



UNIVERSITI PUTRA MALAYSIA

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

LOH YEN NEE

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OF LITHIUM FLUORO AND CHLORO
AND MAGNESIUM CHLORO PHOSPHATE GLASSES**

By

LOH YEN NEE

**Thesis Submitted to the School of Graduate Studies,
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Chairman : Associate Professor Zainal Abidin Talib, PhD

Faculty : Science

A series of lithium fluoro phosphate glass, $(\text{LiF})_x (\text{P}_2\text{O}_5)_{1-x}$ with $x = 0.1$ to $x = 0.6$; lithium chloro phosphate glass, $(\text{LiCl})_x (\text{P}_2\text{O}_5)_{1-x}$ with $x = 0.1$ to $x = 0.6$ both in the interval of 0.05 and magnesium chloro phosphate glass, $(\text{MgCl}_2)_x (\text{P}_2\text{O}_5)_{1-x}$ 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.



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

Oleh

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Kaca lithium fluoro fosfat $(\text{LiF})_x (\text{P}_2\text{O}_5)_{1-x}$ dengan komposisi $x = 0.1$ hingga $x = 0.6$; kaca lithium kloro fosfat $(\text{LiCl})_x (\text{P}_2\text{O}_5)_{1-x}$ dengan komposisi $x = 0.1$ hingga $x = 0.6$, kedua-duanya dengan selangan sebanyak 0.05 dan kaca magnesium kloro fosfat $(\text{MgCl}_2)_x (\text{P}_2\text{O}_5)_{1-x}$ dengan komposisi $x = 0.1$ 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 menunjukan 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 ungu-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.

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LIST OF TABLES

Table		Page
5.1:	Compositions and densities of LiF-P ₂ O ₅ glasses	5.1
5.2:	Compositions and densities of LiCl-P ₂ O ₅ glasses	5.3
5.3:	Compositions and densities of MgCl ₂ -P ₂ O ₅ glasses	5.4
5.4:	The compositions and refractive indices of LiF-P ₂ O ₅ glasses	5.15
5.5:	The compositions and refractive indices of LiCl-P ₂ O ₅ glasses	5.16
5.6:	The compositions and refractive indices of MgCl ₂ -P ₂ O ₅ glasses	5.18
5.7:	Derived characteristic energies of LiF-P ₂ O ₅ glasses	5.26
5.8:	Derived characteristic energies of LiCl-P ₂ O ₅ glasses	5.26
5.9:	Derived characteristic energies of MgCl ₂ -P ₂ O ₅ glasses	5.27
A.1:	Values of the different exponent and circuit element used in equivalent circuit modeling in the glass system of LiF-P ₂ O ₅	A.27
A.2:	Values of the different exponent and circuit element used in equivalent circuit modeling in the glass system of LiCl-P ₂ O ₅	A.33
A.3:	Values of the different exponent and circuit element used in equivalent circuit modeling in the glass system of MgCl ₂ -P ₂ O ₅	A.39

LIST OF FIGURES

Figure		Page
2.1:	Structures of (a) P_4O_6 , As_4O_6 (b) P_4O_{10} , and (c) vitreous P_2O_5	2.5
2.2:	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 effect of Mg cation content on the glass former	2.16
3.1:	Transformation from liquid to crystalline, and liquid to glassy state	3.5
3.2:	Two dimensional analogue of a modified glass; P_2O_5 modified by the addition of some MO_x , network modifier, with shaded circles representing atoms of M	3.10
3.3:	Structure of (a) PO_4 and (b) P_4O_{10} molecules. Darker-shaded circles represent P	3.12
3.4:	Schematic representations of (a) a random network changed by a modifier and (b) of a modified fluoride glass structure consisting predominantly of corner-sharing octahedral	3.15
3.5:	Time dependence of the polarization P after the application of an electric field on an insulator at $t = 0$	3.32
3.6:	The Debye equivalent circuit	3.33
4.1:	Preparation of Samples	4.2
5.1:	Densities of $LiF-P_2O_5$ glasses	5.2
5.2:	Densities of $LiCl-P_2O_5$ glasses	5.3
5.3:	Densities of $MgCl_2-P_2O_5$ glasses	5.4
5.4:	XRD spectrum of $LiF-P_2O_5$ glasses	5.7
5.5:	XRD spectrum of $LiCl-P_2O_5$ glasses	5.7
5.6:	XRD spectrum of $MgCl_2-P_2O_5$ glasses	5.8
5.7:	FTIR spectra of $LiF-P_2O_5$ glasses	5.9
5.8:	FTIR spectra of $LiCl-P_2O_5$ glasses	5.10

5.9:	FTIR spectra of MgCl ₂ -P ₂ O ₅ glasses	5.10
5.10:	Refractive indices of LiF-P ₂ O ₅ glasses	5.15
5.11:	Refractive indices of LiCl-P ₂ O ₅ glasses	5.17
5.12:	Refractive indices of MgCl ₂ -P ₂ O ₅ glasses	5.18
5.13:	The optical absorbance as a function of wavelength in the UV region of LiF-P ₂ O ₅ glasses	5.19
5.14:	The optical absorbance as a function of wavelength in the UV region of LiCl-P ₂ O ₅ glasses	5.20
5.15:	The optical absorbance as a function of wavelength in the UV region of MgCl ₂ -P ₂ O ₅ glasses	5.20
5.16:	Optical absorption coefficient, α , plotted against photon energy, $\hbar\omega$, of LiF-P ₂ O ₅ glasses	5.21
5.17:	Optical absorption coefficient, α , plotted against photon energy, $\hbar\omega$, of LiCl-P ₂ O ₅ glasses	5.22
5.18:	Optical absorption coefficient, α , plotted against photon energy, $\hbar\omega$, of MgCl ₂ -P ₂ O ₅ glasses	5.22
5.19:	The $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy, $\hbar\omega$, of LiF-P ₂ O ₅ glasses	5.24
5.20:	The $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy, $\hbar\omega$, of LiCl-P ₂ O ₅ glasses	5.24
5.21:	The $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy, $\hbar\omega$, of MgCl ₂ -P ₂ O ₅ glasses	5.25
5.22:	The $\ln \alpha$ as a function of photon energy, $\hbar\omega$, of LiF-P ₂ O ₅ glasses	5.28
5.23:	The $\ln \alpha$ as a function of photon energy, $\hbar\omega$, of LiCl-P ₂ O ₅ glasses	5.28
5.24:	The $\ln \alpha$ as a function of photon energy, $\hbar\omega$, of MgCl ₂ -P ₂ O ₅ glasses	5.29
5.25:	Dielectric constant of (LiF) _{0.10} (P ₂ O ₅) _{0.90} at different frequencies and temperatures	5.31

5.26:	Dielectric loss factor of $(\text{LiF})_{0.10}(\text{P}_2\text{O}_5)_{0.90}$ at different frequencies and temperatures	5.31
5.27:	Dielectric constant of $(\text{LiF})_{0.40}(\text{P}_2\text{O}_5)_{0.60}$ at different frequencies and temperatures	5.32
5.28:	Dielectric loss factor of $(\text{LiF})_{0.40}(\text{P}_2\text{O}_5)_{0.60}$ at different frequencies and temperatures	5.33
5.29:	Dielectric constant of $(\text{LiCl})_{0.10}(\text{P}_2\text{O}_5)_{0.90}$ at different frequencies and temperatures	5.34
5.30:	Dielectric loss factor of $(\text{LiCl})_{0.10}(\text{P}_2\text{O}_5)_{0.90}$ at different frequencies and temperatures	5.35
5.31:	Dielectric constant of $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at different frequencies and temperatures	5.36
5.32:	Dielectric loss factor of $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at different frequencies and temperatures	5.36
5.33:	Relative complex permittivity of lithium fluoro and lithium chloro phosphate glasses at 200°C	5.38
5.34:	Dielectric constant of $(\text{MgCl}_2)_{0.10}(\text{P}_2\text{O}_5)_{0.90}$ at different frequencies and temperatures	5.39
5.35:	Dielectric loss factor of $(\text{MgCl}_2)_{0.10}(\text{P}_2\text{O}_5)_{0.90}$ at different frequencies and temperatures	5.40
5.36:	Relative complex permittivity of lithium chloro and magnesium chloro phosphate glasses at 200°C	5.40
5.37:	Dielectric constant of $(\text{MgCl}_2)_{0.40}(\text{P}_2\text{O}_5)_{0.60}$ at different frequencies and temperatures	5.41
5.38:	Dielectric loss factor of $(\text{MgCl}_2)_{0.40}(\text{P}_2\text{O}_5)_{0.60}$ at different frequencies and temperatures	5.42
5.39:	Equivalent circuit for fitting the experimental results	5.43
5.40:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 30°C	5.44
5.41:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 50°C	5.44
5.42:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 100°C	5.45

5.43:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 150°C	5.45
5.44:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 200°C	5.46
5.45:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 250°C	5.46
5.46:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 300°C	5.47
A.1:	XRD spectrum of $\text{LiF-P}_2\text{O}_5$ glasses for mole fraction 0.15-0.55	A.4
A.2:	XRD spectrum of $\text{LiCl-P}_2\text{O}_5$ glasses for mole fraction 0.15-0.55	A.4
A.3:	XRD spectrum of $\text{MgCl}_2\text{-P}_2\text{O}_5$ glasses for mole fraction 0.15-0.45	A.5
A.4:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 30°C	A.5
A.5:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 50°C	A.6
A.6:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 100°C	A.6
A.7:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 150°C	A.7
A.8:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 200°C	A.7
A.9:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 250°C	A.8
A.10:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 300°C	A.8
A.11:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 30°C	A.9
A.12:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 50°C	A.9
A.13:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50} (\text{P}_2\text{O}_5)_{0.50}$ at 100°C	A.10

A.14:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 150°C	A.10
A.15:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 200°C	A.11
A.16:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 250°C	A.11
A.17:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiF})_{0.50}(\text{P}_2\text{O}_5)_{0.50}$ at 300°C	A.12
A.18:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 30°C	A.12
A.19:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 50°C	A.13
A.20:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 100°C	A.13
A.21:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 150°C	A.14
A.22:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 200°C	A.14
A.23:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 250°C	A.15
A.24:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.20}(\text{P}_2\text{O}_5)_{0.80}$ at 300°C	A.15
A.25:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at 30°C	A.16
A.26:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at 50°C	A.16
A.27:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at 100°C	A.17
A.28:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at 150°C	A.17
A.29:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60}(\text{P}_2\text{O}_5)_{0.40}$ at 200°C	A.18

A.30:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60} (\text{P}_2\text{O}_5)_{0.40}$ at 250°C	A.18
A.31:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{LiCl})_{0.60} (\text{P}_2\text{O}_5)_{0.40}$ at 300°C	A.19
A.32:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 30°C	A.19
A.33:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 50°C	A.20
A.34:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 100°C	A.20
A.35:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 150°C	A.21
A.36:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 200°C	A.21
A.37:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 250°C	A.22
A.38:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.10} (\text{P}_2\text{O}_5)_{0.90}$ at 300°C	A.22
A.39:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 30°C	A.23
A.40:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 50°C	A.23
A.41:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 100°C	A.24
A.42:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 150°C	A.24
A.43:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 200°C	A.25
A.44:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 250°C	A.25
A.45:	Experimental and fitted value obtained from equivalent circuit of Figure 5.39 for $(\text{MgCl}_2)_{0.40} (\text{P}_2\text{O}_5)_{0.60}$ at 300°C	A.26

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

	Page
ABSTRACT	ii
ABSTRAK	iv
ACKNOWLEDGEMENTS	vi
APPROVAL	vii
DECLARATION	ix
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS/ NOTATIONS/ GLOSSARY OF TERMS	xvii
 CHAPTER	
1 INTRODUCTION	1.1
2 LITERATURE REVIEW	2.1
2.1 History of glass	2.1
2.2 Network model of glass formers	2.3
2.3 Glass: an important material for optics	2.6
2.4 Structural properties of glasses	2.7
2.4.1 Densities	2.8
2.4.2 X-ray Diffractometry (XRD)	2.9
2.4.3 Fourier Transform Infrared Spectroscopy (FTIR)	2.11
2.5 Optical properties of glass	2.13
2.6 Dielectric properties of glass	2.16
3 THEORY	3.1
3.1 Introduction	3.1
3.2 Theory of glass	3.2
3.3 Nature of the glassy state	3.4
3.4 Glass transformation temperature	3.4
3.5 Structure theory of glass formation	3.8
3.6 The structure of multicomponent glass-forming systems	3.14
3.7 Electronic states in non-crystalline solids	3.16
3.8 Composition and structure of practical glasses	3.18
3.9 Structural properties of the glasses	3.21
3.9.1 Densities	3.21
3.9.2 X-ray Diffractometry (XRD)	3.21
3.9.3 Fourier Transform Infrared Spectroscopy (FTIR)	3.22
3.10 Optical properties of glass	3.23
3.11 Dielectric properties of glass	3.26



4	METHODOLOGY	4.1
4.1	Sample preparation	4.1
	(LiF) _x (P ₂ O ₅) _{1-x} glasses	
	(LiCl) _x (P ₂ O ₅) _{1-x} glasses	
	(MgCl ₂) _x (P ₂ O ₅) _{1-x} glasses	
4.2	Experimental Set-up	4.3
4.2.1	Structural properties measurement	4.3
	4.2.1.1 Densities	4.3
	4.2.1.2 X-ray Diffractometry (XRD)	4.4
	4.2.1.3 Fourier Transform Infrared Spectroscopy (FTIR)	4.4
4.2.2	Optical measurement	4.5
	4.2.2.1 Ellipsometry	4.5
	4.2.2.2 UV-Visible Spectrophotometer	4.5
4.2.3	Dielectric measurement	4.6
5	RESULTS AND DISCUSSION	5.1
5.1	Structural properties measurements	5.1
	5.1.1 Densities	5.1
	5.1.2 X-ray Diffractometry (XRD)	5.6
	5.1.3 Fourier Transform Infrared Spectroscopy (FTIR)	5.8
5.2	Optical measurements	5.14
	5.2.1 Refractive index	5.14
	5.2.2 UV-Visible measurements	5.19
5.3	Dielectric measurements	5.30
6	CONCLUSIONS	6.1
	REFERENCES	R.1
	APPENDICES	A.1
	BIODATA OF THE AUTHOR	V.1



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 $1650\text{ }^\circ\text{C}$. 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