Compositional dependence of density and refractive index in borotellurite glass

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Abstract - Borotellurite glasses with composition (in mol%): 57B₂O₃-20TeO₂-15Bi₂O₃-3TiO₂-(4-x)Na₂O-1TmₓOₓ⁻ₓHo₂O₃ (where x = 0, 0.5, 1.0, 1.5, 2.0, and 2.5) have been fabricated and characterized aims at studying their density, molar volume and refractive index. Glasses were fabricated by melt quenching method. Density measurements were carried at room temperature using picnometer while their refractive indices were determined by applying Brewster angle method. It is observed that both density and molar volume tend to increase with increasing Ho³⁺ ions concentration. The density, molar volume as well as refractive index of the reported glass increases from 4.72 to 4.91 g/cm³, 31.80 – 32.18 cm³/mol, 1.4906 to 1.7253, respectively, with increasing holmium oxide (Ho₂O₃) concentration. Other properties characterized the glasses were also derived, including oxygen packing density, field strength and polaron radius.

1. Introduction
Since the first demonstration of lasing properties on Nd-doped barium crown glasses by Snitzer in 1961 [1], nowadays research on rare earth doped glasses including glasses doped with Tm³⁺ and Ho³⁺ is of interest [2]. Because of shielding effects of 5s and 5p shells on the 4f electrons, absorption and emission spectra of rare earth ions doped in different glasses are unique and relatively invariant. Slightly changes usually relate to peak shifting, relative intensity and spectral bandwidth; and these depend on glass host. For this reason, rare earth doped in various glasses have been investigated. Among them, borotellurite glasses are of interest due to their unique properties, such as high mechanical strength, high solubility of rare-earth ions, low phonon energy, and high refractive index [3-5]. Having these properties, rare earth doped borotellurite glasses have been researched for tailoring many optical devices such as lasers, optical amplifier, and communication systems [6 - 9]. For this purpose, compositional dependence of optical and physical properties has received more attention [10, 11].

This paper presents the compositional dependence of the physical and optical properties of Tm³⁺-Ho³⁺ codoped borotellurite glasses. More attentions are given to study this compositional dependence on parameters such as density, molar volume, oxygen packing density, polaron radius, field strength, and refractive index.

2. Experiment
Borotellurite glasses having compositions (in mol%): 57B₂O₃-20TeO₂-15Bi₂O₃-3TiO₂-(4-x)Na₂CO₃-lTmₓOₓ⁻ₓHo₂O₃ (where x = 0-2.5 mol%) were prepared and fabricated using conventional melt
quenching method. Glasses were named G1, G2, G3, G4 and G5 for \( x = 0, 0.5, 1.0, 1.5, 2.0 \) and 2.5, respectively. For each composition, a total weight of 10 g of materials were weighed according to stoichiometric calculations. For the purpose of homogenization, mixtures were grinding using a mortar for ± 30 minutes. The mixture was then transferred to an alumina crucible and heated in an electric furnace at a temperature of 1000°C for about 60 minutes. Casting was carried out by pouring molten into a pre-heated brass mold at 250°C. Annealing was subsequently carried out at temperature 300°C for about 8 hours and then cooled to room temperature at a cooling rate 1 °C/min. For the purpose of refractive index measurement, all samples were polished down to optical quality.

Density measurement was carried out at room temperature by applying Archimedes principle. Measurement was carried out by using pycnometer and distilled water as an immersion liquid. That is by following equation [12]:

\[
\rho_g = \frac{w_a}{w_a - w_d} \rho_d
\]

where \( w_a \) is the weight of glass in the air and \( w_d \) is the weight of glass in distilled water.

Refractive index of all samples was measured at room temperature and wavelength of 632 nm. The reflected light was then plotted against the incident angle and refractive index was then calculated using Brewster’s angle method by referring to our previous paper [13].

### 3. Results and Discussion

#### 3.1. Density

Density is one of the important properties which can roughly be used to describe atomic distribution in glass matrix. In this respect, density value can be used to calculate several other physical parameters such as molar volume, polaron radius, oxygen packing density, and field strength using relation [14, 15]:

a. Molar volume (\( V_m \))

\[
V_m = \sum x_i M_i \rho_g
\]

b. Oxygen Packing Density (OPD)

\[
OPD = \frac{1000 N_d}{V_m}
\]

c. Polaron Radius (\( r_p \))

\[
r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{\frac{1}{2}}
\]

d. Field Strength (F)

\[
F = \frac{z}{r_p^2}
\]

where \( x_i \) and \( M_i \) are molar fraction and molecular weight of the \( i^{th} \) glass components, \( \rho_g \) is the glass density, \( N_d \) is number of oxygens in the glass system while \( N \) and \( z \) are concentration and atomic number of holmium ion, respectively.

Figure 1 shows the density and molar volume of Tm/Ho co-doped Borotellurite glasses containing different concentrations of \( \text{Ho}_2\text{O}_3 \) and \( \text{Na}_2\text{O} \). \( V_m, \text{OPD}, r_m \) and \( F \) were calculated using equations (2) – (5) and the results are tabulated in Table 1. From definition of density which can be deduced from equation (2) it can be understood that replacement of \( \text{Na}_2\text{O} \) (Mr = 61.979 gr mol\(^{-1}\)) with \( \text{Ho}_2\text{O}_3 \) (Mr = 377.859 gr mol\(^{-1}\)) increases the average molecular weight. From table 1 and Figure 1, it can be clearly seen that density and molar volume increase with increasing \( \text{Ho}_2\text{O}_3 \) concentration. From definition of density, density and molar volume should be inversely related to each other, but in this glass system the relation is different. This abnormal behavior has previously been reported for many glass systems, such as \( \text{TeO}_2-\text{ZnO-Er}_2\text{O}_3 \) [16] \( \text{B}_2\text{O}_3-\text{ZnO-TeO}_2 \) [17], \( \text{TeO}_2-\text{Bi}_2\text{O}_3-\text{ZnO-Na}_2\text{O-Nd}_2\text{O}_3 \) [18] and \( \text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3-\text{SrO-Nd}_2\text{O}_3 \) [19]. The increase in molar volume with the increase of \( \text{Ho}_2\text{O}_3 \) content may be due to several
reasons. Firstly, Ho³⁺ ion has larger ionic radius \((r = 104 \text{ pm})\) than Na⁺ ions \((r = 102 \text{ pm})\). For the case of obtaining the densest atomic arrangement, this replacement increases the volume of the glass. Secondly, this replacement brings more oxygens creating more non-bridging oxygen (NBO) and thus increase the free space in the glass network \([12, 16]\). Further, Ho³⁺ ions are heavier than Na⁺ ions. During glass formation, heavier ions tend to move slower (molten more viscous) which can also result in more free space. Since both mass and volume increase as the content of Ho₂O₃ increase, their contribution to the density change is determined by their significant changes. It can also be seen from Table 1 and Figure 2 that the addition of the concentration of Ho₂O₃ causes an increasing in OPD and field strength, and a decreasing in polaron radius.

**Table 1. Density, molar volume, OPD, polaron radius, and field strength of thulium/holmium co-doped borotellurite glass**

| Glass | Density (g/cm³) | Molar Volume (cm³/mol) | OPD (mol/L) | Polaron Radius \((10^{-8} \text{ ions/cm}^3)\) | Field Strength \((10^{16}\text{ cm}^2)\) |
|-------|-----------------|------------------------|-------------|--------------------------------------|------------------|
| G1    | 4.725           | 31.80                  | 84.60       | -                                    | -                |
| G2    | 4.775           | 31.79                  | 84.93       | 4.103                                | 0.112            |
| G3    | 4.809           | 31.89                  | 84.97       | 3.259                                | 0.356            |
| G4    | 4.850           | 31.95                  | 85.13       | 2.849                                | 0.698            |
| G5    | 4.882           | 32.07                  | 85.13       | 2.592                                | 1.125            |
| G6    | 4.915           | 32.18                  | 85.16       | 2.410                                | 1.628            |

**Figure 1.** Density and molar volume as a function of Ho₂O₃ content
3.2. Refractive Index
Figure 3 is room temperature refractive index of Tm$^{3+}$/Ho$^{3+}$ co-doped borotellurite glasses measured at wavelength 632 nm as compared to that calculated based on compared to glass composition. As seen, refractive index of the glass increases with the increase of Ho$_2$O$_3$ content. Despite higher ionic polarizability the Ho$^{3+}$ ion have as compared to that of Na$^+$ ion, the increase in refractive index from 1.491 to 1.725 as the content of Ho$_2$O$_3$ increases might also because of the formation of non-bridging oxygens (NBOs) in the glass matrix [20], the reason we explained above. Related to the density change, denser material makes more light interacts with atomic lattice and the field it creates and thus will slow down its speed meaning that denser material will create higher refractive index [21].
Figure 3. Refractive index of thulium/holmium co-doped borotellurite glass as a function of \( \text{Ho}_2\text{O}_3 \) content.

4. Conclusions

Glass having composition 57B$_2$O$_3$-20TeO$_2$-15Bi$_2$O$_3$-3TiO$_2$-(4-x)Na$_2$CO$_3$-1Tm$_2$O$_3$-xHo$_2$O$_3$ (with \( x = 0 - 2.5 \) mol\%) have been successfully fabricated. Glasses were studied in term of their density and refractive index change as the content of Ho$_2$O$_3$ was changed. It was shown that both density and refractive index increase with the increase of Ho$_2$O$_3$ content. From the density data, we have also derived other physical properties change as function of Ho$_2$O$_3$ content. They are molar volume, oxygen packing density (OPD), field strength \( (F) \) and polaron radius \( (z) \).

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