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Research Article

Structural and Physical Properties of ZnO Modified Bismuth Silicate Glasses

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Zinc bismuth silicate glasses with compositions $40SiO_2 \cdot xZnO \cdot (60 - x)Bi_2O_3$ ($x = 0, 5, 10, 15, 20, 25, 30, 35$, and 40) have been prepared by conventional melt-quench technique and the solubility limit of zinc in bismuth silicate glass system has been estimated using X-ray diffraction technique. Density has been measured using Archimedes' principle; with increase in ZnO in the samples, the molar volume and density are found to decrease. The glass transition temperature (T_g) has been determined by using differential scanning calorimetry (DSC) and is observed to increase with increase in ZnO content. Raman and FTIR spectra have been recorded at room temperature and the analysis of Raman and FTIR shows that in all the glass compositions, asymmetric and symmetric stretched vibrations of Si–O bonds in SiO_4 tetrahedral units exist and with decrease in Bi_2O_3, the contribution of symmetric vibrations begins to dominate which results in increased compactness of the glass structure.

1. Introduction

Glasses based on heavy metal oxide have attracted attention of researcher's community for their excellent IR transmission compared with conventional glasses [1, 2]. The bismuth oxide glasses have wide range of applications for optical and electronic devices, mechanical sensors, and reflecting windows [3, 4]. Bi_2O_3 is not a classical glass former but due to high polarisibility and small field strength of Bi^{3+} ions, in the presence of conventional glass formers like SiO_2, PbO and B_2O_3, a glass network of BiO_3 and BiO_6 may be built [5]. However, the structural role played by Bi_2O_3 in glasses is complicated. Bi_2O_3 is suitable for forming glass with high refractive index, nontoxicity, wide transmission range, and so forth [6]. SiO_2 in its various amorphous forms has an extremely wide spectrum of industrial applications [7]. Several reports on ZnO-Bi_2O_3 with B_2O_3 and TeO_2, CdO-ZnO-V_2O_5, V_2O_5-Bi_2O_3-B_2O_3, and V_2O_5-ZnO-Bi_2O_3 systems exist in literature [8–14], but physical and structural studies of SiO_2-ZnO-Bi_2O_3 are rare.

The aim of present paper is to investigate the effect of ZnO on physical and structural properties of bismuth silicate glass samples using the techniques of XRD, DSC, FTIR, and Raman spectroscopy.

2. Experimental

The glass samples in the system $40SiO_2 \cdot xZnO \cdot (60 - x)Bi_2O_3$ with composition $x = 0, 5, 10, 15, 20, 25, 30, 35$, and 40 were prepared using analar grade SiO_2, Bi_2O_3, and ZnO chemicals, by conventional melt-quench method. However, the samples with x (ZnO content) higher than 40 had also been tried to synthesize but we could not succeed. For the synthesis of samples, the weighed quantities of SiO_2, ZnO and Bi_2O_3 in appropriate proportions were well-mixed using pestle mortar and then the mixture was taken in silica crucible. The crucible containing mixture was then put in an electrically heated muffle furnace and temperature was slowly raised to 1100°C at which the mixture gets melted. The melt was kept at 1100°C for half an hour and was shaken for proper mixing and homogeneity. The coin shaped glass samples were obtained by pouring and quenching the melt in between two stainless steel plates at room temperature. Density of glass samples was measured using Archimedes' Principle with water as buoyant liquid. X-ray diffraction patterns were taken by using Rigaku Table Top X-ray Diffract meter (XRD) to detect the amorphous character. The glass transition temperature (T_g) was determined from differential scanning calorimetry (DSC) using TA instruments, Model

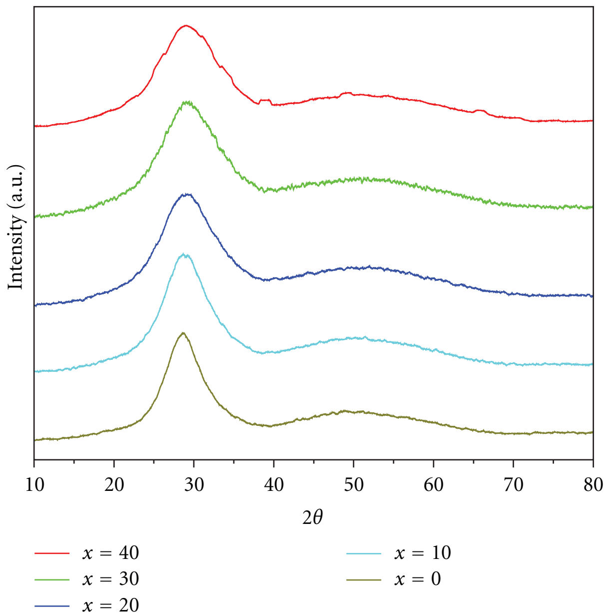

FIGURE 1: XRD of different $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ glass compositions.

No. Q600 SDT. For this purpose glass samples were heated in nitrogen atmosphere at rate of 20°C/min in the temperature range of 40°C to 1000°C. Infrared transmission spectra were recorded at room temperature using Shimadzu FRIT-8001PC spectrometer over the range 400 to 2000 cm^{-1}. The powdered samples were thoroughly mixed with dry KBr in ratio of 1 : 20 by weight and then pallets were prepared under pressure of 8-9 tons. The Raman Spectra were recorded using Renishaw Invia Reflex Micro Raman Spectrometer with Ar ion laser (514 nm) under back scattering configuration.

3. Results and Discussion

The prepared glass samples of $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ with $x = 0, 5, 10, 15, 20, 25, 30, 35$, and 40 were found to be light yellow in colour. The XRD patterns of glass samples with $x = 0, 10, 20, 30$, and 40 are shown in Figure 1. The presence of broad spectrum and absence of any sharp peak in X-ray diffractograms confirms amorphous nature of the synthesized glass samples. The measured values of density (ρ) for all samples are given in Table 1. Perusal of the data presented in Table 1 reveals that the density of samples decreases with increase in ZnO content. This is usual trend as heavier Bi_2O_3 molecules are replaced by lighter ZnO molecules.

The molar volume (V_m) was calculated by using the relation

$$V_m = \frac{\sum x_i M_i}{\rho}, \qquad (1)$$

where ρ is density, x_i, and M_i represent the molar fraction and molecular weight of ith component, and density, respectively. The values of V_m are also presented in Table 1 and its

TABLE 1: Density (ρ), molar volume (V_m), and glass transition temperature (T_g) of $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ glasses with different values of x.

Compositions (x)	ρ (g/cc)	V_m (cc/mole)	T_g (°C)
0	6.73	45.11	451
5	6.60	43.08	471.85
10	6.4948	40.82	459.52
15	6.401	38.41	474
20	6.198	36.57	474
25	5.938	34.93	494
30	5.627	33.45	513
35	5.529	30.56	521
40	5.463	28.87	522

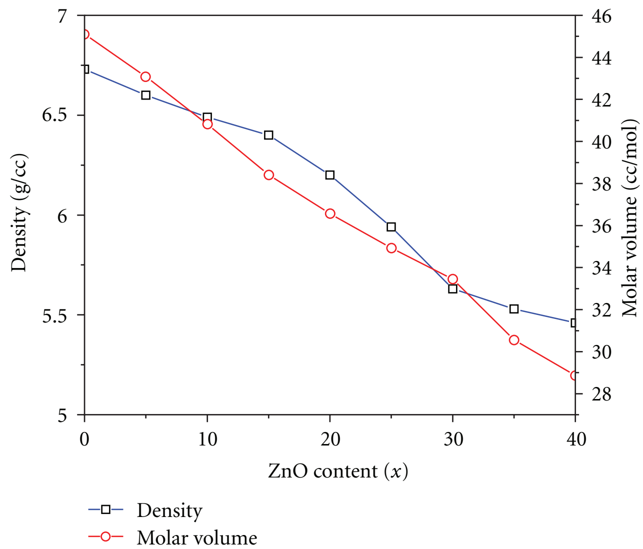

FIGURE 2: Compositional dependence of density (ρ) and molar volume (V_m) for $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ glasses.

variation with composition is shown in Figure 2. Perusal of Figure 2 shows that the molar volume also decreases with increase in ZnO content. Similar results have been reported in the literature for V_2O_5-Bi_2O_3-ZnO [9] and Li_2O-Bi_2O_3-ZnO [15] glass systems. The results of differential scanning calorimetry (DSC) for $40SiO_2$-xZnO-$(60-x)Bi_2O_3$ with $x = 0, 5, 10, 15, 20, 25, 30, 35, 40$ are shown in Figure 3. The glass forming tendency and thermal stability of glasses may be determined from values of T_g. It is observed that T_g increases with increase in ZnO content, indicating the increase in glass thermal stability. A decrease of T_g associated with an increase in heavy metal oxide content in glassy matrix can be attributed to a network opening [16]. So, network compactness of glassy matrix in the present glass system increases with increases of ZnO content.

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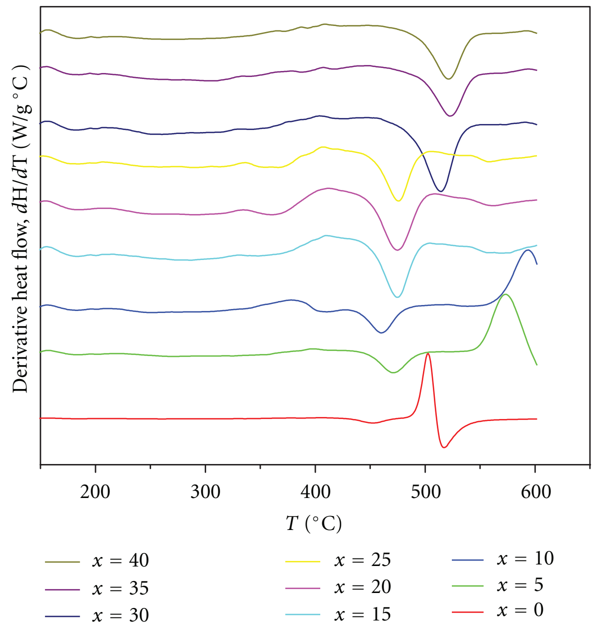

Figure 3: Differential scanning calorimetry (DSC) curves for glass system $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$.

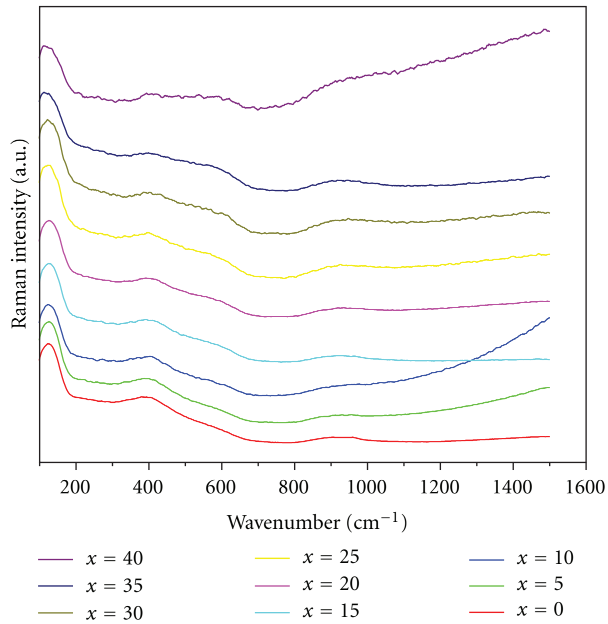

Figure 4: Raman spectra for different $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ glass compositions at room temperature.

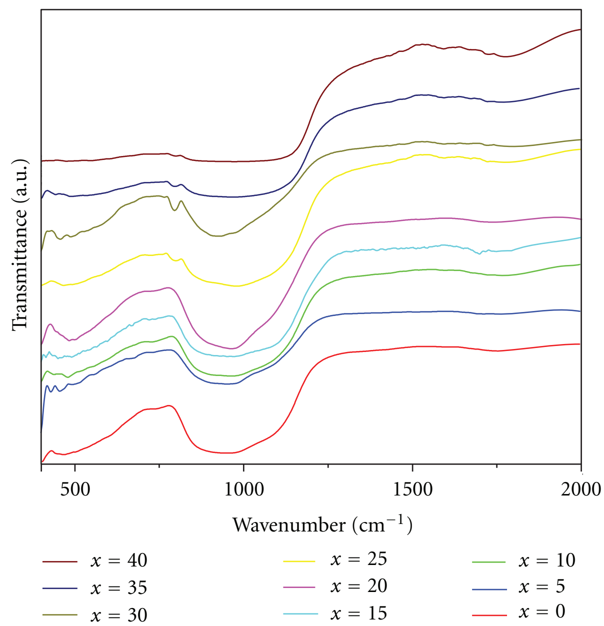

Figure 5: Infrared spectra for different $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ glass compositions at room temperature.

can be attributed to a network opening [16]. So, network compactness of glassy matrix in the present glass system increases with incresase of ZnO content.

The Raman spectra are characterized by three major bands, $\sim 120\,cm^{-1}$, $400\,cm^{-1}$, and a weak broad band $\sim 900\,cm^{-1}$, for all compositions of $40SiO_2 \cdot xZnO \cdot (60-x)Bi_2O_3$ (shown in Figure 4). The FTIR spectra is characterized by two sharp absorption bands between 425 to $550\,cm^{-1}$ (centred at around $475\,cm^{-1}$), 800 to $1200\,cm^{-1}$ (centred at nearly $950\,cm^{-1}$), a small band or flattening at $720\,cm^{-1}$ in all studied glass samples and a small band occurs around $800\,cm^{-1}$ in glass samples for $x = 25, 30, 35$, and 40 as shown in Figure 5. In Raman spectra, the band between 50 and $200\,cm^{-1}$ (centered at around $120\,cm^{-1}$) is usually related to vibrations involving motions of the Bi^{3+} cations in $[BiO_6]$ and/or $[BiO_3]$ units [17, 18]. Another band centred at $400\,cm^{-1}$ may be attributed to the Bi–O–Bi and Bi–O stretching vibrations of BiO_6 Octahedral units [19, 20] and may be due to asymmetric bending vibrations of Si–O–Si in SiO_4 structural units [21, 22].

The intensity of this band decreases with the decrease in Bi_2O_3 content in present glass system, suggesting the presence of bismuth as network modifier in the form of BiO_6 octahedral units. This is also supported by the FTIR data. In FTIR the bands between 425 to $550\,cm^{-1}$ and 800 to $1200\,cm^{-1}$ are attributed to Bi–O–Bi and Bi–O Vibrations of BiO_6 octahedra [17, 20, 23]. Ardelean et al. [24] has reported a band at $715\,cm^{-1}$ due to symmetric stretching vibrations of Bi–O bond in BiO_3 pyramidal units. So, the small kink observed at $720\,cm^{-1}$ in all the glass compositions may be attributed to symmetric stretching vibrations of Bi–O bond in BiO_3 pyramidal units. The Raman spectra of all compositions show a weak band around $920\,cm^{-1}$, which may be attributed to the symmetric stretching vibrations of SiO_4 with three non-bridging oxygens [21]. The position and intensity of this band remains same on wave number scale as per our expectations, as the SiO_2 content remain same in all the compositions. It is also supported by the FTIR, where band between 800 to $1200\,cm^{-1}$ is attributed to the asymmetric stretching vibration mode of SiO_4 tetrahedra [17]. A small but well-distinguished IR band at around $800\,cm^{-1}$ is present in glass samples with $x = 25, 30, 35$, and 40. This band is merged in the broad IR band from 800 cm^{-1} to 1200 cm^{-1} for other glass compositions. The band at around the 800 cm^{-1} in FTIR data is attributed to Si–O symmetric stretched vibrations [25]. The study of Raman and FTIR spectra shows that in all the glass compositions, asymmetric and symmetric stretched vibrations of SiO_4 exist and with decrease of Bi_2O_3, the contribution of symmetric vibrations begins to dominate. This may be due to replacement of larger Bi_2O_3 molecule by smaller ZnO molecule and hence may result in decrease of stretching of silicate network.This may result in the increased compactness of the glass structure, which is also evidenced by decrease in molar volume and increase in T_g. Low frequency band present in FTIR data at around 450 cm^{-1} in all glass samples is assigned to vibrations of Zn^{2+} metal cations [9]. The width of the Raman bands in disordered materials is a measure of the disorder in the local structure [26]. The Raman band width decreases with decrease in bismuth content indicating that the vicinity of bismuth in the present glass system is more distorted.

4. Conclusions

Various investigations like X-ray diffraction, density, and DSC carried out on $40SiO_2 \cdot xZnO \cdot (60 - x)Bi_2O_3$ for $x = 0, 5, 10, 15, 20, 25, 30, 35, 40$, and 45 reveal that stable glasses are obtained for $x = 0$ to 40; the glass forming tendency and thermal stability of these glasses increase with increase in ZnO content. For higher concentration of ZnO that is, more than $x = 40$, glass formation becomes difficult in the present physical conditions and this may be taken as the solubility limit of ZnO in present glass system. The density of these glasses is observed to decrease with increase in ZnO content. On addition of ZnO into bismuth silicate system, contribution of symmetric vibrations of Si–O bonds in SiO_4 tetrahedral units dominate over asymmetric vibrations. Bi_2O_3 plays the role of both glass former as well as modifier in the present system of study.

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