

ELASTIC PROPERTIES
OF GLASSES AND GLASS CERAMICS
AT HIGH PRESSURES AND HIGH TEMPERATURES

by

Salomé Gravett
B Sc (Hons) UOFS

A thesis submitted in fulfilment of the requirements
for the degree of

Master of Science
in the
Department of Physics
University of the Witwatersrand
Johannesburg
1989

(ii)

ABSTRACT

The elastic properties and behaviour of several glasses and glass ceramics have been measured in the 0-300 °C and 0-3 GPa ranges using an ultrasonic method. A solid pressure transmitting capsule with a resistance heater was used. The ultrasonic longitudinal and shear wave velocities through the material were measured with the pulse echo overlap method. C_{11} , C_{44} , E , C_{12} , σ and B were calculated from the velocities and the unit volume variation was established. Zerodur glass ceramic shows a phase transformation around 1.5 GPa and a simple phase diagram have been drawn up, indicating the versatility of this technique. Corning 9658 glass shows a linear unit volume variation with pressure. The results for Corning 9658 glass ceramic shows good agreement with previously published results. 119 MCY glass shows a positive $(\partial B/\partial P)_T$ but a negative $(\partial C_{44}/\partial P)_T$. 119 MCY glass ceramic behaves elastically "normal" for a crystalline material, in that the pressure derivatives are positive and the temperature derivatives are negative.

(iii)

DECLARATION

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

S. J. J. J. J.

10th day of May, 1987.

(iv)

To my husband

Paul, thank you for your patience and encouragement during the completion of this thesis.

CONTENTS

Preface
 Acknowledgements
 Notation
 List of tables
 List of figures

CHAPTER	PAGE
1. INTRODUCTION	1
1.1 Elastic properties	1
1.2 Glasses	3
1.3 Glass ceramics	5
1.4 High pressure and high temperature	7
2. THEORY	11
2.1 Introduction	11
2.2 Elasticity theory	11
2.2.1 Strain components	11
2.2.2 Stress components	14
2.2.3 Elastic constants	16
2.3 Elastic constants of glasses and glass ceramics with pressure and temperature	22
2.4 Measurement of elastic constants	26
3. EXPERIMENTAL TECHNIQUE	29
3.1 Elasticity and its measurement at high pressure and high temperature	29
3.1.1 Review of elasticity measurements	29
3.1.2 The pulse echo overlap method	30
3.1.3 The pulse echo overlap method at high pressure and high temperature	37

(vi)

3.2	The high pressure and high temperature apparatus	37
3.3	The piston assembly	41
3.4	The high pressure and temperature ultrasonic capsule	45
3.5	Experimental procedure	50
3.5.1	Pressure	50
3.5.2	Temperature	50
3.5.3	Frequency	50
4.	DATA ANALYSIS	52
4.1	Pressure	52
4.2	Temperature	56
4.3	Elastic moduli	60
5.	RESULTS AND DISCUSSION	62
5.1	Zerodur glass ceramic	62
5.2	Corning 9658 glass ceramic	78
5.3	Corning 9658 glass	89
5.4	119 MCY glass	98
5.5	119 MCY glass ceramic	107
6.	SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	115
7.	REFERENCES	118

PREFACE

Recently the capability to measure ultrasonic sound velocities in a solid has been extended in this laboratory to measure the velocities at high pressures and high temperatures simultaneously. Fused quartz was the first material to be tested, using this apparatus, and the results were most rewarding. A variety of glassy and glass ceramic samples were supplied by Prof. Ashbee of the University of Tennessee, Knoxville, who is a glass ceramic specialist. The intention was to examine the elastic constants of glasses and glass ceramics, particularly where elastic constant determination is concerned. The major aim was to establish:

- a) phase boundaries,
- b) the phase (glassy or crystalline) within which the phase transition takes place, if it occurs at all, and
- c) if no such transition is seen, to simply establish the unit volume variation in the materials and try to understand them in terms of their composition and structure.

PREFACE

Recently the capability to measure ultrasonic sound velocities in a solid has been extended in this laboratory to measure the velocities at high pressures and high temperatures simultaneously. Fused quartz was the first material to be tested, using this apparatus, and the results were most rewarding. A variety of glassy and glass ceramic samples were supplied by Prof. Ashbee of the University of Tennessee, Knoxville, who is a glass ceramic specialist. The intention was to examine the elastic constants of glasses and glass ceramics, particularly where elastic constant determination is concerned. The major aim was to establish:

- a) phase boundaries,
- b) the phase (glassy or crystalline) within which the phase transition takes place, if it occurs at all, and
- c) if no such transition is seen, to simply establish the unit volume variation in the materials and try to understand them in terms of their composition and structure.

ACKNOWLEDGEMENTS

I would like to acknowledge the following people for their assistance in completing this study:

Dr G G Garrett, the Divisional Director of the Division of Material Science and Technology at the CSIR for the opportunity to perform this study.

Prof J D Comins of the Physics Department of the University of the Witwatersrand for encouragement, interest and assistance as supervisor.

Dr S Hart, former Divisional Head of the Ceramics Group in the previous Institute for Materials Research at the CSIR for sharing his knowledge as a specialist in this field.

Dr I Sigalas as co-supervisor and present programme manager in Composite Materials at the Division of Material Science and Technology, for the inspiration and chance to complete this thesis.

Prof K H G Ashbee of the University of Tennessee for information that he supplied and his interest in this work.

My colleagues for helping out whenever it was necessary and who made a contribution during this study.

NOTATION

α, β, γ	angles
a, b, c, f, g, h	unit cell axes
f', g', h'	distorted axes
i, j, k, l	integers taking the values 1, 2, ..., 6
q, r	letters taking the values x, y, z
$\epsilon_{q,r}$	strain components
e_{qr}	strain components
r, r'	particle position
x	displacement
X_q, Y_q, Z_q	stress components
s_{ij}	elastic compliances or elastic moduli
u, v, w, x, y, z	displacement components
C_{ij}	elastic stiffnesses or elastic constants
C_{12}	Lamé constant
L	longitudinal modulus
v_l	longitudinal wave velocity
S_i	strain component
T_i	stress component
v	velocity
C or M	elastic constant
ρ	density
E	Young's modulus
v_e	extensional sound wave velocity
G	shear modulus
v_s	transverse or shear-polarized sound wave velocity
κ	compressibility
V	volume
P	pressure
T	temperature
B	Bulk modulus
σ	Poisson's ratio

(x)

ϵ_s	transverse strain
ϵ_l	longitudinal strain
A_i	wave amplitude
t	time
f	frequency
ω	wave frequency
k_i	wave constant
l	length of sample
w	natural velocity
P_1	oil pressure
P_2	sample pressure
A_1	ram face area
A_2	piston face area

LIST OF TABLES

Chapter 2

Table 2.1 The connection between elastic constants of isotropic bodies

Chapter 5

Table 5.1.1 Chemical composition of a typical Zerodur sample

Table 5.1.2 Zerodur GC: Elastic properties and their polynomial coefficients

Table 5.1.3 Elastic moduli of Zerodur at room temperature

Table 5.1.4 Values indicating the high-to-low quartz phase boundary for Zerodur

Table 5.2.1 Density and longitudinal and shear phase velocities of 9658 GC

Table 5.2.2 Room temperature elastic properties and their pressure derivatives of 9658 GC

Table 5.2.3 9658 GC: Elastic properties and their polynomial coefficients

Table 5.3.1 9658 glass: Elastic properties and their polynomial coefficients

Table 5.4.1 Chemical composition of 119 MCY glass

Table 5.4.2 119 MCY glass: Elastic properties and their polynomial coefficients

Table 5.5.1 119 MCY GC: Elastic properties and their polynomial coefficients

LIST OF FIGURES

Chapter 1

Fig. 1.1 Two-dimensional representation of an oxide M_2O_3 in (a) the crystalline form (b) the glassy form

Chapter 2

Fig. 2.1 Coordinate axes for the description of the state of strain

Fig. 2.2 Demonstration that $Y_x = X_y$ in order that the body may be in equilibrium

Chapter 3

Fig. 3.1 The essential components of the pulse echo overlap system

Fig. 3.2(a) A series of diminishing echoes

(b) The echo train obtained when using a buffer rod

(c) Two echoes being overlapped

Fig. 3.3 Circuit diagram of the MATEC system

Fig. 3.4 The Kennedy Press

Fig. 3.5 Main components, capsule, piston and cylinder

Fig. 3.6 The cylinder stack

Fig. 3.7 Block diagram of the auxiliary equipment

Fig. 3.8 Cross-sectional diagram of the piston assembly

Fig. 3.9(a) Exploded diagram of the cross-section of the high pressure and temperature ultrasonic capsule

(b) Assembly diagram of capsule

Fig. 3.10 An assembled capsule and components on the pressure plate

Chapter 4

Fig. 4.1 Hysteresis loop obtained when a pressure-dependent variable f is plotted against pressure for a piston-cylinder device

(xiii)

Fig. 4.2 Hysteresis curve for the resistance of a manganin gauge versus pressure

Fig. 4.3 Pressure versus resistance as the independent variable

Fig. 4.4 Upstroke friction versus nominal upstroke pressure. The dotted line is a tangent fitted to the curve at B

Fig. 4.5a) Temperature profiles in the sample space had to be recorded at three points - the top, middle and bottom

b) The temperature read by the reference thermocouple had to be calibrated against the actual temperature read by the test thermocouple in the sample space

Fig. 4.6 Temperature profiles along the sample length at four mean temperatures

Fig. 4.7 Temperature at two end surfaces of sample (top and bottom) as a function of temperature at the middle of the sample

Fig. 4.8 Temperature read by the reference thermocouple versus temperature read by the test thermocouple

Chapter 5

Fig. 5.1.1 Thermal expansion behaviour of c axis

Fig. 5.1.2 Zerodur: Longitudinal frequency (long. freq.) vs pressure (P) for four isotherms

Fig. 5.1.3 Zerodur: Shear frequency (shear freq.) vs pressure for four isotherms

Fig. 5.1.4 Zerodur: Longitudinal modulus (L) vs pressure

Fig. 5.1.5 Zerodur: Shear modulus (G) vs pressure

Fig. 5.1.6 Zerodur: C_{11} vs pressure

Fig. 5.1.7 Zerodur: C_{44} vs pressure

Fig. 5.1.8 Zerodur: Young's modulus (E) vs pressure

Fig. 5.1.9 Zerodur: Lamé constant (C_{12}) vs pressure

Fig. 5.1.10 Zerodur: Poisson's ratio (σ) vs pressure

Fig. 5.1.11 Zerodur: Bulk modulus (B) vs pressure

Fig. 5.1.12 Zerodur: Volume variation (V/V_0) vs pressure

Fig. 5.1.13 Zerodur: Volume variation vs pressure at room temperature as measured with the ultrasonic method and the static-compression method

Fig. 5.1.14 Phase diagram of SiO_2

Fig. 5.1.15 Phase diagram of Zerodur

Fig. 5.2.1 Electron micrograph of a machinable glass ceramic

Fig. 5.2.2 9658 glass ceramic (GC): Isotherms for the longitudinal frequency vs pressure

Fig. 5.2.3 9658 GC: Isotherms for the shear frequency vs pressure

Fig. 5.2.4 9658 GC: Longitudinal modulus vs pressure

Fig. 5.2.5 9658 GC: Shear modulus vs pressure

Fig. 5.2.6 9658 GC: C_{11} vs pressure

Fig. 5.2.7 9658 GC: C_{44} vs pressure

Fig. 5.2.8 9658 GC: Young's modulus vs pressure

Fig. 5.2.9 9658 GC: Lamé constant vs pressure

Fig. 5.2.10 9658 GC: Poisson's ratio vs pressure

Fig. 5.2.11 9658 GC: Bulk modulus vs pressure

Fig. 5.2.12 9658 GC: Temperature dependence of Young's and shear moduli produced by Nakano, et al.

Fig. 5.2.13 9658 GC: Volume variation vs pressure

Fig. 5.2.14 9658 GC: Volume variation vs pressure at room temperature compared with the result of Gerlich and Hart

Fig. 5.3.1 9658 glass: Longitudinal frequency vs pressure at temperature

Fig. 5.3.2 9658 glass: Shear frequency vs pressure at temperature

Fig. 5.3.3 9658 glass: Longitudinal modulus vs pressure

Fig. 5.3.4 9658 glass: Shear modulus vs pressure

Fig. 5.3.5 9658 glass: C_{11} vs pressure

Fig. 5.3.6 9658 glass: C_{44} vs pressure

Fig. 5.3.7 The relationships between $\partial B/\partial P$ and $\partial C_{44}/\partial P$, vs SiO_2 content in the silicate glasses

Fig. 5.3.8 9658 glass: Young's modulus vs pressure

Fig. 5.3.9 9658 glass: Lamé constant vs pressure

(xv)

Fig. 5.3.10 9658 glass: Poisson's ratio vs pressure
Fig. 5.3.11 9658 glass: Bulk modulus vs pressure
Fig. 5.3.12 9658 glass: Volume variation vs pressure

Fig. 5.4.1 119 MCY glass: Longitudinal frequency vs pressure at temperature
Fig. 5.4.2 119 MCY glass: Shear frequency vs pressure at temperature
Fig. 5.4.3 119 MCY glass: Longitudinal modulus vs pressure
Fig. 5.4.4 119 MCY glass: Shear modulus vs pressure
Fig. 5.4.5 119 MCY glass: C_{11} vs pressure
Fig. 5.4.6 119 MCY glass: C_{44} vs pressure
Fig. 5.4.7 119 MCY glass: Young's modulus vs pressure
Fig. 5.4.8 119 MCY glass: Lamé constant vs pressure
Fig. 5.4.9 119 MCY glass: Poisson's ratio vs pressure
Fig. 5.4.10 119 MCY glass: Bulk modulus vs pressure
Fig. 5.4.11 119 MCY glass: Volume variation vs pressure

Fig. 5.5.1 119 MCY GC: Longitudinal frequency vs pressure at temperature
Fig. 5.5.2 119 MCY GC: Shear frequency vs pressure at temperature
Fig. 5.5.3 119 MCY GC: Longitudinal modulus vs pressure
Fig. 5.5.4 119 MCY GC: Shear modulus vs pressure
Fig. 5.5.5 119 MCY GC: C_{11} vs pressure
Fig. 5.5.6 119 MCY GC: C_{44} vs pressure
Fig. 5.5.7 119 MCY GC: Young's modulus vs pressure
Fig. 5.5.8 119 MCY GC: Lamé constant vs pressure
Fig. 5.5.9 119 MCY GC: Poisson's ratio vs pressure
Fig. 5.5.10 119 MCY GC: Bulk modulus vs pressure
Fig. 5.5.11 119 MCY GC: Volume variation vs pressure

1. INTRODUCTION

The main aspects of this study are reviewed in this section.

1.1 Elastic properties

Many scientific-technological advances depend greatly on solid-state elastic properties, especially on their magnitudes as well as their responses to stress and temperature variables. Elastic constants relate to various fundamental solid-state phenomena, such as interatomic potentials or binding forces and equations of state. In thermodynamics they are related to specific heat, thermal expansivity, Debye temperature and Grüneisen's constant. In engineering they are used in calculations for load deflection, residual stress, thermoelastic stress, fracture toughness and elastic instabilities.

Velocities of longitudinal and transverse waves depend entirely on the elastic constants and the mass density. By using velocity methods, the measurements of elastic constants are highly precise. McSkimin and Andreatch (1967) have reported precision of one part in 10^7 , while Papadakis (1969) has reported precision of 5 parts in 10^6 . This capability enables one to use elastic constants in the study of the effects of temperature, pressure, mechanical stress, magnetic field, crystallographic transformations and superconducting transitions.

Thus, elastic constants are applicable to many disciplines: structural design, materials science, and solid-state physics. They may be applied to technological structural economics, safety, and may be used to describe various materials phenomena and fundamental interatomic forces.

In general the atomic structural arrangement of a material and the strength of its interatomic binding forces determine the elastic behaviour of a crystal (Sidek, et al., 1987). The elastic properties of a material are of great importance in determining its behaviour when it is subjected to deformation.

The moduli of elasticity for glass ceramics are higher than those of ordinary glasses and of some conventional ceramics, but they are lower than those of sintered pure oxide ceramics (McMillan, 1979). For glasses, the Young's modulus shows a roughly additive relationship with chemical composition and factors have been derived which enable the modulus to be calculated from the glass composition. The modulus of elasticity of a polyphase ceramic will also be an additive function of the individual characteristics of the crystalline and glassy phases. In a glass ceramic it is to be expected that the Young's modulus will be determined primarily by the elastic constants of the major crystalline phases although the presence in the glass phase of oxides which promote the development of high values of Young's modulus must be allowed for; in particular, calcium oxide, magnesium oxide, and aluminium oxide appear to exert a marked influence upon the elastic moduli of glasses.

Variation of the heat-treatment schedule of a glass ceramic allows different volume fractions of crystal phases to be developed and therefore permits the influence upon elastic properties to be examined.

The effect of temperature upon the elastic constants of glass ceramics can in some cases reveal marked influences resulting from the presence of certain crystal phases. Glass ceramics are remarkable for the very wide range of thermal expansion coefficients which can be obtained. At one extreme, materials having negative coefficients of thermal expansion are available while for other compositions very high positive coefficients are observed. Between these two extremes there exist glass ceramics having thermal expansion coefficients practically equal to zero and others whose expansion coefficients are similar to those of ordinary glasses or ceramics or to those of certain metals or alloys.

In this study the effects of pressure and temperature on elastic constants have been investigated. The focus is limited to several glasses and glass ceramics. In some cases the glassy samples come from the materials used to produce the glass ceramics by annealing.

There exists special merit for applying this high pressure, high temperature ultrasonic technique to solid materials, since not much work

Author Gravett Salome

Name of thesis Elastic Properties Of Glasses And Glass Ceramics At High Pressures And High Temperatures. 1989

PUBLISHER:

University of the Witwatersrand, Johannesburg

©2013

LEGAL NOTICES:

Copyright Notice: All materials on the University of the Witwatersrand, Johannesburg Library website are protected by South African copyright law and may not be distributed, transmitted, displayed, or otherwise published in any format, without the prior written permission of the copyright owner.

Disclaimer and Terms of Use: Provided that you maintain all copyright and other notices contained therein, you may download material (one machine readable copy and one print copy per page) for your personal and/or educational non-commercial use only.

The University of the Witwatersrand, Johannesburg, is not responsible for any errors or omissions and excludes any and all liability for any errors in or omissions from the information on the Library website.