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Band gap and polarizability of boro-tellurite glass: Influence of erbium ions

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HIGHLIGHTS

- The glass samples having composition $30B_2O_3$–10ZnO–(60–x) TeO_2–xEr_2O_3 were prepared by melt-quench technique.
- The absorption band edge was analyzed and refractive indices were determined.
- The amorphous nature was confirmed by X-ray diffraction spectroscopy.
- The variation of density and polarizability are attributed to formation of non-bridging oxygens.

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ABSTRACT

Understanding the influence of rare earth ions in improving the structural and optical properties of inorganic glasses are the key issues. Er^{3+}-doped zinc boro-tellurite glasses with composition $30B_2O_3$–10ZnO–(60–x) TeO_2–xEr_2O_3 are prepared (x = 0, 0.5, 1, 1.5 and 2 mol%) using melt quenching technique. The physical and optical characterizations are measured by density and UV–Vis–IR absorption spectroscopy. The color of the glass changed from light yellow to deep pink due to the introduction of Er^{3+} ions. The maximum density is found to be ~4.73 g cm^{-3} for 1 mol% of Er^{3+} doping. The variations in the polarizability (6.7–6.8 cm^3) and the molar volume (27.987–28.827 cm^3 mol^{-1}) with dopant concentration are ascribed to the formation of non-bridging oxygen. This observation is consistent with the alteration of number of bonds per unit volume. The direct and indirect optical band gaps are increased while the phonon cut-off wavelength and Urbach energy decreased with the increase of erbium content. A high density and wide transparency range in VIS–IR area are achieved. Our results on high refractive index (~2.416) and polarizability suggest that these glasses are potential for photonics, solid state lasers and communications devices.

Introduction

Improving the physical and optical properties of rare-earth (RE) doped inorganic glasses received much interest due their potential applications in optical devices and laser technology [1]. RE ions are extensively used to probe the local structural variations in the host glasses due to their unique spectroscopic properties resulting from the optical transitions in the intra 4f shell [2]. For designing lasing glasses with high performance, knowing the relation between the host composition and radiative (or non-radiative) characters of the RE ions are pre-requisite [3]. In the past, many efforts are dedicated to explore the optical behavior of the Er^{3+} ions due to its broadband emission at 1.53 μm, which is ideal for applications in the field of optical data transmission. The trivalent erbium ion is one of the most important and efficient ion, and its solubility could be attained up to 10 mol% [2].

Recently, the trend is turned to add two or more glass formers to form the glass materials with modified optical properties for various scientific and technical applications. The pure borate glasses possess low refractive index, high melting point and high phonon energies ~1300–1500 cm^{-1}. They are highly suitable in designing new optical devices due to their good RE ion solubility, easy preparation on large scale shaping and cost effectiveness. However, the high vibrational energy in borate based glasses makes them unsuitable for efficient infrared to visible up-convertor. The high non-linear refractive index, low melting point and low phonon energy (~700–800 cm^{-1}) and larger refractive index of tellurite glasses compared to other oxide glasses are beneficial for achieving high rate of radiative transition of RE ions. Tellurite glasses may also be used in the production of optical fibers and planar waveguides. Boro-tellurite glass

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represents favorable compromise between the requirements of low phonon energy and a relatively high thermal stability, high chemical durability and ease of fabrication. Addition of ZnO into boro-tellurite glass network produces low rates of crystallization and increases the glass forming ability [4–6].

We report the Er^{3+} concentration dependent physical and optical properties of erbium doped zinc boro-tellurite glasses (hereafter called as ErBT). The influence of erbium ions on the density, polarizability, molar volume, direct and indirect optical band gaps, phonon cut-off wavelength and Urbach energy are analyzed and discussed.

Experimental

Zinc boro-tellurite glasses of the form $30B_2O_3$–10ZnO–$(60-x)TeO_2$–xEr_2O_3 with x from 0.0 to 2.0 mol% in steps of 0.5 are prepared by melt quenching method. The proper amounts of analytical grades zinc oxide, boric acid, tellurium dioxide and erbium oxide are melted in porcelain crucibles at 950 °C for about 15 min. The melt is stirred thoroughly for proper mixing. The glass samples are annealed for about 3 h at 300 °C to remove the thermal and mechanical stress. The density of samples is measured using the Archimedes' principle with sterilized water as immersion liquid.

Amorphous nature of the glass samples are examined by X-ray diffraction (XRD) measurements at room temperature using Bruker D8 Advance diffractometer performing by the copper target (Kα = 1.54 A1) at 40 kV and 100 mA. The elemental analysis of the glasses was characterized using energy dispersive spectrometry (SwiftED3000 EDX). UV–Vis–IR absorption spectra are recorded using a Perkin–Elmer UVPC3101 spectrophotometer in the range of 400–1800 nm wavelength.

Results and discussion

The increase in erbium content caused a change in the color of glass samples from light yellow to Navajo white. Furthermore, the addition of more than 1.0 mol% erbium trioxide changes the color of the sample from pink to deep pink. The color variation is a consequence of the presence of erbium ion having electronic excited states in the visible region. Fig. 1a shows the XRD spectra of our selective glass samples. The absence of any crystalline sharp peaks and the presence of a broad hump in the range of 20–40° confirms the amorphous nature of the ErBT samples. Fig. 1b presents the EDX of 0.5ErBT glass sample. No signal is recorded for the boron atoms in EDX spectra due to the limit of analysis by equipment for atoms as light as *B*. However, the presence of other chemical and absence of any contamination are confirmed by this method.

The density of the each glass is measured by Archimedes principle. The weight of the sample in water, *A*, and in air, *B* are used to determine the density using the relation, $\rho = \frac{A}{A-B} \times (\rho_0 - d)$, where ρ_0 is the density of immersion liquid, in this case water and d is density of air. The molar volume is calculated via, $V_m = \frac{M}{\rho}$, where M is the molecular weight of sample. The density is found to increase with the increase of Er^{3+} ions concentration up to 1 mol% as summarized in Table 1. The variation of the density is related to the substitution of TeO_2 by Er_2O_3. Since Er_2O_3 has higher molecular weight, the density is expected to increase by increasing the concentration of Er_2O_3. However, the decrease of the density after 1 mol% Er_2O_3 could be associated to the formation of non-bridging oxygen (NBO's) in the network and the clustering of the rare earth ions. (Such clustering is also responsible for luminescence quenching). Finally, it is important to note that the small variation of these parameters is due to the small change in concentration of Er_2O_3.

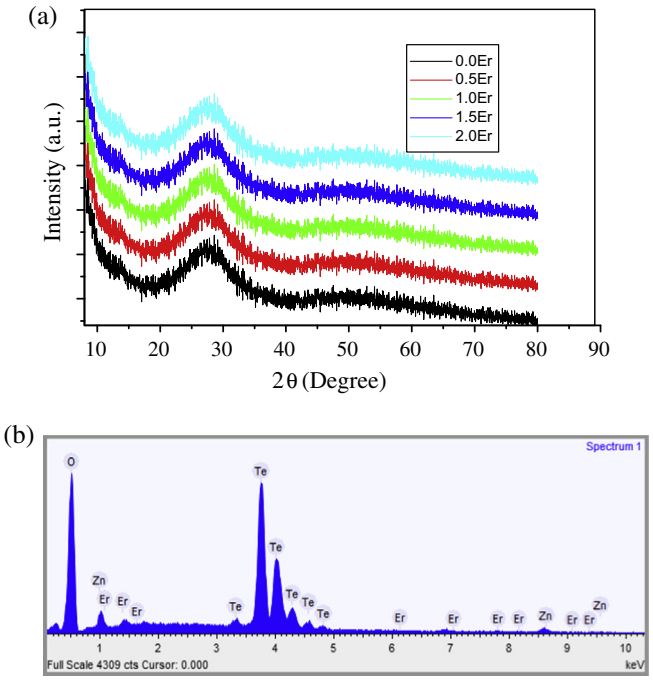

Fig. 1. XRD patterns of prepared Er^{3+}-doped zinc boro-tellurite glasses (a). EDX spectrum of sample 0.5ErBT (b).

The behavior of the molar volume that is mainly guided by the density of the glasses follows an opposite trend as expected [7]. The concentration of erbium ions can be tallied by [8]:

$$N = (\text{mol\% of dopant} \times \rho \times N_A) / (\text{Average molecular weight of glass}) \quad (1)$$

where N_A is the Avogadro's number. The structural change is determined by calculating the average boron-boron separation [9]:

$$\langle d_{B-B} \rangle = \left(\frac{V_m^B}{N_A}\right)^{1/3} \quad (2)$$

where V_m^B is the corresponding volume containing 1 mol% boron, and is obtained from:

$$V_m^B = \frac{V_m}{2(1-X_B)} \quad (3)$$

where X_B is the molar fraction of B_2O_3. The initial decrease in d_{B-B} is related to the densification of the glass. However, it increases as the Er_2O_3 concentration is increased from 1.5 to 2 mol%. Oxygen packing density (OPD) is also evaluated as [10]:

$$\text{OPD} = 1000C\left(\frac{\rho}{M}\right) \quad (4)$$

where C is the number of oxygen atom per each composition. The increase in OPD with the addition of Er^{3+} ions up to 1 mol% indicate that the non-bridging oxygens are not formed in the glasses. However, the decrease in OPD upon further addition of dopant is attributed to the existence of NBOs and broken B–O and Te–O bonds.

The average coordination number is given by [10]:

$$m = \left[\sum_i n_{ci} x_i\right] \quad (5)$$

where n_{ci} is the coordination number of the cations. The coordination number of tellurite, zinc, boron and erbium are 4, 4, 4 and 6, respectively. The average coordination number of glass samples shows steady increase with the increase of Er_2O_3 content.