Magnetic Impacts Of Manganese Oxide Nanoparticles On The Magnetic Behavior Of Eu3+ Doped Boro Tellurite Glasses Impacts Of Manganese Oxide Nanoparticles On The Magnetic Behavior Of Eu^{3+} Doped Borotellurite Glass

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Abstract: Europium ions (Eu^{3+}) activated borotellurite glass with manganese oxide nanoparticles (Mn_3O_4 NPs) inclusion is prepared using the standard melt-quenching technique. Modifications in magnetic parameters are ascribed to the alteration of magnetic properties due to concentrations of Mn_3O_4 NPs. Prepared glass sample is characterized via imaging and spectroscopic instruments. The phase of the glass is determined by an X-Ray Diffractometer (XRD). The XRD pattern confirmed the amorphous nature of glass sample. The Energy-Dispersive X-Ray (EDX) spectra detected appreciated elements presence in the glass including manganese. The presence of manganese oxide nanoparticle inside the host matrix is verified using Transmission Electron Microscope (TEM). The TEM images manifested the growth of Mn_3O_4 NPs with an average diameter of 15.4 ± 1.0 nm. Magnetic properties of Mn_3O_4 NPs are determined by Vibrating Sample Magnetometer (VSM) in terms of saturation magnetization (M_s), remanent magnetization (M_r), susceptibility (χ_m) and coercivity (H_c). The obtained hysteresis loop indicates that the prepared glass systems exhibited paramagnetic behavior at room temperature with positive susceptibility in the range of 4.54×10^{-6} to 7.08×10^{-6} $emuOe^{-1}g^{-1}$. The increase in magnetic performance was observed in coincident with the increased concentrations of Mn_3O_4 NPs. This result indicates that the prepared glass system possibly for the development of magneto-optical devices.

Index Terms: europium, glass, magnetic properties, manganese, VSM

1 INTRODUCTION

P resently, the advancement of multifunctional metallic nanoparticles (NPs) is in full swing [1],[2] due to the practicability of sundry applications. Researches on the improvement in the structural, magnetic, and optical properties of rare earth ions doped glasses by embedding various metallic NPs are still on going. Various magnetic nanoparticles embedded glass systems are prepared such as Ni NPs, Fe_3O_4 NPs and Co_3O_4 NPs [3],[4],[5]. Literatures hinted that these types of glasses with tailored properties are remarkable for the development of magneto-optic devices including data storage and sensors [6]. Modifications in the magnetic properties of rare earth ions doped glasses by embedding various metallic NPs is however a recent research trend. Magnetic properties of borotellurite glass are one of the important characteristics which are significant for the evolution of this new functional material. Inclusion of nanoparticles in borotellurite glass shows notable modifies in magnetic properties of the glass [7]. Among nanoparticles, magnetic nanoparticles are remarkable which is practical for magneto-optic devices. Several researchers have extensively reported about manganese nanoparticles due to its outstanding properties such as large specific surface area, low dimensionality and quantum confinement effect compared with bulk materials [8]. Other than that, it manifests high saturation field, high field irreversibility and extra anisotropy contributions [9],[10]. Despite much researches, the incorporation of Mn_3O_4 NPs on the magnetic properties of borotellurite glass system has not yet explored. The influence of concentrations of Mn_3O_4 NPs in borotellurite glass provides an opportunity to develop new stable magnetic glasses applicable for nonlinear optical sensor and electronics devices. Therefore, in this paper, the Mn_3O_4 NPs embedded borotellurite glass doped trivalent europium has been synthesized and its magnetic studies are presented and reported.

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2 EXPERIMENTAL

Analytical grade powdered chemical reagents of high purity (Sigma Aldrich, 99.9%) such as Tellurium dioxide (TeO_2), Boron oxide (B_2O_3), Magnesium oxide (MgO), Europium oxide (Eu_2O_3) and Manganese oxide (Mn_3O_4) are acquired for the glass preparation. The appropriated amount of the glass constituents (nominal compositions) are weighed using high precession balance (Electronic Balance Precise XT 220A) and mixed rigorously using milling machine for about 30 minutes to ensure homogeneity. Melt-quenching method is used to prepare these glass samples. A platinum crucible containing about 20 g of the mixed glass constituents is placed in an electrical furnace at 900 °C for 1 hour. For homogeneous mixing, the molten liquid is shaken frequently. Subsequently, the sample is transferred to an annealing furnace at 300 °C and kept inside for 3 hours to remove the thermal and mechanical strains completely that cause the embrittlement of glass. Then, the furnace is switched off and the samples are cooled down to room temperature. All the prepared glasses are cut, grinded, polished, and crushed into powder form for further characterizations. The phase of the obtained sample is identified by X-ray Diffraction pattern using the Siemens Diffractometer D5000. Diffraction patterns are collected in the range of diffraction angle (2θ) from 10° to 90°. The energy dispersive X-ray spectrometer (Swift ED3000 EDX) is used to detect any elemental traces in the glass sample. The presence of Mn_3O_4 NPs is detected using Transmission Electron Microscope (TEM) of Philips CM12 equipped with Docu Version 3.2. TEM is operated at an acceleration voltage of 200 kV. Magnetic properties such saturation magnetization (M_s), susceptibility (χ_m), coercive force (H_c) and remanent magnetization (M_r) of the glasses are determined using a Vibrating Sample Magnetometer (VSM) (Model: Lake Shore's new 7400 series) for low moment measurement capabilities with field up to 12 kOe. All measurements are carried out at room temperature.

3 Results and Discussions

Fig. 1 displays the XRD patterns of the prepared glass sample. These XRD patterns demonstrated the amorphous nature of the glass with the absence of any sharp peak. A wide hunch around 25° to 30° which caused by the diffuse scattering remarkably illustrated the existence of disorder atomic arrangement in the glass host matrix [11]. All the samples showed a comparable XRD pattern. It is observed that there is no diffraction peak for Mn_3O_4 NPs, this were possibly due to its smaller percentages in the glass samples.

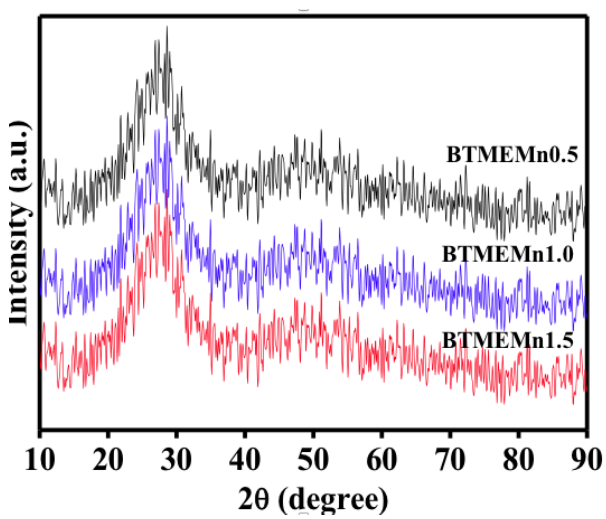

Fig. 1: Mn_3O_4 NPs content (mol %) dependent XRD patterns of prepared glass

The elemental composition of the prepared glass was verified by an EDX analysis. Fig. 2 exemplifies the EDX spectra of BTMEMn1.0 glass sample. The EDX spectra acknowledged that the homogeneous mixing of various elements such as Tellurium (Te), Boron (B) and Europium (Eu) atoms in pure as well as doped manganese as shown in Fig. 2. A small peak of Mn is also noticed. Table 1 lists the nominal and actual percentages of all elements in the present glass sample. It is noted that there are the discrepancies between the nominal and actual percentage of elements (refer Table 1) is ascribed to EDX analysis which quantifies elements by calculating the area under the peak of each identified element that is converted into weight or atomic percent. The spectrum produced by the beam is counted as its accelerating voltage. Both energy of X-ray and density of material will determine the probability of the X-ray escaping the specimen. The emitted X-ray by atom in the sample will spread into any direction that partially may be absorbed by the sample [12]. Hence, this phenomenon contributed to low accuracy of the element traces in rough and inhomogeneous sample.

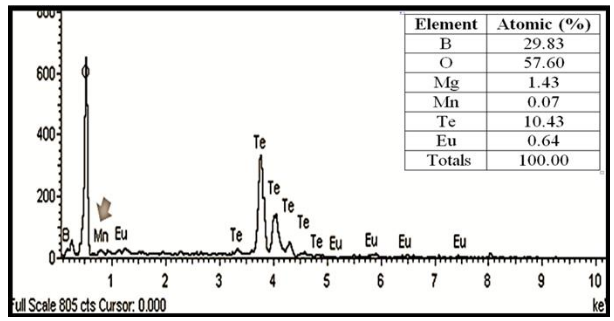

Fig. 2: EDX spectra of BTMEMn1.0 glass sample

Table 1: Nominal and actual composition of elements for BTMEMn1.0 glass

Element / mol %	Tellurium (Te)	Boron (B)	Magnesium (Mg)	Europium (Eu)	Manganese (Mn)
Nominal	58.0	30	10	1.0	2.0
Actual	24.6	70.3	3.3	1.5	0.2

Fig. 3 (a) displays the TEM images of sample BTMEMn1.0. The presence of non-spherical shaped of Mn_3O_4 NPs with different sizes are clearly evinced as black spots in the glass matrix. The occurrence of larger NPs with different sizes and shapes can be interpreted via the mechanism of coalescence of smaller NPs following Ostwald's ripening growth process [13]. Furthermore, these NPs revealed agglomeration tendency. These agglomerations of Mn_3O_4 NPs appeared due to the high attractive force between the particles as reported elsewhere [14]. Moreover, the size distribution of Mn_3O_4 NPs is found to be Gaussian (Fig. 3(b)) with an average diameter of 15.4 ± 1.0 nm.

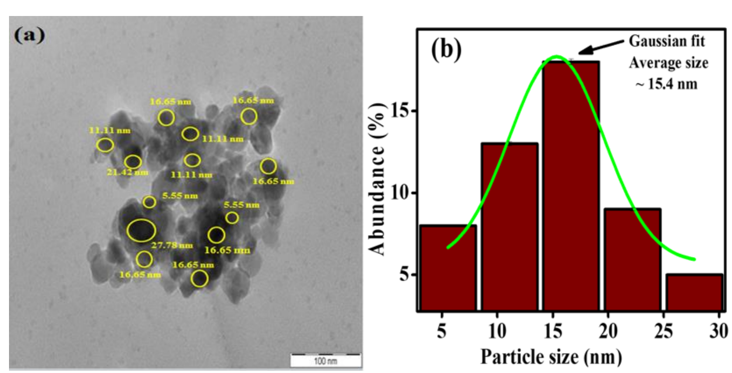

Fig. 3: (a) TEM image of sample BTMEMn1.0 glass sample (b) Size distribution of Mn_3O_4 NPs for the same glass

Fig. 4 presents the typical hysteresis loop of BTMEMn1.0 glass. The insertion of magnetization field (M-H) hysteresis loops as a function of Mn_3O_4 NPs content as well as magnetic field strength for borotellurite system were shown in Fig. 4. The hysteresis loops exhibited strong paramagnetic behavior with an increasing concentration of Mn_3O_4 NPs [18]. Room temperature magnetic properties are measured using VSM under an applied magnetic field of 12 kOe. Table 2 enlists the calculated values of saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c) and magnetic susceptibility (χ_m). These magnetic parameters revealed a gradual towards higher values consistent with the increase of Mn_3O_4 NPs concentrations in the prepared glass.

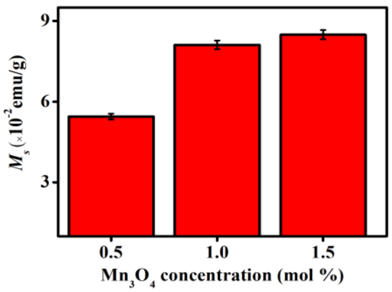

Fig. 4: Hysteresis curve of BTMEMn1.0 glass sample [Insert:

Table 2: Values of saturation magnetization (M_s), remanence (M_r), coercive force (H_c) and magnetic susceptibility (χ_m) of prepared borotellurite glass

Sample	Magnetic parameters			
	M_s (emug^{-1}) $\times 10^{-2}$	M_r (emug^{-1}) $\times 10^{-3}$	H_c (Oe)	χ_m (emuOe^{-1}g^{-1}) $\times 10^{-6}$
BTMEMn0.5	5.45 ± 0.27	0.97 ± 0.04	162.01 ± 8.10	4.54 ± 0.23
BTMEMn1.0	8.11 ± 0.40	4.06 ± 0.20	1424.42 ± 71.22	6.76 ± 0.34
BTMEMn1.5	8.49 ± 0.42	2.30 ± 0.11	81.61 ± 4.08	7.08 ± 0.35

From Fig. 4, the histogram in Fig. 5 illustrates the variations of saturation magnetizations, M_s against the concentrations of Mn_3O_4 NPs.

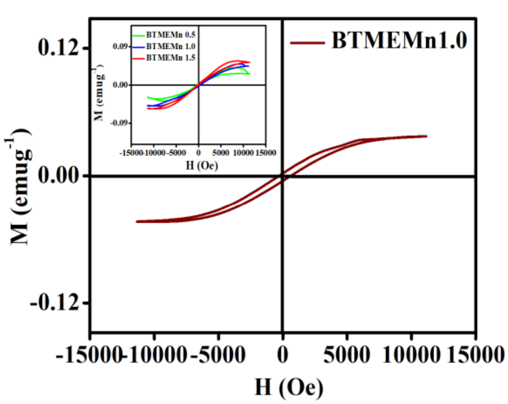

Fig. 5: M_s as a function of Mn_3O_4 NPs concentrations

Fig. 5 shows the saturation magnetization was remarkably increased with the increasing of Mn_3O_4 NPs concentrations. This is attributed by more nanoparticles moment are able to align toward applied field. Glass with 1.5 mol % of Mn_3O_4 NPs possessed the highest saturation magnetization. The increment of magnetization is also associated to the effect of interaction among the magnetic ions of manganese in the glass matrix. Furthermore, this may be attributed to the difference in the surrounding of magnetic atoms which is contributed by the spin configuration and surface area of magnetic particles that has been reported elsewhere [15]. This is presumably due to the single domain possessing a grain structure with a domain specific atomic field direction [16]. Moreover, this atomic direction remains unaffected by the influence of external magnetic field which contributes to the rotation domain and produce large energy thus enhanced the magnetization [17]. The present glass system exhibited that the remanent magnetization significantly increased by the addition of Mn_3O_4 NPs. The coercivity for the studied glasses can be explained by the presence of defects in such amorphous material that leads to magnetic behaviour. Fig. 6 illustrates the variations in coercivity of BTMEMn0.5, BTMEMn1.0 and BTMEMn1.5 glass samples.

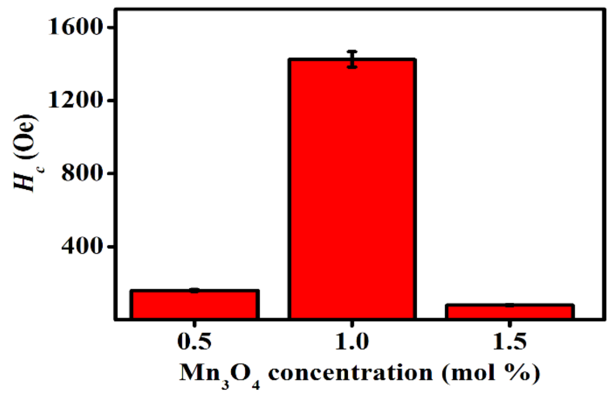

Fig. 6: Mn_3O_4 NPs concentrations (mol %) dependent coercivity, H_c

It is found that the measured value of coercivity, H_c is ranged between 81.61 to 1424.42 Oe in the synthesis glass. With the gradual increment of Mn_3O_4 NPs concentrations (up to 1.0 mol %), the value of H_c is increased but then decreased with further increment. This variation is interpreted in terms of the surface anisotropy and spin glass like state [18]. Meanwhile, susceptibility is assigned to the degree of magnetization of a material in counter to an applied magnetic field [19]. From Table 2, it can be seen that the glass with 1.0 mol % Mn_3O_4 NPs is leading susceptibility than the other glass compositions. For current study, susceptibility is found to increase as Mn_3O_4 NPs' concentrations increased. This indicates that the single ion anisotropy of Eu^{3+} magnetic ions is affecting the Mn_3O_4 NPs local field environment where the main contribution is from the changes of electron spin [20]. It is interesting to note that the incorporation of Mn_3O_4 NPs in BTMEMn glass indeed indicates all the glass samples behaving in paramagnetic nature with positive magnetic susceptibility.

4 Conclusion

Both morphological and magnetic properties of Mn_3O_4 NPs embedded in borotellurite glass have successfully been prepared by conventional melt quenching technique. The influence of various concentrations of Mn_3O_4 NPs on magnetic properties is examined. The amorphous nature of glasses is confirmed by XRD patterns. EDX spectra detected the appropriate stoichiometric elemental compositions while TEM image shows that the manganese has non-spherical shape with a size distribution around 15.4 ± 1.0 nm. The magnetic properties of prepared sample are strongly influenced by the variation of Mn_3O_4 NPs concentrations. The value of the saturation magnetization and coercive force was increased with the increment of Mn_3O_4 NPs concentrations. These NPs affirmed hysteresis characteristic of paramagnetic phase.

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6 References

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