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Structural and magneto-optical properties of ferric oxide quantum dots embedded phosphate glass

Jingbo Yu[a], Qian Zhang[a,b], Yi Gu[a], Anxian Lu[a,*]

[a] School of Materials Science and Engineering, Central South University, Changsha 410083, China
[b] Key Lab. of Power Batteries & Relative Materials, Jiangxi University of Science & Technology, Ganzhou, Jiangxi Prov., 341000, China

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ABSTRACT

In this study, phosphate glasses embedded with Fe_2O_3 quantum dots were prepared via a conventional melt quenching technology with further heat treatment. The effect of Fe_2O_3 content on the structural, optical and magneto-optical properties was investigated. The results showed that the addition of Fe_2O_3 had no obvious influence on the structure units that built up the host glass and the amorphous nature of glass. In the glass matrix, the existence of Fe_2O_3 quantum dots was confirmed by high resolution transmission electron microscope. Meanwhile, optical study clearly demonstrated a red shift in optical cut-off wavelength resulted from the size quantization effect. The highest Verdet constant (22.33°/T-cm) was measured for the glass containing 1 mol% Fe_2O_3, which was ~ 7 times higher than that of the glass matrix. As the increment of Fe_2O_3 contents, a phase evolution of Fe_2O_3 quantum dots from amorphous phase to γ-Fe_2O_3 phase was recorded due to the Ostwald Ripening effect. Interestingly, a concentration quenching phenomenon in Verdet constant was observed along with the phase evolution of Fe_2O_3 quantum dots. When the content of Fe_2O_3 is up to 2 mol%, the glass exhibited paramagnetism with the Verdet constant of − 2.833°/T-cm. This finding can provide a new idea for the development of quantum dot embedded magneto-optical glass.

1. Introduction

The magnetic nanoparticles dispersed glass, a new type of transparent functional magneto-optical material, has been used as the magneto-optically active media for the new field of applied devices, such as optical fiber current sensors [1], optical isolators [2] and magneto-optical current transformers [3].

Different from traditional magneto-optical glass systems [4–6], the size quantization effect (the quantum confinement effect) can be generated in glass due to the presence of small size nanoparticles. Generally, the interaction between nanoparticles and other carriers or quantum mechanical spins can be enhanced by this effect [7]. Besides, the Zeeman splitting can be induced and the electrons energy levels are altered obviously [8]. It is also noteworthy that a unique phenomenon of so-called giant Faraday rotation has been reported resulting from the quantum confinement effect [9]. In the past few years, the magneto-optical properties of the glass doped nanoparticles have been extensively studied [1–3,10]. However, most nanoparticles focus on II–VI semiconductor compounds or related diluted magnetic semiconductors (DMSs) with inserted magnetic dopants (Mn, Fe, Co, Ni). Considering this, exploring newer type of quantum dot is clearly needed before the full possibility potential of the nanoparticles dispersed glass systems are unleashed in the application domains of magneto-optics.

Currently, Fe_2O_3/phosphate composites, a newer type of quantum dot embedded diamagnetic magneto-optical glass, were fabricated by the team of Mahajan and Kale [11,12]. In their studies, Fe_2O_3 quantum dots in small size (4–6 nm) and a noticeably improved magneto-optical Faraday effect were observed. Apart from the excellent Faraday effect, comparatively speaking, the compositions of these glass systems have some advantages. Ferric oxide, as a common magnetic material, can represent the low temperature phase, Maghemite (γ-Fe_2O_3), and it easily evolves into the more stable phase, Hematite (α-Fe_2O_3), when submitted to high temperatures (higher than 500 °C) [13]. Furthermore, ferric oxide has high output and low toxicity. In addition, phosphate glass materials own many merits, such as low melting temperature, low product cost, high luminous ion doped concentration and high transparency for visible light [14–16]. It would be available to use them as a glass matrix for the growth of purity phase Fe_2O_3 quantum dots besides the excellent optical characteristics. However, in their investigations, they focused specifically on the optical and magneto-optical behaviors and did not analyze deeply the structural characteristics of quantum dots and glass matrix. Considering above reasons, in this work, we

* Corresponding author.
E-mail address: axlu@csu.edu.cn (A. Lu).

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modified the compositions of the precursor glass reported in their previous studies and the heat-treatment program. Bi_2O_3 was added in order to improve the optical scattering of glass which was positively related with the Verdet constant. Finally, the Fe_2O_3 quantum dots doped stable phosphate glass system was synthesized. The structure of both the quantum dots and the glass matrix was investigated, and the magneto-optical properties of the glass system were also studied.

2. Experiment

2.1. Preparation of materials

The glasses with the composition of $60P_2O_5$-$15Li_2O$-$8ZnO$-$3B_2O_3$-$3.5Bi_2O_3$-$10.5K_2O$-xFe_2O_3 (mol%), where x = 0, 0.15, 0.25, 0.5, 1, 2, were prepared by a conventional melt quenching technology with further heat treatment. The respective raw materials, procured from reputed firms like Aladdin and had a purity > 99%, were weighed as per the above composition and mixed in a pestle mortar to obtain a homogeneous mixture. Thereafter the mixture was preheated at 450 °C for 1 h to remove H_2O, NH_3 and CO_2 in an electric furnace, and then melted in an alumina crucible at 850 °C for 2 h after. The melt was poured onto a preheated graphite die to obtain glasses and the as-meltedas-melted glasses were annealed in a muffle furnace at 300 °C for 5 h. Subsequently, the glasses were heating treated at 400 °C for 2 h for the growth of the quantum dots, and finally cooled to room temperature. The prepared glass samples with Fe_2O_3 doping amount of 0, 0.15, 0.25, 0.5, 1, 2 mol% were numbered as P0, PF1, PF2, PF3, PF4 and PF5, respectively.

The obtained clear and transparent glasses were cut into desired dimension and polished with emery papers of 2000 meshes on glass polishing machine or ground into fine powder so as to perform different measurements.

2.2. Analytical methods

X-ray Diffraction (XRD, D/max 2500 model, Rigaku, Japan) patterns were measured for all glass samples. The diffractometer scanned the powder at a rate of 4°/min within the Bragg angle (2θ) from 10° to 80°, which operated with working voltage and current of 40 kV and 50 mA. FTIR spectroscopy was performed using FTIR spectrometer (Nicolet 6700, Thermo Electron Scientific Instruments, U.S.A) with the wavenumber range of 400–4000 cm^{-1}. The quantum dots were characterized by the high resolution transmission electron microscope (HRTEM, Tecnai G2 F20, FEI, U.S.A). Before the measurement, glass samples were grounded (less than 100 nm) and then dissolved into the alcohol solution homogeneously. Appropriate amount of solution was dropped on the copper film and subsequently dried under an infrared lamp. The crystalline phase of the quantum dots was identified by matching the SAED patterns with the data of PCPDF standard cards. The transmittance of all samples was investigated with the help of U-3310 spectrophotometer (Hitachi Ltd., Japan) during the wavelength range of 200–800 nm. All test samples had the same thickness (6 mm ± 0.1 mm), and their surfaces were cleaned by Ultrasonic Bath with alcohol as the clearing agent. The Verdet constant was measured with an excitation wavelength of 632.8 nm at room temperature by a self-assembled Faraday effect detector by Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science. All test samples were cylinder and had a diameter of 1 cm and a length of more than 2 cm.

3. Results and discussion

3.1. Structural analysis

XRD patterns of phosphate glass doped with various contents of Fe_2O_3 are displayed in Fig. 1. It can be seen from this figure that all samples are structurally amorphous characterized by the diffused humps and the absence of sharp peaks corresponded to crystalline phase. With the increment of Fe_2O_3 contents, the intensity of scattering peaks heightens and a series of small but sharp diffraction peaks appear. This could be attributed to the growth of quantum dots or nanocrystals. As the Fe_2O_3 contents increase, Fe_2O_3 quantum dots grow in the glass matrix, and then aggregate into larger nanocrystals due to Ostwald Ripening phenomenon [17]. The growth of quantum dots or larger nanocrystals could affect the XRD patterns of testing samples, resulting in the change of intensity of scattering peaks and the appearance of small but sharp diffraction peaks [18]. In spite of this, no obvious crystalline peaks assigned to nanocrystals are recorded because of the insulation of the amorphous glass matrix and lower scanning working voltage [10].

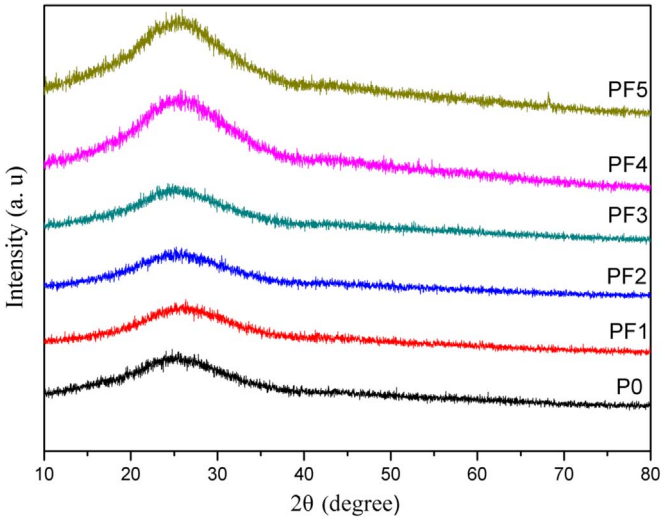

Fig. 1. Effect of Fe_2O_3 content on the XRD patterns of phosphate glasses.

In order to certify the presence of Fe_2O_3 quantum dots or larger nanocrystals inside the amorphous multi-component phosphate glasses and further visualize their microstructures, PF4 and PF5 powder samples were analyzed by HRTEM study. The results are shown in Figs. 2 and 3, respectively.

Fig. 2 reveals the TEM micrographs of PF4 glass with the doping concentration of 1 mol% Fe_2O_3. Fig. 2(a-c) shows the TEM images in morphology and Fig. 2(d) depicts the SAED pattern of the red circle area in the plane-view (c), respectively. It can be seen from Fig. 2(a–c) that abundant quantum dots with the size of less than 5 nm are distributed in the glass matrix homogeneously. Notably, no distinct clusters of quantum dots are noted. Fig. 2(d) exhibits a distinguishable bright spot, indicating the amorphous characteristic of quantum dots. In PF4 glass, Fe_2O_3 quantum dots can be seen as a metastable aggregation constituted by a few ferric ions bonded with other free oxygen ions, where less crystalline phase can be detected, if any. This kind of aggregation in morphology can be melted with the glass matrix in the high transmission voltage, which gives rise to the appearance of an amorphous nature in SAED pattern.

Obviously, clusters of quantum dots can be detected in the PF5 glass doped with 2 mol% Fe_2O_3 in the Fig. 3(a–b), as pointed by the red arrows. To further observe these quantum dots, the HRTEM image with high magnification was obtained and shown in the Fig. 3(c). In this figure, a single quantum dot (or called nanocrystal) with interplanar distance of 2.16 Å can be found. Fig. 3(d) illustrates the SAED pattern corresponding to Fig. 3(c), which is almost identical to the bulk γ-Fe_2O_3 crystal.

It can be seen from the comparison between Figs. 2(d) and 3(c–d) that a significant phase evolution from disordered orientation of quantum dots to ordered arrangement of nanocrystals occurs with the increment of Fe_2O_3 contents. This evolution is mainly a consequence of