

Characterization of aluminum doped zinc borate glasses

R. L. DHIMAN^{*}, V. S. KUNDU^a, A. S. MAAN^b, D. R. GOYAL^b

Post-Graduate Department of Applied Physics, S.D. College, Ambala Cantt. 133 001 India

^a*Department of Electronic Science, Kurukshetra University, Kurukshetra 136 119 India*

^b*Department of Physics, Maharshi Dayanand University, Rohtak 124 001 India*

The role of Al₂O₃ on the structural, physical and photoluminescence (PL) properties in x Al₂O₃ – (40- x) ZnO – 60 B₂O₃; ($0 \leq x \leq 25$) glass system have been investigated by means of FTIR and optical spectroscopic techniques. The samples were prepared by normal melt-quench technique. The absence of absorption band at 806 cm⁻¹ is attributed to the progressive substitution of boroxol ring by triborate (BO₃) and tetraborate (BO₄) structural groups. The PL spectra exhibits four main emission bands, two lies in the blue-red and other two lies in blue-green region. The variation in density and molar volume of the present glass system are found to depend on Al₂O₃ content.

(Received July 14, 2009; accepted July 22, 2009)

Keywords: Aluminum doped Zinc borate glasses, Infrared spectroscopy, Luminescence

1. Introduction

ZnO is a wide band gap semiconductor with hexagonal wurtzite structure. It possesses versatile properties and widely used in various fields such as transducers, chemical gas sensors, transparent conduction electrode, luminescent devices etc [1]. Addition of boric acid (B₂O₃) in ZnO, which form a network structure related to the silicates, creates a glass with higher melting point and greater stability to withstand temperature changes. The borate glasses doped with rare earth metal oxides have been used for high-energy physics scintillation detectors [2]. Since the glasses offers unique advantages over crystals, such as lower cost, easier fabrication and the higher durability and thermal shock resistance. Apart from these applications metal oxides doped borate glasses have tremendous potential applications in photo and radio luminescence technology [3]. The structural investigation of borate glasses by using various physical and chemical methods including Infrared and Raman spectroscopy, Brillouin experiments, NMR and neutron scattering investigations has been the subject of great interest [4-9]. It is well known that addition of a network modifier in borate glasses could produce the conversion of the triangular BO₃ structural units to BO₄ tetrahedra with coordination number of 4, which are incorporated in more complex cyclic groups such as tri-borate B₂O₇, di-triborate B₃O₈, metaborate B₃O₉ and more complicated units, or to the formation of non-bridging oxygen atoms [6-9]. In previous work, we have studied the effect of transitional metal oxides doping on the structure of borate glasses [10-12]. Recently, photoluminescence properties in borosilicate glasses have been reported [3]. Therefore, we have planned to investigate the effect of aluminum oxide doping on the photo luminescence behavior of zinc borate glasses.

In the present work the local structure of zinc borate glasses has been investigated by means of X-ray diffraction and infrared spectroscopy. Furthermore, the effect of aluminum oxide on the structure of zinc borate glasses is also discussed in terms of physical change such as density and molar volume.

2. Experimental Details

2.1 Sample preparation

Aluminum oxide doped zinc borate glasses were prepared from reagent grade powder of Al₂O₃, ZnO and H₃BO₃ which are thoroughly mixed, in appropriate proportions. Aluminum oxide was introduced as Al₂O₃, B₂O₃ was introduced as orthoboric acid (H₃BO₃) and the Zinc oxide was taken in the form of ZnO. The batch materials were dry mixed and melted in silica crucibles placed in an electrically heated muffle furnace at 1250^oC for about two hours, until a bubble free liquid was formed. The molten glass was equilibrated at the melting temperature until a clear and homogeneous melt was obtained. The glass melt was poured and subsequently pressed on a cooled carbon die held at room temperature.

2.2 X-ray diffraction measurements

The X-ray powder diffraction measurements were carried out on Regaku X-ray diffractometer using Cu-K α radiation to check the amorphous nature of the glass samples.

2.3 Infrared measurements

The vibrational spectra of the glass system under study were recorded at room temperature using FTIR spectrometer in the spectral range 500-4000 cm⁻¹. The

measurements were performed using KBr pellets technique.

2.4 Density measurements

The density (D) of the glass samples was determined at room temperature using Archimede's principle with Xylene as an inert immersion liquid. The density was obtained from the relation

$$D \text{ (gm/cm}^3\text{)} = [a/(a-b)] \times \text{density of Xylene}$$

where 'a' is the weight of the glass sample in air and 'b' the weight of the glass sample when immersed in Xylene. The density of Xylene is 0.865 gm/cm^3 . The molar volume (V_M) of each glass sample was calculated using the formula [13]

$$V_M = \sum x_i M_i / D$$

where x_i is the molar fraction and M_i is the molecular weight of the i th component.

2.5 Photoluminescence measurements

The photoluminescence spectra of the glass samples were recorded at room temperature using Fluoromax-3 Spectrophotometer in the wavelength range 350-700 nm.

3. Results and discussion

3.1 X-ray diffraction analysis

The X-ray diffraction pattern of aluminum doped zinc borate glasses depicted in Fig. 1, show no peaks for $x = 0, 5, 10 \text{ mol } \%$, indicating that the samples are completely amorphous in nature.

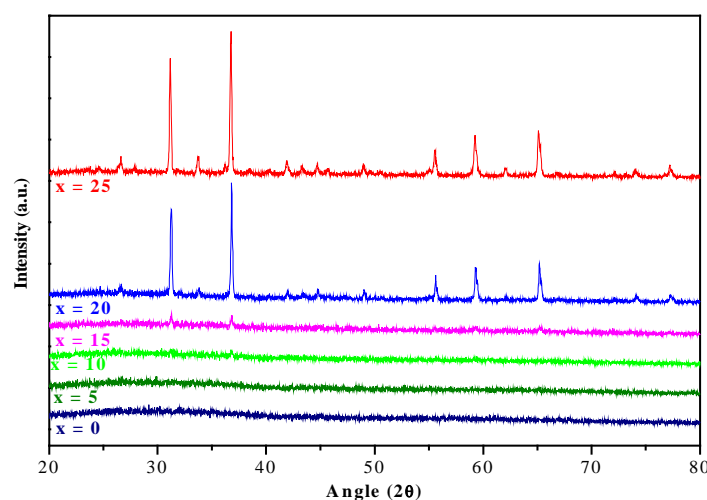


Fig. 1. XRD spectra for $x \text{ Al}_2\text{O}_3-(50-x) \text{ ZnO}-50 \text{ B}_2\text{O}_3$ glass system

However, for $x = 15 \text{ mol } \%$, the appearance of two small peaks indicates the formation of intermediate crystalline phase. For higher concentration ($x > 15 \text{ mol } \%$), appearance of several peaks results in the formation of crystalline phase, some peaks belong to Al_2O_3 and others to ZnO . But the majority of peaks found were belonging to be the hexagonal structure of ZnO .

3.2 Infrared analysis

Infrared spectra of $x \text{ Al}_2\text{O}_3 (50-x) \text{ ZnO}-50 \text{ B}_2\text{O}_3$ glass system with various content of aluminum oxide ($0 \leq x \leq 25 \text{ mol } \%$) are shown in Fig. 2. The observed vibrational bands of the borate network are seen to be mainly active in three infrared regions, which are similar to those reported earlier [10-15]. The first group of bands that occur in the range $1200-1600 \text{ cm}^{-1}$ is attributed to the asymmetric stretching relaxation of the B-O bond of the trigonal BO_3 units. The second group of bands lies between $800-1200 \text{ cm}^{-1}$ is due to the B-O bond stretching of the tetrahedral

BO_4 units. The third group of bands observed at 700 cm^{-1} is due to the bending of B-O-B linkage in the borate network.

According to Krogh Moe's Model [16] the structure of B_2O_3 glass consists of a random network of planar BO_3 triangles with a certain fractions of six member (boroxol) rings. Studies on B_2O_3 glass, the X-ray and neutron diffraction data suggest that the glass structure consists of a random network of BO_3 triangles without boroxol rings. In borate glasses, the appearance of absorption peak at 806 cm^{-1} (in infrared spectra) and 805 cm^{-1} (in Raman spectra) is the characteristics of boroxol ring [17-18]. The absence of this absorption band in the present glass system signifies that no boroxol ring formation occurs in the glasses under study, which in turn suggest the formation of BO_3 and BO_4 structural groups. These groups may be attached in the form of random network. This type of behavior is also observed in our earlier studies [10-12]. The infrared spectra of the present glass system show different absorption peaks as shown in Fig. 2, the peaks

are sharp, medium and broad. The broad bands are generally due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical stretching from the powder samples.

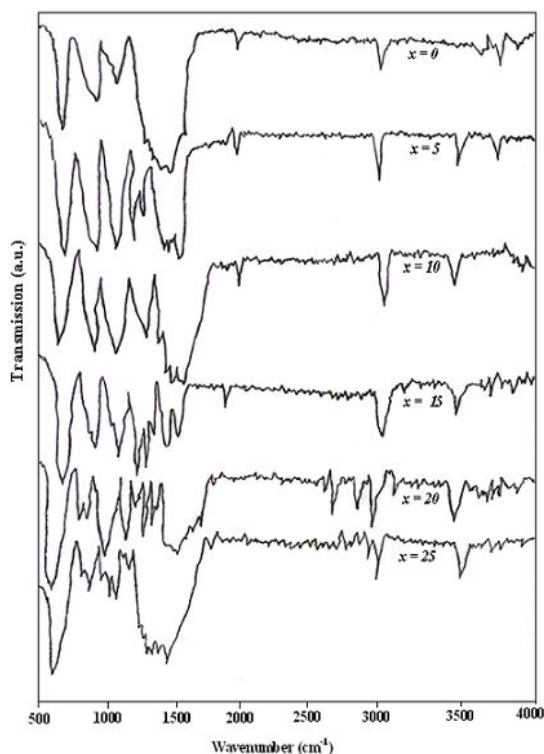


Fig. 2. Infrared spectra for $x\text{Al}_2\text{O}_3(50-x)\text{ZnO}50\text{B}_2\text{O}_3$ glass system.

In IR spectra of the present glass system, nine main absorption peaks are observed for $x = 0$. The first group of bands is located in the region $1198\text{--}1528\text{ cm}^{-1}$ and is associated with the fundamental asymmetrical stretching vibration of the B-O bond of the trigonal BO_3 units. The second group of bands located in the region $927\text{--}1065\text{ cm}^{-1}$, originates from B-O stretching of the tetrahedral

BO_4 units and is due to the vibration of some boron atoms attached to the non-bridging oxygens (NBOs) in the form of BO_4 vibrations [19].

The main dominated peak observed at 683 cm^{-1} is assigned to asymmetric stretching vibration of B-O bond and is due to bending of O-B-O linkage in the borate network [20]. This possibility is more in borate glasses where the boroxol ring is absent. The strong absorption band observed at 927 cm^{-1} is probably due to the B-O stretching vibration of tetragonal BO_4 units in diborate groups. The frequency band located at 1065 cm^{-1} is due to stretching vibration of BO_4 units. This band is shifted to higher frequency region up to 20 mol% of aluminum oxide and then starts decreasing and is attributed to the structural changes that occurred due to the appearance of crystalline phase as detected in X-ray diffraction spectra.

Table 1. Peak frequencies from IR spectra for $x\text{Al}_2\text{O}_3(50-x)\text{ZnO}50\text{B}_2\text{O}_3$ glass system

Peak positions (cm^{-1})						Assignments
$x=0$	$x=5$	$x=10$	$x=15$	$x=20$	$x=25$	
683	698	680	680	688	675	Bending vibrations of O-B-O linkage.
				848	850	ZnO (tetrahedral formation)
927 1065	933 1077	933 1089	930 1090	933 1060	982 1041	B-O bond stretching of the tetrahedral BO_4 units
1282 1318 1432 1528	1205 1270 1342 1433 1522	1276 1364 1440 1552	1198 1243 1288 1352	1199 1286 1354 1442 1535	1083 1318 1384 1385 1456	Asymmetric stretching vibration of B-O bond in the trigonal BO_3 units
1925 2926	1934 2930 3460	1932 2931 3424	1920 2924 3454	2665 2922 3442	1640 2852 3476	Absorption due to hydroxol group

The frequency band observed at 848 cm^{-1} for $x = 20$ mol % is due to the tetrahedral formation of zinc oxide [14]. On addition of aluminum oxide ($x = 5$ mol %), the frequency band observed at 683 cm^{-1} is shifted to higher frequency region i.e. at 699.5 cm^{-1} is assigned to the vibration of Al-O bond with Al^{3+} ion in four-fold coordination. The intensity of this band increases on increasing aluminum oxide content. The main structural units of the borate network lies in the region $1282\text{--}1528\text{ cm}^{-1}$ are assigned to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units. On increasing of aluminum oxide content, these bands are shifted towards the lower frequency region along with the formation of some new absorption bands. The weak frequency band observed at 1205 cm^{-1} is due to the stretching vibration of B-O band of BO_3 units. The absorption bands observed at 1307 and 1318 cm^{-1} are due to stretching vibration of B(III)-O-B(IV) units [20]. The frequency band located at 1432 and 1528 cm^{-1} are due to B-O- vibrations attached to large segments of borate network.

It is clearly seen in the IR spectra that the intensity of frequency bands lies in the region belongs to BO_3 structural units decreases while the intensity of the frequency band observed in the region belonging to BO_4 structural units increases up to 15 mol% of Al_2O_3 suggest that BO_3 structural units are converted in to BO_4 units. It means that NBOs increases with the increase in aluminum oxide concentration. For $x = 15$ mol%, some additional peaks are observed in the middle region belong to BO_3 group and is due to crystalline nature of the sample as

detected in the X-ray diffraction pattern. On further increase of aluminum oxide content the BO_3 structural units start dominating indicating the decrease in NBOs.

3.3 Density and molar volume

The determined values of density (D) and molar volume (V_M) of the glass samples are presented in Table 2.

Table 2. Density (D) and molar volume (V_M) for $x\text{Al}_2\text{O}_3$ ($50-x$) $\text{ZnO}50\text{B}_2\text{O}_3$ glass system

x (mol %)	D (g/cm^3)	V_M (cm^3/mol)
0	3.591	21.023
5	3.420	22.374
10	3.381	22.874
15	3.225	24.365
20	3.150	25.273
25	2.969	27.160

As shown in Fig. 3(a), the density decreases with increase in Al_2O_3 content, although the relative molecular mass of Al_2O_3 is higher than ZnO . As observed in the IR spectra that the addition of aluminum oxide in the glass matrix converts BO_3 to BO_4 units.

The process continues up to 15 mol % where the number of BO_4 units reaches its maximum value. The structure of the present glass for $x=15$ mol% is characterized by large number of non-bridging oxygen's and therefore relatively more open. As explained in IR spectra addition of aluminum oxide randomized the structure, which causes the density to decrease.

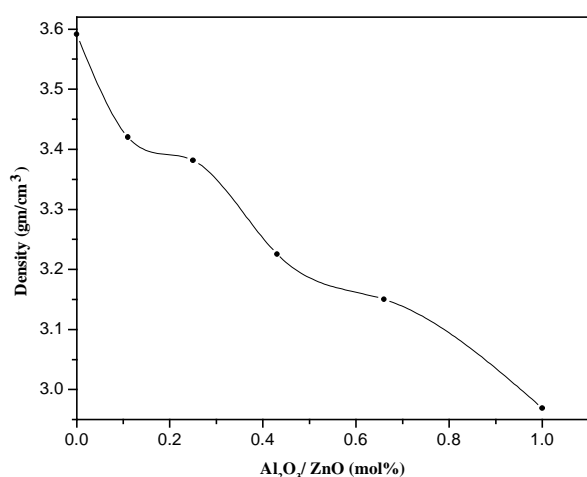


Fig. 3(a) – Variation of density with mol % of $\text{Al}_2\text{O}_3/\text{ZnO}$. However, the molar volume increases with increase in aluminum oxide content and is due the higher relative molecular mass of aluminum oxide compared to zinc oxide.

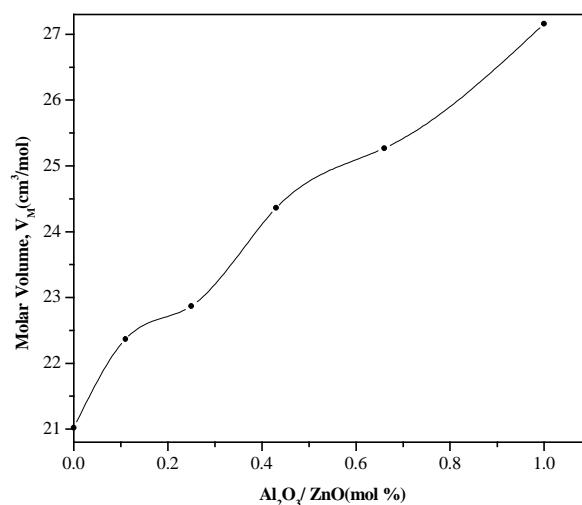


Fig. 3(b) Variation of molar volume with mol % of $\text{Al}_2\text{O}_3/\text{ZnO}$.

A small dip at about 0.1 and 0.4 ($\text{Al}_2\text{O}_3/\text{ZnO}$ mol%) is observed in the density Vs $\text{Al}_2\text{O}_3/\text{ZnO}$ (mol%) plot, which clearly indicate that some structural changes take place at these two particular compositions of Al_2O_3 . This variation is also seen in the molar volume (Fig. 3b) of the present glass system.

3.4 Photoluminescence study

The photoluminescence spectra of the present glass system were recorded at room temperature in the wave length range 350-700 nm are shown in Fig. 4(a-b).

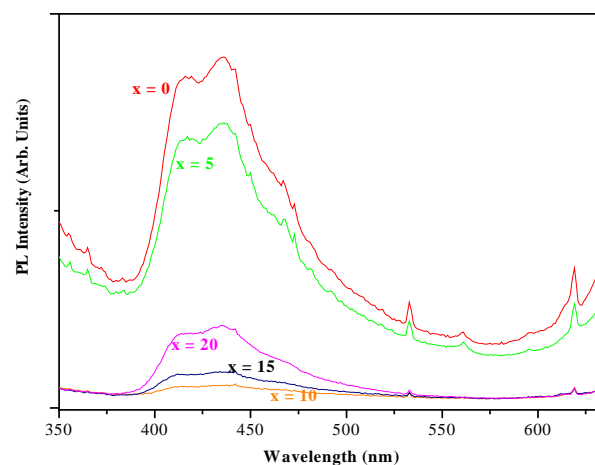


Fig. 4(a). Photoluminescence spectra of glass samples ($x = 0, 5, 10, 15$ and 20 mol%) The main spectral peaks are observed at around 414 nm, 435 nm, 533 nm and 618 nm.

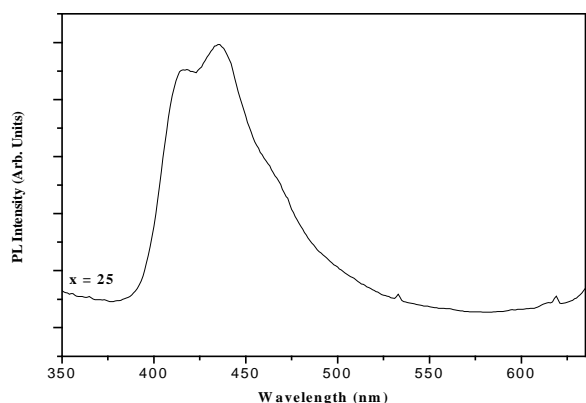


Fig. 4(b). Photoluminescence spectra of glass samples ($x = 25$ mol%).

The peaks around 415 nm, 435 nm show the emission to be in blue–green region and the peaks appeared at 533 nm and 618 nm are due to the emission in the blue-red region. The addition of Al_2O_3 content causes the decrease in PL intensity up to $x = 10$ mol %, however for further increase in Al_2O_3 content the PL intensity increases. It is observed that PL intensity increases abruptly for $x = 25$ mol %. The abruptly increase in PL intensity is understood because of appearance of crystalline phase. It has been reported that zinc borate glasses, exhibit the properties of luminescent material [3]. In the present study it is observed that when zinc borate glasses are diluted sufficiently with Al_2O_3 , results in the formation of crystalline phase causes increase in PL intensity (Fig. 4 (b) and hence it can be used as luminescent material.

4. Conclusions

It is concluded that the structure of zinc borate glasses consist of randomly connected BO_3 and BO_4 structural units. No boroxol ring formation was observed. On addition of aluminum oxide up to 15 mol%, the BO_3 structural units changes to BO_4 units indicate the formation of NBOs. Further addition of aluminum oxide ($x > 15$ mol %) causes the decrease in NBOs. These structural changes are discussed in terms of physical parameters (density and molar volume) and X-ray diffraction results. Tetrahedral formation of zinc oxide was observed at higher aluminum oxide concentration. The appearance of crystalline phase at higher concentration of aluminum oxide causes sudden increase in PL intensity and therefore such materials can be used for photoluminescence applications.

Acknowledgements

The authors are grateful to Dr. R.J. Chaudhary, Scientist, UGC-DAE, Consortium for Scientific Research, Indore Centre (M.P.) for XRD measurements.

References

- [1] S. Roy, A. Basu, Bull. Mater. Sci, **25** 6 513 (2002).
- [2] T. Sekiguchi, S. Miyashita, K. Obara, T. Shishido, N. Sakagami, J Cryst. Growth, **214-215** 72 (2000).
- [3] Chen Guorong, Nikl Martin, Solovieva, Alena Beitlerova, Rao Jinhua, Radiation Measurements, **38** 771 (2004).
- [4] M. Iron, M. Couzi, Levasseur, J. M. Reau, J.C. Brethous, J. Solid-State Chem, **31** 285 (1980).
- [5] F. L. Galeener, G. Lukovski, Jr. J.C. Mikkelsen, Phys. Rev. B, **22**, 3983 (1980).
- [6] J. Lorosch, M. Couzi, J. Pelouz, R. Vacher, A. Lavaseur, J. Non-Cryst. Solids, **69**, 1 (1984).
- [7] Jr. G.E. Jellison, P.J. Bray, J. Non-Cryst. Solids, **29**, 187 (1978).
- [8] P.J. Bray, S.A. Feller, G.E. Jellison, J.H. Yub, J. Non-Cryst. Solids **38-39** 93 (1980).
- [9] A..C. Wright, Vedischcheva, B.A. Shakhmatahin, J. Non-Cryst. Solids, **192-193**, 92 (1980).
- [10] Roshan Lal, N.D. Sharma, H.K.Sharma, Kailash Chandra, Indian J. Pure & Appl Phys, **42** 25 (2004).
- [11] Virender Kundu, R.L. Dhiman, D.R. Goyal, A.S. Maan, J. Opto Adv. Mater., **10**(10), 2765 (2008).
- [12] Virender Kundu, R.L. Dhiman, A.S. Maan, D.R. Goyal, Advances in Condensed Matter Physics, Volume 2008, Article ID 937054.
- [13] E. Mansour, El-Damrawi, Y.M. Moustafa, S. Abel El Maksoud, H. Doweider, Physica B **293** 268 (2001).
- [14] S.P. Yawale, S.V. Pakade, C.S. Adgaonkar, Indian J. Pure & Appl Phys, **33** 35 (1995).
- [15] A.A. Alemi, H. Sedghi, A.R. Mirmohseni, Golsanamlu, Bull.Mater.Sci, **29** 1 55 (2006).
- [16] Krogh-Moe, J. Non-Cryst. Solids, **1**, 269 (1969).
- [17] R.L. Mozi, V. Warren, J. Appl. Cryst, **3**, 251 (1970).
- [18] S. Guha, G. Walrafen, J. Chem Phys, **80**, 3807 (1984).
- [19] Y. Ito, K. Miyauchi, T. OJ, J. Non-Cryst Solids, **57** 389 (1983).
- [20] S.G. Motke, S.P. Yawale, S.S. Yawale, Bull. Mater. Sci, **25** 1 75 (2002).

*Corresponding author: roshandhiman_kuk@yahoo.co.in