International Journal of Applied Natural Sciences (IJANS)
Vol.1, Issue 1 Aug 2012 69-74

International Academy of Science, Engineering and Technology
Connecting Researchers; Nurturing Innovations

SYNTHESIS AND OPTICAL CHARACTERIZATION OF (Pb,Bi)TiO_3 BOROSILICATE GLASS SYSTEM

CHANDKIRAM GAUTAM, ARBIND KUMAR SINGH & AVADHESH KUMAR YADAV

Department of Physics University of Lucknow, Lucknow-226007, India

ABSTRACT

Lead and lead free bismuth titanate borosilicate glasses were prepared by melt quench method using high purity AR grade chemicals. X-ray diffraction has been recorded to confirm the amorphous nature of the prepared glass samples. The optical characterizations were performed by using Infrared (IR) and Raman spectroscopic techniques at room temperature. IR measurements were recorded over a continous wavenumber range 400-5000 cm^{-1} and Raman spectroscopic measurements were caried out in wavenumber range 1000-2000 cm^{-1}. The different absorption peaks / bands were observed in IR spectral patterns. These spectral bands occurs due to Bi and Pb towards lower wavenumber sides while diborate and triborate network units were towards higher wavenumber sides. These glasses are very important for the application of X-rays radiation protection.

KEYWORDS: Lead bismuth titanate glasses; XRD, IR and Raman Spectroscopy.

INTRODUCTION

The structure of oxide glasses is mainly related with the polyhedral oxygen coordination in the structure and it is way to interconnect to each other to form the glassy network. Boric oxide, B_2O_3, is one of the significant glass formers and flux material. In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, and small heat of fusion. In such glasses, B^{3+} ions are triangularly coordinated by oxygen. B_2O_3 units are corner bonded in a random configuration [1]. The structure of borate glasses heavily depend upon the cooling rate of the melt through the range of glass transition temperature [2]. The structural properties of borosilicate glasses can be modified within a wide range by the introduction of oxides of bivalent or monovalent metals that modify the structure of boron [3]. Pb-based glasses are popular as commercial, low temperature sinterable glasses due to their desirable application properties such as low softening temperature, low dielectric constant (<15), and high reflectivity [4]. During the last few decades, the researchers took care towards doped materials because of their unique optical properties and potential applications. Most of the studies are activated by trivalent rare-earth ions, the materials have been found to exhibit favorable spectroscopic properties in many applications [5-7]. Bismuth titanate is a ferroelectric material having wide applications in the electronics as capacitors, memory devices and sensors and also used for optical memory, non-volatile memory, piezoelectric and electro-optic devices [8]. Borate glasses, in particular, have been the subject of numerous infrared studies due to their structural peculiarities. IR spectra of various glasses of (Pb,Bi)TiO_3 borosilicate glass systems show sharp and diffuse absorption peaks. These peaks occur due to different vibrational mode of the borate network and asymmetric stretching relaxation of the B-O bond

of trigonal BO_3 units [9]. More recently (BaSr)TiO_3 borosilicate transparent glasses were prepared successfully [10].

In this research paper, we are reporting the synthesis and optical properties of amorphous bismuth titanate borosilicate glasses studies by Raman and IR spectroscopy.

EXPERIMENTAL PROCEDURE

The AR grade chemicals PbO (Fisher Scientific 99 %), Bi_2O_3(Himedia 99.99%), TiO_2 (Himedia 99%), SiO_2 (Himedia 99.5%), H_3BO_3 (Himedia 99.8%), and La_2O_3 (Himedia 99.9%) were mixed for 2.0 hours in acetone media using mortar and pestle. The well mixed and dried powder were kept in to a high alumina content crucible and then crucible is replaced inside the high temperature SiC electric furnace in the temperature range 1200 - 1300 ^{0}C. The melt was poured into an aluminum mould and pressed by a thick aluminum plate then immediately transferred in to a preheated programmable muffle furnace for annealing at temperature 450 ^{0}C up to 3 hours. The structure of the prepared samples was analyzed using analytical tools such as IR and Raman spectroscopy. XRD of powder glass samples were carried out using a Rigaku Miniflex-II X-ray diffractometer using Cu-K_α radiation to check the amorphous state of the prepared glass samples. To obtain IR spectra of a glass sample, the powdered glass samples were mixed with KBr powder and pressed as pellets. These pellets are carried out for the recording of IR spectra using JASCO FT/IR-5300 in the wave number range 450-4000 cm^{-1} at room temperature. Raman spectra of powdered glass samples were also recorded in the wavenumber range **1000-2000 cm^{-1}**. The nomenclature of glass samples and their compositional distribution is listed in Table 1.

Table 1: Nomenclature of Glass Samples and Compositional Distribution

Glass sample code	$(Pb_xBi_{1-x})TiO_3$		$(2SiO_2$-$B_2O_3)$	La_2O_3
	x	Wheight %		
BT1L0.0	0	65	34	1
PBT1L0.2	0.2	65	34	1
PBT1L0.4	0.4	65	34	1

RESULTS & DISCUSSIONS

X-ray Diffraction Analysis

The XRD patterns of both glass samples BT1L0.0 and PBT1L0.4 are shown in Figure 1.

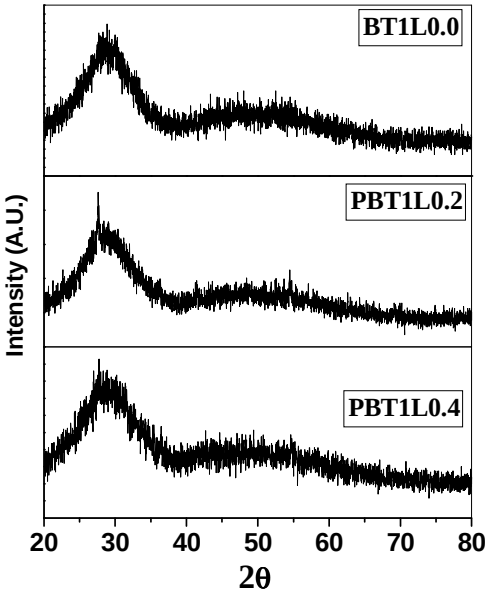

Figure 1: XRD Patterns of Glass Samples BT1L0.0, PBT1L0.2 and PBT1L0.4

These figures exhibit a broad diffuse scattering at different angles instead of crystalline peaks, confirming short range structural order characteristics of glassy amorphous phase.

INFRARED SPECTROSCOPY

IR spectra of various glass samples are shown in the Fig. 2 (a, b and c). IR spectra of these glass samples show six absorption peaks associated with different vibrational modes. IR spectra of all glass samples having broad and sharp bands at different wavenumbers lies between 400-5000 cm^{-1}. All the absorption peaks have been numbered as 1, 2, 3, -----, 6 starting from high wave number side to low wave number side. Wavenumbers of different absorption peaks has been listed in Table 2. The broad absorption band at wavenumber 3657 cm^{-1} are exhibited in IR spectra of glass sample BT1L0.0 (Fig 2 a). This absorption band occurs due to stretching mode of O-H bonds inside the glassy network [11]. The band nature is strongly affected by compositional change and it is observed that band shifted towards higher wavenumber side with increase in the content of lead oxide. Absorption peak no. 2 lies between wavenumber 2867-2943 $cm^{-1}$and it occurs due to hydrogen bonding [12]. This absorption peak disappears in IR spectra of glass sample PBT1L0.4. The absorption peak at wavenumbers 1522-1483 cm^{-1} in these glass samples exhibited due to the vibrational mode of the borate network (peak 3). The vibrational modes of the borate network are attributed due to the asymmetric stretching relaxation in B-O bonds of trigonal BO_3 units. Such types of vibrational modes occur within the wavenumbers range 1200-1750 cm^{-1} [13].

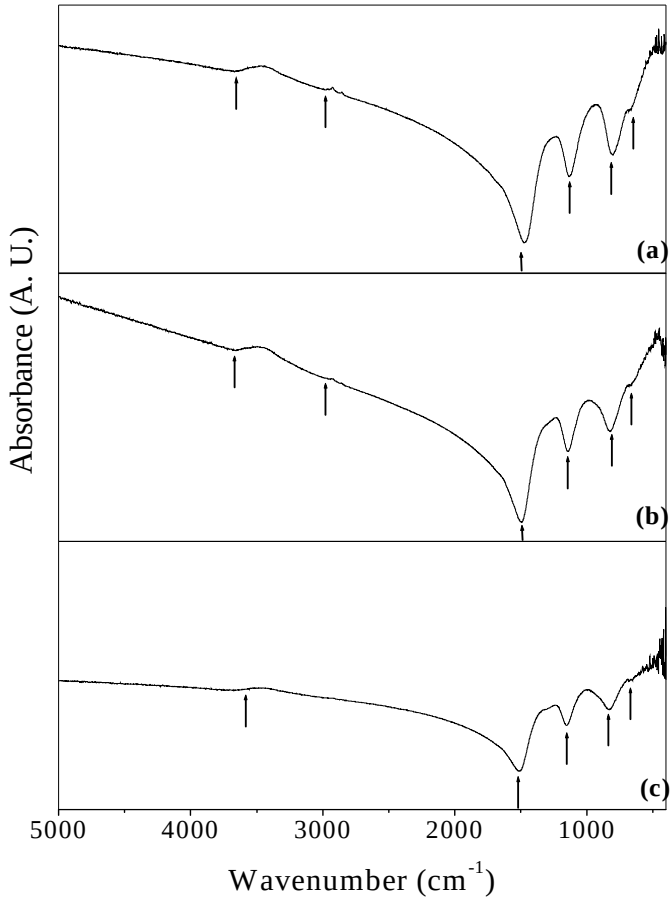

Figure 2: IR Spectra of Glass Samples (a) BT1L0.0 (b) PBT1L0.2 (c) PBT1L0.4

The broad absorption band at around 1120-1153 cm^{-1} peak (no. 4) is attributed to a stretching vibration of B-O-Si linkage [14]. An absorption peak no. 5 is observed within the wavenumber range 816-833 cm^{-1} in IR spectra of all glass samples. This peak was present due to the diborate linkage, B-O-B, in the borate glassy network. In this linkage both boron atoms are tetrahedrally coordinated with triborate super-structural units [15]. An absorption peaks at lower wavenumber side attributed to vibration of metal cation such as Pb^{2+} and Bi^{3+} [16, 17].

Table 2: Wavenumbers of Different Absorption Peaks In IR Spectra of the Glass Samples

Glass Sample code	Wave length of different absorption peaks (cm^{-1})					
	1	2	3	4	5	6
BT1L0.0	3657	2976	1483	1120	816	670
PBT1L0.2	3665	2981	1491	1143	825	669
PBT1L0.4	3584	-	1522	1153	833	676

RAMAN SPECTROSCOPY

Raman spectra of a representative glass sample PBT1L0.2 is shown in Fig. 3. The high intensity peaks are observed at wavenumber 1582 cm^{-1} and 1382 cm^{-1}. The peaks occur due to symmetric mode, where there is no change in dipole moment, therefore, polarizability fluctuates and Raman active. There are not significant results were observed in Raman spectra rest two glass samples.

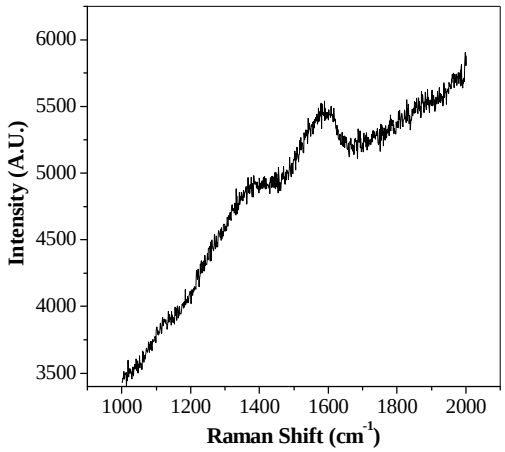

Figure 3: Raman Spectra of Glass Sample PBT1L0.2

CONCLUSIONS

Bulk and transparent glass samples are synthesized successfully in the glass $65[(Pb_xBi_{1-x})TiO_3]$-$34[2SiO_2$-$B_2O_3]$-$1[La_2O_3]$ (x=0.0, 0.2 and 0.4) system. IR spectra of PBT glass samples are attributed to different vibrational modes of BO_3 bonding, asymmetric streching of B-O-Si and B-O-B. It is also concluded that the metalic cations Pb^{2+} and Bi^{3+} are dominating for low wavenumbers.

ACKNOWLEDGEMENTS

The authors are gratefully acknowledged to the UPCST, Lucknow, (India) for financial support under the young scientist major research project no. CSTT/YSS/D-3913.

REFERENCES

[1] S. S. Yawale, S. P. Yawale, C. S. Adgaonkar, “Infrared investigation of some borate glasses,” Indian J. Engg. Mater. Sci., Vol. 7, 2000, pp. 7-13.

[2] W. Soppe C. van der Marel W.F. van Gunsteren H.W. den Hartog, “New insights into the structure of B_2O_3 glass,” J. Non-Cryst. Solids, Vol. 103, 1988, pp. 201-209.

[3] J. S. An, J. S. Park, J. R. Kim, K. S. Hong, and H. Shin, “Effects of Bi_2O_3 and Na_2O on the Thermal and dielectric properties of zinc borosilicate glass for plasma display panels,” J. Am. Ceram. Soc., Vol. 89, 2006, pp. 3658-3661.

[4]. G. H. Hwang, H. J. Jeon, Y. S. Kim, "Physical properties of barrier ribsof plasma display panels: information of pores during sintering of lead borosilicate glass frits," J. Am. Ceram. Soc., Vol. 85, 2002, pp. 2956-2960.

[5] M. Tanaka, Y. Masumoto, "Temperature behaviour of the orange and blue emissions in ZnS:Mn nanoparticles," Chem. Phys. Lett., Vol. 324, 2000, pp. 249.

[6] Jiaqi Yu, Huimin Liu, Yanyun Wang, Weiyi Jia, "Hot luminescence of Mn^{2+} in ZnS nanocrystals", J. Lumin., vol. 79, 1998, pp. 191-199.

[7] R. Jagannathan, K. Athinarayanasamy, A. Mani and C.K. Jayasankar, "Nano-crystallites formation and Eu^{3+} luminescence in zinc boro-sulphate glasses", Opt. Mater. Vol. 5, 1996, pp. 57-62.

[8] M. Villegas, C. Moure, J.F. Fernandez, P. Duran, "Preparation and sintering behaviour of submicronic $Bi_4Ti_3O_{12}$ powders," J. Mater. Sci., Vol. 31, 1996, pp. 949-955

[9] C. R. Gautam, D. Kumar and O. Parkash, "IR study of Pb–Sr titanate borosilicate glasses," Bull. Mater. Sci., Vol. 33, No. 2, 2010, pp. 145-148.

[10] A. K. Yadav, C. R. Gautam and Prabhakar Singh, "Crystallization Kinematics and Dielectric Behavior of (Ba,Sr)TiO_3 Borosilicate Glass Ceramics", New Journal of Glass and Ceramics, 2012 (In press).

[11] P.G. Bray, Interaction of radiation with solids, New York, Plenum, 1967.

[12] G. Sharma, K. Singh, M. Priya, S. Mohan, H. Singh and S. Bindra, "Effects of gamma irradiation on optical and structural properties of PbO-Bi_2O_3-B_2O_3 glasses," Rad. Phys. Chem., Vol. 75, No. 9, 2006, pp. 959-966.

[13] E. I. Kamitsos, M. A. Karakassides and G. D. Chryssikos, "Vibrational spectra of magnesium-sodium-borate glasses: Raman and mid-infrared investigation of the network structure," J. Phys. Chem.Glasses, Vol. 91, No. 5, 1987, pp. 1073-1079.

[14] A. S. Tenny and J. J. Wong, "Vibrational spectra of vapor-deposited binary borosilicate glasses," Chem. Phys., Vol. 56, No. 11, 1972, pp. 5516-5523.

[15] H. Doweidar, M. A. Abou Zeid, G. M. El. Damrawy, "Effect of gamma radiation and thermal treatment on some physical properties of ZnO-PbO-B_2O_3 glasses," J. Phys. D: Appl. Phys., Vol. 24, No. 12, 1991, pp. 2222-2228.

[16] A. K. Yadav and C. R. Gautam, "IR and Raman Spectroscopy of Perovskite (Ba,Sr)TiO_3 Borosilicate Glasses with addition of 1% La_2O_3," Lucknow J. Sci., Vol. 8, 2011, pp. 26-30.

[17] C. R. Gautam, D. Kumar, O. Parkash and Prabhakar Singh **"**Synthesis, I R, crystallization and dielectric study of (Pb,Sr)TiO_3 borosilicate glass ceramics" Bull. Mater. Sci., Vol. 35, No. 8, 2012.