

Physical and Spectroscopic Study of Sm³⁺ ion doped Li₂O-B₂O₃-PbO Glasses

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Abstract:

Samarium doped lithium lead borate in the system 30Li₂O-60B₂O₃-(10-x)PbO-xSm₂O₃ (x=0.5, 1, 1.5, 2 mol %) glasses were prepared by melt quenching method. The addition of modifier oxide to B₂O₃, modifies the glass network by converting three coordinated trigonal boron units to a weaker anionic four co-ordinated tetrahedral borons. The decrease in density with Sm₂O₃ composition is marginal and is found to be consistent with the theoretical values. The increase in molar volume indicates the existence of non-bridging oxygens, leads to openness in the structure of borate glass matrix. From the infrared absorption spectra, the vibrational bending modes (B-O-B), stretching modes (BO₄ and BO₃) of boron atoms and PbO₆ structural units are identified. The IR spectra reveal that the structure of borate glass network is found to be not much affected upon the variation of modifier oxide.

Key words: Borate glass, Structure, Density, Infrared spectra;

Introduction

Glasses are found to be significant attention due to their unique properties like strength, transparency and resistance to corrosion. These properties make the glasses suitable for specific applications in various fields. It is well known that B₂O₃ exhibits unique structural features. Boron atom in B₂O₃ is generally present in both trigonal and tetrahedral coordination of oxygen [1-4]. The B₃ units may be present as B₃ (\equiv [BO_{3/2}]⁰) or as charged units [BO_{2/2}O]⁻ (\equiv B₂), [BO_{1/2}O₂]²⁻ (\equiv B₁) or even [BO₃]³⁻ (\equiv B₀) and these various borate units can often give rise to weakly organized structures resulting in intermediate range order. In general, the formations of groups like boroxol in borates are illustrative of tight connectivities. The concentration of the various borate species in the glass structure is however, determined by the nature and concentration of the modifier oxides. The addition of alkali oxides, not only breaks

the B-O-B bonds but also it weakens the tightly organised borate units. As a consequence of such structural changes, properties of alkali borate glasses vary non-linearly as a function of composition and often give rise to maxima or minima described as “boron anomaly” [1-4].

The addition of PbO to lithium borate forms stable glasses. The glasses containing PbO exhibit high refractive indices and low crystallization tendency [5]. They also exhibit low melting and low glass transition temperatures and in oxide glasses Lead atom play dual role both as network former and modifier depending on its composition. Lithium lead borate glasses doped with samarium ions have potential applications in lasers, memory devices and optical data storage materials. The glasses containing rare earth ions for optoelectronic applications can be developed by understanding its property and structure. In the present work an effort has been made to elucidate the structure of samarium ion doped lead borate glasses.

Experimental:

Glasses in the system, $30\text{Li}_2\text{O} - 60\text{B}_2\text{O}_3 - (10-x)\text{PbO} - x\text{Sm}_2\text{O}_3$ ($x = 0.5, 1, 1.5$ and 2 mol %) were prepared using Li_2CO_3 , H_3BO_3 , PbO and Sm_2O_3 as raw materials. The ratio between B_2O_3 and Li_2O is kept constant, ($\text{B}_2\text{O}_3/\text{Li}_2\text{O}=2$) and PbO content is replaced with Sm_2O_3 . The glass samples were prepared by melting the calculated quantities of analar grade chemicals in porcelain crucibles. The mixtures were melted in an electric furnace in the temperature range of $950\text{ }^\circ\text{C} - 1000\text{ }^\circ\text{C}$ depending on composition. The bubble free and homogeneous melt was poured on to a brass block and pressed with another block to obtain thin glass pieces. The obtained glassy samples were then annealed at a temperature lower than the glass transition temperature in order to remove the internal stresses. All the glasses were checked for amorphous nature by X-ray diffractogram and typical XRD pattern for LPBO, LPB2 and LPB4 samples is shown in Figure1.

Density (ρ) and Molar volume (V_m)

The densities of glasses were measured using acetone as immersion liquid ($\rho=0.789\text{ g/cm}^3$). The molar volumes, V_m were calculated using the relation, M/ρ . Where M is the molecular weight and ρ is the density of the corresponding glass samples. The densities and molar volumes of all the glasses are given in Table 1. The variation of density and molar volume with Sm_2O_3 content is shown in Figure 2.

Oxygen packing density (OPD)

The oxygen packing density of the glasses were calculated using standard relation as given below.

$$OPD = \frac{n \times 1000}{V_m}$$

Where ‘n’ represents the number of oxygen atoms in the respective glass sample.

Infrared Spectroscopy:

The infrared spectroscopic measurements were made on pellets of the glass samples mixed with KBr pellet in the range 400–4000 cm^{-1} using Nicolet 740 FTIR spectrometer.

Results and discussion:

The density of the glasses was found to decrease with increase of Sm_2O_3 content. It is well known that in borate glass boron atom is generally present in both trigonal and tetrahedral coordination of oxygen [1-4]. Addition of modifier oxide such as Li_2O to B_2O_3 glass, breaks the B-O-B network and creates non-bridging oxygen atoms. The formation of non-bridging oxygens, weakens the network structure by providing more voids. This would lead to increase in molar volume. This is well reflected in the variation of molar volume and oxygen packing density against Sm_2O_3 content. The variation of OPD with Sm_2O_3 content is shown in Figure 3. The oxygen packing density found to decrease with increase of Sm_2O_3 . The decrease in OPD clearly indicates the existence of voids in the glass matrix.

It has been reported in the earlier studies that PbO behaves both as network former and as network modifier depending upon its content in the glass [6-8]. PbO enters into glass as a network former particularly when it is at higher concentration, where Pb atoms generally take up four coordinating positions and the lead oxygen polyhedron can be represented as $[\text{PbO}_{4/2}]^{2-}$ [9]. Formation of $[\text{PbO}_{4/2}]^{2-}$ requires additional oxygen atoms which are made available through other mechanisms. But in the present glass system, the highest content of PbO is about 10 mol%. Hence PbO enters into glass as a network modifier, it just behaves like any other alkali oxide by giving away its available oxygen atom (O^{2-}) to boron and Pb atom sits in the vicinity of boron.

The IR spectra of the glasses are shown in Figure 4. It can be seen from IR spectra that the broad absorption peaks in three regions. Absorption in the region of 1200–1400 cm^{-1} is due to stretching modes of $[\text{BO}_3]^0$ trigonal borons [10-12], 850–1100 cm^{-1} is attributed to the stretching modes of $[\text{BO}_4]^-$ tetrahedral borons [10-12] and the 600–800 cm^{-1} to the various B–O–B bending modes in $[\text{BO}_3]^0$ and $[\text{BO}_4]^-$ units [13-17]. These modes are clearly present in all the three systems and in all the compositions. The peaks at 1400 cm^{-1} shift towards to 1200 cm^{-1} suggesting significant weakening of the borate glass network. Similar shift occurs in the $[\text{BO}_4]^-$ frequencies and the peak at 1050 cm^{-1} shifts to 900 cm^{-1} [12,13,18,19]. A fairly sharp but low intensity peak in the region of 670–710 cm^{-1} appearing in all glasses may be attributed to B–O–B (bridge) stretching vibrations [13-17]. The absorption band around 400–450 cm^{-1} can be associated with vibrations of lithium ions [20].

Conclusion

Samarium doped lithium-lead-borate glasses were investigated. The density of glasses found to decrease with increase of Sm_2O_3 content. Addition of modifier oxide to lead borate in the present glass system suggests an increase of voids within the glass matrix. The increase in voids is reflected well in the variation of molar volume. The increase in molar volume and decrease in oxygen packing density indicates the existence of non-bridging oxygens, leads to openness in the structure of borate glass.

Infrared absorption spectra reveal the presence of bending modes (B-O-B), stretching modes (BO_4 and BO_3), Sm^{3+} ions and PbO_6 structural units.

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Table 1: Codes, compositions, densities, molar volumes and oxygen packing density.

Code	Composition				Density (g/cc)	Molar Volume (cc)	OPD (g-atom/litre)
	Li ₂ O	PbO	B ₂ O ₃	Sm ₂ O ₃			
LPB0	0.3	0.1	0.6	0	3.3580	21.7566	101.1186
LPB1	0.3	0.095	0.6	0.005	3.1938	23.0715	95.1389
LPB2	0.3	0.09	0.6	0.010	3.1357	23.6990	92.4089
LPB3	0.3	0.085	0.6	0.015	3.1251	23.9805	91.1156
LPB4	0.3	0.08	0.6	0.020	3.1238	24.1915	90.1143

Table 2: IR band assignments of Sm³⁺ ion doped lithium lead borate glasses.

IR band(cm ⁻¹)	Assignment	References
450	Li ⁺ vibrational frequency	[20]
415	Li-O bond	[20]
600-800	B–O–B bending vibrations	[13-17]
850-1100	Stretching modes of [BO ₄] tetrahedral borons	[10-12]
950-1000	Diborate species	[12,13,18,19]
1200-1400	Stretching modes of [BO ₃] trigonal borons	[10-12]

Figure Captions:

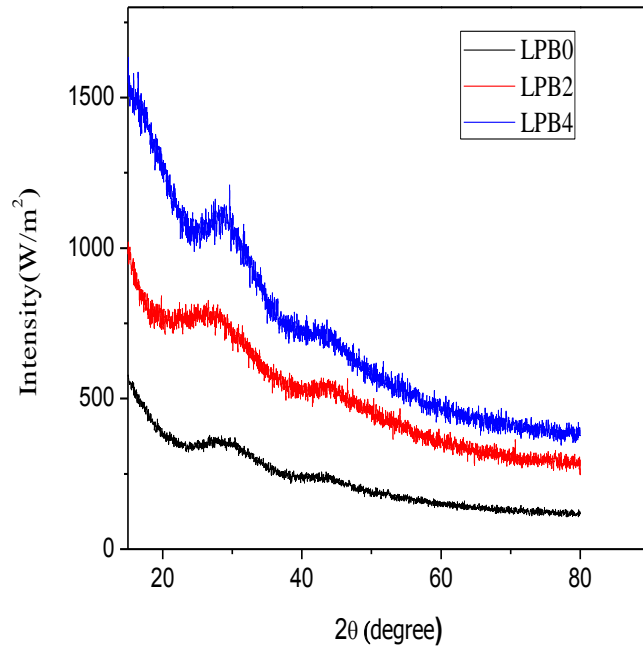


Figure 1: Typical XRD pattern of LPB0, LPB2 and LPB4 glasses.

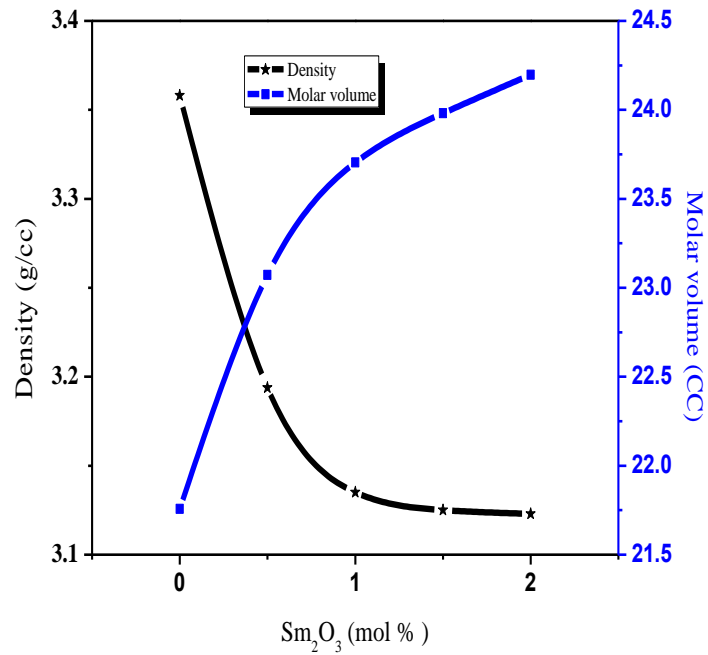


Figure 2: Variation of density and molar volume versus Sm_2O_3 content.

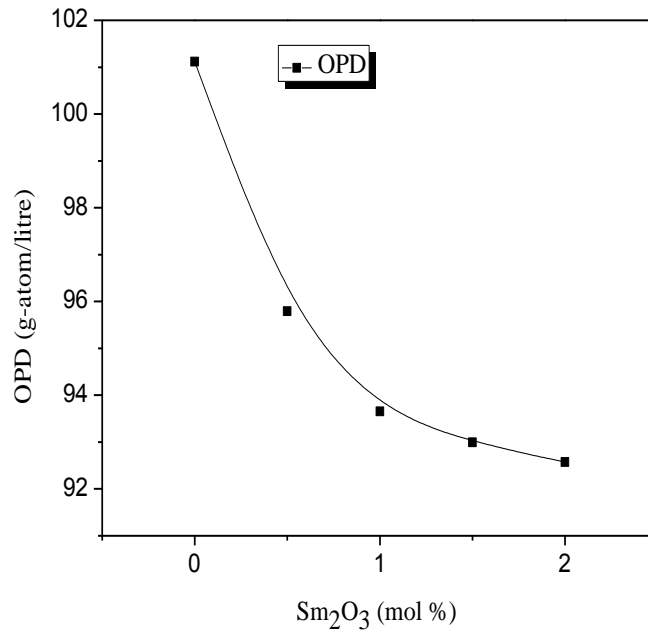


Figure 3: Variation of OPD versus Sm₂O₃ content.

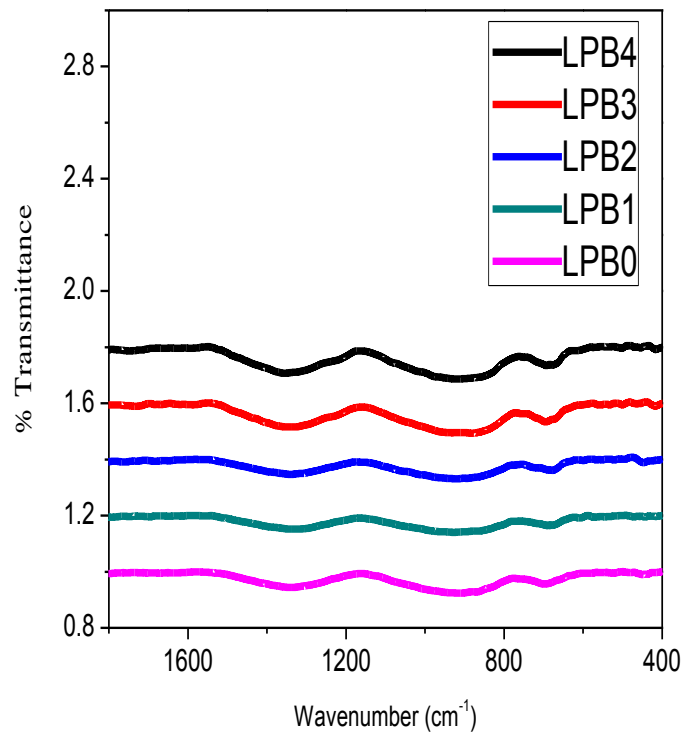


Figure 4: FT-IR spectra of LPB glasses.