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EFFECT OF Mn^{4+} ON THE ABSORBANCE OF EUROPIUM DOPED MAGNESIUM BOROTELLURITE GLASS

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ABSTRACT

A series of europium oxide doped borotellurite glass containing Manganese Nanoparticles (Mn_3O_4 NPs) with composition of (59-x)TeO_2-30B_2O_3-10MgO-1Eu_2O_3-$x$$Mn_3O_4$ (where x = 0.5, 1.0, 1.5 mol %) have been prepared by conventional melt quenching technique. The amorphous nature of glasses is confirmed by X-ray diffraction technique which shows a broad hump at lower 2θ angle. The physical properties glass such as glass density and molar volume are carried out. It is found that glass density and molar volume are in the range of (4.706-4.725) gcm^{-3} and (25.71-25.98) cm^3mol^{-1}, respectively. Meanwhile, the absorption spectra reveals three prominent peaks located at 461 nm, 531 nm and 591 nm which are corresponding to the $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_1 \rightarrow {}^5D_0$ transition, respectively. The absorption features in term of optical band gap (E_{opt}) and Urbach energy (ΔE) are also investigated. It is obtained that the indirect band gap and Urbach energy are ranging from (2.87-3.27) eV and (0.275-0.519) eV, respectively. All the results will be discussed with respect to the modification of Mn_3O_4 NPs concentration.

Keywords: Magnesium Borotellurite Glass; Manganese Nanoparticle; Density; Optical Band Gap; Urbach Energy;

INTRODUCTION

Borate (B_2O_3) is one of the important glass former due to its special physical properties such as high transperancy, low melting point, high thermal stability and good rare earth solubility that make it appropriate for solid state applications [1-3]. Unfortunately, in many circumstances borate possesses a low chemical durability and thus it needs other oxides to enhance its stability as prepared by many workers [4-5]. The presence of both B_2O_3 and TeO_2 in borotellurite glasses has lead to better the glass structure [6]. Furthermore, TeO_2 has useful properties such as low melting temperature, high dielectric constant, high refractive index, low phonon energy and good transmittance of infrared radiation [7]. Therefore, borotellurite glasses have attracted significant interest over many years for non-linear optical devices and lasers applications [8]. In addition, borotellurite also is one of the most attracting materials and have been studied extensively regarding on the structural properties [9]. However, there has been less

extensive reported on the physical and optical properties of borotellurite glass with the presence of magnetic nanoparticle. Thus, the purpose of this study is to identify the influence of Mn_3O_4 NPs on the physical and optical properties of Eu^{3+} doped magnesium borotellurite glass.

EXPERIMENTAL

A 20 gram batch containing a proportion of tellurium dioxide (TeO_2)(purity 99.9 %), orthoboric acid (H_3BO_3) (purity 99.0 %) magnesium oxide (MgO) (purity 99.0 %), europium oxide (Eu_2O_3) (purity 99.0 %) and manganese oxide (Mn_3O_4) (purity 99.0 %) are weighed and well mixed according to detailed nominal composition and codes of synthesized glass samples as entlist in Table 1.

Table1: The nominal composition of (59-*x*)TeO_2-30B_2O_3-10MgO-1Eu_2O_3-*x*Mn_3O_4 glass system where $0.0 \leq x \leq 1.5$ mol % with codes

Glass code	Nominal composition (mol %)				
	TeO_2	B_2O_3	MgO	Eu_2O_3	Mn_3O_4
BTMEuMn0.0	59.0	30.0	10.0	1.0	0.0
BTMEuMn0.5	58. 5	30.0	10.0	1.0	0.5
BTMEuMn1.0	58.0	30.0	10.0	1.0	1.0
BTMEuMn1.5	57.5	30.0	10.0	1.0	1.5

The batch is melted for 1h in an electrical furnace at 900 °C. Then, the melt is transfered to another furnace for annealing process and kept for 3 h at 300 °C to remove the thermal and improve mechanical strains [10] before being cooled down to room temperature. The amorphousity of the sample were identified by X-ray diffraction technique using the Siemens Diffractometer D5000 system operating at 40 kV and 30 mA in the range of 10º - 90º. The density of each glass is measured by Archimedes principle using the relation,

$$\rho = \frac{W_a}{W_a - W_b}(\rho_x) \quad (1)$$

where ρ is the density of immersion liquid (distilled water ρ_x = 0.9987 gm/cm^3), W_a is weight of the glass in air and W_b is the weight of the sample when immersed in distilled water. The molar volume, V_m of the glass samples is calculated from the following expression,

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

where M is molecular weight and ρ is the density. Absorption spectra are recorded using Perkin-Elmer Spectroscopy in the visible range of 200 – 900 nm. The xenon lamp is used as the excitation source.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern for BTMEuMn1.0. From Figure 1, it can be seen that the presence of broad hump in the range of 20º - 35º confirms the amorphous nature of the samples.

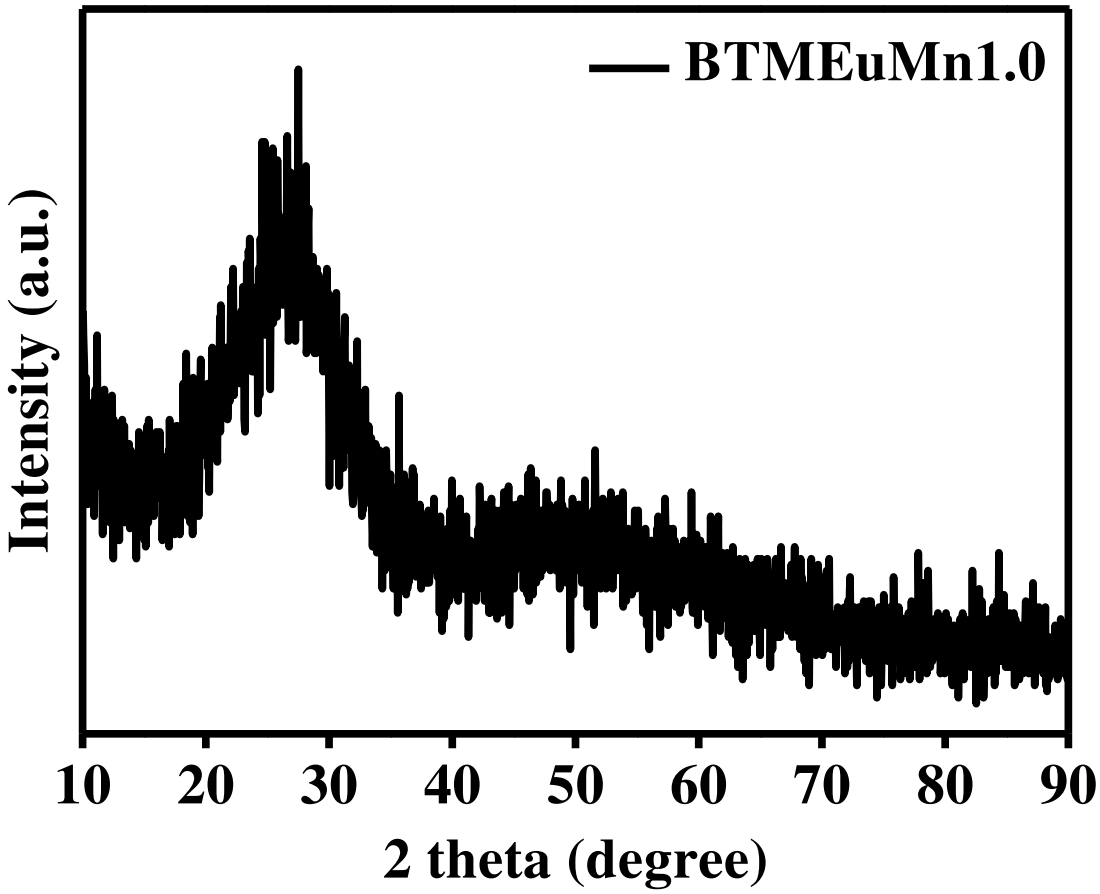

Figure 1: Typical X-ray diffraction pattern of BTMEuMn1.0 glass sample

This result is in a good agreement with the previous study [11] with shows the absence of sharp peaks.

The obtained glass density and molar volume of the samples are summarized in Table 1.

Table 1: Density (ρ) and molar volume (V_m) of the prepared glass system

Glass code	ρ (gcm^{-3})	V_m (cm^{3}mol^{-1})
BTMEuMn0.0	4.717	25.90
BTMEuMn0.5	4.716	25.92
BTMEuMn1.0	4.706	25.98
BTMEuMn1.5	4.725	25.71

From Table 1, the relationship between density and molar volume against Mn_3O_4 NPs concentration can be plotted and presented in Figure 2. From Figure 2, it can clearly seen that the glass density and molar volume exhibits an opposing trend. This is in agreement as reported elsewhere [12].

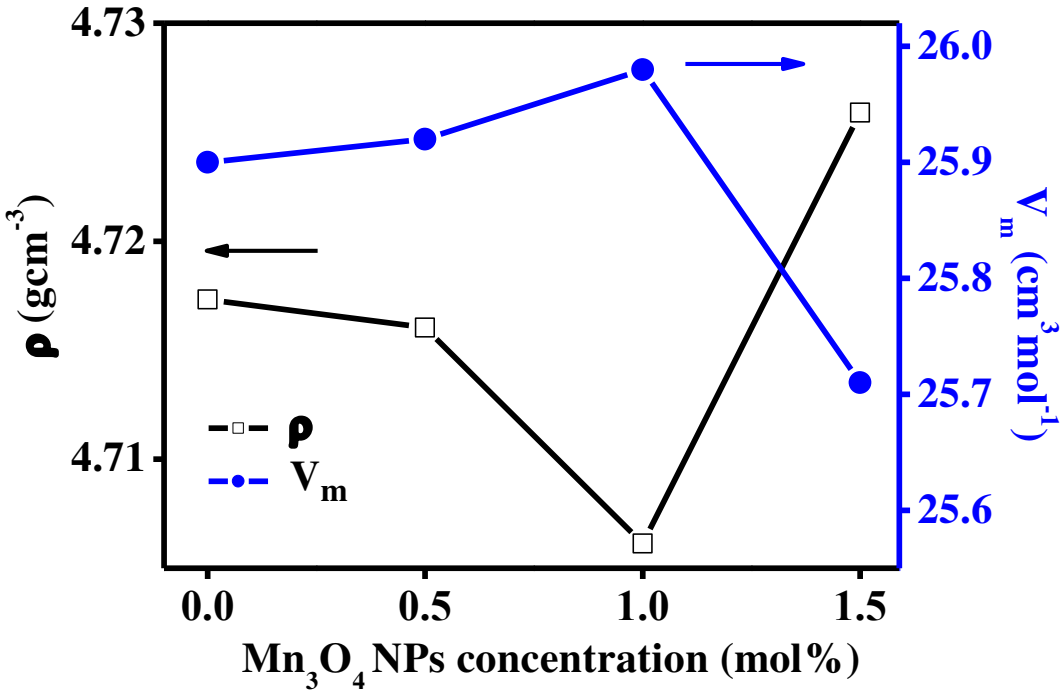

Figure 2: The dependence of density and molar volume with Mn_3O_4 NPs concentration

The glass density is found to decrease with the increase the concentration of Mn_3O_4 NPs up to 1 mol %. This is associated to the formation of non-bridging oxygen (NBO) which subsequently reduce the compactness of glass structure. The increasing number of NBO leads to the increase of excess free volume which resulted in the increase of molar volume [13]. This is through seen the strectching vibration of Mn=O frequency that has been previously observed [14]. However, the glass density decreases as the concentration of Mn_3O_4 NPs is beyond 1.0 mol %. This is due to the increment of Mn_3O_4 (228.812 gmol^{-1}) of the expense of TeO_2 (159.60 gmol^{-1}) which lead to a tightly packed glass structure [13].

The absorption spectrum of 1.0 mol % of Eu^{3+} doped magnesium borotellurite glass in the UV- Vis range are shown in Figure 3.

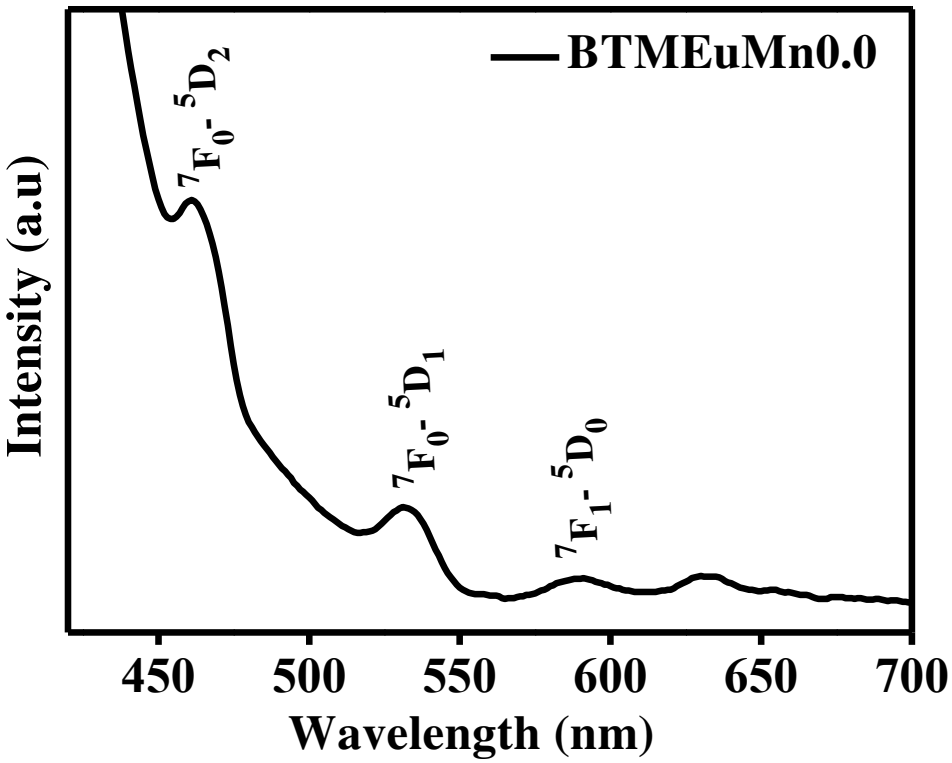

Figure 3: Absorption spectrum of the BTMEuMn0.0 glass

From Figure 3, three absorption peaks are observed which is attributed to the f-f transitions of Eu^{3+}. The absorption peaks are found around 461 nm, 531 nm and 591 nm corresponding to the transition from $^7F_0$ ground state to $^5D_2$, $^5D_1$, respectively and $^7F_1$-$^5D_0$ transition [15].

The optical transitions energy, *α(ω)* can be calculated using Mott and Davis,

$$\alpha(v) = \frac{B\,(hv - E_{opt})^n}{hv} \quad (3)$$

where, E_{opt} is the energy of the optical band gap, *h* is the Plank's constant, *v* is the frequency of the photon, *B* is tailing parameters and *n*=2 for indirect transition is summarized in Table 2. Meanwhile, the Urbach energy, Δ*E* can be determined using equation [16],

$$\alpha(v) = \alpha_o \exp(\frac{hv}{\Delta E}) \quad (4)$$

where, α_o is a constant and Urbach energy, Δ*E* is the width of the band tail of the

electron states. Figure 4 shows the band gap and Urbach energy as a function of Mn_3O_4 NPs concentration. As can be seen from Figure 4, the optical band gap decreases with the increase of the Mn_3O_4 NPs concentrations. This mean that the glass structure becomes less ordered due to the breaking of the regular structure of borate and tellurite, thus decreasing the band gap [17]. This results means that the disorderness of the glass samples increases. However, the optical band gap start to increases when concentration of Mn_3O_4 NPs is more than 1.0 mol %. The increase in optical band gap might be due to the formation of more BO at the local sites. It should be noted that the value of optical band gap is consistent to those reported in the literature [18], thus supported the above arguments.

Table 2: The optical band gap (E_{opt}) for indirect allowed transition and Urbach energy (ΔE) for prepared glasses

Glass code	E_{opt} (eV)	ΔE (eV)
BTMEuMn0.0	3.27	0.275
BTMEuMn0.5	3.03	0.404
BTMEuMn1.0	2.61	0.680
BTMEuMn1.5	2.87	0.519

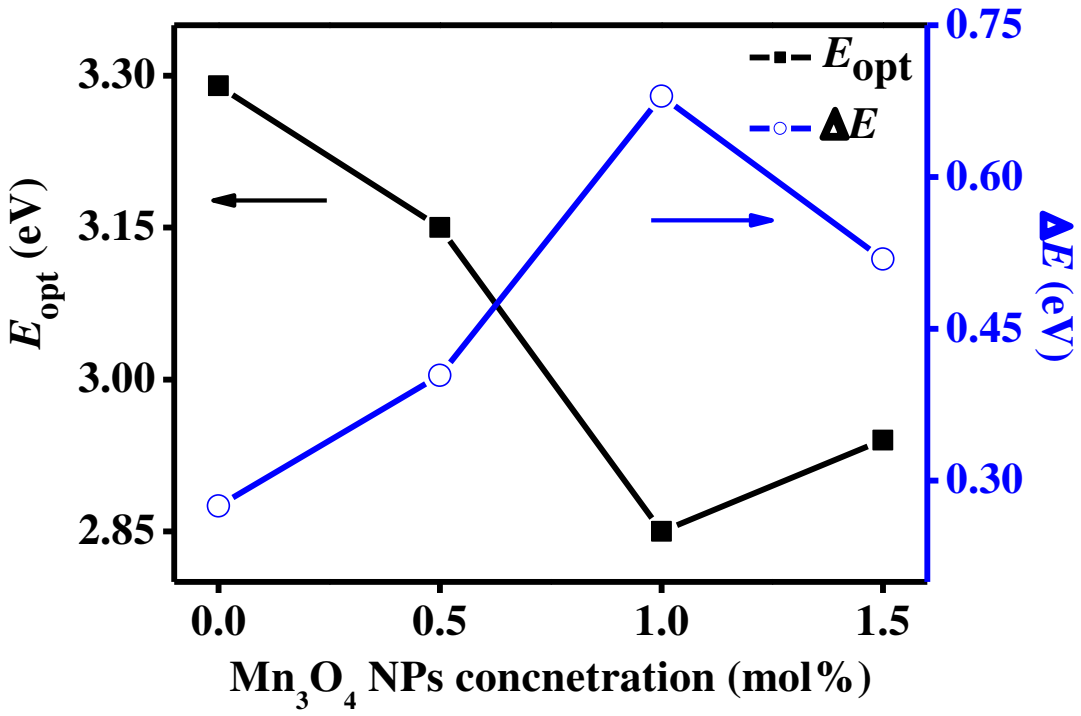

Figure 4: Dependence the E_{opt} and ΔE of Mn_3O_4 NPs concentration

The value of Urbach energy are between 0.275 eV to 0.680 eV and it is quite similar to the values reported in the literature [19]. From Figure 4 also it can be seen that the

Urbach energy is increasing as the concentration of Mn_3O_4 NPs increases up to 1 mol %. This is due to increment of defect in the glass structure. However, beyond 1 mol % the Urbach energy decreases which reflects to the decrement in the number of defect which means that the width of localized state become narrower [20].

CONCLUSION

The influence of Mn_3O_4 NPs concentration on physical and optical properties of borotellurite glasses are successfully investigated and reported. All glass samples are confirmed amorphous in nature. The density, molar volume, energy band gap and Urbach energy are understood in terms of the formation of non-bridging oxygens. It is concluded that those parameters are sensitive to Mn_3O_4 NPs concentration.

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