data, as well as the temperature dependence of the conductivity, in order to correctly identify the contributions to the measured properties of composites has been demonstrated. Furthermore, the use of the characteristic frequencies of the components in identifying their contributions to the composite properties has been demonstrated.

Upon correctly identifying the contributions to the measured properties of the samples, the data could only be satisfactorily fitted to the SEPPE. This model fits the data consistently using the experimentally measured properties of the polyester-resin as well as volume fractions of the silicon as fixed input. The SEPPE also correctly models the dc conductivities extracted from complex impedance plane plots of the composites.

Chapter 7

Liquid-Phase-Sintered Silicon Carbide

7.1 Introduction

Single crystal silicon carbide is a wide band gap semiconductor excellent for high power, high frequency and high temperature devices. Silicon carbide ceramics are widely used as an abrasive, as a refractory, in heating elements and in voltage sensitive resistors (varistors) [Moulson and Herbert¹⁴¹]. There are various forms of sintered polycrystalline silicon carbide, among which is liquid-phase-sintered silicon carbide, produced by sintering silicon carbide powders and additives that form a binder phase. (Other processes for producing polycrystalline SiC include reaction bonding and solid state sintering).

To further understand the ac conductivity of Liquid-Phase Sintered Silicon Carbide (LPSSiC) and its relation to the sintering conditions, additives and microstructure, the electrical properties of samples prepared as described in Section 2.2.4 were investigated and the results are presented and discussed in the sections that follow. It was expected that the LPSSiC system would be similar to the yttria-stabilized zirconia (Chapter 5) but with a grain boundary content of ~ 10 volume %. However, it will be shown that this is not true and that for the samples investigated, all the contributions resolved are due to the multi-component grain boundary/binder phase. This is in contrast to the conclusion of other authors, such as Schroeder et al.²⁹ and Volz et al.³⁰,

who attribute the contributions to the impedance spectra as being due to the silicon carbide grains and the grain boundary phase.

7.2 Results and Discussion

7.2.1 Composition and Microstructure

Figure 7.1 shows scanning electron micrographs of two hot pressed (HP) samples LPSSiC-HP1 and LPSSiC-HP3. It can be seen in the micrographs that the ceramic consists of silicon carbide grains (black) coated by the binder phase (white). Of the samples investigated, the hot pressed samples have the largest binder content $\sim 12\%$ and the smallest average grain size.

An SEM micrograph of the gas pressure sintered (GPS) sample LPSSiC-GPS1 is shown in Figure 7.2. The GPS samples have a larger average grain size and lower binder content ($\lesssim 10\%$) than the HP samples.

Figure 7.3 shows SEM micrographs of two heat treated hot pressed (HTHP) samples LPSSiC-HTHP1 and LPSSiC-HTHP5. Of the samples studied, the HTHP samples have the largest average grain sizes. The samples have a binder content of $\lesssim 10\%$.

The crystalline components of the binder phases, the SiC content and the average grain size of some of the samples investigated are given in Table 7.1. The composition was investigated using x-ray spectroscopy and therefore only the crystalline constituents of the binder phase could be detected. Going from the HP to HTHP samples, the grain size increases while the grain boundary phase content $\sim (100 - \text{SiC content})$ decreases. Note that there was $\sim 1\%$ SiO_2 on the surfaces of the original silicon carbide powder particles. The binder phase of the HP samples, with the exception of LPSSiC-HP1, mainly consist of silicates ($\text{Y}_\alpha\text{Si}_\beta\text{O}_\gamma$) together with yttrium aluminum garnet (YAG) in LPSSiC-HP2 and LPSSiC-HP3 and alumina (Al_2O_3) in the sample LPSSiC-HP5. The binder phase in the GPS samples consists mainly of YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$) and other aluminates ($\text{Y}_\alpha\text{Al}_\beta\text{O}_\gamma$). The binder phase in the

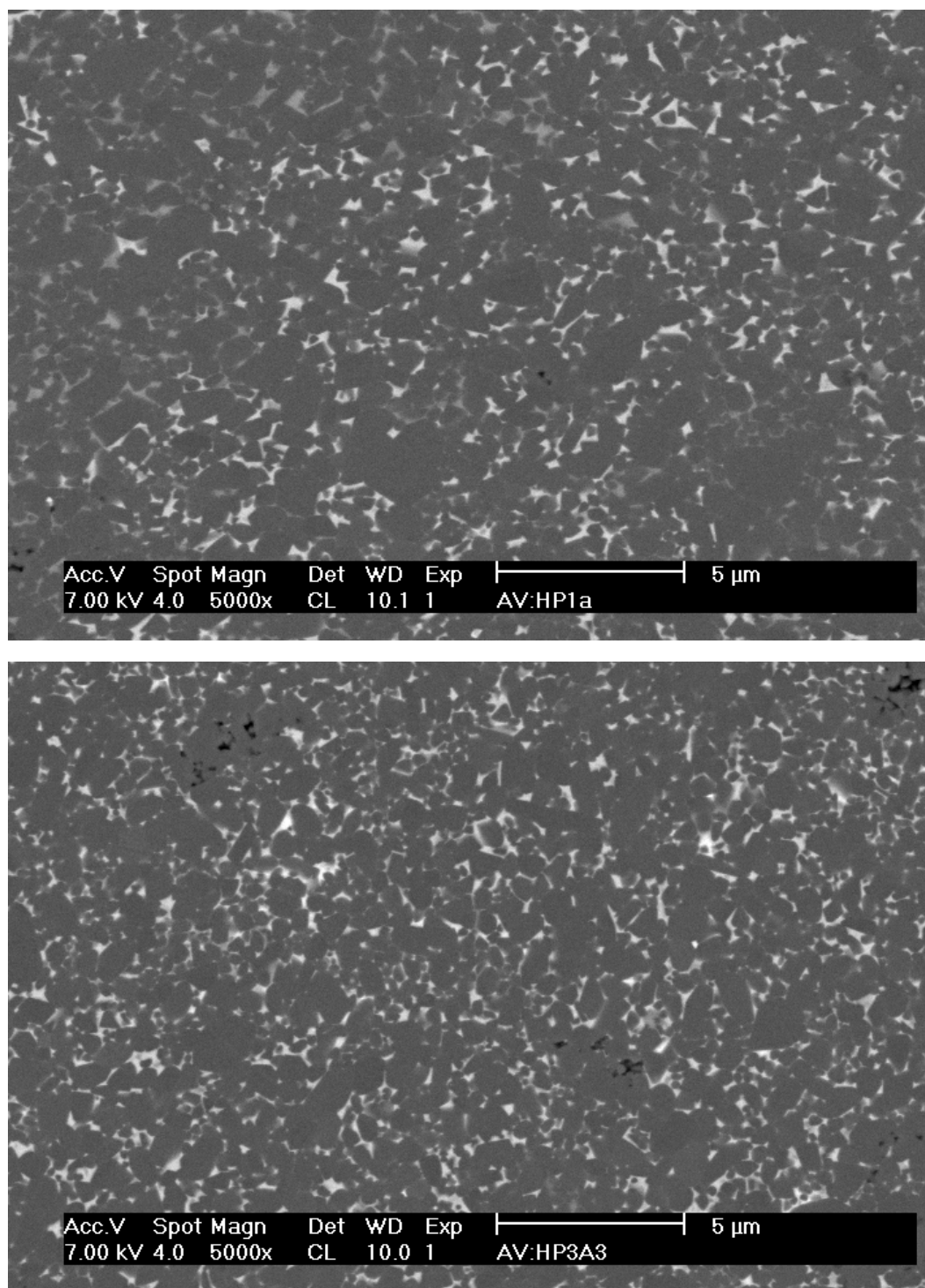


Figure 7.1: Scanning electron micrographs of the hot pressed samples LPSSiC-HP1 and LPSSiC-HP3. (Micrographs courtesy of Mrs A. Can).

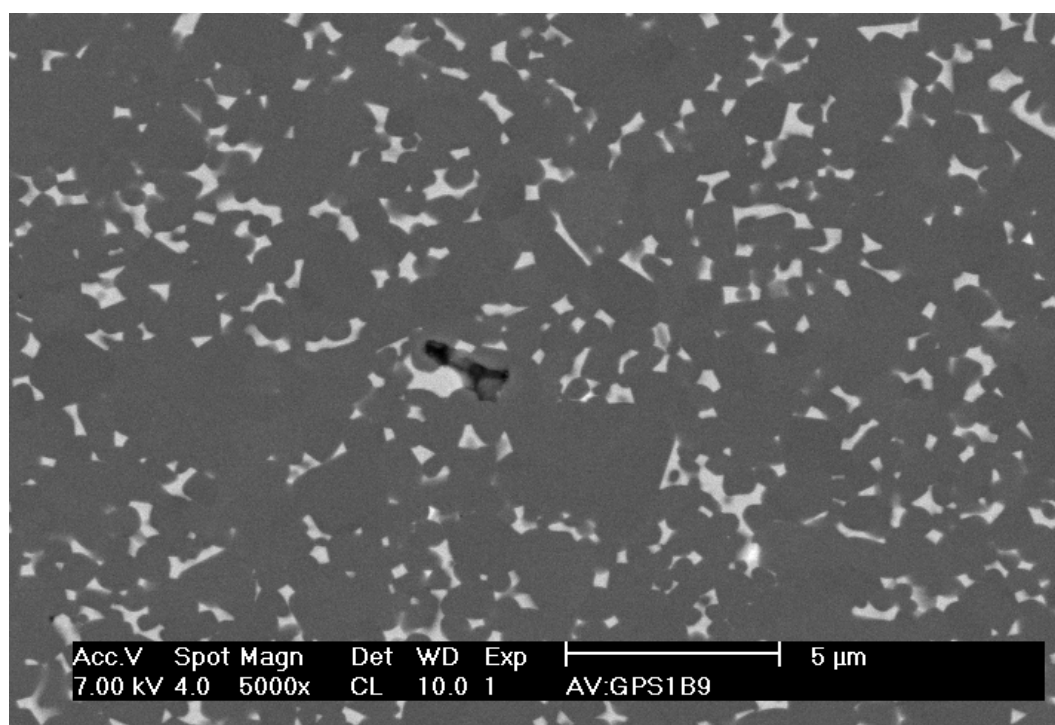


Figure 7.2: Scanning electron micrograph of a gas pressure sintered sample, LPSSiC-GPS1. (Micrograph courtesy of Mrs A. Can).

Table 7.1: The composition of some of the liquid-phase-sintered silicon carbide samples studied. The composition of the sample LPSSiC-HX was not measured. However, the sintering additives did not include any alumina (see Table 2.5), therefore ruling out the presence of YAG or aluminates. (Data courtesy of Mrs A. Can).

Sample Name	Grain boundary composition (% binder phase)	SiC Content (%)	Av. Grain Size (μm)
LPSSiC-HP1	YAG(6.5)	89.41	1.01 ± 0.42
LPSSiC-HP2	YAG(3.9) + Y_2SiO_5 (5.3)	87.66	0.92 ± 0.39
LPSSiC-HP3	YAG(5.6) + $\beta Y_2Si_2O_7$ (4.5)	88.60	0.93 ± 0.39
LPSSiC-HP4	Y_2SiO_5 (9.2)	86.99	0.92 ± 0.39
LPSSiC-HP5	Al_2O_3 (6.3) + $\beta Y_2Si_2O_7$ (3.3)	94.03	1.32 ± 0.56
LPSSiC-GPS1	YAG(9.1)	90.38	2.13 ± 0.85
LPSSiC-GPS2	$Y_4Al_2O_9$ (8.1) + $YAlO_3$ (2.0) + YAG(0.2)	-	-
LPSSiC-GPS3	YAG(5.7) + $Y_4Al_2O_9$ (4.0)	89.21	1.90 ± 0.94
LPSSiC-GPS5	YAG(6.0) + Al_2O_3 (2.7)	93.82	3.24 ± 1.8
LPSSiC-HTHP1	-	90.31	2.86 ± 1.69
LPSSiC-HTHP3	YAG(3.3) + $YAlO_3$ (7.7)	-	-
LPSSiC-HTHP5	YAG(6.3)	93.68	4.17 ± 2.39

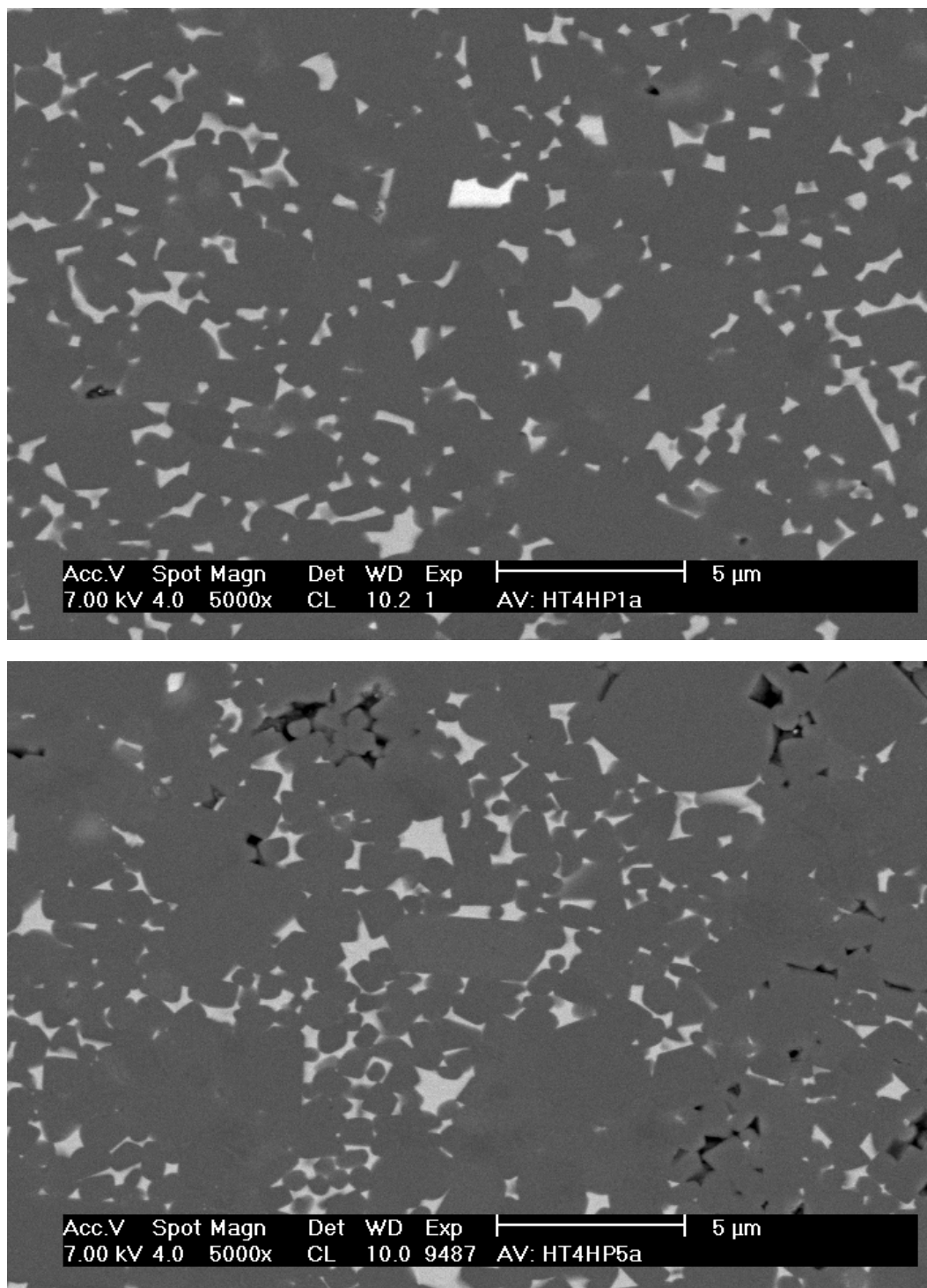


Figure 7.3: Scanning electron micrographs of the heat treated hot pressed samples LPSSiC-HTHP1 and LPSSiC-HTHP4. (Micrographs courtesy of Mrs A. Can).

HTHP samples is mainly YAG and other aluminates. The mechanisms for the formation and change on the binder constituents are described in detail in Can⁸⁴.

Table 7.2: Silicon carbide polytype content (%) of some of the LPSSiC samples (Data courtesy of Mrs A. Can).

Sample Name	6H SiC	4H SiC	15R SiC	3C SiC
LPSSiC-HP1	71.7 ± 1.7	9.7 ± 1.2	9.2 ± 1.1	2.8 ± 1.2
LPSSiC-HP2	68.6 ± 1.4	9.3 ± 1.1	10.4 ± 1.1	2.4 ± 1.2
LPSSiC-HP3	68.9 ± 0.8	7.6 ± 0.8	13.4 ± 1.0	
LPSSiC-HP4	67.3 ± 1.6	11.6 ± 1.2	8.4 ± 1.2	3.5 ± 1.3
LPSSiC-HP5	62.9 ± 3.3	4.0 ± 1.5	5.9 ± 1.8	17.5 ± 2.6
LPSSiC-GPS1	67.6 ± 1.6	10.1 ± 1.1	8.0 ± 1.1	5.2 ± 1.2
LPSSiC-GPS2	65.0 ± 1.0	11.1 ± 0.9	11.4 ± 1.0	2.2 ± 0.8
LPSSiC-GPS3	64.8 ± 1.3	11.6 ± 1.2	9.2 ± 1.2	4.9 ± 1.0
LPSSiC-GPS5	69.9 ± 1.4	6.8 ± 0.9	11.8 ± 1.1	2.8 ± 1.1
LPSSiC-HTHP3	59.6 ± 1.7	15.1 ± 1.7	12.9 ± 1.9	1.4 ± 0.2

Rietveld analysis results, Table 7.2, show the major polytypes (different crystal structures) constituting the SiC grains in several of the samples. It is not expected that the differences in the grain composition will be a factor in explaining the differences in the properties of the polycrystalline materials as all the polytypes are wide band gap semiconductors with energy gaps greater than 1 eV [Persson and Lindefelt¹⁴², Weingärtner et al.¹⁴³ and the references therein].

7.2.2 Impedance data validation

As a first step to analyzing ac conductivity data, as described in Section 2.6.1, it must be proven to be valid and consistent. Therefore, the results for the data validation step of two samples are presented here, before the detailed discussion of all the results in the sections that follow. Figure 7.4 shows two sets of experimental imaginary impedance data and the imaginary impedance calculated using the K-K transform of the experimental real impedance data. Within the accuracy of the numerical integration techniques, the experimental and the calculated data are in agreement. Similar results are obtained for

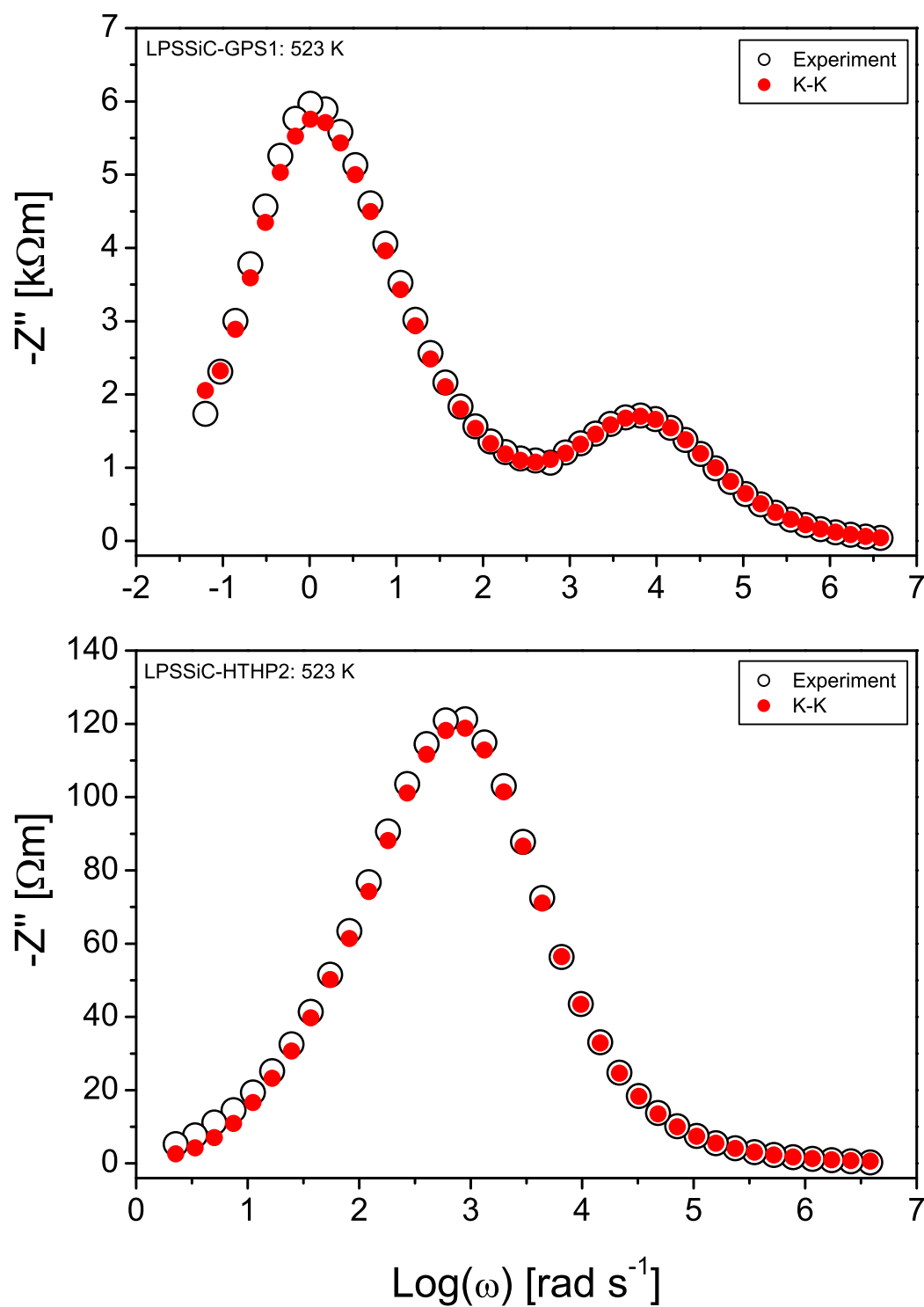


Figure 7.4: The experimental imaginary impedance data and values calculated from the K-K transform of the real impedance data for two LPSSiC at 300 °C, plotted as functions of $\log(\omega)$. Similar results are obtained for other samples and at other temperatures.

other samples and at other temperatures, thereby confirming the validity of the experimental data.

7.2.3 The frequency dependence of the electrical properties of the LPSSiC samples

The frequency dependence of the real dielectric constant and the real conductivity of various LPSSiC samples at 100 °C and 330 °C is shown in Figures 7.5 and 7.6 respectively. From this data, the samples can be classified into three groupings, labeled *A*, *B* and *C* in the figures. The groups will be analyzed in detail starting later in this section. Due to the large differences in the conductivities of the three groups of samples, the properties at different temperatures will be discussed.

Figure 7.7 shows the normalized imaginary impedances of several LPSSiC samples at 100 and 330 °C. It can be seen in this figure that there is a wide distribution of characteristic frequencies (relaxation times) and it is generally difficult to identify common constituents based on this data, as was done for the yttria-stabilized zirconia and the polyester-resin/silicon composites (Chapters 5 and 6). However, it can be observed, particularly at 100 °C (Figure 7.7, top), that the dominant peaks of the HTHP samples and the peaks at the highest frequencies for GPS samples are in a common frequency range. This is still true for both at 330 °C in Figure 7.7 but in this case there is no clear separation of the peaks.

For clarity, Figure 7.8 shows the frequency dependence of the dielectric constants and the conductivities of the **hot pressed (HP)** samples in **group A**, as defined in Figures 7.5 and 7.6. Of the samples studied, those in group *A* were the least conducting. The group consists of the HP samples, except for the samples LPSSiC-HP1 and LPSSiC-HPX, which belong to group *B*. As can be seen in Table 7.1, the HP samples generally contained the lowest SiC content (largest binder phase content). The binder phase of the samples in the group consists mainly of silicates, some YAG in the samples LPSSiC-HP2 and LPSSiC-HP3 and alumina in the sample LPSSiC-HP5. The silicates

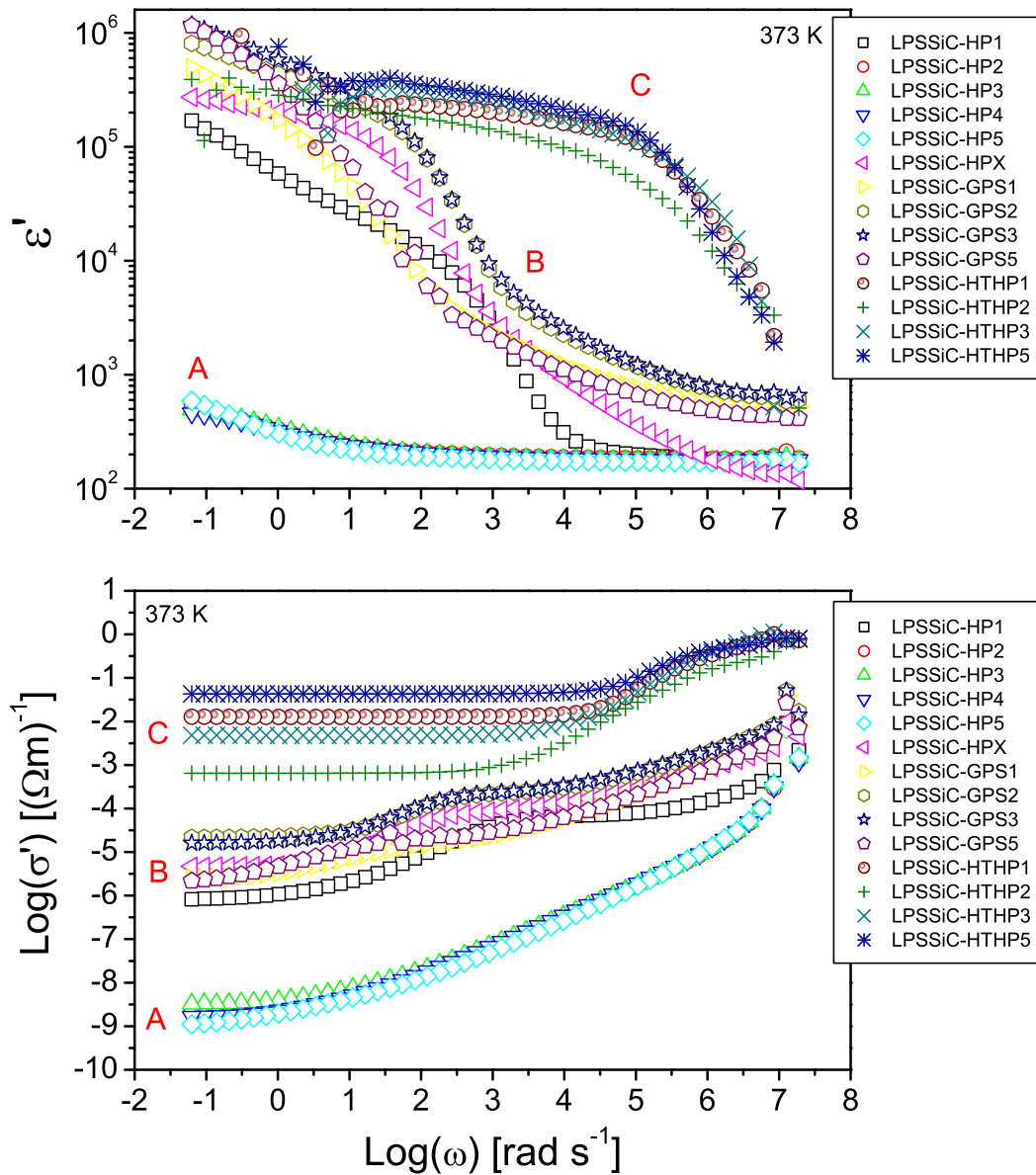


Figure 7.5: The frequency dependence of the real dielectric constants and the real conductivities, at 100 °C, of all the LPSSiC samples studied. The samples can be divided into three groups. The least conducting samples constitute group A, while the samples with intermediate conductivities are in group B and the most conducting samples make up group C.

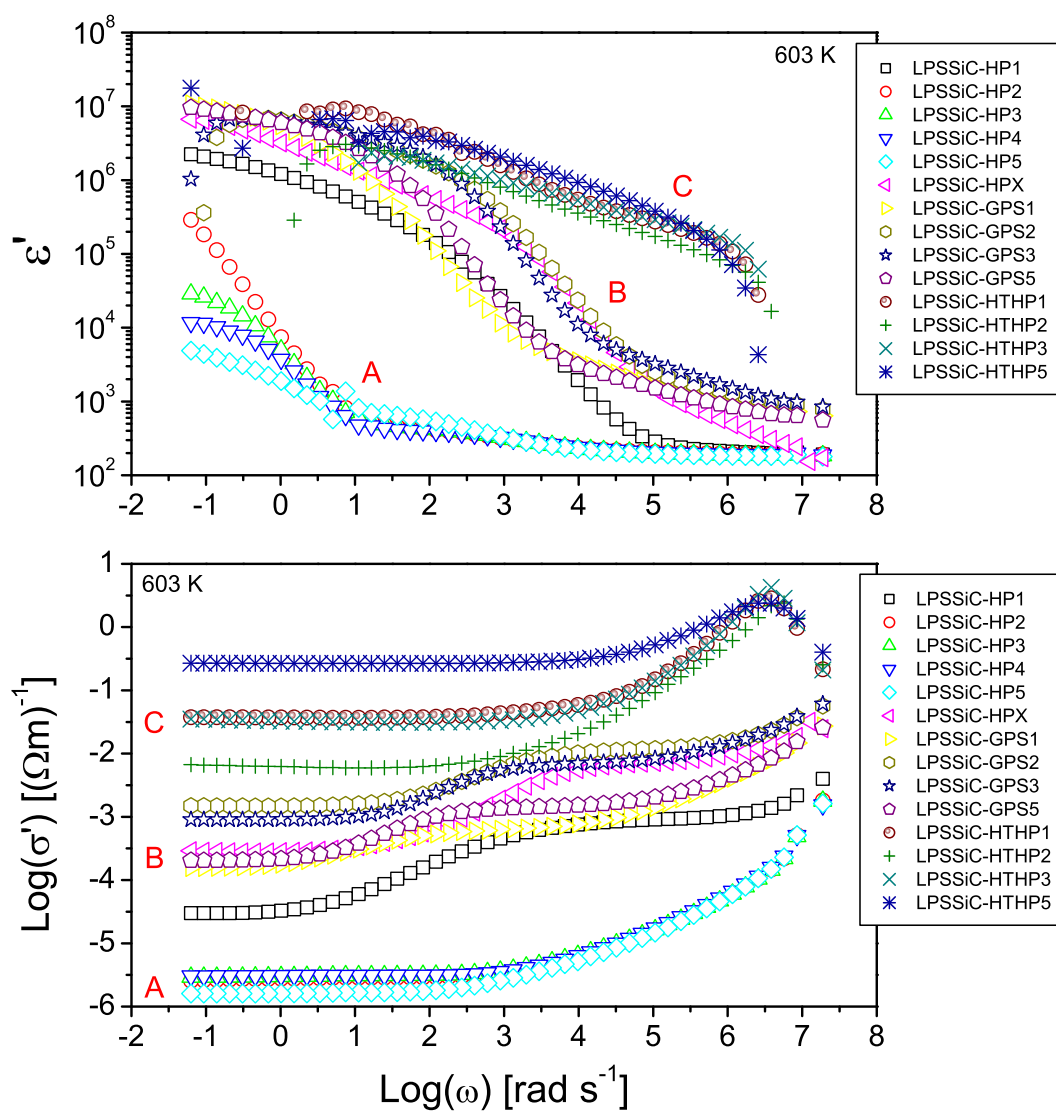


Figure 7.6: The frequency dependence of the real dielectric constants and the real conductivities, at 330 °C, of all the LPSSiC samples studied. (Note that + + + + + is in group C).

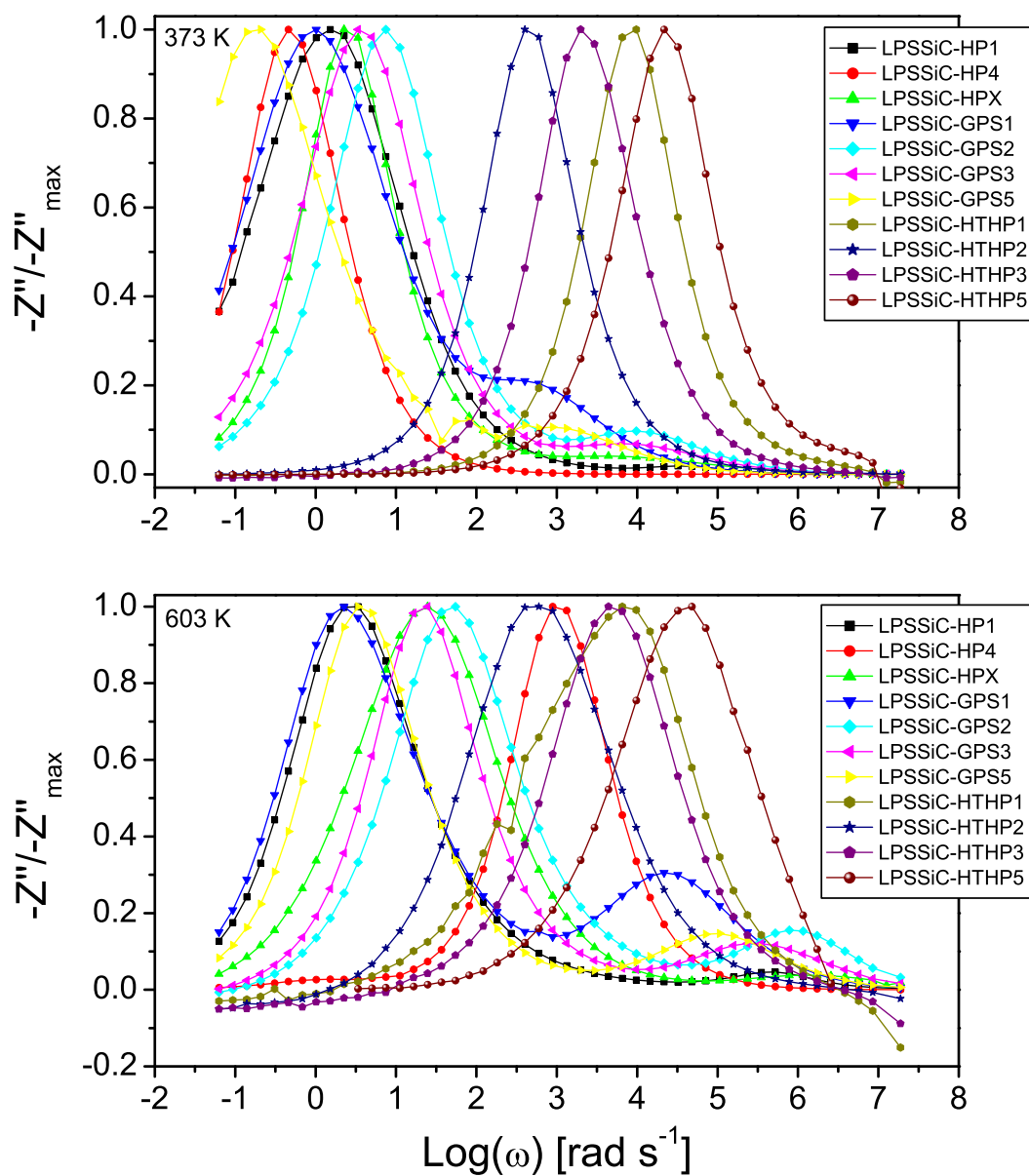


Figure 7.7: The frequency dependence of the normalized imaginary impedance of various LPSSiC samples at 100 and 330 °C. The sample groups are A: HP4, B: HP1, HPX, GPS1-5 and C: HTHP1-5.

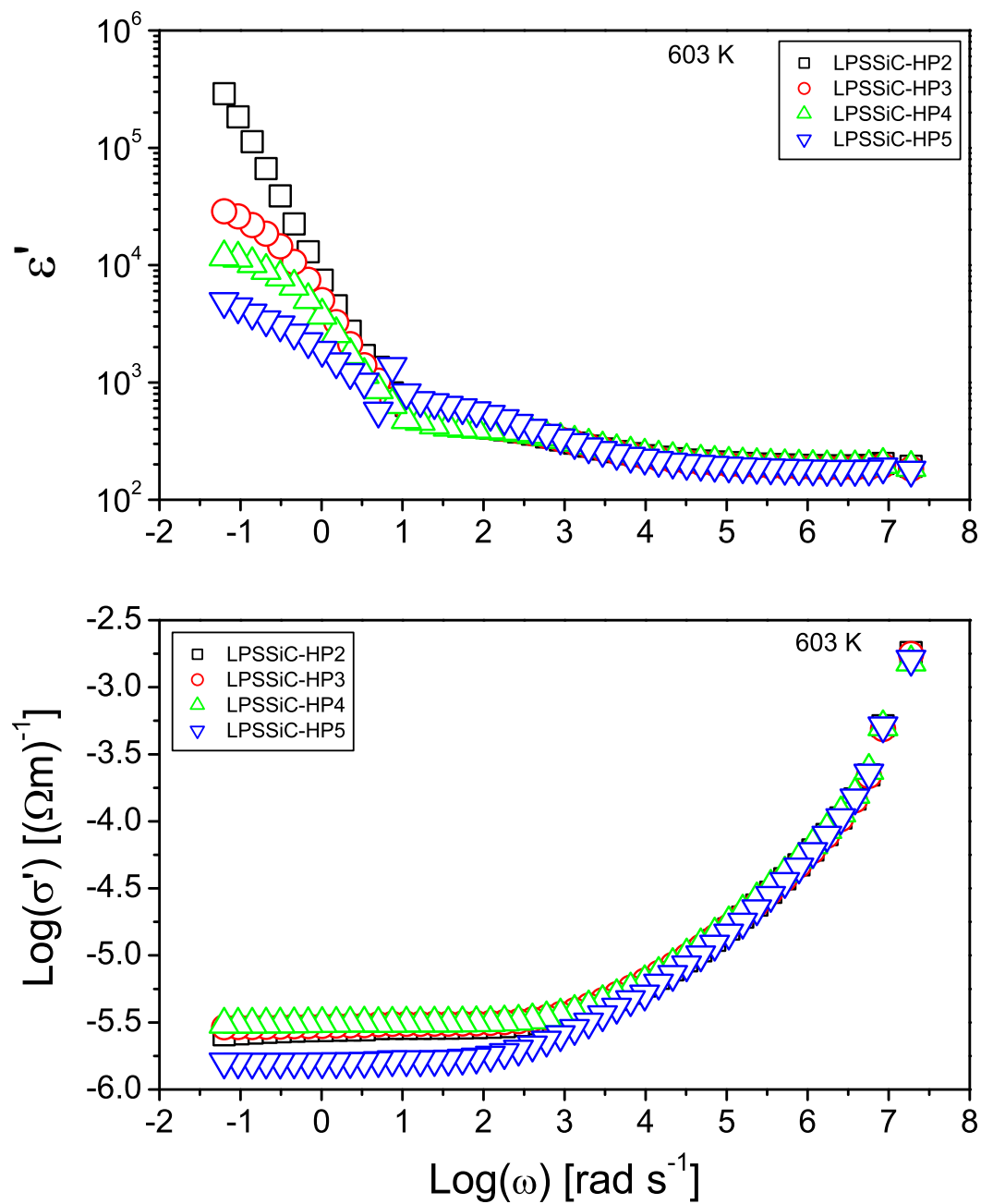


Figure 7.8: The frequency dependence of the dielectric constants and the conductivities, at 330 °C, of the hot pressed samples in group A.

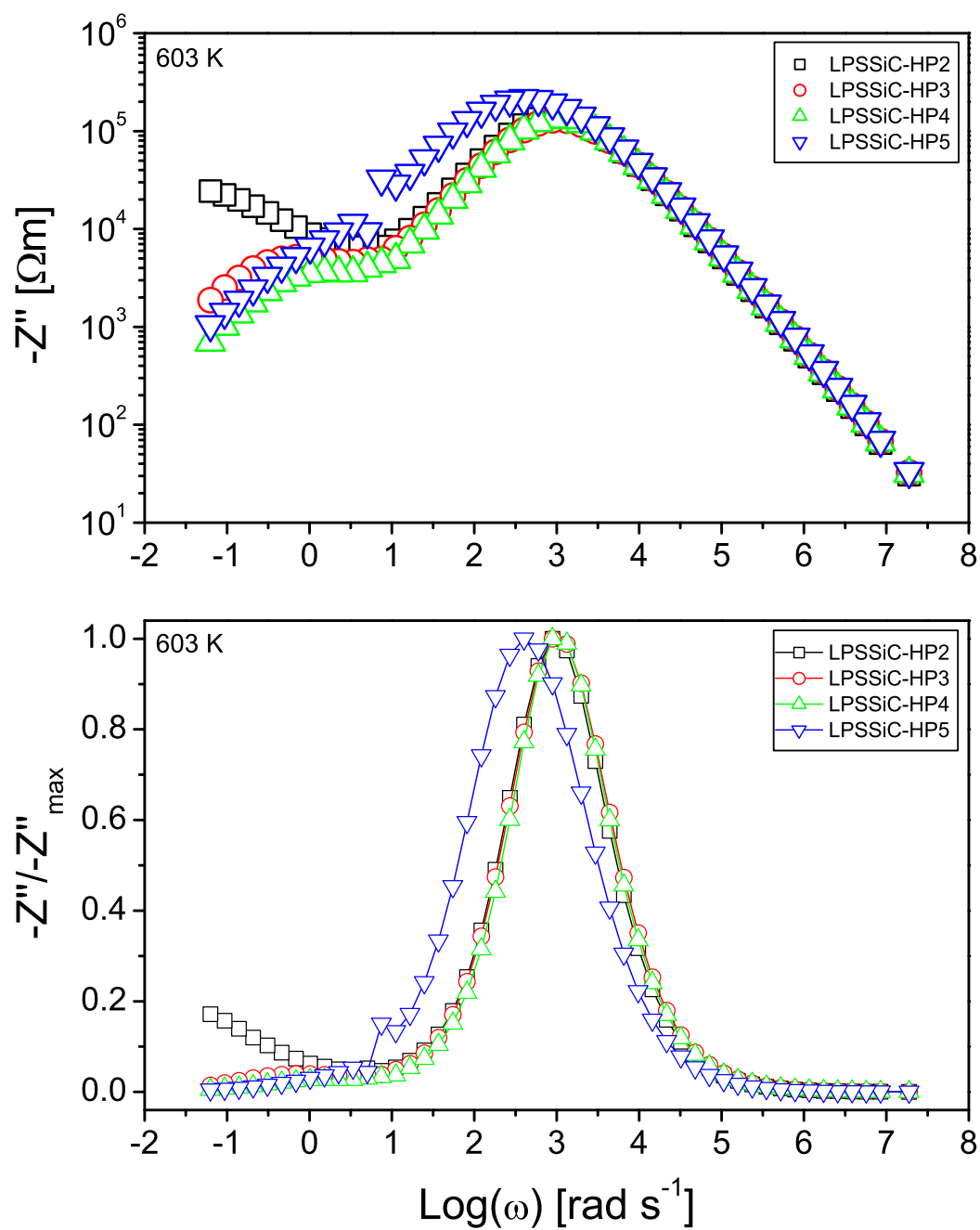


Figure 7.9: The frequency dependence of the imaginary impedances and normalized imaginary impedances, at 330 °C, of the hot pressed samples in group A.

and alumina are generally highly insulating, possibly explaining why this group contains the least conducting samples. Figure 7.9 shows the imaginary impedance (top) and normalized imaginary impedance (bottom) of the group A samples at 330 °C. The common value of $\log(\omega_p) \approx 3.3$ for all the samples except LPSSiC-HP5, indicates that their electrical properties are probably dominated by the same constituent.

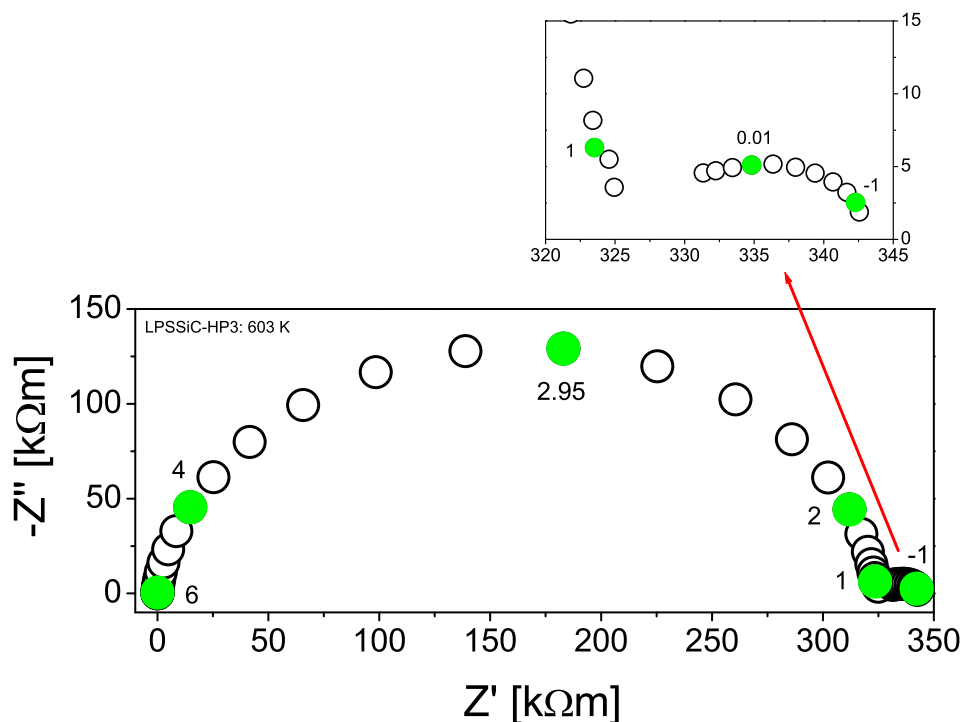


Figure 7.10: The complex impedance plane plot of the data for the sample LPSSiC-HP3 at 330 °C. The low frequency arc also shown in the insert is due to electrode effects. Key values of $\log(\omega)$ are indicated.

Figure 7.10 shows the complex impedance plane plot of the data for the sample LPSSiC-HP3 at 330 °C. Two arcs are resolved, the high frequency arc which dominates the sample impedance and whose characteristic frequency is that common to the HP samples in group A (Figure 7.9) and a smaller arc at low frequencies (high impedance). The low frequency arc is not clearly resolved in 4-probe ac measurements for the same sample and its low frequency intercept with the real axis, ($R_0 \approx 343 M\Omega m$) is greater than the directly measured dc resistance of 320 $M\Omega m$. This suggests that this arc is due to electrode polarization effects.

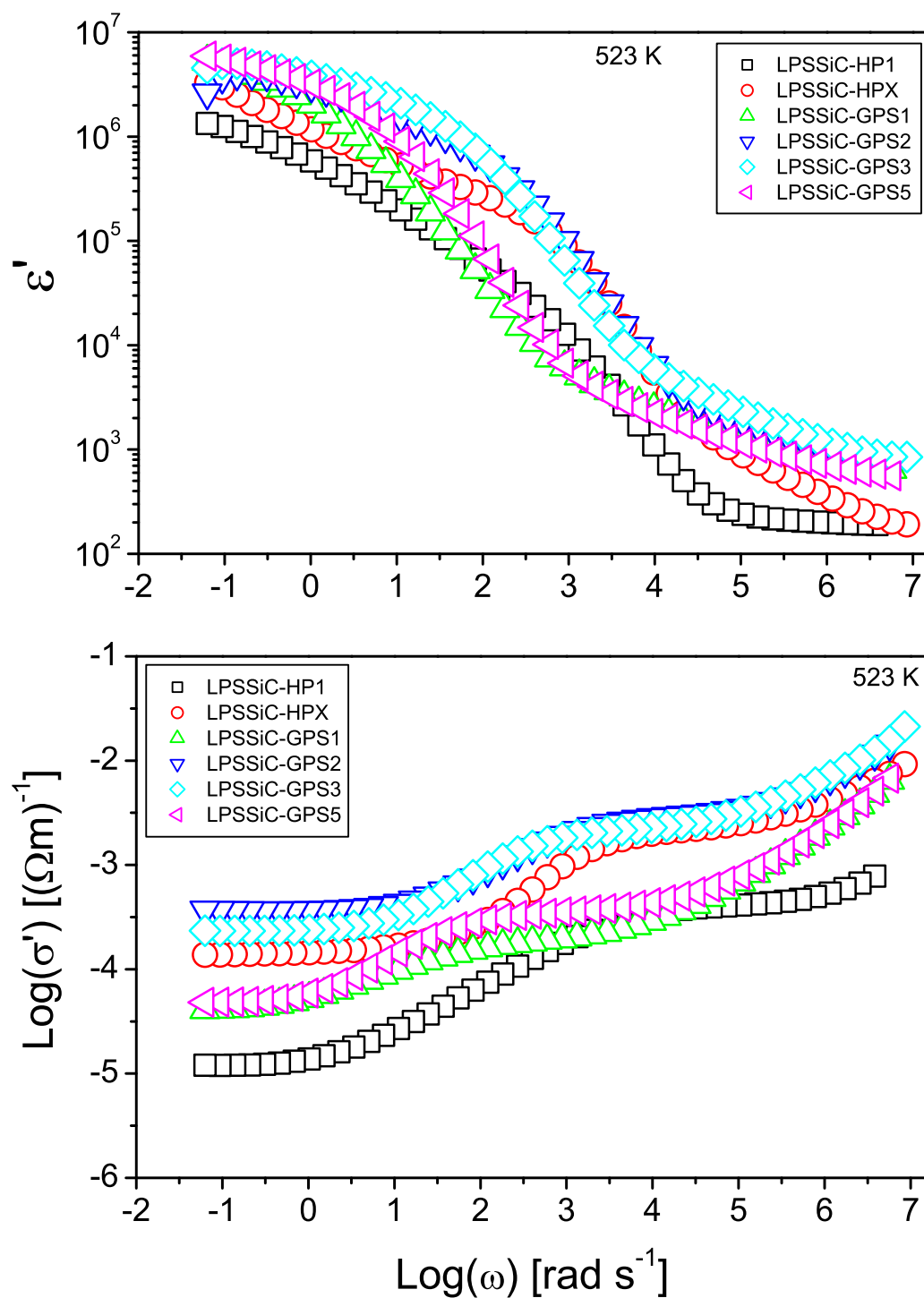


Figure 7.11: The frequency dependence of the dielectric constants and the conductivities, at 250 °C, of the hot pressed samples LPSSiC-HP1 and LPSSiC-HPX and the gas pressure sintered samples in group *B*.

The frequency dependence of the dielectric constants and the conductivities, at 250 °C, of the **gas pressure sintered (GPS)** samples as well as the **hot pressed** samples **LPSSiC-HP1** and **LPSSiC-HPX** in **group B**, as defined in Figures 7.5 and 7.6, is shown in Figure 7.11. For all the samples, the dielectric constant rises from a high frequency value of ~ 100 through a shoulder at intermediate frequencies to a high frequency value $> 10^6$ at the lowest frequencies. The conductivity Figure 7.11 (bottom) drops from its high frequency value, through a shoulder at intermediate frequencies and levels off at low frequencies. The shape of the dielectric constant and conductivity curves are typical of two (or more) component composites (recall the discussion in preceding chapters).

The imaginary impedance and normalized imaginary impedance plots in Figure 7.12 confirm that there are at least two contributions to all the sample impedances, resulting in the two distinct peaks. Unlike for the HP samples, discussed earlier in this section, where the peaks clearly coincide, there is a wide spread in the positions of the peaks due to the GPS samples. It is not possible to clearly identify constituents common to some or all of the samples, from this data.

The complex impedance plane representation of the data for the sample LPSSiC-GPS3 at 250 °C is shown in Figure 7.13. Two arcs can clearly be seen in the figure. Similar plots, clearly showing two contributions, are obtained for all the samples in group B.

Figure 7.14 shows the frequency dependence of the dielectric constants and the conductivities, at 100 °C, of the **heat treated hot pressed (HTHP)** samples in **group C**, as defined in Figures 7.5 and 7.6. The dielectric constants of these samples rise from high frequency values which can not be deduced from the measured data in Figure 7.14 (top), to what appear to be low frequency plateaux. Note that the high frequency properties were not clearly resolved at any of temperatures where measurements were conducted. Therefore the data at 100 °C has been presented, as it highlights the intermediate frequency features that are well resolved. It can be seen in

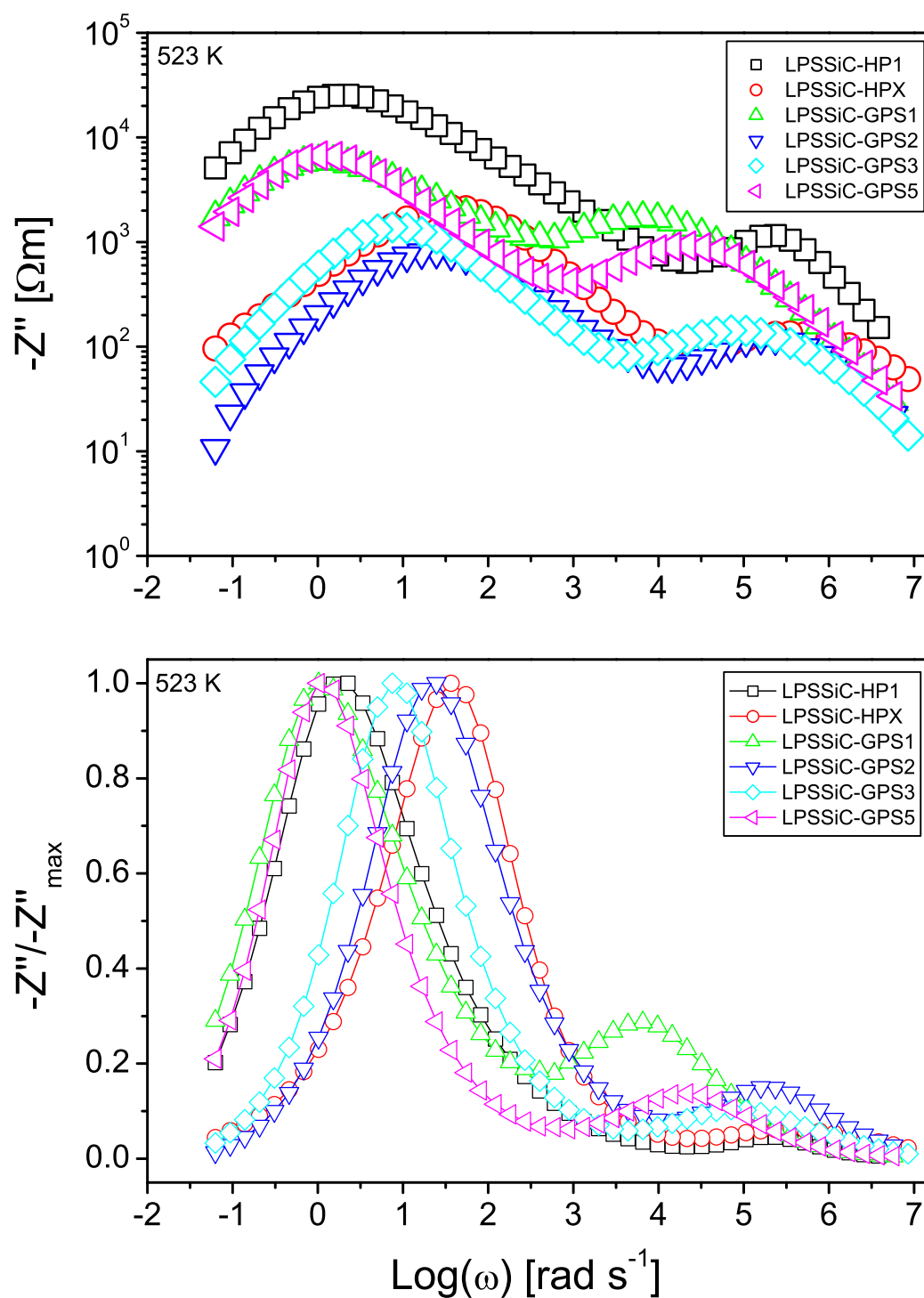


Figure 7.12: The frequency dependence of the imaginary impedances and the normalized imaginary impedances, at 250 °C, of the hot pressed samples LPSSiC-HP1 and LPSSiC-HPX and the gas pressure sintered samples in group *B*.

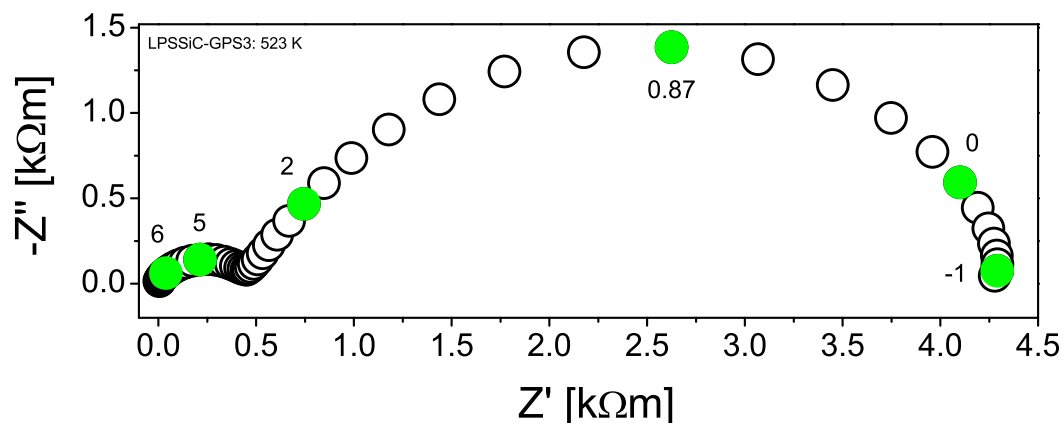


Figure 7.13: Complex impedance plane plot of the data for the sample LPSSiC-GPS3 at 250 °C. Two arcs are clearly observed. Key values of $\log(\omega)$ are indicated.

the conductivity curves, Figure 7.14 (bottom) that there is possibly a high frequency contribution which is not fully resolved.

The frequency dependence of the imaginary impedances and normalized imaginary impedances, at 100 °C, of the group *C* samples is shown in Figure 7.15. It can be seen in the figures that again there is a wide range of characteristic frequencies for a the component giving rise to the peak at intermediate frequencies, which is the only one clearly resolved. The complex impedance plane plot of the data for the sample LPSSiC-HTHP1 at 100 °C is shown in Figure 7.16. One arc is clearly resolved while there is some suggestions of an arc at higher frequencies. Electrode polarization effects are observed at the lowest frequencies (high impedance).

The imaginary impedance and *dielectric modulus* vs $\log(\omega)$ plot, Figure 7.17, shows more clearly the that there are two contributions to the sample electrical properties in the frequency range of the measurements. However, the characteristic frequency of one of these contributions lies above the range of the measurements.

The results presented in this section will be discussed further, in Section 7.2.6, together with the temperature dependence results.

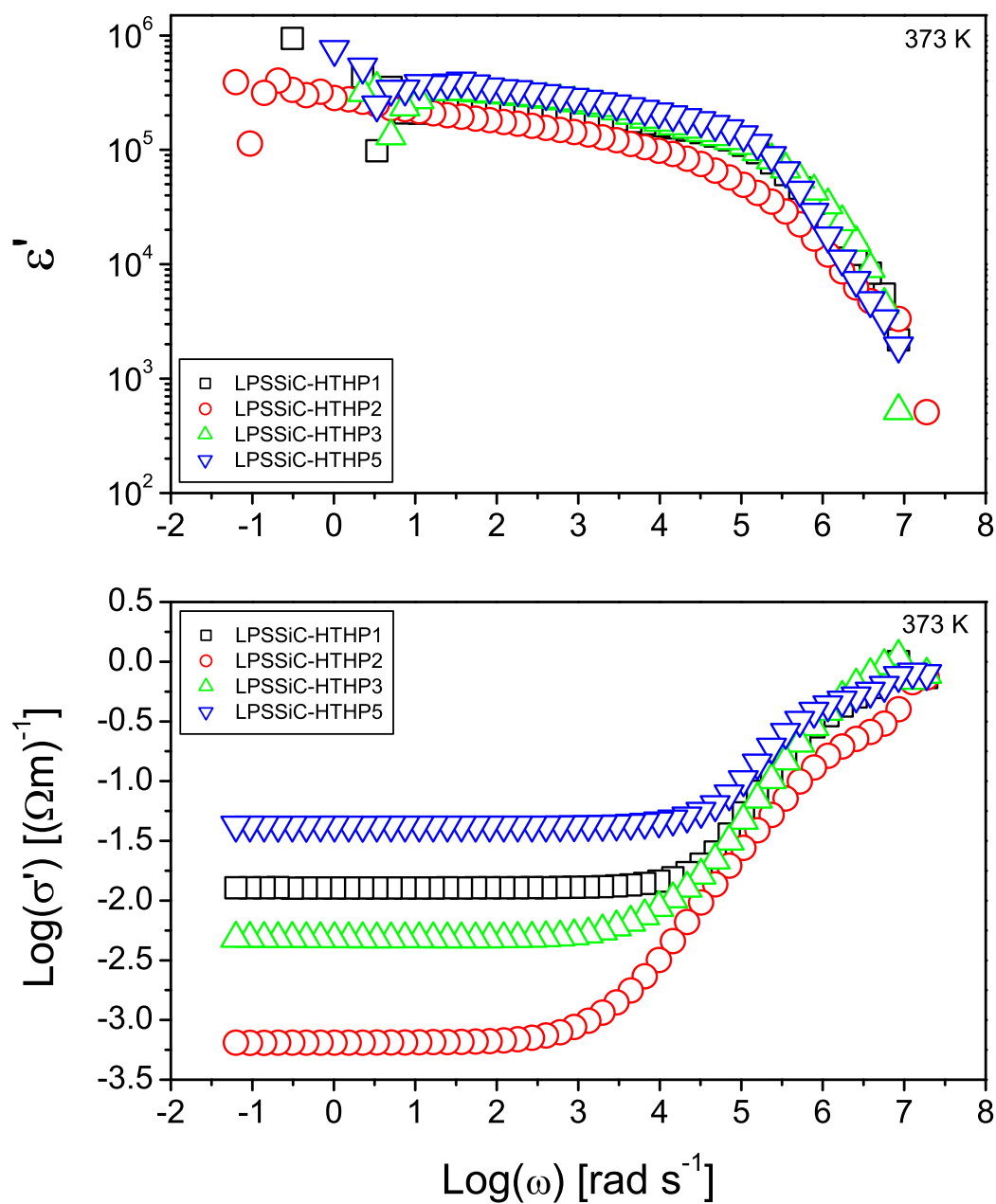


Figure 7.14: The frequency dependence of the dielectric constants and the conductivities, at 100 °C, of the HTHP samples in group *C*. Note that the conductivity data clearly indicates there is another contribution at higher frequencies. This contribution is not clearly resolved at all temperatures investigated in the current work.

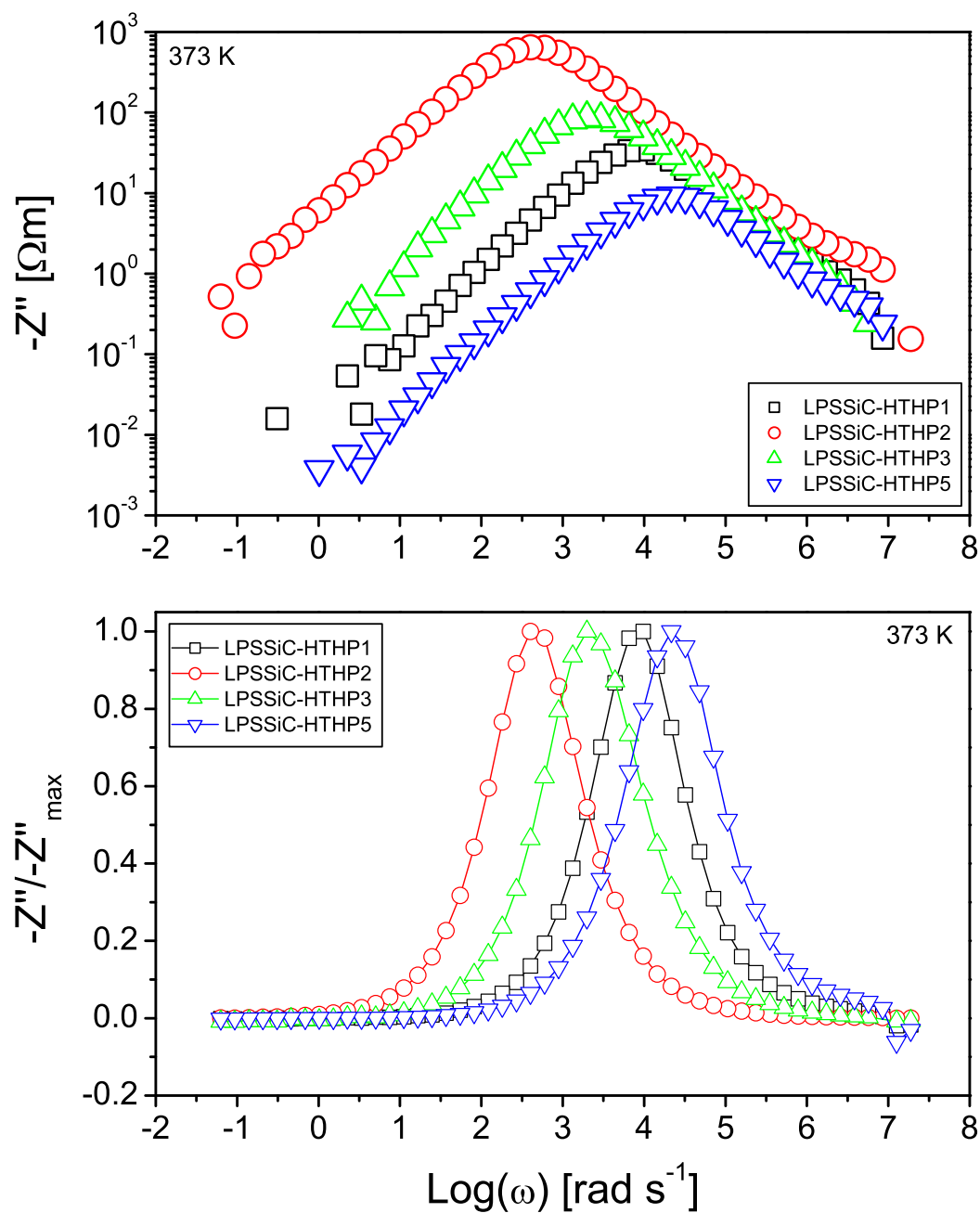


Figure 7.15: The frequency dependence of the imaginary impedances and normalized imaginary impedances, at 100 °C, of the HTHP samples in group C. Note the wide spread in the characteristic frequencies.

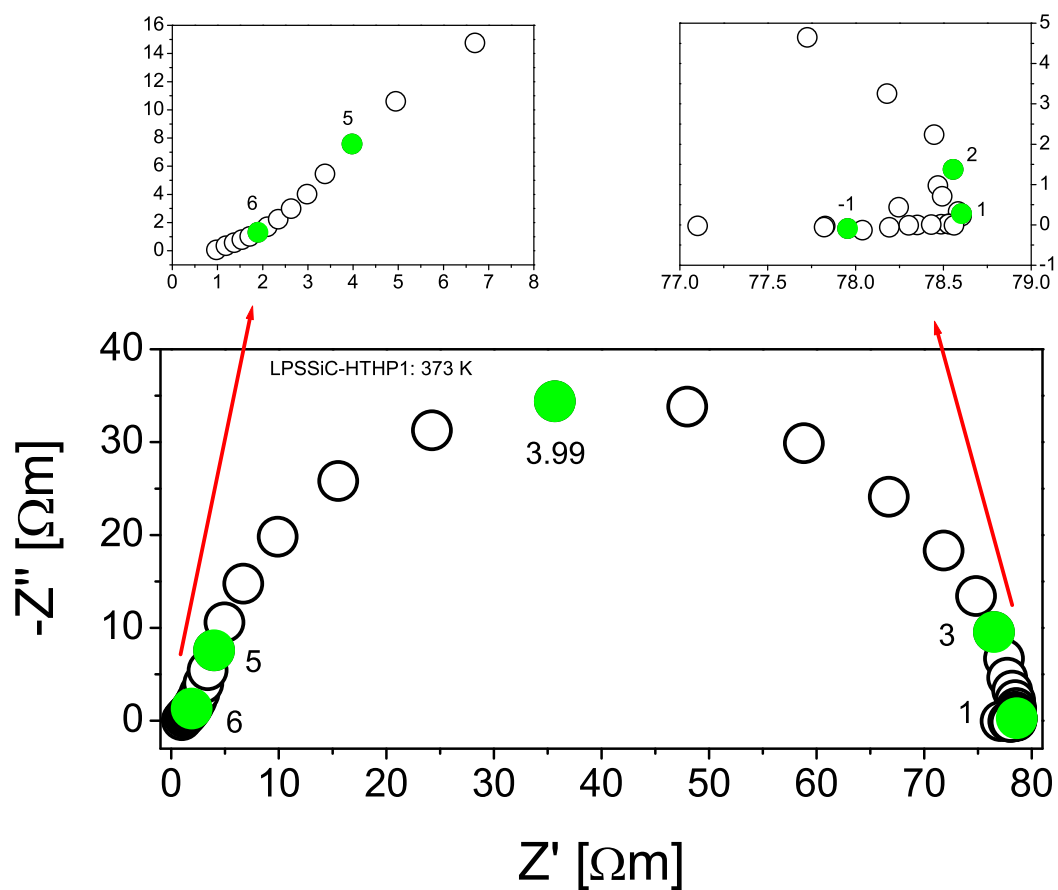


Figure 7.16: Complex impedance plane plot of the data for the sample LPSSiC-HPHT1 at 100 °C. One arc is fully resolved while there are indications of an arc at higher frequencies and electrode polarization effects at low frequencies (see inserts). Key values of $\log(\omega)$ are indicated.

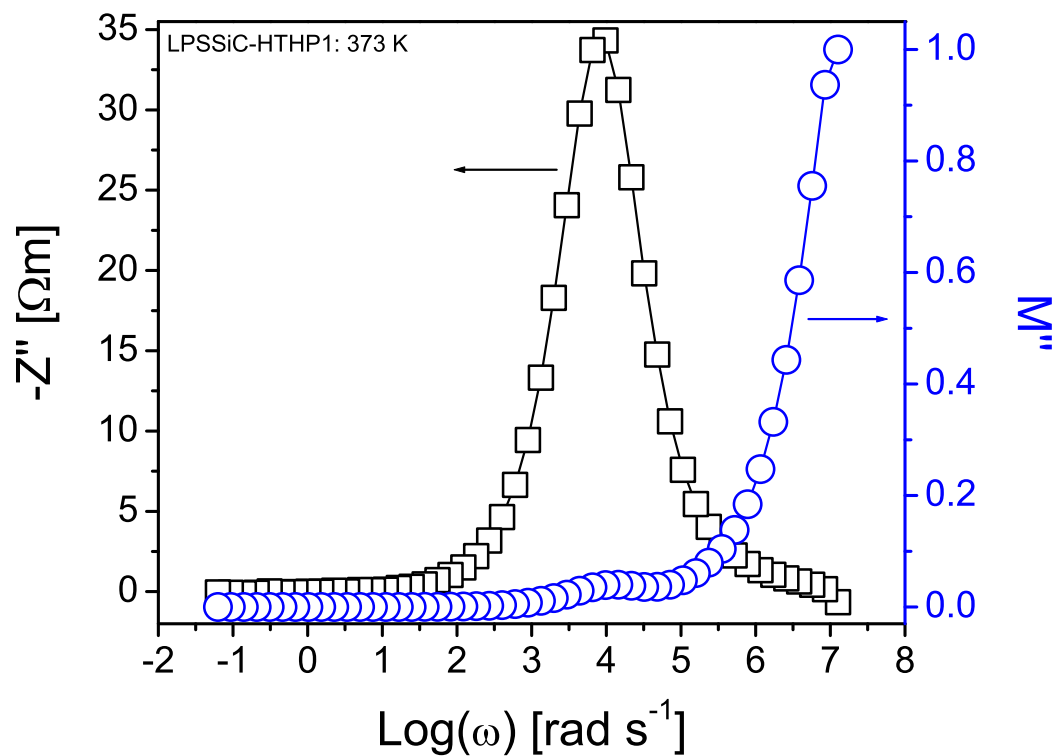


Figure 7.17: The frequency dependence of the imaginary impedance and the imaginary dielectric modulus, of the sample LPSSiC-HPHT1, at 100 °C. It can clearly be seen that there are two contributions to the sample properties in the frequency range presented, one of which can be resolved in both the impedance and dielectric modulus representation of the data ($\log(\omega_p) \approx 4$) while the other is only clearly observed in the dielectric modulus representation of the data ($\log(\omega_p) \geq 7.5$).

7.2.4 The temperature dependence of the electrical properties of the LPSSiC samples

Figure 7.18 shows the temperature dependence of the characteristic frequency (plotted as $\text{Log}(\omega_p)$ vs $100/T^{1/4}$, top) and of the “effective” dc conductivities (plotted as $\text{Ln}(\sigma_{dc}^\dagger)$ vs $100/T^{1/4}$, bottom) of the component giving the arcs at the **highest frequencies** for the samples in **group B** and those of the **very dominant component** for the samples in **groups A and C**. Note that the “effective” dc conductivities of the components ($\sigma_{dc}^\dagger$), extracted from complex impedance plane plots, are normalized to the geometric factors of the samples and not those of the components, which are not known. The discussion in this section will be in terms of these “effective” dc conductivities.

The characteristic frequencies and the dc conductivities are proportional to $1/T^{1/4}$ suggesting a variable range hopping mechanism. Recall from Section 1.5 that for variable range hopping,

$$\sigma_{dc}(\text{or } \nu_p) = \sigma_0(\text{or } \nu_0) \exp[(-T_0/T)^{1/4}], \quad (7.1)$$

where T_0 is a characteristic temperature scale [Helgren et al.⁷⁵].

It can be seen in Figure 7.18 that for the samples in group A, (LPSSiC-HP2 to LPSSiC-HP5), the characteristic frequencies and the dc conductivities of the dominant component in the different samples are tightly grouped at all temperatures. This again suggests that this component has a common constituent, in all the samples. The magnitudes of the characteristic frequencies and the dc conductivities of the component dominant at the highest frequencies in the impedance plots for the samples in group B, mostly GPS samples, which are more widely spread, at each temperature, than those of the samples in group A. The slopes are also notably different for the group B samples. This indicates different activation energies for the hopping conduction in the samples. It can also be seen, in Figure 7.18, that the magnitudes and slopes of the characteristic frequencies and the “dc” conductivities of the samples in group C show a wider spread than those of the samples in group A. From

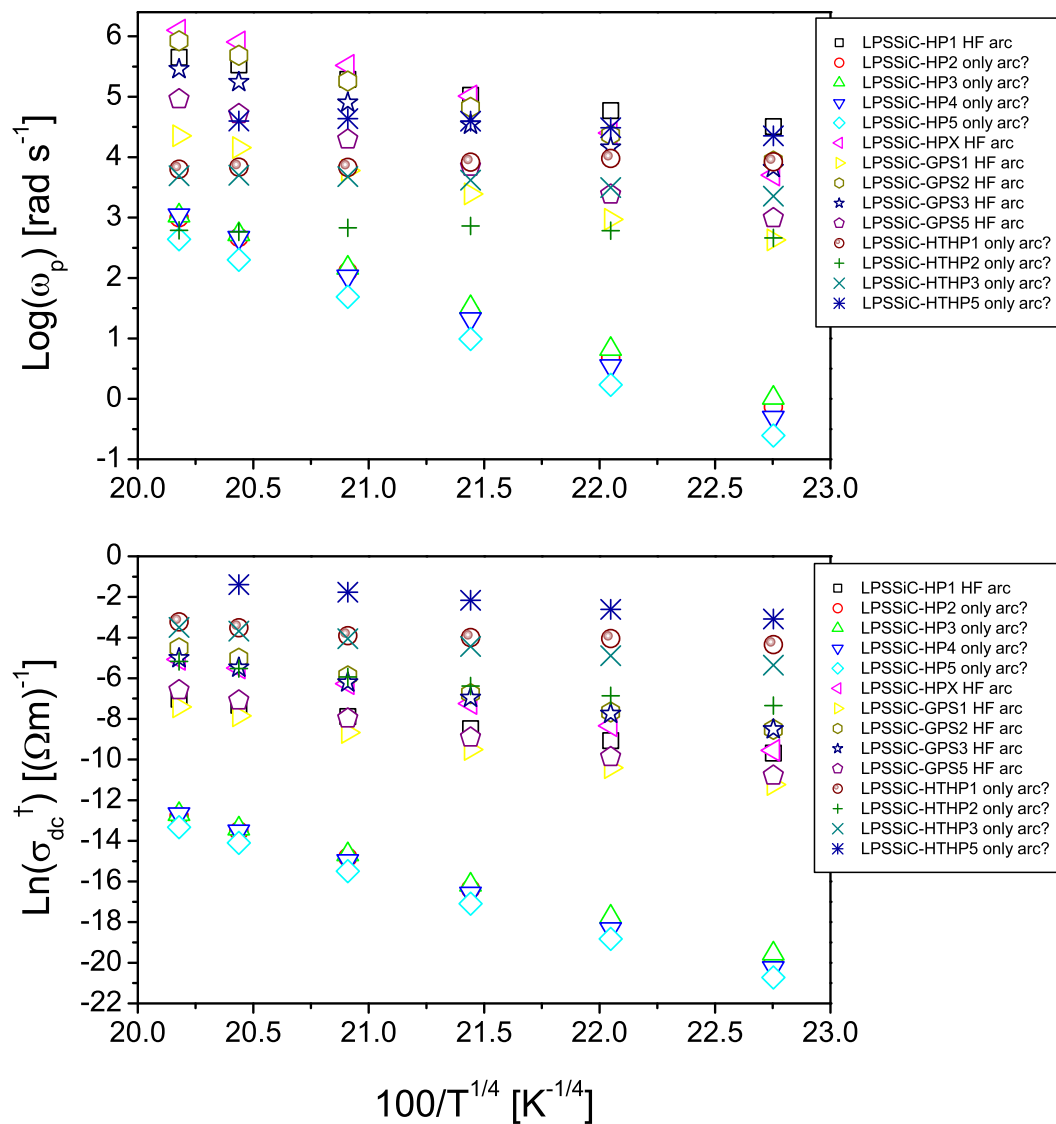


Figure 7.18: The temperature dependence of the characteristic frequencies and the dc conductivities (extracted from complex impedance plane plots) for the component giving the high frequency arc in the samples in group *B* and the dominant arc for the samples in groups *A* and *C*. The sample groups are *A*: HP2-4, *B*: HP1, HPX, GPS1-5 and *C*: HTHP1-5.

the temperature dependence data, it is not possible to clearly identify any constituents common to all or some of the samples in groups *B* or *C*.

Figure 7.19 shows the temperature dependence of the characteristic frequency and the “dc” conductivity from the **arc dominant at low frequencies**, for the samples in **group B** as well as, again, the **very dominant arc** for the samples in **groups A and C**. The latter are again plotted to check if there are any correlations between the properties of the component dominant at low frequencies in the samples in group *B* and the very dominant component in groups *A* and *C*. With the exception of the very dominant components for the HP samples in group *A*, the characteristic frequencies and the dc conductivities of the components of the different samples are all rather widely spread, at each temperature.

Figure 7.20 shows the experimental peak frequency and conductivity data for the component giving the arc at high frequencies (top) and that giving the arc at low frequencies (bottom) for the sample LPSSiC-HPX. This sample was chosen as it contained no aluminum (as alumina) which is a known p-type dopant of silicon carbide [Cree¹⁴⁴, Straubinger et al.¹⁴⁵]. The variable range model, Equation (7.1) is seen to fit the data for both the arcs well. Similar results are obtained for all the other samples.

The best fitting parameters to Equation (7.1), for all the LPSSiC samples investigated, are shown in Tables 7.3 and 7.4.

Figure 7.21 shows the temperature dependence of the “effective” dielectric constants ($\epsilon_p^\dagger$) and the depression angles, of the component giving the arc at high frequencies for the samples in group *B* and the very dominant arc for the samples in groups *A* and *C*. It must again be noted that $\epsilon^\dagger$ is normalized to the sample geometric factor and not to the dimensions of the components, such as grain boundaries, which are not known. The “effective” dielectric constants and the depression angles are both plotted against $1000/T$, a convenient and plausible way of expressing the temperature dependence. It can be seen in Figure 7.21 (top) that the dominant components of the HTHP samples in group *C* have dielectric constants that are significantly higher than those of

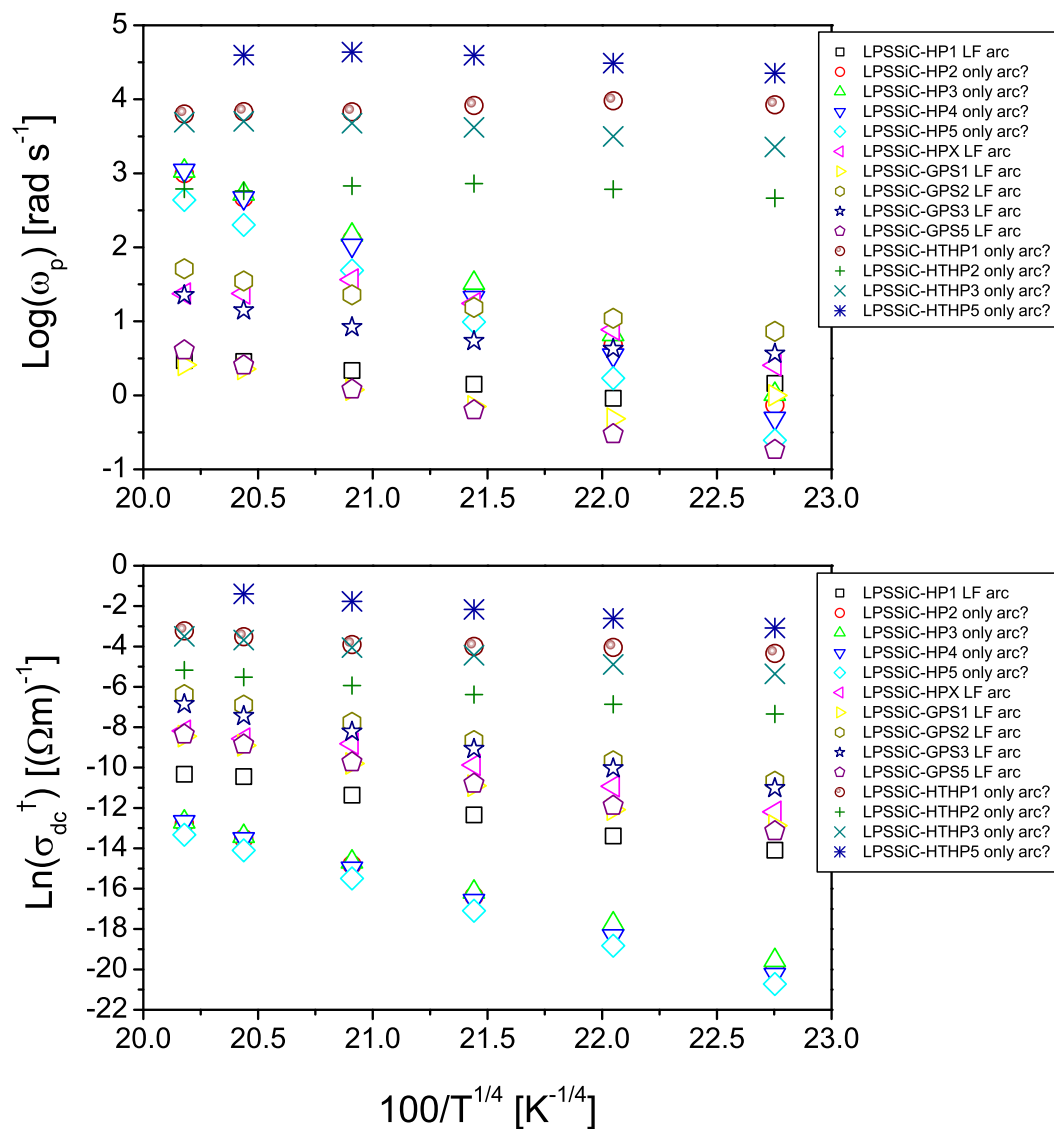


Figure 7.19: The temperature dependence of the characteristic frequencies and the “dc” conductivities (extracted from complex impedance plane plots) for the component giving the low frequency arc in the samples in group *B* and the dominant arc in groups *A* and *C*. Note that the data for the dominant component of the samples in groups *A* and *C* is re-plotted. The sample groups are *A*: HP2-4, *B*: HP1, HPX, GPS1-5 and *C*: HTHP1-5.

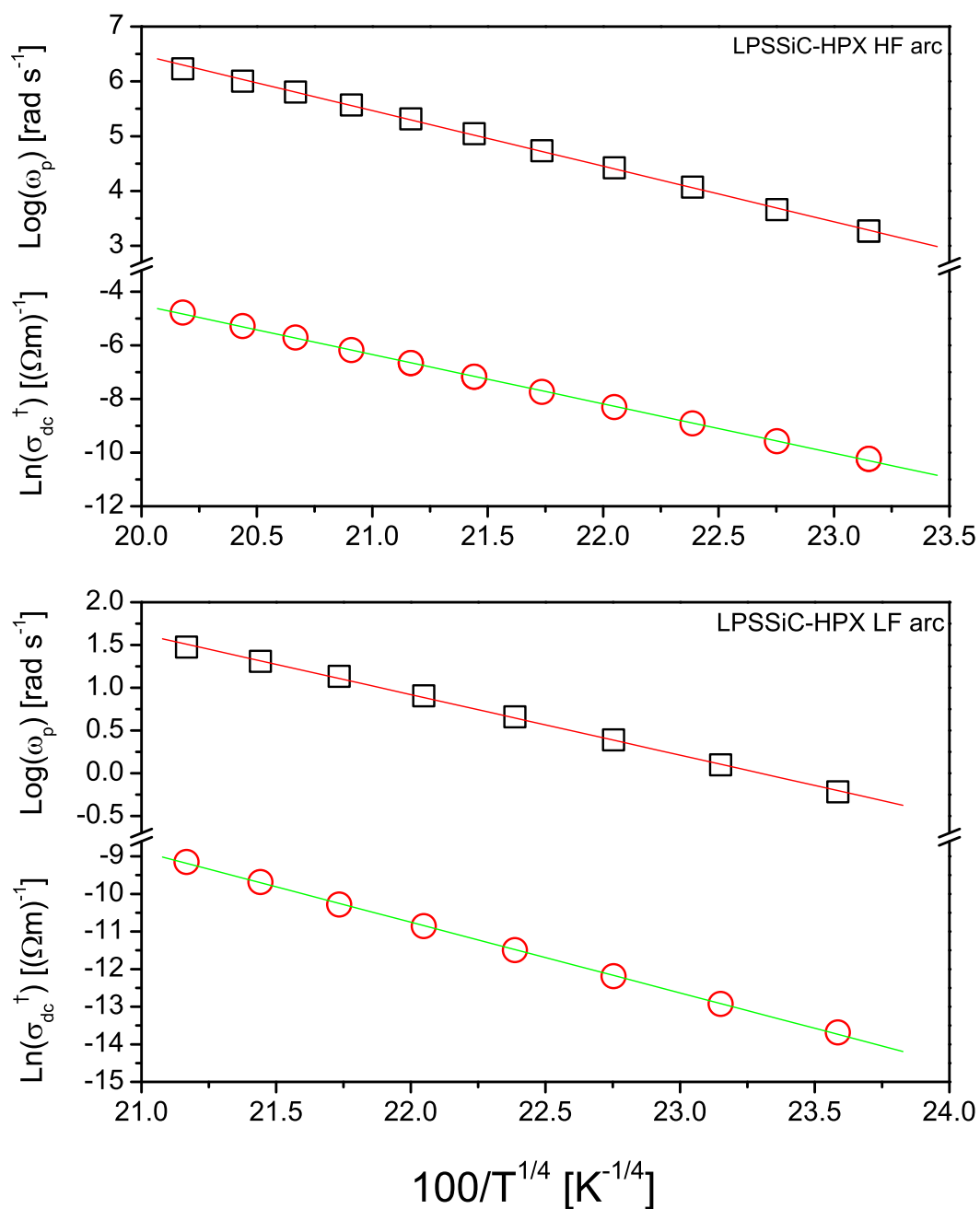


Figure 7.20: The experimental characteristic frequencies (open square) and dc conductivities (open circle) of the components giving the arc at high frequency (top) and the arc at low frequency (bottom) for the sample LPSSiC-HPX and the best fits to the variable range hopping model (solid lines). It can be seen that the model fits the data well.

Table 7.3: The parameters for variable range hopping conductivity in the LPSSiC samples I: dc conductivity parameters.

Sample Name	High Frequency/Only arc		Low Frequency arc	
	$\sigma_0 (\Omega m)^{-1}$	T_0 (K)	$\sigma_0 (\Omega m)^{-1}$	T_0 (K)
HP1	$(11 \pm 5) \times 10^5$	$(12 \pm 2) \times 10^7$	$(3 \pm 2) \times 10^{10}$	$(8 \pm 2) \times 10^8$
HP2	$(5 \pm 2) \times 10^{18}$	$(59 \pm 3) \times 10^8$	-	-
HP3	$(8 \pm 3) \times 10^{17}$	$(51 \pm 2) \times 10^8$	-	-
HP4	$(18 \pm 8) \times 10^{19}$	$(75 \pm 6) \times 10^8$	-	-
HP5	$(3 \pm 1) \times 10^{19}$	$(70 \pm 4) \times 10^8$	-	-
HPX	$(13 \pm 2) \times 10^{13}$	$(117 \pm 2) \times 10^7$	$(17 \pm 2) \times 10^{12}$	$(123 \pm 2) \times 10^7$
GPS1	$(8 \pm 4) \times 10^9$	$(51 \pm 9) \times 10^7$	$(3 \pm 1) \times 10^{13}$	$(15 \pm 1) \times 10^8$
GPS2	$(5 \pm 2) \times 10^{11}$	$(6 \pm 1) \times 10^8$	$(7 \pm 3) \times 10^{11}$	$(8 \pm 1) \times 10^8$
GPS3	$(5 \pm 2) \times 10^9$	$(34 \pm 6) \times 10^7$	$(5 \pm 2) \times 10^{11}$	$(8 \pm 1) \times 10^8$
GPS5	$(3 \pm 2) \times 10^{11}$	$(7 \pm 1) \times 10^8$	$(5 \pm 2) \times 10^{12}$	$(122 \pm 6) \times 10^7$
HTHP1	74 ± 40	$2 \pm 1 \times 10^6$	-	-
HTHP2	$(10 \pm 4) \times 10^4$	$(48 \pm 9) \times 10^6$	-	-
HTHP3	$(7 \pm 2) \times 10^4$	$(28 \pm 2) \times 10^6$	-	-
HTHP5	$(5 \pm 2) \times 10^5$	$(26 \pm 4) \times 10^6$	-	-

Table 7.4: The parameters for variable range hopping conductivity in the LPSSiC samples II: characteristic frequency parameters.

Sample Name	High Frequency/Only arc		Low Frequency arc	
	ν_0 (Hz)	T_0 (K)	ν_0 (Hz)	T_0 (K)
HP1	$(8 \pm 3) \times 10^{13}$	$(12 \pm 2) \times 10^7$	$(3 \pm 1) \times 10^5$	$(18 \pm 6) \times 10^6$
HP2	$(7 \pm 2) \times 10^{26}$	$(63 \pm 3) \times 10^8$	-	-
HP3	$(8 \pm 2) \times 10^{25}$	$(53 \pm 2) \times 10^8$	-	-
HP4	$(3 \pm 1) \times 10^{28}$	$(81 \pm 5) \times 10^8$	-	-
HP5	$(2 \pm 1) \times 10^{27}$	$(72 \pm 4) \times 10^8$	-	-
HPX	$(10 \pm 2) \times 10^{25}$	$(299 \pm 8) \times 10^7$	$(7 \pm 3) \times 10^{12}$	$(32 \pm 5) \times 10^7$
GPS1	$(2 \pm 1) \times 10^{17}$	$(6 \pm 1) \times 10^8$	$(8 \pm 4) \times 10^7$	$(8 \pm 3) \times 10^7$
GPS2	$(6 \pm 3) \times 10^{20}$	$(10 \pm 2) \times 10^8$	$(17 \pm 8) \times 10^6$	$(28 \pm 9) \times 10^6$
GPS3	$(3 \pm 2) \times 10^{17}$	$(47 \pm 9) \times 10^7$	$(15 \pm 7) \times 10^7$	$(6 \pm 3) \times 10^7$
GPS5	$(6 \pm 3) \times 10^{19}$	$(10 \pm 2) \times 10^8$	$(2 \pm 1) \times 10^{10}$	$(22 \pm 6) \times 10^7$
HTHP1	63 ± 30	$(4 \pm 20!) \times 10^4$	-	-
HTHP2	522 ± 300	$(4 \pm 5!) \times 10^3$	-	-
HTHP3	$(4 \pm 2) \times 10^5$	$(9 \pm 4) \times 10^5$	-	-
HTHP5	$(14 \pm 7) \times 10^6$	$(17 \pm 8) \times 10^5$	-	-

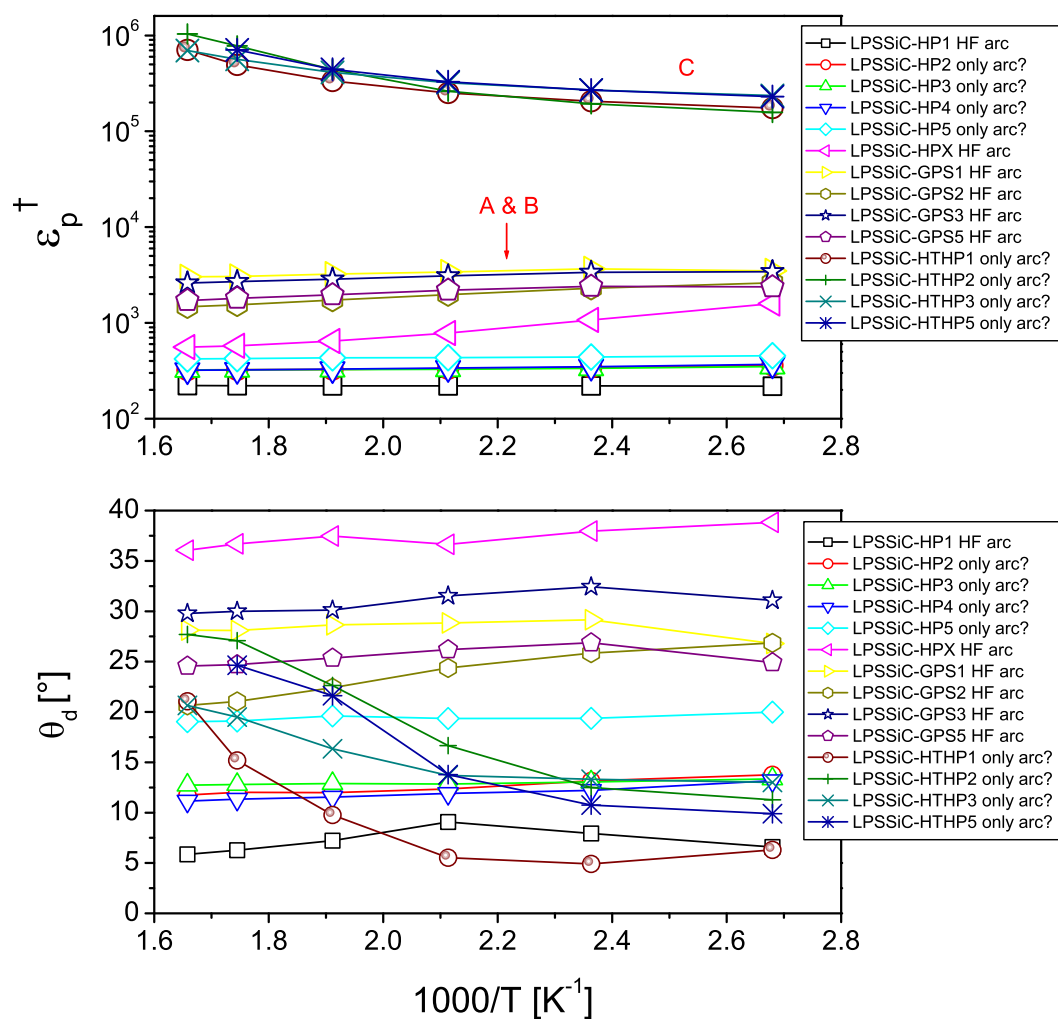


Figure 7.21: The temperature dependence of the real dielectric constants and arc depression angles of the components dominant at **high frequencies** for the LPSSiC samples giving two clearly resolved complex impedance plane arcs (group *B*), and the **very dominant component** for the samples where only one arc is observed (groups *A* and *C*).

the components dominant at high frequencies in the GPS samples and the hot pressed sample LPSSiC-HPX (all in group *B*), which are next highest. The dielectric constants of the dominant component of the HP samples, in group *A* and, somewhat surprisingly, the component dominant at high frequencies in the group *B* sample LPSSiC-HP1 are the lowest.

Figure 7.22 (bottom) shows the wide range of depression angles (θ_d) ranging from 5° to $\sim 40^\circ$ for the various samples. As discussed in Chapter 1, high values of θ_d , as observed for some of these samples, indicate a wide spread of relaxation times for the processes in the components that give rise to the arcs.

Figure 7.22 shows the temperature dependence of the “effective” dielectric constants and the depression angles for the **component dominant at low frequencies** in the samples in **group B** and those of the **very dominant component** for the samples in **groups A and C**, which are re-plotted in this figure. The dielectric constants of the components dominant at low frequencies in the *GPS* samples in group *B* are the highest. These are followed by those of the HP samples also in group *B* (LPSSiC-HP1 and LPSSiC-HPX) which are in a similar range to those of the HTHP samples in group *C*. The very dominant components of the HP samples in group *A* have the lowest “effective” dielectric constants.

Figure 7.22 (bottom) shows a fairly wide spread in depression angles centered at $\sim 15^\circ$ or so.

These results will be incorporated into a later discussion on the relationship between the electrical properties of the LPSSiC samples and their composition and microstructure (Section 7.2.6).

7.2.5 The voltage dependence of the electrical properties of the LPSSiC samples

As mentioned in the introduction to the current chapter, silicon carbide ceramics have been widely used as a varistor material. It has been suggested

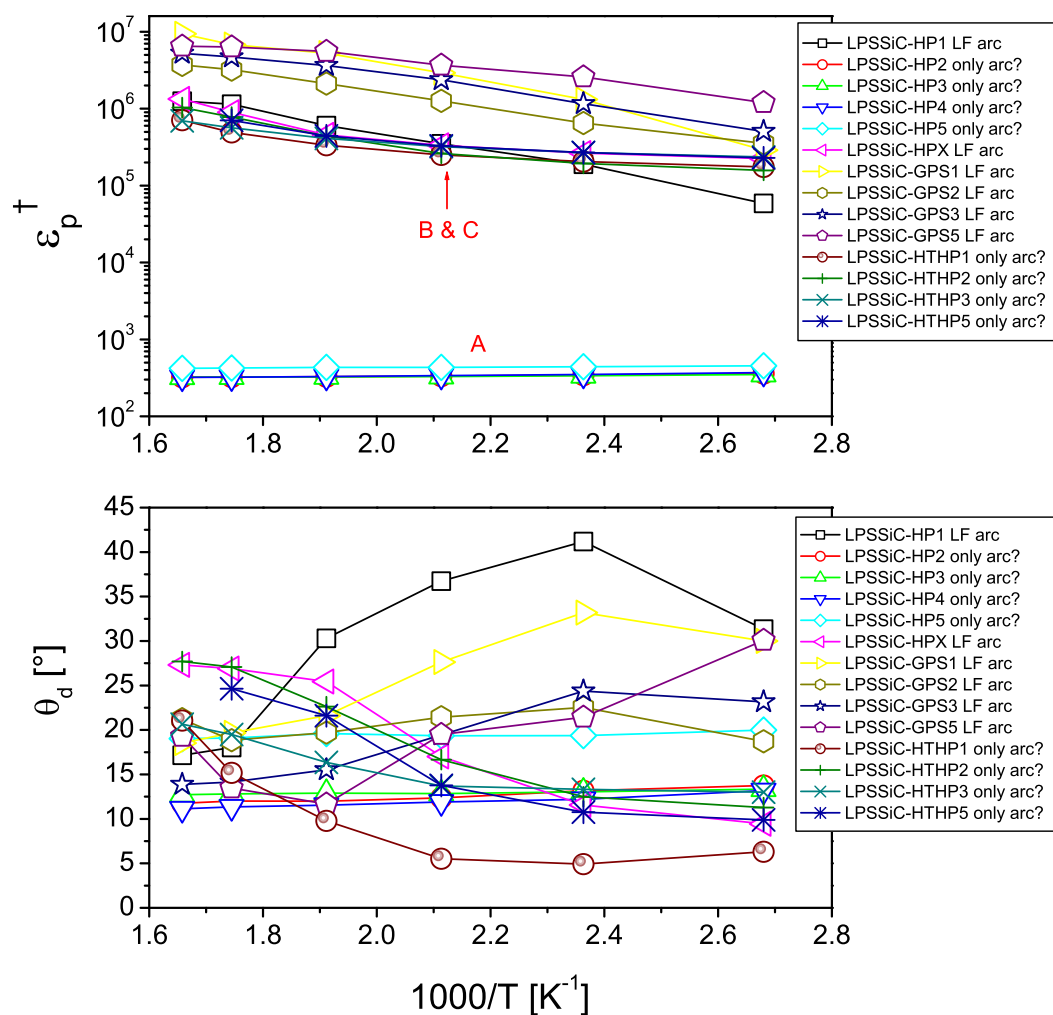


Figure 7.22: The temperature dependence of the real dielectric constants and arc depression angles of the components dominant at **low frequencies** for the LPSSiC samples giving two clearly resolved complex impedance plane arcs (group *B*), and the **very dominant** component for the samples where only one arc is fully resolved, (groups *A* and *C*).

by some authors [such as in Moulson and Herbert¹⁴¹] that the voltage dependent resistance in clay bonded SiC varistors is derived from the contact area between SiC grains. The electrical properties of a component of some of the LPSSiC samples investigated in the current work exhibit a reproducible excitation voltage dependence. This voltage dependence was also seen in 4 probe dc resistance measurements (not presented here), which were consistent with the 2 and 4 probe ac measurements. Therefore, it is concluded that the voltage dependence is due to the LPSSiC ceramic and *not* electrode effects [see also Mason et al.⁸⁵]. Voltage dependence is not observed in the other ceramic system investigated in this work, yttria-stabilized zirconia, except for electrode effects.

The dependence of the IS data on the sample excitation voltage is clearly illustrated, for the group *B* sample LPSSiC-GPS1 at 200 °C, in Figures 7.23 and 7.24. Figure 7.23 shows the complex impedance plane plot of the data for the sample at various excitation voltages. It can be seen in the figure that the sample resistance (intercept of the low frequency arc) decreases with increasing excitation voltage (3 V is the upper limit for the Novocontrol/Solartron dielectric measurement system). It can also be seen in the figure that the non-linearity is notable only for one of the components contributing to the sample impedance, that dominant at lower frequencies ($\log(\omega) < 2$), and is not observed in the impedance of the component dominant at higher frequencies.

Figure 7.24 shows the voltage dependence of the characteristic frequencies (plotted as $\log(\omega_p)$ vs Excitation Voltage) and the “dc” conductivities (plotted as $\ln(\sigma_{dc})$ vs Excitation Voltage) for the components dominant at low and high frequencies, obtained from same data as given in Figure 7.23. For the component dominant at high frequencies, the characteristic frequency and conductivity are virtually constant for the entire voltage range. However, for the component dominant at lower frequencies there are notable changes in the both the conductivity and the characteristic frequency, with change in the excitation voltage.

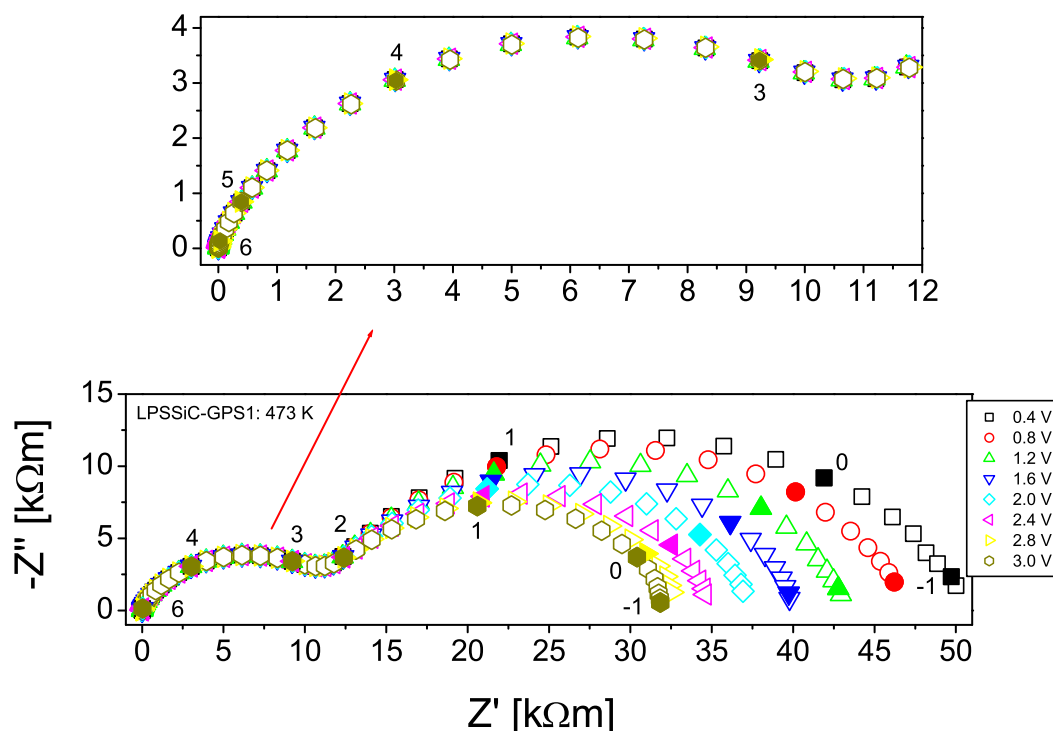


Figure 7.23: Complex impedance plane plot of data from the group *B* sample LPSSiC-GPS1, at 200 °C and various excitation voltages. Note that the impedance of the high frequency arc (insert) does not seem to exhibit this voltage dependence.

Figure 7.25 shows complex impedance plane plots of the data at 0.7 and 1.5 V, for the group *A* sample LPSSiC-HP3, which shows one dominant arc and the group *B* sample LPSSiC-GPS3, for which there are two arcs. Note that the results in Figure 7.25 are at 330 °C for the group *A* sample and ~ 27 °C for the group *B* sample and that the impedances are in the same range for both the samples, which shows that the non-linearity is a real effect and not due to instrument behavior in some particular measurement range. It can be seen in the Figure 7.25 (top) that the dominant high frequency arc for the group *A* sample (LPSSiC-HP3) does not change for the two different voltages. For the group *B* sample (LPSSiC-GPS3), there are notable changes in the dominant (low frequency) arc but no noticeable change in the arc at high frequencies. The results for the two samples, given above, are representative of those obtained from all the samples in their respective groups.

Figure 7.26 shows the complex impedance plane plot of the data for the

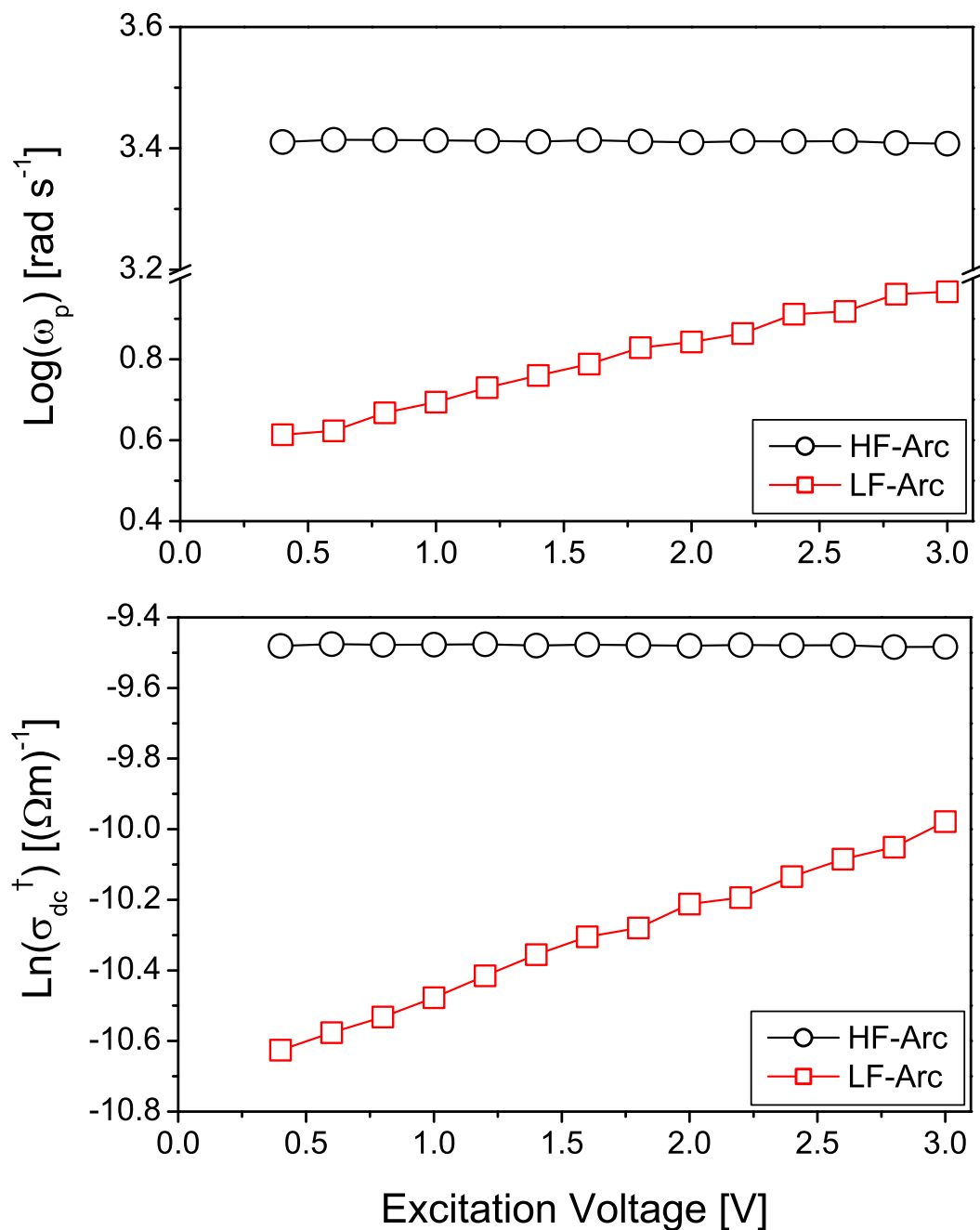


Figure 7.24: The voltage dependence of the characteristic frequencies (top) and the “dc” conductivities (bottom) of the components dominant at high and low frequencies (HF and LF respectively) for the group *B* sample LPSSiC-GPS1. Note that the high frequency component’s properties do not show any significant voltage dependence while the characteristic frequency and dc resistance of the low frequency component are strongly frequency dependent.

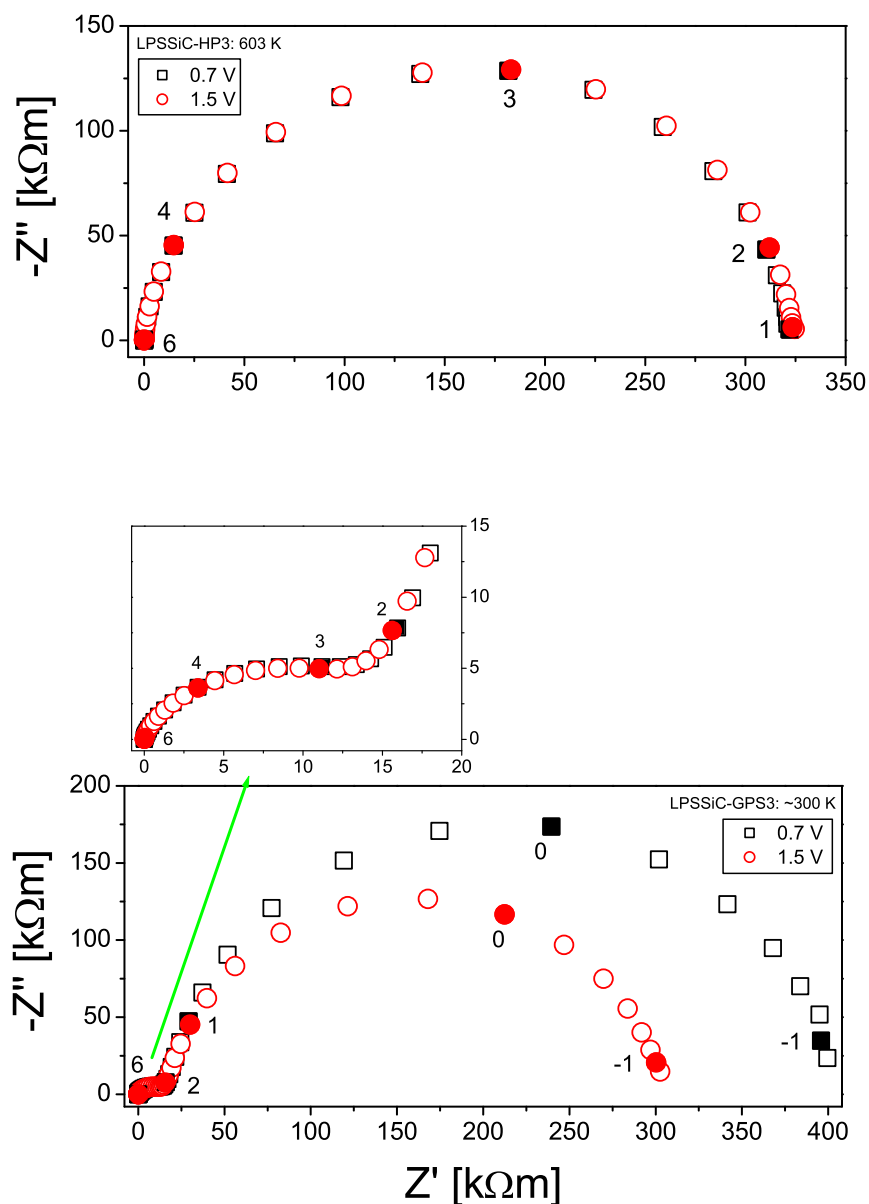


Figure 7.25: Complex impedance plane plots of the data, at 0.7 and 1.5 V, for the group *A* sample LPSSiC-HP3, at 330 °C (top) and that for the group *B* sample LPSSiC-GPS3, at $\sim 27^\circ\text{C}$ (bottom). Note that for the dominant component of the group *A* sample (top) there is no notable voltage dependence of the impedance. For the group *B* sample, the impedance of the component dominant at low frequencies is dependent on the excitation voltage while that of the component dominant at high frequencies is independent of the excitation voltage. Note that the different measurement temperatures, for the two samples, give impedances that are in the same range. Therefore, it can be seen that the non-linearity is a real sample effect and not due to instrument behavior in some particular measurement range.

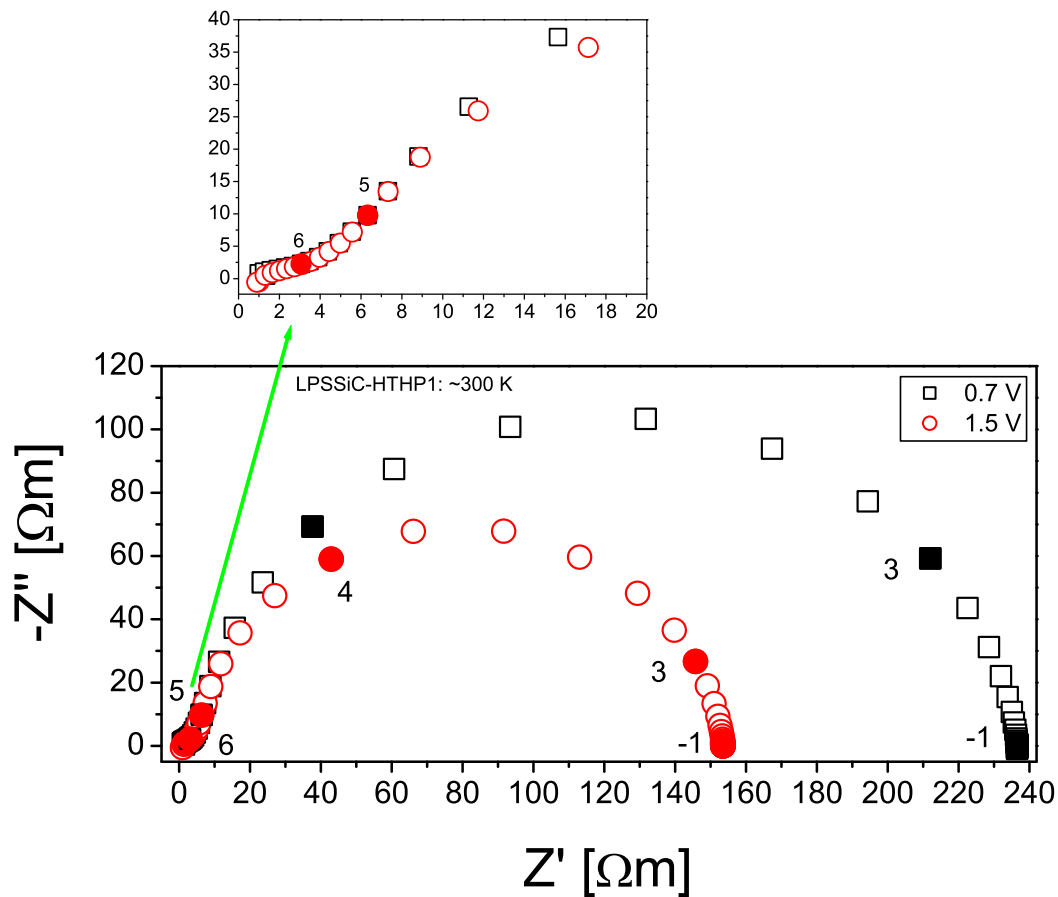


Figure 7.26: Complex impedance plane plot of the data for a group *C* sample, LPSSiC-HTHP1, at two voltages and $\sim 27^\circ\text{C}$. The properties of the dominant component are seen to be clearly voltage dependent. Note the high frequency arc (insert) which is not clearly resolved, and whose properties may or may not be voltage dependent.

group *C* sample LPSSiC-HTHP1 at two different excitation voltages. It can be seen in the figures that the impedance of the dominant component depends on the excitation voltage.

The results described above will also be used, in the following section, as one of the basis for identifying the various components contributing to the measured electrical properties of the LPSSiC.

7.2.6 Microstructure and the electrical properties

From the foregoing, the following can be summed up about the electrical properties of each of the components of the LPSSiC samples that could be

resolved:

- *The only component resolved for the HP samples (group A)*
 - Has similar characteristic frequencies and “dc” conductivity for all the samples
 - Has the lowest conductivity
 - Lowest dielectric constant
 - Impedance independent of excitation voltage
 - Hopping conductor
- *The component dominant at high frequencies in the GPS and HP samples (group B)*
 - Characteristic frequencies and “dc” conductivities fall in a fairly narrow band for the different samples but with a wider spread than for the samples in group A.
 - Impedance independent of the excitation voltage
 - Second lowest dielectric constants
 - Hopping conductor
- *The component dominant at low frequencies in the GPS and HP samples (group B)*
 - Characteristic frequencies and “dc” conductivities more widely spread for the different samples than those of the component dominant at high frequencies.
 - Impedance depends on the excitation voltage
 - Highest dielectric constants
 - Hopping conductor
- *The only component fully resolved in the HTHP samples (group C)*

- Characteristic frequencies and “dc” conductivities for the different samples fall in a wide band
- Highest conductivities
- Impedance depends on the excitation voltage
- Second highest dielectric constants
- Hopping conductor

From the results summarized above and others in the preceding sections it should be noted that:

1. There is no component with a characteristic “signature frequency” that is detectable in *all* the samples (contrast this with the YSZ samples in chapter Chapter 5 and the polyester-resin/silicon samples in Chapter 6).
2. *All* the measurable components are hopping conductors.
3. *All* the components have impedance contributions that are greater than may be expected for unintentionally (shallow level) doped SiC (such as the SiC grains of the LPSSiC ceramics). High resistivities in silicon carbide are *only* obtained for ultra pure crystals or material containing deliberately introduced deep level dopants, such as vanadium [Bickermann et al.¹⁴⁶, Bickermann¹⁴⁷].

There are three possible contributions to the observed electrical properties of LPSSiC ceramics, the SiC grains, SiC-SiC grain boundaries and the binder phase. Note from the compositions shown in Table 7.1 that the binder phase is itself complex and contains one or more crystalline and/or amorphous materials. From the previous results, one must conclude that the silicon carbide making up the grains of the polycrystalline materials is *not* being detected in these measurements. Instead, the effects observed in the LPSSiC samples are all due to the multiphase grain boundary/binder phase. This conclusion is supported by the results given below.

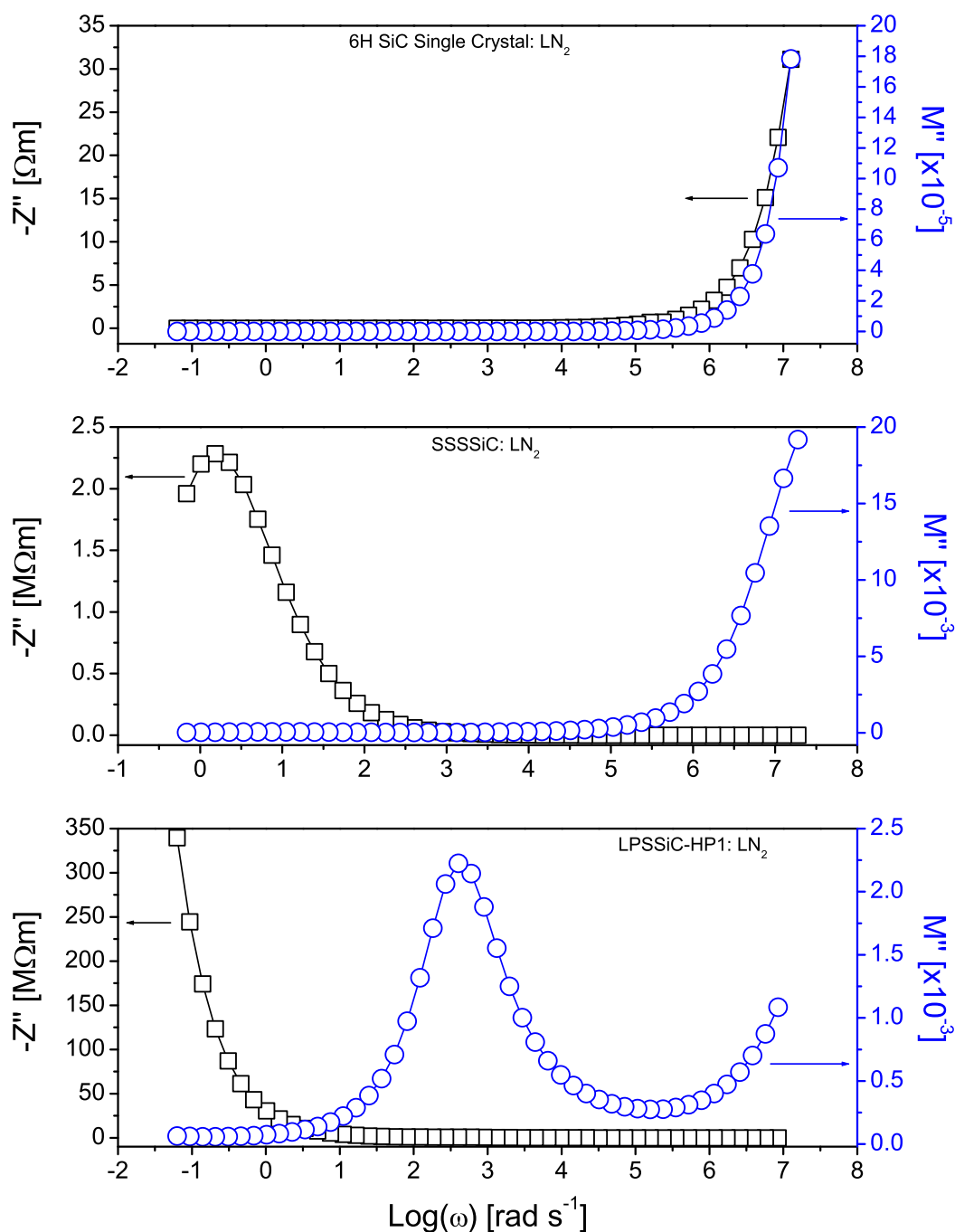


Figure 7.27: The frequency dependence of the imaginary impedance and dielectric modulus of a 6H-SiC single crystal as well as a Solid-State-Sintered-Silicon-Carbide (SSSSiC) sample and the group *B* sample LPSSiC-HP1, measured at liquid nitrogen temperature, to enhance the contribution of the SiC grains.

As mentioned in Chapter 2, the electrical properties of 6H silicon carbide single crystals (with no intentional doping) and a solid-state-sintered silicon carbide (SSSSiC), sample were also measured in this thesis (note from Table 7.2 that 6H is the dominant SiC polytype in the LPSSiC samples). The results of the measurements provide some added information on the possible contributions to the measured LPSSiC samples' electrical properties. Figure 7.27 shows the imaginary impedance and dielectric modulus of a silicon carbide single crystal, a SSSSiC (does not contain a binder phase) and the group *B* sample LPSSiC-HP1, at liquid nitrogen temperature. It can clearly be seen in the top figure that the peak in the impedance and modulus plots for the single crystal is at higher frequencies than could be measured. The data in the top figure indicates, as would be expected, that the single crystal is a highly conducting one component material, as there is the indication of only a single peak in the impedance and the modulus at high frequency.

For the SSSSiC sample Figure 7.27 (middle), one peak is just resolved in the impedance curve and there is the indication of a peak in the modulus at high frequencies. These curves suggest that the SSSSiC is a two component material, with a resistive component (the grain boundaries) giving rise to the low frequency impedance peak and a low resistance component giving rise to the modulus peak, at high frequencies, which is only partially resolved at this temperature (recall the discussion Section 1.2 and the results and discussion in Chapter 6).

From Figure 7.27 (bottom) it is deduced that the group *B* sample, which gave two arcs in the high temperature results previously presented, should be treated as a three component system. The high frequency peak indicated but not fully resolved in the modulus spectrum *must* be associated with the SiC grains such as was done for the SSSSiC sample and the single crystal. There is another peak in the modulus data at intermediate frequencies ($\log(\omega) \approx 3$) which is associated with a first grain boundary component in the material. The impedance peak at the lowest frequencies is associated with the second very high resistance grain boundary component.

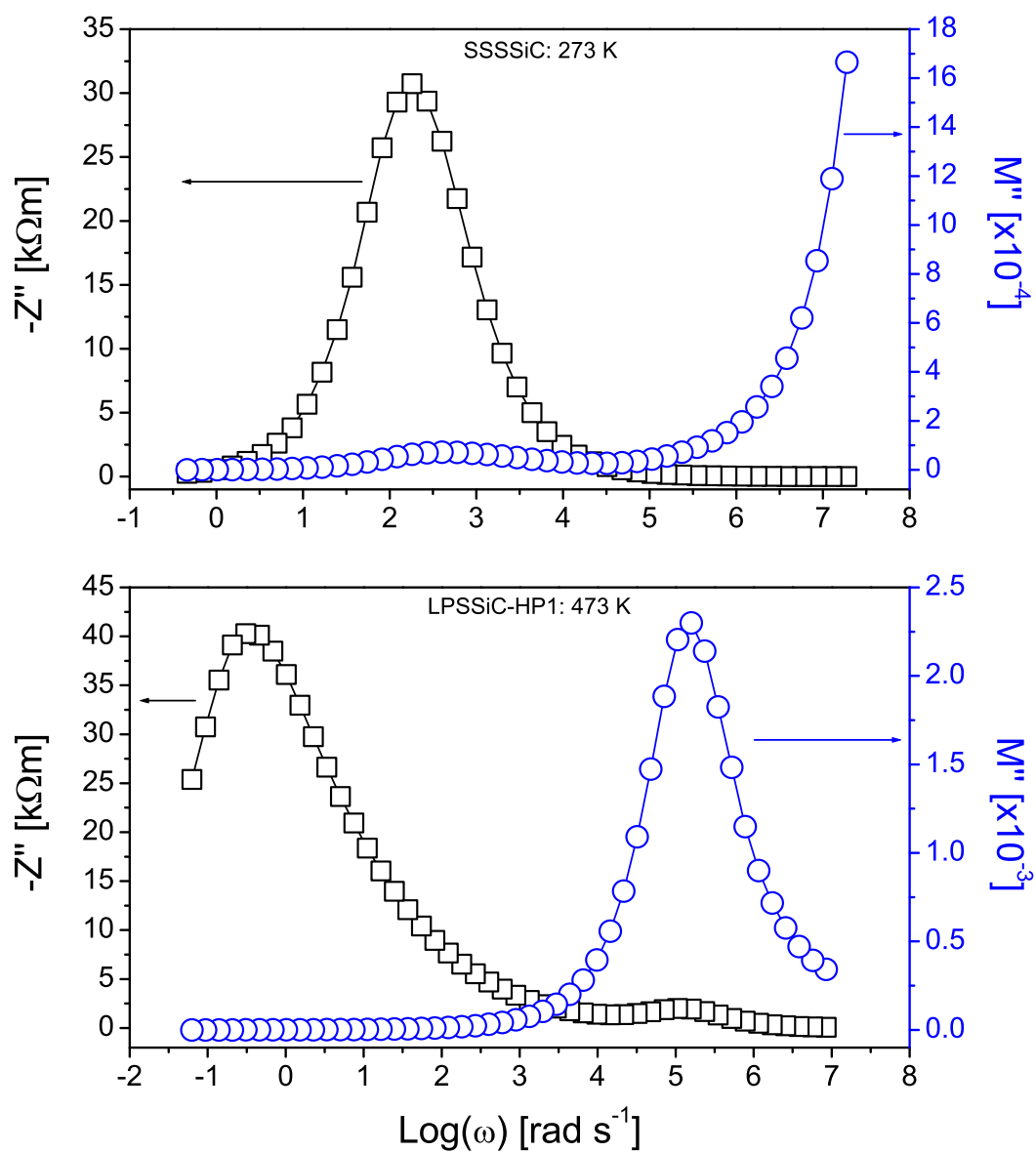


Figure 7.28: The imaginary impedance and dielectric modulus of the SSSiC sample at 0 °C and the sample LPSSiC-HP1 at 200 °C showing the relation of modulus and impedance peaks.

Figure 7.28 shows the results for the SSSSiC and LPSSiC samples at higher temperatures. Figure 7.28 (top) again indicates that the SSSSiC is a two component, grain and grain boundary material. No further component contributions are seen at even higher temperatures. There is one peak in the impedance curve, associated with the dominant grain boundary component (and to which there is a corresponding small peak at similar frequencies in the modulus plot) and the start of the high frequency modulus peak, which was not fully resolved even at liquid nitrogen temperature.

Figure 7.28 (bottom), shows the impedance and modulus plots for the sample LPSSiC-HP1 at higher temperatures. The contributions due to the grain boundary/binder phase components can now be observed in the impedance data, while that of the more conducting grain boundary/binder phase component dominate the dielectric modulus. A comparison of Figures 7.27 and 7.28 shows that the modulus peak that was at intermediate frequencies at liquid nitrogen temperature and which has now moved to higher frequencies, is associated with a peak in the impedance which was not observable in the scale of the data at liquid nitrogen temperature. The low frequency peak in the imaginary impedance, associated with the second grain boundary/binder phase of the material, is now more clearly resolved.

Comparison of the single crystal, SSSSiC and the LPSSiC data confirms an earlier statement that the contributions of the SiC grains in the LPSSiC samples are not observed. Figure 7.27 (top) clearly shows that the conductivity of the silicon carbide is high (and its dielectric constant not anomalously high) and therefore that its characteristic frequency is beyond the range of the measurements. From Figure 7.27 (middle) and Figure 7.28 (top), it can be seen that the SSSSiC is a two component material (grain and grain boundaries) as would be expected for a ceramic containing no added binder phase (see also Chapter 5). Again there is just the suggestion of the effects of the silicon carbide grains at high frequencies and their contributions are not fully resolved. The bottom plots in Figures 7.27 and 7.28 show that the group *B* sample, LPSSiC-HP1, is a three component system, with the SiC grains and

two grain boundary/binder components. The effects of the SiC grains are not fully observed at any of the measurement temperatures and frequencies.

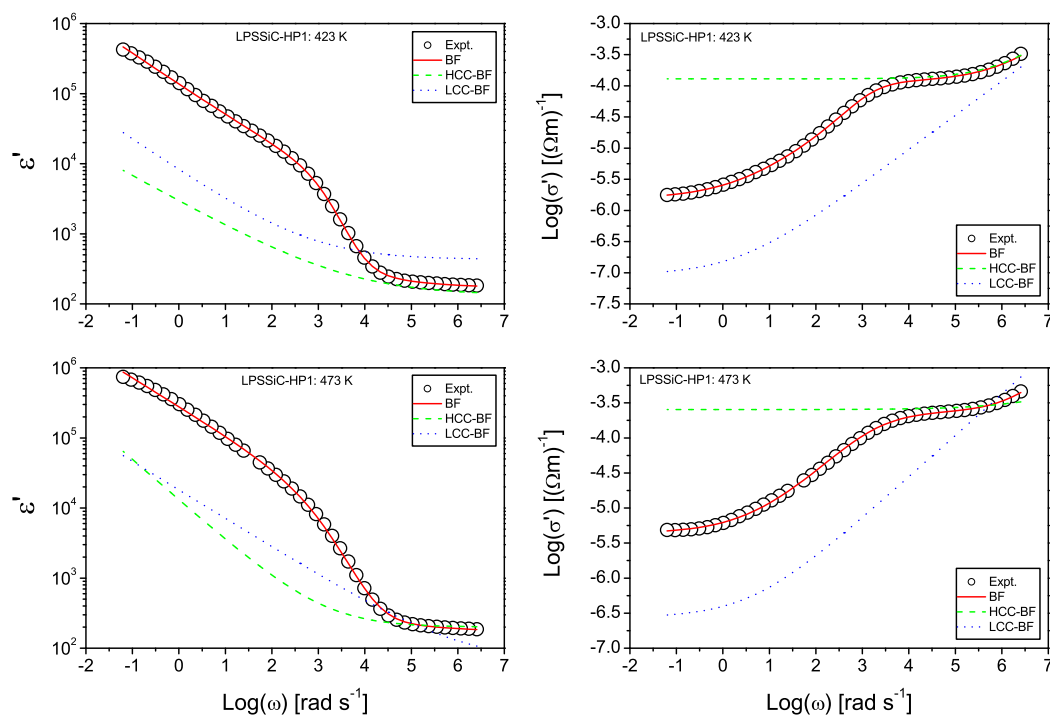


Figure 7.29: The frequency dependence of the dielectric constants and conductivities of the sample LPSSiC-HP1 at 150 °C and 200 °C and the best fit to the UDR-UDR-BLM. $\phi = 0.85$ and the remainder of the parameters are: At 150 °C, $A_g = 5.97 \times 10^{-8}$, $A_{gb} = 1.66 \times 10^{-8}$, $\sigma_{dc-gb} = 9.13 \times 10^{-8}(\Omega m)^{-1}$, $\sigma_{dc-g} = 1.29 \times 10^{-4}(\Omega m)^{-1}$, $s_{gb} = 0.55$, $s_g = 0.63$, $\epsilon_{\infty-gb} = 430$, $\epsilon_{\infty-g} = 133$. At 200 °C, $A_{gb} = 1.20 \times 10^{-7}$, $A_g = 1.47 \times 10^{-7}$, $\sigma_{dc-gb} = 2.75 \times 10^{-7}(\Omega m)^{-1}$, $\sigma_{dc-g} = 2.53 \times 10^{-4}(\Omega m)^{-1}$, $s_{gb} = 0.59$, $s_g = 0.42$, $\epsilon_{\infty-gb} = 64$, $\epsilon_{\infty-g} = 200$.

It is somewhat strange that the electrical properties of the two component grain boundary phase can be modeled using the BLM with dispersive functions for the ac conductivity of both components (UDR-UDR-BLM, see Section 5.2.9; the UDR-UDR-MW model gives similar results). Figures 7.29 to 7.32 show the data for two group *B* samples, LPSSiC-HP1 and LPSSiC-GPS1, fitted to the UDR-UDR-BLM. It can be seen in the figures that the model fits the data well. This suggests that, in the multi-component grain boundary phase of these samples, there is an insulating, probably amorphous, component which must coat a more conducting, probably the crystalline, component. Note that the amorphous component could not be detected using x-ray

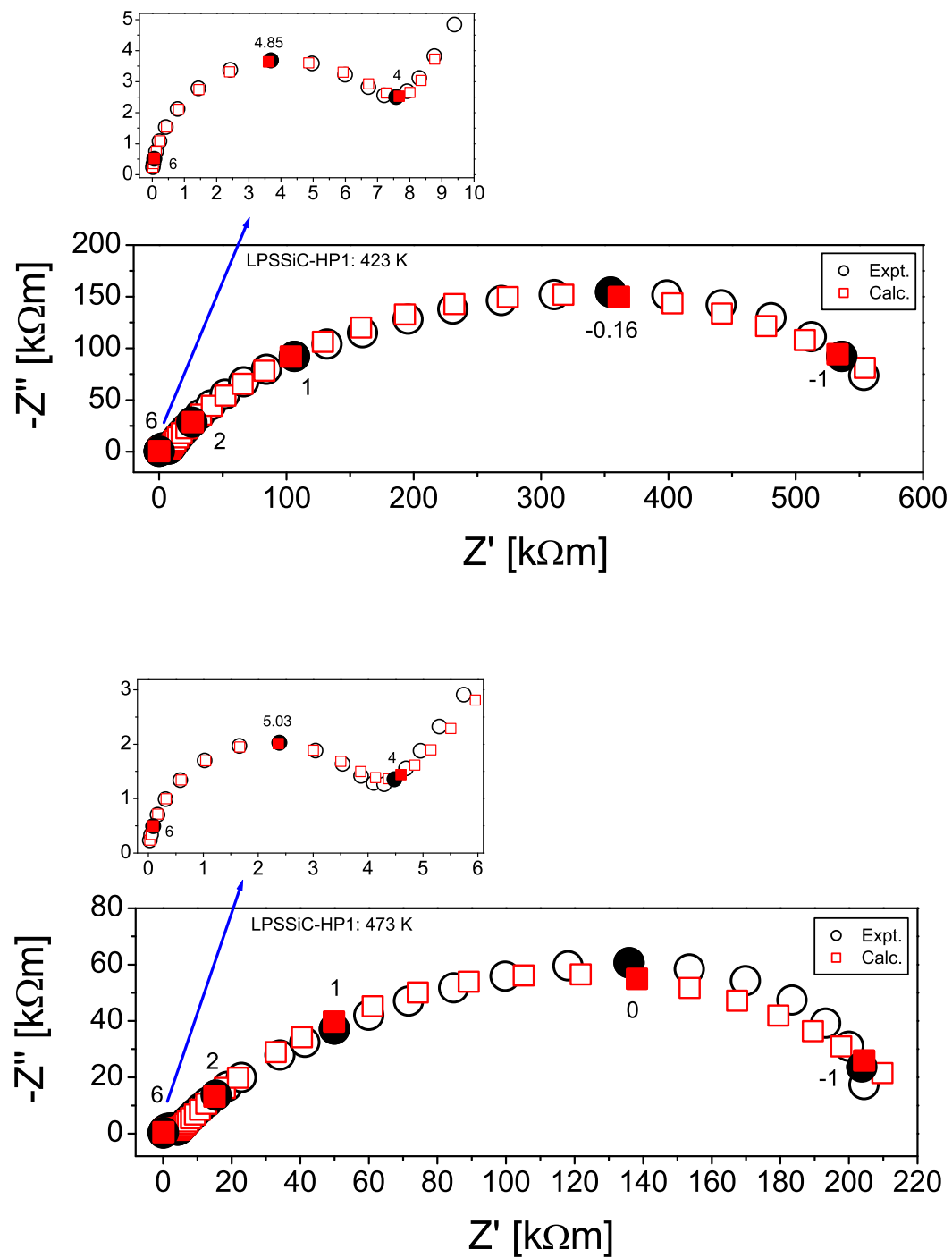


Figure 7.30: The complex impedance plane plot of the data for the sample LPSSiC-HP1 at 150 °C and 200 °C and the best fit to the UDR-UDR-BLM. The parameters for the best fit are given in Figure 7.29.

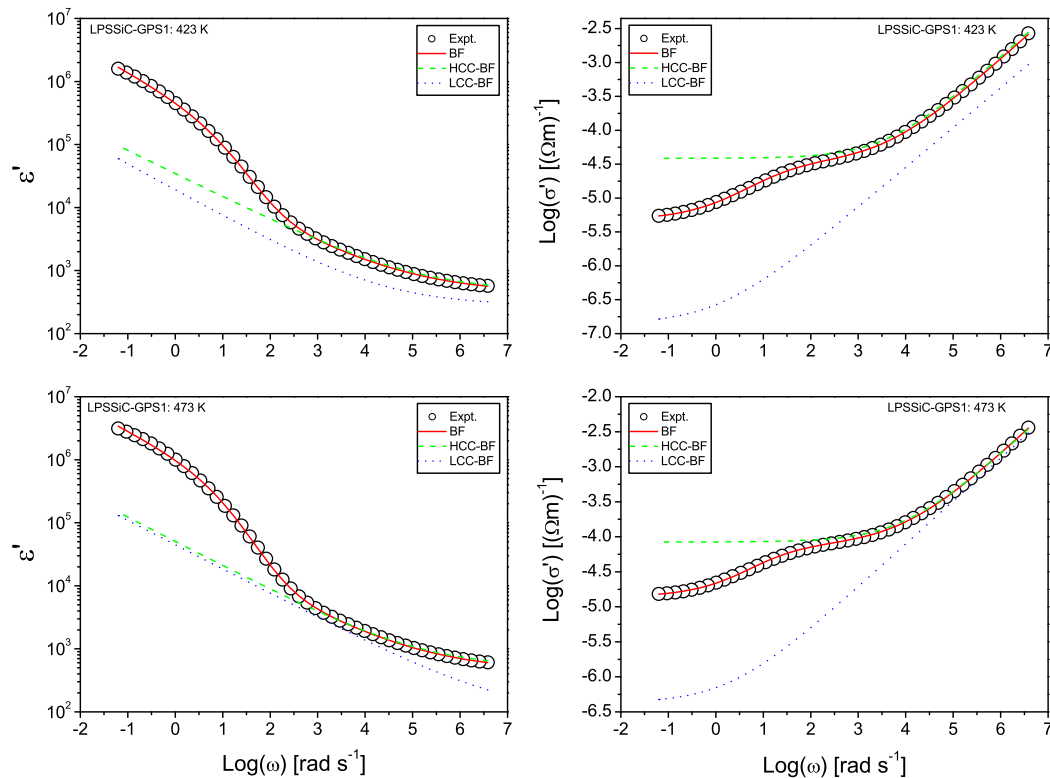


Figure 7.31: The frequency dependence of the dielectric constants and conductivities of the sample LPSSiC-GPS1 at 150 °C and 200 °C and the best fit to the UDR-UDR-BLM. $\phi = 0.928$ and the remainder of the parameters are: At 150 °C, $A_{gb} = 1.27 \times 10^{-7}$, $A_g = 1.99 \times 10^{-7}$, $\sigma_{dc-gb} = 1.39 \times 10^{-7}(\Omega m)^{-1}$, $\sigma_{dc-g} = 3.86 \times 10^{-5}(\Omega m)^{-1}$, $s_{gb} = 0.59$, $s_g = 0.63$, $\epsilon_{\infty-gb} = 284$, $\epsilon_{\infty-g} = 467$. At 200 °C, $A_{gb} = 2.76 \times 10^{-7}$, $A_g = 3.10 \times 10^{-7}$, $\sigma_{dc-gb} = 4.24 \times 10^{-7}(\Omega m)^{-1}$, $\sigma_{dc-g} = 8.44 \times 10^{-5}(\Omega m)^{-1}$, $s_{gb} = 0.61$, $s_g = 0.61$, $\epsilon_{\infty-gb} = 96$, $\epsilon_{\infty-g} = 508$.

spectroscopy. TEM studies might be able to resolve this component. Without more information on the underlying microstructure of the grain boundary phase and of the various components giving rise to features observed and fitted, the interpretation of the results from the fitting and in particular the volume fraction ϕ is difficult. Therefore, the results of fitting to any of the models used in the current thesis will not be discussed in any more detail.

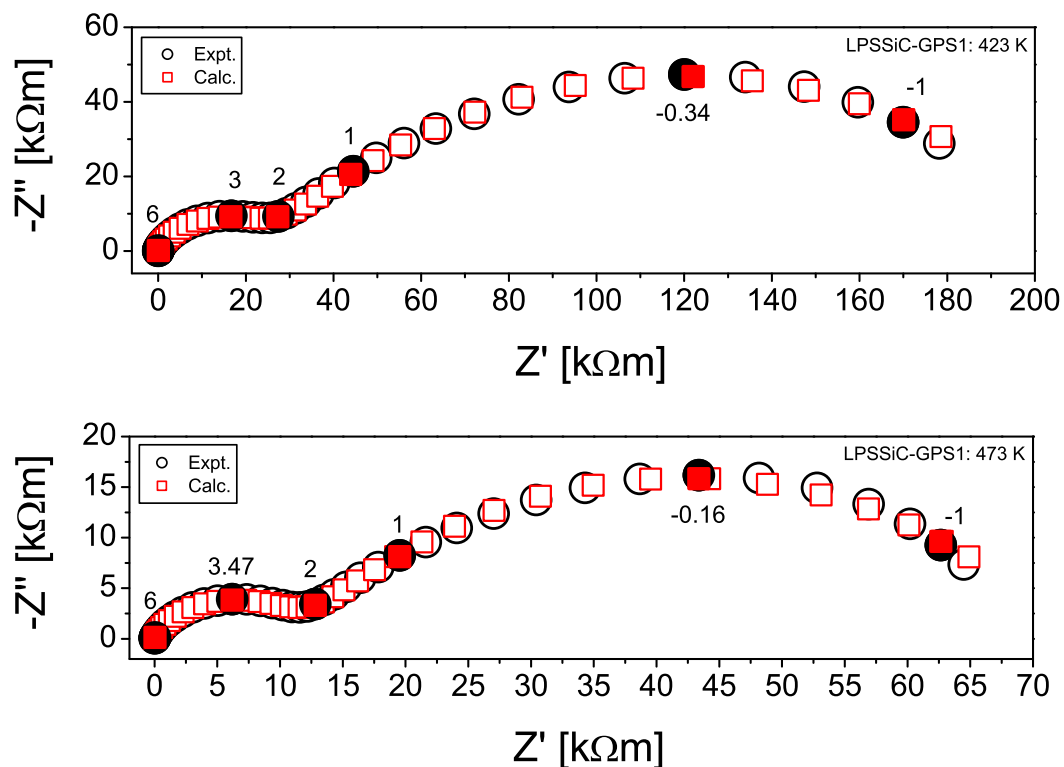


Figure 7.32: The complex impedance plane plot of the data for the sample LPSSiC-GPS1 at 150 °C and 200 °C and the best fit to the UDR-UDR-BLM. The parameters for the best fit are given in Figure 7.31.

7.3 Conclusions

In this chapter, the microstructure, composition and electrical properties of several polycrystalline LPSSiC samples have been described. The frequency dependence of the electrical properties of the samples strongly suggest that the LPSSiC should be considered not as a binary composite with the grains and grain boundaries as the two components, but instead as a three component composite. The three components being the SiC grains and two grain boundary/binder phases.

The temperature dependence of the characteristic frequencies and the conductivities of the components resolved is best fitted by the variable range hopping mechanism. No model could be found to fit the dielectric constants which vary erratically.

One of the components resolved in the GPS and HTHP samples was found

to exhibit a voltage dependent resistance. The component dominant in the HP samples did not exhibit this effect. As previously mentioned, other authors suggest that the variable resistance effect in commercial SiC varistors arises from SiC grain contact areas. It is as yet unclear which particular constituent of the samples studied is leading to this effect and whether or not it is the same constituent in the GPS and HTHP samples.

While it was possible to fit the LPSSiC data to the Brick Layer (and Maxwell-Wagner) models, with dispersive properties for both the components resolved, which may be associated with the multi-component grain boundary/binder phase, such fitting was not pursued in detail as it is unclear what the microstructure of the multi-component grain boundary/binder phase might be. The best fit parameters obtained from such fitting can not be readily assigned to components of the LPSSiC samples.

Summary and Conclusions

In the current thesis, the use of various models and fitting techniques to obtain consistent fitting for series of sample data has been demonstrated. From what has been presented here and, especially the best fit results, the following statements can be made.

- **Simulations and identifying the components of composites**

From simulation results (and later experimental results), it was demonstrated that the components of a composite can be readily and reasonably accurately identified from their characteristic frequencies. For all the models simulated, it was shown that there is a fundamental shifting of the characteristic frequencies, associated with the components, in the composites. This places a limit on how accurately the components can be identified.

However, experimental results clearly demonstrated that, used together with other parameters, the characteristic frequencies of the components can play an important role in correct identification of the contributions to the electrical properties of the composite.

- **Yttria-stabilized zirconia system**

It has been shown that the electrical properties of yttria-stabilized zirconia ceramics can be consistently fitted to the Maxwell-Wagner and Brick Layer models together with the Universal Dielectric Response model, which models the dispersive properties of the grains and in some cases the grain boundaries. While the fitting to the data was generally

satisfactory, non-random residuals as well as the irregular temperature dependence of some of the values of the best fit parameters suggest that, in reality, the Maxwell-Wagner and Brick Layer models, together with the Universal Dielectric Response model only approximately describe the electrical properties of the yttria-stabilized zirconia ceramics. The irregular temperature dependence of the best fit parameter values is of serious practical concern as it makes it impossible to accurately predict the properties of other samples using these models. However, the work on the polycrystalline samples, together with the results on the single crystals, strongly suggests that the major problem is the fitting and modeling of the dispersive properties the grains and not the Maxwell-Wagner or Brick Layer models. Clearly more work needs to be done in obtaining better expressions for the frequency dependent complex conductivities of the grains, $\sigma_h^*(\omega)$ and the grain boundaries, $\sigma_\ell^*(\omega)$. The results obtained in the current work suggest that with accurate and consistent models for the dispersive properties of the grains and grain boundaries the Maxwell-Wagner and Brick Layer models are suitable for semi-quantitative and perhaps even quantitative modeling and fitting the properties of the polycrystalline materials.

- **Polyester-resin/silicon system**

For the polyester-resin/silicon system, the properties of one of the components, the polyester-resin, were independently measurable at all frequencies, where the composite materials' properties were measured. Of the systems investigated in the current work, this system was the closest to the ideal situation that the properties of *both* the components of the composite must be known at *all* frequencies, where the properties of the composites are measured. Unfortunately, there is some uncertainty in the dispersive properties of the silicon. Single crystal silicon, or better still silicon with a similar morphology and doping as that in the composites, could not be obtained, for measurements of the ac conductivity

under the same conditions as for the composites.

In spite of this, it was shown that the Single Exponent Phenomenological Percolation Equation is able to semi quantitatively fit and model the properties of the composites, using the actual component volume fractions and the independently measured properties of the polyester-resin as fixed input (free parameters: σ_h , ϵ_h , ϕ_c and t). It can be argued that the ability to accurately fit data with the actual properties of the components and composition, is the most rigorous test for a model which accurately describes the properties of a system. The current work shows that the SEPPE at least partially meets this rigorous test. To put the matter beyond doubt, further work is required on a system where the dispersive properties of *both* the components can be measured in the same frequency range as that of the composite. Work on the polyester-resin/silicon system also highlighted the importance of using various data representations as well as the characteristic frequencies and the temperature dependence of the properties of the components, in order that the contributions of these components to the properties of the composites are correctly identified. From these results it is suggested that the modulus representation of the data should be used more often, in conjunction with the impedance representation, particularly in systems where one or more of the components is highly conducting.

- **Liquid-phase-sintered silicon carbide system**

The results for the LPSSiC show that it is a much more complex system than the yttria-stabilized zirconia. Further, the results show that the differences between the two systems are not just in the increased amount of the grain boundary component in the LPSSiC.

Using the aforementioned techniques to analyze the data from various LPSSiC samples, it is concluded that the silicon carbide contribution is not observed in the IS spectra, even at liquid nitrogen temperature where the characteristic frequency ω_p is lowest. This conclusion is in

contradiction to the conclusions reached by other authors. It again highlights the importance of using several data representation formats and the temperature dependence of the properties of the components, to correctly identify the contributions of these components to the properties of the composites.

The measured data for the LPSSiC samples where two contributions could be resolved (group *B*) were successfully fitted to the Brick Layer Model. This suggests that, in the multi-component grain boundary phase of these samples, there is an insulating, probably amorphous, component which must coat a more conducting, probably the crystalline component. Note that the amorphous component could not be detected using x-ray spectroscopy. TEM studies might be able to resolve this component.

Appendix A

Examples of the arc separation process

Examples are given of the arc separation process, using the procedure described in Section 2.6.2. The procedure was implemented as the *Mathematica* 5.1 notebook named “*Impedance Arcs Cleanup and Separation (IACS)*” and its associated packages (subprograms). In this section the term “the program”, will be used to refer to this notebook and its packages. The examples in the pages that follow were obtained directly from running this program. The dialogue highlighted in blue in the figures is issued by the program as part of the output. $\gg$ highlights what the program is attempting to do and $\ll$ is the outcome. “I,” is the program referring to itself. The points indicated as “potential arc separation point (s)/arc boundaries”, in red in the dialogue, are *obvious* turning points where there is some notable feature in the data and where the arc(s) could potentially be separated out or “cleaned up” (i.e. boundaries to the arc overlap region). These points have to be confirmed, as actual arc separation or “cleanup” points and the results of this confirmation step are seen in the output that subsequently follows. “Cleanup” is the removal of data points that have been determined, by a particular set of procedures, as not necessarily belonging to the arc or set of arcs. For brevity, some steps, for which there was no difference between the starting and final

data (i.e. where arcs could not be further separated out or “cleaned up”), have been omitted.

A.1 Example 1

The first example is the fairly routine processing of “raw” experimental data and arc separation for the polycrystalline YSZ sample 8YSZ-D1 (note that the actual filename for data from this sample, indicated in magenta in the figures, is *A51R-250.dat*). The experimental data was measured at 250 °C.

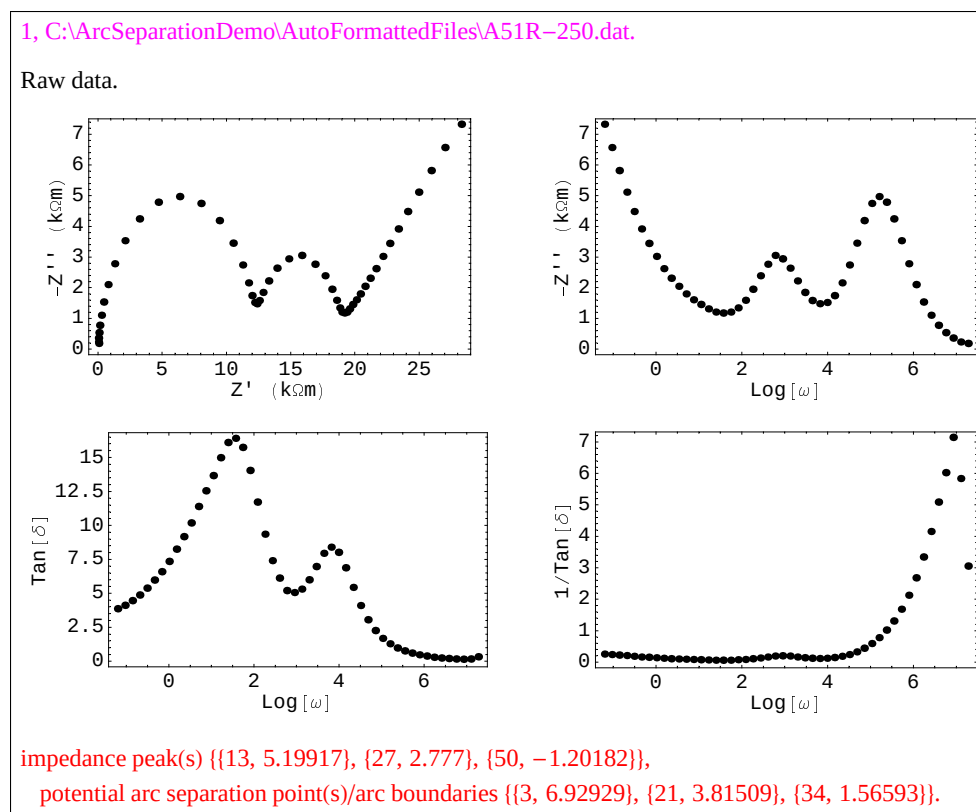


Figure A.1: The raw data prior to the first step in the arc separation procedure presented in various formats for the CSZ sample 8YSZ-D1. The points nearest to the imaginary impedance peaks are indicated as are the potential arc separation points determined using the $\tan(\delta)$, $1/\tan(\delta)$ and $-Z''$ data. The number to identify each point is counted from the highest frequency end, such that the point referred to in the dialogue as {13, 5.19917} is the 13th point and for this point $\log(\omega) = 5.19917$.

The “raw” data, from the input files, for the arc separation process, is shown in Figure A.1. This data had already been reformatted from that of

the output by the measurement control software as described in Section 2.6.2. $\tan[\delta]$ and $1/\tan(\delta)$ data, which by this stage have already been calculated are also plotted in the figure. The frequency points nearest to the peaks have been identified as well the positions where the arcs could be separated (based on $\tan(\delta)$, $1/\tan(\delta)$, $-Z''$). This data is presented at the bottom of the figures. The notation used for the positions is {point number, $\log(\omega)$ }. The numbering of the points is from the highest frequency end. For most measurements, there are 50 points in the raw data set. Non-physical points are dropped from the

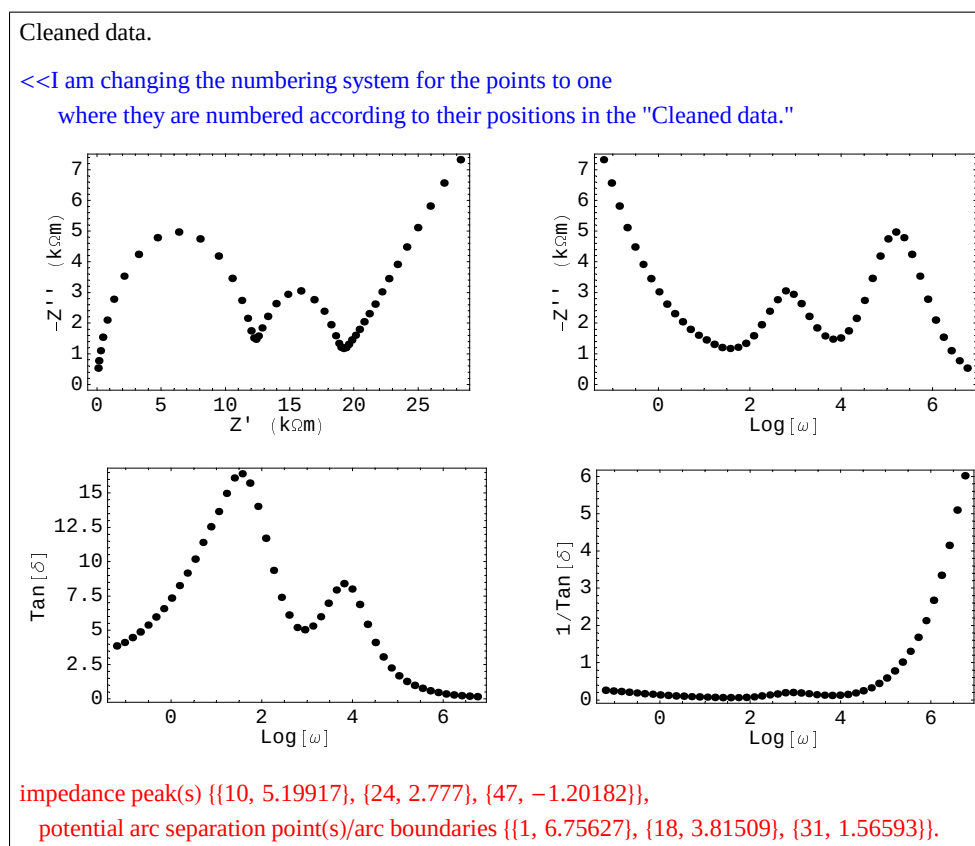


Figure A.2: The “Cleaned data” obtained after the removal of some non-physical points from the “raw” data in Figure A.1. In this case, three points, which were at the high frequency end in the “raw” data, have been dropped.

raw data to leave the “cleaned” data shown in Figure A.2. In this case, three points at the highest frequencies have been dropped. Note that there are two points that are obviously not consistent with the trend in $1/\tan(\delta)$ in Figure A.1. The procedure, set for aggressive cleanup of the data, also removes the point nearest to these two, making up the three points referred

to above. Note also that there is now a change in the numbering system. Whenever points are removed, the numbering system is altered such that the points are always numbered according to their positions in the current “complete” data set.

Figure A.3 shows the first and second derivatives, dZ''/dZ' and d^2Z''/dZ'^2 which are numerically computed. The turning points (maxima and minima), which are not shown in the figure, are also identified at this stage. The combined derivative, imaginary impedance, $\tan(\delta)$ and $1/\tan(\delta)$ data is then used to determine the positions of arc overlap regions. The data remaining after the removal of points in the overlap region and about three points on either side gives the now separated arcs, Figure A.3 (bottom). In this case three arcs have been identified and separated out by the program. Note the start and end points of the separated arcs. The first arc is from point number 1 to point number 15 while the second arc is from point number 20 to point number 28, points 16-19 were determined to be in the overlap region, for the first two arcs. Similarly, points 29-39 are in the overlap region of the second and the third arcs. The three separated out are one more than the user’s expected value of two arcs (an optional input parameter). The program indicates this and also suggests, correctly in this case, that this extra arc may be that due to electrode effects.

After the arcs have been separated out there is then a series of steps to try to remove any points, in the individual arcs, that may have belonged to the overlap region but were not removed in the primary separation step. The sensitivity of the search for points in the data at which $\tan(\delta)$, $1/\tan(\delta)$ or the derivatives are not consistent, with the characteristic patterns for single arcs, is increased from one stage of the “cleanup” process to the next. This is done by decreasing the number of adjacent points matching a specific pattern that is required to identify such stray points i.e. the size of the local neighborhood whose trend they violate. This step is repeated a fixed number of times (5 in the current program).

The “cleanup” of the data for the separated arcs begins with the dropping

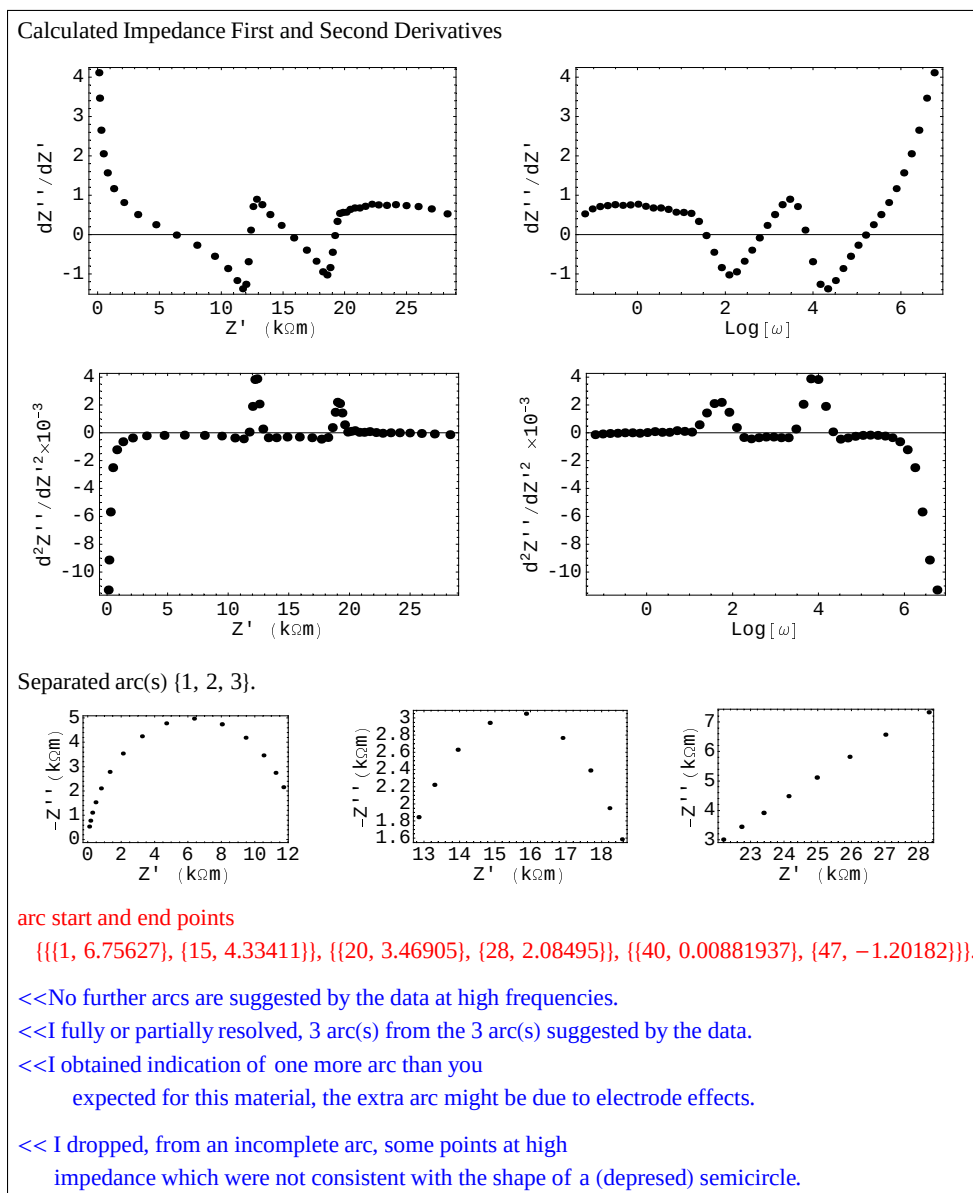


Figure A.3: The calculated first and second derivatives plotted as functions of both Z' and $\log(\omega)$. Together with the imaginary impedance, $\tan(\delta)$ and $1/\tan(\delta)$ data they are used for fine tuning the location of arc overlap regions. The resulting separated impedance arcs are shown at the bottom of the figure.

of the arc due to electrode effects. This is noted in the program dialogue at the top of Figure A.4.

After this, the “cleanup” of the two separated arcs deemed to be due to the sample material (as opposed to electrode effects), commences. The first stage of the “cleanup”, of the two arcs, is based on the $\tan(\delta)$ and $1/\tan(\delta)$ data while the following stages all utilize the first and second derivatives data. Figures A.4 and A.5 show further steps in the cleanup process.

After cleanup of the first arc, cleanup of the second arc is attempted, Figures A.6 to A.8. The same sequence of steps as for the first arc is repeated. Cleanup is started first based on $\tan(\delta)$ data. The procedure recognizes that the peak in $1/\tan(\delta)$ at $\log(\omega) \approx 3$, in Figure A.6, is associated with the peak in the imaginary impedance data and therefore no “cleanup” is possible based on this $1/\tan(\delta)$ peak.

In the second attempt at cleaning up separated arc number 2, based on the derivatives data, a point which does not conform to the characteristic shape of the second derivative of a semicircle is identified, at $Z' \approx 18.5 \text{ k}\Omega m$ ($\log(\omega) \approx 2.1$). The second derivative is expected to monotonically decrease towards $-\infty$ at the edges of single arcs. The inconsistent data is removed. Note that after the non-conforming data points are removed, the derivatives are recalculated, and hence the differences between the values, for the slope, in Figure A.7 and those in Figure A.8.

The “cleanup” procedure is repeated five times as described above for the second arc. The final separated arcs obtained for this particular data set as well as the combined arcs are shown in Figure A.9. The data for the complete spectrum, which includes points in the overlap region, is obtained by taking the “cleaned” data (Figure A.2) points from the start of the first arc to the end of the second arc. This data constitutes the properties of the composite, free of erratic points and electrode effects.

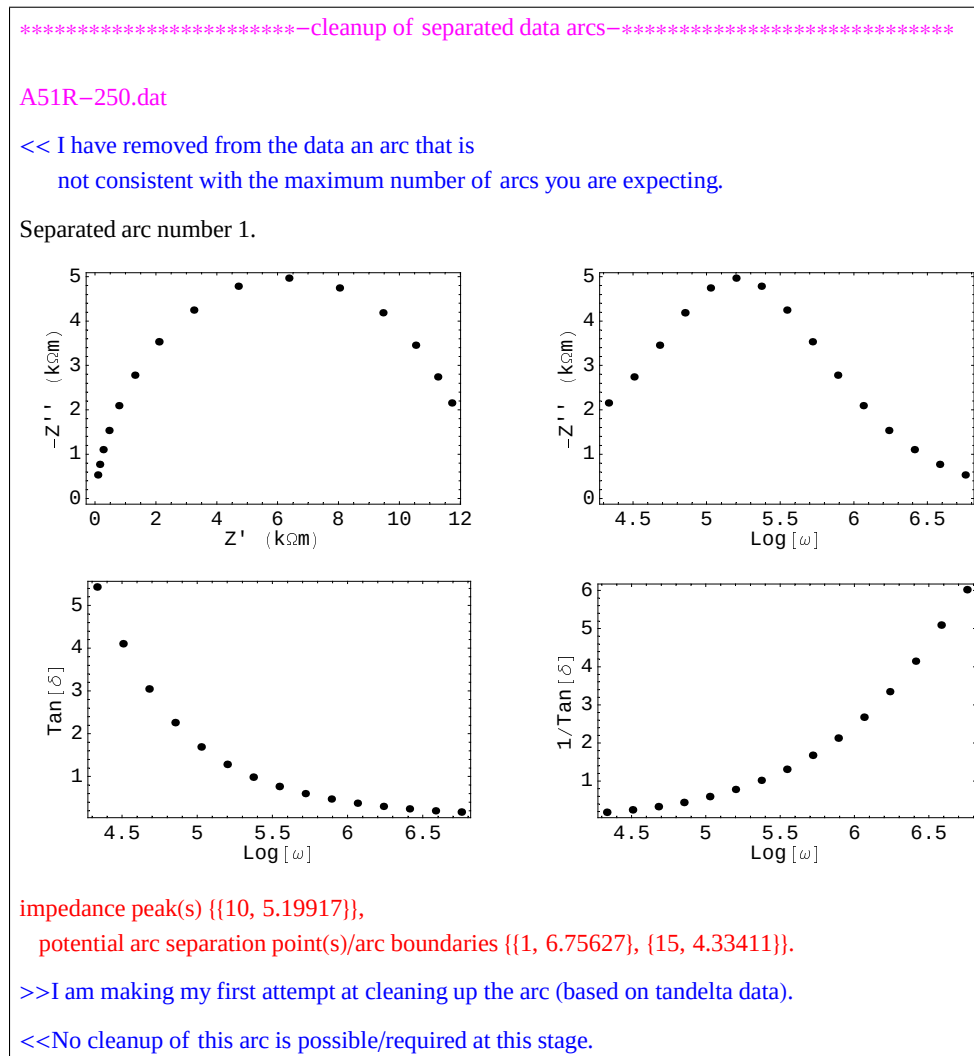


Figure A.4: Prior to the “cleanup” of the first arc (that at the highest frequencies), the third arc (at the lowest frequencies), which was one more than the user expected, is dropped, as can be seen in the dialogue at the top of the figure. The first stage of the “cleanup” of separated arc number 1 is based on $\tan(\delta)$ and $1/\tan(\delta)$ data. The arc “cleanup” ensures that there are no points at the start or end of the arc which belong to the overlap region. At the high frequency end of the arc (low real impedance), $1/\tan(\delta)$ is expected to be monotonically rising while at the low frequency end $\tan(\delta)$ should be rising monotonically.

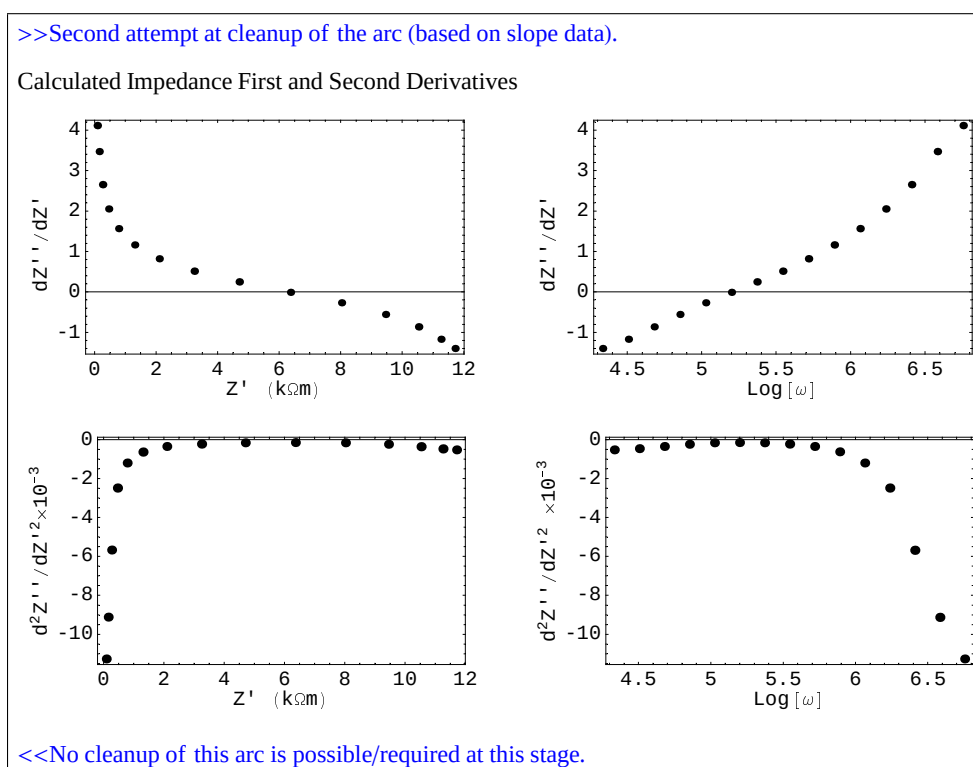


Figure A.5: The second stage of the arc “cleanup” process, for separated arc number 1, based on impedance first and second derivatives. There are no points that, within the error margins of the experimental data, do not conform to the characteristic shapes of the derivatives of semicircles and therefore no cleanup is possible/required.

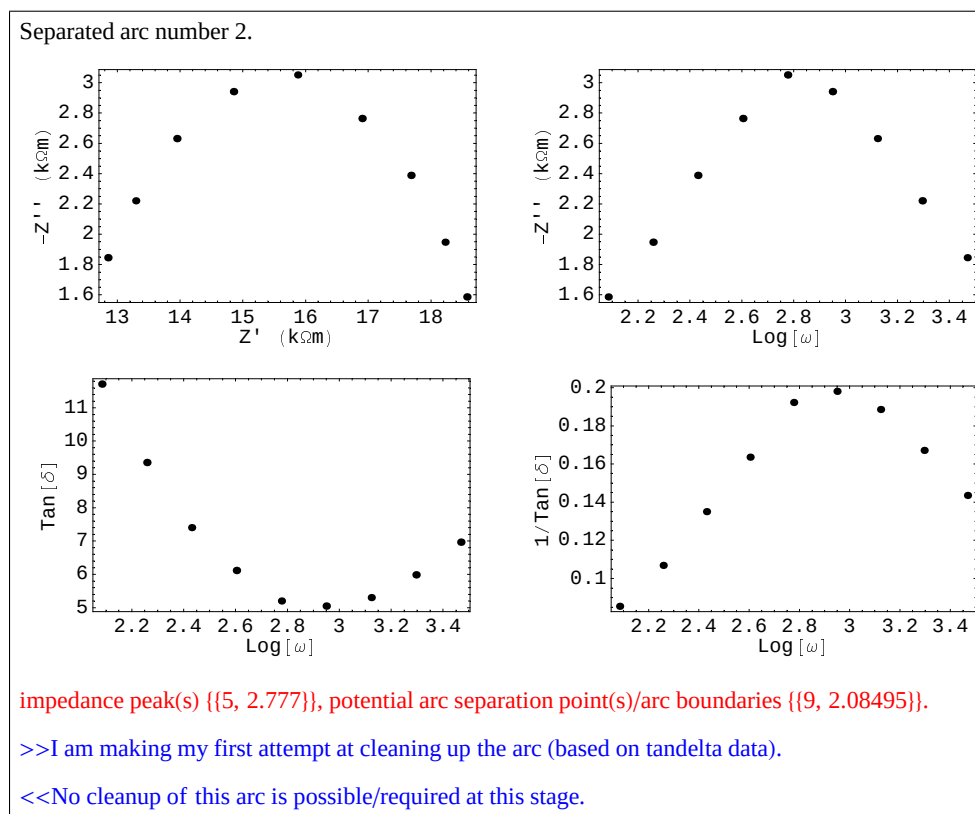


Figure A.6: The first stage in the cleanup of the **second arc** separated out in Figure A.3. The peak in $1/\tan(\delta)$ (trough in $\tan(\delta)$) has not been considered as a potential arc cleanup point because it lies close to the imaginary impedance peak and therefore must be associated with that.

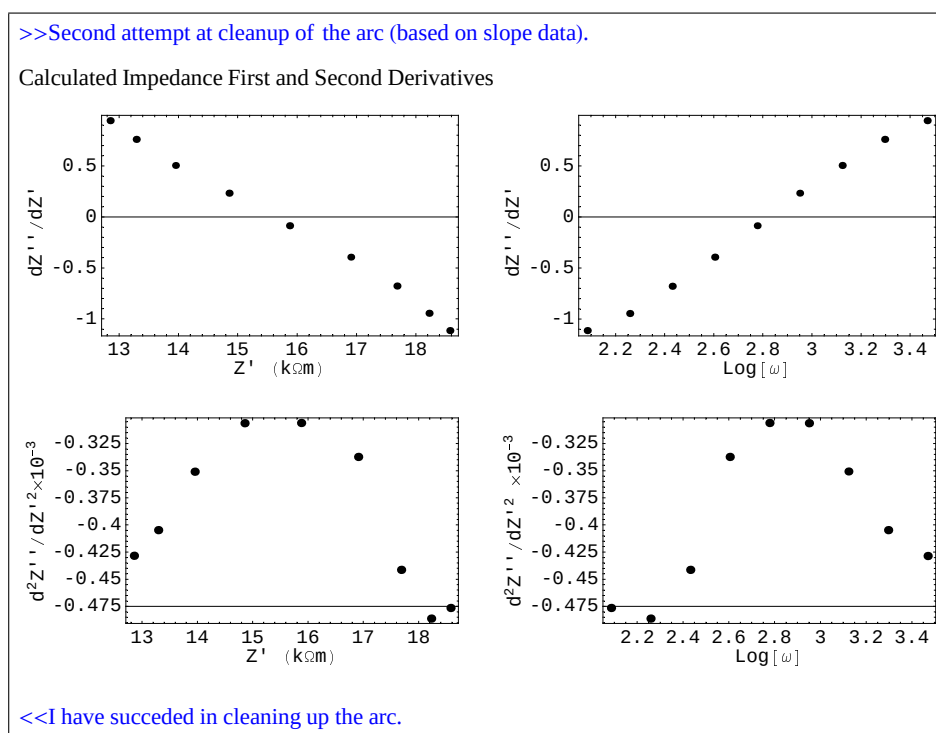


Figure A.7: In the second stage of the cleanup of the second arc, data which does not conform to the characteristic trends in semicircle derivatives, in particular the second derivative (at $Z' \approx 18.5 \text{ k}\Omega\text{m}$, $\log(\omega) \approx 2.1$), is found and this is removed from the separated arc's data. The subsequent stages of the “cleanup” proceed with this data removed, as can be seen in the plots for the third attempt at cleanup (Figure A.8).

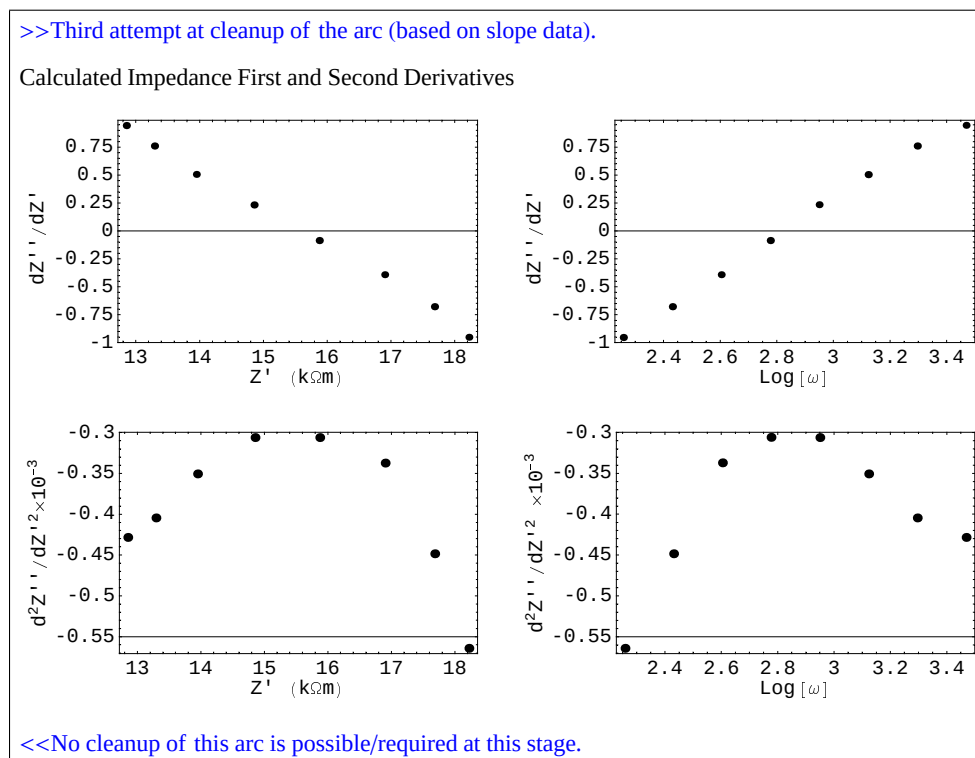


Figure A.8: In these plots for the data for the third stage of the cleanup of the second arc it can be seen that some data was removed during the second stage of the cleanup (as shown in Figure A.7). After the removal of the data, the slopes were recalculated and hence the differences in the y-axis values in the current figure to those in Figure A.7. In this third stage of the clean up, no points are removed.

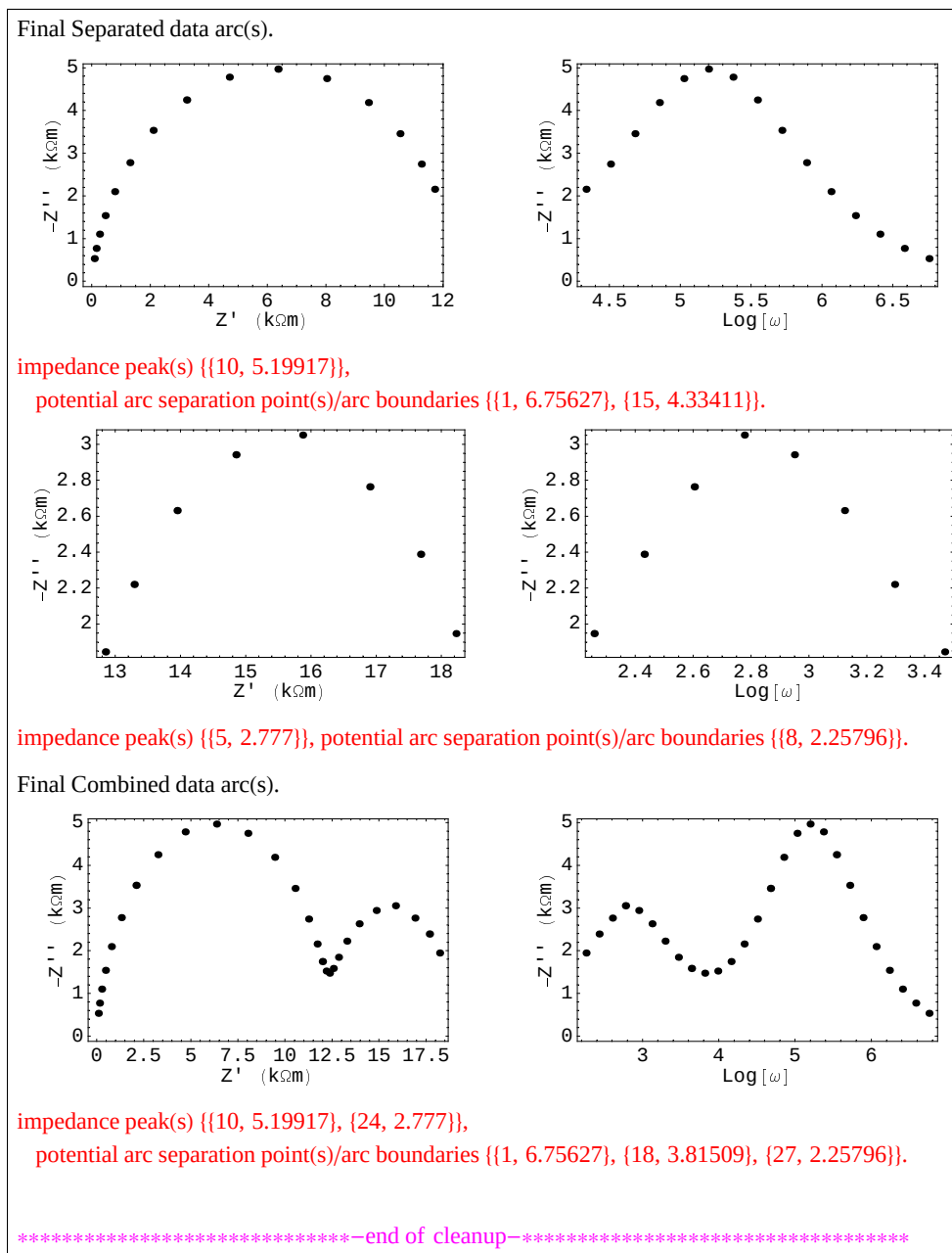


Figure A.9: The final two arcs from the arc separation process are shown individually (top and middle) and then the composite data is shown at the bottom. The composite data is taken from the first point of the first (high frequency) arc to the last point of the second (low frequency) arc and includes the overlap region, but not the stray points and the arc due to electrode effects.

A.2 Example 2

This example shows the arc separation procedure used for a more difficult problem, where the arcs are not very clearly resolved. In this case, independent partial arcs are still unequivocally identified. Again the same sequence of steps, as in the previous example, is followed and explained in the program dialogue and the captions in Figures A.10 to A.15. The sample in this analysis is a LPSSiC sample measured at 100 °C.

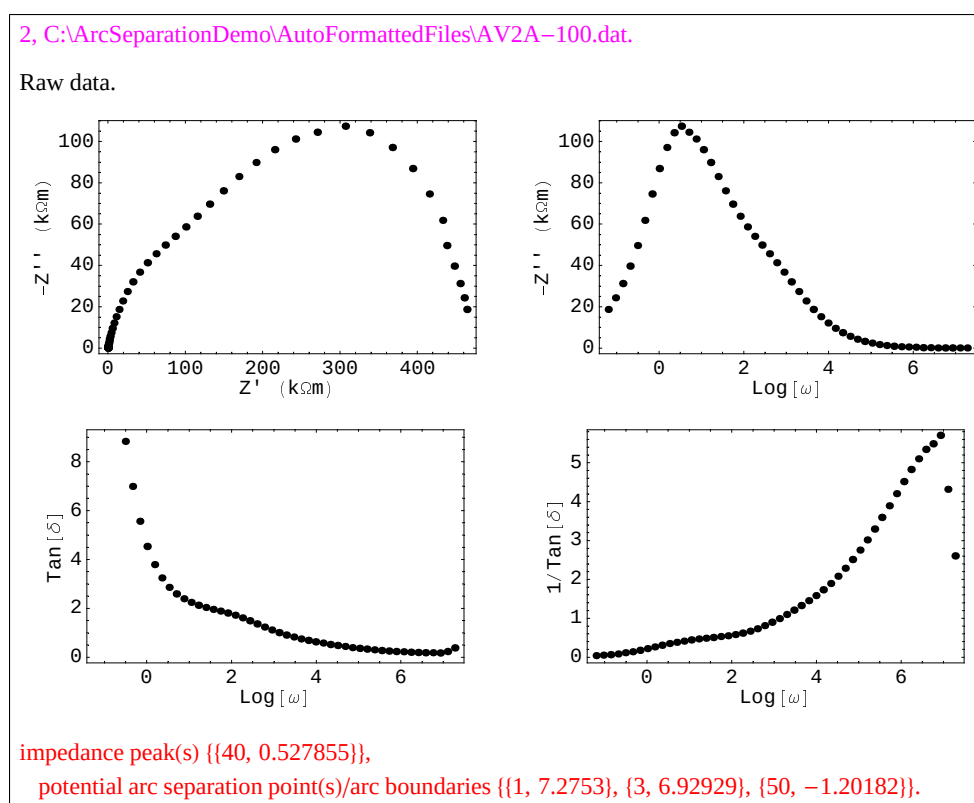


Figure A.10: The “raw” data for the arc separation and cleanup process for a LPSSiC sample, presented in various formats. It can just be seen by eye that there are two features contributing to the distorted semicircle. Two points that are not consistent with the trend in $\tan(\delta)$ and $1/\tan(\delta)$ can also be seen in the plots at the bottom and in particular the $1/\tan(\delta)$ graph (bottom right).

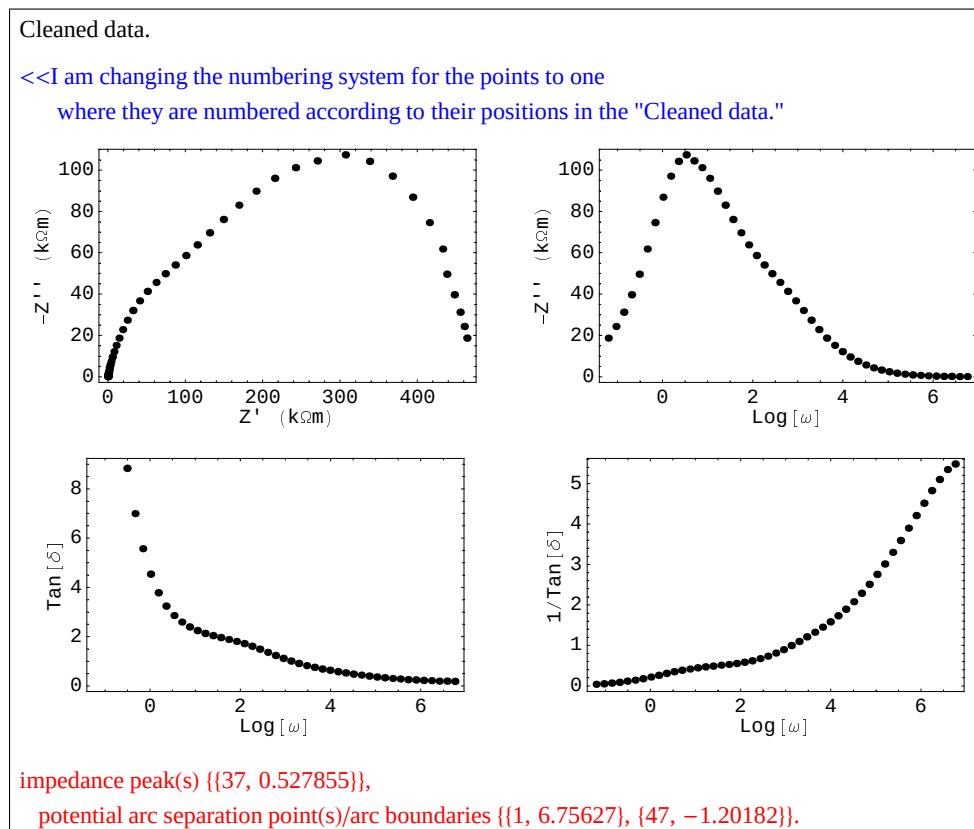


Figure A.11: The data remaining after removing non-physical points from the “raw” data in Figure A.10. Three points at the highest frequency, which were not consistent with the expected increase in $1/\tan(\delta)$ at these frequencies (decrease in $\tan(\delta)$), have been removed from all the data. Note that, based on the data representations in the figure, there are only two *obvious* arc boundaries, the start and end points of the combined arcs. However, in the steps that follow, involving the derivatives, the boundaries of the two arcs that can just be seen by eye will be identified.

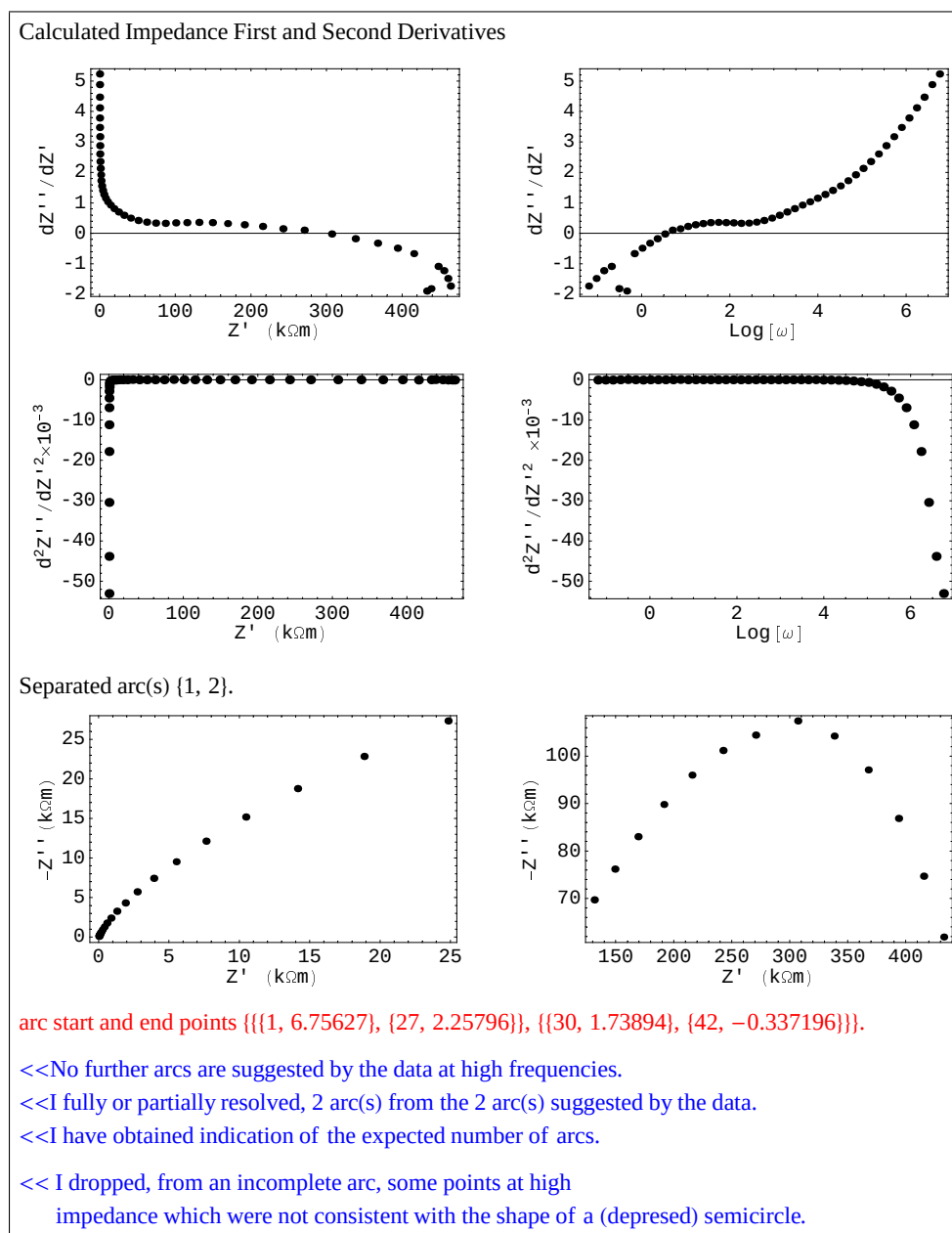


Figure A.12: The first and second derivatives of the cleaned data are shown (top and middle). The turning points of the first derivatives can just be identified by eye in the region $0.5 \leq \log(\omega) \leq 3$ of the dZ''/dZ' vs $\log(\omega)$ plot. The scale of the second derivative allows only the turning points at the ends to be seen. A peak in the middle of the plot cannot be seen by eye using this scale. However, the numerical data is more precise and enough information is obtained from these derivatives to enable the separation of the two arcs (bottom). The stray points that can clearly be seen at low frequencies, in the first derivatives plots are removed in the arc separation step.

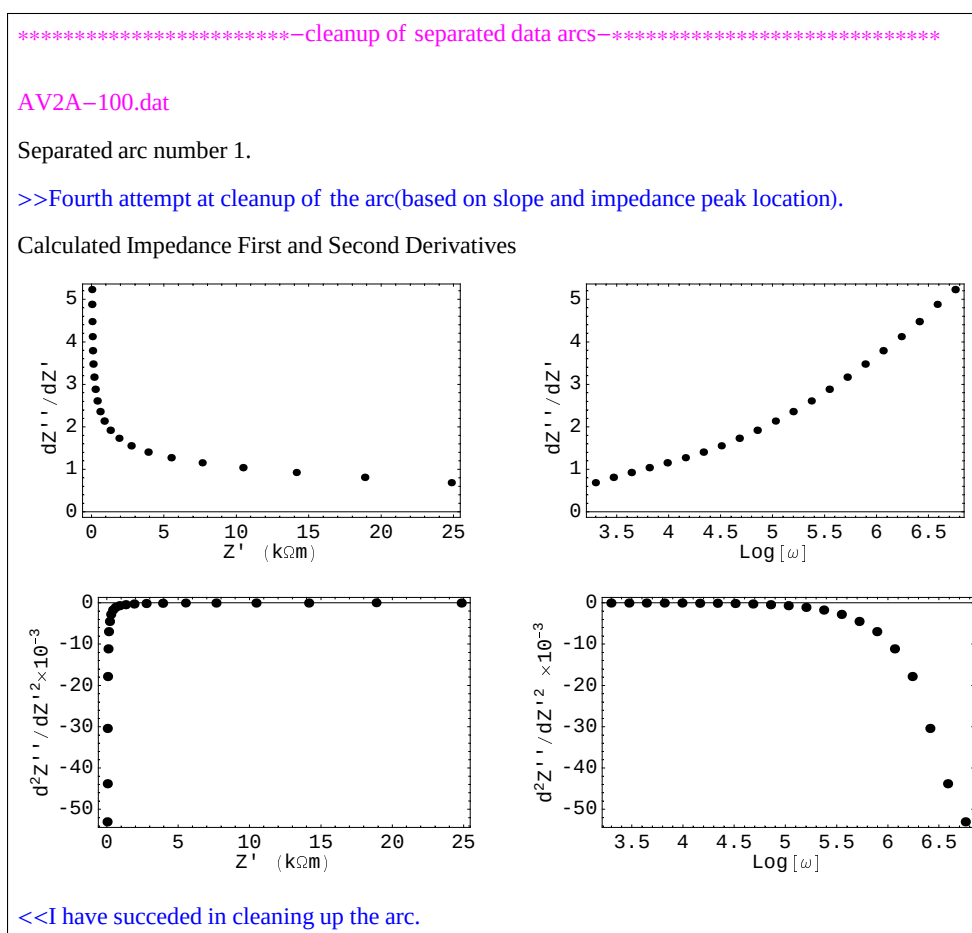


Figure A.13: Fourth attempt at the cleanup of the first arc obtained in the separation of the arcs shown in Figure A.12. Some points at low frequencies (high impedance) where the shapes of the first and second derivatives are not consistent with the patterns expected are removed. The inconsistent region cannot be seen in the scale of the figures.

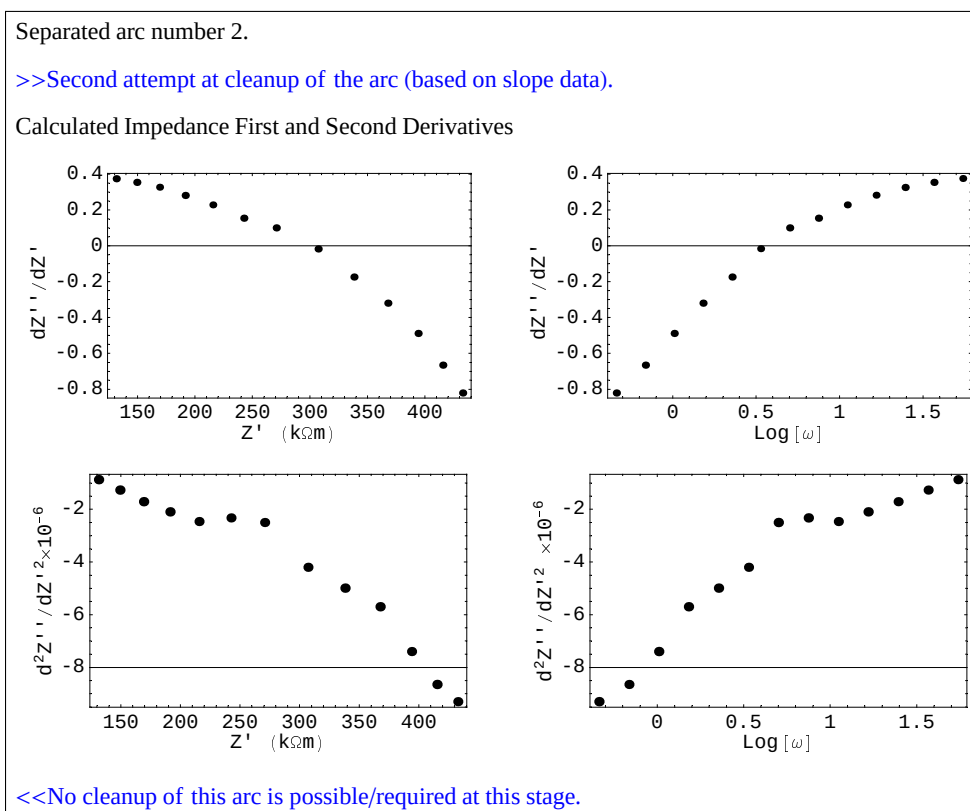


Figure A.14: Cleanup of the second arc obtained in the separation of the arcs shown in Figure A.12. All the points obtained in Figure A.12 remain. Even though there is a bump in the second derivative data, the routine used is robust enough to realize that this is not a turning point where the arcs could be cleaned up. This robustness is achieved by a program setting which requires a fairly high number of points to match a particular trend, for a “true” turning point to be identified.

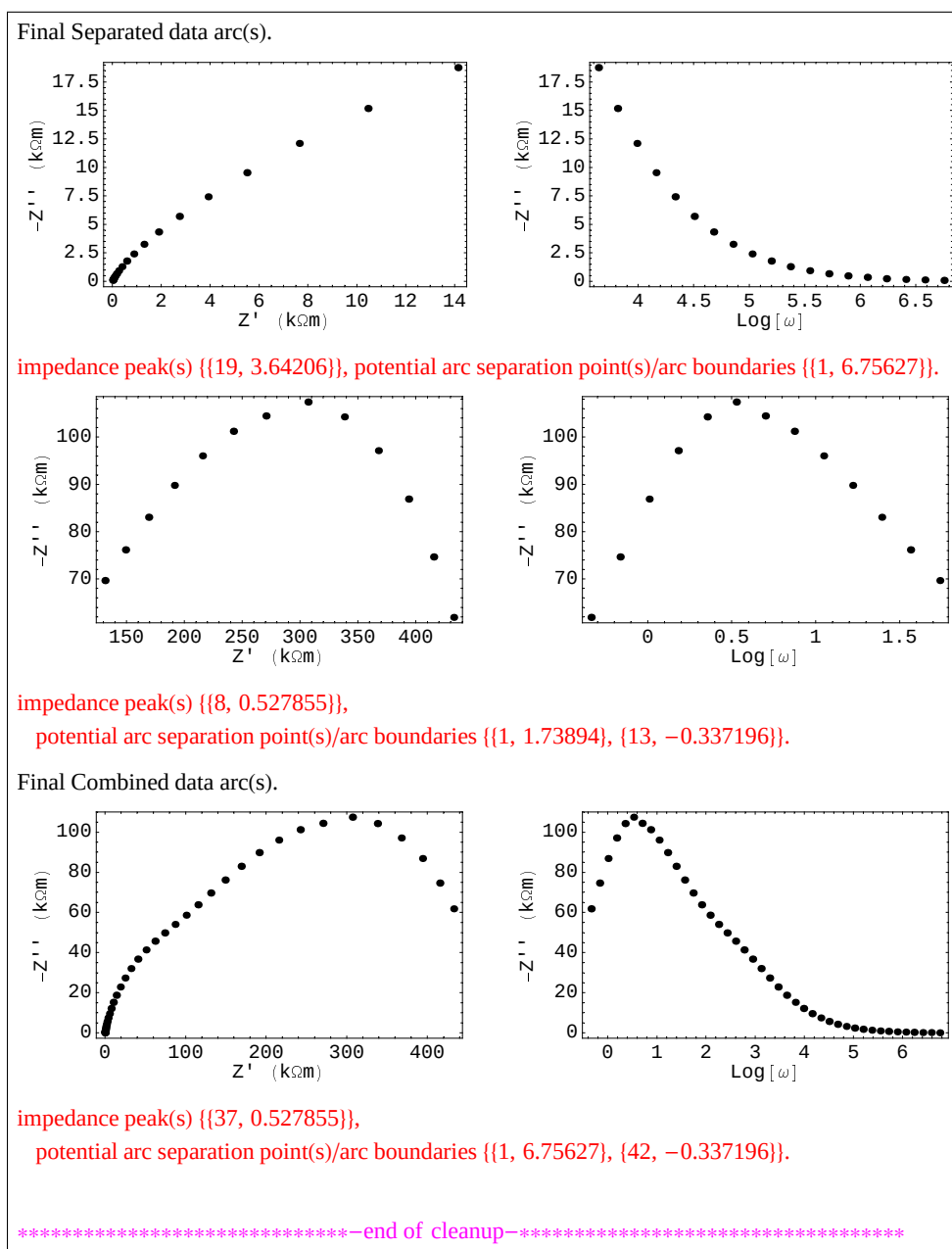


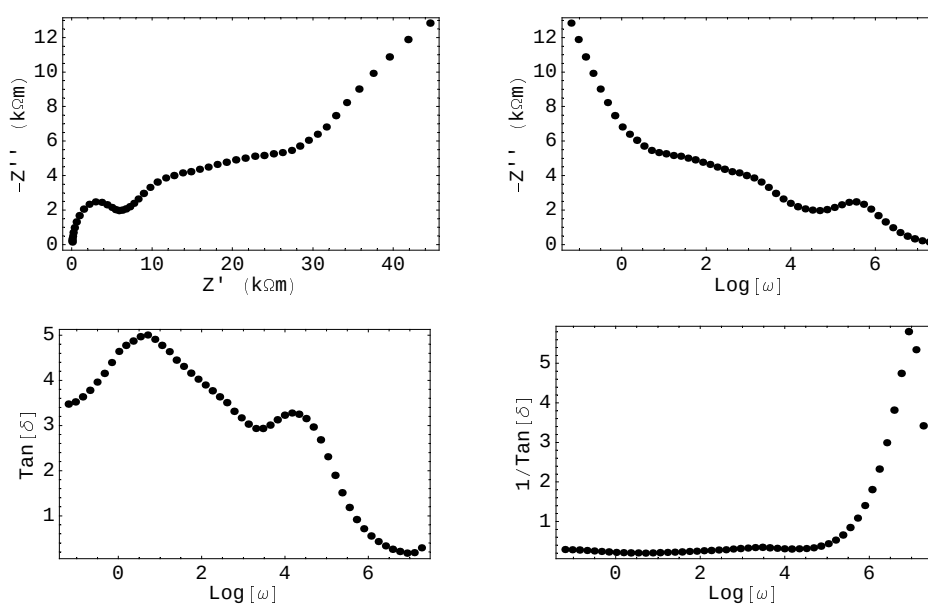
Figure A.15: The final separated arcs for the LPSSiC sample. The routine successfully resolves and separates out the individual arcs (top and middle). The final composite data is shown in the plots at the bottom. Again the composite data is taken from the first point of the first (high frequency) arc to the last point of the second (low frequency) arc and includes the overlap region but not the stray points.

A.3 Example 3

An even more difficult data set is presented in this example and again the program, using the procedure described in Section 2.6.2 is able to resolve and separate out the arcs. While the second arc obtained does not have enough points to be used in finding characteristic frequencies and estimating the dc resistance, the first arc does, making the procedure worth pursuing. Further, data for the composite (first and part of second arc) is obtained which is free of the erratic points and the arc due to electrode effects. There are enough points in this data for direct analysis of the properties of the composite. The experimental data in this example, chosen to highlight the program's handling of more complex data, is from a tetragonal stabilized zirconia (not in the series in Chapter 5) at 250 °C. Three contributions to the data can be readily observed by eye. The process is detailed in Figures A.16 to A.20 and explained in the program dialogue and the figure captions.

3, C:\ArcSeparationDemo\AutoFormattedFiles\B2-250.dat.

Raw data.



impedance peak(s) {{11, 5.54519}, {50, -1.20182}}, potential arc separation point(s)/arc boundaries {{3, 6.92929}, {19, 4.1611}, {23, 3.46905}, {39, 0.700868}}.

Figure A.16: The raw data for the arc separation and cleanup process for a TSZ sample presented in various formats. In this example, which is more difficult than the two previous examples, there is greater overlap of the arcs. Several positions have been identified as potential arc boundaries based on the $-Z''$, $\tan(\delta)$ and $1/\tan(\delta)$ data and these are listed at the bottom.

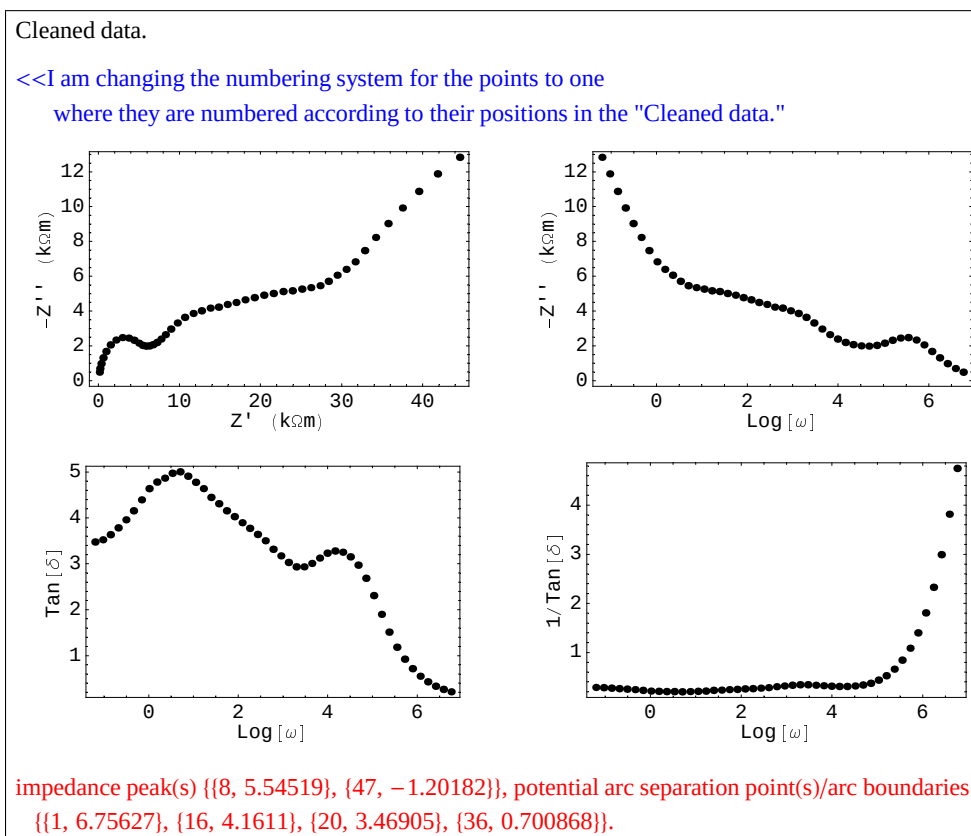


Figure A.17: The figure shows the data from Figure A.16 with the erratic points removed. Cleanup of the data only removes three points at the highest frequencies in the “raw” data. Note also that the points have been renumbered.

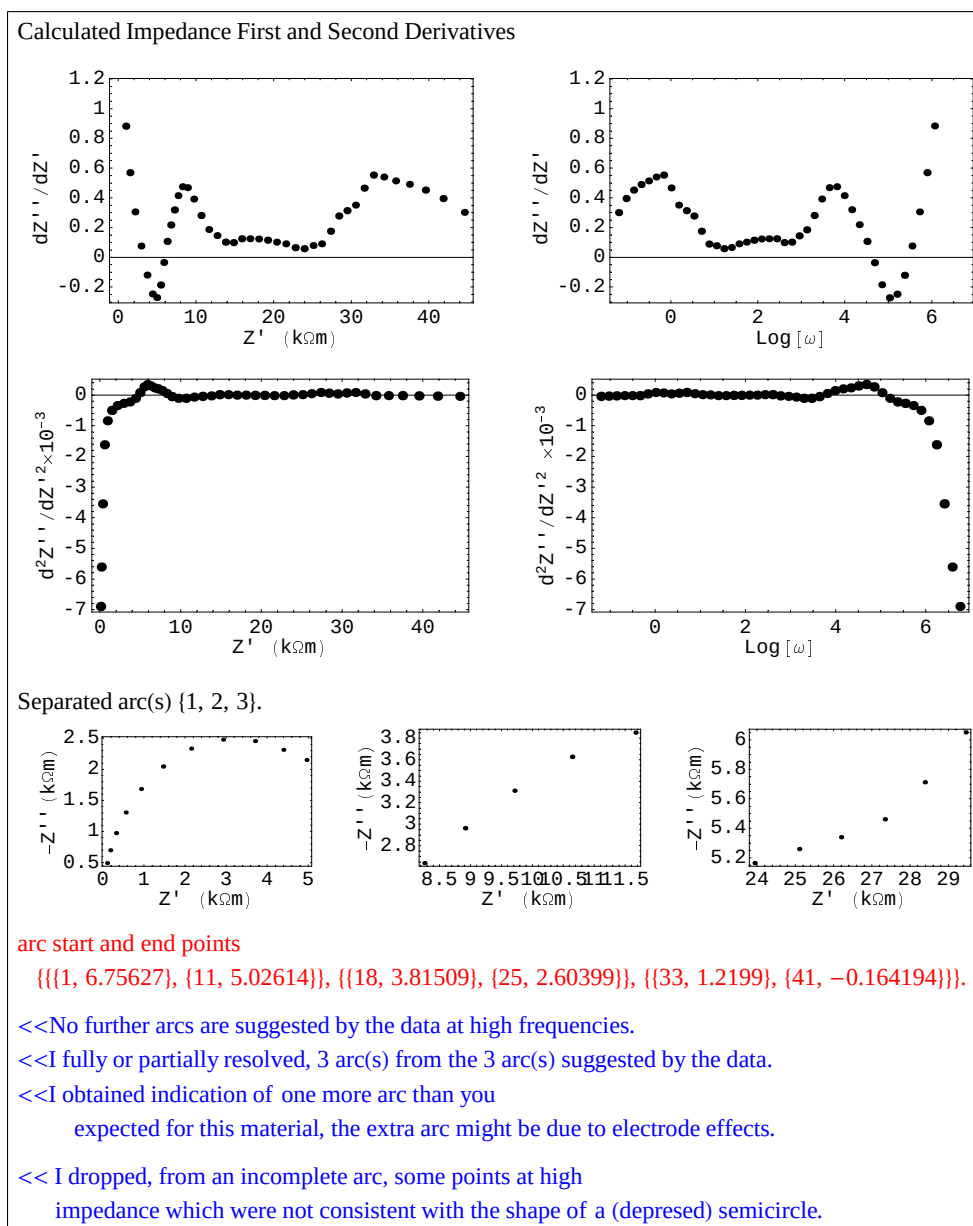


Figure A.18: This figure shows the first and second derivatives (top and middle) of the data in Figure A.17 plotted as functions of Z' and $\log(\omega)$. The derivatives show sharp turning points. Using the derivatives together with the $\tan(\delta)$, $1/\tan(\delta)$ and $-Z''$ data, the arcs are separated out (bottom). All three arcs have been resolved. Note that some points at high impedance in the last two arcs, which do not conform to the pattern for (depressed) semicircles, have been dropped.

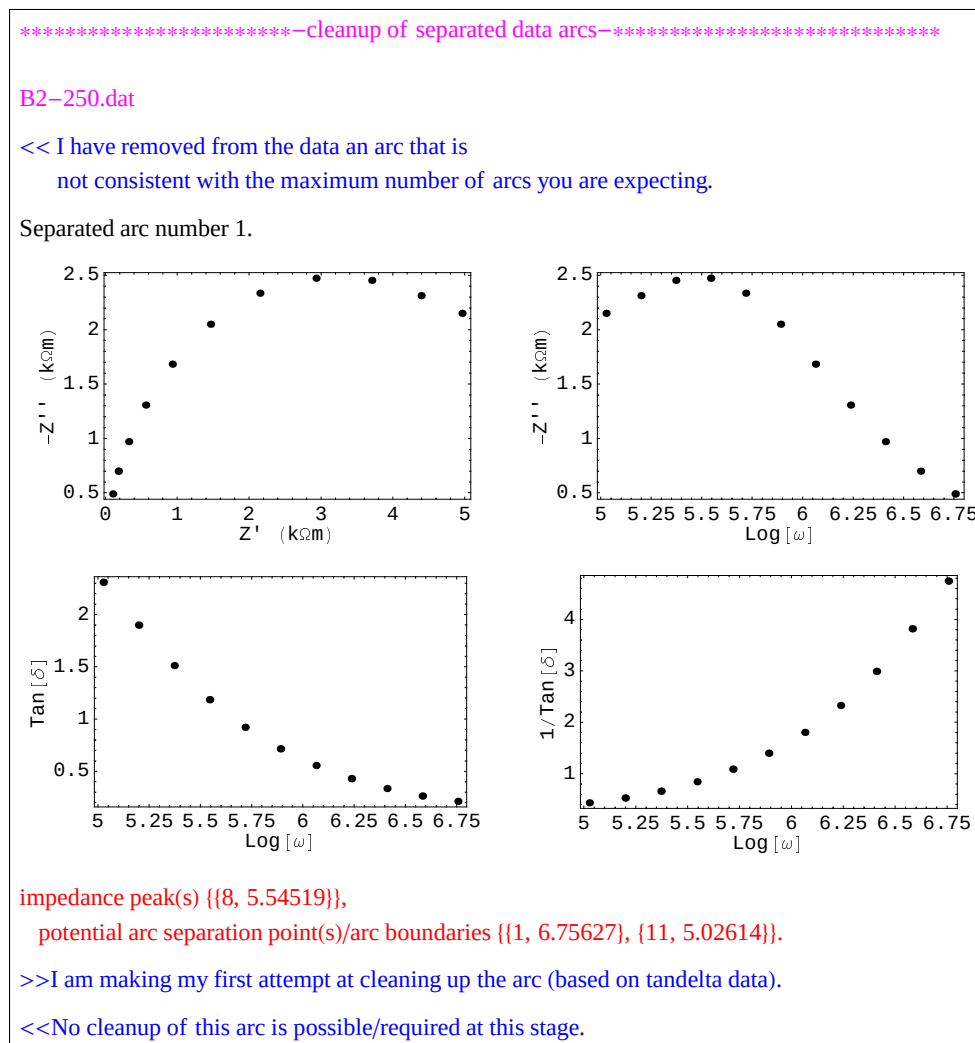


Figure A.19: A user imposed restriction on the number of arcs expected is used as the basis for eliminating one of the three arcs obtained in Figure A.18. No cleanup of the first arc or second arc is possible in this or subsequent stages.

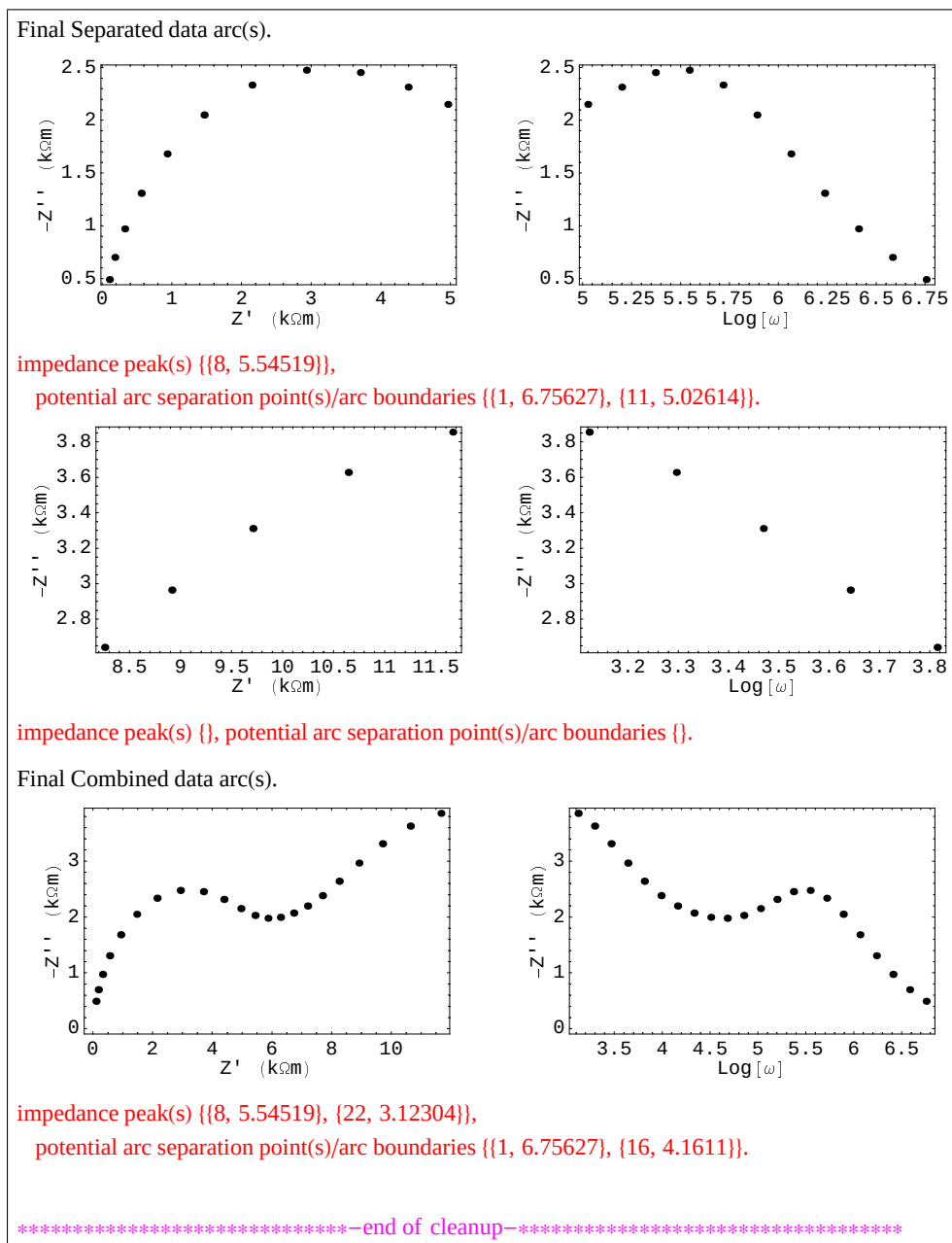


Figure A.20: The final two separated arcs (top and middle) and the composite data, including the overlap region (bottom). Again the routine has successfully resolved and separated out the arcs as well as obtained data for the composite which is free of the erratic points and electrode effects.

A.4 Discussion

The foregoing examples demonstrate the capabilities of the arc separation procedure developed in this work and implemented as a *Mathematica* program. While in practice it is not 100% foolproof, it does provide a quick, easy and automated way for initial data manipulation and for preparing data for more detailed analysis. Large sets of composite sample data can be handled in seconds on a fast PC. The user only needs to specify the optional parameter the *maximum number of arcs expected*.

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