UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, OPTICAL AND DIELECTRIC PROPERTIESOF LITHIUM FLUORO AND CHLOROAND MAGNESIUM CHLORO PHOSPHATE GLASSES

LOH YEN NEE

FPSK(M) 2005 26

STRUCTURAL, OPTICAL AND DIELECTRIC PROPERTIES OF LITHIUM FLUORO AND CHLORO AND MAGNESIUM CHLORO PHOSPHATE GLASSES

By

LOH YEN NEE

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

February 2005

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

STRUCTURAL, OPTICAL AND DIELECTRIC PROPERTIES OF LITHIUM FLUORO AND CHLORO AND MAGNESIUM CHLORO PHOSPHATE GLASSES

By

LOH YEN NEE

February 2005

Chairman : Associate Professor Zainal Abidin Talib, PhD

Faculty : Science

A series of lithium fluoro phosphate glass, $(LiF)_x (P_2O_5)_{1-x}$ with x = 0.1 to x = 0.6; lithium chloro phosphate glass, $(LiCl)_x (P_2O_5)_{1-x}$ with x = 0.1 to x = 0.6 both in the interval of 0.05 and magnesium chloro phosphate glass, $(MgCl_2)_x (P_2O_5)_{1-x}$ with x = 0.1 to x = 0.45 in the interval of 0.05 glasses were prepared by a single-step melting process with LiF, LiCl, $MgCl_2$ and P_2O_5 as starting materials. The amorphous structure of the samples was evident by the XRD spectrum. The short range structures of those binary phosphate samples were examined by Fourier-transform infrared (FTIR) spectroscopy. The densities of the samples were measured as supportive data for the investigations. Ellipsometer is used to determine the samples refractive indices. The results of refractive indices reveal the homogeneity of samples and it was found to be depended on the glass composition. The optical absorption spectra of these glasses were measured using a UV-Vis spectrophotometer and recorded. The Urbach rule has been applied to evaluate the fundamental absorption edges for all the glasses from the obtained spectrum. The optical band gaps were calculated from the absorption edge and it was found that the optical band gap, E_{opt} depended on the glass composition. The value of E_{opt} was found to be erratic although it still shows a decreasing pattern with the increasing mole fraction of network modifier. The dielectric properties of the samples were also measured using a Novocontrol Novotherm High Dielectric Resolution Analyser. The results showed that the dielectric constant and the dielectric loss factor decreased with frequency and increased with temperature.

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

CIRI-CIRI STRUKTUR, OPTIK DAN DIELEKTRIK BAGI KACA LITIUM FLURO DAN KLORO DAN MAGNESIUM KLORO FOSFAT

Oleh

LOH YEN NEE

Februari 2005

Pengerusi : **Profesor Madya Zainal Abidin Talib, PhD**

Fakulti : **Sains**

Kaca lithium fluro fosfat $(LiF)_x (P_2O_5)_{1-x}$ dengan komposisi x = 0.1 hingga x = 0.6; kaca lithium kloro fosfat $(LiCl)_x (P_2O_5)_{1-x}$ dengan komposis x = 0.1 hingga x = 0.6, kedua-duanya dengan selangan sebanyak 0.05 dan kaca magnesium kloro fosfat $(MgCl_2)_x (P_2O_5)_{1-x}$ dengan komposis x = 0.1 hingga x = 0.45, selangan sebanyak 0.05 telah disediakan dengan teknik peleburan tunggal. Bahan asas yang digunakan ialah LiF, LiCl, $MgCl_2$ and P_2O_5. Struktur bahan amorfus dapat dibuktikan dalam spektra serakan sinar-X di mana ketidakwujudan puncak yang tajam dalam spektra yang diperolehi itu. Struktur tertib julat pendek binary kaca fosfat dikaji oleh spektroskopi infra merah (IR). Selain itu, ketumpatan kaca diukur sebagai data sampingan dalam kajian ini. Indeks biasan bahan didapati dengan menujukan sinar monokromat ke atas bahan. Bacaan indeks biasan yang diperolehi membuktikan kesekataan bahan dan ia juga didapati bergantung kepada komposisi bahan. Kaca-kaca ini telah diukur dengan menggunakan spektrofotometer dan spektra penyerapan optik dalam julat lampau unggu-cahaya nampak telah dicatatkan. Peraturan Urbach digunakan untuk menentukur asas pinggir serapan bagi kesemua spektra yang telah diperolehi. Tenaga jurang optik, E_{opt} bagi bahan yang dikaji

adalah berkait-rapat dengan komposisi bahan. Nilai E_{opt} tidak tetap dan selalu berubah-ubah apabila lebih banyak komposisi pengubahsuai rangkaian ditambahkan. Sifat dielektrik bahan kaca juga diukur dengan menggunakan Novocontrol Novotherm Penganalisa Dielektrik Resolusi Tinggi. Data-data pemalar dielektrik dan faktor kehilangan dielektrik menurun dengan peningkatan frekuensi dan meningkat dengan peningkatan suhu.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere appreciation and gratitude to my supervisor, Associate Professor Dr. Zainal Abidin Talib for all his advice, teaching, encouragement, guidance, understanding, correcting and assistance throughout this project and in the preparation of this thesis.

I would like to express my gratitude to my co-supervisors Professor Dr. Wan Mahmood Mat Yunus, Associate Professor Dr. Wan Mohd Daud Wan Yusoff and Associate Professor Dr. Sidek Hj. Abdul Aziz for their valuable comments and suggestions.

I would like to express my deepest appreciation to my grandmother, parents, brother, sister and also my husband Tan Kian Guan for their love care, patience and encouragement.

Finally, I would like to express my special thanks to my colleagues Emma Ziezie Tarmizi, Liu Wei Wen, Sheik Azrif Bux, Hamezan Mohd., Lim Chee Siong and Goh Chee Keong for their sacrificial heart to advice and help me to finish this project. We have learnt many things together thus strengthening our relationship. Thanks to all of you.

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

T_g	glass transition temperature
ASTM	American Society for Testing Material
P_e	electronic polarizability
P_i	ionic polarization
P_o	orientation polarization
P_s	space charge polarization
ε'	dielectric constant
ε''	dielectric loss factor
MIR	mid infrared spectra
DBO	double-bonded oxygen atom
NBO	non bridging oxygen
BO	bridging oxygen
α	absorption coefficient
D	electric displacement
E	electric field
ε_o	permittivity of free space
P	polarization of the dielectric material
A	absorbance
E_{opt}	energy of the optical band gap
$\hbar\omega$	photon energy
ΔE	Urbach energy
E_g	energy gap

NMR	Nuclear Magnetic Resonance
AFM	Atomic Force Microscopy

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

Glass is no exception as a material of archaeological interest. The state in which it was found depends upon its original structure and composition since it was made. The range of glasses made is wider than ever before and now includes chalcogenides, fluorides and metals as well as oxides; the variety of techniques available for producing them has also expanded notably in recent years (Cable, 1996).

Glasses are fused mixtures of inorganic oxides, which are cooled to a solid state without crystallization. They do not have uniquely fixed compositions and thousands of glasses, each with a different composition, are produced commercially. It is often associated with fusion products made from silicates, which are used for windows, bottles, lenses, etc. Beside silicates, a lot of other substances can also be obtained in the glassy state. It is widely understood that the possibility of a material forming glass is not an atomic or molecular property and cannot be measured by chemical or physical properties. It is a state of the solid state which can be reached by a sufficiently high cooling rate.

A wide variety of industrial glasses for packaging, household uses, building and construction, electrical engineering, and optical applications, are manufactured in large industrial plants by the processing of melts, mainly in the open air.

Amorphous substances are formed from solutions when the conditions change at a sufficiently high rate, followed by strong over-saturation. There is often not enough time for the generation of crystalline nuclei and their growth.

Many metal oxides form glasses when melted with a basic glass former oxide such as P_2O_5, B_2O_3, SiO_2, GeO_2, As_2O_3, Sb_2O_3, etc. Network modifier such as Na_2O, Li_2O, CaO and PbO have the function that break up the network. The introduction of large number of network modifiers into a glass leads to an increase in the splitting of the network. An increased mobility of the structural units causes a decrease in the viscosity. Moreover, other physical properties, such as the electrical conductivity, vary greatly. As the network modifiers are irregularly distributed in the whole network, the properties of the glass normally change continuously according to the change in the composition (Naess, 2001).

The vast bulk of these glasses can be considered in three main groups: the soda-lime-silica, the borosilicate and the lead silicate glasses. The largest percentage of all manufactured glass is soda-lime glass, which are mixtures of silica (SiO_2), sodium oxide (Na_2O) and calcium oxide (CaO). This group form by far the largest group of glasses in terms of tonnage produced and includes the common sheet and plate glasses used for windows as well as the glasses used for most bottles and jars. This type of glass supplies most of the world's needs for bottles, food jars, drinking glasses, tableware, lamp bulbs, plate glass and window glass.

Borosilicate glasses, which are mixtures of silica sand and boric oxide, have a high chemical durability, high thermal resistance, high electrical resistivity and low thermal expansivity. Materials of this group are in common use for cooking utensils, domestic ovenware, chemical process equipment and laboratory glassware.

Lead silicate glasses, which are mixtures of silica sand, potash and lead oxide, have a very high electrical resistivity and refractive index. The presence of lead makes the glass heavy. These lead glasses are known as crystal and are used for most of the high-quality decorative cut glass and fine tableware. Relatively costly raw materials and melting difficulties make this group of glasses expensive to produce, but nevertheless they are used for special purposes: for decorative, high-quality tableware, where the very high refractive index gives the classical 'sparkle' when prismatic cuts are used to decorate the surfaces, and for the glass-to-metal seals in the bases of electric lamps and electronic valves (Holloway, 1973). Lead glass is also the "paste" used in making imitation diamonds. Glass with a high lead content can be used as a shield in nuclear energy installations industry.

Fused silica which are made from pure silicon dioxide (SiO_2), with no additives have the characteristics of high hardness, a low thermal coefficient of expansion, and a high melting point of 1650 ^{o}C. It is a very stable material which can be used for making astronomical telescope mirrors with very large diameters. Its strength and mechanical stability also make it a good material for laboratory apparatus.

Another classification is the alkali silicate family of glasses which are made by adding an alkali such as sodium or potassium to the silica which lowers the melting point and makes the resulting glass become soluble in water. Proper preparation can yield a liquid solution of glass and water known commercially as water glass. This substance is used as a protective coating, for fire proofing and as an adhesive.

Phosphate glasses are of technological interest due to their several advantages over conventional silicate and borate glasses. Among the superior physical properties of phosphate glasses are high thermal expansion coefficient, high thermal conductivity, low glass transition temperature (T_g), low melting and softening temperatures. Because of these behaviours, phosphate glasses were the candidates for fast ion conducting material and other important applications such as lasers hosts, wave guides, thick film paste, the molding of optical elements, low temperature enamels for metals, glass to metal seals and bio-compatible materials or biomedical implants (Shih *et al.*, 2003).

Phosphate glasses also have the characteristics of high ultraviolet transmission for hosting lasing ions, and are potential candidates for making solid state electrolytes, machinable glass ceramics, amorphous semiconductors, laser glasses, optoelectronics and nuclear waster storage (Subbalakshmi *et al.*, 2002, and Hezzat *et al.*, 2003).

Phosphate glasses have considerable potential for applications in optical data transmission, detection, sensing and laser technologies. For example, neodymium phosphate glasses have been widely used in lasers because of the characteristic of high ultraviolet transmission which is suitable for hosting lasing ions (Higazy *et al.*, 1995). Phosphate glasses are relatively easy to prepare and offer an important range of compositional possibilities, which facilitate tailoring of the physical and