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ABSORPTION STUDIES OF ERBIUM DOPED SODIUM MAGNESIUM BORO-TELLURITE GLASS

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ABSTRACT

A series of erbium doped sodium magnesium boro-tellurite transparent glasses of composition (30-x) B_2O_3-45TeO_2-15MgO-10Na_2O-xEr_2O_3 (where x=1.0, 1.5 and 2.0 mol %) has been prepared by the conventional melt-quenching technique. X-Ray Diffraction (XRD) pattern confirms the amorphous nature of the prepared glasses. The physical and optical properties of glass samples are characterized in terms of density, molar volume and UV–VIS–NIR, respectively. The glass density increases as it is found to be in the range of 3.928 up to 3.982 (g/cm^3) and and molar volume are found vary from 27.57 to 27.93 (cm^3 mol^{-1}). The absorption spectra reveals eight absorption bands with transition from $^4I_{15/2}$ to $^4F_{5/2,}$ $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2,}$ $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$. The optical energy band gap, E_{opt}^{I} and Urbach energy, ΔE are calculated from the observed absorption spectra which are found to be decreased in the range of 3.32 to 3.26 eV while the Urbach energy values increase between 0.18-0.21 eV respectively. The variations of E_{opt}^{I} and ΔE values are depending on the Er_2O_3 content in the host matrix. The optical properties of the prepared glasses with the change in Er_2O_3 content have been studied and compared with previous results.

Keywords: Boro-tellurite glass; Erbium, Density; Optical band gap; Urbach Energy;

INTRODUCTION

Rare earth doped glass materials have made the largest interest to develop photonic system for various applications such as solid state lasers, sensors, optical data transmission and display device [1]. Among the lanthanide group, Er_2O_3 is one of the most potential candidates in the pursuit of photonic materials research regard to its advance optical properties [2]. Recently, the trend is turned to add two or more glass formers to form the glass materials with modified optical properties [3]. B_2O_3–TeO_2 glass system has drawn attention of many researcher regarding to the requirement of low phonon energy and a relatively high thermal stability, high chemical durability and ease of fabrication which are also of interest for the fabrication of various new optical devices [4]. Several authors have studied and reported the properties of Er_2O_3 doped boro-tellurite glasses by varying the chemical composition [5, 6].

The studies on these boro-tellurite glasses have shown progressive changes in boron and tellurium coordination with the addition of other ions [7]. Therefore, the aim of the present study is to synthesize Er_2O_3 doped boro-tellurite glass through melt quenching technique and to measure the density, molar volume, optical band gap energy (E_{opt}) and Urbach energy (ΔE) of glass sample with varies Er_2O_3 concentration.

EXPERIMENTAL

Glass samples with composition of $(30\text{-}\varkappa)B_2O_3\text{-}45TeO_2\text{-}15MgO\text{-}10Na_2O\text{-}\varkappa Er_2O_3$ (where $\varkappa$ = 1, 1.5 and 2 mol%) have been prepared by the conventional melt-quenching technique. The nominal compositions and their corresponding label of all samples are presented in Table 1. A proper amounts of all the weighed chemicals are mixed and then were milled for an hour to obtain homogeneity. Afterward, the mixture is transferred to a platinum (Pt) crucible for being pre-heated at 150ºC for 45 minutes and melted at 960ºC for about an hour. The melts then are quenched by annealing at 300ºC for 3 hour in order to avoid the formation of crack, to remove the formation of air bubbles, thermal strains and to improve the mechanical strength [8]. After annealed, the prepared glasses are cooled down to ambient temperature. The prepared glasses were cut and polished to obtain planar and smooth surfaces before measuring their optical properties.

The amorphous nature of the prepared Er_2O_3 doped sodium magnesium boro-tellurite glasses were confirmed through the X-ray diffraction using Bruker D8 Advance diffractometer (Kα = 1.54Å) at 40 kV and 100 mA, at room temperature. The optical absorption measurement was made using a Shimadzu UVPC-3101 spectrophotometer in the range of 350-1600 nm wavelength with a resolution of ±1 nm. The glass density was measured following the Archimedes principle using distilled water as an immersion liquid. Density is calculated from,

$$\rho = \frac{A_\alpha}{A_\alpha - B_w} \times (\rho_0 - \rho_\alpha) \quad (1)$$

where A_α and B_w are the weight of the sample in the air and in liquid, respectively; ρ_0 is the density of liquid (distilled water; 1gcm^{-3}) and ρ_α is the density of air (approximately 0.001gcm^{-3}). The molar volume (V_m) in terms of the molecular weight (M) yields,

$$V_m = \frac{M}{\rho} \quad (2)$$

Table 1: Nominal composition of Er_2O_3 doped with sodium magnesium boro-tellurite glass (mol%) and their corresponding labels

Glass	B_2O_3	TeO_2	MgO	Na_2O	Er_2O_3
S1	29	45	15	10	1.0
S2	28.5	45	15	10	1.5
S3	28	45	15	10	2.0

RESULT AND DISCUSSION

X-Ray Diffraction

Figure 1 shows the XRD pattern for the glass. From Figure 1, a broad peak in the range of 20–35° can be seen which is and confirms the amorphous nature of the prepared glasses.

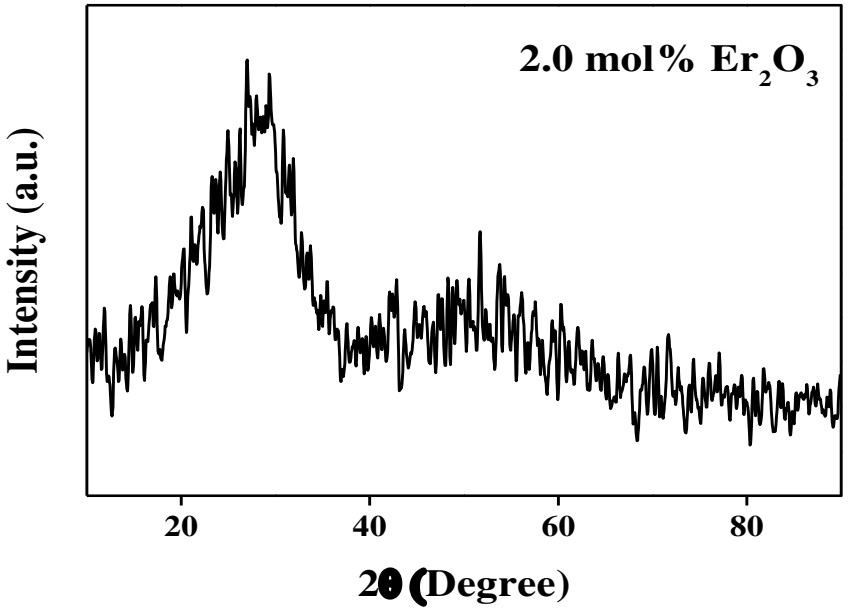

Figure 1: XRD pattern of the Er_2O_3 doped with sodium magnesium boro-tellurite glass

Glass density and molar volume

The value of density and molar volume for all glass samples are shown in Table 2 and also illustrated in Figure 2. From Figure 2, it can be seen that the increase in Er_2O_3 concentration from 1.0 to 2.0 mol% at the expense of B_2O_3 will cause the increase in density value from 3.928 up to 3.982 (g/cm^3). It might be due to the substitution of Er_2O_3 from B_2O_3 where the molar mass of Er_2O_3 (382.52 g/mol) is higher than B_2O_3 (69.62 g/mol). When lower molar mass substance is substituted by higher molar mass substance net molar mass increase resulting strong connectivity in glass network [9]. The molar volume is found to decrease by concentration of Er^{3+} ions up to 1.5 mol%

and then increase for 2.0 mol%. A possible reason for this increment in molar volume could be due to the elongation in the bond length or inter-atomic spacing between the atoms [10].

Table 2. Physical properties of Er_2O_3 doped sodium magnesium boro-tellurite glass

Parameters	S1	S2	S3
Density ρ (g/cm^3)	3.928	3.977	3.982
Molar volume (cm^3 mol^{-1})	27.59	27.57	27.93
Indirect band gap; E_{opt}^{I} (eV)	3.32	3.27	3.26
Urbach energy (eV)	0.18	0.20	0.21

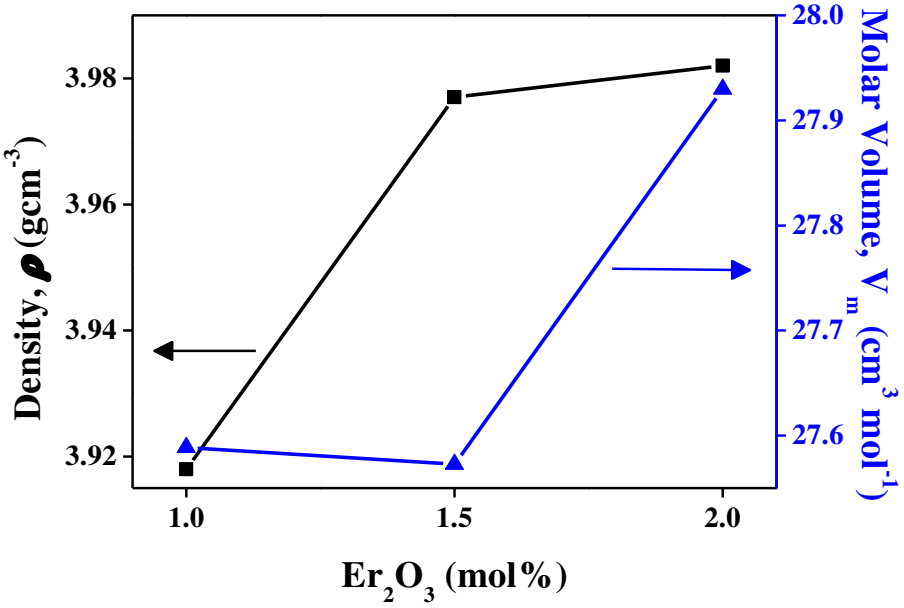

Figure 2**:** Variation of density and molar volume with mol % of Er_2O_3

Absorption spectra

The absorption spectra of Er_2O_3 doped sodium magnesium boro-tellurite glass are recorded in the range of 300-1600 nm as shown in Figure 3. The spectrum of absorption is quite similar to other Er_2O_3 -doped glasses [7, 11, 12]. The absorption band arise from the $^4I_{15/2}$ ground state to the various excited state due to f-f transition interaction in the Er^{3+} ions[1]. The spectra consist of eight absorption transition such as $^4F_{5/2,}$ $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2,}$ $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ which correspond to the band positions of 450, 488, 524, 549, 654, 800, 977 and 1527 nm respectively. A weak peak around 549nm at $^4S_{3/2}$ energy level is due to the small absorption cross-section and overlap from upper level of $^2H_{11/2}$ [13].

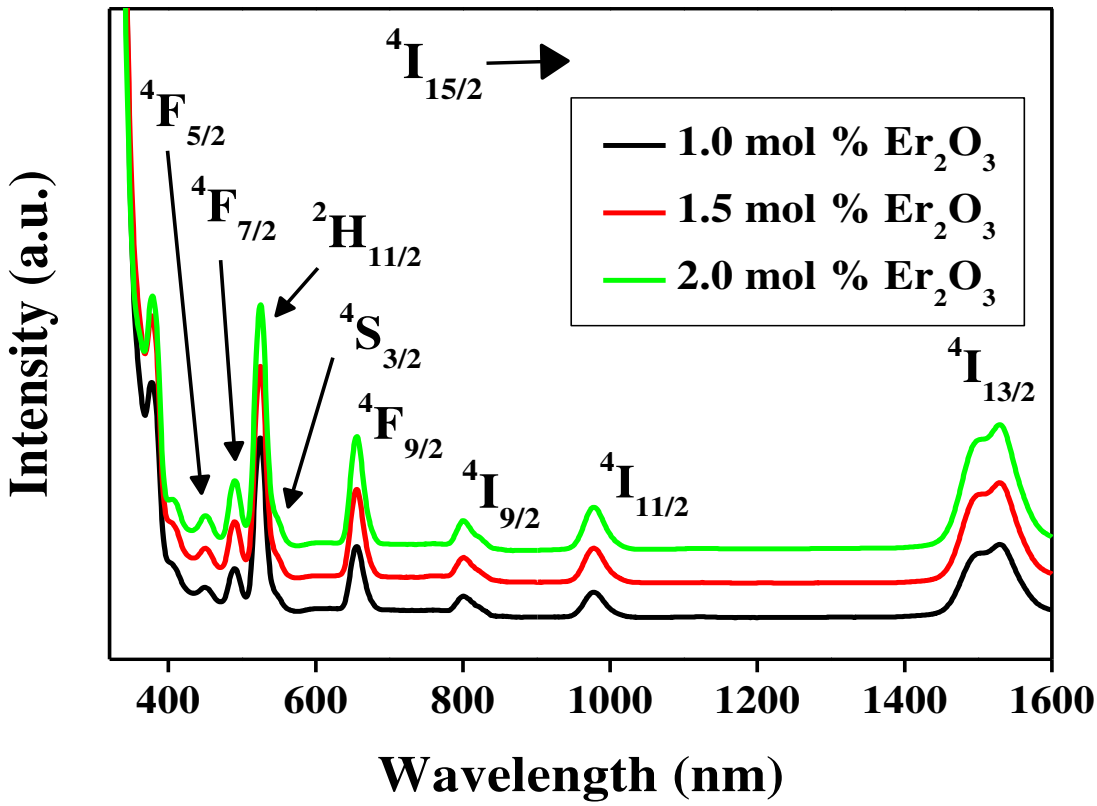

Figure 3: Absorption spectra of glasses for varying concentration of Er^{3+} ions

Optical band gap (E_{opt}^{I}) and Urbach energy (ΔE)

The fundamental of absorption edges in the UV region is used to explore the optical transition and electronic band structure of the crystalline and non-crystalline materials [14]. The optical absorption coefficient for each photon energy can be determined using the relation

$$\alpha(\omega) = \frac{2.303A}{t} \quad (3)$$

where t is the thickness of the sample and A correspond to absorbance. In amorphous material, the absorption due to electronic transition within the band in relation with the optical bandgap can be described using Davis and Mott theory [15]. The absorption coefficient α(ω)as a function of photon energy ħω or direct and indirect optical transition as proposed by Mott and Davis is given by

$$\alpha(\omega) = \frac{B(\hbar\omega - E_{opt})^n}{\hbar\omega} \quad (4)$$

where B is a constant called band tailing parameter, and n = 2 for indirect transition. E_{opt} is the optical energy band gap between the valence band and conduction band. The relation can be written as

$$(\alpha\hbar\omega)^{1/2} = B(\hbar\omega - E_{opt}) \quad (5)$$

Using this relation, the optical band gap values (E_{opt}) for all glass samples are determined by extrapolation the straight line of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ to $(\hbar\omega)^{1/2} = 0$ as in Figure 4(a) and are listed in Table 2. As given in Table 2, an indirect optical band gap decrease from 3.32 to 3.26 eV, as the concentration of Er^{3+} ions is increase up to 2 mol%. The band gap values changes due to the structural changes and the formation of greater number of non-bridging oxygen taking place in the glass network [16].

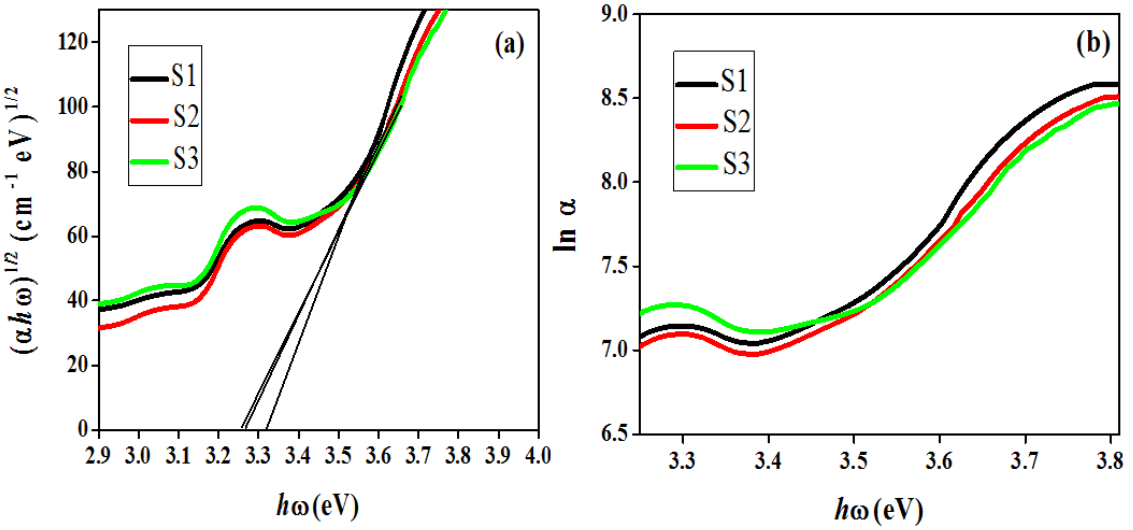

Figure 4: (a) Plot of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ for indirect band gap (b) Plot of ln α versus $\hbar\omega$ for Urbach energy of Er_2O_3 doped sodium magnesium boro-tellurite glass

The absorption coefficient α(υ) in the optical region near the absorption edge, at certain temperature, always obey the Urbach equation and is given by

$$\alpha(\upsilon) = \beta \exp\left(\frac{\hbar\omega}{\Delta E}\right) \quad (6)$$

where β is a constant, $\hbar\omega$ is the photon energy, and ΔE is the Urbach energy which is interpreted as the width of the localized states in the normally forbidden band gap which is used to characterize the degree of disorder in the amorphous and crystalline materials [16]. The tendency of materials to convert weak bonds into defects become

greater when it have larger Urbach energy [7]. From Figure 4(b), Urbach energy is determined from the slope of plot ln (α) against photon energy (ħω) and is found to be in the range of 0.18-0.21 eV as listed in Table 2. The optical band gap (indirect) energy (E_{opt}) and band tail (Urbach) energy as a function of Er_2O_3 mol% are shown graphically in Figure 5. It is observed from Figure 5 that when the Er_2O_3 mol% increased, the non-bridging oxygen ion increases by shifting the band edge to lower energies, which in turn decreased the optical band gap energy values and increases the Urbach energy values which is in agreement as reported elsewhere [3, 17, 18].

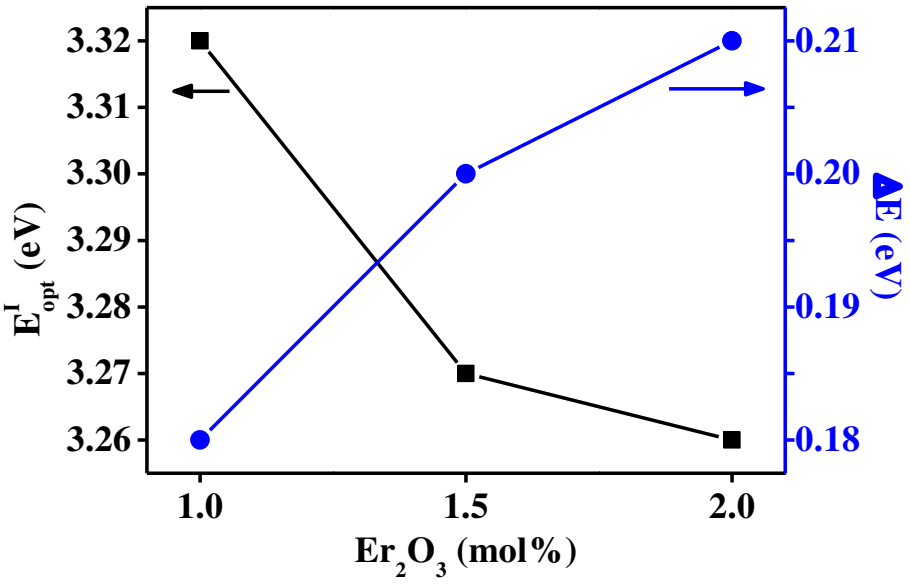

Figure 5: Optical band gap energy (E_{opt}) and Urbach energy ΔE of Er_2O_3 doped sodium magnesium boro-tellurite glass

CONCLUSION

A series of Na_2O-MgO-B_2O_3-TeO_2 glasses with different Er_2O_3 concentration has been prepared by melt-quenching technique and their amorphous nature is confirmed by XRD. The density, molar volume, band gap and Urbach energy dependent on variation in Er_2O_3 concentration are discussed and understood in term of the formation of non-bridging oxygen. The role of Er^{3+} ions in modifying the physical and optical properties is understood.

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