UNIVERSITI PUTRA MALAYSIA

# PHYSICAL AND ELECTRICAL PROPERTIES OF ZINC-MAGNESIUM-PHOSPHATE GLASSES

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**MASTER OF SCIENCE**
**UNIVERSITI PUTRA MALAYSIA**

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# PHYSICAL AND ELECTRICAL PROPERTIES OF ZINC-MAGNESIUM-PHOSPHATE GLASSES

**By**

**NG BENG HONG**

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

**June 2007**

For my beloved parents, siblings and family

Ng Ching Ai @ Ooi Ah Peng

Lim Chin Lan

Chuah Bee Kuan

Ng Beng Tiong

Ng Beng Wei

Ng Beng Kiat

For showering me with love, understanding and encouragement

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

**PHYSICAL AND ELECTRICAL PROPERTIES OF ZINC-MAGNESIUM-PHOSPHATE GLASSES**

By

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**June 2007**

**Chairman : Associate Professor Zainal Abidin Talib, PhD**

**Faculty : Science**

Glasses in a wide range of composition in the ternary system x(ZnO)-y(MgO)-z($P_2O_5$) where x ranges from 5 to 20 mol %, y ranges from 5 to 20 mol % and z ranges from 50 to 70 mol % have been prepared by traditional melt quenching technique with ZnO, MgO and $P_2O_5$ as the starting raw materials. X-ray diffraction (XRD), refractive index and electrical properties have been used to characterize the structural, optical and electrical features. All the sample glasses at present work have been confirmed to be amorphous by X-ray diffraction technique using Philips Model 7602 EA Almelo. The refractive indices of ternary glasses were measured by Ellipsometer and were found to agree with Lorentz-Lorenz equation where the refractive index increased with the increase of the density ($\rho$) and the decrease of the molar volume ($V_m$) of the glass. The density of the glass was determined by Archimedes Principle. From the empirical data, other values such as molar volume and molar refractivity have been computed. The variations in the molar volume were resulting in variation on the

density and refractive index of the glasses. From the results obtained, it is obvious that the refractive index varies with molar refractivity, which depends on the polarizability of the ions, density and molecular weight in the sample glass. Those physical properties were found to be sensitively depending on its composition. Electrical conductivity ($\sigma$) was measured in the temperature 30 $^{o}$C to 300 $^{o}$C. Conductivity for the ternary series glasses increased with addition composition of ZnO or MgO with temperature. Activation energy ($E_a$) was calculated by the slope of graph log σ versus 1000/T with Arrhenius equation. The values of activation energy in the ternary series were recorded in the range of 0.023 eV to 0.112 eV.

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

**SIFAK FIZIK DAN ELEKTRIK BAGI KACA
ZINK-MAGNESIUM-PHOSPHATE**

Oleh

**NG BENG HONG**

June 2007

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

**Falkulti : Sains**

Kaca dalam satu julat komposisi diantara system pertigaan x(ZnO)-y(MgO)-z(P2O5) di mana x dalam julat 5 hingga 20 mol %, y dalam julat 5 hingga 20 mol % dan z dalam julat 50 hingga 70 % telah dihasilkan menggunakan teknik sepuh lebur dengan ZnO, MgO dan P2O5 sebagai bahan asal mulaan. Pembelauan sinar-X (XRD), index biasan dan kajian elektrik telah digunakan untuk menggambarkan ciri struktur, optik dan elektrik yang berlaku dalam semua sampel. Semua sampel dalam pengajian ini telah disahkan sebagai amorfus melalui pengukuran pembelauan sinar-X dengan menggunakan mesin Philips Model 7602 EA Almelo. Indeks biasan pertigaan kaca telah diukur menggunakan mesin Ellipsometer dan didapati menepati presamaan Lorentz-Lorenz yang mana nilai indeks biasan tersebut meningkat dengan peningkatan ketumpatan ($\rho$) dan penurunan isipadu molar ($Vm$) bagi sampel kaca. Ketumpatan kaca telah diukur menggunakan prinsip Archimedes. Dari nilai data empirihal yang diukur, nilai-nilai lain seperti isipadu molar dan pembiasan molar telah dikira. Perubahan isipadu molar mempengaruhi ketumpatan dan indeks biasan dalam kaca. Hasil kajian jelas menunjukkan bahawa indeks biasan berkadar songsang dengan pembiasan molar yang bergantung kepada pengutuban ion, ketumpatan dan berat molekul dalam kaca. Semua sifat fizikal didapati begitu sensitif pergantungannya kepada komposisi bahan tersebut. Kekonduksian elektrik ($\sigma$) telah diukur dalam julat suhu 30 $^{o}$C hinggan 300 $^{o}$C. Kekonduksian bagi sistem pertigaan kaca didapati meningkat dengan penambahan komposisi ZnO atau MgO dan peningkatan suhu. Tenaga pengaktifan ($E_a$) telah dikira daripada kecerunan graf log $\sigma$ lawan $1000/T$ yang mematuhi persamaan Arhenius. Nilai bagi tenaga pengaktifan dalam sistem pertigaan kaca diperoleh dalam linkungan 0.023 eV hingga 0.112 eV.

## ACKNOWLEDGEMENTS

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This thesis submitted to the Senate of Univrsiti Putra Malaysia has been accepted as fulfillment of the requirement for the Degree of Master of Science. The members of the Supervisor Committee are as follows:

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# DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that is has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**NG BENG HONG**

Date: 10 September 2007

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# LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS

| | |
|---|---|
| a.c. | alternating current |
| A | absorption |
| $A_2O$ | alkali oxides |
| $\alpha(\omega)$ | absorption coefficient |
| BO | bridging oxygen |
| C | capacitance |
| CN | coordination number |
| $c$ | velocity of light in vacuo ($c = 3 \times 10^8$ ms$^{-1}$) |
| d | thickness |
| d.c. | direct current |
| DBO | double bond |
| $e$ | electronic charge |
| $\varepsilon'$ | permittivity or dielectric constant |
| $\varepsilon''$ | dielectric loss factor |
| $E_a$ | activation energy |
| $E_g$ | energy gap |
| $E_{opt}$ | optical band gap |
| FTIR | Fourier transforms infrared |
| G | conductance |
| $I$ | current |
| IR | infrared |

| | |
|---|---|
| k | extinction coefficient |
| K | dielectric constant |
| M | mass of particle |
| Me | metal |
| MeO | metal oxide |
| NBO | non-bridging oxygen |
| NMR | nuclear magnetic resonance |
| n | refractive index |
| $\rho$ | density |
| $Q^i$ | number of the BO atoms in a $PO_4$ group |
| $Q$ | charge |
| $R$ | resistor |
| R | reflectance |
| RO | alkaline-earth oxides |
| $R_m$ | molar refractivity |
| $T$ | temperature |
| $T_g$ | transformation temperature ($^oC$) |
| $tan\ \delta$ | loss angle (measure of dielectric losses) |
| TM | transitional metal |
| TO | terminal oxygen |
| $V$ | volume |
| V | voltage |
| v | valency of Me |

| | |
|---|---|
| $V_m$ | molar volume |
| λ | wavelength |
| ω | angular frequency |
| XRD | x-ray diffraction |
| Z | impedance |

# CHAPTER 1

# INTRODUCTION

Glass is by definition an amorphous substance and an inorganic oxide. In other words, all glasses are amorphous but not all amorphous solid are necessarily glasses. Glass can simply be signified as transparent material that is made from silica with the addition of a few alkali oxides.

Glasses have no underlying regular structure. Glass formed by the process called “super cooling” processing. A liquid (melt) cool very rapidly below its freezing point. If the cooling rate is fast enough, the molecules cannot organize themselves into crystals. Instead, the atoms or molecules making up the glass jumbled together. They may be packed in tightly until the glass cannot be moved, and are not packed in a regular way. As the temperature drops, the liquid becomes more viscous and the molecules more sluggish, thus not giving enough time for the liquid (melt) to form a regular crystal lattice [1].

Amorphous materials exhibit many properties which are unique to them and are not shared by crystalline solids. The absence of periodicity, or long-range order, characteristic of an amorphous solid is most clearly evidenced in a diffraction experiment, for example using X-rays. Where instead of the sharp Bragg spots or rings produced by single crystal or polycrystalline samples respectively, broad diffuse haloes are observed. The observation of diffuse haloes in a diffraction experiment is a prerequisite to characterization of an amorphous material.

## 1.1 Structure and Properties of Rare-Earth Phosphate Glasses

In this study, magnesium-phosphate (M-P) glasses are chosen as the base glass. The appearance of the base glass is colourless and transparent. The phosphate ion is a polyatomic anion. It consists of one central phosphorus atom surrounded by four identical oxygen atoms in a tetrahedral arrangement with the empirical formula $PO_4^{3-}$ [2]. The structure of vitreous $P_2O_5$ is thought to consist of a 3-dimensional network of corner-sharing $PO_4$ tetrahedral each of which is decorated with a non-bridging P=O bond.

As alkali and transition metals (network-modifying elements) is added to form a binary or ternary of phosphate glass, a structural transformation from a 3-D network of $P_2O_5$ to a complex chain structure takes place through the generation of additional non-bridging oxygen. However, the chemical durability of glasses was improved with the addition of mixed oxide [3].

To their chemical durability, the phosphate glasses can be melted at lower temperatures (1000$^{o}$C to 1200$^{o}$C) than many silicate glasses. Phosphate glasses are fluid and easily poured, do not easily devitrified, and can contain large amounts of alkali and alkaline earth oxides without any serious reduction in their chemical durability [4]. Based on the properties, these glasses are excellent materials for use in the vitrification and safe disposal of nuclear and other hazardous wastes [5]. Therefore, understanding the correlation between the structure modification induced by various metal-oxide additives and the physical and chemical properties represents one of the most important aspects of materials research on phosphate glass.

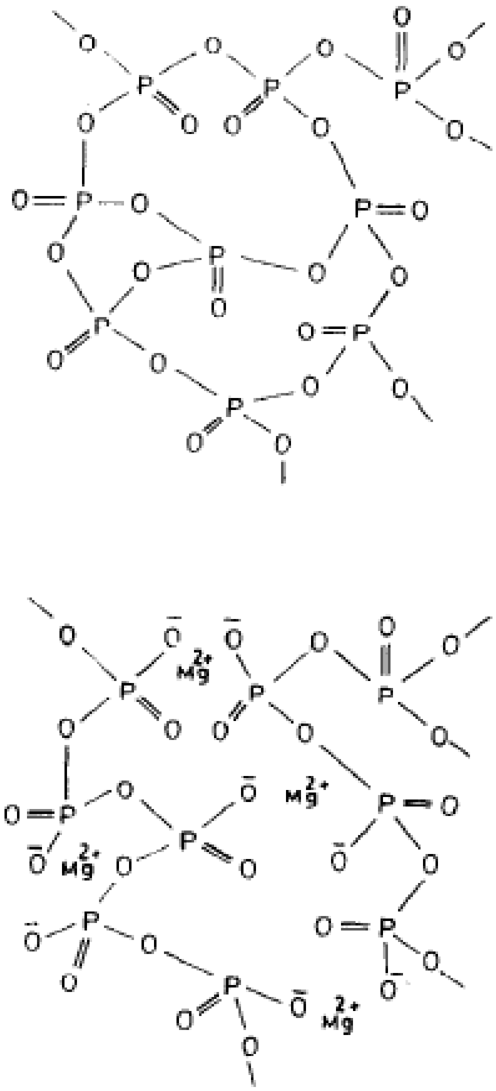
Alkali, alkaline-earth and many of others metal oxides form glasses when melted with $P_2O_5$ materials. Phosphate glasses are of technological interest due to their several unique properties, such as high thermal expansion coefficient, low glass transition temperature and low softening temperature would make them characterized by good infrared (IR) transmissions [5, 6, 7]. Due to their physical properties, the phosphate glass have several advantages that more conventional than silicate glass [8].

Alkaline-earth phosphate glasses are important for technological applications in various fields of optics. These glasses are structurally interesting because they accept a wide range of alkaline-earth. Properties of a glass are governed by its structure which in turn depends on its chemical composition.

It is well known that several transition metal oxides viz. $V_2O_5$, ZnO, MgO, etc. when heated with a glass former like $P_2O_5$, $B_2O_3$, etc. form binary or ternary glasses on quenching the melt. The MgO-$P_2O_5$ glasses have been studied extensively by several authors [9, 10]. The pure $MgO$-$P_2O_5$ glasses are, in general, very unstable (hygroscopic) and their conductivity is also low. Both the conductivity and the stability of these glasses are found to increase by the small addition of various oxides of alkaline earth.

Magnesium phosphate glasses are classified into so-called "anomalous phosphate" since $MgO$-$P_2O_5$ glasses has anomalies in many of its physical properties [9]. The properties of the magnesium phosphate glasses are strongly influenced by the strengthening effect of $Mg^{2+}$ and the characteristic of binary phosphate glasses depended on the availability of terminal oxygen (TO) to coordination to the cations in phosphate system.

In 1995, Higazy [10] measured the electrical conductivity and electrical constant of $MgO$-$P_2O_5$ glasses. He stated that Mg appear to belong to the category of ions which can occupy interstitial positions in glasses as cations forming, $Mg^{2+}$. In glasses, cations forming strongly ionic conduction and therefore directional bonds with oxygen are described as part of the glass network. So consider for the studied glass system the Mg ions enter the glass network interstitially (see Fig. 1.1). Hence, some network bonds (P-O-P) are broken and replaced by ionic force between Mg ion and singly bonded oxygen atoms.



(a)

(b)

**Fig.1.1. Schematic two-dimensional representation of the structure of $MgO-P_2O_5$ binary phosphate glasses; (a) composed of the basic glass former, $P_2O_5$ and (b) showing the effects of Mg cation content on the glass former (taken from Ref. [10]).**