Structural and Electron Spin Resonance analysis of Eu^{3+} doped Borotellurite Glass containing Manganese Oxide Nanoparticles

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Abstract:- **Structural properties of $30B_2O_3$-(59-x)TeO_2-10MgO-xEu_2O_3-1Mn_3O_4 glass are prepared via melt quenching method. The glass samples are characterized by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy and Electron Spin Resonance (ESR) Spectroscopy. The glass nature is confirmed by XRD pattern. FTIR spectra display a shift in vibrational modes of TeO_4 and TeO_3 units thus indicate an alteration in the glass network structure due to an incorporation of Eu_2O_3. Influence which varies Eu_2O_3 concentrations on the structural due to the nature of spin-spin interaction are determined. Both g value and resonance magnetic field (H_r) are found to be in the range of (189-198) and (211-226) Oe respectively. The obtained g value of glass samples will modify the structural of europium doped magnesium borotellurite glass due to this presence of manganese oxide nanoparticles (Mn_3O_4 NPs) which may be useful for developing efficient photonic devices.**

Keywords—Borotellurite glass, structural properties, nanoparticles, ESR analysis (key words)

I. INTRODUCTION

Glasses are unique materials that have been benefitted years ago. Glass has been extensively investigated due to its high temperature resistance, high dielectric constant and good mechanical strength [1-3]. Furthermore, glass is not only known because of its excellent thermal and mechanical properties [4] but also of its potential in becoming a good medium for luminescence due to its enhancement of absorption efficiency of rare earth ions [5,6]. This excellent property has motivated researcher to further the study in optimizing luminescent thus develop to a more suitable material specifically in the development of laser and solid state device. To this day, rare earth ions (REIs) doped glass materials turn out to be an interesting topic in luminescence material. Dehelean *et al*. [7] acknowledged that REIs doped glasses exhibit high brightness and improved efficiency thus are very prospective for broad array of technological applications [8]. Trivalent Eu^{3+} ion is a well-known activator with simple electronic transitions [9]. The Eu^{3+} ions possess prominent laser emissions in the orange or red region [10] and narrow band emission [11] with longer lifetime. Both synthesis and characterizations of REIs doped binary and ternary glasses are intensively performed due to its advantages in [12]. Combination of TeO_2 and B_2O_3 is an intrinsically interesting subject of study due to the stability of borotellurite (BT) compound [13]. BT glasses have promising optical materials due to its high refractive index, low phonon energy and higher transparency in the infrared spectrum [14,15]. Further, BT glass needs another element known as glass modifier such as alkaline earth metal oxide and transition metal oxide [16] to improve the network connectivity then produce a stable BT glass with increasing non-bridging oxygen (NBO)[17]. The substitution of network modifier such as MgO would produce stable BT glass [18]. The addition of such modifiers would modify and increase the NBO, consequently open up the glass structure [19]. BT glass is emerged as a favorable host for accommodating large amount of REIs. Maheshvaran *et al.* [20] reported that Eu^{3+} doped BT glass has potential for red-emitting glass due to excellent luminescent properties and can be used as optical materials. Hence, Eu^{3+} doped glass has drawn much interest in technological applications especially for optoelectronic materials [21-23]. Luminescence properties of BT glass is one of the important characteristic which can be used as a strong indicator to hunt for a new functional material. Incorporation of nanoparticles in BT glass shows remarkable changes in optical properties of lanthanides [24]. Synthesis and characterization of magnetic Mn_3O_4 NPs have ever-growing interest. The incorporation of Mn_3O_4 in glass has paramount importance due to its excellent physical and structural properties [25]. However, not many efforts are dedicated

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towards the incorporation of europium in this glass system. This motivated an investigation of the REIs doped glasses containing Mn_3O_4 NPs. In this paper, a new series of Mn_3O_4 NPs embedded BT glass doped with different concentrations of trivalent europium have been prepared and its structural studies are performed and reported.

II. EXPRIMENTAL

Raw materials for the glass preparation of magnesium BT glasses embedded Mn_3O_4 NPs are commercially obtained in powder form. Analytical grade glass constituents of B_2O_3 (purity 98.94%), Te_2O (purity 99%), MgO (purity 99%), Eu_2O_3 (purity 99%) and Mn_3O_4 (purity 99.7%) in powder form are well-mixed with nominal glass compositions of (59-x)TeO_2-30B_2O_3-10MgO-$x$$Eu_2O_3-1Mn_3O_4$ (where x = 0.5, 1.0, 1.5 and 2.0 mol %). Required proportion of B_2O_3, Te_2O, MgO, Eu_2O_3 and Mn_3O_4 powders are weighed using an electronic balance (Precisa 205 A SCS). Then the total of batched mixture is placed in a platinum crucible before being melted at 900 °C for 1 hrs in an electric furnace. The melt is then transferred to an annealing furnace and poured into the brass mould before being annealed at 350 °C for 3 hrs to reduce the mechanical and thermal stress that causes embrittlement [26]. The melt is then cooled down to room temperature. Synthesized glasses are characterized using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy and Electron Spin Resonance (ESR) measurements.

III. RESULT AND DISCUSSION

Fig. 1 shows XRD patterns of the synthesized glass sample. The XRD pattern of the glass recorded in the range of $10^\circ \leq \theta \leq 90^\circ$ as shown in Fig. 1.

A broad hump is exhibits in the range of 15°-40°, which confirms the characteristic of amorphous nature of the glass [27, 28]. Conversely, peaks that indicate the existence of Mn_3O_4 NPs were hardly detected by XRD due to its fairly low concentration compared with host and modifier.

FTIR spectra of prepared glasses in the range of 400 cm^{-1} - 4000 cm^{-1} are shown in Fig. 2 and the corresponding peak positions with the assignments of vibrational modes are listed in Table 1.

The FTIR spectra in Fig. 2 clearly comprise of main sharp distinctive and characteristic absorption bands. These bands are due to main BT network group vibration. From Fig. 2, it is noticed that the peak at 665-682 cm^{-1} is referred to the TeO_4 tbp group in the present glass [29]. It is observed that, as the amount of Eu_2O_3 is increased, the peak of TeO_4 tbp is displaced from 665 cm^{-1} toward a higher wavenumber and reaches 682 cm^{-1} at 1.0 mol % of Eu_2O_3. This is attributed to the formation of more TeO_3 units at the expense of TeO_4 units [30]. Formation of large number of Te-O bonds in TeO_3 units has strengthened the glass network. However, as the amount of Eu_2O_3 is beyond 1.0 mol %, the vibration peaks slightly shifted toward a lower wavenumber. This shift might indicate structural alteration.

Electron Spin Resonance (ESR) studies of Eu^{3+} doped BT glasses embedded with various concentrations of Eu_2O_3 have been investigated and represented in Fig. 3 at room temperature. ESR is used to detect paramagnetic behaviour and to provide information on the coordination of isolated sites [35]. The calculated values of magnetic parameters such as resonance magnetic field (H_r), peak-to-peak line width (ΔH_{pp}) and g value which can be obtained from ESR spectra are presented in Table 2.

For various concentrations of Eu_2O_3, it is observed that the intensity of the signal g value at 4.3 is more intense compared to g value that close to 2. It pointed out that Mn^{2+} center is present dominantly in a rhombic environment. Additionally, a positive shift in the g value as concentration of Eu_2O_3 increase would indicate that the Mn^{2+} is in a covalent environment [36]. The value of g = 1.89 is the minimum amount where the bond is in covalence environment as shown by BTME1.0Mn sample. Meanwhile, variations of line width (ΔH_{pp} = peak to peak distance) with concentration of Eu_2O_3 is another sensitive indicator of changes in the environment of Mn ions [37]. Overall, the ESR strongly indicates that Mn^{2+} centers are in asymmetric sites and the nature of the bonding is dominantly covalent bond.

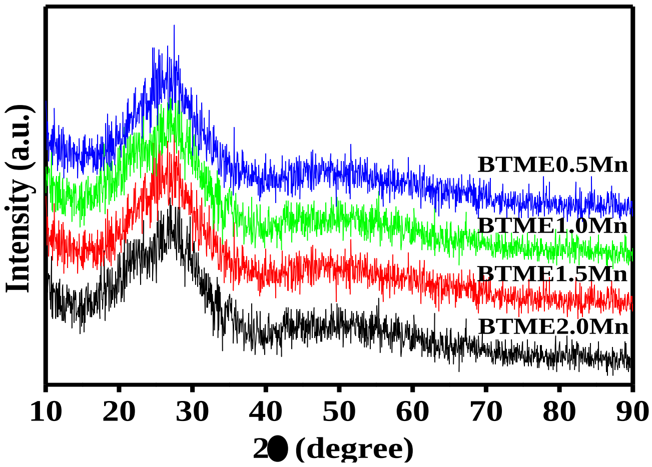

Fig. 1 X-Ray Diffraction (XRD) patterns of glass system

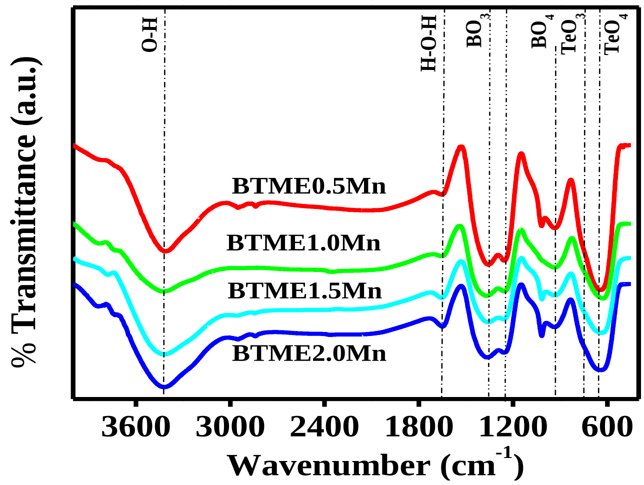

Fig.2. Fourier Transform Infrared (FTIR) spectra of the prepared glass system

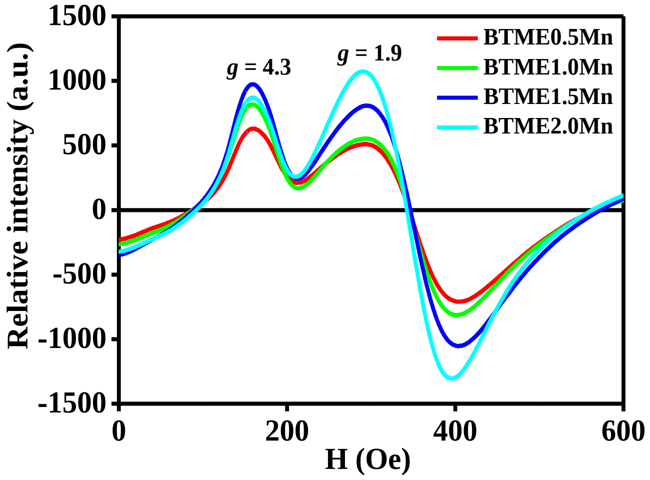

Fig.3. Electron Spin Resonance (ESR) spectra of prepared glass samples

VI. CONCLUSIONS

The structural and magnetic properties of Eu^{3+}:Mn doped BT glass has successfully been studied and prepared by melt quenching technique. The amorphous nature of glasses is confirmed by XRD. The FTIR spectra are strongly influenced by the variations of Eu_2O_3 concentration. For the ESR spectra, manganese ions exhibit two resonance signals at g values 1.9 and 4.3. ESR spectra strongly indicated that Mn^{2+} centers were in asymmetric sites (octahedral) and the nature of the bonding is dominantly covalent type.

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TABLE 1. The IR peak positions and band assignments of the present glass systems

Glass code	Assignments IR Band (cm^{-1})						Ref.
	TeO_4 (tbp)	TeO_3 (tp)	BO_4 unit	BO_3 unit	H-O-H	OH	
B_2O_3-TeO_2-ZnO	643	725	921	1355	-	-	[31]
B_2O_3-TeO_2-MgO-K_2O	678	1082	1382	1745	3432	-	[32]
B_2O_3-TeO_2-Al_2O_3	643	664	930	1360	-	-	[33]
TeO_2-B_2O_3-ZnO-V_2O_5	643	660	940	1355	-	-	[34]
BTME0.5Mn	648	685	933	1259	1734	3422	
BTME1.0Mn	651	681	936	1259	1738	3425	
BTME1.5Mn	639	678	936	1259	1741	3428	
BTME2.0Mn	638	676	936	1259	1742	3420	

TABLE 2. Magnetic properties of prepared BT glasses at various concentration of Eu_2O_3

Glass code	Magnetic parameters		
	g value	H_r (Oe)	ΔH_{pp} (Oe)
BTME0.5Mn	1.91	218	137
BTME1.0Mn	1.89	226	136
BTME1.5Mn	1.90	225	138
BTME2.0Mn	1.98	211	138

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