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Optical response and magnetic characteristic of samarium doped zinc phosphate glasses containing nickel nanoparticles

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ABSTRACT

A magnetic glass of composition $40ZnO–(58-x)\,P_2O_5–1Sm_2O_3–xNiO$, with $x=0.0$, 1.0, 1.5 and 2.0 mol% is prepared by melt-quenching technique. The glass is characterized by X-ray diffraction, high-resolution transmission electron microscope (HRTEM), photoluminescence (PL) spectroscopy and vibrating sample magnetometer (VSM) analysis. The X-rays diffraction confirms the amorphous nature of the glass while the HRTEM analysis reveals the presence of nickel nanoparticles in the glass samples. High-resolution TEM reveals that the lattice spacing of nickel nanoparticles is 0.35 nm at (100) plane. Photoluminescence emission shows the existence of four peaks that correspond to the transition from the upper level of $^4G_{5/2}$ to the lower level of $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2,}$ and $^6H_{11/2.}$ It is observed that all peaks experience significant quenching effect with the increasing concentration of nickel nanoparticles, suggesting a strong energy transfer from excited samarium ions to the nickel ions. The glass magnetization and susceptibility at 12 kOe at room temperature are found to be in the range of $(3.87\pm0.17\times10^{-2}–7.19\pm0.39\times10^{-2})$ emu/g and $(3.24\pm0.16\times10^{-6}–5.99\pm0.29\times10^{-6})$ emu/Oe g respectively. The obtained hysteresis curve indicates that the glass samples are paramagnetic materials. The studied glass can be further used towards the development of magneto-optical functional glass.

1. Introduction

Many studies have been conducted especially in the material science field and have significantly improved the quantum efficiency of the lasers material [1–3]. Phosphate is enormous materials that give many excellent properties as a host glass by incorporating with rare-earth (RE) ions [4,5]. Phosphate glasses are very excellent materials to accommodate other oxide materials [6]. By controlling the RE doped phosphate glass embedded with metallic nanoparticles (NPs), quenching in luminescence intensity due to energy transfer from RE ions into the surface of metallic NPs can be overcome [3]. The significance of lasing transition of $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ evaluated from the photoluminescence spectra originating from samarium (Sm^{3+}) shows wide potential applications for efficient visible optical devices [1,7,8]. Zinc oxide as a metal transition is able to modify the structural, physical and chemical durability properties of the host glass former [6,9–12].

The metallic NPs such as silver and gold have been studied to improve RE luminescence and enhance the non-linear optical properties [13,14]. NPs can increase the yield of their weak optical transitions by generation of intense electric fields upon electromagnetic excitation where plasmonic metal nanostructures in the vicinity of the rare-earth (RE) ions alter their free space spectroscopic properties [15]. This mechanism so-called nanometal enhanced fluorescence (NMEF) and it is due to the localized surface plasmons resonance (LSPR). Three main phenomena that govern the origin of the electromagnetic field enhancement are the localized surface plasmons (LSP), the change confinement at the metallic nanoparticles extremities and coupling the effect [16]. The magneto-optical material is another promising area to study the magnetic properties on RE ions environment in glasses [17,18]. In addition, nanometers magnetic particles give a more sensitive response to the change of applied magnetic field and thus exhibit super-paramagnetic coexistence of single domain materials [19]. This reveals interesting optical and magnetic properties such as surface plasmon resonance (SPR) absorption and super-paramagnetism [20–22]. The investigation on Mn^{2+}, Fe^{2+} and Co^{2+} (transition metal ions) with RE doped host glasses have significantly increasing the interest in their properties for magneto-optical devices such as isolator, switches and sensing application [18,21,22].

In this work, samarium doped zinc phosphate glasses embedded with nickel (Ni) nanoparticles have been prepared by conventional melt quenching technique. The aims of the present study are to investigate the influence of Ni NPs in the glass matrix

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on the structural, magnetic and luminescence properties. The mechanisms of the embedded Ni NPs are also analyzed and understood.

2. Experimental procedure

Homogeneous samarium doped zinc phosphate glasses embedded with nickel nanoparticles are prepared using conventional melt quenching technique with molar composition of 40ZnO–$(58-x)$ P_2O_5–$1Sm_2O_3$–xNiO, where x=0.0, 0.5, 1.0, 1.5 and 2.0 mol%. Starting powder of ZnO (99%), P_2O_5 (98%), Sm_2O_3 (99%) and NiO (99.8%) are used as nominal composition. The batched mixture around 15 g is placed in an alumina crucible and melted in a furnace at 900 °C for 20 min. The melt is then poured into a mold of steel before annealing at 350 °C for 3 h to reduce the residual stress. The melt is then cooled down to room temperature. Finally, the samples are cut, ground and polished for the optical measurements. Grinding and polishing is done by grit silicon carbide sandpaper up to 1000 μm and diamond paste with grit size up to 3 μm respectively. X-ray diffraction (XRD) analysis is performed on Siemens Diffractometer D5000 using CuKα radiations (λ=1.54 Å) at 40 kV and 100 mA, with scanning angle 2θ ranges between 10° and 80° to verify the amorphous nature of all glass samples.

The microstructures and compositional analysis of Ni NPs in the glass are determined using high resolution transmission electron microscopy (HRTEM) image on JEOL 2100F at an acceleration voltage of 200 kV. Powder samples are ultra-sonicated in toluene before dropping on copper grids, which are the most frequently used TEM grids. The glass density is determined by standard principle of Archimedes following

$$\rho = \frac{W_a}{W_a - W_b}\rho_x \tag{1}$$

where w_a is weight of the glass sample in air and w_b is the weight of the sample when immersed in toluene of density $\rho_x = 0.8669\ \mathrm{g\ cm^{-3}}$. In other dimension, ionic packing density is calculated by [23,24]

$$V_t = \left(\frac{1}{V_m}\right)\sum (V_i x_i) \tag{2}$$

where V_m is molar volume of the glass sample, x_i is molar fraction (mol%) and V_i is packing density parameter ($\mathrm{m^3/mol}$) that indicates the effect of Ni NPs on the glass network. The relations of an oxide M_XO_Y and V_i can be expressed as follow

$$_i = \left(\frac{4\pi N_A}{3}\right)\left[Xr_M^3 + Yr_O^3\right] \tag{3}$$

where N_A is Avogadro's number ($\mathrm{mol^{-1}}$) while r_M and r_O are the ionic radius of metal and oxygen respectively, [25].

From the measured density, ρ and calculated average molecular weight, $\bar{M}$, nickel ion concentration, N_i and mean nickel ion separation R_i can be determined using relations

$$N_i = \frac{N_A x \rho}{\bar{M}} \tag{4}$$

and

$$R_i = \left(\frac{1}{N_i}\right)^{1/3} \tag{5}$$

mol% of Ni NPs, x was tabulated in Table 1.

Perkin-Elmer LS-55 photoluminescence (PL) spectrometer (UK) is used to measure emission properties of respected samarium doped zinc phosphate embedded nickel nanoparticles glasses. The decay lifetime is calculated using following relation

$$\tau = \frac{A_1\tau_1{}^2 + A_2\tau_2{}^2}{A_1\tau_1 + A_2\tau_2} \tag{6}$$

where A_1 and A_2 are constants, and τ_1 and τ_2 are the rapid and slow lifetimes respectively. However if $\tau_1=\tau_2$, and $A_1=A_2$, then Eq. (6) can be rewritten as,

$$\tau = \frac{2A_1\,\tau_1{}^2}{2A_1\,\tau_1} = \tau_1 \tag{7}$$

Meanwhile, the exponential component can be calculated through relations of direct transfer

$$I(t) = I_o + A_1\exp\left(\frac{-t}{\tau_1}\right) + A_2\exp\left(\frac{-t}{\tau_2}\right) \tag{8}$$

and can be rewritten as,

$$I\,(t) = A\exp\left(\frac{-\tau}{\tau}\right) \tag{9}$$

where I is the luminescence intensity when I_o of initial luminescence intensity is constant and t is time, which excited at 401 nm with operating power at 20 kW for 8 μs duration.

Saturation magnetization (M_s), coercive force (H_c), remanence (M_r) and squarness M_r/M_s of the glasses is determined using vibrating sample magnetometer (VSM) Lake Shore's 7400 series at room temperature in the fields up to 12 kOe. Vibrating sample magnetometer (VSM) is used to measure magnetic moment and hysteresis loop of a sample when it is vibrated perpendicularly to a uniform magnetic field [26]. Data on hysteresis loop are presented for magnetic materials without substrate (glass host) for low moment measurement capabilities using the Lake Shore VSM. Magnetic susceptibility, χ_m are obtained by relations,

$$M = \chi_m H \tag{10}$$

where χ_m is magnetic susceptibility, M is magnetization and H is magnetic field. It is measured using magnetic field strength with a maximum value of 12 kOe.

Table 1
Calculated physical and magnetic properties of 40ZnO–$(58-x)$ P_2O_5–$1Sm_2O_3$–xNiO glasses; density (ρ), ionic packing density (V_t), mean Ni NPs ion separation, R_i, Ni ion concentration (N_i), saturation magnetization (M_s), remanence (M_r), coercive force (H_c), squarness (M_r/M_s)and magnetic susceptibility (χ_m).

x (mol%)	Density, ρ ($\mathrm{g/cm^3}$) ± 0.001	Ionic packing density, V_t (in %) ± 0.001	Mean Ni NPs ion separation, $R_i \times 10^{-21}$	Ni ion concentration, $N_i \times 10^{20}$ (ions/$\mathrm{cm^3}$)	M_s (emu/g) $\times 10^{-2}$	M_r (emu/g) $\times 10^{-3}$	H_c (Oe)	M_r/M_s (emu/g) $\times 10^{-2}$	χ (emu/Oe g) $\times 10^{-6}$
0.0	2.839	40.552	–	–	4.17 ± 0.21	2.62 ± 0.13	787.82 ± 39.40	6.27 ± 0.31	3.47 ± 0.17
0.5	2.893	41.147	4.57 ± 0.27	0.729 ± 0.039	5.67 ± 0.27	0.42 ± 0.02	103.15 ± 5.15	0.72 ± 0.04	4.73 ± 0.23
1.0	2.875	40.717	2.29 ± 0.11	1.453 ± 0.073	3.87 ± 0.17	0.45 ± 0.01	260.74 ± 13.04	1.15 ± 0.05	3.24 ± 0.16
1.5	2.893	40.814	1.52 ± 0.08	2.199 ± 0.111	7.19 ± 0.39	0.11 ± 0.01	22.20 ± 1.12	0.16 ± 0.01	5.99 ± 0.29
2.0	2.918	40.985	1.12 ± 0.06	2.966 ± 0.148	5.30 ± 0.25	0.17 ± 0.01	1653.50 ± 82.65	0.32 ± 0.01	4.42 ± 0.22