Structural, dielectric and optical properties of transparent glasses and glass-ceramics of SrBi$_2$B$_2$O$_7$

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**Abstract**

Optically clear glasses of SrBi$_2$B$_2$O$_7$ (SBBO) were fabricated via the conventional melt-quenching technique. The amorphous nature of the as-quenched samples of this compound was confirmed by X-ray powder diffraction (XRD) studies. Its glassy nature was established by differential scanning calorimetry (DSC). However, the optical microscopy revealed the presence of isolated hexagonal shaped crystallites especially at the edges of the as-quenched glasses. The glass plates that were heat-treated around the onset of the glass transition temperature (670 K) for 12 h yielded transparent (C24/60% transmission) glass-ceramics of SrBi$_2$B$_2$O$_7$ (SBBO) with well defined microstructure. These were found to be textured associated with an orientation factor of about 0.77 (77%). The optical transmission studies carried out in the 100–1200 nm wavelength range confirmed both the as-quenched and heat-treated samples to be transparent from 400 to 1200 nm. The dielectric properties of the as-quenched as well as the heat-treated (670 K/12 h) samples were studied as a function of frequency (100 Hz–10 MHz) at various temperatures (303–873 K). The dielectric dispersion at higher temperatures in the as-quenched glass was rationalized using Jonscher's dielectric dispersion relations. The prefactor $A(T)$ and the exponent $n(T)$ in the Jonscher's expression were found to be maximum and minimum respectively around the crystallization temperature ($T_{cr}$) of the as-quenched SBBO glasses.

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**1. Introduction**

Transparent glass-ceramics have been of industrial interest because of their potential use in a variety of devices [1,2]. These are becoming increasingly important because of the flexibility that is associated with this route of fabricating intricate sizes and shapes as per the requirement. A number of glass-ceramics, based on well known ferroelectric crystalline phases (LiNbO$_3$ [3], LaBGeO$_5$ [4], SrBi$_2$Nb$_2$O$_9$ [5], Bi$_2$WO$_6$ [6], etc.) were fabricated and their polar and electro-optic properties were reported. In general, there are two approaches that are known in the literature to obtain transparent glass-ceramics. The first one has been to exercise a strict control over the crystallite size in such a way that it is comparable with the wavelength of the visible light at which these are intended to be employed. Alternate approach would be to grow the crystals of the desired size within the bulk glass matrix (same/different chemical composition) wherein the refractive index mismatch between these two phases would be significantly small. For certain applications even surface crystallized glasses would be interesting. For instance, transparent surface crystallized glasses were found to exhibit promising non-linear optical properties [7].

Recently SrBi$_2$B$_2$O$_7$ (SBBO) and CaBi$_2$B$_2$O$_7$ (CBBO) phases that were synthesized by the solid-state reaction route were reported to be non-centrosymmetric [8]. SrBi$_2$B$_2$O$_7$ (SBBO) crystallizes in P6$_3$ space group with $a = 0.91404(4)$ and $c = 1.30808(6)$ nm, while the other compound CaBi$_2$B$_2$O$_7$ is orthorhombic associated with Pna$_2$$_1$ space group. Keeping the potential applications of transparent glass-nano/microcrystal composites in view, attempts were made to fabricate SrBi$_2$B$_2$O$_7$ glasses and glass-microcrystal composites. In this paper, we report the results pertaining to the glass formation and evolution of crystalline SBBO phase in its own glass matrix. Structural, thermal, optical and dielectric properties of the as-quenched as well as the transparent glass-ceramics comprising micrometer sized crystallites of SrBi$_2$B$_2$O$_7$ are elucidated. An attempt has been made to rationalize the dielectric behavior in terms of Jonscher’s model.

**2. Experimental**

Glasses under investigation were fabricated by two different routes. In the first one, the pre-reacted SrBi$_2$B$_2$O$_7$ polycrystalline powders were melted and quenched into glasses. In the other...
method the glasses were made from constituent carbonates/oxides and the results of which are reported here. Stoichiometric amounts of reagent grade Bi₂O₃, SrCO₃, and B₂O₃ were mixed well by using mortar and pestle in the acetone medium and the resultant mixture was melted in a platinum crucible at 1273 K for about 30 min. The melt was then poured on to a stainless steel plate and pressed with another one to obtain transparent glass plates of 1–2 mm thick. These as-quenched samples were annealed at 623 K (below the glass transition temperature) for 12 h and cooled slowly to ease out the thermal stresses associated with them. The glassy nature of the as-quenched samples was confirmed by subjecting the samples to differential scanning calorimetric (DSC) (Perkin Elmer, Diamond DSC) analysis, in the 600–795 K temperature range at a heating rate of 10 K/min. X-ray powder diffraction (XRD) studies were performed using Philips PW1050/37 diffractometer (CuKα radiation) to confirm the amorphous nature of the as-quenched glasses and also the crystalline nature (phase-analysis) of the heat-treated samples.

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. Microstructural analyses on the heat-treated sample were done by using a JEOL JSM-5600LV scanning electron microscope (SEM) and alone with an optical microscope (Olympus BX51). Dielectric studies on the as-quenched and heat-treated glass samples were carried out as a function of frequency (10⁵–10⁷ Hz) 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 sample. 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 (Bruker IFS 66v/s Vacuum Fourier Transform Interferometer) in the 100–1200 nm wavelength range. The optical band gap energy, E_{opt}, was calculated for the as-quenched and heat-treated glasses under study.

3. Results and discussion

3.1. Thermal studies

DSC studies were carried out to determine the glass transition (T_g) onset of crystallization (T_c) and the peak crystallization (T_p) temperatures. Fig. 1(a) and (b) shows the DSC traces obtained for the as-quenched bulk glass-plate and pulverized glass. Both the samples exhibit endotherms (associated with the glass transition) which confirm the glassy nature of the as-quenched samples. However, in the case of the bulk platy (Fig. 1(a)) sample the thermal behavior is sluggish and the T_g and T_c are broad suggesting the surface crystallization mechanism to be dominant in this system. Also there is a considerable amount of upward shift in the crystallization peak of the bulk platy sample.

When a glass crystallizes during a DSC run, the heat of crystallization is evolved and one or more exothermic peaks appear on the DSC curve. The glass devitrification is as a result of two individual processes: nucleation and crystal growth. Nucleation can occur either in the volume or on the surface of the glass sample. The total number of nuclei per unit volume is the sum of surface nuclei, proportional to the specific surface area of the sample, and of the bulk nuclei formed during the heat-treatment [9]. It is known that the shape of the exothermic peak is strongly influenced by the crystallization mechanism. Sharp and broad peaks correspond to the bulk and surface crystallization, respectively [9]. Further, higher the number of nuclei, the lower the peak temperature, T_p [10].

The endotherms are followed by exotherms in both the cases which were confirmed (by XRD) to be associated with the crystallization of SBBO phase. The values for T_g, T_c, and T_p for the powdered glass are 670, 713, and 724 K respectively whereas for the bulk platy sample these values are 670, 730, and 764 K.

3.2. X-ray structural studies

Fig. 2(a)–(e) shows the XRD patterns obtained for the as-quenched and heat-treated (670 K (around T_g)/12 h) SBBO glasses along with that of the polycrystalline SBBO powder prepared via the solid-state reaction route. The pattern (Fig. 2(a)) recorded for the powdered sample of the as-quenched glass clearly establishes the overall amorphous nature of the sample.

Interestingly, the XRD pattern recorded for the bulk platy sample of the as-quenched glass shows the presence of a sharp peak (at 2θ = 41.28°) which suggests the presence of either isolated crystallites or completely oriented surface crystallized sample. Indeed this sharp XRD peak for the as-quenched glass-plate matches well with that of the (006) reflection of the polycrystalline SBBO and for comparison the XRD pattern of the polycrystalline SBBO (obtained by solid-state reaction route) is depicted in Fig. 2(e).

The XRD pattern corresponding to the bulk glass-plate that is heat-treated at 670 K/12 h is shown in Fig. 2(c). It shows the presence of sharp Bragg-peak indicates the crystallization of the glass. All the peaks are found to match with that of SBBO which confirms that the crystallized phase is indeed that of SBBO. The (001) peaks are found to be more intense than the rest of the peaks unlike in the case of the heat-treated pulverized glass (Fig. 2(d)) implying that there is a preferred orientation of crystallites on the surface of the sample. In order to reinforce these facts, XRD patterns were recorded for the samples after removing the surface layers of a few micrometers thick. These patterns did not reveal the presence of any well defined diffraction peaks suggesting that the crystallization is mostly confined to the surface at this stage of heat-treatment (670 K/12 h).
The preferred orientation of the crystallites (texture) was quantified by using Lotgering’s method, in which the orientation factor \( f \) is given by the formula

\[
f = \frac{(P - P_0)}{1 - P_0},
\]

where \( P = \sum I_{hkl} \) for the textured sample and \( P_0 = \sum I_{hkl} \) for the randomly oriented SBBO powder prepared via the conventional solid-state reaction route. \( I_{hkl} \) is the sum of X-ray intensities, reflected from \( (00l) \) family of planes and \( I_{hkl} \) is the sum of X-ray intensities reflected from all the planes. The value of \( f \) is 0.77 for the sample heat-treated at 670 K/12 h, implying that 77% of the crystallites are oriented with their \( a-b \) plane parallel to the surface of the glass-plate. To confirm the phase purity of the crystallized SBBO phase, the heat-treated sample was powdered and subjected to XRD study and the corresponding pattern is shown in Fig. 2(d). This pattern is in complete agreement with that of the polycrystalline SBBO powder which confirms the absence any secondary phase.

### 3.3. Transmission electron microscopic (TEM) studies

Fig. 3 shows the transmission electron micrographs of the as-quenched and heat-treated samples accompanied by the corresponding selected area electron diffraction (SAED) patterns. The TEM micrograph (Fig. 3(a)) along with the corresponding selected area electron diffraction (SAED) pattern which shows the absence of any sharp diffraction rings confirm its amorphous nature. The heat-treated samples exhibit the presence of crystallites embedded in an amorphous matrix and a typical micrograph recorded for one such sample is shown in Fig. 3(b). The corresponding SAED pattern shows the presence of sharp diffraction rings and the calculated d-spacing (1.086, 1.811, 2.71 and 4.075 Å) are in good agreement with that obtained for a polycrystalline SBBO.

### 3.4. Optical and scanning electron microscopic studies

To have more insight into the nature of the crystallization and the morphology of the crystallites, the as-quenched and heat-treated samples were subjected to optical and scanning electron microscopic studies. The optical micrograph of the as-quenched glass-plate is shown in Fig. 4(a). It indeed reveals the presence of isolated hexagonal shaped crystallites of more than 10 μm size on the surface (mostly confining to the edges) of the sample. The morphology of the crystallites is hexagonal and is a true reflection of the crystal structure of the SBBO, which is reported to be hexagonal. Also these crystallites are found to be slightly birefringent on examination under crossed polars. The optical micrograph of the heat-treated (670 K/12 h) glass-plate (Fig. 4(b)) shows a mosaic of crystallites on the surface of the sample. The average crystallite size is in the range of 5–12 μm and is consistent with the presence of sharp peaks in the XRD patterns. It is to be emphasized that these samples are still optically transparent (≈60% transmission). The surface and the cross-sectional SEM micrographs of the heat-treated (670 K/12 h) samples are shown in Fig. 5(a) and (b), respectively. The micrograph shows well crystallized surface with closely packed grains (5–12 μm sized) and this corroborates the optical micrographic studies. The cross-sectional SEM micrograph reveals the surface crystallization layer thickness to be about 30–40 μm. It also clearly exhibits the presence of well defined growth fronts with the crystallites growing towards the bulk of the sample from the surface.

The development of the texture is generally attributed to the surface crystallization where the growth is confined to the surface associated with a two dimensional spread. A plane crystallization front of many crystalline grains moved inward into the glass and the grains of this layer grow in competition with each other, similar to the grain growth of a polycrystalline film on a substrate. The texture evolves in such a way that the grains with the fast growing c-axis orientation perpendicular to the growth front are preferentially selected. Therefore the crystallites on the surface grow mainly in the lateral direction. When the crystallized surface area reaches a critical limit, impingement precludes further growth of the faster growing crystals, and only the crystals that are oriented with the c-axis normal to the surface continue to grow towards the specimen center, forming a crystallized layer. The optical clarity of both the as-quenched and heat-treated samples prompted us to carry out optical transmission studies to quantify its transmission range vis-à-vis optical band gap.

The optical transmission spectra (uncorrected for reflection losses) recorded for the as-quenched and heat-treated (at 670 K/12 h) SBBO samples in the wavelength range of 100–1200 nm are shown in Fig. 6(a) and (b), respectively. In the case of as-quenched SBBO glass, the percentage transmission is almost constant in the 1200–500 nm range vis-à-vis optical band gap. The optical band gap that is observed is around 2.9 eV. The preliminary work that was carried out with regard to the establishment of the non-centrosymmetric nature of this glass-ceramic using SHG study as a tool yielded interesting positive results. The detailed investigations have been in progress and the full report of this work along with IR studies will be reported shortly.
Fig. 3. TEM micrographs and the corresponding SAED patterns for (a) the as-quenched and (b) heat-treated (670 K/12 h) SBBO glasses.

Fig. 4. Optical micrographs of the (a) as-quenched and (b) heat-treated (670 K/12 h) SBBO glasses.

Fig. 5. Scanning electron micrographs of the SBBO heat-treated (670 K/12 h) glasses (a) top view of the crystallized surface, and (b) cross-sectional view of crystallized surface.
3.5. Dielectric studies

The frequency dependence of the dielectric constant ($\varepsilon_r$) at various temperatures (303–803 K) for the as-quenched and heat-treated (670 K/12 h) samples are depicted in Fig. 7(a) and (b), respectively. In general, the dielectric constant decreases with increase in frequency at all the temperatures under study for both the as-quenched and heat-treated glasses. At low temperatures (room temperature to 403 K) the dielectric constant is independent of frequency. However, the dielectric constant is marginally higher ($\sim$28 at 1 kHz at room temperature) for the heat-treated glasses than that ($\sim$24 at 1 kHz at room temperature) of the as-quenched glasses. This small difference in the dielectric constant is attributed to the microstructure associated with the heat-treated glasses in which SBBO crystallites of 5–12 µm range are embedded leading to an enhanced interfacial polarization.

The variations in the dielectric loss as a function of frequency at different temperatures (303–803 K) for both the as-quenched and heat-treated glasses are depicted in Fig. 8(a) and (b), respectively. The dielectric loss data at various temperatures for the heat-treated glasses at all the frequencies under study are comparable with that of the as-quenched samples. The loss is reasonably low (0.01–0.03 at 1 kHz) in the 303–503 K temperature range at all the frequencies under study. The increase in loss is significant with increase in temperature especially at low frequencies. The variation of the dielectric constant and the loss as a function of temperature at various (100 Hz–10 MHz) frequencies for the as-quenched glasses are depicted in Fig. 9(a) and (b), respectively. The increase in dielectric constant with increase in temperature from room temperature to 600 K is insignificantly small especially at high frequencies as shown in the inset of Fig. 9(a). Subsequently, it exhibits two maxima in the 738–818 K temperature range. These temperatures are consistent with that of $T_g$ and $T_{cr}$ of the as-quenched glasses. However, the onset of the anomalies is in the vicinity of the glass transition temperature (as confirmed by the DSC studies) of the as-quenched glass-plate. There is a slight upward shift in the onset of the dielectric maximum temperature with increase in frequency. The loss also increases steeply around the glass transition and crystallization temperatures of the as-quenched glass. Broad peaks in the dielectric loss are observed which are indeed incident at lower temperatures than those of dielectric maxima, referred to relaxation phenomena, shift towards higher temperatures with increasing frequency, akin to that observed in other ionic conducting systems [12]. The incidence of the dielectric anomaly around the $T_{cr}$ in general was explained in the literature in terms of conduction related polarization. Doi [13] suggested that this type of polarization could be treated as ori-
presentation polarization of the pseudo-dipoles created by the non-bridging oxygens. As the viscosity of the system drastically decreases in this temperature range and as a result, the dipoles and ions can easily respond to the external field. The temperature-dependent dielectric behavior of the heat-treated samples (Fig. 10(a) and (b)) is similar to that of the as-quenched sample. However, the maximum that is observed in \( \varepsilon_r \) is beyond the glass transition temperature of the as-quenched glass. The temperature at which this maximum occurs is well within the area under the exothermic curve obtained in the DSC experiment suggesting that this is due to the crystallization of the residual glass in the heat-treated one. The same sample on cooling down to the room temperature and on repeating the dielectric experiment as a function of temperature did not exhibit a peak in \( \varepsilon_r \).

3.5.1. Dielectric dispersion relations and rationalization of the experimental results

The dielectric dispersion with frequency is significant at higher temperatures (Fig. 7(a)), suggesting that this phenomenon at low frequencies is coupled with space charge effects. The dielectric behavior of the present glass is rationalized by invoking Jonscher’s universal law [14]

\[
C = A(T) (i\omega)^{n(T)^{-1}},
\]

\( n(T) \) is the temperature-dependent exponent and the prefactor \( A(T) \) determines the strength of the polarizability arising from the universal mechanism. In this case, the complex dielectric constant as a function of the radian frequency \( (\omega = 2\pi f) \), is given by the following relation (taking into account the true dc conductivity contribution)

\[
\varepsilon' = \varepsilon_{\infty} + \frac{\sigma}{i\omega\varepsilon_0} + \frac{a(T)}{\varepsilon_0} (i\omega)^{n(T)^{-1}},
\]

where \( \varepsilon_{\infty} \) is the ‘high frequency’ value of the dielectric constant, \( \sigma \) is the dc conductivity and \( a(T) \) can be given as \( A(T) L / S \), where \( S \) and \( L \) are the area and the thickness of the sample respectively. The real and imaginary parts of the complex dielectric constant are given by the following relations:

\[
\varepsilon_r' = \varepsilon_{\infty} + \sin \left( n(T) \frac{\pi}{2} \right) \omega^{n(T)^{-1}} a(T) / \varepsilon_0,
\]

\[
\varepsilon_i' = \frac{\sigma}{i\omega\varepsilon_0} + \cos \left( n(T) \frac{\pi}{2} \right) \omega^{n(T)^{-1}} a(T) / \varepsilon_0,
\]

where the first term in Eq. (4) determines the lattice response and that in Eq. (5) corresponds to the dc conduction part, while the second term in both the equations reflects the charge carrier contribution to the dielectric constant. We have been successful in fitting the experimental dielectric data to the dielectric dispersion relations given in Eqs. (4) and (5). Fig. 11(a) and (b) show the experimental values of the real (\( \varepsilon_r' \)) and the imaginary (\( \varepsilon_i' \)) parts of the dielectric constants at 633 K as a function of frequency. The lines
in both the plots are the theoretical fits obtained using Eqs. (4) and (5). The $e_1$ value was chosen as the dielectric constant obtained at 10 MHz, as the dispersion is negligibly small around this frequency. The exponent $n(T)$ and the coefficient $a(T)$ were determined from the curve fittings. The temperature dependence of $n(T)$ and log $A(T)$ (= $a(T)$S/L) are shown in Fig. 12. The exponent $n(T)$ is almost constant up to 730 K and shows a minimum around $T_{cr}$ and subsequently increases with further increase in temperature. The plausible explanation for the observed minimum around $T_{cr}$ has been to consider the interaction of the charge carriers with the lattice. On the other hand, the prefactor $A(T)$, which determines the strength of polarizability, and the lattice contribution, $e_1$, (Fig. 13) exhibits a sharp peaks around the $T_{cr}$ has been to consider the interaction of the charge carriers with the lattice.

4. Conclusions

The as-quenched and the heat-treated (glass-ceramic) samples of SrBi$_2$B$_2$O$_7$ were transparent in the 400–1200 nm wavelength range associated with an optical band gap of 2.9 eV. The glass-ceramics were found to have a mosaic of crystallites associated with preferred orientation. The dielectric constants of both the as-quenched and the glass-ceramic at room temperature were almost independent in the 100 Hz–10 MHz frequency range. However, the dielectric relaxation that was encountered at higher temperatures was rationalized by invoking Jonscher’s universal law.

References