Journal of Non-Crystalline Solids 411 (2015) 53–58

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Modification of structural and physical properties of samarium doped zinc phosphate glasses due to the inclusion of nickel oxide nanoparticles

Siti Amlah M. Azmi, M.R. Sahar *, S.K. Ghoshal, R. Arifin

Advanced Optical Material Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310, UTM Skudai, Johor, Malaysia

ARTICLE INFO

Article history:
Received 18 September 2014
Received in revised form 11 December 2014
Accepted 19 December 2014
Available online xxxx

Keywords:
Nickel oxide nanoparticles;
Samarium;
FTIR;
Raman;
Phosphate

ABSTRACT

A series of nickel oxide (NiO) nanoparticles (NPs) embedded samarium (Sm^{3+}) doped zinc phosphate glass of the form $(58 - x)P_2O_5$–40ZnO–$1Sm_2O_3$–xNiO, with x = 0.0, 0.5, 1.0, 1.5 and 2.0 mol% are synthesized via melt quenching technique and the influence of NPs (at fixed concentration of Sm^{3+}) on their overall behaviors are examined. XRD pattern verifies the amorphous nature of prepared glass samples. TEM images reveal the existence of NiO NPs with average size ~8 ± 1 nm. Physical properties such as glass density (2.8 ± 0.1–3.0 ± 0.1 g cm^{-3}), molar volume (42.2 ± 0.1–40.6 ± 0.1 cm^3 mol^{-1}) and hardness (173.2 ± 0.1–465.1 ± 0.1 Hv) are all found to increase with the increase of NPs concentrations. The absorption spectra exhibit surface plasmon resonance (SPR) peak of NiO centered at 433 nm. The vibrational modes are obtained using Fourier transform infrared (FTIR) and Raman analyses. Four major IR absorption bands centered at 723, 916, 1081 and 1280 cm^{-1} are evidenced. Raman spectra display two significant peaks at 708 and 1201 cm^{-1} attributed to the symmetric and asymmetric stretching vibrations of P – O – P bridging oxygen in Q^1 units and non-bridging oxygen (NBO) in Q^2 units respectively. NPs assisted alteration in structural and physical properties are majorly attributed to the strong local field effect in the proximity of rare earth ion, generation of NBO ions and energy transfer. Our observation may contribute towards the development of NPs embedded rare earth doped glass photonics.

1. Introduction

Lately, phosphate glasses doped with trivalent rare-earth (RE^{3+}) ions containing NPs received major attraction due to various striking features [1–5]. Among other host glass, RE doped phosphate glasses are preferred in optical communication, photonic devices and lasing materials [6,7]. The low melting temperature, insulating behavior, high thermal expansion and excellent ability in accommodating large amount for rare-earth (RE) ions make them promising [7–9]. Moreover, incorporation of metal oxide modifiers such as ZnO, Al_2O_3 and MgO in the phosphate host alters the structural units of the network and thereby improves their chemical durability and physical properties [10–12]. However, the changes in the overall structure depend very much on their compositions [6]. For example, the Zn ions give different forms of phosphate chain through the delocalization of P═O and $P-O^-$ bonds [6,12]. The addition of other metal oxides is needed to understand the disorder nature of the glassy state and the contribution of P – P bonds.

Currently, the significant optical enhancement in phosphate glasses caused by embedding metal oxide NPs became fascinating [1,2]. Ferromagnetic magnetic NiO NPs owing superior optical and electronic properties are well known for diverse applications in catalysis, gas sensor and magnetic devices [13–15]. NiO NPs also offer high thermal stability and possess a compromised size and surface effects which are fit for many optical applications. Furthermore, Ni^{2+} ions in octahedral sites exhibit several strong absorption bands in the visible and NIR regions [16,17]. In the IR region, the displayed emission peak around 1.5 μm is similar to that of the luminescence characteristics of erbium doped glasses [16,18]. In nickel–zinc phosphate glasses, the ability of NiO NPs in occupying the tetrahedral zinc site with cubic symmetry is reported [19]. Despite some efforts the notable modifications in the structural, thermal, physical and optical properties of RE doped phosphate glasses containing NiO NPs is far from being understood.

In this paper, the NiO NP concentration dependent alteration in physical and structural characteristics of Sm^{3+} doped zinc-phosphate glasses synthesized via the melt-quenching method. The sizes of NPs are estimated and the role of NPs in stimulating SPR effects is discussed.

2. Experimental

Glasses with composition 40ZnO–(58 − x) P_2O_5–$1Sm_2O_3$–xNiO (where x = 0.0, 0.5, 1.0, 1.5 and 2.0 mol%) are prepared using the conventional melt quenching method. Starting powdered materials (analytical grade with high purity) of ZnO (99%), P_2O_5 (98%), Sm_2O_3 (99%) and NiO (99.8%) are mixed thoroughly with appropriate proportion. The homogeneous mixture is placed in an alumina crucible and melted in a furnace at 900 °C for 20 min before being annealed at 350 °C for 3 h to reduce the mechanical stress avoiding embrittlement. The melt is

* Corresponding author.
E-mail address: mrahim057@gmail.com (M.R. Sahar).

http://dx.doi.org/10.1016/j.jnoncrysol.2014.12.024
0022-3093/

then cooled down to room temperature. Finally, the samples are cut and polished for the optical measurements. X-ray diffraction (XRD) analysis is performed on a Siemens Diffractometer D5000 using CuK_α radiations ($\lambda = 1.54$ 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. Glass densities are measured by Archimedes method via analytical balance with specific density (Precisa XT 220 A) using toluene as an immersion liquid while the hardness is determined using the Vickers hardness test at a constant loading of 98.1 N. Transmission electron microscopic (TEM) measurements are performed using a Philips CM12 operating at 200 kV with Dock version 3.2 image analyses. The room temperature absorption spectra in the range of 200 to 700 nm are recorded by using a Shimadzu UV-3101PC (Kyoto, Japan) scanning spectrophotometer. A Perkin-Elmer 1710 Fourier transform infrared spectrometer in the range of 400–4000 cm^{-1} is employed to record the transmission spectra following KBr disc technique. Transparent disc pallets of surface area ~1 cm^3 are formed by compressing the homogeneous mixture of relatively fine glass powder and anhydrous KBr at ratio of 1:100. The Raman measurement is performed using a confocal Horbia Jobin Yvon (Model HR800 UV) with Argon ion laser (excitation wavelength 514.55 nm) that operates at 20 mW in the range of 400–4000 cm^{-1}. The errors are mainly due to the instrumental and experimental which has been estimated to be around 5%.

3. Results and discussion

The XRD patterns of all Sm^{3+} doped zinc phosphate glass samples containing NiO NPs as shown in Fig. 1 displaying a broad diffraction band verify their amorphous nature.

TEM image in Fig. 2 displays the presence of non-spherical NiO NPs in the glass matrix. The black spots with red circles verify the occurrence of NiO NPs having different sizes and shapes. The inset illustrates the Gaussian size distribution of NiO NPs. The average diameter of NPs is found to be 8.0 ± 0.1 nm. The occurrence of varying sizes and shapes of NPs are attributed to the formation of bigger NPs (refer to red circle) via coalescence of smaller NPs following well known growth principle called Ostwald's ripening process where particles with different morphology tend to assemble for free energy minimization.

Fig. 3 shows the SPR band in the UV–Vis absorption spectra. It can be seen that, the prominent plasmon peak evidenced at 433 nm. This is due to the strong local electro-magnetic field of NiO NPs [20,21]. The appearance of a strong SPR band at 335 nm for pure NiO NPs is reported [14]. The SPR bands of NiO NPs are found to be red-shifted [20,21]. The influence of surrounding local field of NPs is responsible for such optical

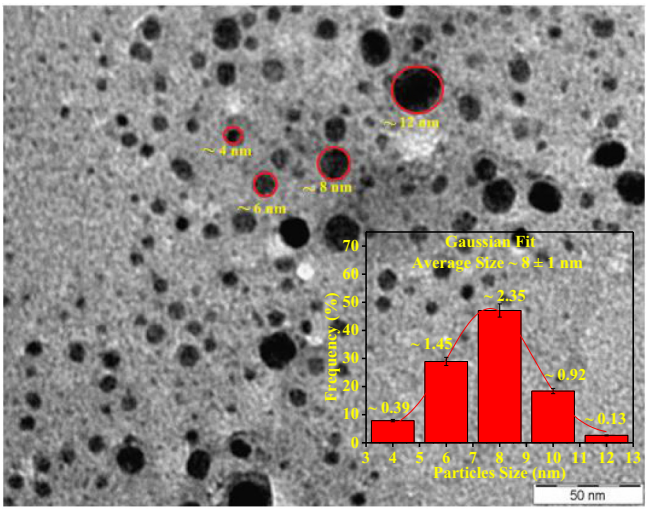

Fig. 2. Typical TEM micrograph for the glass sample showing the existence of NiO NPs with varying sizes. The inset shows the NP size distribution.

enhancement. The variation in the size and shape of NPs influences the wavelength (λ_{SPR}) of SPR band [21,22]. The position of SPR peaks is known to depend upon the nominal percentage of metallic NPs added in host and the glass refractive index [35]. This red-shift of the SPR wavelength can be explained through Mie's scattering theory following:

$$\lambda_{max}^2 = (2\pi c)^2 mNe^2\left(\varepsilon_\infty + 2n^2\right)/\varepsilon_0 \quad (1)$$

where c is the speed of light, N is the concentration of free electrons, m is the conduction electrons' effective mass, ε_0 is the permeability of free space and ε_∞ is the metal optical dielectric function. It is higher refractive index of the dielectric media responsible for such red-shift of the SPR peak positions.

The refractive index n of each sample (Table 1) is calculated following [42]:

$$\frac{n^2-1}{n^2+1} = 1-\sqrt{\frac{E_{opt}}{20}} \quad (2)$$

where E_{opt} is the optical band gap energy of the glass obtained from absorption data.

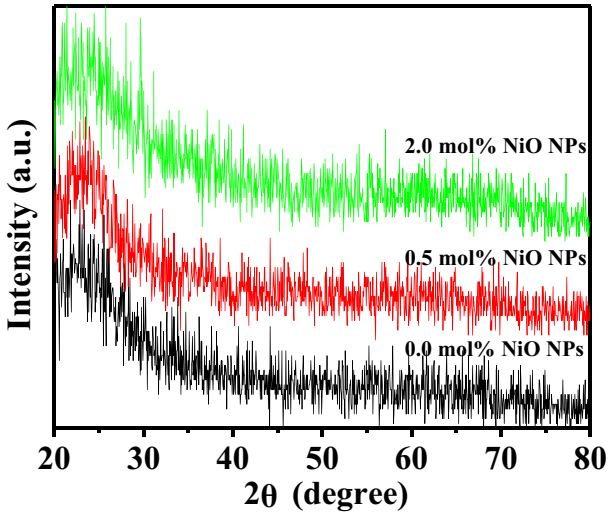

Fig. 1. The XRD patterns of NiO NPs embedded Sm^{3+} doped zinc phosphate glasses.

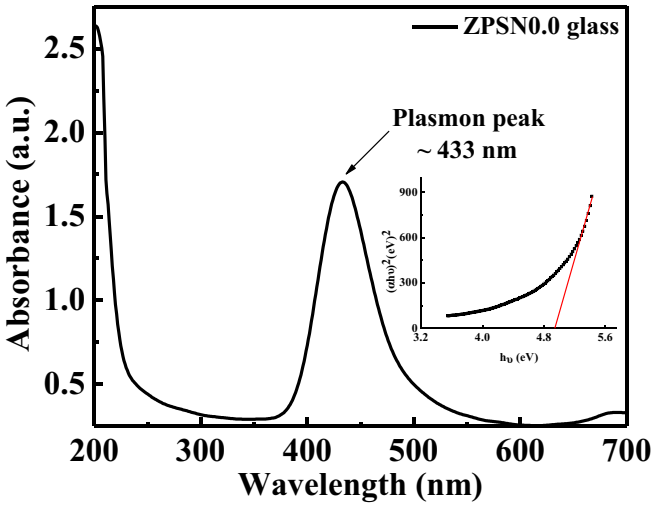

Fig. 3. UV–Vis absorption spectra of glasses without Sm_2O_3 and with 1 mol% NiO NPs.