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Structural and dielectric properties of $(100 - x)B_2O_3$-$(x / 2)Bi_2O_3$–$(x / 2)Fe_2O_3$ glasses and glass-ceramic containing $BiFeO_3$ phase

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ABSTRACT

Glasses of the compositions $(100 - x)B_2O_3$-$(x / 2)Bi_2O_3$–$(x / 2)Fe_2O_3$ with x = 50, 60 and 70 (in mol%) were prepared. The glassy phase of the samples was established by X-ray diffraction (XRD) and Differential thermal analysis (DTA) studies. The formation of the $BiFeO_3$ phase inside the glass matrix (glass-ceramic) by the heat treatment of the sample at x = 60 was identified by XRD, DTA and Fourier transform infrared (FTIR) studies. FTIR results revealed that the glass samples are composed of BO_3, BO_4, BiO_3, BiO_6, FeO_4 and FeO_6 basic structural units. The trends of the glass transition temperature (T_g), density (ρ), molar volume (V_m), oxygen packing fraction (OPD) and theoretical optical basicity (Λ_{th}) were discussed in terms of the structural modifications that take place in the glass matrix. The variation of the dielectric constant (ε_r), dielectric loss ($\tan\delta$) and the ac conductivity of the glass samples cannot be explained on the basis of the distance between iron ions (R_i) only but on the space charge polarization. The dielectric properties of the glass-ceramic were affected by the presence of $BiFeO_3$ phase inside the glass matrix.

1. Introduction

Borate glasses containing heavy metal and transition metal oxides have attracted much attention because of their manifold possible applications [1,2]. Boron trioxide (B_2O_3) is known as a very good glass former and is characterized by a large variety of structural units [3,4]. These units such as diborate, triborate, and tetraborate make the borate glasses act as one of the best choices for incorporated both heavy metal and transition metal oxides [5]. Among the heavy metal oxides, Bi_2O_3 is known as an unconventional glass former because of the small field strength of Bi^{3+} ions and is characterized by a high density, high polarizability and excellent IR transmission [6–8]. The Bi_2O_3 structure in the glasses have two possible coordinations [BiO_3] pyramidal and [BiO_6] octahedral units because of its dual role, one as modifier with BiO_6 and the other as glass former with BiO_3 structural units [9,10]. These properties make the borate glasses containing Bi_2O_3 oxides have wide range of applications such as thermal and scintillation detectors in high-energy physics [7]. In addition to, the transition metal oxide Fe_2O_3 is characterized by multiple valence states and act as both network former and glass modifier [6,11]. These properties make the borate glasses containing Fe_2O_3 oxide have strong bearing on electrical and magnetic properties as well as used to formulate a suitable glass matrix for storage media for nuclear wastes [10,11]. H. H. Qiu et al. [1] have employed press quenching technique to obtain Fe_2O_3–Bi_2O_3–B_2O_3 system of glasses. They found that the glass formation region was determined to be in the range of composition as $0 \le Fe_2O_3 \le 40$ mol%, $0 \le Bi_2O_3 \le 100$ mol% and $0 \le B_2O_3 \le 100$ mol%. Moreover, the presence of different values of the activation energy for two temperature regions and the variations of dielectric constant in glass system were interpreted to be due to the formation of non-bridging oxygen and phase separation, respectively.

The glass-ceramic containing multiferroic such as $BiFeO_3$ have been widely used in developing new devices and expected to be used in various application [12,13]. The glass crystallization method is one of the most appropriate ways of synthesizing the multiferroic glass-ceramic with fine grain without pores and defects at relatively low temperature [13]. A. A. Egorysheva et al. [13] have used glass crystallization method for the first time to obtain the new composite material containing of $BiFeO_3$ crystallites inside the glass matrix. They found that the phase equilibrium and glass formation region of the Bi_2O_3–Fe_2O_3–B_2O_3 system (0–50 mol% B_2O_3) and the $BiFeO_3$ crystallites grow in anisotropic glass-ceramic. Moreover, the magnetic properties of $BiFeO_3$ crystals phase in the glass matrix are similar to those of multiferroic $BiFeO_3$ crystalline nanoparticles. Takahashi et al. [12] have prepared the $2Bi_2O_3$–$2Fe_2O_3$–1BaO–$2B_2O_3$ system and fabricate the polycrystalline material consisting of $BiFeO_3$ phase via glass-

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ceramics processing. They found that the crystallization of the $BiFeO_3$ phase is obtained at low temperature (480 °C) compared with the temperature of $BiFeO_3$ phase formation by solid state method. Additionally, they found that also the coexistence of both ferroelectricity and ferromagnetism in the glass-ceramics consisting of $BiFeO_3$ phase.

Despite numerous studies on the B_2O_3–Bi_2O_3–Fe_2O_3 glass system, to the best of our knowledge there is no report describing the influence of both highly Bi_2O_3 and Fe_2O_3 in these glasses. Besides, there is few works available about preparation of $BiFeO_3$ crystal phase inside the glass matrix (glass-ceramic). Therefore, the objective of the present work is to synthesize glasses of the compositions $(100 - x)B_2O_3$-$(x/2)Bi_2O_3$–$(x/2)Fe_2O_3$ with x = 50, 60 and 70 (in mol%) and study the influence of both highly Bi_2O_3 and Fe_2O_3. In addition to this study also aiming to fabricate the $BiFeO_3$ phase inside the glass matrix (glass-ceramic) by the heat treatment of the sample at x = 60 mol%. In this study, the glass and glass-ceramic samples were comprehensively investigated by means of X-ray diffraction (XRD), Differential thermal analysis (DTA), Fourier transform infrared (FTIR), Ac conductivity and dielectric properties.

2. Experimental procedures

2.1. Samples preparation

Glass samples with the molar composition $(100 - x)B_2O_3$-$(x/2)Bi_2O_3$–$(x/2)Fe_2O_3$ with x = 50, 60 and 70 (in mol%) were prepared by melt quenching method. The glass samples under investigation were prepared from reagent grade B_2O_3 (99.99%), Bi_2O_3 (99.99%) and Fe_2O_3 (99.95%). The stoichiometric amounts of these chemicals were milled in an agate mortar. These batches were melted in porcelain crucible at 1050 °C for 1 h in an electric furnace in air. The melt was quickly poured on a copper plate and then pressed by another one. To obtain partially glass-ceramic sample for x = 60, smaller lots were heat treated in air for 5 h at 823 K (HT823) on the basis of the DTA results.

2.2. Samples characterization

X-ray diffraction (XRD) patterns of the glass and glass-ceramic samples were performed by Philips type PW3710 diffractometer using CuKα radiation at room temperature. The differential thermal analysis (DTA) of the glass and glass-ceramic samples were performed by Shimadzu DTA-50 analyzer with heating rate 40 K/min and an accuracy of ± 1 K. The density (ρ) of the glass samples at room temperature were determined by the Archimedes's method using toluene as an immersion liquid ($\rho_{toluene}$ = 0.866 g/cm^3). The molar volume (V_m) of the glass samples has been calculated using the relation

$$V_m = \sum_i (X_i M_T)/\rho \quad (1)$$

where x_i is the molar concentration and M_T is the total molecular weight of the ith component. The random errors in the density measurements are evaluated by taking the standard deviation of the mean of the density values for three specimens of each concentration. The oxygen packing fraction of the glass samples has been calculated using the relation

$$OPD = 1000C(\rho/M) \quad (2)$$

where C is the number of oxygens per formula unit. The oxygen molar volume of the glass samples has been calculated using the relation

$$V_0 = \left(\sum_i (X_i M_i)/\rho\right)\left(1/\sum_i (X_i n_i)\right) \quad (3)$$

where n_i is the number of oxygen atoms in each oxide. The theoretical optical basicity (Λ_{th}) of the glass samples has been calculated using the relation

$$\Lambda_{th} = X_{B_2O_3}\Lambda_{B_2O_3} + X_{Bi_2O_3}\Lambda_{Bi_2O_3} + X_{Fe_2O_3}\Lambda_{Fe_2O_3} \quad (4)$$

where X_{B2O3}, $X_{Bi2O3}$and X_{Fe2O3} are the equivalent fractions of the different oxides and Λ_{B2O3}, $\Lambda_{Bi2O3}$and Λ_{Fe2O3} are the optical basicity values which equal 0.425, 1.19 and 1.02 respectively [1,14]. The oxide ion polarizability (α_0) of the glass samples has been calculated using the relation which suggested by Duffy [14,15].

$$\Lambda_{th} = 1.67\left(1 - \frac{1}{\alpha_0^2}\right) \quad (5)$$

The FTIR absorption spectra of the glass and glass-ceramic samples in the 400–860 cm^{-1} wavenumber range with a resolution of 2 cm^{-1} were recorded by a JASCO FTIR-430 spectrophotometer using KBr pellets. The obtained spectra are deconvoluted to enable us to know the structural groups of the glass and glass-ceramic samples. The Ac conductivity and dielectric measurements of the glass and glass-ceramic samples were carried out using a Stanford Research RCL Bridge (Model: SR-720) as a function of temperature (300–675 K) and frequency (0.120–100 k Hz).

3. Results and discussion

3.1. XRD and DTA, studies

Fig. 1(a) and (b) shows the XRD patterns of the $(100 - x)B_2O_3$-$(x/2)Bi_2O_3$–$(x/2)Fe_2O_3$ with x = 50, 60 and 70 (in mol%) glass samples. From Fig. 1(a), it noticed that the XRD pattern for glass samples exhibit broad hump without any crystalline peaks, which indicate the amorphous nature of the glass samples. From Fig. 2, it noticed that the XRD patterns for the glass-ceramic sample at x = 60 are not fully amorphous and contain some crystalline peaks [12,13]. It can be seen that all the peaks in Fig. 2 correspond to XRD spectrum of rhombohedral $BiFeO_3$ with space group *R3c* (card number 72-2035) [12,13,16]. But there is shift in XRD peak positions towards higher angles than those of the card number 72-2035 [16]. These shifts may be due to the presence of amount of strain which arising out of the anisotropic growth of $BiFeO_3$ phase in glass matrix during heat treatment.

Fig. 2 shows the DTA curves of the $(100 - x)B_2O_3$-$(x/2)Bi_2O_3$–$(x/2)Fe_2O_3$ with x = 50, 60 and 70 (in mol%) glass samples. From this figure, it is noticed that the DTA curves exhibit one endothermic dip which represents the glass transition temperature (T_g). At still higher temperatures for x = 0.50 and 0.60, these curves exhibit shoulder and exothermic peaks (T_{p1} and T_{p2}) which can be attributed to the crystallization of two phases. Thus, the shoulder and exothermic peak (T_{p1} and T_{p2}) may be due to the formation of the $BiFeO_3$ and $Bi_2Fe_4O_9$ phases, respectively [12]. These results are agreement with those reported for $2Bi_2O_3$–$2Fe_2O_3$–1BaO–$2B_2O_3$ glass by Takahashi et al. [12]. For x = 0.70, the curve exhibits three exothermic peaks (T_{p1}, T_{p2} and T_{p3}) which may be attributed to the crystallization of three phases. The thermal characteristic temperatures of the DTA curves for glass samples are listed in Table 1. From this table, it can be seen that the decrease in T_g with increasing Fe_2O_3 and Bi_2O_3 content on expense of B_2O_3. It is known that, there is a correlation between T_g and both the change in the coordination number of the network former and the number of nonbridging oxygen atom [17]. Thus, the decrease of T_g can be attributed to the increase of the number of Bi—O linkages (the bond strength of Bi—O is 81.9 kcal/mol) which are weaker than B—O linkages (the bond strength of B—O is 192.7 kcal/mol) [17,18]. In addition to, the change in the coordination number of the boron, bismuth and iron ions and the number of nonbridging oxygen atom in the glass matrix with increasing Fe_2O_3 and Bi_2O_3 content, which are an agreement with the following IR results [19]. From Table 1, it is noticed that the values of T_{p1} and T_{p2} shift to lower temperatures with increasing Fe_2O_3 and Bi_2O_3 content which indicate lower thermal stability [18].

The DTA curve of the glass-ceramic sample is shown in Fig. 3. From this figure, it can be seen that the clear glass transition and