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Fabrication of $Tb_3Al_5O_{12}$ transparent ceramics using co-precipitated nanopowders

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ABSTRACT

Terbium aluminum garnet (TAG) precursor was synthesized by a co-precipitation method from a mixed solution of terbium and aluminum nitrates using ammonium hydrogen carbonate (AHC) as the precipitant. The powders calcined at different temperatures were investigated by XRD, FTIR and FESEM in order to choose the optimal calcination temperature. Fine and low-agglomerated TAG powders with average particle size of 88 nm were obtained by calcining the precursor at 1100 °C for 4 h. Using this powder as starting material, TAG transparent ceramics were fabricated by vacuum sintering combined with hot isostatic pressing (HIP) sintering. For the sample pre-sintered at 1700 °C for 20 h with HIP post-treated at 1700 °C for 3 h, the average grain size is about 3.9 μm and the in-line transmittance is beyond 55% in the region of 500–1600 nm, reaching a maximum transmittance of 64.2% at the wavelength of 1450 nm. The Verdet constant at 633 nm is measured to be −178.9 rad T^{-1} m^{-1}, which is 33% larger than that of the commercial TGG single crystal (−134 rad T^{-1} m^{-1}).

1. Introduction

Magneto-optical materials are essential components of Faraday isolators which are widely used in high-average-power laser systems and advanced optical communications [1–4]. Recently, the demand for Faraday isolators that work at visible and near-infrared range has significantly increased, where conventional $Y_3Fe_5O_{12}$ (YIG) is inapplicable due to its poor transparency in this region [5,6]. Among all the transparent materials available, $Tb_3Al_5O_{12}$ (TAG) is considered to be an excellent candidate used in the visible and near-infrared spectral regions thanks to its excellent optical quality, high thermal conductivity, and higher Verdet constant than the most commonly used $Tb_3Ga_5O_{12}$ (TGG) single crystal [7–9]. However, it is extremely difficult to grow TAG single crystal from the melt for its incongruent melting nature [10]. Although considerable efforts have been devoted to solving this problem [11–15], the size of TAG single crystal is still limited, leaving it far away from practical application.

In the past decades, transparent polycrystalline ceramics have aroused widespread concern due to their excellent properties [16–20]. TAG transparent ceramics which can avoid the incongruent melting problems for its lower fabrication temperature than melting point have been considered as a preferable candidate for Faraday isolators. The TAG transparent ceramic was first reported in 2011 [21], and its in-line transmittance reached about 75% in the 400–1600 nm range. Its Verdet constant was measured to be −172.72 rad T^{-1} m^{-1} at 632.8 nm and the thermal conductivity was approximately 6.5 W $m^{-1}K^{-1}$ at room temperature. Chen et al. investigated the proper dosage of the sintering aids for the fabrication of TAG transparent ceramics, and the optical transmittance of TAG ceramics was improved to above 80% in the region of 550–1500 nm [22]. Researchers have found that the magneto-optical, thermal and mechanical properties of TAG transparent ceramics are comparable to those of TAG single crystals [23,24].

In general, garnet transparent ceramics can be fabricated by two main methods. One is solid-state reaction method which uses primary oxide powders as raw materials [25–27]. The other one is vacuum sintering of powders synthesized by wet-chemical approaches [28–31]. Up to now, TAG transparent ceramics are usually fabricated by solid-state reaction method ever reported in the

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literature [21,22,32–34]. However, impurities are easily introduced during the ball milling process, and it requires a high temperature for the TAG phase formation. The impurities and incomplete reaction during the solid-state reactive sintering would severely degrade the optical quality of TAG ceramics. It is well recognized that wet chemical methods such as co-precipitation [35,36], spray pyrolysis [37], hydrothermal synthesis [38,39], sol–gel [40,41] and combustion synthesis [42–44] offer considerable advantages in terms of atomic level mixing of high-purity precursors and excellent chemical homogeneity of the final product. Among these wet-chemical methods, the co-precipitation method is one of the most promising techniques to synthesize TAG nanopowders with excellent chemical homogeneity, pure phase and good crystallinity at low temperature. Therefore, the co-precipitation synthesis process and the properties of the as-prepared TAG powders need to be studied, which is aimed to fabricate fully dense and transparent ceramics by vacuum sintering of TAG powders with high sinterability.

In this work, we synthesized TAG precursors by a co-precipitation method using AHC as the precipitant. Phase evolution of the precursors and properties of the resultant TAG powders were investigated. Subsequently, TAG transparent ceramics were fabricated by vacuum sintering of the prepared powders calcined at 1100 °C followed by hot isostatic pressing (HIP) post-treatment. The optical quality, microstructure, and magneto-optical property of the resultant TAG ceramics were also investigated.

2. Experimental procedure

$Tb(NO_3)_3$ solution was prepared by dissolving Tb_4O_7 (99.99%, Yuelong New Materials Co., Ltd., Shanghai, China) in the heated high-purity nitric acid. $Al(NO_3)_3$ solution was prepared by dissolving the $Al(NO_3)_3 \cdot 9H_2O$ (99.0%, Sinopharm Chemical Reagent Co., Ltd.) in the deionized water. Tb^{3+} and Al^{3+} concentrations of the nitrate solutions were assayed by chemical analysis. The metal nitrates were then mixed according to the stoichiometric ratio of $Tb_3Al_5O_{12}$ and further diluted with deionized water to the concentration of 0.3 M for Al^{3+}. Ammonium hydrogen carbonate (AHC) (Analytical grade, Aladdin) was dissolved in deionized water with a concentration of 1.5 M as the precipitant solution. Ammonium sulfate (99.0%, Sinopharm Chemical Reagent Co., Ltd.) was added into the precipitant solution as the dispersant. The precursor precipitate was prepared by the reverse-strike technique (adding salt solution to the precipitant solution). 500 ml of the mixed salt solution was dripped into 640 ml of the AHC solution at a dripping speed of 20 ml/min under mild agitation at room temperature. After aging for 1 h, the resultant suspension was washed four times with deionized water and rinsed twice with absolute ethanol by repeated dispersion and centrifugal filtration. After that, the precursor was dried at 70 °C for 48 h. Then, the precursor was sieved through 200-mesh screen and calcined at different temperatures for 4 h in air. Finally, the powders calcined at 1100 °C were uniaxially dry-pressed into pellets at 20 MPa and then the green bodies were cold isostatically pressed at 250 MPa. The pellets were sintered at 1450–1700 °C for 10–20 h in a tungsten mesh-heated vacuum furnace under 10^{-3} Pa during holding. The heating and the cooling rates were 2 °C·min^{-1} and 10 °C·min^{-1}, respectively. The sample sintered at 1700 °C for 20 h was finally hot isostatic pressing (HIP) post-treated at 1700 °C for 3 h under 200 MPa Ar atmosphere.

Phase identification of the powder was identified by X-ray diffraction (XRD, Model D/max2200 PC, Rigaku, Japan). XRD analysis was performed on a Huber Imaging Plate Guinier Camera G670 (Cu $K_{\alpha 1}$ radiation, k = 1.54056 Å, 40 kV/30 mA, Ge monochromator). The 2θ for all data ranged from 10° to 80° with 0.02° step size. The compositions of the powders were investigated by a Fourier transform infrared spectroscopy (FTIR, Bruker VERTEX 70 spectrophotometer, Ettlingen, Germany). Thermogravimetry analysis and differential thermal analysis (TG–DTA) of the precursor were performed on a TG-DTA analyzer (Thermo plus EVO II, Rigaku, Japan) in flowing air atmosphere with a heating rate of 10 °C/min. Specific surface area analysis was performed using a micromeritics (Model ASAP 2010, Norcross, USA) with N_2 as the absorption gas at 77 K. Morphologies of the powders were observed with a field emission scanning electron microscopy (FESEM, SU8220, Hitachi, Japan). The in-line transmittance of mirror-polished ceramics (1.5 mm thick) was measured by a UV-VIS-NIR spectrophotometer (Model Cary-5000, Varian, USA). Microstructures of the thermal-etched surfaces of as-sintered ceramics (thermally etched at 1400 °C for 3 h) were observed by a field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). Grain sizes of the sintered samples were measured by the linear intercept method and the average grain size was calculated by multiplying the average linear intercept distance by 1.56 [45]. The Verdet constant was measured with an instrument consisting of a He–Ne laser, an electromagnet and two polarizers. The measurement was carried out at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized precursor and the powders calcined at 800 °C-1200 °C for 4 h. XRD analysis shows that the as-synthesized precursor is amorphous. The powder remains amorphous when the calcination temperature is increased to 800 °C. For the powder calcined at 900 °C, terbium aluminum perovskite ($TbAlO_3$, TAP) phase accompanied with cubic TAG crystalline phase are detected. When calcined at 1000 °C, the precursor completely transforms to TAG phase without the formation of intermediate phase. With the calcination temperature increased from 1000 °C up to 1200 °C, diffraction peaks corresponding to the cubic structure of TAG (JCPDS 76-0111) are higher and sharper, indicating the improved crystallinity of the powders. The XRD result indicates that pure TAG powder could be obtained by the co-precipitation method at a lower temperature, which is beneficial to the synthesis of nanoscaled and highly sinterable TAG powders. The mean crystallite size (D_{XRD}) of the TAG powders can be calculated from peak broadening of XRD spectrum using the Scherrer's formula:

$$D_{XRD} = 0.89\lambda/(\beta \cdot \cos\theta) \quad (1)$$

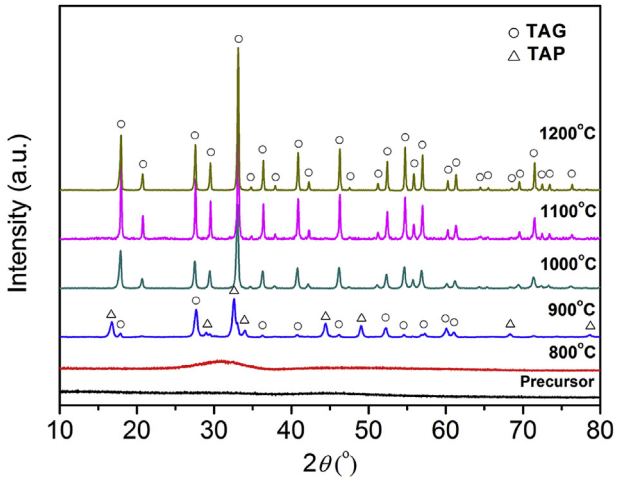

Fig. 1. XRD patterns of the as-synthesized precursor and the powders calcined at different temperatures for 4 h.