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Magneto optical properties of rare earth Tb_2O_3 doped PbO-Bi_2O_3-B_2O_3 glass

Qiuling Chen[a,*], Qiuping Chen[b], Hui Wang[a], Gaimin Wang[a], Shuai Yin[a]

[a] School of Material Sciences & Engineering, Henan University of Technology, Zhengzhou 450007, Henan, China
[b] Department of Applied Science and technology, Politecnico di Torino, Corso duca degli Abruzzi, 24, Torino 10129, Italy

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ABSTRACT

Terbium dioxide is intensively studied in luminescence and magneto optical applications. The fabrication and characterization of diamagnetic glass with composition of xTb_2O_3 – 30PbO – $60Bi_2O_3$ – (10 − x) B_2O_3 (x = 0, 0.1, 0.2, 0.4, 0.5 and 1 mol%) is reported. The influence of Tb_2O_3 on glass forming ability, glass structure and properties has been studied by means of DSC, XRD, Raman, UV–vis/FTIR spectral and Faraday rotation measurement by a home-made optical bench.

Due to the high optical basicity and high polarization of host glass, the formation of Tb^{4+} in 0.1% Tb_2O_3 doped PBB glass contributes to an improvement on density, refractive index, thermal stability (106 °C), optical cutoff wavelength (501 nm) and Verdet constant (0.1301 min/G·cm).

1. Introduction

Magneto optical (MO) Faraday rotation glass is interesting for optical isolators, bio-sensor, magnetoplasmonics and magneto optical current technology [1–3]. Rare earth doped glass has been studied for photoluminescence, electrical conductivity, high refractive index, optical amplifiers, up conversion lasers and Faraday rotation [4–8]. Among rare earth ions, Tb^{3+} ion exhibits highest magnetic moment and paramagnetic effects because of its electronic transition of $4f_n \rightarrow 4f_{n-1}5d$, and has been extensively doped in silicate [9–11], aluminate [12], borate [13–15], phosphate [16–19], germanium [20], fluoride [21] glass and crystal [22] to enhance Faraday rotation. But Faraday rotation of Tb doped MO glass mainly comes from heavy Tb^{3+} doping which arouses some drawbacks: 1) highly concentrated Tb breaks the glass network, and degrades the thermal/chemical stability and glass transparency, increases the glass intrinsic loss and the difficulties of further fiber processing. 2) Tb^{3+} are paramagnetic ions whose Verdet constant is highly temperature-dependent. In addition, rare earth doped paramagnetic glass always exhibits saturation and sharp decrease of magnetization under high magnetic field [23]. So compared with high melting temperature silicate glass and thermal /chemical unstable phosphorous glass, heavy metal oxide glass, for example lead-bismuth-boron glass, is a very interesting host of rare earth (Er, Yb, Tb, Dy, Tm, La) in optical laser [24], amplifier [25], nonlinear [26], photoluminescence [27,28] and photocatalysis [29] applications.

Bi_2O_3 and PbO based glass possesses low-melting temperature, big mass and high polarizable Bi^{3+}/Pb^{2} ions. Their relatively low phonon energy, high refractive index, high dielectric constant and good corrosion resistance are interesting in photonics and MO devices [30–35]. B_2O_3 can modify Bi^{3+} and Pb^{2+} into vitreous network [36] since they cannot form glass by themselves.

Tb doped lead-bismuth-glasses were found in photoluminescence and laser applications based on emitting property of Tb^{3+} ions. To the best of our knowledge, the Faraday rotation of such system is an opening yet, because the Tb^{3+} ion shows paramagnetic effect, but lead-bismuth glass presents diamagnetic performance [37]. Recently a Faraday rotation study of rare earth La^{3+} doped diamagnetic TeO_2–WO_3–PbO glass was reported [38].

Qiu et al. [39,40] reported the study on the relationship between glass matrix and paramagnetic Eu^{2+} ions. According to this study, the paramagnetic Eu^{2+} ions show diamagnetic performance at a wavelength longer than 635 nm in heavy metal glass.

Actually, the big index and high magnetic moment characters of Tb_2O_3, especially the high dipole polarization of Tb ions, are very interesting to diamagnetic glass [41]. The paramagnetic contribution of Tb comes from the emission properties of Tb^{3+} state. But Tb^{3+} state is not the only state of terbium in glass. An oxidizing glass melting atmosphere, or a high optical basicity glass host can suppress the Tb^{3+} emission through forming Tb^{4+} [42,43]. Tb^{4+} was recently studied for photocatalysis [32] due to its inhabitation of electron/hole pair's recombination. This property can increase the polarization and can improve the Faraday rotation. Tb^{4+} can be realized by adjusting the glass melting condition or using Femi-second laser irradiation [44].

In addition, besides the primary optical and MO properties, high thermal stability of MO glass is necessary and important for subsequent fiber drawing and MO device integration. According to literature [45],

* Corresponding author.
E-mail address: qlchen2016@163.com (Q. Chen).

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Table 1
Composition (mol%) of Tb_2O_3 doped glasses and their glass forming appearance.

Code	PbO	Bi_2O_3	B_2O_3	Tb_2O_3	Glass-forming
PBB	30	60	10	0	Glass
PBBT1	30	60	9.9	0.1	Glass
PBBT2	30	60	9.8	0.2	Glass
PBBT3	30	60	9.6	0.4	Glass
PBBT4	30	60	9.5	0.5	Crystalline
PBBT5	30	60	9	1	Crystalline

Tb doped glass exhibits improved thermal properties. However, it is difficult to prepare Tb doped glass because Tb has susceptibility to phase separation and crystallization at high melting temperature [46]. On the other hand, the paramagnetic property comes from the electron transition of Tb^{3+}, high optical basicity and low melting temperature of lead-bismuth-boron glass is helpful to form Tb^{4+}.

Based on previous study [47–51], we doped low concentration (< 1%) Tb into diamagnetic glass in oxidizing melting atmosphere in this paper, in order to get a good quality diamagnetic glass with improved thermal, optical and Faraday rotation through investigating the influence of Tb to glass structure and properties. The Verdet constant obtained in this study was compared with published results from other diamagnetic glasses [52–63].

2. Experiments

2.1. Tb_2O_3 doped magneto optical glass fabrication

Glass was fabricated by melt-quenching method and the composition of $30PbO\text{-}60Bi_2O_3 - (10 - x)\ B_2O_3$: xTb_2O_3 (where x = 0, 0.1, 0.2, 0.4, 0.5 and 1 mol%) is listed in Table 1. Chemical reagents (99.99% purity) were weighted in 20 g batches which was melted in Al_2O_3 crucibles at 1000 °C for 1 h. The melts were cast onto a brass plate followed with an annealing, cutting and optically polishing (λ-Logitech PM).

2.2. Glass characterization

Glass transition temperature (T_g) and crystallization temperature (T_c) were determined through differential scanning calorimetry (Perkin-Elmer DSC7) under N_2 atmosphere at a heating rate of 10 °C/min. We measured the density following the Archimedes' principle using water as immersion liquid. Refractive index (n) at 633 nm was measured by a prism coupling method using Metricon 2010. UV-VIS absorption spectra were recorded between 200 nm and 800 nm by means of an UV–VIS spectrophotometer (Varian Cary 500). Absorption coefficient was calculated by Eq. (1):

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

where α is the absorption coefficient, A is the absorbance obtained from UV spectra, z is sample thickness. Fourier transforms infrared spectra (FT-IR) of 400–4000 cm^{-1} wave number were recorded using a Varian Cary 500 spectrophotometer. XRD (Philips X'Pert diffractometer) for crystalline quality was scanned. Raman spectra were recorded using a MKI Renishaw Raman spectroscopy of 840–1900 cm^{-1}wavenumber.

Glass Verdet constant was measured using a home-made single light DC magnetic optical bench as reported in our previous paper [48]. The Verdet constant can be calculated according to Eq. (2)

$$\theta = VBl \quad (2)$$

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 [52] is used as reference. Before each measurement, magnetic field at different position was measured using a magnetometer to ensure a homogenous distribution in solenoid.

3. Results and discussion

3.1. Glass forming

Table 1 lists glass forming appearance as a function of Tb_2O_3 content under the same melting condition. PBB glass matrix is very sensitive to Tb_2O_3 content. Bubble free transparent glasses with high homogeneity and yellowish color were obtained for Tb_2O_3 lower than 0.5%.The Bi^{3+} concentration in these glasses is very high (60%), so the Bi^{3+} tends to have 3 coordination number. Pb^{2+}, being larger and more polarizable, behaves a coordination number of 4. B^{3+} ion in glass was replaced by much bigger radius Tb^{3+} ion, this increases the glass network gap and improves the ability to accommodate rare earth ions, and eventually enlarges the glass-forming region [46].

From Table 1, the melts containing Tb_2O_3 content > 0.5% could not form into glass. This is due to the atomic size mismatch between magnetic Tb and PBB amorphous network [46]. In ternary PBB system, the B—O bond strength is very big (498 kJ/mol), so B_2O_3 prevents the growth and crystallization of Pb^{2+} and Bi^{3+} through occupying certain space and inhibiting their accumulation, and finally suppresses crystals formation. But in PBBT system, overmuch Tb_2O_3 (such as > 0.5% Tb_2O_3), at the cost of losing good forming B_2O_3, introduces non-bridging oxygen, high electronic strength and polarizable Tb^{3+} or Tb^{4+} ions. These factors induce coordination number change from layered triangular [BO_3] to tetrahedral [BO_4], and change from tetrahedrons [BiO_3] to pyramids [BiO_6] [54] which collapsed the network.

3.2. XRD structure

Fig. 1 shows the XRD spectra of PBB glass containing Tb_2O_3 contents. Melts with Tb_2O_3 of 0%, 0.1%, 0.2%, 0.4% show typical glassy morphology nature without crystalline phase. Two broad diffraction peaks find at 2θ = 30° and 50°, respectively, representing the typical diffraction pattern of lead bismuth glass [49]. The introduction of Tb ions changes the network bonds and thus improves the relative packing efficiencies of cations in $PbO\text{-}Bi_2O_3\text{-}B_2O_3$ glasses since Tb ions replace much smaller B ions. Table 2 shows the physical properties of Tb doped glasses, the density is much increased with Tb_2O_3 content which is desirable for most applications. The relatively higher molar volume of Tb_2O_3 (365.85 $g{\cdot}mol^{-1}$) than B_2O_3 (69.622 $g{\cdot}mol^{-1}$) contributes to the density increase.

3.3. FT-IR spectra

FT-IR spectra of glasses recorded in range of 400 cm^{-1}–4000 cm^{-1} are displayed in Fig. 2. We notice Tb_2O_3 doped glass presents higher FT-IR transmission compared with pure PBB. Since Tb_2O_3 has high polarization and big mass, so it exhibits similar FT-IR performance with heavy metal oxides. However, the transmission decreased in the

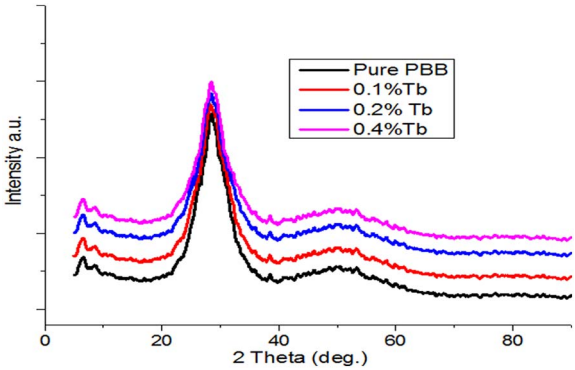

Fig. 1. XRD spectra of PBB glass and PBB glass with different Tb_2O_3 dopants.

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