UNIVERSITI PUTRA MALAYSIA

EFFECT OF PbO ON THE ELASTIC PROPERTIES OF BORATE AND PHOSPHATE GLASS SYSTEM

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By

AZMAN B. KASIM

Thesis Submitted in Fulfilment of the Requirements for the Degree of Master of Science in the Faculty of Science & Environmental Studies
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July 2000

DEDICATIONS

To…

My wife, Nazrah

My Dad, Hj. Kasim

My Mum, Hjh. Jamilah

My Brother, Azrin Kasim

My Sister, Noor Azah Kasim

… Thanks for your support
And endless love…

Abstract of the thesis presented to the Senate Of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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Faculty: Science and Environmental Studies

The effect of PbO on the elastic properties phosphate of glass and borate glass system has been studied. A series of lead borate glasses [PbO_x. $(B_2O_3)_{x-1}$ (0.30 $\leq$ X $\leq$ 0.45)] and lead phosphate glasses [PbO_x. $(P_2O_5)_{x-1}$ (0.10 $\leq$ X $\leq$ 0.60)] were successfully synthesized. By using ultrasonic measurement system, the velocities of the propagated waves attained could be used to estimate the elastic properties of glass. In this studies, the velocities of propagated waves in lead borate and lead phosphate are found to decrease with the mole fraction of PbO. Meanwhile, the addition of PbO increases the density of glasses. It shows that lead borate and lead phosphate glasses become more rigid but undergone a weakening structure. Hence, an addition of PbO will affect the elastic properties of glass. From the

experimental results `the elastic modulus C_{11} and C_{44}, Young's modulus (E); bulk modulus (B) and Poisson ratio (σ) are also found to vary with the mole fraction of PbO. The Debye temperatures, which describe the thermal behaviour for isotropic materials such as glass also show a decreasing trend with the mole fraction of PbO. It seems that an addition of PbO into the borate and phosphate glass systems changes the coordination of the glass structure and weakens the glass network by the increase of non-bridging oxygens (NBOs).

From the structural aspect, the lead borate glass consists of BO_3 and BO_4 units, which change markedly with the PbO content. At low PbO concentration ($x \leq 0.15$), lead is assumed to assist in the formation of BO_4 tetrahedral. Whereas, for high PbO content ($x > 0.15$), some of lead act to form PbO_4 pyramid. Meanwhile, for lead phosphate glasses, since the basic structure is PbO_4 tetrahedral, hence an increment of PbO content tend to reduce the number of cross-linking P-O-P bonds between pairs of tetrahedral and increase the number of chains of PO_4 tetrahedral.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk memperolehi ijazah Master Sains.

KESAN PbO TERHADAP SIFAT KENYAL KACA BORAT DAN KACA FOSFAT

Oleh

AZMAN BIN KASIM

Julai 2000

Pengerusi : Prof. Madya Sidek Hj. Ab. Aziz, Ph.D

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Kesan PbO terhadap sifat-sifat kenyal kaca borat dan fosfat telah dikaji. Satu siri kaca borat [PbO_x. $(B_2O_3)_{x-1}$ ($0.30 \leq X \leq 0.45$)] dan kaca fosfat [PbO_x. $(P_2O_5)_{x-1}$ ($0.10 \leq X \leq 0.60$)] telah pun disediakan. Dengan menggunakan sistem pengukuran ultrasonik, halaju perambatan gelombang yang diperolehi telah digunakan untuk menganggar sifat kenyal bagi kaca. Dalam kajian ini didapati halaju gelomb-ang yang merambat dalam kaca borat dan fosfat berkurangan terhadap pertambahan PbO. Pertambahan PbO juga turut meningkatkan ketumpatan kaca-kaca tersebut. Ini menunjukkan kaca plumbum borat dan plumbum fosfat menjadi lebih keras tetapi mempunyai struktur yang lemah. Pertambahan PbO telah memberi kesan terhadap sifat kenyal kaca. Daripada hasil ujikaji didapati modulus kenyal C_{11} dan C_{44}, modulus Young (E), modulus pukal (B) dan nisbah

Poisson (σ) turut berubah terhadap plumbum oksida. Suhu Debye yang menerangkan tentang ciri-ciri terma bagi bahan isotropik seperti kaca juga menunjukkan penurunan terhadap kandungan PbO. Maka, pertambahan ion plumbum ke dalam sistem kaca borat dan kaca fosfat telah mengubah koordinasi struktur kaca dan melemahkan rangkaian kaca disebabkan oleh pertambahan bilangan oksigen bebas (NBOs).

Dari aspek struktur, kaca plumbum borat yang mengandungi unit BO_3 dan BO_4 turut mengalami perubahan terhadap kandungan PbO. Bagi kandungan PbO rendah ($x<0.15$), plumbum dikatakan membantu pembentukkan BO_4 tetrahedra. Manakala, untuk kandungan PbO tinggi ($x>0.15$), sebahagian daripada plumbum bertindak membentuk piramid PbO_4. Bagi kaca plumbum fosfat yang mempunyai struktur asas PO_4 tetrahedra, pertambahan PbO telah mengurangkan hubungan silang ikatan P-O-P antara pasangan tetrahedra dan meningkatkan sejumlah bilangan rantaian PO_4 tetrahedra.

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LIST OF SYMBOLS AND ABBREVATIONS

SOEC	-	Second Order Elastic Constants
IR	-	infra red
NBOs	-	Nonbridging oxygens
DTA	-	Differential Thermal Analysis
EDX	-	Energy Dispersive X_ray
XRD	-	X_ray Diffraction
SEM	-	Scanning Electron Microscope
σ	-	stress
ε	-	strain
e_{ij}	-	strain components
σ_{ij}	-	stress components
C_{rs}	-	components of elastic constant
λ,μ	-	Lame's constants
V_L	-	longitudinal velocity
V_S	-	shear velocity
ν	-	Poisson's ratio
B	-	bulk modulus
E	-	Young's modulus
d	-	fractal dimension
W_{air}	-	weight of the sample in the air

$W_{acetone}$	-	weight of the sample in acetone
ρ_s	-	density of the glass sample
$\rho_{acetone}$	-	absolute density of acetone ~ 0.7899 g/cm^3

CHAPTER 1

INTRODUCTION

A wide spread interest of the science and technology of glass has attracted considerable attention to scientists and researchers throughout the world. Glass is believed to have been found in the Middle East 3000 BC but it was not well developed. The development of glass has advanced a great deal in early 20th century but a rapid growth of glass technology was only started in the last sixty years. One of the earliest developments was air tempering to improve their strength.

Glass is one of man's most valuables and versatile materials in daily uses. Glass has found applications in optical data transmission, detection, sensing, laser technologies and batteries application. By glass we usually understand it as hard material, often transparent or translucent, which is made by heating together a mixture of materials such as sand, limestone and soda at a very high temperature.

Glass History

The word `glass' is derived from an Indo European root meaning `shiny', which has also been given the words glare, glow and glaze. Glasses and glazes were manufactured far back in human history. According to Sir W.M. Flinders Petrie, the earliest known glaze dates from about 12000 B.C. and the earliest pure glass from about 7000 B.C. Both glasses were found in Egypt. In the West, glass manufacturing was dispersed to isolated sites after the fall of the Roman Empire but was continued in Byzantium and later in the Middle East by the Arabs.

Progress in techniques of glass manufacture and in the application of glass was subsequently rapid, in parallel with many other areas of technology. Until the twentieth century most of these advances were made empirically, using common sense to guide experimentation. The application of basic scientific understanding to the improvement of glass manufacture and to new application of glass occurred only in the last few decades. Among the first to study glass in a more basic way was Micheal Faraday (1830).

He studied the electrolysis and conductivity of various glasses. Later, Warburg and Tegetmeier (1884) found that the electrolysis of glass followed the Faraday's law. At the same time, Tammann (1884) initiated work on the viscosity of glass, glass transition, the relationship of crystallization rate and viscosity and the reasons for glass formation. Schulz (1913) made a detailed study of exchange and diffusion of silver ions for sodium ions in a commercial glass.

Joseph Fraunhopper (1787-1826) was successful in preparing the optical glass. Until the twentieth century, the Department of Glass Technology at Shelfield University, England carried out a great experimental and theoretical approach of glass technology under Prof. W.E.S.Turner's research group. They were active in measuring such properties as density, electrical conductivity, chemical durability, viscosity and thermal expansion of a wide variety of commercial and lab glasses. Griffith proposed his hardness and brittleness theorem and Zachariasen (1935) with his Random Network Theory after the World War II. To date, glass technology appication has produced various types of glass for commercial use.

Research Background

Various researches had been carried out on the physical properties of the borate and phosphate glasses. The works on the elastic properties of these glasses were extremely scarced. Previously, a research done on glass was reported by the well-known Saunders and his co-workers (1990). In order to give information about the elastic properties of borate and phosphate glasses, the ultrasonic velocity and attenuation measurements have been carried out. They were found to be successful in their works. Many researchers and scientists then continued this type of work.

Since then, works on glass and its properties were burst rapidly worldwide. For example, Soga (1985) was carried out an investigation on the elastic moduli and fracture toughness of glass. Santokh and co-workers (1989) investigated the elastic moduli of some mixed alkali borate glasses. From the measured ultrasonic velocities and densities, the elastic moduli were calculated. Senin (1994) studied the second order elastic constants of the rare earth phosphate glasses as a function of temperatures and pressure. Later, his co-worker carried out works on the elastic, inelastic and nonlinear acoustic properties of zincchloro-phosphate glass.

As mentioned previously, investigation towards the glass property is extremely scarced especially on the elastic properties of the glass. A number of works had been carried out on the physical properties of the borate and phosphate glasses. In spite of the vigorous investigation towards glass properties, to date not much work on the elastic properties of borate and phosphate glass was reported.

Objective of Study

The purpose of this project is to prepare and study the elastic properties of binary lead borate $(PbO)_X(B_2O_3)_{1-X}$ and binary lead phosphate $(PbO)_X(P_2O_5)_{1-X}$ glass system as function of x mole fraction. In this work, we also studied the effect of PbO on the physical properties of both glass systems.

The present work concerns the entire range of glass that can be prepared by melting respectively, PbO and B_2O_3 reagents and PbO and P_2O_5 reagents in alumina crucibles. After synthesizing the glass, the ultrasonic measurements were carried out at the room temperature in order to obtain the longitudinal and shear wave velocity. Together with the density measurements, the data for elastic constant was obtained and hence the compositional dependence of the elastic moduli could be determined. Thus, knowing the strength of a glass is of practical interest, since it may determine the durability of the glass use and it may also decide the suitability of the materials for special application (Salama et.al 1994).

Chapter Organization

In the next chapter the glass technology will be discussed including the uses of the glass and also about the glass family of interest. Then, chapter 3 describes the theory of glass, which includes the definition of glass and the explanation of the glass structures and components. The random network theory and the glass melting transition are also discussed. In chapter 4, the theory of elasticity and related elastic parameters will be described. In chapter 5, the methodology of the research is explained where the synthesizing of the glasses and the preparation of the glasses for the elastic measurements are given in detail. Chapter 6 and 7 report on the experimental results and give all the