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Optical Properties of Lithium Borate Glass $(Li_2O)_x (B_2O_3)_{1-x}$

(Sifat Optik Kaca Litium Borat $(Li_2O)_x (B_2O_3)_{1-x}$)

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ABSTRACT

A series of $(Li_2O)_x(B_2O_3)_{1-x}$ has been synthesized with mole fraction x=0.10, 0.15,0.20,0.25 and 0.30 mol% using melt quenching method. The structure of the glass system was determined by FTIR and X-ray diffraction. The density and molar volume were determined and the density increases with Li_2O content whereas molar volume decreases with Li_2O. Refractive index of glass samples were measured by ellipsometer. Refractive index increases with increase of Li_2O. The absorption spectra of the studied glass showed that position of fundamental absorption edge shifts to longer wavelength with Li_2O. Optical band gap varies from 0.10 to 2.22 eV and Urbach energy varies from 2.91 to 1.55 eV. The variation in optical band gap and Urbach energy were due to the variation in the glass structure.

Keywords: Borate glass; optical band gap; refractive index

ABSTRAK

Satu siri kaca $(Li_2O)_x(B_2O_3)_{1-x}$ telah disintesis dengan pecahan mol x = 0.10, 0.15,0.20,0.25 dan 0.30 mol% dengan menggunakan kaedah sepuh lindap. Struktur sistem kaca ditentukan oleh FTIR dan sinar belauan X. Ketumpatan dan isi padu molar telah ditentukan dan ketumpatan meningkat dengan kandungan Li_2O dan isi padu molar berkurang dengan Li_2O. Indeks biasan sampel kaca diukur dengan ellipsometer. Indeks biasan meningkat dengan peningkatan Li_2O. Spektra serapan bagi kaca yang dikaji menunjukkan pinggir asas serapan berubah ke jarak gelombang yang lebih panjang dengan Li_2O. Jurang jalur optik berubah daripada 0.10 kepada 2.22 eV dan tenaga Urbach berubah daripada 2.91 kepada 1.55 eV. Perubahan jurang jalur optik dan tenaga Urbach adalah disebabkan oleh perubahan struktur kaca.

Kata kunci: Indeks biasan; jurang jalur optik; kaca borat

INTRODUCTION

Glass plays an important role in the world especially in science and industry. In recent years the development of glass-ceramics has extended the range of glass-based engineering materials (Oliver 1975). Glasses are important optical materials usually made to be transparent in the visible spectrum (Abdel Baki & El-Diasty 2006). Borosilicate has the advantage of chemical durability and better thermal shock resistance. It can be used for cooking ware, laboratory apparatus and automobile headlamps. Most of the bottles and jars are made from soda-lime-silica glass. Borate glasses which consist of boron oxide can be used for optical lenses because it has high refractive index. Lithium borate glass has a wide range of application. It is used for detecting penetration of radiation which is applied in homeland security and nonproliferation. The main objectives of the present work were to study the refractive index and optical band gap with variation of lithium borate glass composition.

METHODS

Lithium borate glass $(Li_2O)_x (B_2O_3)_{1-x}$ glass with x = 0.10,0.15,0.25 and 0.30 mol% were fabricated using Li_2O(99%) and B_2O_3 (97.9%). The chemical powder was weight accurately by electric balance with accuracy of ±0.0001 g and mixed thoroughly. The mixture in the alumina crucible was then put in electric furnace and preheat it at 400°C for 30 min. The mixture then melted at 1000°C for 1 h. The melts were poured into stainless cylindrical shaped split mould. The mould was preheated to reduce thermal shock. The mould was then put into furnace at 300°C for 2 h for annealing process. The sample was cut into desired dimension and polished with sand paper so that the sample had flat and parallel surface.

The prepared samples were ground into powder form for x-ray diffraction measurement by using X'pert Pro Panalytical. The density of glass sample was measured at room temperature by Archimedes Principle by using distilled water as the buoyancy liquid. Optical band gap and absorption measurement of the sample was measured by UV-1650PC UV-Vis Spectrophotometer (Shidmadzu) with wavelength of 190-1100 nm at room temperature. Refractive index measurement was done by Ellipsometer with 632.80 nm wavelength of light source.

RESULTS AND DISCUSSION

XRD patterns of different composition of lithium borate glass show a broad peak which indicates that all samples

have the characteristic of long range structure disorder, this shows that samples are amorphous. Figure 1 shows density increases with Li_2O content. Density increases from 2012 to 2263 kg/m^3 with Li_2O. The density is affected by the structural softening or compactness, change in coordination number, cross-link density and dimension of interstitial spaces of glass (Moustafa et al. 2008). The tetrahedral BO4 groups that form at low lithium content are stronger bonded compared to the triangular BO3 groups and increase its density (El-ALaily & Mohamed 2003). Lithium oxide act as modifier in the glass samples network. When Li_2O is introduced into glass network, transition from tetrahedral BO4 groups to triangular BO3 groups with non-bridging oxygen (NBO) occurred. The increase in density is due to increase in the number of non-bridging oxygen (NBO) atoms (Mohapatra 2009).

Molar volume decreases with content of Li_2O which is shown in Figure 1. The decrease in molar volume is because of the compact structure (Moustafa et al. 2008). The molar volume decreases with increasing Li_2O content also due to Li_2O occupies interstitial position in the network (Kashif et al. 2010).

Refractive index of lithium borate glass system increases with Li_2O as shown in Figure 2. Refractive index is inversely proportional to the molar volume (El-ALaily & Mohamed 2003). The refractive index increases with decreasing molar volume and which in turn increases the density. The coordination number of lithium borate glass also leads to the increase of refractive index. An addition of Li_2O causes changed in coordination number and creates more non-bridging oxygen. Thus has a higher average coordination number of studied glass which results in the increase of the refractive index (Saddek et al. 2008). The formation of non-bridging oxygen forms more ionic bonds, which manifest themselves in a large polarizability, thus results in a higher index value.

The absorption coefficient $\alpha(\omega)$ as a function of photon energy $\hbar\omega$ for direct and indirect optical transition according to Rockett (2007) is given by:

$$\alpha(\omega) = \frac{B\left(\hbar\omega - E_{opt}\right)^n}{\hbar\omega}, \quad (1)$$

n=2 for indirect allowed transition and n= ½ for allowed direct transitions. In both cases electromagnetic waves interact with the electrons in the valance band, which were raised across the fundamental gap to the conduction band (Abdel Baki & El-Diasty 2006).

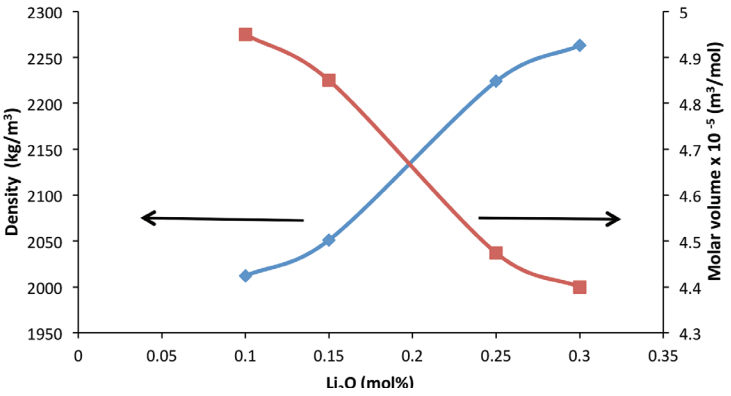

FIGURE 1. Density and molar volume of $(Li_2O)_x$ $(B_2O_3)_{1-x}$ glass system

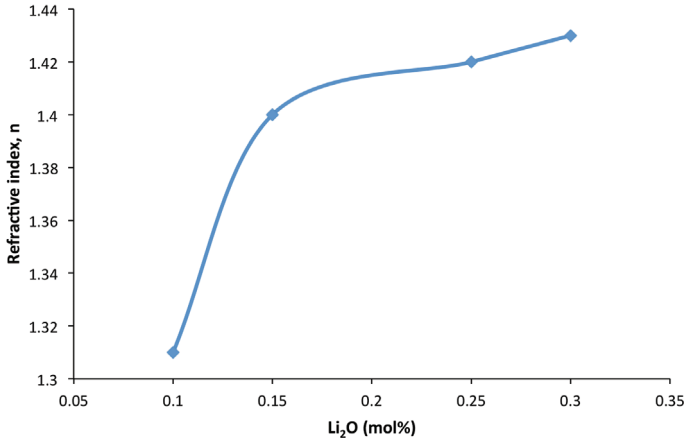

FIGURE 2. Refractive index $(Li_2O)_x$ $(B_2O_3)_{1-x}$ glass system

The absorption coefficient $\alpha(\omega)$ was determined near the absorption edge of all different glass samples. It is well known for that amorphous materials, a reasonable fit to (1) with n=2 is achieved (Chimalawong et al. 2004).

In amorphous material, the plot of $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ is also plot for direct band gap to see whether optical data on the sample glasses fit better to direct or indirect band gap and (1) for n =1/2 becomes,

$$(\alpha\hbar\omega)^2 = B(\hbar\omega - E_{opt}). \quad (2)$$

The relation in (2) is used to plot $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ for different composition of sample glasses. The values of indirect optical band gap and direct optical band gap can be obtained by extrapolating the straight line on the curve to the axis at $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^2 = 0$, respectively.

Figure 3 shows the optical band gap values for indirect transition vary between 0.1 and 2.3 eV, while direct band gap vary from 3.8 to 4.8 eV. The results showed that direct band gap values were larger than the indirect band gap and both values are decreased with the increase of Li_2O content. The indirect transition is the most probable transition mechanism and Li_2O ions increase the excitation-phonon coupling which results in the dynamic disorder (Abdel Baki & El-Diasty 2006). It can be seen that both direct and indirect transitions were involved from the theoretical fitting of the experiment absorption coefficient (Halimah et al. 2005). It is noted that with the increase of Li_2O content, the optical band gap energy, E_{opt} first increases and then decreases, the increase in lithium ions causes structural change in the glass network. The formation of non-bridging oxygen NBO, which binds excited electrons less tightly than bridging oxygen increases with Li_2O results in the decrease of optical energy band gap (Gayathri Pavani et al. 2011). When lithium ions were added in small amount, there was an increase in the number of BO4 units against BO3 units. With further increase of Li_2O content, the six-membered borate rings with only one BO4 tetrahedron appeared and it can be in triborate, tetraborate or pentaborate forms. Thus, the numbers of NBO increase with further addition of Li_2O and break up the regular structure of the borate and boroxyl rings and as a result the band gap decreases (Hager 2009).

The absorption edge in many disordered materials follows the Urbach rule given (Subhadra & Kistaiah 2010) by:

$$\alpha(\omega) = B \exp(\hbar\omega/\Delta E) \quad (3)$$

where $\alpha(\omega)$ is the absorption coefficient at an angular frequency of $\omega = 2\pi f$, ΔE is the width of tailed of localized states in the band gap (Urbach energy) and was determined from the reciprocal of the slope of the plot ln $\alpha(\omega)$ versus $\hbar\omega$. The Urbach energy is well known that the shape of the fundamental absorption edge in the exponential (Urbach) region can yield information on the disorder effects (Kesavulu et al. 2010). Materials with larger Urbach energy would have greater tendency to convert weak bonds into defects (Rani et al. 2009). The value varies between 1.55 and 2.91 eV which has nonlinear variation, Urbach energy decreases with addition of Li_2O content. Figure 4 shows that Urbach energy decreases with Li_2O, this decreasing trend suggested that the degree of disorder decreases in glass structure with increase of Li_2O content (Upender et al. 2010).

Conclusion

The physical and optical properties of studied glass sample were dependent on the glass composition. The increased in density with Li_2O content was due to the number of non-bridging oxygen. The molar volume decreased as a result from Li_2O occupied interstitial position in the network. The formation of non-bridging oxygen increased with Li_2O resulted in the decreased of optical energy band gap for both direct and indirect band gap. This is because non-bridging oxygen binds excited electrons less tightly than bridging oxygen. The decreased in Urbach energy is owing to the decrease of degree of disorder in glass structure with Li_2O.

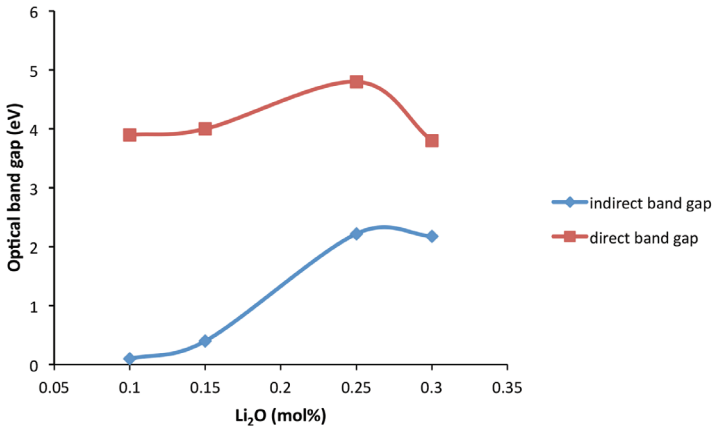

FIGURE 3. Indirect and direct optical band gap of $(Li_2O)_x (B_2O_3)_{1-x}$ glass system

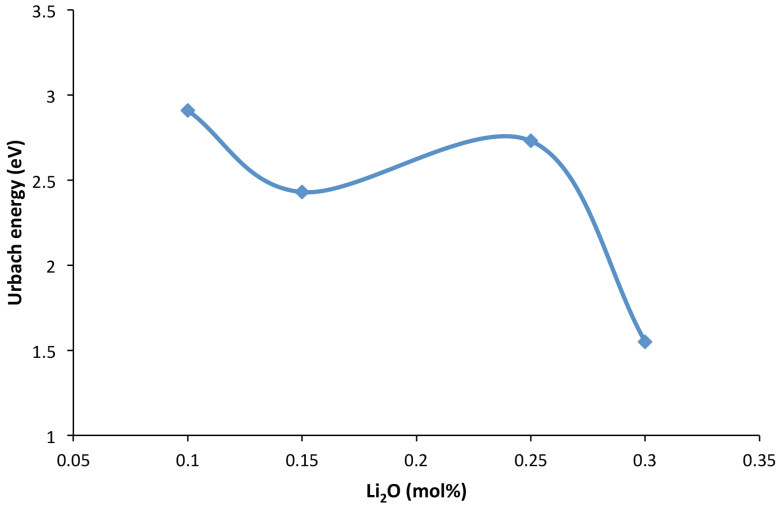

FIGURE 4. Urbach energy of $(Li_2O)_x$ $(B_2O_3)_{1-x}$ glass system

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