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Structural and other physical properties of lithium doped bismuth zinc vanadate semiconducting glassy system

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HIGHLIGHTS

- Glass transition and crystallization temperature decreases with increase in Li_2O.
- VO_5 structural units are converting into VO_4 tetrahedral units.
- Bi_2O_3 is present in both BiO_6 octahedral and BiO_3 pyramidal units.

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ABSTRACT

Glass samples with compositions xLi_2O. $(100-x)$ $(50V_2O_5{\cdot}20\ Bi_2O_3{\cdot}30\ ZnO)$ have been prepared by standard melt quench technique. The amorphous nature of the glass samples has been ascertained by X-ray diffraction. It is found that density, molar volume (V_m), crystalline volume (V_c) and the difference ($V_m - V_c$) of the studied glass samples decreases with increase in Li_2O content. The glass transition temperature (T_g), crystallization temperature (T_c) and the difference ($T_c - T_g$) also decreases with increase in Li_2O content, indicating that stability and glass formation tendency decreases. Raman and IR studies reveal that on addition of Li_2O, VO_5 structural units are converting into VO_4 tetrahedral units and Bi_2O_3 is present in both BiO_6 octahedral and BiO_3 pyramidal units with Bi—O—Bi, Bi—O—V and Bi—O—Zn linkages.

Introduction

Glasses containing heavy metal oxides, mainly Bi_2O_3 has been vastly studied because of their excellent optical properties such as long wavelength cutoff, high third-order optical susceptibilities and their appropriateness in the field of glass ceramics, layers for optical and electronics devices, thermal and mechanical sensors and photonic devices [1–4]. Bi_2O_3 is not a classical network former due to small field strength of Bi^{3+} ions whereas there exists many reports in literature where it acts as a network former with $[BiO_3]$ pyramidal units in presence of oxides such as V_2O_5, PbO, B_2O_3, and SiO_2 [2,5,6]. Generally, V_2O_5 is also not known as a primary glass network former, but it forms network with other oxides like ZnO, Bi_2O_3, etc [5–7]. Recently, the structural and electrical properties of Bismuth modified zinc vanadate semiconducting glasses have been studied in detail [6,8,9]. The introduction of lithium oxide in bismuthate glasses usually enhance their electrical conductivity and make them suitable candidates for sensors and solid state electrolytes in high density batteries [10–14]. It is observed that with low Li content, Li^+ ions generally go into the structural interstices to compensate the excess negative charge of the BiO_6 octahedra [15]. So, doping of lithium in bismuth zinc vanadate semiconducting glassy system may modify the conduction mechanism. In order to explore the technological applications of lithium doped bismuth zinc vanadate glasses, the study of structural, thermal and physical properties of these glasses is mandatory.

The aim of the present paper is to study the effect of Li_2O on structural, thermal and physical properties of bismuth zinc vanadate glasses.

Experimental

Glass samples of compositions xLi_2O. $(100-x)$ $(50V_2O_5{\cdot}20\ Bi_2O_3{\cdot}30\ ZnO)$; $x = 2$, 4, 6, 8 and 10 were prepared using analar

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grade chemicals V_2O_5, Bi_2O_3, ZnO and Li_2CO_3. The weighed quantities of these chemicals in appropriate proportions were thoroughly mixed in an agate pestle–mortar. The mixture was put in a silica crucible and melted by heating in a muffle furnace; the temperature was raised slowly to 1050 °C, where it was maintained for 1 h and melt was shaken frequently to ensure proper mixing and homogeneity. The melt was then poured on to a stainless steel block and quickly pressed with another stainless steel block at room temperature. The color of the pressed samples was found to be black.

X-ray diffraction of the samples was taken using the Rigaku Table-Top X-ray diffractometer. Density (ρ) of the samples was measured by Denver Instruments (model no. SI-234) physical balance by Archimedes principle with taking xylene as the buoyant fluid. The different characteristics temperatures like glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and liquidus temperature (T_l) were measured from differential scanning calorimetry (DSC) by TA instruments, model no. Q600 SDT, at a heating rate of 20 °C/min and in the N_2 ambience. Infrared transmission spectra were recorded at room temperature on Perkin Elmer model no. 5700 FTIR spectrometer over the spectral range 400–1250 cm^{-1}. For recording the Infrared transmission spectra, the powdered samples were thoroughly mixed with KBR in the ratio 1:20 by weight and pellets were made under a uni-axial pressure of 9–10 tons. The number of scans taken for each spectrum was 32. The Raman spectra of the polished samples were recorded using Renishaw Invia Reflex Micro Raman spectrometer with Ar ion laser (514 nm) under back scattering configuration over the spectral range 50–1125 cm^{-1}. The FTIR and Raman spectra were found to be consisting of broadened bands that are comprised of a number of overlapping peaks. In order to resolve the peaks, the deconvolution of FTIR and Raman spectra was performed using the inbuilt "multiple peaks fit" module of Origin Pro 8.6 software. The detailed procedure of deconvolution has been published elsewhere [16]. The statistical validation of the fitting has also been tested by applying the *F*-test [16,17].

Results and discussion

X-ray diffractograms (XRDs) of glasses xLi_2O. $(100-x)$ $(50V_2O_5 \cdot 20\ Bi_2O_3 \cdot 30\ ZnO)$; x = 2, 4, 6, 8 and 10 are shown in Fig. 1, the presence of a broad band and no sharp peaks, confirmed the amorphous nature of the prepared samples. Density is explained in terms of a competition between the masses and size of the various structural units present in the glass and measure of how tightly the ions and ionic groups packed in the structure. The values of density (ρ) measured for all the glass samples are presented in Table 1 with probable error of ±0.001 gm/cm^3. Perusal of the data presented in Table 1 shows that density of the glass samples decreases with increase in Li_2O content. This is not an unexpected result as Li_2O (lighter material) replaces the parent $(50V_2O_5 \cdot 20\ Bi_2O_3 \cdot 30\ ZnO)$ heavier composition in the present glass system. The molar volume (V_m) of the prepared samples was calculated using the following relation [18]

$$V_m = \sum_i x_i M_i / \rho \quad (1)$$

where x_i is the mole fraction and M_i is the molecular weight of ith component and ρ is the density of the sample. The values of V_m so calculated are given in Table 1 the crystalline volume (V_c) is given by the formula

$$V_c = \sum_i x_i V_i \quad (2)$$

where V_i is the molar volume of ith component in the crystalline phase. The calculated values of crystalline volume V_c are also given in Table 1. The values of molar and crystalline volume have been plotted in Fig. 2 for all compositions. The molar volume of the glass samples was found to decrease with increase in Li_2O content. Similar results have been reported in literature for Bi_2O_3—Li_2O/Na_2O—ZnO—B_2O_3 glasses [19,20]. Perusal of the data plotted in Fig. 2 indicates that molar volume of all the studied glass samples is greater than the corresponding values of V_c, indicating the presence of excess structural volume in these samples; this is the characteristics of their glassy nature. Whereas, the difference of V_c and V_m i.e. $(V_m - V_c)$ represented by ΔV, decreases with increase in lithium content, indicating the decrease in glassy nature.

The glass forming ability and thermal stability of the glasses can be determined from the characteristic temperatures viz T_g, T_c, T_m and T_l. The values of T_g, T_c, T_m and T_l have been determine from the DSC curves as shown in Fig. 3 for the glass sample with x = 2 and are presented for all the studied glass samples in Table 1. The higher value of difference of T_c and T_g i.e. ΔT $(T_c - T_g)$ hampers the process of crystallization and hence favors the glass formation [6]. Perusal of the data presented in Table 1, it is observed that both T_g and ΔT for the studied glass compositions decreases with increase in Li_2O content signifies the decrease in glass formation tendency and thermal stability. The assertion of the molar and crystalline volume about the glass formation tendency is supported by the results of thermal analysis. The variation in the T_g may also be accredited to change in tightness of packing in the oxide network which may be measured in terms of the oxygen packing density (OPD) given by the following relation [21]

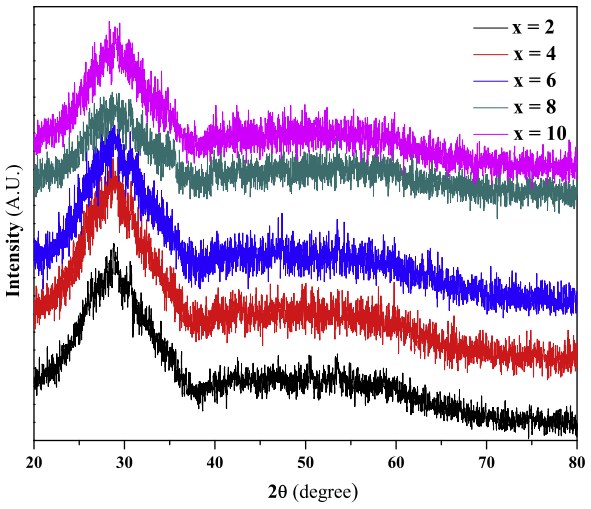

Fig. 1. XRD of different xLi_2O. $(100-x)$ $(50V_2O_5 \cdot 20\ Bi_2O_3 \cdot 30\ ZnO)$ glass compositions.

Table 1
Density (ρ), molar volume (V_m), crystalline volume (V_c), ΔV (V_m–V_c), oxygen packing density (*OPD*), glass transition temperature (T_g), crystalline temperature (T_c), ΔT ($T_c - T_g$) melting temperature (T_m) and liquidus temperature (T_l) of xLi_2O. $(100-x)$ $(50V_2O_5 \cdot 20\ Bi_2O_3 \cdot 30\ ZnO)$ glasses with different values of x.

Parameters	X = 2	X = 4	X = 6	X = 8	X = 10
ρ (gm/cm^{-3})	4.516	4.502	4.484	4.466	4.445
V_m (cm^3/mol)	45.375	44.719	44.103	43.483	42.880
V_c (cm^3/mol)	40.332	40.124	39.911	39.692	39.467
ΔV (cm^3/mol)	5.043	4.595	4.192	3.791	3.413
OPD (gm atm/l)	73.531	73.218	72.829	72.438	72.007
T_g (°C)	308	303	298	293	290
T_c (°C)	368	356	350	340	336
ΔT (°C)	60	53	52	47	46
T_m (°C)	590	595	573	565	534
T_l (°C)	625	627	594	589	554