ZnO Modified Bismuth Silicate Glasses Structural and Physical Properties

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Abstract— *Zinc bismuth silicate glasses with compositions* $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ $(x = 0,5,10,15,20,25,30,35, and\ 40)$ *were prepared using standard melt-quench techniques and zinc solubility limits were estimated using X-ray diffraction techniques in the bismuth silicate glass scheme. Density was measured using the principle of Archimedes; the molar volume and density decreased with a rise in ZnO in the samples. The temperature of the glass transition (T_g) was determined using differential calorimetry scanning (DSC) and is expected to raise with a rise in ZnO content. Raman and FTIR spectra were registered at room temperature and Raman and FTIR analysis demonstrates that in all glass compositions there are asymmetric and symmetric extended vibrations of Si-O bonds in SiO_4 tetrahedral units and with reduction in Bi_2O_3, the input of symmetric vibrations starts to dominate resulting in enhanced compactness of the glass composition.*

Keywords— ZnO, Bismath silicate, DSC,Raman spectra, Infrared spectrum.

I. INTRODUCTION

Heavy metal oxide-based glasses have drawn community attention for their outstanding IR transmission relative to standard glasses [1,2]. Bismuth oxide lenses are suitable for a broad spectrum of applications for optical and electronic instruments, mechanical sensors and window reflection [3,4]. Bi_2O_3 is not a classic glass former, but owing to elevated polarization and low field strength of Bi^{3+} ions, a glass network of BiO3 and BiO6 may be constructed in the presence of standard glass formers such as SiO2, PbO and Bi_2O_3 [5]. The structural function Bi_2O_3 plays in glasses, however, is complex. Bi_2O_3 is appropriate for forming elevated refractive index, non-toxicity, broad range of transmission, and so on [6]. SiO2 has an incredibly broad range of industrial apps in its multiple amorphous forms [7]. Several reports are available in literature on ZnO- Bi_2O_3 with Bi_2O_3 and TeO_2, CdO-ZnO-V_2O_3, V_2O_3- Bi_2O_3-B2O3 and V_2O_5-ZnO- Bi_2O_3 systems [8–14], but SiO_2-ZnO- Bi_2O_3 physical and structural trials are uncommon.

The objective of this document is to use XRD, DSC, FTIR, and Raman spectroscopy methods to explore the impact of ZnO on the physical and structural characteristics of bismuth silicate glass specimens.

II. EXPERIMENTAL

The glass samples in scheme $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ with composition x=0,5,10,15,20,25,30,35,and 40 were prepared by standard melt-quenching technique using anal grade SiO_2, Bi_2O_3, and ZnO chemicals. However, we also tried to synthesize the samples with x(ZnO content) higher than 40 but we couldn't achieve. The weighed amounts of SiO_2, ZnO and Bi_2O_3 were well mixed with pestle mortar for the synthesis of samples and then the blend was drawn in silica crucible. The mixed crucible was then placed in an electrically heated muffle furnace and the temperature was slowly raised to 1100 ° C where the mixture was melted. For half an hour, the melt was kept at 1100 ° C and shaken for adequate mixing and homogeneity. The samples of coin-shaped glass were obtained by pouring and quenching the melt at room temperature between two plates of stainless steel. Glass sample density was evaluated using the Principle of Archimedes with water as a buoyant liquid. X-ray diffraction patterns were used to detect the amorphous character using the Rigaku Table Top X-ray Diffract meter (XRD). The glass transition temperature (T_g) was determined using TA tools, Model No, from differential calorimetry scanning (DSC). Q600 SDT. Glass samples were heated to a temperature range of 40 ° C to 1000 ° C in the nitrogen atmosphere at a rate of 20 ° C / min. Infrared transmission spectra were registered over the range of 400 to 2000 cm^{-1} at room temperature using Shimadzu FRIT-8001PC spectrometer. The powdered samples were carefully blended in a proportion of 1:20 by weight with dry KBrand then pallets were prepared under 8-9 tonnes stress. The Raman Spectra was registered using the back-scattering setup of the Renishaw Invia Reflex Micro Raman Spectrometer with Ar ion laser (514 nm).

III. RESULTS AND DEBATE

$40SiO_2\ .xZnO.(60-x)Bi_2O_3$ prepared glass samples with x=0,5,10,15,20,25,30,35,and 40 were discovered to be colored light yellow. Figure 1 shows the XRD patterns of x=0,10,20,30 and 40 glass samples. The existence of wide spectrum and lack of any sharp peak in X-ray diffractograms confirms the synthetic glass samples ' amorphous nature. Table 1 shows the measured density values (π) for all specimens. Perusal of the information described in Table 1 shows that sample density reduces as ZnO content increases. As heavier Bi_2O_3 molecules are substituted with lighter ZnO molecules, this is the usual trend.

TABLE 1
$40SiO_2\ .xZnO.(60-x)Bi_2O_3$ CRYSTAL TRANSITION TEMPERATURE (T_g), MOLAR VOLUME (V m), AND DENSITY (ρ)[27]

Compositions (x)	$\rho\ (g/cc)$	$V_m\ (cc/mole)$	T_g (℃)
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

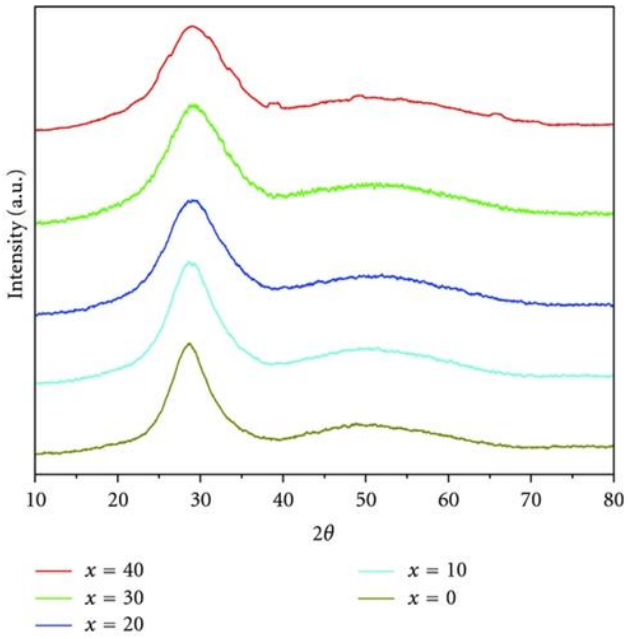

FIGURE 1: XRD of various crystal compositions $40SiO_2\ .xZnO.(60-x)Bi_2O_3$.[27]

Calculation of the molar quantity (V m) using the relationship

$$V_m = \frac{\sum x_i M_i}{\rho},$$

Wherever the density isρ, x_i and M_i respectively, represents the molar fraction and molecular weight of the component of i^{th} and density. V_m values are also shown in Table 1 and their composition variation is shown in Figure 2. Figure 2's perusal demonstrates that molar volume also reduces as ZnO content increases.

Similar results for V_2O_5-Bi_2O_3-ZnO [9] and Li_2O-Bi_2O_3-ZnO [15] glass structures were recorded in the literature. The results for $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ with x=0,5,10,15,20,25,30,35,40 differential scanning calorimetry (DSC) are shown in Figure 3. The tendency to form glass and the thermal stability of glasses can be determined from T g values. T g is

noted to improve with a rise in the content of ZnO, suggesting an increase in the thermal stability of glass. A reduction in T g connected with an rise in the content of heavy metal oxide in glass matrix may be linked to the opening of a network [16]. In the current glass scheme, therefore, the network compactness of the glass matrix improves with an increase in the content of ZnO.

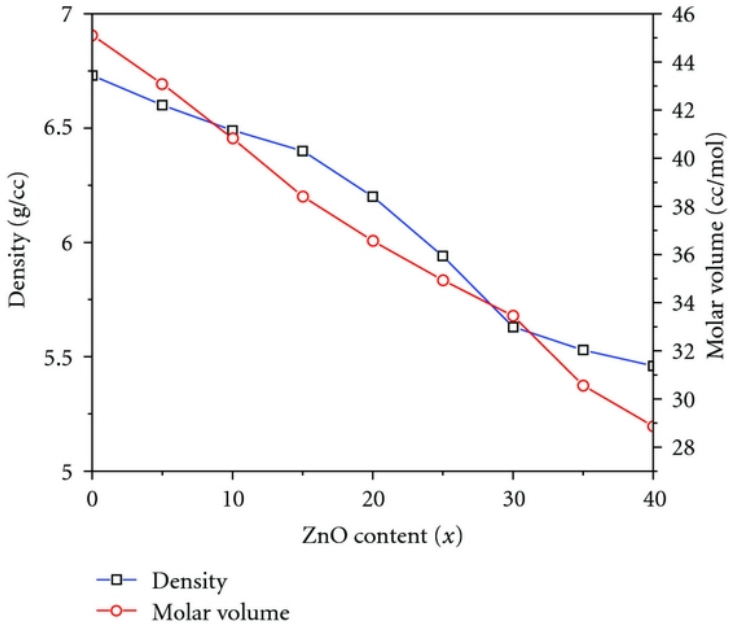

FIGURE 2: Density (π) and molar quantity (V_m) compositional reliance for $40SiO_2 . xZnO. (60 - x)Bi_2O_3$ lenses.[27]

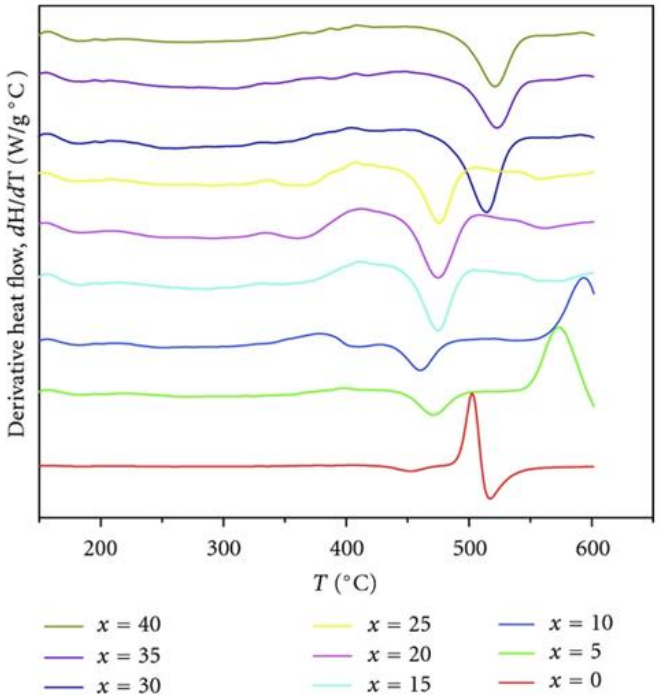

FIGURE 3: Calorimetry differential scanning (DSC) curves for the $40SiO_2 . xZnO. (60 - x)Bi_2O_3$ crystal scheme.[27]

The tendency to form glass and the thermal stability of glasses can be determined from T g values. T g is noted to improve with a rise in the content of ZnO, suggesting an increase in the thermal stability of glass. A reduction in T g connected with a rise in the content of heavy metal oxide in glass matrix may be linked to the opening of a network [16]. In the current glass scheme, the network compactness of the glass matrix rises as the content of ZnO rises.

For all $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ compositions, the Raman spectra are defined by three significant bands,~120 Cm^{-1}, 400 Cm^{-1}, and a small wide band ~900 Cm^{-1}. The FTIR spectrum is defined by two sharp absorption bands ranging from 425 to 550 Cm^{-1} (centered at about 475 Cm^{-1}), 800 to 1200 Cm^{-1} (centered at approximately 950 Cm^{-1}), a tiny band or flattening at 720 cm−1 in all the glass specimens studied, and a tiny band occurs at around 800 cm−1 in glass specimens 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 about 120 Cm^{-1}) is usually associated with vibrations involving Bi^{3+} cation movements in[BiO_6] and/or[BiO_3] units[17, 18]. Another 400Cm^{-1} centered band can be attributed to the Bi–O–Bi and Bi–O stretching vibrations of BiO_6 octahedral units [19, 20] and can be attributed to asymmetric Si–O–Si bending vibrations in SiO_4 structural units [21, 22].

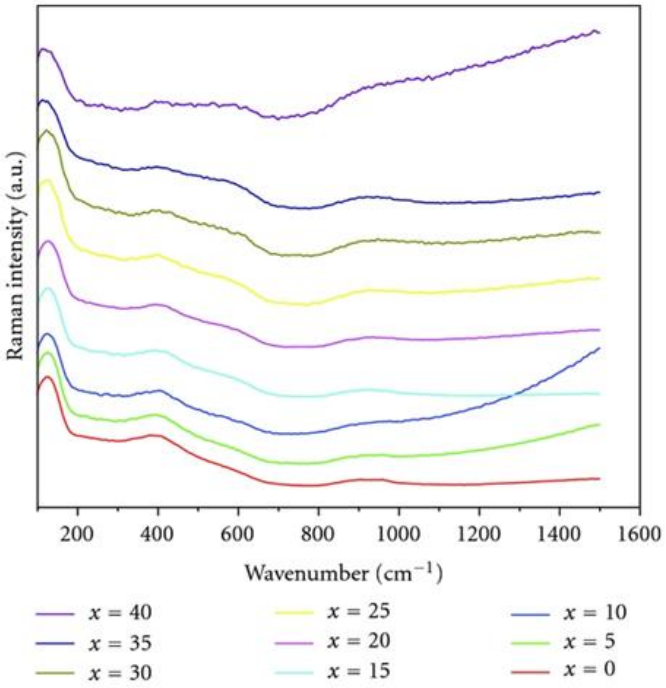

FIGURE 4: Raman spectra at room temperature for various $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ crystal compositions.[27]

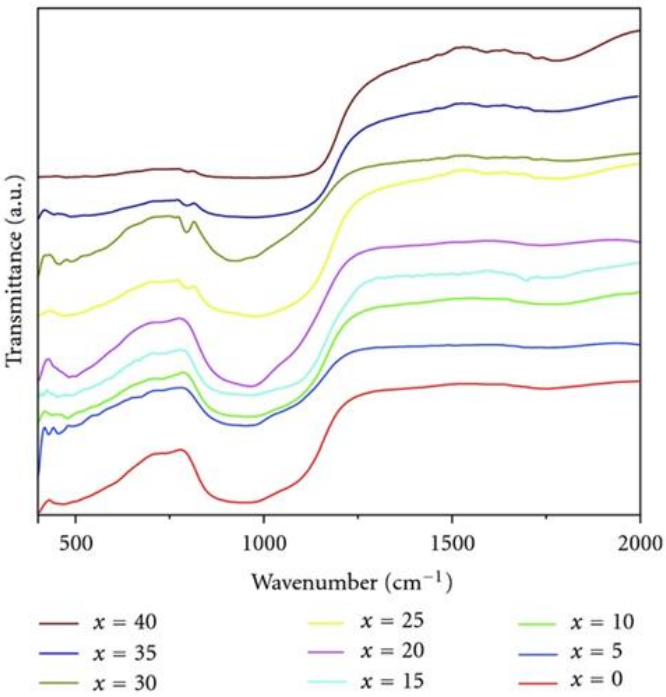

FIGURE 5: Infrared spectrum for various compositions of $40SiO_2\ .xZnO.(60-x)Bi_2O_3$ at room temperature.[27]

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, bands ranging from 425 to 550 cm^{-1} to 800 to 1200 cm^{-1} are attributed to Bi–O–Bi and Bi–O BiO_6 octahedra vibrations [17, 20, 23]. In BiO_3 pyramidal units, Ardelean et al.[24] recorded a band at 715 cm^{-1} owing to symmetric stretching vibrations of the Bi-O bond. Thus, the tiny kink found in all the glass compositions at 720 cm^{-1} can be ascribed to symmetrical stretching vibrations of Bi-O bond in BiO_3pyramidal 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 is attributed to SiO_4 tetrahedra's asymmetric stretching vibration mode between 800 and 1200 cm^{-1}[17]. In glass samples with x=25,30,35, and 40, there is a small but well-distinguished IR band at about 800 cm^{-1}. For other glass compositions, this band is merged in the wide IR band from 800 cm^{-1} to 1200 cm^{-1}. The band is ascribed to Si–O symmetric stretched vibrations at around 800 cm^{-1} in FTIR data [25]. The research of Raman and FTIR spectra demonstrates that there are asymmetric and symmetric extended SiO_4 vibrations in all glass compositions and the input of symmetric vibrations starts to dominate with decreased Bi_2O_3. This may be due to the substitute of the bigger Bi_2O_3 molecule with a lower ZnO molecule, leading to a reduction in the stretching of the silicate network. This may lead in an enhanced compactness of the glass framework, which is also demonstrated by a reduction in molar volume and an increase in T_g. Low frequency band present in FTIR data is assigned to vibrations of Zn^{2+} metal cations at around 450 cm^{-1}in all glass samples [9]. A measure of the disturbance in the local framework is the length of Raman bands in disordered materials [26]. With a reduction in bismuth content, the Raman band length reduces indicating that the environment of bismuth in the current glass scheme is more distorted.

IV. CONCLUSION

Different studies such as X-ray diffraction, density and DSC conducted on $40SiO_2\,.xZnO.(60-x)Bi_2O_3$ for, (x=0,5,10,15,20,25,30,35,and 40) show that stable glasses are acquired for up to 40 glasses; the glass forming trend and thermal stability of these glasses increases with an rise 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. It is noted that the density of these glasses decreases with an rise in ZnO content. The input of symmetric vibrations of Si-O bonds in SiO_4 tetrahedral units dominates asymmetric vibrations when ZnO is added to the bismuth silicate structure. Bi_2O_3 plays both the former glass and the modifier role in the current study system.

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