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OPTICAL AND STRUCTURAL BEHAVIOR OF Sm^{3+} DOPED TELLURITE GLASS CONTAINING MN NPS

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ABSTRACT

Metallic nanoparticles (NPs) embedded rare earth (RE) doped tellurite glasses due their unique and exotic nonlinear optical properties became attractive in nanophotonic research. Lately, magnetic NPs (Fe, Ni, Mn and Co) incorporated tellurite glasses received much attention due to their distinctive structural, optical, magnetic and physical properties promising for assorted applications. Most of the tellurite based glasses with varying modifiers, magnetic NPs and RE dopants displaying ferrimagnetic behavior are useful for magneto-optic devices. Tunable modifications of physical and optical properties of samarium (Sm^{3+}) doped oxy-chlorite tellurite glasses containing manganese (Mn) NPs remain challenging. Developing RE doped magneto-optic plasmonic nanoglasses with superior properties by stimulating surface plasmon resonance (SPR) of embedded magnetic nanostructure in the glass network is a long standing quest. It is needless to mention, that tellurite glasses have saveral advantages over conventional silicate, phosphate and borate glasses. However, their low absorption and emission cross-section and luminescence quenching at higher RE concentration are major drawback for efficient device fabrication. Improving the optical performance by avoiding the concentration quenching is the key issue. Incorporation of metal NPs of controlled sizes are opted as alternative route for spectral modifications. Following melt-quenching method we prepared a series of Mn NPs embedded Sm^{3+} doped oxy-chlorite tellurite glass of composition $68.5TeO_2+5Li_2O+15MgO+10LiCl+1.5 Sm_2O_3+y$Mn (where $0.00 \leq y \leq 0.1$ mol %) and determined their optical properties. Glasses are characterized using XRD, TEM, PL and VSM measurements. TEM image display the existence of spherically shaped Mn NPs with means size ~31.34 nm. Emission spectra exhibit four intense peaks in the visible region with remarkable intensity quenching. Presence of NPs is found to influence strongly the emission behaviours. Significant modification of physical, structural, optical, magnetic properties and local environment of RE caused by the insertion of NPs are evidenced. The notable features of the results demonstrate diversified prospective applications of these glass compositions. The financial support from MOE, Malaysia via GUP/RU research project grant (Vote: 05H36) and MyBrain15 is gratefully acknowledged.

Keywords: Nanoparticles; Absorption; Energy band gap; Luminescence.

INTRODUCTION

Unique nonlinear optical properties of metallic nanoparticles (NPs) embedded rare earth (RE) doped tellurite glasses became attractive in nanophotonic research field. Recently, magnetic NPs such as Fe, Ni, Mn and Co incorporated tellurite glasses received much attention due to their distinctive structural, optical, magnetic and physical properties promising for many applications like bio-imaging and magnetic energy storage. Tellurite glasses is a great glass former which posses several advantages over conventional silicate, phosphate and borate glasses. Most of the tellurite based glasses with varying modifiers, magnetic NPs and RE dopants displaying ferrimagnetic behaviour which are useful for magneto-optic devices.

From the previous study it is claimed that RE elements have typical relaxation characteristics, which directly dependent on electromagnetic properties of magnetic particle like ferrite. It is also reported that ion substituition such as ion 2+ subtitute to ion 3+ improve their properties and characteristic[1]. For manganese oxide particles it is observed that Mn^{2+} is obscured by Mn^{3+} at higher concentration of MnO[2]. Mn^{3+} ions, take part modifying the glass network.

Current study gives us view that manganese ion have strong influence on optical, magnetic and electrical properties of the glass. Tunable modifications of physical and optical properties of samarium (Sm^{3+}) doped lithium-magnesium-oxycloride-tellurite glasses containing manganese (Mn) NPs remain the key issues.

EXPERIMENTAL

Series of tellurite glass were prepared via melt quenching technique with molecular composition $68.5TeO_2 + 5Li_2O + 15MgO + 10LiCl + 1.5\ Sm_2O_3 + y$Mn, where y is 0.00, 0.02, 0.04, 0.06, 0.08 and 0.1 mol percent. Raw materials with high purities (Sigma Aldrich analytical grade purity, 99.99%) are weight to prepare samples of 15 gram each. Then, the homogenized mixed compound is melted in the furnace at 900^oC for an hour by using platinum crucible. The melted compounds are casted on metal molding plates and undergo annealing at 300^oC for about two hours before it is cooled down into room temperature. The specimen is polished, grind and the thickness is fixed at 2mm for characterization purposes.

In order to investigate the magnetic and optical responses occurred due to concentration changes of Mn NPs, certain characterization process was conducted. The emission spectra are recorded by Perkin Elmer LS-55 photoluminescence (PL) spectrometer (UK). Magnetic behavior of the glasses is determined using Lake Shore’s new 7400 series vibrating sample magnetometer (VSM) at room temperature in a field of 12000 O.e. Meanwhile sizes, shapes, and distribution of NPs were recorded using TEM spectroscopic. XRD pattern were recorded using Siemen Diffractometer model D5000.

RESULTS AND DISCUSSION

Appearances of prepared glass are orange in color, transparent and become darker with incorporation of metallic Mn NPs. The amorphous nature of the glass is proven by XRD pattern. Figure 1, show XRD pattern for a sample with Mn NPs concentration at 0.1 mol percent. Broad ham is observed at 15° – 40° exhibit the existence of long range structural disorder in the prepared glass. All glass displays same pattern.

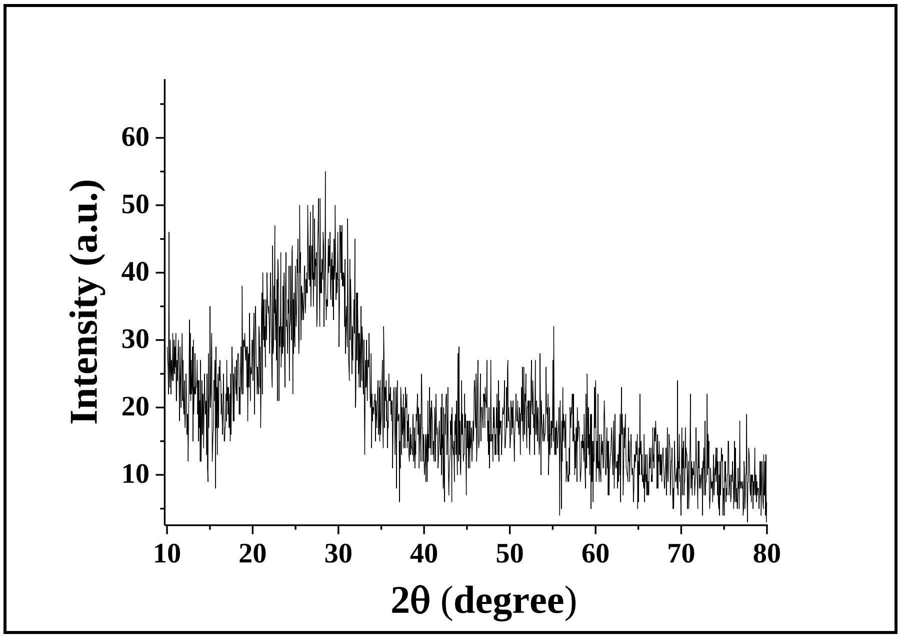

Figure 1: XRD pattern for 0.1 mol percent of Mn NPs

PL emission spectra were recorded in room temperature with excitation wavelength at 402nm and emits four emission band in the visible region with FWHM at 577nm (green), 614nm (yellow), 658.5nm (red) and 719.5 nm (red) corresponding to the transitions from $^4G_{5/2}$ excited state to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, and $^6H_{11/2}$ ground states. Among all energy transition, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ exhibit most intense spectra. Other paper reported that transition of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ have the highest value of branching ratio for Sm^{3+} energy level which are excelent for laser transition [3]. In the other hand, the radiative properties of Sm^{3+} are dependent on the glass former network, modifier, and its local field. The radiative transition rates which correlates to radiative decays are also depend upon Judd–Ofelt parameters and energy gap between initial level and terminal level.

Figure 2 shows that the intensity of emission spectra decreased dramatically as the Mn NPs is inserted. Reduce of intensity are assign to be due to non radiative decays. For examples energy might have lost in the form of heat or multi-phonon processes during energy transition associated with magnetic nature of Mn NPs. The observed concentration quenching due to Mn NPs, might be attributed to the energy transfer through cross-relaxation mechanism mediated via dipole-dipole interaction within the RE atom and also an energy transfer from Sm^{3+} ion to its local field of NPs [4].

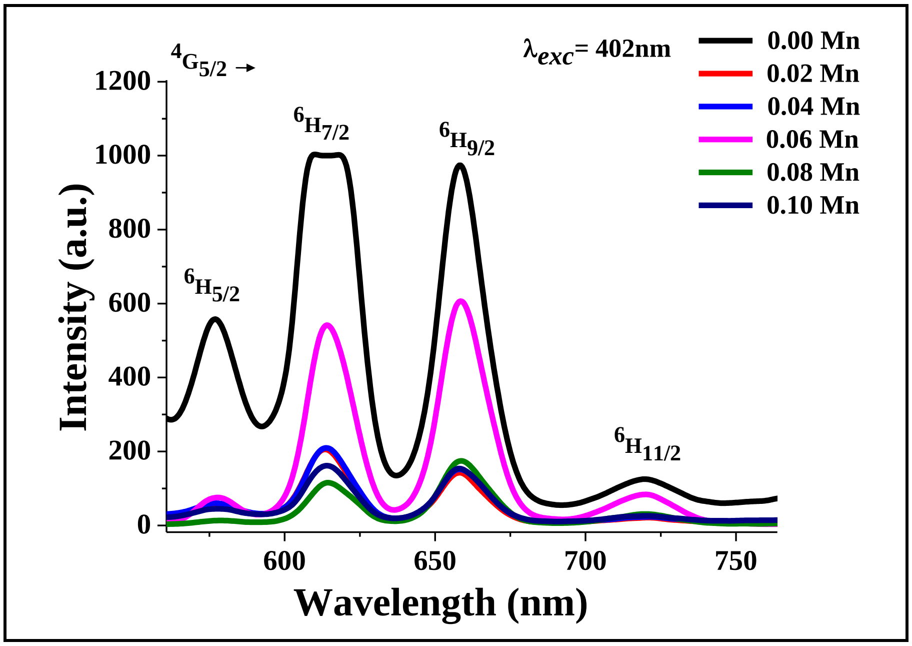

Figure 2: NPs concentration dependent emission spectra for all samples

VSM were conducted to determine the changes on magnetic properties of samples. Figure 3 illustrates hysteresis loop for current glass with and without Mn NPs. The hysteresis magnetization loop for both glasses exhibit ferrimagnetic behaviors. Magnetic properties of the glass, become stronger with the presence of Mn NPs. Five magnetic parameter obtained are saturation magnetization Ms, remanent magnetization Mr, susceptibility χ, squareness Mr/Ms, and coercivity Hc. Susceptibility is determined by using equation 1.

$$\chi = \frac{Ms}{H} \quad (1)$$

H is stand for external magnetic field. All the magnetic parameters for tellurite glass with and without Mn NPs were listed in table 1.

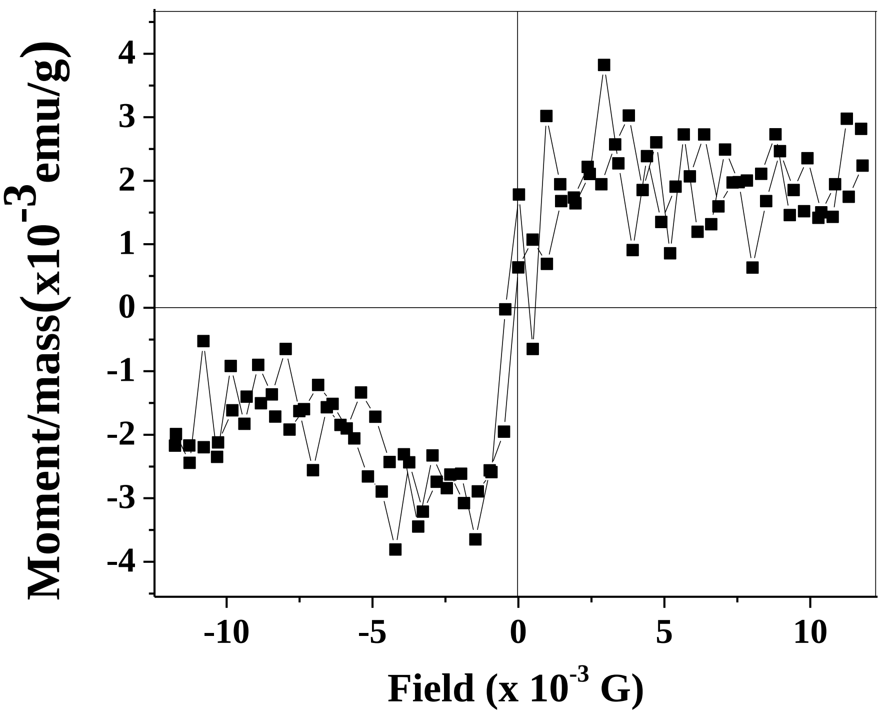

Figure 3 (a): Hysteresis loop of glass with 0.0 mol percent of Mn NPs.

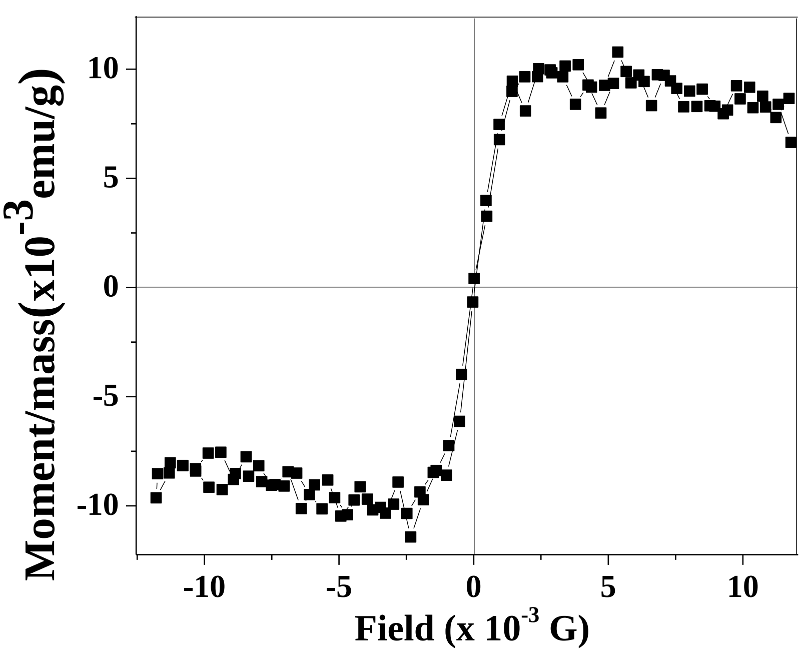

Figure 3 (b) : Hysteresis loop for glasses with and without Mn NPs.

Table 1: Magnetic parameter for tellurite glass with and without Mn NPs

Mn NPs concentration (Mol %)	0.00	0.10
Saturation magnetization, Ms (x 10^{-03} emu/g)	47.060	37.410
Remanent magnetization, Mr (x10^{-6} emu/g)	531.54	310.53
Susceptibility, χ (x10^{-6})	3.9200	3.1200
Squareness, Mr/Ms (x 10^{-02})	1.1300	0.8300
Coercivity, Hc (G)	4.7938	1300.2

Image of Mn NPs in the glass matrix were captured by TEM and shown in Figure 4 with scale ratio of 100nm to 1cm. Black spots show the Mn NPs with irregular shapes. Red line is the highlighted diameter. The distribtuion of Mn NPs is compared to other reported paper [5-7]. Instead of scattering like gold and silver NPs, Mn NPs tend to cluster with each other [8-10]. This might be due to the high surface charge onto the nanoparticles and magnetic dipole–dipole interaction[11].

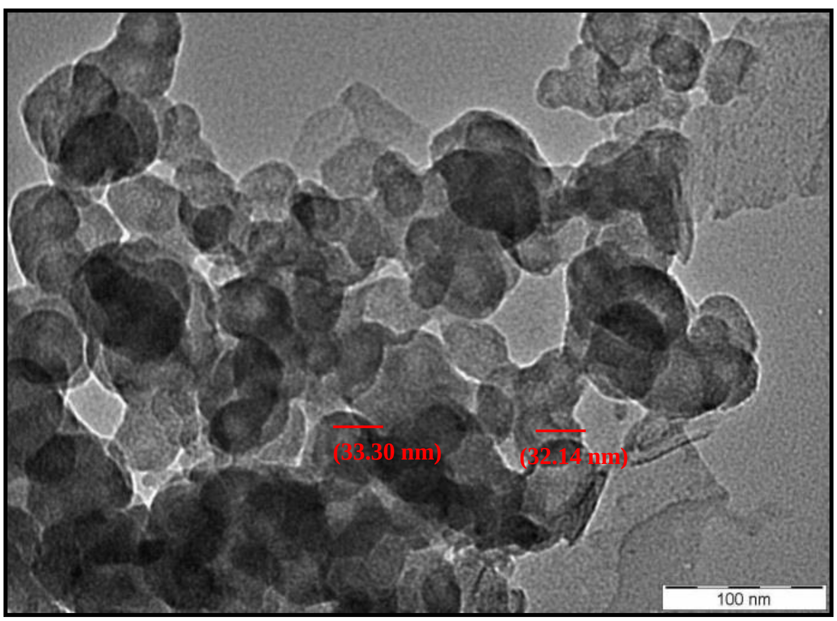

Figure 4: TEM image of Mn NPs in the glass matrix

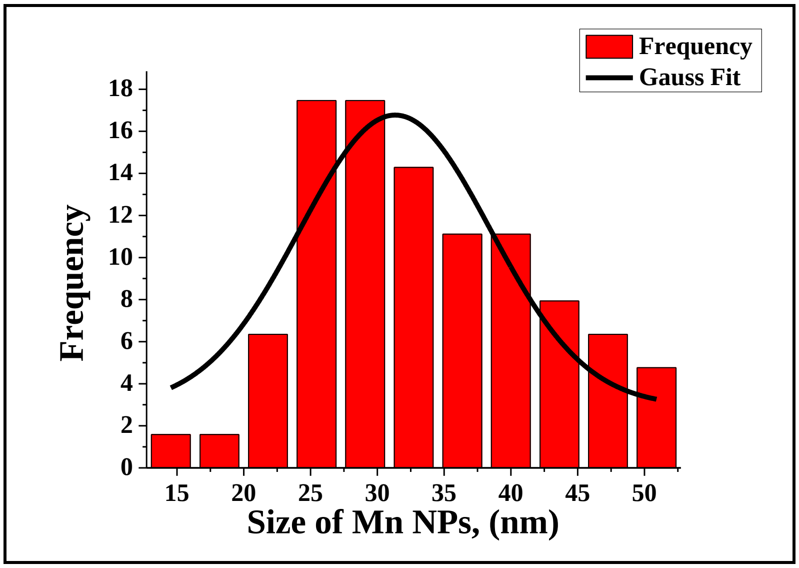

Figure 5: Gaussion fit of sizes distribution Mn NPs

Figure 5, shows the Gaussian fit for sizes distribution of Mn NPs in the glass. 60 of seen NPs, are chosen randomly and the size is measured. The sizes are ranged within 15nm to 50nm. Most frequent size is at 25nm to 30nm. Average size of Mn NPs in TEM image is ~31.34nm approximately.

CONCLUSION

Glass systems with molar composition 68.5TeO_2–15MgO–5Li_2O–10LiCl–1.5Sm_2O_3 – *x*Mn, where *x* is 0.02, 0.04, 0.06, 0.08 and 1.0 mol percent were prepared by using conventional melt-quenching method and the influences of Mn NPs on optical and magnetic properties ware determined. Long range structural disorder of XRD pattern confirmed the glass nature. The observed quenching in luminescence intensities in all samples containing Mn NPs is understood in terms of various mechanisms. Hysteresis loops evidenced that magnetic polarization is influenced by Mn NPs. The TEM image shows Mn NPs with mean size of ~31.34nm and irregular spherical shapes. Our observation may be useful for knowledge and development in potential lasing glass materials.

ACKNOWLEDGMENT

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