THINK INDIA (Quarterly Journal)
ISSN:0971-1260
Vol-22-Issue-4-October-December-2019

Effect of Magnesium Ions on the Structural and Thermal Properties of Lead Borate Glasses

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ABSTRACT

B_2O_3-PbO-MgO glasses with different concentration of MgO (3-12 mol. % in the steps of 3) were prepared by melt quench technique. Structural characterizations of these glasses were studied through FT-IR and DTA measurements. The amorphous nature of the glasses was checked by X-ray diffractometry. The transformation of BO_3 trigonals to BO_4 tetrahedral units has evidenced from the FT-IR spectra of the prepared glass samples and the BO_4 structural units increases with an increasing concentration of MgO content. The transition temperature, melting temperature and crystallization temperature have been identified using DTA measurements. The transition temperature increases with an increase of MgO content. The structural properties of these glasses were discussed in terms of the relative proportion of lead and magnesium oxides.

Keywords: Melt quench technique, XRD, FTIR, DTA.

1. INTRODUCTION

Borate glasses are one of the important amorphous materials which offer varying physical and chemical properties with changes in chemical composition and thus find wide applications [1]. Boron possess the ability to change the coordination with oxygen between three and four hence form various structural units in the glass network and such behavior is quite different than that of silicon and phosphorous which form only tetrahedral coordinate units with oxygen [2]. Structural characterization of lead doped borate glasses have always been an interesting subject due to numerous applications in modern technology [3]. Glasses containing PbO show high refractive indices with low crystallization tendency, as well as lower melting point and glass transition temperatures [4,5]. Dumbaugh [6] classified PbO as glass- modifier/formers because of the high polarizability of Pb^{2+} ions that makes a periodic arrangement of PbO_6 or PbO_4 polyhedral difficult. Although lead borate glasses particularly with high lead content have low glass transformation temperature and characteristic light yellow colour due to a tail of Pb^{2+} ion absorption. MgO doped PbO system has been found to form glass over a wide composition range and has got many applications in making ultrasonic delay cables, electron multiplier, TV picture tubes, glass to metal seals, etc. [7-10]. Wide applications for the preparation of compression type glass to metal seals, because of their compatible, thermal expansion co-efficient and appropriate mechanical strength. The properties of alkaline oxide doped lead borate glass system can be modified either by changing their composition or by adding different additives which changes the structure in the glass network. Consequently, various physical properties like mechanical strength, electrical and thermal conductivity, etc. get affected.

Many studies have focused on metal oxide addition such as MgO, SdO, CaO which are usually incorporated as network modifiers/formers. Among the various metal oxides, MgO is of interest in the biological viewpoint because Mg^{2+} is known to play a physiological role in positively influencing bone

strength when it is substituted into apatites [11]. The authors are interested to study the influence of MgO on lead borate glass system by various characterization techniques such as XRD, FTIR and DTA.

2. EXPERIMENTAL METHODS

Lead borate based glasses $68B_2O_3$ - (32-x) PbO – x MgO (where x =3, 6, 9 and 12 mol %) were prepared by melt quench technique. The Analytical Reagent grade powders of boron trioxide (B_2O_3), lead oxide (PbO) and magnesium oxide (MgO) of appropriate proportion were grind in an agate mortar thoroughly for 60 minutes to form a homogeneous mixture and then melted in a silica crucible in an electrically heated furnace under ordinary atmospheric conditions at around 900 °C. The melt was poured into a brass mould to form samples of dimensions 10mm diameter and 6mm thickness. To avoid the mechanical strain developed during the quench process, the glass samples were annealed at 450 ºC for 2 hours. Then the furnace was switched off and allowed to cool gradually to room temperature.

2.1. Characterization

2.1.1 XRD analysis

The amorphous nature of glasses were determined by X-ray diffraction technique using PAN Alytical x' Pert PRO Powder X-ray Diffractometer, 15KVA UPS support.

2.1.2 FTIR analysis

The infrared spectra of the powdered glasses were recorded at room temperature (303K) in the wavenumber range 400-4000 cm^{-1} with a resolution of 4 cm^{-1} by RXI Perkin Elemer FTIR spectrometer using potassium bromide (KBr) pellet technique.

2.1.3 DTA analysis

The Differential Thermogravimetric Analysis (DTA) was carried out on a NETZSCH-STA 449F3 JUPITER thermal analyzer between RT to 1400°C temperature range at heating rate of 20°C min^{-1}.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

X-ray diffraction is a useful method to detect readily the presence of crystals in a sample. From the result of X-ray diffraction spectra, the prepared glasses (Fig. 1) was found to be in the form of broad halo, which is characteristic of amorphous structure [12]. This indicates the absence of long range atomic order and lack of periodicity of the three dimensional network.

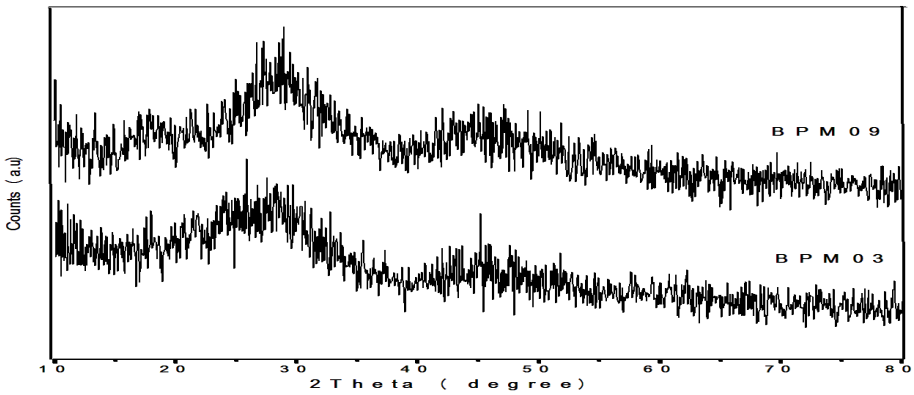

Fig. 1 XRD pattern of BPM03 and BPM09 glasses

3.2 FTIR analysis

ISSN:0971-1260
Vol-22-Issue-4-October-December-2019

The infrared spectra of $68B_2O_3$-(32-x)PbO - xMgO glasses are recorded at 303K in the frequency range between 400 and 4000 cm^{-1} as shown in Fig. 2, The observed bands along with their vibrational assignments of samples have been tabulated in Table 1. The obtained broad bands confirm the amorphous nature of the studied glass samples and are in good agreement with XRD pattern. The FTIR spectra can provide information about molecular vibration or rotation associated with a covalent bond and is usually used to survey the variation of glass structure with change in compositions.

In general, borate glasses exhibited three characteristic groups of bands representing vibrations of the molecules. 1200 – 1400 cm^{-1} region of band which occurs due to the asymmetric stretching vibrations of B-O bond of trigonal BO_3 units. The band in the range of 800- 1200 cm^{-1} is due to B-O bond stretching vibration of tetragonal BO_4 units and the band around 700 cm^{-1} represents bending of B–O–B linkages in the borate networks.

Fig. 2 explains the stretching vibration of the B-O bond of the trigonal BO_3 units (at 1380 cm^{-1}) with the progressive substitution of MgO. This band decreases in intensity and gradually gets shifted to lower wavenumber (at 1324 cm^{-1}) for the glasses from BPM03 to BPM12. The bands in the region (1016-1025 cm^{-1}) are assigned to symmetric stretching vibrations of B-O bonds in BO_4 units. The intensity of this band increases with increasing MgO content. i.e., the lower wavenumber is shifted to higher wavenumber [13-15].

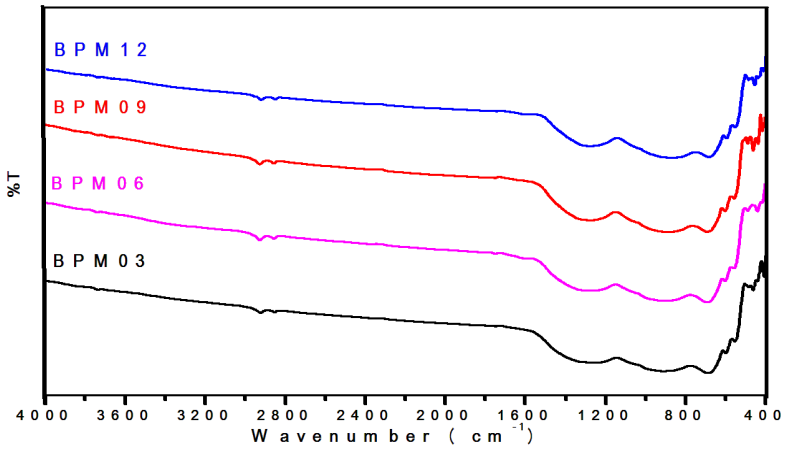

Fig. 2 FT-IR spectra of BPM glass samples

Modifier oxide MgO enters the glass network; it alters the structure of the glass to substantial extent by converting BO_3 trigonal units to BO_4 tetrahedral units. In addition, the oxide breaks the local symmetry of B-O-B and B-O-Pb linkages and occupies the interstitial position by forming covalent B-O-Mg linkages and creates more polymerized glass structure. As the concentration of MgO increases, the intensity of the band due to BO_3 units decreases with the corresponding increase in intensity of band due to BO_4 units. This is due to the increasing presence of modifying action of the modifier. Another band is also observed around 710 cm^{-1} due to the bending vibration of B-O-B linkages in the borate glasses. The bands are located at around 925 cm^{-1} which is due to MgO_4 tetrahedra [16]. The band at 475 cm^{-1} shows the existence of divalent ions in the network vacancies [17].

Table 1 Band positions and their corresponding assignments of infrared spectra of BPM glass system

ISSN:0971-1260
Vol-22-Issue-4-October-December-2019

Wavenumber cm^{-1}	Assignment
~1380	B-O stretching of BO_3 units
~1016	Stretching vibration of BO_4 tetrahedral
~925	MgO_4 tetrahedral
~710	Bending vibration of B-O-B
~475	Specific vibration of Mg^{2+} ions

3.3 DTA analysis

Fig. 3 show the DTA curves of the studied glasses and the values of glasses transition temperature (T_g), crystalline temperature (T_c), melting temperature (T_m), thermal stability (S) and Hruby's parameter (K_{gl}) are summarized in the Table 2. The T_g, T_c and T_m values increase from 279 °C to 368 °C, 537 °C to 656 °C, 804 °C to 888 °C. These revealed that the formation of new linkages with the addition of MgO that contribute to a volume contraction [18, 19]. Besides, the Mg^{2+} ions tend to occupy the interstitial sites within the glass matrices.

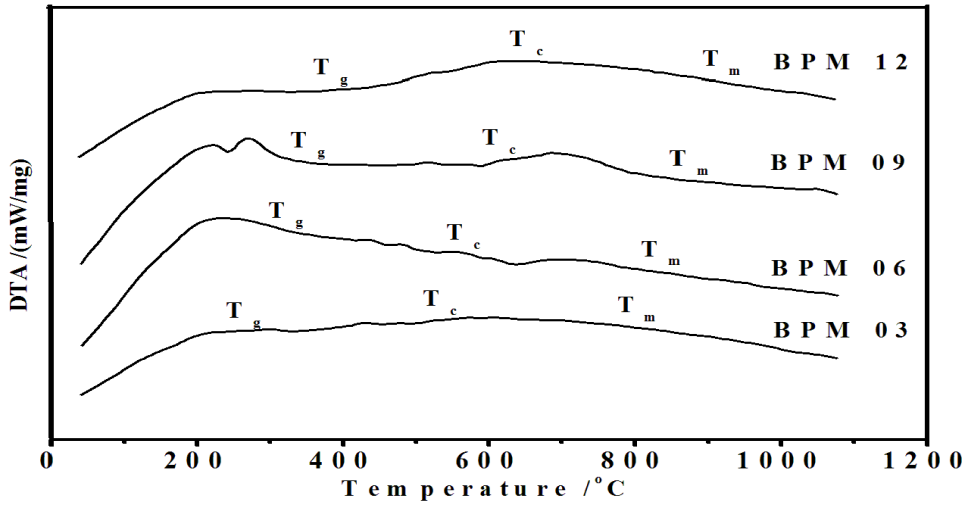

Fig.3. DTA curve of prepared glass samples

At lower concentration of MgO, the BPM03 glasses are less stable and the gradual replacement of PbO by MgO increases the values of S and K_{gl}. This proclaims that for the studied glasses, the stability against devetrification increases with increasing concentration of MgO. Besides, the Mg^{2+} ions tend to occupy the interstitial sites within the glass matrices.

Table 2 Values of glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), thermal stability (S) and Hruby's parameter (K_{gl}) of BPM glasses

Sample Code	Glass transition temperature T_g/°C	Crystallization temperature T_c/°C	Melting temperature T_m/°C	Thermal temperatur S	Hruby's parameter K_{gl}
BPN03	279	537	804	258	0.9662
BPM06	294	562	837	268	0.9745
BPM09	350	628	865	274	1.1308
BPM12	368	656	888	288	1.2413

4. CONCLUSION

ISSN:0971-1260
Vol-22-Issue-4-October-December-2019

Lead borate glasses with compositions $68B_2O_3$ - (32-x)PbO – xMgO (where x=3, 6, 9 and 12 mol %) have been successfully developed which is transparent, moisture resistant and stable. The XRD spectra confirmed the amorphous nature of the prepared glasses. From IR spectroscopy, it is clear that the doping of magnesium oxide leads to the formation of BO_3 and BO_4 units and the increase in concentration of BO_4 with MgO. This can also be proved by the DTA data, and the stability of the investigated glasses increases with increasing MgO content at the expense of PbO.

ACKNOWLEDGMENT

The authors wish to express their grateful thanks to Dr. P. Vasantharani, Professor and Head, Department of Physics, Annamalai University, for her kind help and encouragement, which she extended to them throughout the period of this study.

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