



Structural, optical and thermal properties of glass and anti-glass phases in strontium tellurite and borotellurite systems doped with europium



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ABSTRACT

Glass sample of the composition: 10SrO-90TeO₂ was prepared by melt-quenching technique and found to contain triangular, rectangular, and spherical shaped micro-inclusions of the average size ~803 μm in the glassy matrix. The inclusions grow to an average size of ~1347 μm and assume flower-like morphology upon adding 1 mol% Eu₂O₃ in the 10SrO-90TeO₂ sample. X-ray diffraction studies showed that the micro-inclusions exhibit sharp peaks, but their Raman spectra have broad phonon bands that are indistinguishable or very similar to that of the glassy matrix phase. The addition of 10 mol% B₂O₃ in the samples inhibits the growth of inclusions of anti-glass phases and forms purely amorphous samples. B₂O₃ significantly enhances the photoluminescence properties of Eu³⁺ doped samples. Furthermore, B₂O₃ converts the four-fold co-ordinated Te-O structural units into three-fold co-ordinated Te-O units.

1. Introduction

Tellurium oxide (TeO₂) based glasses have a wide range of applications in gas sensors, memory switching devices, upconversion lasers, and in optical waveguides due to their several attractive properties such as high thermal stability against crystallization, chemical durability, low melting points, non-hygroscopic nature, and low phonon energies etc. [1–3]. TeO₂ is a conditional glass former and it requires high quenching rate of ~10⁵ K s⁻¹ [4] to form glassy phase, however, when it is mixed with alkali, alkaline-earth, and transition metal oxides; it forms glasses easily at a moderate quenching rate of ~10² Ks⁻¹. The modifiers enhance the glass forming ability (GFA) in tellurite systems by breaking the TeO₄ structural units and by lowering the average Te-O coordination number [5]. The short-range order in tellurite glasses can be described in terms of Q_mⁿ structural units, where *n* denotes the number of bridging oxygen and *m* is the coordination number. There are five types of tellurite polyhedral units namely Q₃⁰, Q₃¹, Q₃², Q₄³, and Q₄⁴ [6,7]. The Q₄⁴ unit represents a fully interconnected network of four coordinated tellurium ion containing four bridging oxygens; Q₃² and Q₃³ polyhedra contain one non-bridging oxygen, while Q₃¹ and Q₃⁰ represent triangularly coordinated TeO₃ and TeO₃₊₁ units with one bridging oxygen and all non-bridging oxygens respectively [6]. The short-range structural variability of tellurite glasses create a range of electric-dipole environments, which make these glasses exhibit novel

optical and mechanical properties [8]. The glass forming range of SrO-TeO₂ system lies between 4.8 mol% to 11 mol% of SrO [1].

Tellurite systems are reported to form “anti-glass” materials [9–14]. An anti-glass is a solid in which the cations (Te⁴⁺, Bi³⁺, Nb⁵⁺, and Sr²⁺ etc.) have a long-range order but these are statistically distributed at their sites. On the other hand, the anions (oxygen ions) are randomly distributed in the structure resulting in anionic disorder and moreover, there is a significant concentration of oxygen vacancies [9], hence a prominent long-range order of cations contrasts with the highly disturbed short-range order of the anions i.e. there is a co-existence of order and disorder in the anti-glass materials. Due to the statistical distribution of cations among themselves and disordered arrangement of anions, the anti-glass structure generates large Debye-Waller factors in excess of that produced by the thermal motion of the atoms. This consequently produces considerable vibrational disorder and results in broad phonon bands in the Raman and infrared spectra (similar to that in glasses). However, due to the long-range order of the cations, X-ray and neutron diffraction patterns of anti-glasses exhibit sharp peaks similar to that in crystalline materials [9,11]. Very few anti-glass tellurite materials have been studied in the literature: Bi₂Te₄O₁₁ [13], SrTe₅O₁₁ [10], and LiHo_{0.045}Y_{0.955}F₄ [15] etc.

Tellurite glasses are promising host materials for the rare-earth ions due to the high rare-earth ion solubility, wide optical transmission window ~0.35 μm to 5 μm, the maximum phonon energies of less than

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780 cm^{-1} , and high refractive index which make the local fields around the rare-earth ion site more prominent, leading to the enhancement of the radiative transition rates [16,17]. Generally, highly concentrated rare-earth ion doped glasses are unstable and difficult to synthesize [17,18]. Among all the lanthanide ions, Eu^{3+} is the preferred ion probe to study the inhomogeneity and symmetry of the host matrices, because of the non-degenerate nature of the ${}^7\text{F}_0$ (ground) state and ${}^5\text{D}_0$ (excited) state, which makes its energy-level structure much simpler. The optical properties of Eu^{3+} ions are critically dependant on the local environment and chemical composition of the glass matrix, which makes them convenient to study the structure and nature of the bonds in disarrayed systems [16,17,19,20].

The co-existing anti-glass inclusions in the glassy matrix in tellurite systems [9,13] is analogous to the phenomenon of “poly-amorphism” that is observed in $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses (YAG) [21]. Polyamorphism is the existence of two or more condensed amorphous phases, which can be obtained by varying the synthesis method or by applying high pressure, intense radiation or by varying the temperature. The different phases have the same chemical composition but quite different structures and properties. The study of polyamorphic substances provides profound insights about the relationship of a liquid with its glass and on the influence of melts’ local structure on the glass forming ability. The materials that show coexisting phases can be used to produce a new class of nano to microscale composite materials with enhanced mechanical and optical properties [22,23]. Further, oxygen deficient structures such as tellurite anti-glasses are reported to show enhanced luminescence properties [24].

Therefore, it is important and interesting to study the structural, optical, and thermal properties of rare-earth ion doped glass and anti-glass materials from the fundamental point of view to understand the conditions of glass formation and for the synthesis of materials with special optical and mechanical properties. The present study aims at the elucidation of structure-property relationships in SrO-TeO_2 , $\text{SrO-B}_2\text{O}_3\text{-TeO}_2$ glass and anti-glass samples containing Eu^{3+} for luminescent applications.

2. Experimental

Glass samples of the composition: $10\text{SrO-xB}_2\text{O}_3\text{-(90-x)TeO}_2$ and $9\text{SrO-1Eu}_2\text{O}_3\text{-xB}_2\text{O}_3\text{-(90-x)TeO}_2$, where ($x = 0, 10, 20$ mol %), were prepared by melt-quenching technique. The appropriate amounts of TeO_2 (Alfa Aesar 99.9%), SrCO_3 (Sigma Aldrich India 99.9%), H_3BO_3 (Sigma Aldrich India 99%), and Eu_2O_3 (Sigma Aldrich India 99.9%) were weighed and ground in a mortar-pestle for about 30 min to obtain a homogeneous mixture. The batch mixture was then transferred to a platinum (Pt) crucible (25 cm^3) and melted at 750°C in a muffle furnace. The melt was kept at this temperature for ~ 30 min and homogenized by occasionally swirling the Pt crucible inside the furnace. The melt was subsequently poured on a heavy brass plate to obtain disk-shaped samples. The samples were immediately annealed at 250°C for 1 h to reduce thermal stresses that are generated inside the samples by rapid-quenching. Clear, bubble free, and yellow colored samples were prepared. The color of the samples lightened with increase in B_2O_3 concentration from 10 to 20 mol%. The samples were characterized by density, X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC), Photoluminescence spectroscopy (PL), optical microscopy, ${}^{11}\text{B}$ Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR), and Raman spectroscopy. The composition, density, and molar volume data of the samples is given in Table 1.

XRD studies were carried out on powdered samples on Shimadzu XRD-7000 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$) in the 2θ range of $10^\circ\text{--}65^\circ$. The X-ray tube was operated at 40 kV and 30 mA current. The scattered X-ray intensity was measured with a scintillation detector.

The optical microscope images of the two disk samples: 10SrTe and 9Sr1EuTe , that contained anti-glass inclusions were studied on a Nikon

Eclipse Ti microscope at magnifications of $40\times$, $50\times$, and $100\times$.

The density of the samples was determined at room temperature by Archimedes method using dibutylphthalate (DBP) as the immersion fluid. The error in density was in the range: ± 0.001 to 0.003 g cm^{-3} and it depended on the precision of the electronic balance (0.1 mg) and the mass of the sample. The density of each sample was calculated by using the following relation [25]:

$$\rho = \frac{W_A \rho_L}{W_A - W_L} \quad (1)$$

where ρ_L is the density of the DBP at the laboratory temperature, W_A and W_L are the weight of the sample in air and in the liquid, respectively.

The molar volume was calculated by using the following relation:

$$V_m = \frac{xM_A + yM_B + zM_C}{\rho} \quad (2)$$

where x, y, z are mol% of the components $A, B,$ and C and $M_A, M_B,$ and M_C are their respective molecular weights.

DSC studies were performed on the powdered samples on SETARAM SETSYS 16 TG-DSC system at a heating rate of $10^\circ\text{C min}^{-1}$ under air-flow conditions in the temperature range of $200\text{--}800^\circ\text{C}$. Sample amounts of 20–40 mg were taken in a platinum pan for DSC analysis. The maximum uncertainty in the measurement of glass transition temperature (mid-point), crystallization temperature (peak-point) and melting temperature (peak-point) was $\pm 1^\circ\text{C}$.

The photoluminescence (PL) spectra of strontium tellurite and strontium borotellurite disk samples containing Eu^{3+} were recorded at room temperature on the Perkin Elmer LS 55 fluorescence spectrometer. The PL spectra were recorded at an excitation wavelength of 395 nm generated by a xenon lamp. The PL studies were carried on the disk samples.

${}^{11}\text{B}$ MAS-NMR studies were performed on powdered samples using Bruker AVIII HD NMR spectrometer operating at a magnetic field of 11.74 T with a 4 mm Bruker MAS probe. The sample spinning rate was 14 kHz and Larmor frequency of ${}^{11}\text{B}$ nuclei at this magnetic field was 160.5299 MHz. Short RF pulses ($\sim 15^\circ$) with a recycle delay of 20 s were used. The NMR spectra were collected after 4096 scans and referenced to ${}^{11}\text{B}$ resonance peak in solid NaBH_4 at -42.16 ppm.

Raman studies were performed on the disk-shaped samples using Renishaw In-Via Reflex micro-Raman spectrometer. The Raman spectra were excited by 514.5 nm light generated by argon ion laser (50 mW). Measurements were carried out at room temperature using an edge filter for Stokes spectra with a diffraction grating containing 2400 lines mm^{-1} and a Peltier cooled CCD detector in an un-polarized mode using backscattering geometry. The spectra were recorded in the Raman shift range of $30\text{--}4500\text{ cm}^{-1}$ at a spectral resolution of 1 cm^{-1} .

3. Results and discussion

3.1. Structure

The XRD patterns of the samples are shown in Fig. 1. The pure 10SrTe and europium doped 9Sr1EuTe sample show several sharp peaks at $27.2^\circ, 31.6^\circ, 45.3^\circ, 53.6^\circ,$ and 56.2° superimposed on the broad hump and reveals the co-existing glass and anti-glass phases in these two samples. The sharp peaks match well with the cubic $\text{SrTe}_5\text{O}_{11}$ phase having a face-centered cubic unit cell and ‘Fm3m’ space group (powder diffraction file #36-1235) as reported by Burckhardt et al. [10]. The addition of B_2O_3 into 10SrTe and 9Sr1EuTe samples destroys the growth of anti-glass phases and the samples containing B_2O_3 show only broad humps (no sharp peaks) in the angular range of 20° to 35° , which confirms their wholly amorphous nature.

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