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Synthesis and properties of nanocrystal $BiPO_4$ in diamagnetic PbO-Bi_2O_3-B_2O_3 glass

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ABSTRACT

In this study, we synthesized of $BiPO_4$ nanocrystals in diamagnetic glass (45PbO–45Bi_2O_3–8B_2O_3–2P_2O_5mol %) by melt quenching technique and studied its influence to glass Faraday rotation. The 9 nm irregular $BiPO_4$nanocrystals formed in glass and changed glass structure, spectral and properties through the characterization of X-ray diffraction, field Emission scanning electron microscopy, differential scanning calorimetry, UV–Vis optical absorption, Vicker's hardness and Verdet constant etc. The $BiPO_4$ –induced local plasmon effect and bigger polarization gave glass improvements on optical cutoff wavelength, Faraday rotation and Vicker's hardness which is very attractive to magneto optical glass devices.

1. Introduction

There has been an increasing interest on nanoparticles/nanocrystals in scientific and technological aspects. Magneto optical glass containing magnetic/optical functional nanoparticles is attractive to optical isolator, light emitting diodes, magneto-optical (MO) current transformers and optical fiber sensor [1–3]. Especially,the big mass, high polarizable and low phonon energy Bi_2O_3 and PbO based diamagnetic glass [4–8] has shown big advantages over paramagnetic counterpart, such as temperature-independent Faraday rotation property, wide transmission in UV and FTIR range etc. [9–11]. Studies found that nanoparticle such as Fe_3O_4 can help diamagnetic glass to get a bigger Faraday rotation due to surface plasmon effect induced by its nano-scale [12–14]. And the high optical basicity and low melting temperature of diamagnetic glass are also good for optical functional nanoparticles/nanocrystal formation [15–17].

Bismuth phosphate ($BiPO_4$) nanostructure was found to have special applications in catalysis particularly for the separation of radioactive elements and ion sensing [18–24]. They exhibit unique chemical and physical properties, differing substantially from those of the corresponding bulk solids. The differences in quantum size and relatively large specific surface ratio usually excite the surface plasmon effect and superparamagnetic effect [24–28]. And these effects are beneficial to Verdet constant [29,30]. A recent study on $BiPO_4$ found that $BiPO_4$ nanocrystal could improve the Faraday rotation in phosphate glass, but the reason was not addressed [21].

The glass properties were usually influenced through compositional and structural changes. The inclusion of nanocrystals or nanoparticle would inevitably and accordingly change the glass properties. For a good magneto optical glass, its thermal stability, mechanical, optical, magneto optical properties and chemical resistance are all crucial for sensing devices. Based on previous studies [31–35], in this paper, we synthesized the $BiPO_4$ nanocrystals in lead- bismuth diamagnetic glass, and investigated its influence on glass thermal, mechanical, optical and magneto optical properties. The aim is to understand the modification of $BiPO_4$ nanocrystal and obtain an efficient way to improve the diamagnetic glass Verdet constant. In addition, considering the influence of P_2O_5 on chemical resistance, the chemical property also was evaluated. The Verdet constant obtained in this study was compared with published results from other diamagnetic glasses [36–42].

1.1. Experiment

All chemicals (PbO, Bi_2O_3, B_2O_3 and P_2O_5 99.99% purity) were used as received. The pure PBB (45PbO–45B_2O_3 –10B_2O_3) host and $BiPO_4$ nanocrystals contained PBBP glass (45PbO–45Bi_2O_3 –5B_2O_3–5P_2O_5) were fabricated by melt quenching technique after thoroughly mixing of reagents. The slow preheating to 450°Cin a platinum crucible is performed to remove H_2O, NH_3 and CO_2 from impurities. The mixture was melted at 950 °C and 1050 °C for 1 h for pure PBB and PBBP, respectively, and then cast on highly polished brass panel. PBB glass was annealed to 300 °C at 0.5 °C/min heating/cooling rate. The PBBP glass was annealed at 370 °C for 5 min and then quickly cool down to 300 °C for 2 h. Both glasses were cut and optically polished (λ-Logitech PM) after annealing.

Different characterizations on samples were performed. X-ray

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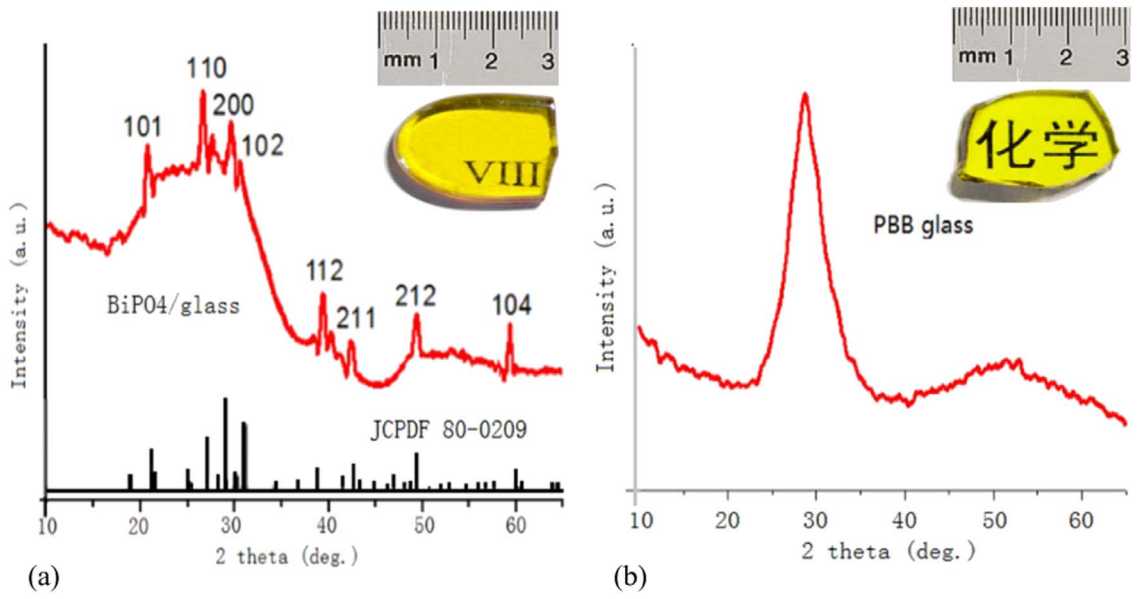

Fig. 1. XRD spectra of PBB containing $BiPO_4$ nano-crystal (a) and PBB (b).

diffraction (XRD) measurement was taken for all both samples (powder) at room temperature using Philips PW 1343 X-ray diffractometer at 40 kVand 40 mA (X'pert MPD) with monochromatized Cu-Ka(λ = 1.5406 Ä) radiation. The morphology and particle distribution were characterized by FESEM spectrascope. 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 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 with 30 mg powder in aluminum crucible. We measured the density using alcohol as immersion liquid and refractive index (n) at 633 nm wavelengths by prism coupling method using Metricon 2010. Optical absorption spectra were recorded between 200 nm - 800 nm at room temperature using a UV–VIS spectrophotometer (Varian Cary 500). The absorption coefficient was calculated by Eq. (1):

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

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 200 g, the value was calculated through Eq. (2): where P is the applied load in Kg, and d is mean length diagonal of the indentation in mm.

$$HV = 1.854P/d^2 \quad (2)$$

The chemical stability is assessed by weighting mass lose before and after dipping the glass into water, 0.05 mol/L HCl and NaOH solution for 24–72 h, respectively.

Verdet constant was measured as described in our previously published article using a home-made single light beam DC magnetic technique [35]. The Verdet constant (V) was calculated according to Eq. (3).

$$\theta = VBl \quad (3)$$

where θ is the Faraday rotate angle, B is the magnetic field and l is the sample length. A pure silica with a known Verdet constant [42] is used as reference. The magnetic flux was tested before each measurement using a magnetometer for homogenous magnetic field distribution in solenoid. Considering the errors (systematic or random) during experiment, data reported in this paper was the mean value of 10 measurements.

2. Results and discussion

2.1. Formation of $BiPO_4$ nanocrystals in glass

The formation of $BiPO_4$ nanocrystals can be theoretically divided into three sequential steps: (1) creation of tiny primary $BiPO_4$ nanoparticles as nuclei, (2) growth of $BiPO_4$ nuclei via self - assemble, (3) formation of regular and bigger $BiPO_4$ nanocrystals. During the process, the primarily formed nanocrystals aggregate in an oriented fashion, resulting in larger crystals, or they may randomly aggregate and reorient, undergo phase transformations (for example v2, v3 and v4 in Raman spectra in Fig. 2), or recrystallize into large and regular crystals.

However, this aggregation-growth mechanism is constrained by glassy network bonding energy, the viscosity, and tension which were determined by glass composition, glass structure, annealing temperature and duration. In this study, after a very short period (5 min), the generation and growth of nanocrystals was inhibited by the decreased viscosity caused by temperature fall downing from 370 °C to 300 °C, the sharply declined viscosity prevented the self-assemble and growth of nuclei. And meanwhile the increased surface tension of melt also prevented the $BiPO_4$ nuclei to grow and to rearrange. On the other hand, with the temperature decrease, the crystalline energy is not enough to support their growth any more. So the nuclei had no enough time nor enough energy to grow into bigger crystals or rearrange into regular shape. This can be observed in FESEM images (Fig. 3), the majority of the nanocrystals appeared to be irregular ranging in size from 7 to 10 nm.

Actually, there are some factors influencing the glass crystallization, they are composition, quenching rate and impurities which act as nucleation centers [24]. According to crystalline-like ordering theory [44], there is always partial phase separation of crystallite former -poor region and crystallite former -rich region in glass. During glass quenching from liquid state, the crystalline-like groups continuously break up and reform in super-cooled state between T_c and T_g temperature range [44]. These nanocrystalline groups are frozen-in in most glasses, especially if the glass is multi-component. Moreover, the glass containing tiny nanocrystallines still exhibit homogenous and transparent nature, this can be observed from XRD in Fig. 1.

2.2. Structure analysis (XRD spectra)

XRD spectrum in Fig. 1 can give information about the glass