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Structural and electric–dielectric properties of B_2O_3–Bi_2O_3–Fe_2O_3 oxide glasses

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ABSTRACT

In the present study, glasses with composition $(80\text{-}X)\cdot B_2O_3\cdot XBi_2O_3\cdot 20Fe_2O_3$ ($X=10$, 15 and 20 mol%) have been prepared by the conventional melt quenching technique. The glassy state of the samples is characterized using DTA and X-ray diffraction. The infrared spectra of these glasses are recorded over a continuous spectral range (400–2000 cm^{-1}) as an attempt to study their structure systematically. Systematic variation in density and molar volume in these glasses indicates the effect of Bi_2O_3 on the glass structure. It is found that the thermal stability decreases with increasing Bi_2O_3 content. From the electric–dielectric measurements, it is found that σ_{dc}, $\sigma_{ac}(\omega)$ decrease and $(\theta_D/2)$, increases with increasing Bi_2O_3 content. It is also observed that the dielectric constant, ε_1 (ω), and the loss factor, tan δ, decreases with increasing Bi_2O_3 content in this glassy system.

1. Introduction

B_2O_3 is one of the most important glass formers incorporated into various kinds of glass systems as a flux material, in order to attain materials with specific physical and chemical properties suitable for high-technological applications. The boron atom in borate crystals and glasses, usually coordinated with either three or four oxygen atoms, forming [BO_3] or [BO_4] structural units [1–4]. These two fundamental units can be combined arbitrary to form either the so-called super structure or different B_xO_y structural groups like boroxol ring, pentaborate, tetraborate, diborate groups, etc. the number of structural units depends on the total concentration of the added modifiers. On the other hand, glasses containing the heavy metal oxide (Bi_2O_3) have attracted considerable attention, due to their wide applications in the field of glass-ceramics, thermal and mechanical sensors, reflecting windows, or their use as layers for optical and opto-electronic devices, etc. [5,6]. As reported earlier, Bi_2O_3 is not a classical glass former, due to high polarizability and small field strength of Bi^{3+} ions, in the presence of conventional glass formers (such as B_2O_3, SiO_2, etc.) it may build a glass network of [BiO_n] ($n=3$, 6) pyramids [7–9]. Because of its dual properties, as a modifier with [BiO_6] octahedral and as glass former with [BiO_3] pyramidal units, bismuth ions may influence the electrical properties of oxide glasses [10]. However, the structural role played by Bi_2O_3 in glasses is complicated and poorly understood. This is because the [BiO_n] polyhedra are highly distorted due to the pair lone electrons [11]. Transition metal ions are being extensively used in the present day to probe the glass structure, since their outer d-electron orbital functions have broad radial distribution and due to their high sensitive response to the changes in the surrounding actions [12]. Among various transition metal ions, iron ions have strong bearing on electrical, optical and magnetic properties [13]. The present work has been carried out to investigate the effect of bismuth ions on the density, molar volume, electric–dielectric properties and structural properties of the ternary B_2O_3–Bi_2O_3–Fe_2O_3 glass system.

2. Experimental procedures

The ternary $(80\text{-}X)\cdot B_2O_3\cdot XBi_2O_3\cdot 20Fe_2O_3$ ($X=10$, 15 and 20 mol%) system is prepared and the obtained samples are coded by the symbols BBF1, BBF2 and BBF3, respectively. The preparation is carried out by melting homogeneous mixtures of reagent grade B_2O_3, Bi_2O_3 and Fe_2O_3 in porcelain crucibles, using an electric furnace at 1200 °C for 1 h. The melt is quenched between the two pre-cooled copper plates in air to form ($2\times 2\times 2$ mm^3) sample. The prepared samples are powdered to suit the X-ray, DTA and IR measurements. The formation of glass (non-crystallinity) is confirmed by the X-ray diffraction measurement of the as quenched samples, using a Philips X-ray diffractometer PW/1710 with Ni filtered, Cu Kα radiation ($\lambda=1.542$ Å) powered at 40 kV and 30 mA. Since the XRD results are not presented here.

The densities of the glass samples are measured using the suspension weight method based on the Archimedes principle,

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using toluene as an immersion liquid whose density is known (0.868 g/cm^3).

The calorimetric measurements are carried out using the Shimadzu (50) differential thermal analysis with an accuracy of ±0.1 K. The calorimeter is calibrated using the well-known melting temperatures and melting enthalpies of zinc and indium supplied with the instrument. The value of the glass transition, T_g, the crystallization extrapolated onset, T_c, and the crystallization peak, T_p, temperature is determined with an accuracy ±2 K by using the microprocessor of the thermal analyzer. The infrared (IR) absorption spectra of the glasses in the wave number range (from 400 to 2000 cm^{-1}) with a resolution of 4 cm^{-1} are measured at room temperature by an infrared spectrophotometer type JASCO, FT/IR-430 (Japan). For the electrical measurements, the glass samples are polished to obtain optically parallel surfaces of 1.5 mm thickness. The total conductivity, σ_{tot}, dielectric constant, $\varepsilon_1(\omega)$, and loss factor, tan δ, of the investigated glasses are measured by computerized LCR Bridge MODEL SR 720. Silver paste has been coated on both faces of the pellet, in order to achieve the best electrical contact.

3. Results and discussion

3.1. Density and molar volume

The change in density with composition in oxide glass system can be expressed in terms of apparent volume occupied by 1 g atom of oxygen (molar volume V_m), which can be calculated from the density and composition using the following formula:

$$V_m = \Sigma(n_i M_w)/\rho \tag{1}$$

where, M_w, is the molecular weight of oxide, n_i, is the molar fraction and, ρ, is the density of the sample. Both density and molar volume increase with increasing Bi_2O_3 content. This may be due to the higher molecular mass of Bi_2O_3 when compared to B_2O_3 [11–15]. The values of the density and the molar volume are listed in Table 1.

3.2. DTA measurements

Fig. 1 shows the DTA trace of the $70B_2O_3\cdot10Bi_2O_3\cdot20Fe_2O_3$ (BBF1) glass sample at 10 K/min heating rate as an example. The investigated glass sample exhibits glass transition temperature, T_g, followed by two crystallization peaks temperature, T_{p1}, and, T_{p2}. The inset in this figure shows the variation of the glass transition temperature, T_g, as a function of Bi_2O_3 concentration. It is found that the thermal transition data, T_g, T_c, T_{p1} and T_{p2} are shifted to lower temperature with increasing Bi_2O_3 content [16]. This means that the thermal stability of the investigated glasses decreases with increasing Bi_2O_3 content. The decreasing values of, T_g, with increasing Bi_2O_3 content are assigned for the following reasons. The increase in the inter-ionic bond distance is attributed to the larger ionic size of Bi^{3+} (0.108 nm) than that of B^{3+} (0.02 nm) [17]. The bond strength plays a competitive role in decreasing, T_g. The bond strengths of Bi–O and B–O are 80.3 and 192.7 kcal mol^{-1}, respectively [18], so the decrease in, T_g, is attributed to the replacement of a B–O linkage by the weaker Bi–O linkage. Similarly, the observed decrease in, T_g, for glasses that are studied may be due to the increasing number of non-bridging oxygen atoms.

Table 1
The density and molar volume of the (80-X)$\cdot B_2O_3\cdot XBi_2O_3\cdot20Fe_2O_3$ (X=10, 15 and 20 mol%) glass samples.

Sample code	M_w g/mol%	ρ g/cm^3	V_m cm^3/mol%
BBF1	127.27	3.04	41.86
BBF2	147.1	3.46	42.5
BBF3	166.90	3.68	45.35

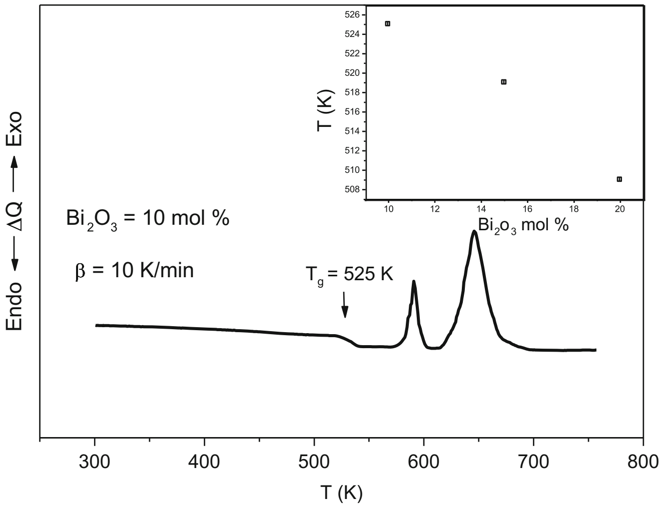

Fig. 1. The DTA trace of the $70B_2O_3\cdot10Bi_2O_3\cdot20Fe_2O_3$ as quenched glass sample at 10 K/min heating rate. The inset shows the relation between the glass transition temperature, T_g, and Bi_2O_3 content.

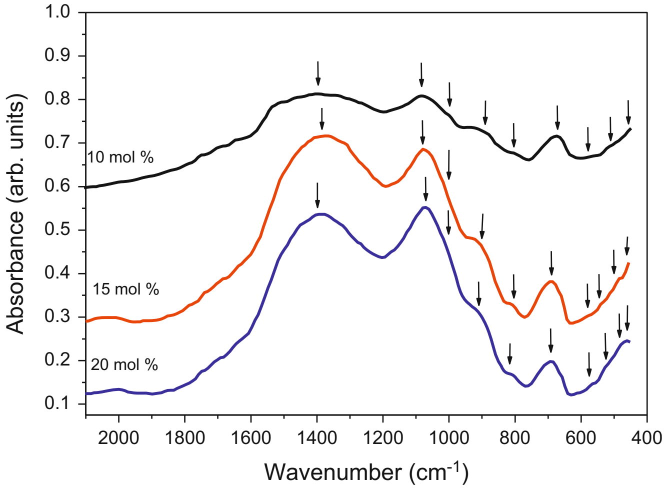

Fig. 2. Infrared absorption spectra of the (80-X)$\cdot B_2O_3\cdot XBi_2O_3\cdot20Fe_2O_3$ (X=10, 15 and 20 mol%) glass samples.

3.3. Infrared spectral studies

In order to determine main features concerning the local structure of glasses under study FTIR absorption measurements are carried out. The room temperature IR spectra in the region (from 400 to 2000 cm^{-1}) of the studied samples (BBF1, BBF2 and BBF3) are shown in Fig. 2. According to the IR structural studies at around ~465 cm^{-1}, a band appeared and this band can be attributed to the vibration of Fe–O bonds of FeO_6 units (GNM) [19–21]. Also it is observed that, at around ~480 cm^{-1}, a band appeared and this band can be attributed to the Bi–O bonds vibration in BiO_6 units [22].

The band around ~530 cm^{-1} is assigned to the Bi–O bending vibrations in BiO_6 units [23]. At around ~558–657 cm^{-1}, bands appeared and these bands may be attributed to the vibration Fe–O