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Multiferroic $BiFeO_3$ enhanced Faraday rotation effect in magneto optical glasses

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ABSTRACT

Single phase multiferroic $BiFeO_3$ nanocrystals and $BiFeO_3$ doped magneto optical $BiFeO_3$–PbO–Bi_2O_3–B_2O_3 glasses have been synthesized and characterized in this study. Through the X-ray diffraction, Scanning electron microscopy, differential scanning calorimetry, UV–Vis optical absorption, Vicker's hardness and Verdet constant measurement, the glass structure and spectral were found to be modified by $BiFeO_3$ nanocrystal, and Faraday rotation, absorption edge and mechanical performance of glasses were improved by such modification due to the low band gap, high polarization, ferromagnetic & superparamagnetic property of nanocrystal $BiFeO_3$. Glass of 5%$BiFeO_3$–40%PbO–50%Bi_2O_3–5%B_2O_3 exhibits a Verdet constant of 0.1615 min/G·cm at 633 nm, thermal stability of 105 °C and a 510 nm cutoff wavelength which is very attractive to magneto optical glass devices.

1. Introduction

Magnetic/multiferroic/optical functional nanoparticles are attractive for numerous applications in opto-electronics and bio-sensors [1–3], especially in big mass, high polarizable and low phonon energy Bi_2O_3 and PbO based diamagnetic glass [4–6] which exhibits temperature-independent Faraday rotation advantage over paramagnetic counterpart [7]. Fe_3O_4 or Fe_3O_4/Ag core/shell nanoparticles could show superparamagnetic character and improve Verdet constant of diamagnetic glass [8–12].

Perovskite $BiFeO_3$ is a most promising multiferroic material due to its relative lower band gap, ferromagnetism and high phase-transition temperature from antiferromagnetic to paramagnetic [13–16]. Importantly, $BiFeO_3$ shows a rhombohedrically distorted perovskite structure with a big magnetic polarization [17]. Moreover the multifunctional bismuth ferrite is appealing to spintronics, magnetically modulated transducers, magnetic field sensors and ultrafast optoelectronic applications [18,19,21].

Extensively studies have been conducted on magnetic, ferroelectric, dielectric and photocatalytic properties of $BiFeO_3$ nanocrystals [22,23], thin film [24], nanoceramic [25] and bulk [26]. In contrast, the magneto optical character of $BiFeO_3$ is rarely investigated especially in homogeneous glass matrix although $BiFeO_3$ shows high optical transparency and high Faraday rotation constant at 1550 nm [27–29]. Faraday rotation of $BiFeO_3$ mainly origins the electric dipole transitions of Fe^{3+} cation [27] and significant spin-orbit interaction between 6p orbitals of bismuth and 2p orbitals of oxygen [23]. Verdet constant of $BiFeO_3$ thin film at 1550 nm was measured to be 18 ± 2°/cm/kOe due to its no clear hysteresis magnetization which is attractive to diamagnetic glass. Meanwhile, Bi^{3+} ions have strong covalent interactions with octahedral complexes, this enhances the non-degeneracy of the spin-orbit coupling levels as well as the Faraday rotation [30]. $BiFeO_3$ has not been used in magneto optical devices mainly due to their linear birefringence properties induced by low-symmetry crystal structure: the refractive indices and dielectric constants along each of the crystalline axes are not necessarily equal. This rouses a phase lag as light propagates through the material and limits the total Faraday rotation possible for any given length of material [31].

However, their high intrinsic Faraday rotation, high polarization, low energy gap (2.17 eV) and even potential nanosize-excited superparamagnetic character are interesting to diamagnetic glass. A recent magneto optical study on $BiFeO_3$ thin film has shown a big Kerr effect for magnetic field sensing applications [30]. $BiFeO_3$ also has a large curie temperature (830 °C) and high Neel temperature (397 °C) [32,33] which paves a possibility to be incorporated into low-melting PbO-Bi_2O_3-B_2O_3 glass by melt-quenching method.

The thermal stability, mechanical, optical and magneto optical properties are all important for magneto optical glass and sensing devices. Based on previous studies [34–36], in this paper, we synthesized single phase $BiFeO_3$ nanoparticles successfully by low temperature sol-gel method to avoid bismuth volatilization and impurity phases ($Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$). The obtained $BiFeO_3$ and $BiFeO_3$ doped diamagnetic glasses were characterized using XRD, SEM and energy dispersive X-Ray(EDX) to describe their structure, grain size, surface

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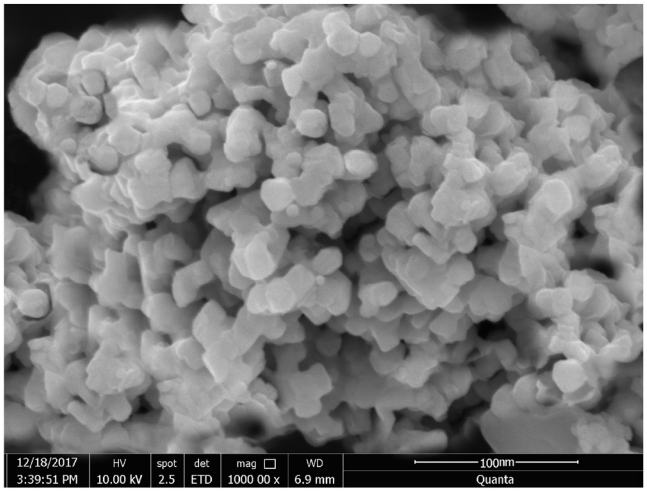
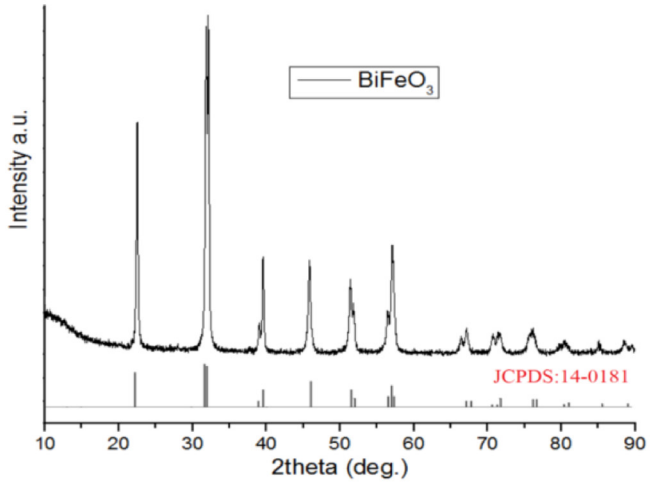


(a)

(b)



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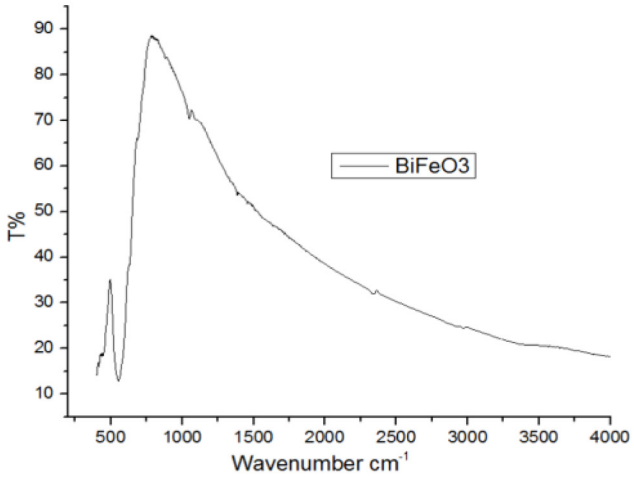

Fig. 1. SEM image (a), XRD pattern (b) and FT-IR spectra (c) of nanocrystalline $BiFeO_3$.

morphology and composition along with thermal, mechanical, optical and magneto optical measurements for a comprehensive investigation on $BiFeO_3$ nanocrystal modified structure and properties. The Verdet constant measured in this study was compared with published results from other diamagnetic glasses [37–43].

2. Experiment

0.2 M $Fe(NO_3)_3.9H_2O$ and 0.2 M $Bi(NO_3)_3.5H_2O$ were mixed in a 500 ml beaker under stirring condition. Poured the mixture cautiously into solution of Tartaric acid and Ethylene glycol (1:1) in a 80 °C water bath under magnetic stirring. The ammonia solution was then dropwise added into the mixed solution with continuous stirring to adjust the PH = 1 until a dark red gel was obtained. After a 80 °C drying for 12 h in vacuum furnace, the obtained powder was subjected to calcination at 500 °C to remove the volatile substance, moisture and other undesired components.

Glass/ceramic with composition of $40PbO–50Bi_2O_3$ –(10-x) B_2O_3–x$BiFeO_3$ (BFO) (x = 0, 0.2%, 0.5%, 2%, 5%, 8% and 10% in molar) were fabricated by melt quenching technique after thoroughly mixing of reagents (PbO, Bi_2O_3 and B_2O_3 99.99%). The mixture was melted at 850 °C for 1 h followed with casting on a brass panel. The glasses were cut and optically polished (λ-Logitech PM) after annealing at 280 °C for 2 h.

Different characterizations on $BiFeO_3$ nanocrystalline and glasses were performed: X-ray diffraction (XRD) at room temperature was done using Philips PW 1343 X-ray diffractometer at 40 kV and 40 mA (X'pert MPD) with monochromatized Cu-Ka (λ = 1.5406 Å) radiation. The grain size and morphology were characterized by SEM spectrascope along with an EDX analysis on composition. Fourier transforms infrared spectra (FT-IR) of 400–4000 cm^{-1} were recorded using a Varian Cary 500 spectrophotometer. Raman spectra were recorded using a MKI Renishaw Raman spectroscopy of 50–1100 cm^{-1}. Glass transition temperature (T_g) and crystallization temperature (T_c) were measured using differential scanning calorimetry (DSC) (Perkin-Elmer DSC7) under N_2 atmosphere at a heating rate of 10 °C/min with 30 mg powder in aluminum crucible. The refractive index (n) at 633 nm was measured by prism coupling method using Metricon 2010. Optical absorption spectra were recorded between 200 nm–1100 nm at room temperature using a UV–vis spectrophotometer (Varian Cary 500). The absorption coefficient was calculated by Eq. (1):

$$\alpha = \frac{\log\left(I_0/I\right)}{z} = A/z \tag{1}$$

where α is the absorption coefficient, A is the absorbance obtained from UV spectrum, z is sample thickness. Vicker's hardness was tested using a 136° pyramidal diamond indenter at a weight load of 50 g, the value was calculated through Eq. (2): where P is the applied load in Kg, and d