Physical and Optical Studies of Bi³⁺-Modified Erbium Doped Tellurite Glasses

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Abstract. Er³⁺-doped tellurite glasses with various compositions (in mol%): 54TeO₂-(41-x)ZnO-xBi₂O₃-2Na₂O-3Er₂O₃ (x = 1, 2, 3, 4, and 5) were prepared with melt quenching method. Studies was aimed at investigating the effect of Bi³⁺ ion content on the physical and optical properties of the glasses. The density, refractive index, optical absorption, and optical energy band gap measurements were carried out at room temperature using pycnometer, Brewster angle method, and UV-VIS-NIR spectrophotometer, respectively. From the experiment, it was shown that the density and refractive index of the glasses increased with the increase of Bi³⁺ ions concentration. The absorption band intensity of electronic transition from ⁴I₁₅/₂ to ⁴H₁₁/₂ exhibited an increase as the Bi³⁺ ions concentration increase suggesting that incorporating Bi³⁺ ions into this glasses might improve the pumping efficiency.

Keywords: Tellurite glasses, Erbium doped glasses, Glass density, glass refractive index, glass band gap.

1. Introduction

In the last view decades, tellurite glasses have been the subject of several spectroscopic investigations mainly due to their potential for laser glass host [1-5]. These glasses are characterized by their high index of refraction [6], low phonon energy [7, 8], and thermally stable against devitrivication [8, 9]. Large numbers of tellurite glasses compositions have been synthesized. Among them are doped with rare-earth ions Y³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Lu³⁺, Er³⁺, Nd³⁺, Ho³⁺, Tm³⁺ and Yb³⁺ [8, 10-12].

Erbium doped glasses are one those intensively investigated mainly for the optical amplifier application used in the third window telecommunication corresponding to the electronic transition from ⁴I₁₃/₂ → ⁴I₁₅/₂ emitting 1.5 µm. A lot of works on the spectroscopic properties of Er-doped tellurite glasses have been done by different researchers [13-15].

In order that the optical amplifiers can be connected to the installed optical fiber network with better confinement and high quantum yield, optical amplifiers are formed in a defined optical path either in the form of planar waveguide or optical fiber. In either form, slightly different composition of Er-doped tellurite glasses have to be tailored to from a thin film of Er-doped tellurite glass with higher refractive index. Similarly, a fiber core containing Er³⁺ ions having slightly higher refractive index than that for the cladding is required. Adding small amount of heavy ions with higher ionic polarizability into the chosen glass substrates is a common way done by most researchers to increase glass refractive index. This index change, however, can lead to change to any other spectroscopic properties of the glasses.

This paper aims at investigating the spectroscopic properties change of tellurite glasses as small amount of Zn²⁺ ions concentrations were substituted by Bi³⁺ ions. Studies were focused on the effect of the incorporation of Bi³⁺ ions to the physical and optical properties glasses: density, refractive index, absorption spectra, and optical energy band gap.
2. Experiment
The composition of Er-doped tellurite glasses used in this experiment is (in mol%): 54TeO₂-(41-x)ZnO-xBi₂O₃-2Na₂O-3Er₂O₃ (x = 1, 2, 3, 4, and 5). The purity of all chemicals were more than 99.9%. Mixture of these chemicals were prepared in a glove box. After thoroughly mixed, mixture was contained in a platinum crucible and heated in an electric furnace. Na₂O used in these glass compositions were obtained from Na₂CO₃ that upon heating released CO₂ and left Na₂O. In order that this reaction to occur, mixtures were initially heated at 300°C for 30 minutes and then brought to 900°C. Molten was hold at this temperature for about 60 minutes and periodically stirred using platinum rod. Casting was performed by pouring the melt in a preheated square brass mold and let it to cool to room temperature. To remove any inhomogeneity in the glass occurs during natural rapid cooling, glass was then annealed at 375°C for 6 hours. Cooling at 1°C/minute was performed to ensure that all part of the glass at any time during cooling is at the same temperature.
For optical characterization, the obtained glasses were cut and polished to optically polished. Glass density was measured at room temperature by applying Archimedes law using pycnometer. Glass refractive index was determined from Brewster’s angle measured using spectrometer. Spectroscopic properties of all glasses were studied from the glasses absorption spectra measured within UV-VIS-NIR region. All of these measurement were carried out at room temperature.

3. Results and Discussion
3.1. Density and refractive index
Figure 1 shows densities and molar volume of tellurite glasses containing different concentration of Bi₂O₃. As shown, glass density increases with the increase of Bi₂O₃ content. This result is mainly attributed by the high value of Bi₂O₃ molecular weight which is 465.96 g/mol. This value is higher than those for other oxides composing glass structure which are 159.60 g/mole for TeO₂ and 81,379 g/mole for ZnO. Linear increase of sample molecular weight (Figure 1b) and linear decrease of ionic packing ratio (Figure 1c) as Bi₂O₃ content increases do not make the glass density change in the same way (linear increase).
Glass molar volume is another factor affecting glass density. Figure 1d is molar volume of the glass calculated using equation [15]

\[ V_m = \frac{\sum{x_iM_i}}{\rho} \]

Where \( \rho \) is glass density, \( x_i \) and \( M_i \) are molar fraction and molecular weight of an oxide composing the glass. As molar volume can be associated with the spatial dispersion of oxygen in the glass matrix characterized by oxygen packing density (OPD) expressed by [15]

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

where \( N_O \) is number of oxygen atom present in the glasses, the abrupt change in molar volume within the range of the increasing Bi₂O₃ content from 2 mol% to 4 mol% can then be interpreted as the abrupt change in the number of the non-bridging oxygen. The way the molar volume change as the Bi₂O₃ content change which is not similar to both the change in molecular weight and ionic packing ratio can be linked to the appearance of a very little change in glass density within the range of Bi₂O₃ content from 2 mol% to 4 mole% (Figure 1d).
Figure 2 shows refractive index of tellurite glasses which changes as function of Bi₂O₃ content. As shown, refractive index of glasses increase with the increase of Bi₂O₃ content. The cationic molar polarizability of Bi³⁺ (1.508 Å³), which is higher than that of Zn²⁺ (0.283 Å³), is the main caused of this increase. In addition, creation of non-bridging oxygen in the glass network resulted from the substitution of ZnO by Bi₂O₃ can also be considered as an additional factor contributing to the refractive index increase.
3.2. Absorption spectra

UV-VIS-NIR absorption spectra of Er-doped tellurite glasses containing different concentration of Bi$^{3+}$ are given in Figure 3. All the observed absorption bands; which have peaks at 414 nm, 451 nm, 460 nm, 498 nm, 532 nm, 555 nm, and 665 nm; correspond to electronic transitions from ground state ($^4I_{15/2}$) to the exited states of $^2H_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$, respectively. Among them, absorption corresponding to electronic transition from $^4I_{15/2}$ to $^4H_{11/2}$ is the strongest one. The intensity of this band increases with the increase of Bi$^{3+}$ content. This result might be attributed by the glass density which leads to the increase of Er$^{3+}$ density and consequently increase the absorption coefficient. Moreover, it is seen that the fundamental absorption of all glasses raise rapidly just below the absorption band at 414 nm and therefore absorption band below this band cannot be observed.

Figure 3b can roughly illustrate the fundamental absorption change as the Bi$^{3+}$ content increases. Although, incorporating Bi$^{3+}$ ions into the Er-doped tellurite glasses might benefit in term of pumping efficiency, it is seen that the UV absorption edge is blue-shifted as the Bi$^{3+}$ ions content is increased.
Figure 2. Refractive index of tellurite glasses as function of Bi$_2$O$_3$ content.

Figure 3. Absorption spectra of tellurite glasses as function of Bi$_2$O$_3$ content.

Figure 4a is UV absorption edge from which optical energy band gap was calculated. In this paper, the optical energy band gap was calculated using expression

$$(ahv)^{1/2} = C(hv - E_{opt})$$

where $a$, $hv$, $E_{opt}$, and $C$ are absorption coefficient, photon energy, optical band gap, a Constance which is independent to the photon energy, respectively. In term of the optical energy band gap, incorporating Bi$^{3+}$ ions into the glasses can lead to decreasing energy band gap. Figure 4b indicates how the optical energy band gap changes as the Bi$^{3+}$ ions content in the glass changes. The energy band gap decreases as the Bi$^{3+}$ ions content in the glass increases. This decrease of energy band gap indicates that incorporating Bi$^{3+}$ ions into the glass causes the glass becomes more ionic which is in a good agreement with has been mention above that the increase of Bi$^{3+}$ ions content increases the number of non-bridging oxygen, and therefore increases the number of free electrons in the glass matrix.

Figure 4. (a). UV-absorption edge of tellurite glasses with different concentration of Bi$^{3+}$ ions. (b). Optical energy band gap of glasses as function of Bi$^{3+}$ ions content.

4. Conclusions

Series of Erbium doped tellurite glasses containing different concentration of Bi$_2$O$_3$ were fabricated using conventional melt quenching method. The changes in density, refractive index, absorption spectra, and optical energy band gap for the same concentration of Er$^{3+}$ ions concentration were analyzed in order to determine the effect of Bi$^{3+}$ ions concentration on the glass properties. The obtained density and refractive index of the glasses were increase with the increase of Bi$^{3+}$ ions concentration.
The absorption band intensity of electronic transition from $^4I_{15/2}$ to $^4H_{11/2}$ exhibited an increase as the Bi$^{3+}$ ions concentration increase suggesting that incorporating Bi$^{3+}$ ions into these glasses might improve the pumping efficiency.

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