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Structural, dielectric, impedance and optical properties of $CaBi_2B_2O_7$ glasses and glass-nanocrystal composites

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ABSTRACT

Optically clear glasses were fabricated by quenching the melt of $CaCO_3$–Bi_2O_3–B_2O_3 (in equimolecular ratio). The amorphous and glassy characteristics of the as-quenched samples were confirmed via the X-ray powder diffraction (XRD) and differential scanning calorimetric (DSC) studies. These glasses were found to have high thermal stability parameter (S). The optical transmission studies carried out in the 200–2500 nm wavelength range confirmed both the as-quenched and heat-treated samples to be transparent between 400 nm and 2500 nm. The glass-plates that were heat-treated just above the glass transition temperature (723 K) for 6 h retained ≈60% transparency despite having nano-crystallites (≈50–100 nm) of $CaBi_2B_2O_7$ (CBBO) as confirmed by both the XRD and transmission electron microscopy (TEM) studies. The dielectric properties and impedance characteristics of the as-quenched and heat-treated (723 K/6 h) samples were studied as a function of frequency at different temperatures. Cole–Cole equation was employed to rationalize the impedance data.

1. Introduction

The suitability of lithium and strontium borate glasses as effective hosts to evenly disperse the nano/microcrystals of the Aurivillus family of oxides was demonstrated [1–3]. In the process of exploring the possibilities of using the other borates such as $CaBi_2B_2O_7$ (CBBO) and $SrBi_2B_2O_7$ (SBBO) as hosts for the nanocrystallization of Aurivillus family of ferroelectric oxides, to begin with we investigated $CaBi_2B_2O_7$ in its glassy state apart from studying the physical properties of these glasses consisting of 50–100 nm sized crystallites of the same composition. Recently, the non-linear optical property of crystalline CBBO has been reported by Barbier and Cranswick [4]. The CBBO crystallizes in an orthorhombic polar crystal class associated with the space group $Pna2_1$. The objective of investigating into the glasses and the glass nano/microcomposites of polar materials has been to critically examine them from their pyroelectric [5,6], non-linear optic [7,8] and electro-optic [9–11] properties view point. It was known that the dielectric properties of these materials have direct influence on the device characteristics. The measurements concerning the dielectric constant, dielectric loss and electrical conductivity of CBBO glasses over the range of frequencies and temperatures that are normally of interest in the application of these materials were carried out. We have also examined the structural aspects of the glass and crystalline samples using X-ray powder diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). An attempt has been made to rationalize the temperature dependence of the impedance behavior in terms of the Cole–Cole equation.

2. Experimental

CBBO glasses were fabricated via the conventional melt-quenching technique. For this, $CaCO_3$ (99.95%, Aldrich); Bi_2O_3 (99.9%, Merck); and B_2O_3 (99.9%, Aldrich) were thoroughly mixed and melted in a platinum crucible at 1373 K for 1 h. Melts were quenched by pouring on a steel plate and pressed with another plate to obtain 1–1.5 mm thick glass-plates. X-ray powder diffraction (XRD) study was performed at room temperature on the as-quenched samples to confirm their amorphous nature. The differential scanning calorimetric (DSC) (Model: Diamond DSC, PerkinElmer) run was carried out in the 550–900 K temperature range at a heating rate of 10 K min^{-1} on the as-quenched CBBO glass-plate. The experiment was conducted in dry nitrogen ambience. The as-quenched glass-plates weighing 15 mg were used for the experiments.

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Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies of the as-quenched and heat-treated glasses were conducted using a JEOL JEM 200CX microscope. Dielectric and impedance studies on the as-quenched glass samples were carried out as a function of frequency (1 kHz to 10 MHz) and temperature using an impedance/gain phase analyzer (HP 4194A). For this purpose the samples were sputtered with gold and silver epoxy was used to bond silver leads to the samples. The as-quenched glass samples were mirror polished prior to the optical measurements. The optical spectra of these glasses were recorded using a UV–Vis spectrophotometer (PerkinElmer LAMBDA 750 UV/VIS/NIR) in the 200–2500 nm wavelength range. The refractive indices of the as-quenched polished samples were determined using Brewster angle method at λ = 543 nm using He:Ne laser. It is to be noted that this λ is slightly away from the absorption edge of the CBBO glasses. The optical band gap energy, E_{opt}, was calculated for the as-quenched glasses under study.

3. Results and discussion

3.1. Thermal studies

The glass transition (T_g), the onset of the crystallization (T_{cr}) and the peak crystallization (T_p) temperatures were determined using DSC studies. Fig. 1 shows the typical DSC trace obtained for the as-quenched CBBO glass-plate. A significant difference that exists between the glass transition, T_g (686 K) and the onset of the crystallization T_{cr} (825 K) temperatures accounts for good thermal stability of the CBBO glasses. A parameter usually employed to estimate the glass stability is the thermal stability (ΔT) [12] which is defined by

$$\Delta T = (T_{cr} - T_g) \tag{1}$$

Larger the difference between the T_{cr} and T_g, higher the thermal stability of the glasses.

According to Saad and Poulin [13], the thermal stability parameter (S) could be expressed as

$$S = \frac{(T_p - T_{cr})(T_{cr} - T_g)}{T_g} \tag{2}$$

S reflects the resistance to devitrification of the glass. In the above equation ($T_p - T_{cr}$) is related to the rate of devitrification transformation of the glassy phases. The value of S calculated using Eq. (2) is 4.86, for the present glasses (CBBO) reflecting the higher thermal stability than the other Bi_2O_3–B_2O_3 (S = 3.7) based glasses [14].

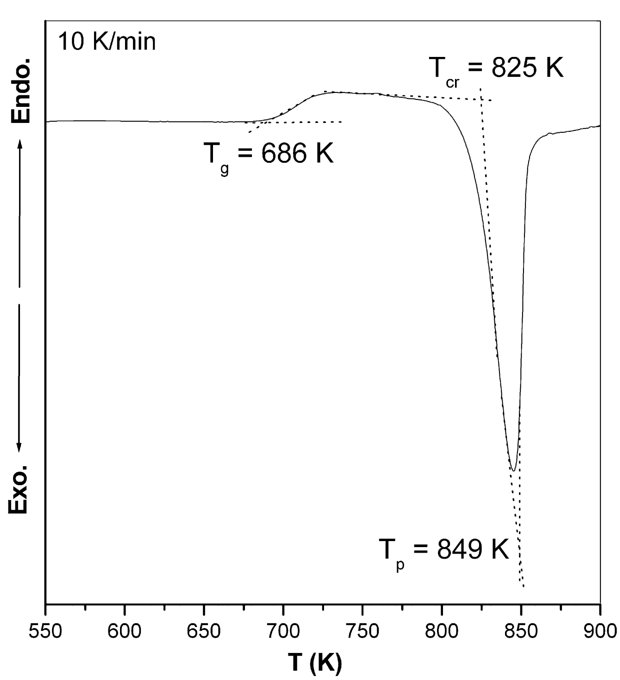

Fig. 1. DSC trace for the as-quenched CBBO glass-plate.

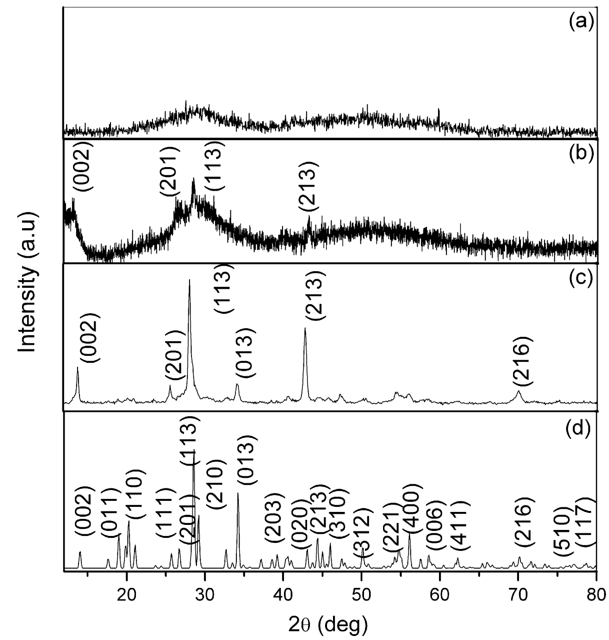

Fig. 2. XRD patterns for the (a) as-quenched glass-plate, (b) heat-treated glass-plate at (723 K/6 h) CBBO, (c) glass-plate heat-treated at 923 K/12 h, and (d) polycrystalline powdered sample of CBBO.

3.2. X-ray structural studies

XRD patterns obtained at room temperature for the CBBO glass-plates are depicted in Fig. 2(a)–(d). Fig. 2(a) shows the XRD pattern recorded at room temperature for the as-quenched glasses. The pattern clearly reveals their amorphous nature. Interestingly, the sample heat-treated at 723 K (just above the T_g) for 6 h shows X-ray peaks (Fig. 2(b)) that are assigned to the (0 0 2), (2 0 1), (1 1 3) and (2 1 3) planes of polycrystalline CBBO. These peaks are fairly broad, suggesting the presence of fine crystallites of the CBBO phase. The crystallite size as determined by Scherrer analysis at this stage of heat treatment is about 60 nm. Fig. 2(c) shows the XRD pattern recorded for the samples heat-treated at 923 K (beyond the T_{cr}) for 12 h which could be index to an orthorhombic CBBO phase. The XRD pattern obtained for a polycrystalline CBBO prepared by the solid-state reaction route is included in the same figure (Fig. 2(d)) for comparison. These results clearly demonstrate that it is possible to obtained transparent CBBO glasses embedded with about 60 nm sized crystallites of the same composition by heat treating the as-quenched glasses just above their glass transition temperature.

3.3. Transmission electron microscopic studies

Transmission electron micrographs along with the corresponding selected area electron diffraction (SAED) patterns for the as-quenched and heat-treated CBBO glasses are shown in Fig. 3(a) and (b) respectively. The electron diffraction pattern of the as-quenched CBBO glass (Fig. 3(a)) confirms its amorphous nature which is consistent with that of the XRD studies. The electron micrograph that is obtained for the heat-treated (723 K/6 h) glass reveals the existence of nano-crystallites (≈50–100 nm) within the glass matrix (Fig. 3(b)). The corresponding SAED pattern shows the presence of sharp diffraction rings and the calculated d-spacings are in good agreement with that of the polycrystalline CBBO.

3.4. Optical studies

The optical clarity of both the as-quenched and heat-treated samples prompted us to carry out optical transmission studies to