

Structural Characterization of Lead Sulphide Doped Lithium Borate Glasses

P S NICHIT

Department of Physics,
Govt. Vidarbha Institute of Science and
Humanities,
AMRAVATI (M.S.) INDIA
nichitpratiksha@gmail.com

S P YAWALE

Department of Physics,
Govt. Vidarbha Institute of Science and
Humanities,
AMRAVATI (M.S.) INDIA
spyawale@rediffmail.com

S S YAWALE

Department of Physics,
Govt. Vidarbha Institute of Science and
Humanities,
AMRAVATI – 444604 (M.S.) INDIA

Abstract— Glasses of various compositions in the system $42.5\text{Li}_2\text{O} : x\text{PbS} (57.5-x) \text{B}_2\text{O}_3$ where x is the molar concentration in mol% were prepared via melt quenching technique. The amorphous nature of all the compositions of the as-quenched glasses under study was confirmed by X-ray powder diffraction (XRD) studies. The glassy nature of the as-quenched glasses was established by differential thermal analyses (DTA). The analysis of Infrared (IR) spectra shows that the formation of boroxol ring and tetrahedral coordination inside the glassy matrix was not observed, while the conversion of three-fold to four-fold coordination of boron atoms in the structure of glasses was observed.

Keywords- XRD, FTIR, TG, DTA

I. INTRODUCTION

XRD is considered as the most versatile non-destructive analytical tool for identifying the constituents of a multiphase mixture (Solid or powder sample) qualitatively and quantitatively and also to determine the amorphous content of the sample. A diffraction pattern contains information not only about the phase composition of a crystalline sample but also contains information about crystallite sizes, crystalline solid-solution, stress and texture. Thermal analysis is made up of various techniques for studying the thermal behavior of materials. When a material is heated or cooled, its structural and chemical composition undergoes changes: fusion, melting, crystallization, oxidation, decomposition, reaction, transition, expansion etc. To measure these various transformations the variation in different parameters is followed up as a function of the temperature. Infrared spectroscopy has been proven to be a useful tool for investigating the structure and dynamics of amorphous solids. It is used to know the existence of different bonds and bond transformation if any. Infrared spectroscopy has also been used for obtaining information about the coordination number of ions in simple crystal structures [1]. In borate glasses B_2O_3 is basic glass former because of its higher bond – strength, lower cation size, smaller heat of fusion and valence ($=3$) of B. In borate glasses, B^{3+} ions triangularly coordinated by oxygen, form glasses easily. In B_2O_3 the units are triangles, which are corner bonded in a random configuration [2]. The structure of borate glasses is different from other glasses such as phosphate, silicate etc.

Structural characterization of lead based binary and ternary glass system was carried out by Vasantharani et al [3] using FT-IR spectroscopy, X-ray diffraction and SEM analysis. Synthesis and characterization of cadmium doped lead–borate glasses were studied by Alemi et al [4] using FT-IR spectroscopy. The glass transition temperature of lithium borate glasses with various isotopic compositions was

determined by differential thermal analysis and by impedance spectroscopy [5].

In the present paper the structure of $\text{Li}_2\text{O-PbS-B}_2\text{O}_3$ glasses is discussed with the help of XRD and infrared spectra. To elucidate the conduction mechanism in present glass system, one has to know the structure. Since infrared spectroscopy is the most advantageous tool for the study of amorphous materials, we have used it to determine the structure of lithium borate glasses containing varying amount of PbS.

II. EXPERIMENTAL

A. Preparation of Glass Samples

The glasses of various compositions having general formula $42.5\text{Li}_2\text{O} : x\text{PbS} (57.5-x) \text{B}_2\text{O}_3$ where $x = 4, 6$ and 8mol% of PbS were prepared from Analytical Reagent (AR) grade chemicals Li_2O , B_2O_3 and PbS of different compositions. Appropriate amounts in mol% of Li_2O , B_2O_3 and PbS in powder form having accuracy of $\pm 0.00001\text{g}$ were taken. Repeated grinding of mixture was done to ensure homogenization. Homogeneous mixture was then transferred to fire clay crucibles, which was then subjected to melting in an automatically temperature controlled muffle furnace at temperature ranging from 1000 to $1200^\circ\text{C} \pm 10^\circ\text{C}$. The duration of melting was generally four hours. The homogenized molten mass was cast in steel discs of 2.5 cm

length and 0.7 cm thicknesses. The samples were quenched at 200°C to avoid cracking and shattering of glass.

B. X-ray diffraction (XRD)

The X-ray powder diffraction data of all glasses was obtained from Vishveshwarya National Institute of Technology (VNIT), Nagpur India. The Philips PW 3050/60

X-ray powder diffractometer was used. Details of the operating conditions were as mentioned: generator settings: 45KV, 40mA, radiation: CuK α (angle range $2\theta = 10-80^\circ$, step size: 0.0170, Scan Step Time = 10.3377, Divergence Slit Size [$^\circ$] = 0.4785.

C. Infrared spectra (FTIR)

The FTIR spectra of lead sulphide doped lithium borate glasses were recorded on 4100typeA FTIR spectrophotometer at room temperature in the wavelength range 400 to 4000 cm^{-1} . All spectra were collected from department of Physics, Govt. Vidarbha Institute of Science and Humanities, Amravati India.

D. Thermogravimetry (TG) and Differential thermal analysis (DTA)

TG, DTA data of lead sulphide doped lithium borate glasses was obtained from department of material engineering, Vishveshwarya National Institute of Technology (VNIT), Nagpur. The samples were analyzed by Perkin Elmer Instruments Diamond TG/DTA model no. PYRIS Diamond K-A 101005820, which is interfaced with computer to record simultaneously TG/DTA data. All the thermal reactions of the dried powder were carried out in a static system by simultaneous thermo-gravimetric (TG) and differential thermal analysis (DTA) at the rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C in Ar gas flow 200 ml/min.

III. RESULTS AND DISCUSSION

A. XRD:

The X-ray diffraction technique has been used to check for the possible crystallinity in the sample after quenching and annealing. It is known that the absence of peak in the intensity versus 2θ curve represents complete amorphous state of the sample. Indication of peaks in the curve suggests the formation of phases in the glass during annealing time or slow cooling. The X-ray diffractograms of $\text{Li}_2\text{O}:\text{PbS}:\text{B}_2\text{O}_3$ glass samples with 4, 6 and 8mol% of PbS are given in figure 1.

The absence of peak in the X-ray spectra, confirmed the amorphous nature of glass samples. All the spectra for different mol% of PbS doped lithium borate glasses reveal a hump in low 2θ region. It is due to short range order and indicating that these lithium borate glasses doped with PbS are amorphous. Increase in concentration of PbS does not induce any crystallinity in these glass samples. This also explains the homogeneous nature of the samples.

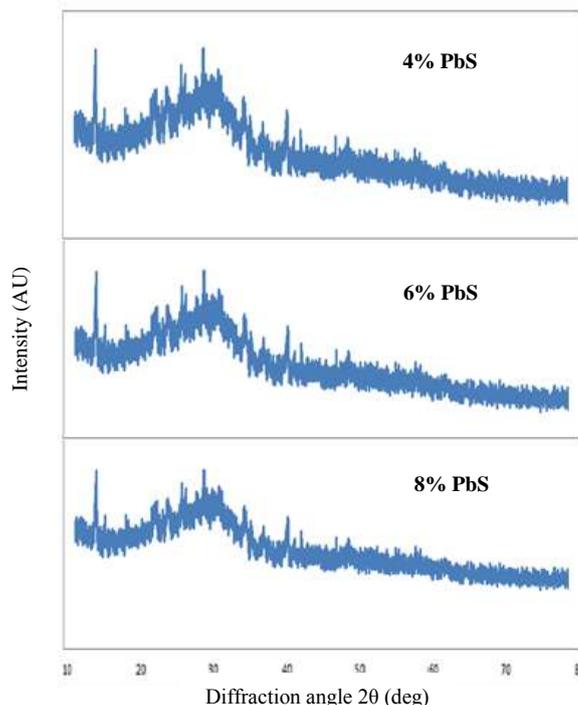


Figure 1: X-Ray diffraction pattern of PbS doped Lithium borate glasses

B. FTIR:

The infrared spectral investigation of $\text{Li}_2\text{O}-\text{PbS}-\text{B}_2\text{O}_3$ glasses in the frequency range $400-4000\text{cm}^{-1}$ is done. The infrared spectra of all the glasses under study are given in figure 2. Eight to ten absorption peaks are observed in all the samples. The shapes of the peaks are sharp, medium and broad. The peak positions of the frequencies λ^{-1} are tabulated in table 1. The broad bands are exhibited to 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. The vibrational modes of the borate network are seen to be mainly active in three infrared spectral regions, which are similar to those reported by several workers[6-8] (i) the first group of bands which occur at $1200-1600\text{cm}^{-1}$ is due to the asymmetric stretching relaxation of the B-O band of trigonal BO_3 units, (ii) the second group lies between 800 and 1200cm^{-1} which is due to the B-O bond stretching of the tetrahedral BO_4 units and (iii) the third group is observed around 700cm^{-1} and is due to bending of B-O-B linkages in the borate networks.

In the present glass system the absence of absorption peak of 806cm^{-1} indicates the absence of boroxol ring formation. The progressive substitution of boroxol rings by triborate and tetra borate groups is observed. In pure B_2O_3 glass, the 806cm^{-1} frequency is a characteristic of boroxol ring. The vanishing of 806cm^{-1} means no boroxol ring in the glass structure. This type of behaviour is observed in $\text{B}_2\text{O}_3:\text{Li}_2\text{O}$ glasses [9, 10].

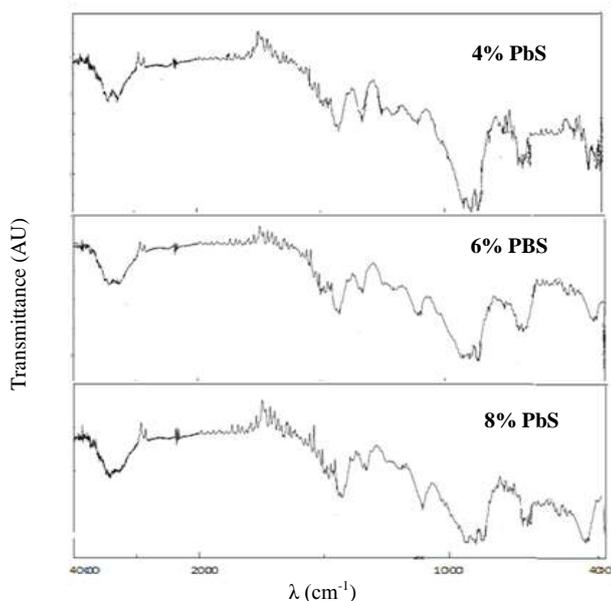


Figure 2: FTIR spectra of PbS doped lithium borate glasses

The absorption bands at wave numbers range 1300-1700 cm^{-1} are attributed to the bending vibration and stretching vibration of B-O-B in $[\text{BO}_3]$ triangles [11, 12]. The absorption bands below 620 cm^{-1} are attributed to vibration of PbO [13]. Therefore, PbO acts as a network participant filled in the interspaces of $[\text{BO}_3]$ units in the form of Pb^{2+} ions. The most intense peak at 1500 cm^{-1} region and a sharp peak at 863 cm^{-1} are characteristic of Li_2CO_3 . The absorption band at 993 cm^{-1} in the IR spectra in these glasses may be attributed to a stretching vibration of B-O-M (B-O-Pb) linkage where M represents a metal ion. Absorption at 616 cm^{-1} is due to bending of O-B-O. The lead play dual role of Pb^{2+} cations in glass structure. First it act as a network modifier in the glassy matrix when these cations are ionically bonded and secondly, if Pb-O bond is covalent Pb^{2+} cation will act as glass former [14]. The low frequency bands near 453 cm^{-1} in IR spectra of borate glasses can be attributed to vibration of Pb^{2+} metal cations [15-18].

Table 1: Peak frequencies from IR spectra for $\text{Li}_2\text{O} : \text{PbS} : \text{B}_2\text{O}_3$ glasses

Glass composition $\text{Li}_2\text{O} : \text{PbS} : \text{B}_2\text{O}_3$	Peak position (cm^{-1})										
42.5 : 4 : 53.5	454.17	615.71	863.1	993.2	1110.8	1208.1	1333.5	1426.1	1510.9	3263.8	3494.3
42.5 : 6 : 51.5	453.34	616.42	865.8	992.5	1106.9	1207.2	1333.5	1426.1	1511.9	3185.8	3421.1
42.5 : 8 : 49.5	452.21	617.25	863.9	991.9	1105.9	-	1332.5	1431.8	1501.2	3186.8	3587.3

C. Thermogravimetry (TG) and Differential thermal analysis (DTA):

Figure 3(a) to 3(c) shows TG, DTA curve for 4, 6 and 8mol% of PbS doped lithium borate glasses. TG curve gives the information about the weight loss in the sample. From the TG curve it is observed that the weight loss in the range room temperature to 370 $^{\circ}\text{C}$ is due to loss of absorbed moisture in the glass sample, because these glasses are hygroscopic. Minor weight loss is observed (nearly equal to 1%) in the temperature range 370 to 450 $^{\circ}\text{C}$. This may be attributed to a structural decomposition. The total weight loss observed in all the samples is nearly equal to 10%. Thus we can say that all the glass samples are thermally stable. From the DTA curve the glass transition temperature T_g , change in heat capacity ΔC_p and change in enthalpy ΔH_c are determined and mention in table 2. The possibility of formation of crystallization and phase separation in these glasses is tested. From the DTA curve it is observed that only one endothermic peak exists in each curve is due to glass transition and no exothermic peaks are obtained which suggest that there is no crystallization or phase transition. Similar type of behaviour is confirmed with the help of X-ray diffraction spectra.

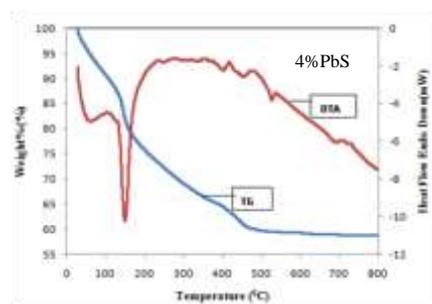


Figure 3(a): TG, DTA curve of 4 mol% of PbS doped $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ glasses

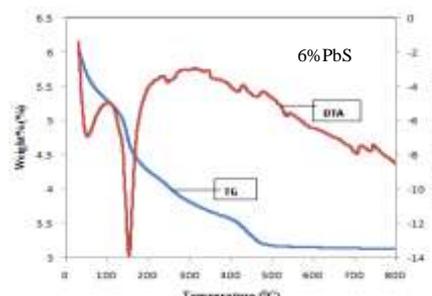


Figure 3(b): TG, DTA curve of 6 mol% of PbS doped $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ glasses

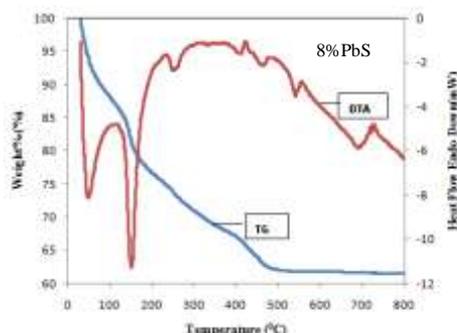


Figure 3(c): TG, DTA curve of 8 mol% of PbS doped $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$

Table 2: Kinetic parameter data from TG and DTA curves

Glass composition $\text{Li}_2\text{O}:\text{PbS}:\text{B}_2\text{O}_3$	Glass Transition temperature (T_g) (°C)	Specific Heat (ΔC_p) $\text{J/g } ^\circ\text{C}$	Endothermic peak			
			Onset Temp. (°C)	Peak Temp. (°C)	End Temp. (°C)	Enthalpy (ΔH_c) (J/g)
42.5 : 4 : 53.5	140.48	1.57	134.75	154.14	170.85	221.77
42.5 : 6 : 51.5	146.78	1.09	132.29	151.03	167.05	160.90
42.5 : 8 : 49.5	234.80	0.64	134.80	152.41	169.29	102.31

IV. CONCLUSION

The percent crystallinity is found to be negligible as compared to the amorphous state hence the overall behaviour in the properties would be due to amorphous nature. It consists of randomly connected BO_3 and BO_4 groups. The connection of BO_3 triangles and BO_4 groups heavily depends on the rate of cooling of the melt hence the structure of the glass. The structure of lead sulphide doped lithium borate glass without boroxol ring formation is observed. TG, DTA data shows that there are two degradation steps in each glass sample. The total weight loss observed in the entire samples is minimum which indicated that the present glass is thermally stable.

ACKNOWLEDGMENT

Authors are very much thankful to Director and Head, Dept. of Physics, both from Govt. Vidarbha Institute of Science and Humanities, Amravati for providing necessary facility at the time of research work. We are also highly obliged to Dr. Pathak, Head, Dept. of Instrumentation, Visvesvarya National Institute of Technology, Nagpur for providing XRD and TG/DTA characterization of materials.

REFERENCES

[1] Franke Duchille and R.Roy, Zeit Krist vol.111, 1959, pp.462-470.
 [2] S.G.Motke, P.Yawale and S.S.Yawale, Bull.MaterSci.vol.25, 2002 pp.75-78.
 [3] P.Vasantharani and N. Sangeetha, International Journal of Research in Pure and Applied Physics, vol.3 (1), 2013, pp.1-6
 [4] A. A. Alemi, H. Sedghi, A.R. Mirmohseni and V.Golsanamlu, Bull. Mater. Sci., vol.29 (1), 2006, pp.55-58.

[5] Takanori Nagasaki, R. Morishima, Tsuneo Matsui, Journal of Nuclear Science & Technology, vol.39, 2002, pp.386-390.
 [6] S.G.Motke, S.P.Yawale & S.S. Yawale, Bull. Mater. Sci., vol.25, 2002, pp.75-78.
 [7] F.M. Ezz Eldin, E.L.Alaily, F.A. Khalifa&H.A.Batal Fundamentals of glass science and Technology (3rd ESG conference) 1995.
 [8] E.L.Ghoneun, H.A.Batal, N. AbdelShafi & M.H.Azooz, Proceeding of Egyptian conference of Chemistry, Cairo Egypt, 1996, pp.162.
 [9] Kulkarni, H. S. Maiti & A.Paul, Bull. Mater Sci., vol.6, 1984, pp.201-221.
 [10] M. A. Kanehisa & R. J. Elliot, Mater. Sci. Engg., Vol. B3, 1989, pp.163- 166.
 [11] Y. Cheng, H. Xiao, W. Guo, W. Guo, Ceram. International, vol.33, 2007, pp.1341-1347.
 [12] E.I. Kamitsos, A.P. Patsis, M.A. Karakassides, G.D. Chryssikos, J. Non-Cryst. Solids, vol.126, 1990, pp.52-67.
 [13] A.K. Hassan, L. Borjesson, L.M. Torell, J. Non-Cryst. Solids, vol.172/174, 1994 pp.154-160.
 [14] A.M Azhra., C.Y.Zahra, J. Non-Cryst. Solids, vol.155, 1993, pp. 45-55.
 [15] J.G. O' Bray, J.G.OKeefe, J. Phys. Chem. Glasses, vol.4, 1963, pp.37-46.
 [16] H. Doweidar, M. A. Abou Zeid, G. M. El-Damrawi, J. Phys. D: Appl. Phys., vol. 24, 1991, pp.2222-2228.
 [17] S. P. Yawale, S. V. Pakade, C. S. Adgaonkar, Indian J. Pure Appl. Phys., vol.33, 1995, pp. 34 -37.
 [18] S. A. Feller, N. Lower, M Affatigato., Phys. Chem. Glasses, vol.42, 2001.