The Physical Properties Of Lead Borate (PbO-B_2O_3)Glass

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Abstract: Due to its special properties for optical material and excellent glass forming materials, borate glass with composition xPbO-(100-x)B_2O_3 where x varying from 20 to 40 mol % are prepared by melt quenching techniques. The physical properties of glasses have been identified such as density, molar volume, X-ray diffraction(XRD), microhardness and FTIR spectroscopy measurement. The glass densities were found to be increased from 4.1848 gcm^{-3} to 5.2099 gcm^{-3}. Besides, the increment in molar volume from 23.9757 cm^3mol^{-1} to 25.1536 cm^3mol^{-1} PbO–B_2O_3 glasses with an increase in the PbO content has been observed and discussed. The X-ray diffraction pattern of PbO-B_2O_3 shows the broad humps which comfirms amorphous nature in the glass networking since no peak has been observed in the diffraction pattern. The FTIR study shows that the incorporation of PbO as network modifier helps in converting BO_3 group to BO_4 units. This reveals that when PbO ions enter the glass structure it can alter the glass networking. Based on the microhardness study, it was found that the microhardness showed linear decrease from 386 kg/mm^2 to 280 kg/mm^2 with an increase in the PbO contents. The results will be discussed and presented in details.

Keywords: FTIR, Lead borate, Melt-quench, Molar volume, X-ray diffraction

1. Introduction

Recently, borate glasses received more interest due to their useful physical properties. Borate is a glass forming oxide as B_2O_3 based glass is an attractive optical material that have been used as electro-optic switches, electro-optic modulators, non-linear parametric converters and solid state laser materials by incorporating with heavy metal oxides. Borate glasses show high transparency, low melting point, high thermal stability and good glass forming nature. The structure of the borate glasses is not a random distribution of BO_3 triangle and BO_4 tetrahedra, but a gathering of these units forms well defined and stable borate groups such as diborate, triborate, and tetraborate that constitute the three-dimensional random network (Yasser et al., 2009)

PbO has many extra-ordinary properties such as a high refractive index, large density, excellent infrared transmission and high nonlinear optical susceptibility. Therefore, lead oxide has been used as a constituent in several borate and phosphate glasses in order to achieve useful physical properties. For example, glasses containing Pb provide low melting glass, which are suitable for sealing applications. The high density of this glass makes it a nominee for radiation shielding material. Even though PbO is not a glass-forming oxide by itself, it can be incorporated in substantial quantities into the other glass-forming oxide systems such as ZnO-B_2O_3 (P. Limkitjaroenporn et al., 2011). Also, the optical properties and photo-elasticity of PbO–B_2O_3 glasses were investigated by A.A. Soliman (2009) and K. El-Egili et al. (2011) respectively. It is concluded that, PbO–B_2O_3 glass systems have been observed to be promising gamma-ray shielding materials (G. Sharma et al., 2006). Lead borate based glass formulations with high chemical durability and lower melting temperatures compared to the currently used glasses were developed as candidates for the vitrification of radioactive waste (Y. Cheng et al., 2007).

In this study, the aim is to study the physical properties of the PbO-B_2O_3 glass system. The physical properties were determined by mean of their density, molar volume, X-ray

diffraction as well as the microhardness. Meanwhile, fourier transforms infrared (FTIR) transmission spectra have been measured for obtaining the structural information of these glasses. The result obtained were analysed and presented in detailed.

2. Experiment Details

Glass samples of composition (100 - x) B_2O_3 + xPbO with x varying from 20% to 40% mol are prepared using a conventional melt quenching technique. A proportional amount of raw materials such as boric oxide (B_2O_3) and lead oxide (PbO) are well mixed to ensure that the sample is homogeneous. The mixtures are then melted in a alumina crucible at temperature around 1000 °C for 30 minutes at room temperature until a bubble free liquid has been formed. The melts was cast onto flat surface mould before being annealed at 300 °C for five hours. Then the furnace was switched off until it has slowly cooled down to room temperature. The glass samples were then ready for the physical and structural characterization.

3. Sample Characterization

The amorphous/crystalline nature of glass sample is comfirmed by X-ray diffraction(XRD). It is sensitive to neither the type of atom nor the relative position of atoms in the material as well as the length scale over which the crystalline order persists. The x ray diffraction is determined by using Bragg's law equation :

$$n\lambda = dsin\theta \quad (1)$$

where n is index of refraction, λ is wavelength and d is crystal spacing.

The infrared transmission spectra of the glasses were measured at room temperature in the wave number in a range 400- 4000 cm^{-1} using Perkin Elmer model Spectrum One fourier transform infrared spectrometer (FTIR) under the Attenuated Total Reflectance (ATR) method. The prepared glasses were in the form of fine powder.

The density of glass sample at room temperature was measured by standard principle of Archimedes principle using a electronic densitometer MD-300s. The weights of the prepared glass were measured in air and in bath water using a sensitive microbalance. Then, the density, ρ, was determined from the relation

$$\rho = \frac{W_a}{W_a - W_b}\rho_b \quad (2)$$

where W_a is the weight in air, W_b is the weight in bath water and ρ_b is the density of water bath (ρ_b =0.9997 g/ cm^3).

Meanwhile, the molar volume was calculated by following equation

$$\rho = \frac{m}{V} \quad (3)$$

where ρ is glass density, m is the mass of glass and V is the molar volume

Microhardness has been determined by Vickers hardness test method, also referred to as a microhardness testing method, which is mostly used for small parts, thin sections, or case depth work. To identify the micro hardness of the sample, the following equation was used

$$HV = \frac{1.72\,F}{d^2} \quad (4)$$

where HV is Vickers harness, F is load in kg and d is the average length of diagonal

4. Results and discussion

X-ray diffraction

X-ray diffraction patterns of all glass samples with nominal composition of (100 - x) B_2O_3 + xPbO is shown in Fig 1,which confirms their amorphous nature, since there is no sharp peak observed in the diffraction pattern. The similar trend of results was also been found by G. Pal Singh et al. (2009) and A. Mardhiah et al. (2013)

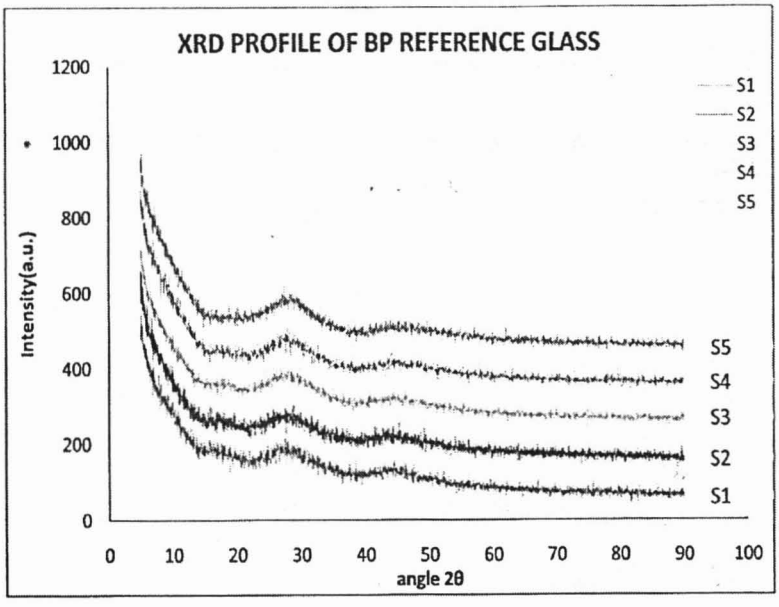

Fig. 1 X-Ray diffraction pattern of PbO-B_2O_3 glasses

Molar Volume and Density

The density, ρ and molar volume, V of prepared PbO-B_2O_3 glasses is given in Table 1. From Table 1, the result of the density and molar volume of the glass system are found to increase with the substitution of PbO, from 4.1848 gcm^{-3} to 5.2099 gcm^{-3} and 23.9757 cm^3mol^{-1} to 24.5709 cm^3mol^{-1} respectively. It may be observed that the density increases gradually with the increasing of lead oxide content in the glass composition. The increase in the density is due to the fact that the replacement of PbO with higher molecular weight of PbO compared to that of B_2O_3 tend to increase the packing density of glass structures. Similar trend of results were also been found by A. Noranizah et al. (2014) in their research work.

Molar volume is one of the important parameter to be determined for the physical properties. As depicted from Table 1, it is found that the molar volume of the glasses increased from 23.9757 cm^3mol^{-1} to 24.5709 cm^3mol^{-1} with the gradual increase of the PbO content in the borate glasses. However, results show slightly decrease from 24.5709 to 24.3634 m^3mol^{-1} as the PbO content increases from 25 mol% to 30 mol% that might due to some changes in glass structure. Decreasing trend in molar volume is attributed to the decreases in bond length or interatomic spacing among the atoms of glass network which causes compaction of structure. Meanwhile, the increasing trend implies that the incorporation of PbO with higher atom radii than radii of B_2O_3 tend to increase the molar volume of glass structure of the free volume of glass networking S. D. Patil et al. (2004).

Table 1. Density and molar volume of $PbO-B_2O_3$

Sample	B_2O_3	PbO	Density (g/cm^3)	Molar Volume (cm^3/mol)	Remarks
S01	80	20	4.1848	23.9757	Yellow
S02	75	25	4.3959	24.5709	Yellow
S03	70	30	4.7486	24.3634	Light yellow
S04	65	35	4.9174	25.0884	Light yellow
S05	50	40	5.2099	25.1536	Light yellow

Microhardness

Fig. 2 represents the Vicker's values of the glass as a function of the PbO content. From Fig. 2, it is clearly been seen that the the micro hardness values (Hv) indicates systematic decrease with the increasing PbO contents in the B_2O_3 system. The value of micro hardness are found to decease from 386 N/mm^2 to 280 N/mm^2 with respect to mol% of PbO content. The decreasing trend of Vicker's hardness values might be due to formation of more depolymerize boron structural unit from more covalent rigid to the less covalent rigid in structural unit. An addition of mol% PbO also will cause the expansion of glass network by creating more non-bringing oxygen (NBO) that give less rigidity to the structure and hence resulting in decreasing in microhardness. According to D. Singh.et.al.2010, the microhardness of lead borate glass mainly depends on the nature of the different types of structural units of the Pb and B ions presents in the glass and extend of plastic flow. The similar trend of results also has been found by V. K. Shrikhande et al. (2001) in their research work.

Table 2. Hardness of $PbO-B_2O_3$

Sample	B_2O_3	PbO	Length 1 (mm)	Length 2 (mm)	Load (N)	Vickers Hardness (HV)
S01	80	20	68.640	69.910	9.807	386.000
S02	75	25	69.370	69.370	9.807	385.000
S03	70	30	74.120	74.120	9.807	338.000
S04	65	35	75.090	75.090	9.807	329.000
S05	50	40	84.290	78.470	9.807	280.000

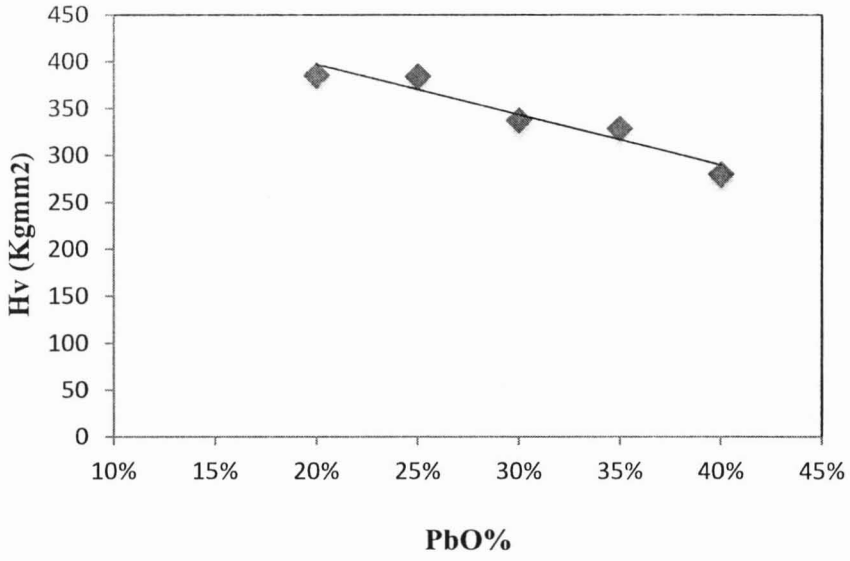

Fig. 2 The Vicker's hardness (Hv) vs PbO mol%. A line is drawn for the guide of the eye

FTIR spectra of PbO-B_2O_3 glasses

The FTIR spectra of PbO-B_2O_3 glass series are shown in Figure 3. There are five IR peak regions observed from 450 cm^{-1} to 4000.0 cm^{-1}. The absorption regions around 600 cm^{-1} to 710 cm^{-1} were due to the bending vibrations of the B-O-B linkages in the BO_3 group (P. Limkitjaroenporn et al., 2011). Whereas, the band at around 800-1200 cm^{-1} is assigned to the stretching vibration of B-O bonds of tetrahedral BO_4 unit in metaborate, pyroborate and orthoborates (Yasser B. Saddeek et al., 2009). Meanwhile, the transmission peak around 1200-1600 cm^{-1} is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 unit.

Pal Singh, G. et al. (2011) confirmed that a band around 691 cm^{-1} indicates that the B-O- bending vibration of BO_3 and BO_4 group with PbO vibration in the borate network and its indicates that the lead enters the glass structures. Whereas the peaks observed at around 943 cm^{-1} is attributed to the B-O stretching vibrations of the BO_4 groups. The peak also shows the overlapped of Pb-O bond. Meanwhile, the shifting peaks from 1384.08 cm^{-1} to 1476.37 cm^{-1} with increasing the PbO content is attributed to the asymmetric stretching vibration relaxation of the B-O bond of trigonal BO_3 group in ortho and meta-borate unit. The near-infrared bands in the region 3000–4000 cm^{-1} are related to vibrations of water, OH or B–OH groups. It is reported that, the broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples (G. Lakshminarayana et al., 2006).

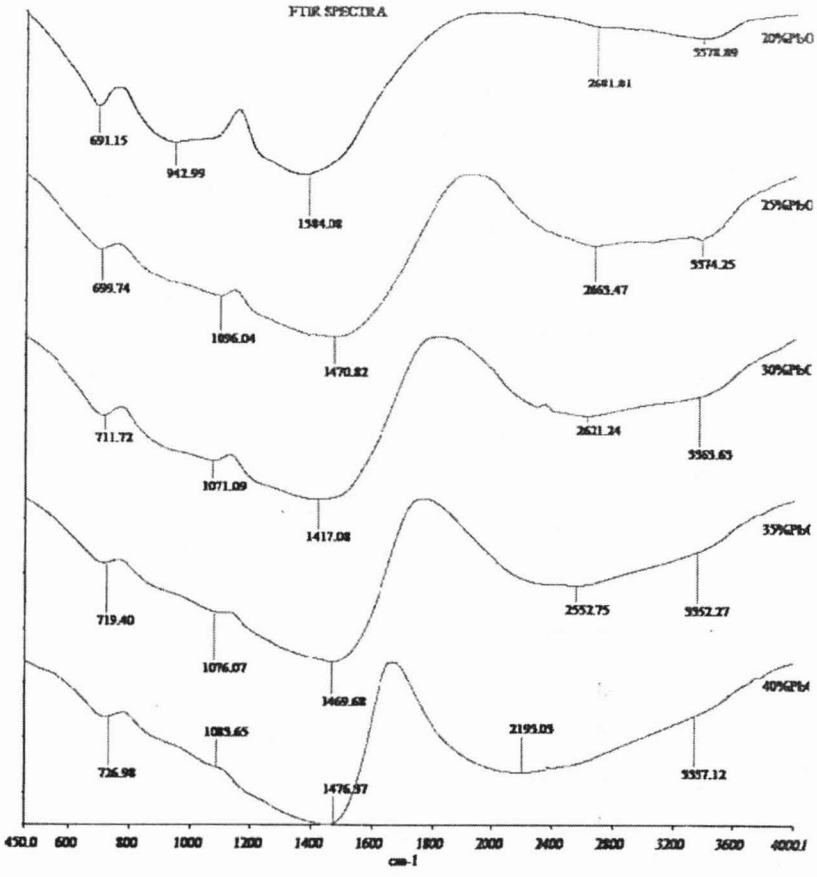

Fig. 3 FTIR spectra of (90 - x) B_2O_3 + 10ZnO + xPbO samples

5. Conclusion

The physical properties of PbO-B_2O_3 glasses system with respect to PbO content has been investigated. Both density and molar volume was found to increase with respect to mol% of PbO. result respectively. The replacement of PbO with higher molecular weight compared to that of B_2O_3 tend to increase the packing density of glass structures. Meanwhile, incorporation of PbO with higher atom radii than radii of B_2O_3 tend to increase the molar volume of glass structure of the free volume of glass networking. The X-ray diffraction pattern of the glass syatem shows broad humps which confirms amorphous nature in the glass structure since no peak has been observed in the diffraction pattern. Meanwhile, the microhardness study shows linear decrease with increase in the PbO contents in the B_2O_3 content. In FTIR study, we have found that the formation of tetrahedral BO_4 groups has been established with an addition of PbO in the glass system and thus alter the glass networking.

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