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Role of Er^{3+} and Bi^{3+} ions on thermal and optical properties of $Li_2B_4O_7$ glasses: Structural correlation

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ABSTRACT

Glasses with general formulae $xBiCl_3$-(100-x)$Li_2B_4O_7$ where $10 \le x \le 30$ and x Er_2O_3-(10-x)$BiCl_3$-90$Li_2B_4O_7$, where $0.1 \le x \le 0.5$ mol% have been prepared to study the effect of $Er_2O_3/BiCl_3$ on their physical, thermal and optical properties. Thermal stability parameter (ΔT) extracted from DSC thermograms reveals that the ΔT (> 100°C) depends on Er_2O_3 content and the glasses are suitable for fiber drawing process. Optical properties of both the investigated glass systems exhibit composition dependent trends and the properties are critically dependent on polarizabilities and ionicity of the dopant ions. The variations observed in the physical properties of investigated glasses were correlated to the structural changes occur due to the addition of $BiCl_3/Er_2O_3$. ^{11}B MAS NMR studies reveal the opening up of a tightly bound $[B_4O_7]^{2-}$ structural units with the formation of NBOs in the network. The variation of N_4 (fraction of 4-coordinated boron to the total boron content) with $BiCl_3/Er_2O_3$ clearly indicates the presence of different proportion of 3- and 4-coordinated borons in the glass network.

1. Introduction

Glasses containing heavy metal oxides such as Bi_2O_3, PbO, WO_3, TeO_2, GeO_2, etc. are promising materials for infrared technologies, lasers and non-linear optics [1]. Bismuth doped glasses have attracted considerable attention in recent years because they serve as new medium for broad band optical amplifier in the telecommunication window [2–4]. Further, Bi^{3+} ions acts as emission center over several other materials [5, 6]. Bi_2O_3 has low field strength and high polarizability but it cannot be vitrified by itself. It forms good glasses in presence of archetypal glass formers such as B_2O_3, P_2O_5, GeO_2, SiO_2 etc. Generally, Bi_2O_3 tends to occupy octahedral coordination and the additional oxygen required for the coordination is provided by host matrix [7]. The boron in modified borate glasses coordinates with either 3- or 4- oxygen atoms to form $[BO_{3/2}]^0$ or $[BO_{4/2}]^-$ structural units. The conversion of $[BO_{3/2}]^0 \rightarrow [BO_{4/2}]^-$ is maximum when the ratio $\frac{\text{modifier oxide}}{B_2O_3}$ is equal to 0.5. Further increase in modifier oxide results in re-conversion of $B_4 \rightarrow B_3$, this anomaly is termed as "boron anomaly". At this composition the structure is dominated by diborate ($R_2B_4O_7$) units where modifier R = Na, Li, Rb, K, etc., in which case the trigonal and tetrahedral boron are in the ratio 1:1 [8]. Therefore, it is interesting to study optical properties of $BiCl_3$-$Li_2B_4O_7$ glasses.

Rare earth oxide doped glasses have potential technological applications viz. optical amplifiers, remote sensing thermometers, solid state lasing materials, etc. [9–11]. Also, the doping of rare earth ions improves chemical durability, glass forming ability and thermal stability [9]. Recent literature reports reveal that doping with Er_2O_3 enhance the glass formation range (25–65 mol% B_2O_3) [12, 13] and exhibit broad band properties [14, 15]. Dimitrov and Komatsu [16] have reported that B_2O_3 glasses containing Bi_2O_3 possess high refractive index, polarizability, optical basicity and low metallization criterion which find applications in opto-electronic devices. These glasses are stable hosts for getting efficient luminescence in rare earth ion devices [17–20]. The emission quantum efficiency from a given energy level depends on phonon energy of the host matrix. This can be achieved by introducing heavy metal ions because nonradioactive loss will be small [21–24].

2. Experimental

$Er_2O_3/BiCl_3$ doped lithium diborate glasses in the system of $xBiCl_3$-

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(100-x) $Li_2B_4O_7$ where $10 \le x \le 30$ and x Er_2O_3-(10-x) $BiCl_3$-90$Li_2B_4O_7$ where $0.1 \le x \le 0.5$ were prepared by well-known melt quenching technique. Bismuth chloride ($BiCl_3$), lithium carbonate (Li_2CO_3), boric acid (H_3BO_3) and $Er(NO_3)_35H_2O$ (all analytical grade) were weighed according to the stoichiometry of the glass system and thoroughly mixed and ground using pestle agate mortar. The ground mixture was poured into a silica crucible. The crucible was then kept inside an electric furnace set at a temperature of 400 °C to decompose Li_2CO_3 and $Er(NO_3)_35H_2O$ to Li_2O and Er_2O_3. The batches were melted at 1000 °C for about 15 min to ensure homogeneity and then poured on to a preheated brass plate and quenched. All the glass samples were then annealed at 180 °C for 3 h to remove the thermal strains, developed during quenching.

The amorphous nature of the glass samples was tested using powder X – ray diffractometer. ^{11}B MAS NMR spectra of the invested glasses were recorded using solid state high resolution Jeol-II spectrometer operating at 9.4 Tesla and the MAS rotor speed is 10 kHz. The pulse frequency of 400 MHz is employed. The optical absorption spectra of glasses were recorded using a Perkin Elmer (Lamda 35) spectrometer in the UV–Vis-NIR region in the range of 200–1000 nm. The glass transition temperature (T_g) and thermal stability parameter, $\Delta T = T_x - T_g$, where T_x is onset of crystallization temperature were determined using the thermograms obtained from Differential Scanning Calorimeter (Perkin Elmer DSC -2) tuned at a heating rate of 5 K/min. Densities of annealed glass pieces free from cracks and air bubbles were measured by Archimedes method with xylene as the immersion liquid. The molar volume of each composition was calculated as $V_m = M/\rho$, where M is the molecular weight of the formula unit.

3. Results and discussion

X-ray diffraction patterns of two representative samples are presented Fig.1. The spectra contains broad hump-like features at low angles ($2\theta = 20° - 30°$) without any sharp peaks, which confirms amorphous nature of the investigated glasses [25]. Sample code, composition, density (ρ), molar volume (V_m), glass transition temperature (T_g), crystallization temperature (T_x), thermal stability parameter (ΔT) and oxygen packing density (OPD) are presented in the Table. 1.

3.1. Physical and thermal properties

Density and molar volume are important physical parameters which have been used to explore the degree of structural compactness or openness of the glass network. The density and molar volume of LB glasses lies in the range of 2.55 to 3.042 g/cm^3 and 32.22 to 44.108 cm^3 respectively. In the case of LBE glasses the values lie in the range of 2.536 to 2.587 g/cm^3 and 32.54 to 31.943 cm^3 for density and molar volume respectively. The variation of density and molar volume in LB and LBE series are as shown in Fig. 2 and Fig. 3 respectively. Interestingly in LB series both density and molar volume increases with $BiCl_3$ mol%. The variations seen in density can be attributed to the substitution of heavier $BiCl_3$ (315.74 g) to $Li_2B_4O_7$ (169.12 g) and the increase in density is 19% when $BiCl_3$ is varied from 10 to 30 mol%. The molar volume increases by 28.83% for the corresponding increases in $BiCl_3$ content. This increase in molar volume is due to the incorporation of Cl^- into interstitials of the network and structural transformations occurred. It is evident from Fig. 3 that the density increases while molar volume decreases when Er_2O_3 is substituted to $BiCl_3$. The observed increase in density is only 2%, when heavier Er_2O_3 (382.56 g) is substituted to $BiCl_3$ from 0.1 to 0.5 mol%. The volume increasing effect is primarily due to the formation of non-bridging oxygens (NBOs) created in the structure during the modification of the glasses structure.

Oxygen packing density (OPD) is a measure of compactness of the glass network, which can be calculated using the relation, $OPD = \frac{1000}{M.V} \times n_0$,where n_0 is number of oxygen atoms per formula unit. The calculated values of OPD for LB and LBE glasses are presented in Table 1. It can be seen from Table 1 that OPD depends on $BiCl_3$ content. As the concentration of $BiCl_3$ increases OPD decreases, which can be attributed to the fact that as $BiCl_3$ is substituted to $Li_2B_4O_7$, the tight diborate units (B_4O_7) are replaced by Bi^{3+} and Cl^-. Occupation of Cl^- in the interstitials of network causes the volume increasing effect. This results in the formation of a more open macromolecular network leading to the decrease in T_g [26, 27]. There is a marginal increase in OPD with Er_2O_3 content indicating the structural compactness due to efficient packing of oxygens leading to structural rigidity, which is also reflected in variations observed in thermal stability. $\Delta T = T_x - T_y$ is chosen as a measure of glass formability or thermal stability. It is desirable for a glass host to have ΔT as large as possible. The glass to which ΔT is 100 $^\circ C$ is stable against devitrification and they are more stable for fiber drawing. The DSC thermograms obtained by plotting heat flow versus temperature (LB and LBE glasses) are shown in the Fig. 4 and inset. The glass transition temperature (T_g) determined as the intersection of the extra plotted linear portions around the glass transition region lie in the range of 314 to 283 °C for LB glasses and for that of LBE glasses the values lie in the range 382 to 370 °C. The thermal stability (ΔT) of LB glasses lies in the range (120 to 127 °C) and increases with increasing $BiCl_3$ content. Whereas in the case of LBE glasses, ΔT lies in the range 167 to 170 °C and increases with Er_2O_3 concentration. It is evident from Fig. 5 that T_g decreases with dopant concentration in both LB and LBE glasses and $(T_g)_{LB} < (T_g)_{LBE}$ indicating that the addition of halide lowers T_g. The thermal stability increases with increasing $BiCl_3/Er_2O_3$ content and $(\Delta T)_{LBE} > (\Delta T)_{LB}$, indicating that Er_2O_3 containing glasses are more stable than halide doped glasses. This is attributed to the fact that the lower T_g in network is due to the volume increasing effect with increasing halide content. All though, T_g decreases with $BiCl_3/Er_2O_3$content but thermal stability (ΔT) and strength increases in both LB and LBE glasses. It is necessary to investigate of glasses for better understanding of the kinetics of glasses. Further, the desirable condition for fiber drawing process is that ΔT > 100°C. It is evident from the Fig. 6 that both LB and LBE glasses possess ΔT > 100 °C, indicating that the investigated glasses are satisfying the condition for conventional fiber drawing process [28–35]. In support of the above, Table 2 presents the literature values of ΔT for different glass matrices.

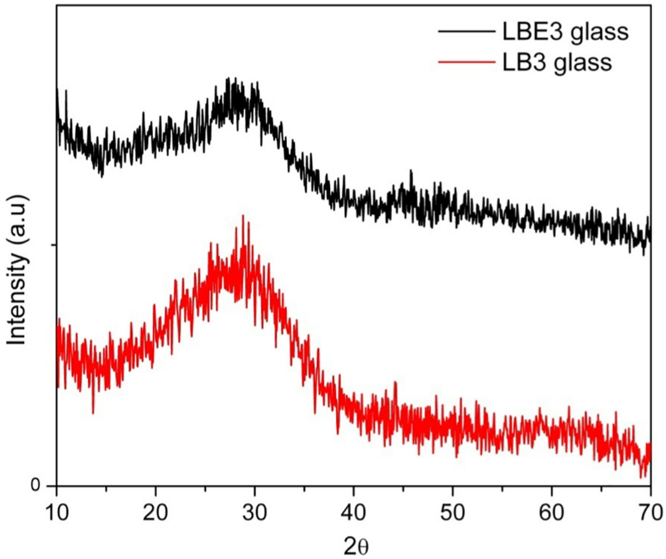

Fig. 1. XRD pattern of LBE3 and LB3 glasses.

3.2. Optical absorption

In both LB and LBE glasses the absorption edge is extended over a wide wavelength range seen in the UV-region. LB glasses exhibit blue