ELSEVIER

Ceramics International 30 (2004) 1715–1717

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Optical absorption spectrum of $(LiCl)_x(P_2O_5)_{1-x}$ glass

Z.A. Talib*, Y.N. Loh, H.A.A. Sidek, W.M.D.W. Yusoff, W.M.M. Yunus, A.H. Shaari

Department of Physics, Faculty of Science and Environmental Studies, University Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

Received 24 November 2003; received in revised form 11 December 2003; accepted 23 December 2003

Available online 2 July 2004

Abstract

A series of glasses $(LiCl)_x(P_2O_5)_{1-x}$ with $x = 0.1$–0.6 in the interval of 0.05 were prepared by a single-step melting process with LiCl and P_2O_5 as starting materials. Their density and absorption spectra in the ultra-violet visible (UV-Vis) region have been recorded at room temperature. 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 optical band gap decreases to lower energies and shifts to longer wavelength with the increase in LiCl content in glass. The absorption edge is attributed to indirect transitions. The densities of glasses were found to be varying between 2.33 and 2.52 g cm^{-3} for mole fraction of 0.1–0.6. The average density was 2.42 g cm^{-3} and no evidence of anomalous densities' behaviour was observed.

Keywords: $(LiCl)_x(P_2O_5)_{1-x}$ glass; Density; Absorption edge; Optical band gap

1. Introduction

Vitreous P_2O_5 is a transparent hygroscopic glass that has superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures and high ultra-violet (UV) transmission. However, P_2O_5 still can not be used to replace the conventional glasses in a wide range of technological applications [1] due to its poor chemical durability, high hygroscopic and volatile nature. The present investigation is on the UV absorption where lithium ions are introduced into glasses as LiCl, which acts as a modifier in P_2O_5 network glass.

2. Experimental procedure

The glass samples were prepared from reagent grades of lithium chloride LiCl and phosphorous pentoxide P_2O_5. The starting materials were weighted by using electronic balance to get 30 g batches of LiCl and P_2O_5. The batches were thoroughly mixed in alumina crucible, and were covered by a lid before heating. Firstly, the chemicals were heated in the first furnace at 400 °C for 30 min, to allow the phosphate to decompose completely before melting and react with other batch. Then the crucible was transferred to the second furnace at 1000 °C for 1 h. The substance melts at that temperature and chemical will react with one another of calculated amount of LiCl and P_2O_5. The melt was then poured into a disc shaped (dimension: diameter ~20 mm and thickness ~2 mm) preheated steel mould at 400 °C. It was then pressed with solid mould immediately to get samples of desired thickness ~1–2 mm. After solidification, the glass was transferred to another furnace set at 150 °C for annealing. After 15 min, the furnace was switched off and the glasses were then allowed to cool to room temperature, under initial cooling rate of ~3 °C min^{-1}. This is done to remove residual stresses before cutting and polishing procedures. After that, silicon carbide abrasive papers were used to polish the samples until both surfaces of the samples were flat, smooth and parallel. The sample's thickness was then measured using a digital micrometer.

3. Structural, density and optical measurements

The binary glasses that were successfully prepared were free of bubbles, transparent and colorless. The densities of the glasses were determined by using Archimedes's principle with acetone (C_3H_6O) as an immersion liquid. The

* Corresponding author.
E-mail address: zainalat@fsas.upm.edu.my (Z.A. Talib).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.146

densities were calculated from the equation:

$$\rho_{\text{glass}} = \rho_{\text{acetone}} \times \frac{\text{weight of glass in air}}{\text{weight of glass in acetone}}, \quad (1)$$

where $\rho_{\text{acetone}} = 0.7899\,\text{g cm}^{-3}$.

The procedure involves filling a biker with acetone, and weight it as x. The glass sample was tied with a string and was dipped into the acetone by holding the end tail of the string, without touching the base of the biker and recorded as y. The weight of glass in acetone can be obtained by $(y-x)$. From that, the densities of the glasses can be determined through Eq. (1).

Optical absorption measurements in the wavelength range of 200–800 nm were performed at room temperature using a Camspec M350 Double Beam UV-Vis Spectrophotometer. The optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance, A, using the following equation:

$$\alpha(\lambda) = 2.303\frac{A}{d}, \quad (2)$$

where d is the thickness of the samples.

4. Results and discussions

The compositions of the samples used are listed in Table 1. Fig. 1 showed that the densities of glasses varying between 2.33 and 2.52 g cm^{-3} for mole fraction of 0.1–0.6. The average density was 2.42 g cm^{-3} and we found no evidence of anomalous densities' behaviour as compared to previous workers [2].

The data for Fig. 2 were obtained from the relation (2). As can be seen from figure, it is clear that there is no sharp absorption edge and this is a characteristic of the glassy state [4]. From the result presented, the absorption edges shifted back and forth as the mole fraction was increased. This observation has been observed before in phosphate glasses [5] and is attributed to the changes in the bonding that take place in the glass as the metal content increased. For photon energies higher than the mobility gap E_o, the absorption coefficient $\alpha(\omega)$ varies with angular frequency of radiation ω according to

$$\alpha(\omega) = \frac{\text{constant}}{\hbar\omega}(\hbar\omega - E_{\text{opt}})^r, \quad (3)$$

where E_{opt} is the energy of the optical band gap, $\hbar\omega$ is the photon energy of the incident radiation and r is an index which can assume values of 1, 2, 3, 1/2 and 3/2 depending on the nature of the interband electronic transitions. By assuming indirect transitions, the value of $r = 2$ was chosen and can be illustrated as below:

$$(\alpha\hbar\omega)^{1/2} = \text{constant}(\hbar\omega - E_{\text{opt}}). \quad (4)$$

Fig. 3 was plotted by using Eq. (4). Thus, the values of E_{opt} were obtained by extrapolation of the linear region of the plots of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ to $(\alpha\hbar\omega)^{1/2} = 0$ and are given in Table 1.

The value of E_{opt} was found to be erratic although it still shows a decreasing pattern with the increasing mole fraction of LiCl. It was believed that these variation may be due

Table 1
Variation of optical band gap, E_{opt}, and density with different mole fraction of LiCl in phosphate glass

Glass sample no.	LiCl content (mol%)	P_2O_5 content (mol%)	Density (g cm^{-3})	E_{opt} (eV)
1	10	90	2.39	3.90
2	15	85	2.52	3.67
3	20	80	2.33	3.46
4	25	75	2.38	3.95
5	30	70	2.39	3.55
6	35	65	2.40	3.96
7	40	60	2.33	3.83
8	45	55	2.43	3.91
9	50	50	2.48	2.83
10	55	45	2.42	3.64
11	60	40	2.52	3.04

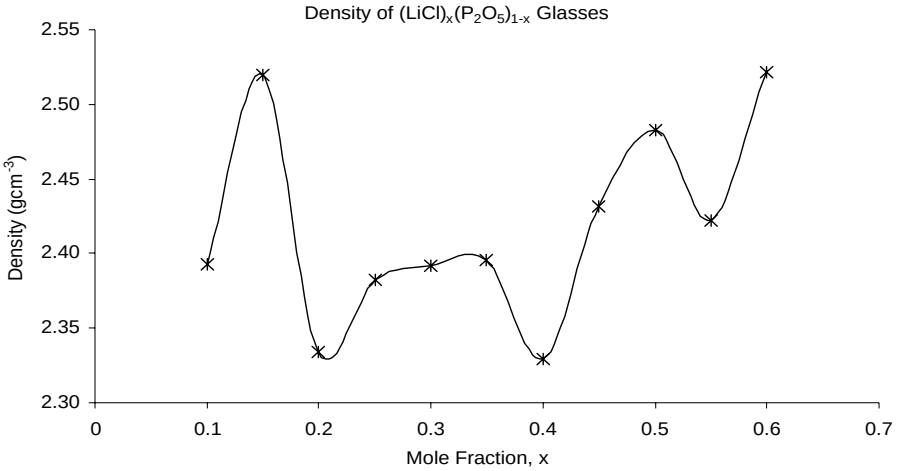

Fig. 1. Density measurement of LiCl–P_2O_5 glasses.

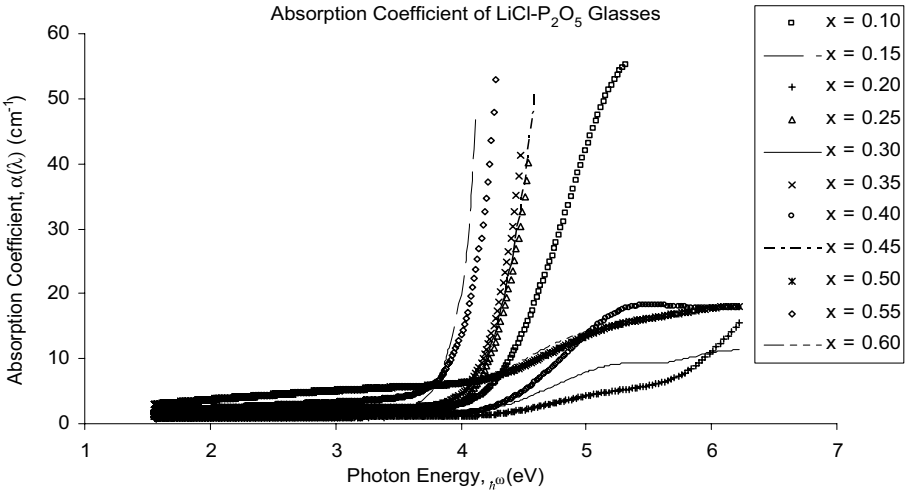

Fig. 2. Optical absorption coefficient, α, plotted against photon energy, $\bar{h}\omega$, for LiCl–P_2O_5 glasses.

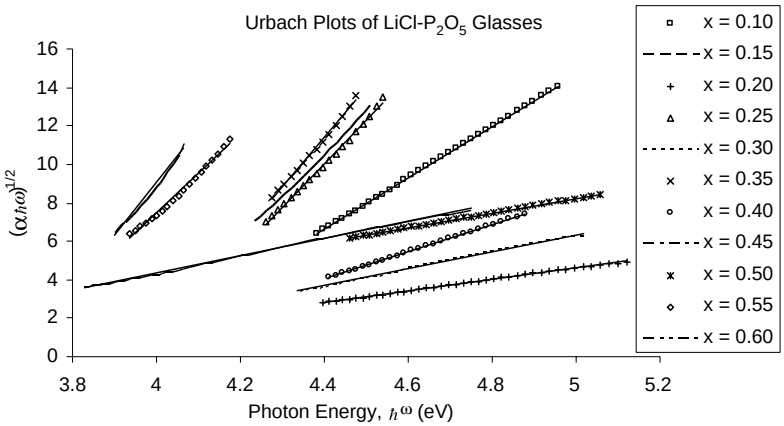

Fig. 3. The $(\alpha\bar{h}\omega)^{1/2}$ as a function of photon energy, $\bar{h}\omega$, for LiCl–P_2O_5 glasses.

to the addition of higher proportions of the LiCl seems to cause progressive breakdown of the phosphate network [3]. Graph of optical absorption coefficient, α, against photon energy, $\bar{h}\omega$, for LiCl–P_2O_5 glasses was plotted and shown as Fig. 2. The measurements of optical absorption and the absorption edge are important especially in connection with the theory of electronic structure of amorphous materials [5]. Observations of the variation of E_{opt} with increase in the modifier content can be attributed to the changes in the bonding that takes place in the glass. From Fig. 3 and Table 1, we can conclude that the optical band gap decreases with increase in LiCl content in the glass. Since the basic building units of LiCl phosphate glasses are known to be PO_4^{3-} tetrahedral, probably the internal vibrations of the molecular ion groups PO_4^{3-} take part in the transitions. In this work, the shift of the longer wavelength and the decrease of E_{opt} to lower energies with increase in LiCl content is probably related to the progressive increase in the concentration of non-bridging oxygen (NBO). This increase in turn gives rise to a possible decrease in the bridging (P–O–P) oxygen (BO) [3]. The shift is attributed to structural changes which are a result of the differing site occupations, i.e., interstitial or substitutional of the Li^+ ions which add to the phosphate matrix and modify the network. We assume that as the cation concentration increases, the BO develop bonds with Li^+, which in turn leads to the gradual breakdown of the glass network.

References

[1] M. Ganguli, M. Harish Bhat, K.J. Rao, Lithium ion transport in Li_2SO_4–Li_2O–P_2O_5 glasses, J. Solid State Ionics 122 (1999) 23–33.
[2] S.K.J. Al-Ani, I.H.O. Al-Hassany, Z.T. Al-Dahan, The optical properties and ac conductivity of magnesium phosphate glasses, J. Mater. Sci. 30 (1995) 3720–3729.
[3] C. Dayanand, R.V.G.K. Sarma, G. Bhikshamaiah, M. Salagram, Optical properties of lead phosphate glasses, J. Non-Cryst. Solids 167 (1994) 122–126.
[4] S.K.J. Al-Ani, A.A. Hogazy, Study of optical absorption edges in MgO–P_2O_5, J. Mater. Sci. 26 (1991) 3670–3674.
[5] Y.C. Ratnakaram, A. Viswanadha Reddy, Electronic spectra and optical band gap studies in neodymium chlorophosphate glasses, J. Non-Cryst. Solids 277 (2000) 142–154.