UNIVERSITI PUTRA MALAYSIA

DIELECTRIC, THERMAL, OPTICAL, AND DEGRADATION CHARACTERISTICS OF MgO/ZnO-CONTAINING PHOSPHATE GLASSES

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By

KHOR SHING FHAN

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

August 2011

SPECIALLY DEDICATED TO

- *Father, Mother, Siblings and Brother-in-law for their loves, patients and spirits courage*
- *All my Friends for their supports and helps*

Wish them peace and happiness

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Chairman : Associate Professor Zainal Abidin Talib, PhD

Faculty : Science

Investigation was carried out on binary $(MgO)_x(P_2O_5)_{1-x}$ with $x = 20, 25, 30, 35, 40, 45$ and 50 mol % and ternary series $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$, $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ and $(ZnO)_x(MgO)_{30-x}(P_2O_5)_{70}$ with $x = 5, 8, 10, 13, 15, 18$ and 20 mol % in order to determine the role of zinc and magnesium ions in phosphate glasses. All the samples were prepared by traditional melt quenching technique. X-ray diffraction (XRD) measurement confirmed that the samples were amorphous. Dielectric spectroscopy, laser flash technique, differential thermal analyzer (DTA), UV-visible spectrophotometer, ellipsometry and inductively coupled plasma-optical emission spectrometry (ICP-OES) have been used to characterize the electrical, thermal, optical features and ion released concentration respectively as well as to shed further light on the structure of the glasses. The dielectric permittivity (ε') and loss factor (ε'') were measured in the frequency range of 0.01 Hz to 1 MHz and in the temperature range between 303 and 573 K.

The empirical data were sufficiently fitted and modeled with a superposition of Harviliak-Negami (HN) dielectric relaxation functions and a conductivity term. The results showed that the dielectric constant and dielectric loss factor decreased with frequency and increased with temperature. These interesting variations have been explained in the light of polarization and ionic interaction. At low frequencies, the dielectric loss factor spectrum was dominated by dc conduction which was manifested by the $1/\omega$ slope. Activation energy of dielectric relaxation (E_ω) was in the range 0.05 to 0.14 eV, 0.40 to 0.51 eV, 0.05 to 0.11 eV and 0.06 to 0.09 eV for binary glasses (MP) and ternary glasses with constant mole fraction of zinc (CZ), mangnesium (CM) and phosphate (CP), respectively. Activation energy of dc conduction (E_σ) was in the range 1.00 to 1.15 eV, 1.04 to 1.16 eV, 0.92 to 1.07 eV and 1.06 to 1.12 eV for MP, CZ, CM and CP glass systems, respectively. The values of E_σ is higher than those for E_ω which suggest both the conduction and relaxation processes are due to different mechanisms. Thermal diffusivity measurements were carried out in the temperature range of ambient to 573 K. The values decreased from 0.32 to 0.23 mm^2/s. The response was explained based on phonon mean free path. The greater the network connectivity the greater the phonon mean free path which makes it easier for the phonon to propagate and eventually lead to higher values of thermal diffusivity. The glass transition temperature (T_g) of the glasses was measured by DTA from 25 °C to 700 °C and the values of T_g was found in the range of 396 to 544 °C. The variation is proportional to the length of phosphate chain, cross-linking density and bonding strength of the structure. The decreases in T_g reflects the bond strength of the glass structure is weakened on account of the rupture of phosphate cross-linked network. The UV spectra of the glasses were measured in the wavelength range of 190 to 1100 nm at ambient temperature. The Urbach rule was applied to evaluate the values of optical energy band gap (E_{opt}) and Urbach energy (E_U) for all the samples from the absorption spectrum. The E_{opt} was found to be in the range of 3.64 to 3.78 eV, 3.36 to 3.44 eV, 3.47 to 3.79 eV and 3.54 to 3.81 eV for MP, CZ, CM and CP glass systems, respectively. Meanwhile E_U was found to be in the range 0.26 to 0.28 eV, 0.29 to 0.47 eV, 0.27 to 0.32 eV and 0.27 to 0.45 eV for MP, CZ, CM and CP glass systems, respectively. The behavior of both E_{opt} and E_U was correlated with structural disorder in the sample. As the non-bridging oxygen sites increase in the glassy matrix the valence bands were broadened resulting in a lower E_{opt} and higher E_U. Refractive index of the glasses was measured at ambient temperature with helium-neon laser of 632.8 nm wavelengths. The measured refractive index was found varying in between 1.508 and 1.575 and was dependent on the amount of non-bridging oxygen which has higher polarizability than bridging oxygen. This is because the depolymerization effect brought about retardation of light propagating through the phosphate network. The refractive index was found to vary proportionally with density as well. Chemical durability of the studied glasses has also been investigated in acidic, neutral and basic buffer solutions for 30 days to express the resistance offered by a glass towards attack by aqueous solutions. In the corrosion test, all the glass specimens experienced hydration, hydrolysis and precipitation steps. The dissolution rate (D_R) of these glasses was in the range of 10^{-6} to 10^{-8} g/cm^2 min and subjected to the relative concentration of Zn^{2+} or Mg^{2+} ions and glass compositions. The binary compositions exhibit excellent chemical durability which is comparable to window glass. The surface morphology of the CZ glass system was found to be the most affected by the buffer solutions on account of the formation of asymmetric bridging oxygen which tend to accelerate the hydrolysis process once the surface is hydrated. The pH values of all the solutions decreased as a function of time and this was attributed to the release of phosphate species from the dissolving glasses and subsequently the formation of phosphoric acid in the solution. Ion released measurement showed that all ions in the glass structure leached out of the glass surface when reacted in an aqueous solution. In addition, the ion leaching concentration strongly depended on the glass composition and the pH of the aqueous solution.

Abstrak tesis yang dikemukakan kepada Senat of Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doctor Falsafah

DIELEKTRIK, TERMA, OPTIK, DAN KETAHANAN KIMIA BAGI MENGANDUNGI MgO/ZnO-KACA FOSFAT

Oleh

KHOR SHING FHAN

Ogos 2011

Pengerusi : Profesor Madya Zainal Abidin Talib, PhD

Fakulti : Sains

Kajian telah dibuat ke atas system perduaan $(MgO)_x(P_2O_5)_{1-x}$ dengan $x = 20$, 25, 30, 35, 40, 45 dan 50 mol % dan pertigaan $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$, $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ dan $(ZnO)_x(MgO)_{30-x}(P_2O_5)_{70}$ dengan $x = 5$, 8, 10, 13, 15, 18 dan 20 mol % untuk menentukan peranan ion zink dan magnesium dalam system asas kaca fosfat. Semua sampel kaca yang dikaji telah dihasilkan dengan menggunakan teknik sepuh lebur. Semua sampel dalam pengajian ini telah disahkan sebagai amorfus melalui pengukuran pembelauan sinar-X (XRD). Spektroskopi dielektrik, teknik sinaran laser, perbezaan terma analisis, UV-visible spektrofotometer, ellipsometer dan inductively coupled plasma-optical emission spektrometer (ICP-OES) telah digunakan untuk menggambarkan ciri-ciri dielektrik, haba, optik dan perlepasan ion termasuk juga struktur yang tersirat dalam semua sampel. Ketelusan dielektrik dan factor kehilangan dielektrik telah diukur pada frekuensi dari 0.01 Hz hingga 1 MHz dan julat suhu dari 303 hingga 573 K. Semua empirikal data didapati padan dengan model yang terdiri daripada dua fungsi istirahat dielektrik Harviliak-Negami (HN) dan satu konduksi. Data menunjukkan ketelusan dielektrik dan faktor kehilangan dielektrik bagi semua sampel menurun dengan peningkatan frekuensi dan meningkat dengan peningkatan suhu. Perubahan tersebut telah dijelaskan berdasarkan polarisasi dan ionik interaksi. Di frekuensi rendah, spektrum factor kehilangan dielektrik didominasi oleh arus terus di mana dinyatakan dengan kecerunan $1/\omega$. Tenaga pengaktifan dielektrik istirahat (E_ω) didapati di dalam julat 0.05 ke 0.14 eV, 0.40 ke 0.51 eV, 0.05 ke 0.11 eV dan 0.06 ke 0.09 eV untuk kaca binari (MP) dan ternari dengan malar fraksi mol zink (CZ), magnesium (CM) dan fosfat (CP) masing-masing. Tenaga pengaktifan pengaliran arus terus (E_σ) didapati di dalam julat 1.00 ke 1.15 eV, 1.04 ke 1.16 eV, 0.92 ke 1.07 eV dan 1.06 ke 1.12 eV untuk MP, CZ, CM dan CP sistem kaca masing-masing. Nilai E_σ didapati lebih tinggi daripada E_ω dicadangkan kedua-dua prosess konduksi dan istirahat adalah berlainan mekanism. Pengukuran keresapan haba dilakukan dari suhu bilik hingga 573 K. Data keresapan terma didapati menurun dari 0.32 to 0.23 mm^2/s. Perubahan tersebut dijelaskan dari segi fonon mean free path. Sambungan rangkaian yang lebih besar meningkatkan fonon mean free path dimana memudahkan phonon merebak dan akhirnya membawa kepada nilai-nilai yang lebih tinggi kemeresapan haba. Suhu peralihan kaca dikaji dari suhu 25 °C kepada 700 °C. Nilai T_g didapati berada di dalam julat 396 to 544 °C. Nilai T_g berkadar langsung terhadap panjang rantai fosfat, persilangan dan kekuatan ikatan struktur. Penurunan nilai T_g mencerminkan kekuatan struktur kaca menjadi lemah disebabkan oleh pemecahan rangkaian fosfat. Spektra UV sampel kaca diukur dalam suhu bilik dengan julat panjang gelombang 190 ke 1100 nm. Melalui kajian pinggir penyerapan, nilai bagi jurang tenaga jalur optik (E_{opt}) dan jurang tenaga Urbach (E_{U}) telah dinilai dengan menggunakan peraturan penyerapan Urbach keatas semua spektra yang telah diperolehi.. Nilai E_{opt} didapati berada di dalam julat 3.64 ke 3.78 eV, 3.36 ke 3.44 eV, 3.47 ke 3.79 eV dan 3.54 ke 3.81 eV untuk MP, CZ, CM dan CP sistem kaca masing-masing. Manakala nilai E_{U} didapati berjulat 0.26 ke 0.28 eV, 0.29 ke 0.47 eV, 0.27 ke 0.32 eV dan 0.27 ke 0.45 eV untuk MP, CZ, CM dan CP sistem kaca masing-masing. Sifat E_{opt} dan E_{U} dikaitkan dengan struktur rawak dalam sampel. Kuantiti oksigen-tidak-terikat meningkat di kaca matriks telah mengembangkan jalur valens dan menyebabkan E_{opt} yang lebih rendah dan lebih tinggi E_{U}. Indek biasan telah diukur dalam suhu bilik pada 632.8 nm. Nilai indek biasan yang diukur berada dalam julat 1.508 hingga 1.575 dan bergantung kepada bilangan oksigen-tidak-terikat dimana mempunyai polarisasi yang lebih tinggi berbanding dengan oksigen-terikat. Ini adalah kerana kesan depolymerization telah menghalang cahaya menyebar melalui rangkaian fosfat. Nilai indek biasan juga didapati berubah secara berkadar langsung dengan ketumpatan kaca. Kajian terhadap ketahanan kimia juga telah diteliti dalam larutan buffer berasid, neutral dan beralkali selama 30 hari untuk menyatakan rintangan yang ditawarkan oleh kaca terhadap serangan atas larutan berair. Dalam ujian kakisan semua kaca specimen mengalami prosess penghidratan, hidrolisis dan pemendakan. Kadar larut kepada sampel kaca berada dalam julat 10^{-6} hingga 10^{-8} g/cm^2 min dan bergantung kepada konsentrasi relatif Zn^{2+} atau Mg^{2+} ion dan komposisi kaca. Kaca berkomposisi binary menunjukkan ketahanan kimia yang sangat baik setanding dengan tingkap kaca. Permukaan morfologi sistem kaca CZ dipengaruhi oleh larutan buffer disebabkan pembentukan ikatan oksigen tak simetri telah mempercepatkan prosess hidrolisis sekali permukaan terhidrat. Nilai pH kepada semua larutan bufer menurun dengan masa disebabkan perlepasan spesies fosfat dari kaca dilarut dan menghasilkan asid fosforik di dalam larutan. Kajian perlepasan ion menunjukkan semua jenis ion di dalam struktur kaca diluluhkan dari permukaan kaca apabila reaksi di dalam larutan bufer. Konsentrasi ion yang diluluhkan bergantung kepada komposisi kaca dan nilai pH kepada larutan akuous.

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"I can no other answer make but thanks/ And thanks; and ever thanks."

- Shakespeare's Twelfth Night

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that is has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

KHOR SHING FHAN

Date : 11 August 2011

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LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS

A	absorption
A_2O	alkali oxides
$\alpha(\omega)$	absorption coefficient
α_m	polarizability
BO	bridging oxygen
c	velocity of light in vacuum ($c = 3 \times 10^8\ ms^{-1}$)
C	capacitance
CN	coordination number
CTE	coefficient of thermal expansion
d	thickness (mm)
d.c.	direct current
D	diffusion coefficient $\left(cm^2/sec\right)$
D_R	dissolution rate ($g/\ cm^2\ min$)
DBO	double bond
DSC	differential scanning calorimeter
G	shear modulus
G	conductance of the dielectric
e	electronic charge
ε'	permittivity or dielectric constant
ε"	dielectric loss factor
ε_o	free space permittivity
ε_∞	high frequency dielectric permittivity
$\Delta\varepsilon$	dielectric strength

E_σ	total activation energy for ionic conduction
E_a	activation energy
E_g	energy gap
E_{opt}	optical band gap energy (eV)
E_U	Urbach energy (eV)
E_S	strain energy
E_B	electrostatic binding energy
E_d	activation energy for diffusion
FTIR	Fourier transforms infrared
G	conductance
I	current
I_o	intensities of incident beam
I_t	intensities of transmitted beam
IR	infrared
j	current density
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
N_A	Avogadro number
ρ	density (g cm^{-3})

γ	gamma
Q^i	number of the BO atoms in a PO_4 group
O/P	ratio of oxygen and phophorous
Q	charge
Q	radiant energy, (J m^{-2})
R	resistor
RO	alkaline-earth oxides
R_m	molar refractivity
R_S	specific refractivity
RMC	reverse Monte Carlo
T	temperature
T_g	transformation temperature (^oC)
T_D	thermal diffusivity in cm^2/s
TSP	thermally stimulated polarization
TSD	thermally stimulated depolarization
TPS	transient plane source
$\tan\delta$	loss angle (measure of dielectric losses)
TM	transitional metal
TO	terminal oxygen
$t_{1/2}$	time corresponding to which measured temperature reaches half of the final temperature.
t_R	rear face temperature
μ	Mobility
V_m	molar volume (cm^3 mol^{-1})
V_p	phase velocity of light in material

V	voltage
v	valency of Me
λ	wavelength (nm)
ω	angular frequency
ω_p	relaxation frequency
XRD	x-ray diffraction
XPS	X-ray photoelectron spectroscopy
Z	impedance

CHAPTER 1

INTRODUCTION

1.1 Introduction

Glasses are noncrystalline or amorphous substances. “Amorphous”, meaning structureless or capable of assuming any structure (Feltz, 1993). In the other words, glass has no long-range order or regularity in its molecular (Doremus, 1973) and exhibit glass transformation behaviour (Elliott, 1990). Glass has numerous empty sites or vacancies and do not contain planes of atoms. Thus, Bragg reflection is unavailable.

Glasses are amazing material no matter as an artistic medium or an industrial material and its properties have always intrigued man. Even nowadays in 21st century, scientists and researchers still keeping the enthusiasm and passion for new glass research in term of fundamental understanding and develop the physics of amorphous solids to impetus further commercial exploitation development.

In recent years, there was a great awareness of the need to study the relation between the structure and properties of materials. Once the atomic concentration has been fixed, the properties and the structure are largely defined (Gaskell, 1997). Glass is a complex material and its electrical properties as measured over a wide frequency range are a considerably interesting subject. The study on dielectric behavior of glasses over a wide range of frequency and temperatures is expected not only to reveal comprehensive idea about the nature and origin of the loss occurring in these materials as well as conduction mechanism but also provide information on the structural aspect of the glasses (Murali Krishna et al. 2008 & Sahaya Baskaran et al. 2008). Dielectric measurements are also performed in an attempt to identify how local motions of charge carrier might be affected by the structural changes induced from modification effect (Button et al., 1981). The dielectric properties of usual interest are the real (ε') and imaginary (ε'') components of the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. Worth for noting until today is that there has been no theory of ionic transport which is accepted widely. Thus, ionic diffusion in ionic conducting glass material has been an issue of interest because of its importance in technological uses. Therefore, a better understanding of its electrical conductivity is required.

Glasses are considered ideal host materials for athermalisation as they are versatile and can be physically and compositionally tailored to meet various optical and thermal requirements (Owen, 2007). Athermalization, in the context of temperature measuring instruments, is the practice of designing an instrument so that temperature changes do not affect what is being measured. Thermal properties of glass are getting important and its thermal diffusivity is one of the most important parameters when heat transfer phenomena are involved. Therefore, study on thermal diffusivity is important to investigate the dynamical aspect of atoms and molecules in materials and also the structure of the materials with the help of the knowledge of the dynamical properties obtained (Hiki et al., 1994). In addition, DTA measurement also provides some useful information on the structure of glasses.

In optical field, glasses are among the few solids which transmit light in the visible region of the spectrum (Fuxi, 1992). Glass is the basic elements in all optical instruments and refractive index is a fundamental parameter that is intimately connected to optical devices performance and reliability. However, refractive index varies with structural or compositional changes. To figure out the relationship between the refractive index and compositions of the present glass systems it is crucially important to study their optical properties.

Study of the optical absorption edge in UV-region has proved to be very useful method for clarification of optical transitions and electronic band structure of the materials (Mott and Davis, 1979). Glass has generally an inherent absorption in the ultraviolet range (Abdel-Baki & El-Diasty, 2006). However, the prediction of the location of the ultraviolet absorption edge of oxide glasses especially phosphate glasses is expected to be quite complex, since its structural changes occur with change in the composition (Dayanand et al., 1994). Therefore, understanding the mechanism responsible for the optical absorption edge of the glass system under investigation in this study would shed further light on the structural of those glasses.

Good chemical durability is a very important parameter for operation glasses which should not exhibit any noticeable degradation caused by environment under normal conditions. For this reason, knowledge of chemical durability is becoming more important and good chemical durability is a critical requirement as these glasses are either in use or proposed for use in applications (Desirena et al., 2009). Hence, the present study focus on the chemical durability improvement of phosphate glasses with the mixture of magnesium oxides and zinc oxide to investigate how the current finished new products: zinc magnesium phosphate glasses will stand up to aqueous attack.

Phosphate glass can be prepared over a wide range of composition. It is well known that addition of different oxides to phosphate (P_2O_5) results in depolymerization of the network and formation of different structures. Phosphate glass structure is strongly dependent on the ratio of its oxygen and phosphate (O/P ratio) as set by glass composition and properties of the other participating oxides (Maczka et al., 2006). The structural units in phosphate network are classified according to their connectivities by Q^i notation, where i represents the number of bridging oxygen atoms per PO_4 tetrahedron. In the present study, the structural units in phosphate network were mainly composed of ultraphosphate, Q^3 and Q^2 units.

1.2 Potential of Phosphate Glass

The intent of the present work was to study dielectric properties on phosphate-based glasses consisting of zinc oxide and magnesium oxide. Over the years, phosphate glasses have been developed for numerous applications on account of phosphate glasses having several advantages over conventional silicate and borate glasses. Its superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures have helped to promote them as an ideal candidate for sealing to high expansion metals such as stainless steels and aluminium alloys (Brow et al., 1988).

Phosphate glasses are high ultra-violet and far infrared transmissible. The ultra-violet absorption edge in alkaline-earth phosphate glasses can be varied by the choice of the metal ion (Matz et al., 1988). Phosphate glasses have also considerable potential for applications in optical data transition, detection, sensing, laser technologies (Higazy, 1995) even as nuclear waste storage (Devidas et al., 2007). Phosphate glasses are also suitable materials for high power lasers because of low thermo-optical coefficient and large emission (Marek Nocun, 2004). It also could provide superior laser characteristics which are line width, laser cross section, etc., as well as low, nonlinear refractive index and essentially zero dependence of optical path length on temperature (Kurkjian & Prindle, 1998).

Poor chemical durability of phosphate glasses is a unique physical property that is being exploited in biomedical field especially for tissue engineering industry. Phosphate-based glasses are a range of glasses made up of components which all occur naturally in the body, and are suited to applications for devices in areas related to guided tissue regeneration and treatment of bone defects. By tailoring the composition of phosphate-based glasses it is possible to control the dissolution rates ranging from those that would completely degrade in water in a few hours to those that are stable for years (Drake and Allen, 1985). Controlling degradation behavior is a critical property in order to give enough time for the cells to lay down their own extracellular matrix and regenegrate the injured bone and at the same time to ensure that the biomaterial does not last longer than needed (Wang 2009). Poor durability of phosphate glasses is also useful for applications like the controlled release of oligo-elements in soils (Pyare et al., 1996).

Phosphate glasses can generally be formed at lower temperatures than silicate based systems. For this reasons, a number of phosphate glasses have been identified as being potentially applicable to disposition of nuclear waste especially of plutonium (Nirex Report, 2004). The most extensive use of phosphate glasses for vitrifying nuclear wastes has occurred in the former Soviet Union (Polykov et al., 1994). Magnesium phosphate glass with up to 55 mol % P_2O_5 can accommodate up to 45 mass % of simulated high level nuclear wastes (HLW) (Toshinori Okura, 2006) while iron phosphate glasses of composition $40(Fe_2O_3)60(P_2O_5)$ (mol%) can accommodate in excess of 50% of certain HLW constituents while maintaining excellent chemical durability (Day et al., 1998).

The wide use of incandescent lamps and gaseous discharge devices generated a need for sealing metal conductors through glass envelopes (Wei et al., 2001). Phosphate glasses are attractive as glass-metal seals due to their low melting temperature, low viscosity and high thermal expansion coefficient. For instant, zinc polyphosphate glasses have thermal expansion coefficients similar to many metals, and find it is practical use for sealing and welding between glassy and metallic parts (Tischendorf et al., 2003).

1.3 Research Aim

$MgO-P_2O_5$ and $ZnO-P_2O_5$ glasses well-known as anomalous glass (Kordes et al., 1953). However, it is of interest to investigate the properties of simultaneous admixture of MgO and ZnO into the phosphate compositions. The aim of this study is to investigate the dielectric, thermal, optical properties and chemical durability of binary $(MgO)_x(P_2O_5)_{1-x}$ and ternary $(ZnO)_{30}(MgO)_x(P_2O_5)_{70-x}$, $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$, $(ZnO)_x(MgO)_{30-x}(P_2O_5)_{70}$ glass systems. The different properties between these glass systems will help in assessing the insulating character of these glasses and may throw some light on the structural aspects, and to understand in more detail the natural behavior of phosphate glasses. In addition, the study will also attempt and elucidate the role undertaken by zinc and magnesium ions introduced into the phosphate network.

1.4 Objectives

The main objectives of the present study are summarized below:

1. Studying the frequency and temperature dependencies of dielectric response parameters on binary $(MgO)_x(P_2O_5)_z$ glasses and ternary $(ZnO)_x(MgO)_{y-x}(P_2O_5)_z$ glasses and deducing the nature of dielectric polarization involved.
2. Determination of an equivalent electrical circuit model that well describes the AC response of the sample.
3. Characterization of the thermal and optical properties in order to deduce the information on structural aspect of the studied glass samples.
4. Characterization of the effect of composition to chemical durability of the glass and to evaluate the dissolution rate of the glass in solution with pH 4.01, pH 7.00 and pH 10.01.
5. Examining the pH changes of solutions in order to understand the behavior of the glass corrosion.

1.5 Chapter Organization

This thesis is divided into six chapters. Chapter 1 gives general introduction of glass. Chapter 2 discusses on the literature review of phosphate glass. Chapter 3 mentions about the general theory of glassy state, phosphate glass fundamental structure, dielectric, thermal, optical and chemical durability. Chapter 4 discusses the experimental procedures and theoretical aspects that have been employed in this research. Chapter 5 is about results and discussion. The experimental results and findings with discussion will be presented in this chapter. Finally, the conclusion and suggestions for future work are described in Chapter 6. Various derivations of equations and calculations are included in the Appendices to supplement the main text within this thesis.

REFERENCES

Abay, B., Guder, H. S. and Yogurtchu, Y. K. 1999. Urbach-Martienssen's tails in layered semiconductor GaSe. *Solid State Communications* 112: 489-494

Abdel-Baki, M. and El-Dasty, F. 2006. Optical properties of oxide glasses containing transition metals: case of titanium- and chromium-containing glasses. *Current opinion in solid state and materials science* 10: 217-229

Abd El-Ati, M. I. and Higazy, A. A. 2000. Electrical conductivity and optical properties of gamma irradiated niobium phosphate glasses. *Journal of Materials Science* 35: 6175-6180

Ahmad, M. M., El Sayed Yousef, and El Sayed Moustafa. 2006. Dielectric properties of the ternary $TeO_2/Nb_2O_5/ZnO$ glasses. *Physica B* 371: 74-80

Al-Ani, S. K. J. and Higazy, A. A. 1991. Study of optical absorption edges in $MgO-P_2O_5$ glasses. *Journal of Materials Science* 26: 3670-3674

Al-Ani, S. K. J., Al-Hassany, I. H. O. and Al-Dahan, Z. T. 1995. The optical properties and a.c. conductivity of magnesium phosphate glasses. *Journal of Materials Science* 30: 3720–3729

Ali Omar, M. 1993. Elementary Solid State Physics, Addison-Wesley Publishing Company, Inc., pp. 389. United State of America,.

Altaf, M. and Ashraf Chaudhry, M. 2006. Dielectric behavior and conductivity $CdO-P_2O_5$ glasses. *Journal of Research Science* 17: 201-206

Altaf, M., Ashraf Chaudhry, M. and Zahid, M. 2003. Study of optical band gap of zinc borate glasses. *Journal of Research Science* 14: 253-259

Andersson, O. H. 1992. Glass transition temperature of glasses in the $SiO_2-Na_2O-CaO-P_2O_5-Al_2O_3-B_2O_3$ system. *Journal of Materials Science: Materials in Medicine* 3: 326-328

Angus Rockett. 2008. The materials science of semiconductors. Springer. Pp.362

Arai, Y., Itoh, K., Kohara, S. and Yu, J. 2008. Refractive index calculation using the structural properties of $La_4Ti_9O_{24}$ glass. *Journal of Applied Physics* 103: 094905

Bae, B. S. 1994. Chemical Durability of Copper Phosphate Glasses. *Glass Technology* 35: 83-88

Bahgat, A. A., El-Samanoudy, M. M. and Sabry, A. I. 1999. Optical and electrical properties of binary WO_3-Pb_3O_4 glasses. *Journal of Physics and Chemistry of Solids*: 1921-1931

Balaji Rao, R., Gopal, N. O. and Veeraiah, N. 2004. Studies on the influence of V_2O_5 on dielectric relaxation and ac conduction phenomena of Li_2O-MgO-B_2O_3 glass system. *Journal of Alloys and Compound* 368: 25-37

Bano, N. and Hashmi, R. A. 1996. Electrical studies of leaves over wide frequency range. *IEEE Transactions on Dielectrics and Electrical Insulation* 3: 229-232

Barsoum, M. W. 1997. Fundamentals of ceramics. McGraw-Hill Inc., New York. pp 543.

Bergo, P., Pontuschka, W. M. and Prison, J. M. 2008. Dielectric properties and physical features of phosphate glasses containing iron oxide. *Materials Chemistry and Physics* 108 :142-146.

Bertolotti, M., Liakhou, G., Li, Voti, R., Ricciardiello, F. G., Sparvieri, N. and Sibilia, C. 1992. Thermal diffusivity measurements for Mg-Mn ferrites. *Materials Letter* 13, issue 1: 51–54.

Bhanu Prashanth, S. B. and Asokan, S. 2009. A composition dependent thermal behavior of GexSe35-xTe65 glasses. *Journal of Non-Crystalline Solids* 355: 1227-1230

Bhide, A. and Hariharan, K. 2007. Sodium ion transport in $NaPO_3$-Na_2SO_4 glasses. *Materials chemistry and physics* 105: 213-221.

Bih, L., Abbas, L., Mohdachi, S. and Nadiri, A. 2008. Thermal and electrical properties of mixed alkali in Li_2O-Na_2O-WO_3-P_2O_5 glasses. *Journal of Molecular Structure* 891: 173-177

Boiko, G. G., Andreev, N. S. and Parkachev, A. V. 1998. structural of pyrophosphate $2ZnO.P_2O_5$-$2Na_2O.P_2O_5$ glasses according to molecular dynamics simulation. *Journal of Non-Crystalline Solids* 238: 175-185

Brauer, D. S., Christian Russel, Kraft, J. 2007. Solubility of glasses in the system P_2O_5-CaO-MgO-Na_2O-TiO_2: Experimental and modeling using artificial neural networks. *Journal of Non-Crystalline Solids* 353: 263-270.

Brow, R. K., Tallant, D. R., Meyer, S. T. and Phifer C. C. 1995. The short range structure of zinc polyphosphate glass. *Journal of Non-Crystalline Solids* 191:

45-55

Brow, R. K. 2000. Section 1: Structure. Review: The structure of simple phosphate glasses. *Journal of Non-Crystalline Solids* 263&264: 1-28

Brow, R. K., Click, C. A. and Alam, T. M. 2000. Modifier coordination and phosphate glass networks. *Journal of Non-Crystalline Solids* 274: 9-16

Bunker, B. C., Arnold, G. W. and Wilder, J. A. 1984. Phosphate glass dissolution in aqueous solutions. *Journal of Non-Crystalline Solids* 64: 291-316

Bunker, B. C. 1994. Molecular mechanisms for corrosion of silica and silicate glasses. *Journal of Non-Crystalline Solids* 179: 300-308

Button, D. P., Tandon, R. P., Tuller, H. L. and Uhlmann, D. R. 1981. Fast Li^+ ion conductance in chloroborate glasses II-diborates and metaborates. *Solid State Ionics* 5: 655-658

Byun, J. O., Kim, B. H., Hong, K. S., Jung, H. J., Lee, S. W. and Izyneev, A. A. 1995. Properties and structure of $RO-Na_2O-Al_2O_3-P_2O_5$ (R = Mg, Ca, Sr, Ba) glasses. *Journal of Non-Crystalline Solids* 190: 288-295.

Cape, J. A. and Lehman, G. W. 1963. Temperature and finite pulse-time effects in the flash methods for measuring thermal diffusivity. *Journal of Applied Physics* 34: 1909-1913

Carslaw, H. S. and Jeager, J. C. 1959. Conduction of heat in solids. Oxford Universiti Press 2nd , 101

Carta, D., Knowles, J. C., Smith, M. E. and Newport, R. J. 2007. Synthesis and structural characteristic of P_2O_5-CaO-Na_2O sol-gel materials. *Journal of Non-Crystalline Solids* 353: 1141-1149

Catlow, C. R. A. 1994. Defects and disorder in crystalline and amorphous solids (Nato Science Series C: Mathematical and physical Sciences). 1st Edn., Kluwer Academic Publishers, Netherlands, ISBN-10: 0792326105, pp:511.

Charles, A. Harper. 2001. Handbook of ceramics, glasses, and diamonds, Chapter 2: Ceramics, glasses, and micas for electrical products. McGraw-Hill: pp2.36

Charles, B. Boss, and Kenneth, J. Fredeen. 1997. Concept, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectroscopy, 2nd Edition. Perkin Elmer, USA.

Chaudhry, M. A. and Bilal, S. 1995. Concentration-dependent electrical conductivity of phosphate glasses containing zinc oxide. *Journal of Materials Chemistry and Physics* 41: 299–301

Chaudhry, M. A., Bilal, M. S., Altaf, M., Ahmed, M. A. and Rana, A. M. 1995. The optical absorption study of cadmium-zinc phosphate glasses. *Journal of Materials Science Letters* 14: 975-977

Chaudhry, M.A. and Altaf, M. 1998. Optical Absorption studies of sodium cadmium phosphate glasses. *Materials Letters* 34: 213-216

Chen Ang, Jurado, J. R., Zhi Yu, Colomer, M. T., Frade, J. R., Baptista, J. L. 1998. Variable-range-hopping conduction and dielectric relaxation in disordered $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$. *Physical Review B* 57: 11858-11861

Chowdari, B. V. R. and Gopalakrishnan, R. 1988. Investigation of AgX: Ag_2O:MoO_3:P_2O_5 glassy system (x = I, Br, Cl). *Journal of Non-Crystalline Solids* 105: 269-274

Chowdari, B. V. R. and Pramoda Kumari, P. 1996. Thermal, electrical and XPS studies of $Ag_2O.TeO_2.P_2O_5$ glasses. *Journal of Non-Crystalline Solids* 197: 31-40

Claudia Altavilla. 2006. Nanotechnology applied to glass surface protection. *CERC 3 Young Chemist's Workshop: Chemistry for the conservation of cultural Heritage: Present and future perspectives*. Perugia, Italy.

Clark, L. M. and Taylor, R. E. 1975. Radiation loss in the flash method for thermal diffusivity. *Journal of Applied Physics* 46: 714-719

Corbridge, D. E. C. 1985. Phosphorus. An outline of its chemistry, biochemistry and technology (3rd Edition). Elsevier Science Publishers B. V., Amsterdam. PP.37, 169.

Corrie T. Imrie, Ioannis Konidakis, Malcolm D. Ingram. 2004. What variable-prresure variable-temperature measurements are telling us about ion transport in glass. *The Royal Society of Chemistry, Dalton Transaction*: 3067-3070

Cowan, R. D. 1963. Pulse method of measuring thermal diffusivity at high temperatures. *Journal of Applied Physics* 34: 926

David Jiles. 1994. Introduction to the electronic properties of materials. Chapter 7: Electronic properties of semiconductors, pp131. Chapman and Hall, London, UK.

Davis, E. A. and Mott, N. F. 1970. Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. *Philosophical Magazine* 22: 903-922

Day, D. E., Wu, Z., Ray, S. and Hrma, P. 1998. Chemically durable iron phosphate glass wasteforms. *Journal of Non-Crystalline Solids* 241: 1-12

Dayanand, C., Sarma, R. V. G. K., Bhikshamaiah, G.. and Salagram, M. 1994. Optical properties of lead phosphate glasses. *Journal of Non-Crystalline Solids* 167: 122-126

Desirena, H., Schulzgen, A., Sabet, S., Ramos-Ortiz, G.., de la Rosa E. and Peyghambarian N. 2009. Effect of alkali metal oxide R_2O (R = Li, Na, K, Rb and Cs) and network intermediate MO (M = Zn, Mg, Ba and Pb) in tellurite glasses. *Optical Materials* 31: 784-789

Devidas, G. B., Sankarappa, T., Chougule, B. K., Prasad, G.. 2007. DC conductivity in single and mixed alkali vanadophosphate glasses. *Journal of Non-Crystalline Solids* 353: 426-434

Duffy, J. A. 2001. Ultraviolet transparency of glass: a chemical approach in terms of band theory polarisability and electronegativity. *Physics and Chemistry of Glasses* 42: 151-157

Doremus, R. H. (1973). Glass Science. A Wiley-Interscience Publication

Drake, C. F., Allen, W. M. 1985 The use of controlled release glasses for the controlled delivery of bioactive materials. *Biochemical Society Transactions* 13: 516–520.

Edward, D. Palik. 1998. Handbook of Optical Constants of Solids. Academic Press.

Elliott, 1990. Physics of Amorphous Materials, 2^{nd} Edition. Longman Group UK Limited.

Elliott, R. J. and Gibson, A. F. 1974. An Introduction to solid State Physics and its Applications. Macmillan Press LTD, pp:196

El-Mallawany, R. 1992. The optical properties of tellurite glasses. *Journal of Applied Physics* 72: 1774-1777

Eraiah, B. 2006. Optical properties of samarium doped zinc-tellurite glasses.

Bulletin Materials Science 29: 375-378

Eraiah, B. and Bhat, S. G., 2007. Optical properties of samarium doped zinc-phosphate glasses. *Journal of Physics and Chemistry of Solids* 68: 581-585

Eric Tong Yih Lee. June 2004. *Development and characterization of phosphate glasses for athermalisation.* University Southampton, Faculty of Engineering, Science and Mathematics, Optoelectronic Research Centre, PhD Thesis.

Fayon, F., Massiot, D., Suzuya, K. and Price, D. L. 2001. ^{31}P NMR study of magnesium phosphate glasses. *Journal of Non-crystalline Solids* 283: 88-94

Feltz, A. (1993). Amorphous inorganic materials and glasses. New York, USA. VCH Publishers, Inc.

Fernandez, E., Gil, F.J., Ginbera, M.P. 1999. Calcium Phosphate Bone Cements for Clinical Applications. Part 1. Solution Chemistry. *Journal of Material Science. Materials in Medicine*10: 169-176

Frohlich, H. 1958. Theory of dielectrics. Oxford University Press.

Fujino, S. and Kuwabara M. 2006. Dielectric properties of phosphate glasses in the region from 1 to 10 GHz. *Key Engineering Materials* 320: 209-212

Fuxi G.. 1992. Optical properties of glass. Springer, Berlin.

Gaskell, P. H. 1997. Structure and properties of glasses – how far do we need to go? *Journal of Non-Crystalline Solids* 222: 1-12

Gerald Burns. 1985. Solid State Physics. Academic Press, Inc, Orlando Florida.

Germa Garcia-Belmonte, Franc ois Henn and Juan Bisquert. 2006. Dielectric relaxation strength in conducting glasses caused by cluster polarization. *Chemical Physics* 330: 113-117

Ghauri, M. A. 1983. The optical properties of cadmium zinc phosphate glasses. *Journal of Materials Science Letters* 2: 660-662

Ghauri, M. A., Siddiqi, S. A., Shah, W. A., Ashiq, M. G.. B. and Iqbal, M. 2009. Optical properties of zinc molybdenum phosphate glasses. *Journal of Non-Crystalline Solids* 355: 2466-2471

Ghoneim, N. A., Ahmed, A. A. and Gharib, S. 1983. Effect of transition metal oxides on the thermal conductivity of glass. *Thermochimica Acta* 71: 43-51

Gliemeroth, G.. 1982. Optical properties of optical glass. *Journal of Non-Crystalline Solids* 47: 57-68

Gorachand Ghosh. Handbook of thermo-optic coefficients of optical materials with applications. Chapter 2: Refractive index. Pp: 5-114. Academic Press, 1998.

Hager, I. Z. 2009. Optical properties of lithium barium haloborate glasses. *Journal of Physics and Chemistry of Solids* 70: 210-217

Hassan, M.A. and Hogarth, C. A. 1988. A study of the structural, electrical and optical properties of copper tellurium oxide glasses. *Journal of Materials Science* 23: 2500-2504

Hasselman, D. P. H. and Merkel Gregory, A. 1989. Specimen size effect of the thermal diffusivity/conductivity of aluminum nitride. *Journal of American Ceramics Society* 72: 967-971.

Hasselman, D. P. H. 1990. Temperature dependence of the thermal diffusivity/conductivity of aluminum nitride. *Journal of American Ceramics Society* 73: 2511-2514.

Helmut Mehrer. 2007. Diffusion in solids: Fundamentals, methods, materials, diffusion-controlled processes. Springer-Verlag Heidelberg.

Hench, L.L. 1977. Physical Chemistry of Glass Surfaces. *Journal of Non-Cryst. Solids* 25: 343-369

Higazy, A. A. 1995. Electrical conductivity and dielectric constant of magnesium phosphate glasses. *Journal of Materials Letters* 22: 289–296

Hiki, Y., Takahashi H. and Kogure Y. 1994. Study of the thermal transport properties of superionic conducting glasses. *Solid State Ionics* 70/71: 362-367

Hogarth, C. A. and Ghauri, M. A. 1979. The preparation of cadmium phosphate and cadmium zinc phosphate glasses and their electrical and optical properties. *Journal of Materials Science* 14: 1641-1646

Hogarth, C. A. 1983. Some studies of the optical properties of Tungsten-Calcium-Tellurite Glasses. *Journal of Materials Science* 18: 1255-1263

Holloway, D. G. 1973. The physical properties of glass. Wykeham, London, pp. 41, 92-95

Hoppe, U., Walter, G., Kranold, R., Stachel, D. and Barz A. 1995. The dependence of structural peculiarities in binary phosphate glasses on their network modifier content. *Journal of Non-Crystaline Solids* 192 & 193: 28-31

Hoppe, U. 1996. A structural model for phosphate glasses. *Journal of Non-Crystalline Solids* 195: 138-147

Hoppe, U., Walter, G., Kranold, R. and Stachel, D. 2000. Structural specifies of phosphate glasses probed by diffraction methods: A review. *Journal of Non-Crystalline Solids* 263&264: 29-47

Hoppe, U., Walter, G.., Carl, G., Neuefeind, J. and Hannon, A. C. 2005. Structural of zinc phosphate glasses probed by neutron and x-ray diffraction of high resolving power and by reserve Monte Carlo simulations. *Journal of Non-Crystalline Solids* 351: 1020-1031

Hudgens, J. J., Brow, R. K., Tallant, D. R. and Martin, S. W. 1998. Raman spectroscopy study of the structure of lithium and sodium ultraphosphate glasses. *Journal of Non-Crystalline Solids* 223: 21-31

Hummel, R. E. 2001. Electronic properties of materials, Third Edition. Springer-Verlag Berlin Neidelberg

Isard, J.O., Allnatt, A.R., and Melling, P.J. 1982. An Improved Model of Glass Dissolution. *Physics and Chemistry of Glasses* 23 (6): 185-189

Jacinto, C., Feitosa, C. A. C., Mastelaro, V. R. and Catunda, T. 2006. Thermal properties of barium titanium borate glasses measured by thermal lens technique. *Journal of Non-Crystalline Solids* 352: 3577-3581

Jermoumi, T., Mustapha Hafid, Niegisch, N., Mennig, M., Sabir, A. and Toreis, N. 2002. Properties of (0.5-x)Zn-$x$$Fe_2O_3-0.5P_2O_5$ glasses. *Materials Research Bulletin* 37: 49-57

Jermoumi, T., Hassan, S. and Hafid, M. 2003. Structural investigation of vitreous barium zinc mixed metaphosphate. *Vibrational Spectroscopy* 32: 207-213

Jonscher, A. K. 1981. Review a new understanding of the dielectric relaxation of solids. *Journal of Materials Science* 16, 2037-2060

Jonscher, A. K. 1983. Dielectric relaxation in solids. Chelsea Dielectrics Press Limited, London. Pg. 66

Jonscher, A. K. 1989. Interpretation of non-ideal dielectric plots. *Journal of Materials Science* 24, 372-374

Jonscher, A. K. 1990. The universal' dielectric response. II. *IEEE Electrical Insulation Magazine* 6: 24-28

Jonscher, A. K. 1999. Review Article. Dielectric relaxation in solids. *Journal Physics D Applied Physics* 32: R57-R70

Jung, B. H., Kim, D. N. and Kim, H. S. 2005. Properties and structural of (50-x)BaO-xZnO-50P_2O_5 glasses. *Journal of Non-Crystalline Solids* 351: 3356-3360

Kanazawa, T. 1982. Structural characteristics of MgO-P_2O_5 glasses. *Journal of Non-Crystalline Solids* 52: 187-194

Khafagy, A. H., El-Adawy, A. A., Higazy, A. A., El-Rabaie, S. and Eid A. S. 2008. Studies of some mechanical and optical properties of (70-x)TeO_2+15B_2O_3+15P_2O_5+$x$$Li_2O$ glasses. *Journal of Non-Crystalline Solids* 354: 3152-3158

Kim, D. J., Kim, D. S., Kim, S. W., Troitsky, O. Y., Kim, J. C. and Lee, S. H. 2000. One-Level Two Points Method for estimation of thermal diffusivity by the converging thermal wave method. Proceedings of the 4th Korea-Russia International Institute Symposium 3: 184-189

Kim, J. R., Choi, G. K., Yim, D. K., Park, J. S. and Hong, K. S. 2006. Thermal and dielectric properties of ZnO-B_2O_3-MO_3 glasses (M = W, Mo). *Journal of Electroceramics* 17: 65-69

Kittel, C., 1962. Introduction to solid state physics, 5th edition, Wiley, New York.

Koudelka, L., Mosner, P. 2001. Study of the structure and properties of Pb-Zn borophosphate glasses. *Journal of Non-Crystalline Solids* 293-295: 635-641

Kreidl, N. J., in: Kreidl, N. J. and Uhlmann, D. R., (Eds.), Glass Science and Technology, Glass-forming Systems, Academic Press, New York, 1983, Vol. 1: 192

Kremer, F. and Schonhals, A. 2003. Broadband Dielectric Spectroscopy. Springer-Verlag Berlin Heidelberg.

Krishna Mohan, N., Rami Reddy, M., Jayasankar, C. K. and Veeraiah, N. 2008 Spectroscopic and dielectric studies on MnO doped PbO-Nb_2O_5-P_2O_5 glass system. *Journal of Alloys and Compound* 458: 66-76

Kurkjian, C. R. and Prindle, W. R. 1998. Perspectives of the history of glass composition. *Journal of Amorphous Ceramics Society* 81: 795-813

Larson, K. B. and Koyama, K. 1967. Correction for finite-pulse effects in very thin samples using flash method for measuring thermal diffusivity. *Journal of Applied Physics* 38: 465-474.

Laskar, J. M., Bagavathiappan, S., Sardar, M., Jayakumar, T., John Philip and Raj, B. 2008. Measurement of thermal diffusivity of solids using infrared thermography. *Materials Letter* 62: 2740-2742

Licina, V., Mogus-Milankovic, A., Reis, S. T. and Day D. E. 2007. Electronic conductivity in Zinc iron phosphate glasses. *Journal of Non-Crystalline Solids* 353: 4395-4399

Lippma, E., Magi, M., Samoson, A., Englehardt, G.. and Grimmer, A. R. 1980. *Journal of American Ceramics Society* 102: 4889-4893

Liu, H. S., Chin, T. S. and Yung, S. W. 1997. FTIR and XPS studies of low-melting $PbO-ZnO-P_2O_5$ glasses. *Materials Chemistry and Physics* 50: 1-10

Maczka, M., Macalik, B., Hanuza, J. and Bukowska, E. 2006. Synthesis and characterization of $M_2O-MgO-WO_3-P_2O_5$ (M = K, Rb, Cs) glass system. *Journal of Non-Crystalline Solids* 352: 5586-5593

Maglic, K. D., Cezairliyan, A. and Peletsky, V. E. (Eds.) 1992. Compendium of thermophysical property measurement methods, Volume 2, Plenum Press, New York: 281-314.

Marek Nocun. 2004. Structural studies of phosphate glasses with high ionic conductivity. *Journal of Non-Crystalline Solids* 333: 90-94

Marino, A. E., Arrasmith, S. R., Gregg, L. L., Jacobs, S. D., Chen, G. R. and Duc, Y. J. 2001. Durable phosphate glasses with lower transition temperatures. *Journal of Non-Crystalline Solids* 289: 37-41.

Matsubara, E., Waseda, Y., Ashizuka, M. and Ishida, E. 1988. Structural study of binary phosphate glasses with MgO, ZnO, and CaO by X-ray diffraction. *Journal of Non-Crystalline Solids* 103: 117-124

Matz, W., Stachel, D. and Goremychkin, E. A. 1988. The structure of alkaline earth metaphosphate glasses investigated by neutron diffraction. *Journal of*

Non-Crystalline Solids 101: 80-89

Mcswain, B. D., Borrelli, N. F. and Gouq-Jen Su. 1963. Infrared. Spectra of Vitreous Boron Oxide and Sodium Borate glasses. *Physics Chemistry Glasses* 4:11-21

Metwalli, E. and Brow, R. K. 2001. Modifier effects on the properties and structures of aluminophosphate glasses. *Journal of Non-Crystalline Solids* 289: 113-122

Mercier, C., Montage, L., Sfihi, H., Palavit, G., Boivin, J. C. and Legrand, A. P. 1998. Local structural of zinc ultraphosphate glasses containing large amount of hydroxyl groups: ^{31}P and ^{1}H solid state nuclear magnetic resonance investigation. *Journal of Non-Crystalline Solids* 224: 163-172

Meyer, K. 1997. Characterization of the structure of binary zinc ultraphosphate glasses by infrared and raman spectroscopy. *Journal of Non-Crystalline Solids* 209: 227-239

Milos, B. Volf. 1984. Chemical approach to glass. *Glass Science and Technology*, 7. Elsevier Science Publishers, Netherlands.

Mogus-Milankovic, A., Licina, V., Reis, S. T. and Day, D. E. 2007. Electronic relaxation in zinc iron phosphate glasses. *Journal of Non-Crystalline Solids* 353: 2659-2666

Mogus-Milankovic, A., Santic, A., Gajovic, A. and Day, D. E. 2003. Spectroscopy investigation of MoO_3-Fe_2O_3-P_2O_5 and SrO-Fe_2O_3-P_2O_5 glasses. Part I. *Journal of Non-Crystalline Solids* 325: 76-84

Mogus-Milankovic, A., Santic, A., Karabulut, M. and Day, D. E. 2003. Study of electrical properties of MoO_3-Fe_2O_3-P_2O_5 and SrO-Fe_2O_3-P_2O_5 glasses by impedance spectroscopy. Part II. *Journal of Non-Crystalline Solids* 330: 128–141

Montagne, L., Palavit, G. and Delaval, R. 1997. ^{31}P NMR in (100-x)($NaPO_3$)-xZnO glasses. *Journal of Non-Crystalline Solids* 215: 1-10

Montagne, L., Palavit, G. and Delaval, R. 1998. Effect of ZnO on the properties of (100-x)($NaPO_3$)-xZnO glasses. *Journal of Non-Crystalline Solids* 223: 43-47

Moridi, G. R. and Hogarth, C.A. Some properties of semiconducting copper-calcium phosphate glasses. In: W.E. Spear, Editor, Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, CICL, Edinburgh (1977), p. 688

Mott, N. F. and Davis, E. A. 1979. Electronic processes in non-crystalline materials, 2nd Edition. Clarendon Press, Oxford: 273.

Murali Krishna, G., Veeraiah, N., Venkatramaiah, N. and Venkatesan, R. 2008. Induced crystallization and physical properties of Li_2O-CaF-P_2O_5:TiO_2 glass system: Part II. Electrical, magnetic and optical properties. *Journal of Alloys and Compounds* 450: 486-493

Munoz-Martin, D., Villegas, M. A., Gonzalo, J. and Fernandez-Navarro, J. M. 2009. Characterisation of glasses in the TeO_2-WO_3-PbO system. *Journal of The European Ceramic Society* 29: 2903-2913

Naoyuki Kitamura, Kohei Fukumi, Junichi Nakamura, Tatsuo Hidaka, Hidekazu Hashima, Yoshitaka Mayumi and Junji Nishii. 2009. Optical Properties of zinc bismuth phosphate glass. *Journal of Materials Science and Engineering* B 161: 91-95

Nirex Report. Sep. 2004. A review of international literature on immobilization matrices for separated stock of plutonium. United Kingdom Nirex Limited. Pp 20

Nishida, T. and Takashima, Y. 1986. Mossbauer and DTA studies of K_2SO_4-$ZnSO_4$-$Fe_2(SO_4)_3$ glasses. *Bulletin Chemical Society Japan* 59: 2789-2794

Onyiriuka, E. C. 1993. Zinc phosphate glass surfaces studied by XPS. *Journal of Non-Crystalline Solids* 163: 268-273

Owen, A. E. 1963. Prog. Ceram. Sci. Vol. 3, Ed. J. E. Burke (Pergamon Press, New York, 1963): 77

Owen, G. Gardens. 2007. Trends in Optical material research. Chapter 5: Study of the optical and thermal properties of phosphate glasses. Nova Science Publishers, Inc. Pp:137-183

Padma Kurma, P. and Yashonath, S. 2006. Ionic conduction in the solid state. *Journal Chemical Sciences* 118: 135-154

Padmasree, K. P. and Kanchan, D. K. 2006. Conductivity and dielectric studies on $20CdI_2\text{-}80[xAg_2O\text{-}y(0.7V_2O_5\text{-}0.3B_2O_3)]$ super ion conducting system where $1 \leq x/y \leq 3$. *Journal of Non-Crystalline Solids* 352: 3841-3848.

Palavit, G., Mercier, C., Montagne, L. Drache, M. and Abe, Y. 1998. Chemical reactions of ultraphosphate glasses with water at various temperatures. *Journal of American Ceramics Society* 81: 1521-1524

Pan, A. and Ghosh, A. 1999. Ionic conductivity and relaxation dynamics in lithium tellurite glasses. *Journal of Physical Review B* 60: 3224–3229

Parker, W. J., Jenkins, R. J., Butler, C. P. and Abbott, G. L. 1961. Thermal diffusivity measurement using the flash technique. *Journal of Applied Physics* 32: 1679-1684

Parrot, J. E. and Struckes, A. D. 1975. Thermal Conductivity of solids. Pion Limited, London.

Paul, A. 1982. Chemistry of glass. Chapman and Hall. London, New York. PP 108-139

Peter, F. Green. 2005. Kinetics, transport, and structure in hard and soft materials. Taylor and Francis Group, LLC.

Pollock, D. D. 1982.Physical properties of materials for engineers, Volume III. CRC Press, INC. Boca Raton, Florida. Pp. 188

Polykov, A. S., Borisov, G. B., Moiseenko, N. I., Osnovin, V. I., Dzekun, E. G., Medvedev, G. M., Bel'tyukov, V. A., Dubkov, S. A. and Filippov, S. N. 1994. Experience in ceramic EP-500/1P type melter operation for HLW vitrification. *Atomnaya Energiva* 76: 183-188

Prasad, P. S. S. and Radhakrishna, S. 1988. Transport and dielectric studies on silver based molybdo-tungstate quaternary superionic conducting glasses. *Solids State Ionics* 28-30: 814-820.

Pye, L. D., Stevens, H. J. and LaCourse, W. C. 1972. Introduction to glass science. Plenum Press, New York

Pyare, R., Lal, L. J., Joshi, V. C., Singh, V. K. 1996. Leachability of molybdenum from ternary phosphate glasses. *Journal of American Ceramic Society* 79: 1329-1334

Radha Krishnan, S., Srinivas, R. S. 1976. Phys. Rev. B 14: 6967

Rani, S., Sanghi, S., Agarwal, A. A., Kishore, N. and Seth, V. P. 2008. Effect of ZnO/CdO on the structure and electrical conductivity in $Li_2O.MO.Bi_2O_3.B_2O_3$ glasses (M = Zn, Cd). *Journal of Physics and Chemistry of Solids* 69: 1855-1860

Ratnakaram, Y. C. and Reddy, A. V. 2000. Electronic spectra and optical band gap studies in neodymium clorophosphate glasses. *Journal of Non-Crystalline Solids* 277: 142-154

Ravi Kumar, V., Veeraiah, N., Buddhudu, S. and Tyaga Raju, V. J. 1997. Dielectric dispersion in CuO doped ZnF_2-PbO-TeO_2 glasses. *Journal de Physique III France* 7: 951-961.

Rawson, H. 1980. Properties and applications of glass. Glass science and technology 3. Elsevier science publishers B. V. Pg. 262

Reis, S. T., Karabulut, M. and Day, D. E. 2001. Chemical durability and structure of zinc-iron phosphate glasses. *Journal of Non-Crystalline Solids* 292: 150-157

Reis, S. T., Mogus-Milankovic, A., Licina, V., Yang, J. B., Karabulut, M., Day, D. E. and Brow, R. K. 2007. Iron redox equilibrium, structure and properties of zinc iron phosphate glasses. *Journal of Non-Crystalline Solids* 353: 151-158

Richerson David W., 1944. Modern ceramics engineering: Properties, processing, and use in design. 3rd Edn. CRC, Taylor & Francis

Rockstad, H.K. 1970. Hopping conduction and optical properties of amorphous chalcogenide film. *Journal of Non-Crystalline Solids* 2: 192-202

Rohsenow, W. M., Hartnett, J. P. and Ganic, E. N. 1985. Handbook of heat transfer fundamentals. Chapter 4: Conduction. McGraw-Hill, Inc. pp.4-3

Rothenberg, G. B. 1976. Glass Technology Recent Developments. Noyes Data Corporation.

Rosenberg, H. M. 1988. The Solid State. Third Edition. Oxford Science Publications.

Sahaya Baskaran, G., Ramana Reddy, M. V., Krishna Rao, D. and Veeraiah N. 2008. Dielectric properties of PbO-P_2O_5-As_2O_3 glass system with Ga_2O_3 as additive. *Journal of Solid State Communications* 145: 401-406

Salama, S. N., Salman, S. M. and Gharib, S. 1987. Thermal conductivity of some silicate glasses and their respective crystalline products. *Journal of Non-Crystalline Solids* 93: 203-214

Sales, B. C., Otaigbe, J. U., Beall, G. H., Boatner, L. A. and Ramey, J. O. 1998. Structure of zinc polyphosphate glasses. *Journal of Non-Crystalline Solids* 226:

287-293

Sales, B. C., Boatner, L. A. and Ramey, J. O. 2000. Chromatographic studies of the structures of amorphous phosphate: a review. *Journal of Non-Crystalline Solids* 263 & 264: 155-166

Salman, F. E., Shash, N. H., El-Haded Abou and El-Mansy M. K. 2002. Electrical conduction and dielectric properties of vanadium phosphate glasses doped with lithium. *Journal of Physics and Chemistry of Solids* 63: 1957–1966

Saltas, V., Vallianatos, F., Soupios, P., Makris, J. P. and Triantis, D. 2005. Application of dielectric spectroscopy to the detection of contamination in sandstone. International Workshop, Greece.

Sankarappa, T., Prashant, M., Devidas, G. B., Nagaraja, N. and Ramakrishnareddy, R. 2008. AC conductivity and dielectric studies in V_2O_5-TeO_2 and V_2O_5-CoO-TeO_2 glasses. Journal of Molecular Structure 889: 308-315

Saxena, N. S., Imra, M. M. A. and Kedar Singh. 2002. Simultaneous measurements of thermal conductivity and diffusivity of Se80Te20-*x*Inx (*x* = 2, 4, 6 and 10) chalcogenide glasses at room temperature. *Bulletin Materials Science* 25: 241-245

Scaife, B. K. P. 1989. Principle of Dielectrics. Clarendon Press, Oxford.

Shaaban, M. H., El Nimr, M. K. and Ahmed A. A. 1993. Electrical conductivity of field-assisted ion-exchanged glass with molted $PbCl_2$ salt. Journal of Materials Science: *Materials in Electronics* 4: 208-214

Shafi N. A. El Batal, H. A., Ezz El Din, F. M., Gharib, S. and Halawa M. M. 1985. Thermal conductivity of gamma-irradiated ternary borate glasses. *Thermochimica Acta* 96: 121-128

Shawoosh, A. S. and Kutub, A. A. 1993. An investigation of the electrical, optical, and DSC properties of a copper-phosphate glass composition. *Journal of Materials Science* 28: 5060-5064

Sheikh, M. A., Taylor, S. C., Hayhurst, D. R. and Taylor, R. 2000. Measurement f thermal diffusivity of isotropic materials using a laser flash method and its validation by finite element analysis. *Journal of Physics D: Applied Physics* 33: 1536-1550

Shelby, J. E. 2000. Properties of alkali-alkaline earth metaphosphate glasses. *Journal of Non-Crystalline Solids* 263 & 264: 271-276

Shelby, J. E. 2005. Introduction to glass science and technology. The royal society of chemisty

Shelby, J. E., 1985. Formation and properties of calcium aluminosilicate glasses. *Journal of American Ceramic Society* 68: 155-158

Shih, P. Y., 2003. Properties and FTIR spectra of lead phosphate glasses for nuclear waste immobilization. *Materials Chemistry and Physics* 80: 299-304

Simon, V., Muresan D., Takacs A. S., Neumann M. and Simon S. 2007. Local order changes induced in calcium-sodium phosphate glasses by transition metal. *Journal of Solid State Ionics* 178: 221-225

Singh, A. K., Pushpendra Kumar, Kedar Singh, Saxena, N. S. 2006. Thermal transport in $Se_{81}Te_{15}Sb_4$ Chalcogenide glass. *Chalcogenide Letters* 3: 139-144

Soliman, A. A. 2008. XRD, DTA and density studies of lithium borate glasses containing copper. *Armeniun Journal of Physics* 1: 188-197

Song, C. H., Choi, H. W., Kim, J. E., Lee, J. K., Kim, S. J. and Yang Y. S. 2005. Dielectric properties of $KNbGeO_5$ glass. *Journal of the Korean Physical Society* 46: 167-170

Sparvieri, N., Penco, E., Sibilia, C., Bertolotti, M., Suber, G. and Ferrari A. 1987. A laser interferometric method applied to thermal diffusivity measurement of ferrites. *Material Letter* 5, issues 11-12: 449–452

Stevals, J. M. 1953. Proc. 11th Cong. Pure and Applied Chemistry 5: 519

Subcik, J., Koudelka, L., Mosner, P., Montagne, L., Revel, B. and Gregora, I. 2009. Structure and properties of MoO_3-containing zinc borophosphate glasses. *Journal of Non-Crystalline Solids* 355: 970-975

Suzuya, K., Price, D. L., Loong, C.-K. and Kohara, S. 1999. The structure of magnesium phosphate glasses. *Journal of Physics and Chemistry of Solids* 60: 1457-1460

Suzuya, K., Itoh, K., Kajinami, A. and Loong, C. –K. 2004. The structure of binary zinc phosphate glasses. *Journal of Non-crystalline Solids* 345&346: 80-87

Syam Prasad N. and Varma K. B. R. 2005. Evolution of ferroelectric $LiNbO_3$ phase in a reactive glass matrix ($LiBO_2$-Nb_2O_5). *Journal of Non-Crystalline Solids* 351: 1455-1465

Szu Sungping and Chang Fu-Shyang. 2005. Impedance study of V_2O_5-TeO_2-BaO. *Solids State Ionics* 176: 2695-2699

Takebe, H., Baba, Y. and Kuwabara M. 2006. Dissolution behavior of ZnO-P_2O_5 glasses in water. *Journal of Non-Crystalline Solids* 352: 3088-3094

Tauc, J. and Menth, A. 1972. State in the gap. *Journal of Non-Crystalline Solids* 8-10: 569-585

Tauc, J., Grigorovici, R. and Vancu, A. 1966. Optical Properties and electronic structure of amorphous germanium. *Physica Status Solidi* 15: 627-637

Tauc, J., in: Abeles F. (Ed). 1970. Optical properties of Solids, North-Holland, Amsterdam.

Taylor, R. 1980. Construction of apparatus for heat pulse thermal diffusivity measurementsfrom 300-3000 K. *Journal of Physics E: Scientific Instruments* 13: 1193-1199

Taylor, R. E. and Cape, J. A., 1964. Finite Pulse-time effects in the flash technique. *Applied Physics Letters* 5: 212-213

Taylor, R. E. and Clark III, L. M. 1974. Finite Pulse Time Effects in Flash Diffusivity Method. *High Temperatures-High pressures* 6: 65-71

Ticha, H., Schwarz, J., Tichy, L. and Mertens, R. 2004. Physical properties of PbO-ZnO-P_2O_5 glasses II. Refractive index and optical properties. *Journal of Optoelectronics and Advanced Materials* 6: 747-753

Tischendorf, B. C., Otaigbe, J. U., Wiench, J. W., Pruski, M. and Sales, B. C. 2001. A study of short and intermediate range order in zinc phosphate glasses. *Journal of Non-Crystalline Solids* 282: 147-158

Tischendorf, B. C., Alam, T. M., Cygan, R. T. and Otaigbe, J. U. 2003. The structure and properties of binary zinc phosphate glasses studied by molecular dynamics simulations. *Journal of Non-Crystalline Solids* 316: 261-272

Tischendorf, B. C. 2005. *Interactions between water and phosphate glasses*, PhD Thesis, Dept. Ceram. Eng., University of Missouri-Rolla

Toshinori Okura, Tomoko Miyachi and Hideki Monma. 2006. Properties and vibrational spectra of magnesium phosphate glasses for nuclear waste immobilization. *Journal of the European Ceramic Society* 26: 831-836

Urbach, F. 1953. The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. *Physical Review* 92: 1324-1324.

Van Wazer, J. R. 1958. Phosphorus and its Compounds. Interscience: New York.

Van Wazer, J. R., Griffith, E . J. and McCullough, J. F. 1955. Structure and properties of the Condensed phosphates. VII. Hydrolytic degradation of pyro-and tripolyphosphate. *Journal of The American Chemical Society* 77: 287-291

Veeranna Gawda, V. C., Anavekar, R. V. 2005. Transport properties of Li_2O-MnO_2-B_2O_3 glasses. *Solid State Ionics* 176: 1393-1401.

Volf, M. B., 1990. Technical approach to glass. Karel Nemecek: pp. 202

Walter, G., Hoppe, U., Baade, T., Kranold, R. and Stachel, D. 1997. Intermediate range order in MeO-P_2O_5 glasses. *Journal of Non-Crystalline Solids* 217: 299-307

Walter, G, Vogel, J., Hoppe, U. and Hartmann, P. 2003. Structural study of magnesium polyphosphate glasses. *Journal of Non-Crystalline Solids* 320: 210-222

Wang, Q., Wang, Q., Wang, J., Zhang, X., Yu, X. and Wan, C. 2009. Degradation kinetics of calcium polyphosphate bioceramic: an experimental and theoretical study. *Material Research* 12: 495-501

Wei, T. Y., Hu, Y. and Hwa, L. G 2001. Structure and elastic properties of low temperature sealing phosphate glasses. *Journal of Non-Crystalline Solids* 288: 140-147

Wei Gao and Nigel M. Sammes. 1999. An introduction to electronic and ionic materials. World Scientific Publishing, pp. 207

Weng, C. Z., Chen, J. H. and Shih, P. Y. 2009. Effect of dehydroxylation on the structure and properties of $ZnCl_2$-ZnO-P_2O_5 glasses. *Materials Chemistry and Physics* 115: 628-631.

West, A. R. 1991. Solid state chemistry and its applications. John Wiley and Sons. Pp. 109

Weyl, W. A. and Marboe, E. C. 1962. The Constitution of Glasses, A dynamic interpretation, Vol. 1, Wiley, New York.

Wiench, J. W., Pruski, M., Tischendorf, B., Otaigbe, J. U. and Sales, B. C. 2000. Structural studies of zinc polyphosphate glasses by nuclear magnetic resonance. *Journal of Non-Crystalline Solids* 263&264: 101-110

Xiaolin Chen, Yonghong Cheng, Xiaojun Xie, Wutong Feng and Hong Wang, Calculation of the relaxation time of h-BN based on dielectric data. International Conference on Solid Dielectric, Winchester, UK, 2007: 639-642

Xu, Q. and Ichikawa, K. 1985. Thermal diffusivity of Ge-Te glass near the glass-supercooled-liquid transition. *Journal of Physics C: Solid State Physics* 18: L985-989

Yu, X., Day, D. E., Long, G. J. and Brow, R. K. 1997. Properties and structure of sodium-iron phosphate glasses. *Journal of Non-Crystalline Solids* 215: 21-31

Yusoff, A. R. M. and Abd. Majid, W. H. 2005. Pyroelectric behavior and dielectric properties of linear copolysiloxane/eicosylamine superlattice. *European Physical Journal B* 45: 33-37

Zachariasen W. H. 1932. The atomic arrangement in glass. *Journal of Chemical Society* 54: 3841-3851