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Optical Characterization of Lead-Bismuth Phosphate Glasses

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Abstract: Systematic series of lead-bismuth phosphate glasses, where PbO, Bi_2O_3 and P_2O_5 content change for every series based on their weight percentage have been prepared. The optical properties were measured and their amorphous nature was confirmed by X-ray diffraction technique. Both experiments were conducted at room temperature. The fundamental absorption edge for all the glasses was analyzed. The values of refractive index, also the position of absorption edge and hence the optical band gap were found to vary depending on the composition of the glass.

Key words: X-ray diffraction, optical, phosphate, bismuth, lead oxide, refractive index, optical band gap

INTRODUCTION

Phosphorus pentoxide (P_2O_5) acts as one of the most important glass former and flux materials. Phosphate glass exhibit very important physical properties such as low melting temperature, high thermal expansion coefficient, low glass transition temperature, low softening temperature and high ultra-violet (UV) transmission[1, 2]. Despite their solubility, the lower processing temperature has led these glasses to be used in applications such as glass to metal seals, low temperature enamels for metals and for optical elements[3]. On phosphate-based glasses, several works have been carried out in the last decade, especially concerning an optimization of glass preparation, investigation of their properties and information about the glass structure. Phosphates glasses with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties[4, 6].

Combining bismuth oxide (Bi_2O_3) and lead oxide (PbO) with phosphorus pentoxide allows one to tune the optical properties in a wide range depending on the glass composition. The present work intends to study the optical properties of this glass system (PbO-Bi_2O_3-P_2O_5) over a wide range of composition. Their amorphous nature was confirmed by X-ray diffraction technique and their densities were measured by the Archimedes methods. Meanwhile the absorption and refractive indices were measured and described numerically by appropriately fits.

MATERIALS AND METHODS

Analar PbO, Bi_2O_3 and P_2O_5 were used to prepare 12 glass samples with different composition using the conventional method. These reagents were weighed and mixed together with appropriate amounts where P_2O_5 content ranged from 65.0 to 38.2%. The PbO and Bi_2O_3 content increase ranging from 31.5 to 55.7% and 3.5 to 16.6% respectively. X-ray diffraction measurement was made at room temperature using a Philips X-ray Diffractometer.

The density of each glass was measured, based on the Archimedes method using acetone as the immersion liquid. A glass disc was weighed in air (W_{air}) and immersed in acetone and reweighed (W_{ac}). The acetone density is 0.789 gcm^{-3} and the relative density is given by the following relation[7]:

$$\rho_s = \rho_{ac}\frac{W_{air}}{W_{ac}} \quad (1)$$

The optical absorption of the polished samples was obtained in the wavelength range of 200 nm-800 nm, at room temperature by using Camspec M350 Double Beam UV-Visible Spectrophotometer. The absorption coefficient (α (λ)) was calculated from the absorbance (A) using the following equation[4]:

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

where, d represents the thickness of the glass samples.

High precision refractive indices of glasses of the system PbO-Bi_2O_3-P_2O_5 for every series were measured at room temperature. The measurements were carried out on an ellipsometer using the prism method and were done at discrete wavelengths of 632.80 NM with the method of minimum deviation using one prism cut from the glass bodies for each glass composition, respectively.

A correction of the measured refractive indices (n_{meas}) that takes the refractive index of air (n_{air}) and its dispersion into consideration is necessary for the determination of the refractive indices. The refractive index of air is calculated using Edlén's approximation[8] (wavelength (λ) in μm):

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$$n_{air}(\lambda) = 1.000083421 + \frac{0.0240603}{130.0 + \lambda^{-2}} + \frac{1.5997 \times 10^{-4}}{38.9 + \lambda^{-2}} \quad (3)$$

The data are then corrected by:

$$n(\lambda) = n_{meas}(\lambda) \times n_{air}(\lambda) \quad (4)$$

RESULTS AND DISCUSSION

The XRD patterns of the glasses obtained are shown in Fig. 1a-c. All the selected quenched materials were found to be fully in the glass form and a broad halo, which is a characteristic of amorphous structure, was obtained at around $2\theta \cong 30^{o}$. This indicates the absence of long-range atomic arrangement and also the periodicity of the three dimensional network in the quenched material[9].

The densities of all glass samples are tabulated in Table 1. From the results, it can be seen that the values of the density increase with the addition of PbO and Bi_2O_3. The addition of Pb^{2+} and Bi^{3+} atoms, will modify the glass structure by creating a non-bridging oxygen (NBOs) in the network[10]. The NBOs created were believed to alter the glass structure in a way that the packing of the molecule becomes denser as more network modifier ions (in this case Pb^{2+} and Bi^{3+}), attempt to occupy the interstices within the network[7]. The increase of the density of the glasses accompanying the addition of Bi_2O_3 is probably due to a change in cross-link density and coordination number of Bi^{3+} ions[11]. The results from this work are consistent with several studies by others on the phosphate-based glasses[12, 13].

The variety of refractive index (n) (for λ = 632.8 NM) with the composition are also presented in Table 1. The *n* the values that obtained from this measurement could be used to calculate the values of the dielectric constant (ε). It has been observed that the composition dependence of both *n* and ε for all series of the samples show a similar linear behavior. The refractive index and the optical dielectric constant are related through the following equation

$$\varepsilon = n^2 = [(1 + R^{1/2}) / (1 - R^{1/2})] \quad (5)$$

where, R is the optical reflection spectra[14].

The refractive indices of the glasses in this work show a linear trend where the value increases with the increasing modifier content in the system. It has been reported that the linear refractive index of alkali borate glasses increase with the increase in alkali content[14] and the values of refractive index increases with the addition of Bi_2O_3 content in Bi_2O_3-B_2O_3 glasses[8]. Meanwhile for this study we assume that in the phosphate glass, the increase in refractive index values is also related to the increase of non-bridging oxygen (NBOs) and network changes by addition of Pb^{2+} and Bi^{3+} ions in the system.

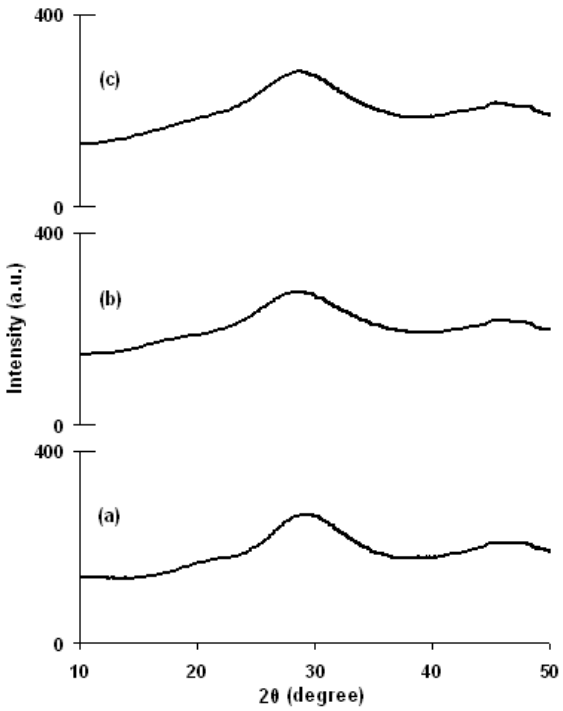

Fig. 1: XRD patterns of the glasses, where (a) sample A3, (b) sample B3 and (c) sample C3

Spectroscopic ellipsometry method is also an important factor in characterizing the physicochemical properties of the glass system[15]. Furthermore, it can provide information about surface and interface quality, layer inhomogeneity and material absorption[16], which is important for high power laser coating application.
The optical absorption spectra of the glass samples are shown in Fig. 2. There are no sharp absorption edges in the figure, indicating a characteristic of the glassy state[4]. The position of the fundamental absorption edge shifts to longer wavelengths as the content of glass modifier, PbO and Bi_2O_3, increases in the glass. Although the absorption edge shifts to approximately 320 nm-330 nm wavelength, the shift is still short as compared with the earlier study on PbO- P_2O_5 glass system[6]. It is suggested that the introduction of Pb^{2+} ion into the phosphate network in the form of PbO disrupts two bridging oxygens, or alternatively creates two non-bridging oxygens (NBOs)[17]. On the other hand, the introduction of Bi^{3+} ion into the phosphate network in the form of Bi_2O_3 probably disrupts the activity of creating the NBOs. Thus, the creation of smaller number of NBOs seems to be the reason for absorption edge shifting towards shorter wavelengths [17] with an increase in Bi_2O_3 content.

The absorption coefficient (α (ω)) near the fundamental absorption edge for each curve in Fig. 2a-c was calculated as the wavelength interval of 1.0 NM from the relation[6]:

$$\alpha(\omega) = (1 / d)\ln(I / I_o) \quad (6)$$

where, $\ln(I / I_o)$ corresponds to absorbance. Thus, the data are related by Mott and Davis[14] to the optical band gap (E_{opt}) through the following relation proposed for amorphous materials:

$$\alpha(\omega) = \text{const}(\hbar\omega - E_{opt})^r / \hbar\omega \quad (7)$$

where, $\hbar\omega$ 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 transition, where r = 2 agrees well for oxide glasses[5]. The equation (7) can be readjusted to represent linearity between $(\alpha\hbar\omega)^{1/2}$ and $(\hbar\omega - E_{opt})$ as

$$(\alpha\hbar\omega)^{1/2} = \text{const}(\hbar\omega - E_{opt}) \quad (8)$$

Figure 3 was plotted by using Equation (8). 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 the values are given in Table 1.

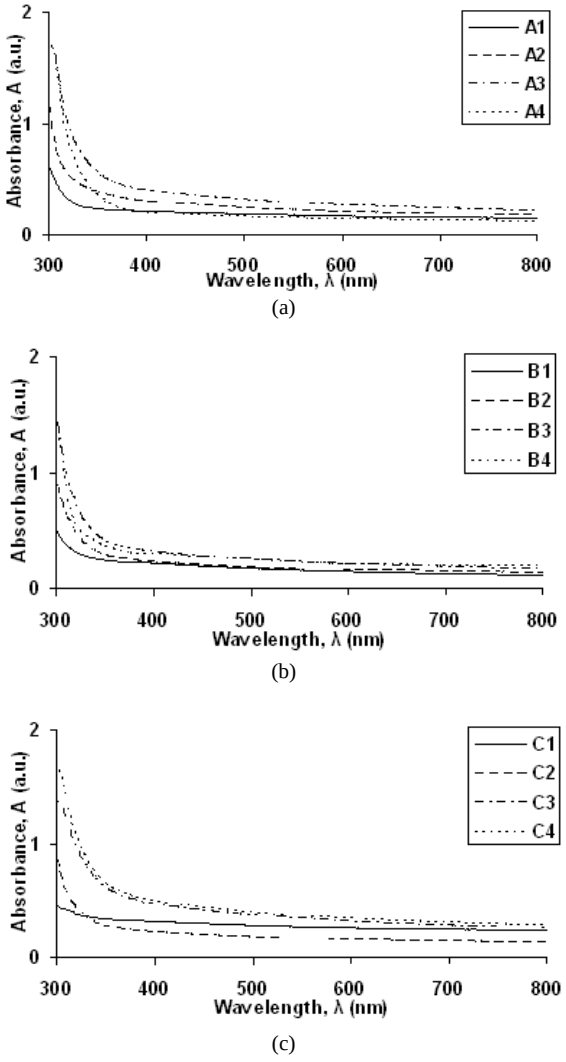

Fig. 2: Optical absorbance of (a) glass sample A1-A4, (b) glass sample B1-B4, (c) glass sample C1-C4

A slight decrease of E_{opt} to lower energies with an increase of lead oxide and bismuth oxide content, were probably related to the progressive increase in the concentration of non-bridging oxygen, where this increase in turn gives the rise to a possible decrease in the bridging (P–O–P) oxygen[6].

Also, the shift is attributed to structural changes which are the result of the different site occupation for example in this study, the interstitial or substitutions of Bi^{3+} and Pb^{2+} ions which add to the phosphate matrix and modify the network, which in turn cause a progressive breakdown of the phosphate network[6]. Talib *et al.*[2] and Dayanand *et al.*[6] suggested that, since the basic building units of phosphate based glasses are known to be PO_4^{3-} tetrahedral, probably the internal vibrations of the molecular ions group PO_4^{3-} take part in the transition. The gradual decrease in E_{opt} also shows the tendency towards the semiconducting behavior consistent with the observations made earlier on phosphate based glasses[18].

However, it should be noted that the results on E_{opt} and other optical behaviors obtained in lead-bismuth phosphate glasses in the present work are entirely different from those obtained in the case of lead-phosphate glasses[6]. This fact must be attributed to the network structural differences brought about by the presence of Bi^{3+} ion. For an example, there is not even one value of E_{opt} in lead-bismuth phosphate glasses greater than that in lead-phosphate. Even in the lowest composition of phosphate content in lead-phosphate glasses (45 mol%, E_{opt} = 4.206 eV) their values are still higher than the highest composition of phosphate content in lead-bismuth phosphate glasses(E_{opt} = 3.37 eV (sample A1), 3.50 eV (sample B1), 3.71 eV (sample C1)). This finding clearly shows the character of Bi^{3+} ion in the glass network as mentioned before.

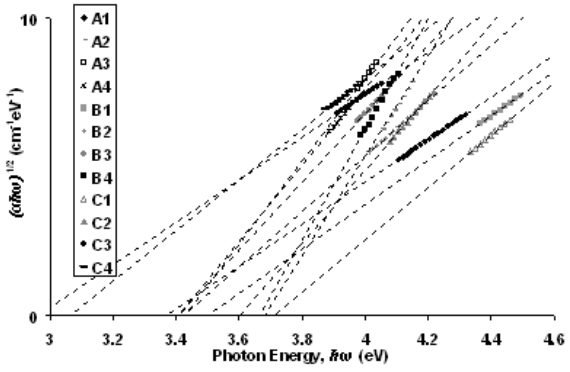

Fig. 3: The $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for lead-bismuth phosphate glass system

Table 1: Glass composition, density and optical band gap in lead-bismuth phosphate glass system.

Glass sample	Weight %			Density			E_{opt}
	PbO	Bi_2O_3	P_2O_5	(kgm^{-3})	n	ε	(eV)
A1	31.5	3.5	65.0	4330.93	1.514	2.293	3.37
A2	41.5	4.5	54.0	5346.08	1.747	3.052	3.68
A3	49.4	5.4	45.2	5690.63	1.799	3.238	3.43
A4	55.7	6.1	38.2	5697.64	1.812	3.284	3.40
B1	28.5	6.5	65.0	3952.27	1.347	1.815	3.50
B2	37.4	8.6	54.0	4825.79	1.668	2.784	3.42
B3	44.5	10.3	45.2	5003.04	1.708	2.919	3.40
B4	50.2	11.6	38.2	5428.22	1.765	3.117	3.66
C1	25.6	9.4	65.0	4009.99	1.582	2.502	3.71
C2	33.6	12.4	54.0	4832.39	1.693	2.868	3.60
C3	40.0	14.8	45.2	5415.94	1.767	3.123	2.96
C4	45.2	16.6	38.2	5448.43	1.767	3.123	3.06

CONCLUSION

New ternary lead-bismuth phosphate glasses were successfully prepared and their glassy natures were determined by using the XRD method and supported by the trend in plotting graphs of optical absorption edge. Some physical properties of the glass have been measured. The optical band gap and refractive index values have been determined either from the experiment or theoretical fitting of the absorption. The linear variation $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ shows good a correlation for all glass samples. An addition of Bi_2O_3 in the glass system affects their physical and optical properties.

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