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SnO_2 modified thermal, mechanical and magneto optical property improvement of $PbO\text{-}Bi_2O_3\text{-}B_2O_3$ glass

Qiuling Chen[a,*], Kai Su[a], Hui Wang[a], Qiuping Chen[b]

[a] School of Material Sciences & Engineering, Henan University of Technology, Zhengzhou 450001, Henan, China
[b] Department of Applied Science and Technology, Politecnico di Torino, Italy

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ABSTRACT

SnO_2 is a widely accepted room temperature ferromagnetic material and has found applications in rapidly growing fields of spintronics and magneto electronics. Faraday rotation diamagnetic glass has attracted research attentions in photonics, sensing and magneto optical devices due to their high refractive index, wide transmittance in UV and Fourier transform infrared (FT-IR) range and temperature independent Faraday rotation. In this paper, we report for the first time the fabrication of SnO_2 modified diamagnetic glass with composition of $xSnO_2$-(10-x) B_2O_3-30PbO-60Bi_2O_3 (x = 0, 2, 4, 6, 8 and 10 mol%) by melt-quenching method. The influence of SnO_2 on glass forming ability, thermal, mechanical properties and Faraday rotation were evaluated through X-ray Diffraction (XRD), FT-IR, Raman, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), Vicker's hardness and Verdet constant measurements. Good vitrification was achieved with SnO_2 amount ≤ 6 mol%. XRD spectra confirmed that too much SnO_2 exist as distorted SnO_6 polyhedra and there is obvious direct interaction between tin and Bi_2O_3 structural units. FT-IR, Raman and XPS spectra ascertain the existence of characteristic vibration of SnO_4, SnO_6, PbO_4, BiO_3 and BO_3 units. Glass with 4%SnO_2 exhibited significant good glass thermal stability (102 °C), big Vicker's hardness (369 HV), high Verdet constant (0.1424 min/G.cm at 633 nm) and big cutoff wavelength (432 nm) due to the enhanced network connectivity, brought about by inclusion of high polarization and magnetization strong Sn–O linkages.

1. Introduction

Faraday Effect based magneto optical technology is growing in popularity in optical fiber sensors, isolators and magneto-optical current transducer [1–3]. Heavy metal oxides (HMO) diamagnetic glasses show promising advantages over magnetic crystals and paramagnetic counterparts. These advantages include high ultraviolet (UV) and FT-IR transmission, high refractive index, low melting point and temperature-independent Verdet constant [4–6]. The relative lower Verdet constant of diamagnetic glass can be enhanced through doping Fe_3O_4 nanoparticles or diamagnetic ions, such as Ti^{4+} [7–9].

The HMO SnO_2 is a wide band gap dilute magnetic material with excellent optical transmission in visible and UV regions, high refractive index and high magnetization, that has been extensively used for optoelectronic devices [10–13]. A number of studies have been carried out on the structural and redox behavior of tin silicate glasses [14–16]. For example, Ziemath et al. performed studies on structural and thermophysical properties of $22Na_2O$–8CaO–$70SiO_2$ glasses containing up to 5 wt% SnO_2 [14]. They observed that SnO_2 incorporation is associated with an increase of microhardness and a decrease of thermal expansion coefficient. Actually SnO_2 is found to be very helpful for mechanical hardness and thermal shock resistance improvement [15]. However, few study on the properties, especially magneto optical property of SnO_2 incorporated diamagnetic glasses was reported, nor information regarding the modification of tin in lead/bismuth matrix and their interaction. This information will be beneficial to understand the influence of SnO_2 to structure, spectra and properties of diamagnetic glass, and new magneto optical glass with enhanced performance is expected from the inclusion of SnO_2.

Among HMO glasses, Bi_2O_3&PbO based glass possesses big mass, high polarizing Bi^{3+}/Pb^2 ions, especially their low melting point, low phonon energy and high refractive index are attractive in photonics and MO devices [16,17]. B_2O_3 is usually used to help Bi_2O_3 or PbO to form into glass since they cannot form glass by their own [18]. Importantly, the high optical basicity and low melting temperature are good for Sn^{4+} state which has high diamagnetic susceptibility [19] and high polarization [20]. Such diamagnetic character of Sn^{4+} has been utilized to enhance the temperature stabilities and magnetic performance in

* Corresponding author.
E-mail address: qiulingchen1972@gmail.com (Q. Chen).

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varies thin film compounds such as $CuFe_2O_4$ [21], $CoFe_2O_4$ [22], $Sn_{1-x}Zn_xO_2$ [23], $BaFe_{12-2x}M_xSn_xO_{19}$ [24], $Sn_{1-x}Co_xO_2$ [25], $La_{0.7}Sr_{0.3}Mn_{1-x}$ Sn_xO_3 [26] and α-Fe_2O_3(α-$Sn_xFe_{2-x}O_3$) nanoparticles [27].

The diamagnetic susceptibility for atom or ion is mainly dependent on the electron number and the attracting electron ability of atomic nucleus [28]. The diamagnetic susceptibility of Sn^{4+} (-30×10^{-6} emu/mol) is close to that of Pb^{2+} (-46×10^{-6} emu/mol) [19] and Bi^{3+} (-25×10^{-6} emu/mol) [29], so Sn^{4+} is expected to be helpful for Verdet constant improvement of PbO-Bi_2O_3-B_2O_3 glass.

Based on previous studies [30–35], in this paper, we investigated the synthesis and properties of SnO_2 doped PbO-Bi_2O_3-B_2O_3 glass through different characterization methods. The aim of this paper is to obtain a new diamagnetic glass system with enhanced magneto optical performance through the modification of SnO_2.

2. Experiments

2.1. SnO_2 doped magneto optical glass fabrication

The glasses were obtained by melting a chemically pure PbO, Bi_2O_3, H_3BO_3 and SnO_2 with the molar composition of 30PbO–60Bi_2O_3 − (10–x) B_2O_3: xSnO_2(where x = 0, 2, 4, 6, 8 and 10 mol%) in amounts 30 g batches in pure Al_2O_3 crucibles at 900 °C–1000 °C temperature for 1 h. Good vitrification was achieved by rapid cooling of the melt on a brass plate. The glasses were subjected to cutting, optical polishing (λ-Logitech PM) and grounded into powder for characterization studies.

2.2. Glass characterization

X-ray studies were carried out on a X'Pert-PRO diffractometer using CuKα radiation at 1.5418 Å and diffractometer settings in the 2θ range from 10 °C–80 °C by changing the 2θ with a step size of 0.020. Differential Scanning calorimetry investigation of glass specimens was performed using Perkin-Elmer DSC7 instrument. DSC scans were conducted using 5–10 mg ground as-cast sample at a heating rate of 10 °C/min from room temperature to 600 °C in an alumina crucible and another empty crucible was used as reference. The density of glass sample was determined by the Archimedes principle, using water as immersion liquid. In the present studies IR spectra were recorded in order to study the effect of SnO_2 substitution in the place of B_2O_3 in glass system.

The refractive index of the samples was measured at 633 nm by using a refractometer (Metricon 2010) based on the prism coupler technique. Samples of 2 mm thick with optically polished surfaces were faced on a prism and mounted on a high-resolution rotary table with step size of 0.3 min and nominal resolution of refractive index 5×10^{-5}. The UV absorption spectra were recorded in 200 nm–800 nm range by means of UV–VIS spectrophotometer (Varian Cary 500). 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 840–1900 cm^{-1}.

Glass Verdet constant measurement was described in our previously published articles [35]. The Verdet constant was calculated according to Eq. (1).

$$\theta = VBl \tag{1}$$

where θ, V, B and l are Faraday rotate angle, Verdet constant, magnetic field and sample length, respectively. A pure silica with a known Verdet constant [40] is used as a reference.

The microhardness was tested using a 136° pyramidal diamond indenter at a weight load of 100 g. Vicker's hardness can be calculated through Eq. (2): where P is the applied load in Kg, and d is mean length diagonal of the indentation in mm.

Table 1
Composition (mol%) of glasses and glass forming appearance.

Code	PbO	Bi_2O_3	B_2O_3	SnO_2	Glass-forming
S_0	30	60	10	0	Glass
S_1	30	60	8	2	Glass
S_2	30	60	6	4	Glass
S_3	30	60	4	6	Glass
S_4	30	60	2	8	Crystallized (ceramic)
S_5	30	60	0	10	Crystallized (ceramic)

$$HV = 1.854P/d^2 \tag{2}$$

3. Results and discussion

3.1. Glass forming

Table 1 lists the glass composition and glass forming appearance. SnO_2 content is critical for vitrification. Bubble-free transparent glasses with high homogeneity and light yellowish color were obtained for $SnO_2 \leq 6\%$. In this case, low concentrated large ionic radius Sn^{4+} (0.71 Å) plays the modifier role and produces non-bridging oxygen (NBO) in glass matrix. According to our previous investigation on PBB glass [32], the Bi^{3+} tends to have coordination number 4 due to very high content. Pb^{2+} being larger and more polarizing, behaved in a more similar way like Bi^{3+}in glass. The tetrahedron SnO_4 could well match with frame tetrahedron PbO_4 and BiO_4 units and forms homogeneous glassy network. In addition, the big Sn−O bond strength (528 kJ/mol) of SnO_4 inhibits structural changes of Bi polyhedral, and maintains a homogenous glass network [33].

However, the doped SnO_2 acted as impurities of host glass, if the impurities were excessive, they would be precipitated as crystallines when their solubility in PBB matrix reaches to the limit point. On the other hand, excessive SnO_2 with strong reduction capability could probably reduce the PbO into black crystalline Pb^0. Due to the non-bridging oxygen and high electronic strength Sn^{4+} ions, the continuous growth of SnO_2 amount could accelerate the conversion of tetrahydra [BO_4] → trigonal [BO_3] units which is not helpful for glass forming.

3.2. XRD spectra analysis

Fig. 1 displays the XRD spectra of PBB glasses/ceramic with different SnO_2 amounts. It is clear that glasses with 0%, 2%, 4% and 6% SnO_2 exhibit a typical glassy morphology nature without any crystalline phase or peak. It is known that if crystallites formed in glass matrix, the width of the main diffraction peak is sensitive to crystallite size and thermal history. Therefore, any significant growth of crystalline nuclei in the process of quenching and/or annealing would lead to a corresponding slight change in the shape/width of the diffraction peak [17]. From Fig. 1, the shape/intensity varies very slightly from different SnO_2 doping amounts indicating the SnO_2 modified glass matrix by forming tiny (undetectable) crystallites [30].

When SnO_2 amount reaches to 8% or higher, crystal phases can be seen in spectrum at 2θ values of 26.5°, 26.6°, 33.9°, 37.8°,51.9° and 64.8° of tetragonal rutile SnO_2 associating with (110), (101), (200), (211) and (112) of respectively (Fig. 1.b) [13]. High SnO_2 content accelerates the interaction of units by offering group [SnO_6] due to its higher negative attractive force to positive Bi^{3+} and Pb^{4+} cations. Another second phase in Fig. 1 is defined to be $Bi_2Sn_2O_7$ crystalline from the reaction between SnO_2 and glass matrix [36].

The maximum SnO_2 crystallite size was measured to be around 15 nm using Debye-Scherrer formula in Eq. (3):

$$D = \frac{0.9\lambda}{W\cos\theta} \tag{3}$$

where λ is wave length of X-ray (0.1541 nm), W is FWHM (full width at

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