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

by

Salomé Gravett
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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. $C_{11}$, $C_{44}$, $E$, $C_{12}$, $\sigma$ 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 $\left(\partial B/\partial P\right)_T$ but a negative $\left(\partial C_{44}/\partial P\right)_T$. 119 MCY glass ceramic behaves elastically "normal" for a crystalline material, in that the pressure derivatives are positive and the temperature derivatives are negative.
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.

[Signature]

11th day of May, 1951.
To my husband

Paul, thank you for your patience and encouragement during the completion of this thesis.
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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.
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My colleagues for helping out whenever it was necessary and who made a contribution during this study.
NOTATION

\( a, \beta, \gamma \) 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
\( e_{q,r} \) strain components
\( e_{qr} \) strain components
\( E, E' \) 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
\( \rho \) density
\( \rho \) Young's modulus
\( \nu \) extensional sound wave velocity
\( G \) shear modulus
\( \nu_s \) transverse or shear-polarized sound wave velocity
\( \lambda \) compressibility
\( V \) volume
\( P \) pressure
\( T \) temperature
\( B \) Bulk modulus
\( \sigma \) Poisson's ratio
\( \varepsilon_s \) transverse strain
\( \varepsilon_l \) longitudinal strain
\( A_1 \) wave amplitude
\( t \) time
\( f \) frequency
\( w \) wave frequency
\( k \) wave constant
\( \ell \) length of sample
\( w \) natural velocity
\( P_1 \) oil pressure
\( P_2 \) sample pressure
\( A_1 \) ram face area
\( A_2 \) piston face area
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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, thermelastic 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 10⁷, while Papadakis (1969) has reported precision of 5 parts in 10⁶. 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