UNIVERSITI PUTRA MALAYSIA

ELASTIC PROPERTIES AND IONIC CONDUCTIVITY OF LITHIUM PHOSPHATE AND LITHIUM BORATE GLASSES

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FSAS 1999 9

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1999

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By

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Thesis Submitted in Fulfilment of the Requirements for the Degree of Master of Science in the Faculty of Science and Environmental Studies, Universiti Putra Malaysia

June 1999

ACKNOWLEDGEMENT

First and foremost, I wish to thank my supervisor, Associate Professor Dr. Sidek Hj. Abd. Aziz for his supportive and friendly supervision. It is also my great privilege to have Associate Professor Dr. Chow Sai Pew as my co-supervisor. He has been kind and helpful to me over the past two years and I can never thank him enough for all his help and guidance.

I would like to extend my appreciation to Associate Professor Dr. Hj. Wan Mohd Daud Wan Yusoff and Dr. Mansor Hashim for their kindness in allowing me to explore the possibility of using their equipment for the ionic conductivity measurement. I would also wish to thank Associate Professor Dr. Zainal Abidin Talib for the beneficial discussions.

I would like to extend my gratitude to the government for granting the PASCA scholarship to me to support my daily expenditure. Finally, thanks to my heavenly Father for His grace and mercy throughout this two years.

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LIST OF ABBREVIATIONS

Mol%	Mole percent
fcc	Face-centered cube
T-T-T	Time-Temperature-Transformation Curve
NMR	Nuclear Magnetic Resonance
NBO	Non-Bridging Oxygen
BO	Bridging Oxygen
NDT	Non-Destructive Testing
RF	Radio Frequency
DUT	Device Under Test
IR	Infrared
ADWP	Asymmetric Double Well Potential

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

THE STUDIES OF ELASTIC PROPERTIES AND IONIC CONDUCTIVITY OF LITHIUM PHOSPHATE AND LITHIUM BORATE GLASSES

By

LOW YEE SAN

June 1999

Chairman : Associate Professor Sidek Hj. Abd. Aziz (Ph.D.)

Faculty : Science and Environmental Studies

Glasses are of scientific interest because their compositions can be varied over a very wide range and it is possible to produce glasses for a particular application. In this work, lithium glasses with phosphate and borate as the glass formers are studied. Four series of lithium glasses, lithium phosphate $(Li_2O)_x(P_2O_5)_{1-x}$ (x = 0.10 to 0.50), lithium chlorophosphate $(LiCl)_y[(Li_2O)_{0.4}(P_2O_5)_{0.6}]_{1-y}$ (y = 0.10 to 0.50), lithium borate $(Li_2O)_x(B_2O_3)_{1-x}$ (x = 0.15 to 0.40) and lithium chloroborate $(LiCl)_y[(Li_2O)_{0.25}(B_2O_3)_{0.75}]_{1-y}$ (y = 0.05 to 0.25) glasses have been prepared for the elastic property and ionic conductivity measurement using the rapid quenching technique. The ultrasonic velocities of the glass samples were measured by using the MBS 8000 ultrasonic data acquisition system. The densities were determined using the Archimedes' principle. The elastic properties and Debye temperatures of these glasses were then obtained. Young's modulus, bulk modulus and Debye temperature of binary lithium phosphate and borate glasses were found to increase with the mole fraction of Li_2O. The elastic moduli and Debye temperature of lithium chlorophosphate glasses were found decrease with the addition of LiCl whereas anomalous trend of elastic moduli and Debye temperature were observed in the case of lithium chloroborate glasses. The elastic properties of these glasses are closely related to the strength of glass networks and structures. The ionic conductivities of these glasses were measured by using the HP LCR meter. The conductance G was measured and used to calculate the ionic conductivity. Unusual frequency-dependent ionic conductivity was encountered in these glasses at lower mole fractions of Li_2O or LiCl content. Anomalous trend of temperature-dependent ionic conductivity was observed for binary glasses with lower mole fractions of alkali content. Generally, the ionic conductivity of these glasses was found to increase with the Li_2O or LiCl content.

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

KAJIAN CIRI-CIRI KENYAL DAN KEKONDUKSIAN IONIK UNTUK KACA JENIS LITIUM FOSFAT DAN LITIUM BORAT

Oleh

LOW YEE SAN

Jun 1999

Pengerusi : Profesor Madya Sidek Hj. Abd. Aziz (Ph.D.)

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Kaca mempunyai kepentingan saintifik kerana ia dapat dihasilkan dalam pelbagai komposisi untuk aplikasi tertentu. Dalam kajian ini, kaca litium dengan fosfat dan borat sebagai pembentuk kaca telah dikaji. Empat siri kaca litium telah dihasilkan iaitu lithium fosfat $(Li_2O)_x(P_2O_5)_{1-x}$ (x = 0.10 hingga 0.50), litium kloro-fosfat $(LiCl)_y[(Li_2O)_{0.4}(P_2O_5)_{0.6}]_{1-y}$ (y = 0.10 hingga 0.50), litium borat $(Li_2O)_x(B_2O_3)_{1-x}$ (x = 0.15 hingga 0.40) dan litium kloro-borat $(LiCl)_y[(Li_2O)_{0.25}(B_2O_3)_{0.75}]_{1-y}$ (y = 0.05 hingga 0.25) menerusi teknik penyejukan mendadak. Pengukuran halaju ultrasonik telah dijalankan dengan menggunakan sistem pemperolehan data ultrasonik MBS 8000. Ketumpatan kaca-kaca diukur dengan mengunakan prinsip Archimedes. Daripada halaju ultrasonik dan

ketumpatan, ciri-ciri kenyal kaca-kaca ini dihitung. Modulus Young, modulus pukal dan suhu Debye untuk kaca litium fosfat dan litium borat didapati meningkat dengan kandungan Li_2O atau LiCl. Modulus kenyal dan suhu Debye untuk kaca litium kloro-fosfat berkurangan dengan penambahan LiCl manakala corak anomalus bagi modulus kenyal dan suhu Debye telah diperhatikan dalam kes kaca litium kloro-borat. Ciri-ciri kenyal kaca-kaca ini didapati berkait rapat dengan kekuatan struktur kaca. Kekonduksian ionik bagi kaca-kaca ini telah diukur dengan menggunakan mesin meter pengukuran HP LCR. Konduktan G telah diukur untuk semua sampel kaca dan diguna untuk pengiraan kekonduksian ionik. Pemerhatian yang agak luar biasa didapati untuk hubungan antara frekuensi dan kekonduksian ionik pada kandungan Li_2O atau LiCl yang rendah. Corak anomalus telah diperhati untuk kekonduksian ionik yang bersandarkan suhu untuk kaca litium fosfat dan litium borat pada kandungan alkali yang rendah. Umumnya, kekonduksian ionik bagi kaca-kaca ini meningkat dengan penambahan Li_2O atau LiCl.

CHAPTER I

RESEARCH OVERVIEW

Introduction

Glasses are among the most ancient materials in human civilisation but the strong interaction between fundamental research and glass technology appeared only in the middle of this century. The reason is perhaps that the glassy materials are out of thermodynamic equilibrium and that their physical properties depend on their thermal histories. In addition, classical theories about crystal structures and classical investigation technique seem to be ineffective in the studies of these kinds of disordered structures.

In spite of the difficulties, glasses are still of scientific interest because their compositions can be varied over a very wide range and it is possible to produce glasses for particular applications. As our knowledge about glasses is growing, glasses have found a lot of applications of technological importance such as optical wave guides, glasses for lasers, amorphous semiconductors in xerography and solar cells or electrolytes in high density batteries.

In this research, lithium glasses with phosphate and borate as the glass formers are studied. Lithium glasses are well known for their ionic conductivity but the elastic properties of this type of glasses have not gained much interest from researchers. A brief review of the ionic conductivity and elastic properties of these glasses will first be described in this chapter. The objective of this work and the chapter organisation will be discussed subsequently.

Literature Reviews

There are numerous publications on the ionic conductivity of lithium glasses but few are found on the ultrasonic properties. Most of the researchers are more interested on borate glasses rather than phosphate glasses.

Phosphate Glasses

The hygroscopic behaviour of crystalline and vitreous phosphate is one of the reasons for little investigations on the structure and the properties of these glasses. However, phosphate-based glasses still contribute to some important technological applications, such as bioceramic, glass to metal seals, fast ionic conducting electrolytes, high quality micro-optic lenses and host material for rare-earth solid state laser. In addition, a lead-iron phosphate glass is used as a stable medium for storage of high level nuclear waste.

In the study of lithium phosphate glasses, Martin and Angell (1986) have studied the electrical conductivity of lithium phosphate glasses over a wide