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Short Communication

Synthesis of $Tb_3Al_5O_{12}$ (TAG) transparent ceramics for potential magneto-optical applications

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ABSTRACT

$Tb_3Al_5O_{12}$ transparent ceramics have been prepared by solid state reaction and vacuum sintering. The optical quality and the microstructure of the samples were investigated. The sample sintered at 1650 °C possessed relatively good optical transparency from 400 nm to 1600 nm. The Verdet constant measured at 632.8 nm of the quasi-pore-free $Tb_3Al_5O_{12}$ transparent ceramic was −172.72 rad T^{-1} m^{-1}, which was close to the counterpart of $Tb_3Al_5O_{12}$ single crystal. The thermal conductivity of the sample was also measured. To the best of our knowledge, this is the first time that $Tb_3Al_5O_{12}$ transparent ceramic with relatively good optical quality and magneto-optical property has been reported.

1. Introduction

Magneto-optical materials based on Faraday effect are fundamental components in optical communication, optical parameter amplifier, optical modulators, and high pulse energy and high average power lasers, etc. To date, the most commonly used crystalline Faraday magneto-optical material is $Tb_3Ga_5O_{12}$ (TGG) single crystal [1]. Though being a congruent melting material, growing TGG of high quality is not an easy task for the evaporation of Ga_2O_3 from the melt during the crystal growth process [2]. Actually, TGG is the next-best thing of $Tb_3Al_5O_{12}$ (TAG) single crystals, which is caused by the great growth difficulty of the latter for its incongruent melting nature and unstable TAG phase in the Tb_2O_3–Al_2O_3 system [3]. But still, considerable efforts have been made in growing TAG single crystals from the melts: Tm^{3+} [4], Lu^{3+} [5], Ga^{3+} [6], Sc^{3+} [7], and Yb^{3+} [8], etc. were doped to partially substitute Tb^{3+} or Al^{3+} to obtain a congruent melting composition or a stable TAG phase. Ganschow et al. tried micro-pulling down method to grow TAG single crystals. Al_2O_3 inclusions were detected in the crystal [9]. Murata Manufacturing Co., Ltd. has grown out pure TAG fiber crystals by the hybrid floating zone method [10]. However, the size of the crystals was limited by the above two methods. Very recently, relatively large-sized Lu^{3+}, Sc^{3+} co-doped $\{Tb_3\}[Sc_{2-x}Lu_x](Al_3)O_{12}$ single crystals has been grown out by the Czochralski method, which has better growth characteristics and still has the good magneto-optical property [11]. On the other hand, during the past two decades, the optical quality of pore free transparent ceramic materials has been greatly enhanced [12,13]. Scattering loss turned lower and lower [14]. Due to the cubic garnet structure, TGG and TAG transparent ceramics with good optical quality could be made. TGG transparent ceramics have been made and showed very similar magneto-optical properties to TGG single crystals [15]. For TAG, the benefit of transparent ceramic is obvious: since the fabrication process of transparent ceramics is free from melting, obtaining pure TAG phase will not be a problem. So here we first report TAG transparent ceramics as an ideal Faraday magneto-optical material working in the visible and near infrared range. The optical quality, microstructure, magneto-optical property, and the thermal conductivity of the samples were investigated.

2. Experimental details

Firstly, Tb_4O_7 and Al_2O_3 powders of high purity (99.999%) were mixed according to the $Tb_3Al_5O_{12}$ formula with ethanol by ball milling for 48 h. 0.5 wt.% tetraethyl orthosilicate (TEOS) and 1 wt.% polyethylene glycol 400 (PEG-400) were added as the sintering aid and dispersion aid, respectively. The slurry was dried at 80 °C. After meshing, the powders were uni-axially pressed into pellets under 10 MPa. The pellets were subsequently cold-isotropically pressed (into green body) under 200 MPa. The green body was pre-sintered in air at 650 °C for 3 h to remove the organic ingredients. Then vacuum sintering was carried out at 1550 °C, 1600 °C, 1650 °C and 1700 °C for 5 h under a base pressure of 1.0×10^{-3} Pa. The obtained samples were named T1, T2, T3 and T4, respectively. All the samples were double-side polished to 2.4 mm thick (see Fig. 1).

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The crystal structure of the samples was investigated by X-ray diffraction (XRD) (Ultima IV, Rigaku, Japan). The optical transmittance spectra of the samples were measured on an ultraviolet/visible/near-IR spectrophotometer (V-570, JASCO, Japan). Scanning electron microscopy (SEM) (JSM-6360LA, JEOL, Japan) was employed to investigate the microstructure of the samples. The thermal conductivity of the sample with the best quality was measured by the well-known flash method on a Xenon Flash Apparatus (LFA447/1 NanoFlashR300, Netzsch, Germany). The Verdet constant at 632.8 nm of the sample was measured by a home made instrument consisting of a He–Ne laser, two polarizers and an electromagnet. For the Verdet constant measurement, the size of the clinic-shaped sample was Φ-10 mm × 8.7 mm.

3. Results and discussion

Fig. 1 shows a picture of the four as-sintered transparent ceramic samples after double-side mirror polishing. Except for the translucent T1, the characters behind the other three samples could be seen. Fig. 2 presents the XRD θ–2θ scans of the samples. XRD results showed that T1 sintered at lower sintering temperature (1550 °C) was of perovskite structure terbium aluminate (TAP) and TAG mixed phases. For T2, T3, and T4, all the peaks could be well assigned to the diffraction of TAG (JCPDF No. 76-0111). Almost no secondary phase or impurities were detected, which indicated that the obtained ceramic samples sintered ⩾1600 °C were of almost pure TAG phase. Typically, TAP always has lower phase formation energy than TAG does [16].

The optical transmittance of the samples is given in Fig. 3. For T1, T2 and T3, the transparency of the samples got better with higher sintering temperatures. From 500 nm to 1500 nm, the transmittance of T3 was close to 70%. The transmittance of T4 became lower than that of T3, which might be caused by over-heating when sintered at 1700 °C. The absorption peak at 484 nm was due to the Tb^{3+}: $^7F_6 \rightarrow {}^5D_4$ transition. No absorption of Tb^{4+} was observed, thanks to the vacuum sintering for suppressing the introduction of Tb^{4+}. No further annealing in a reducing atmosphere (like H_2) is needed. Through calculation from the refractive index, the authors of Ref. [10] predicted that the optical transmittance limitation of TAG from 500 nm to 1300 nm could reach more than 95%. In our experiment, since sintering temperature was the only one varying factor for all the four samples, the transparency could be further enhanced by optimizing the preparation process, for instance, to improve the temperature schedule, to select a better shaping method, or to improve the morphology of the raw material powders, etc.

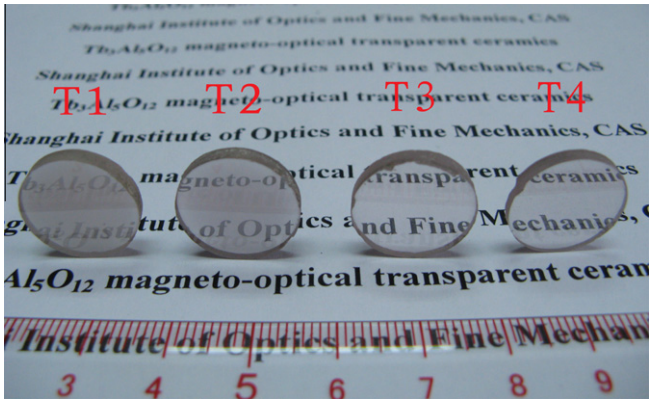

Fig. 1. A picture of the mirror polished ceramic samples.

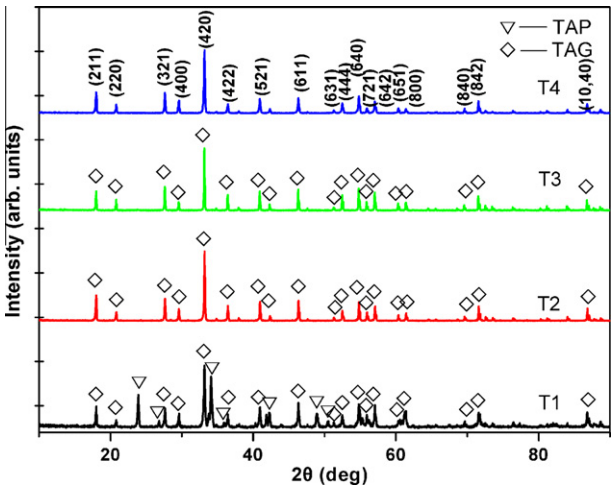

Fig. 2. XRD θ–2θ scans of the four transparent ceramic samples.

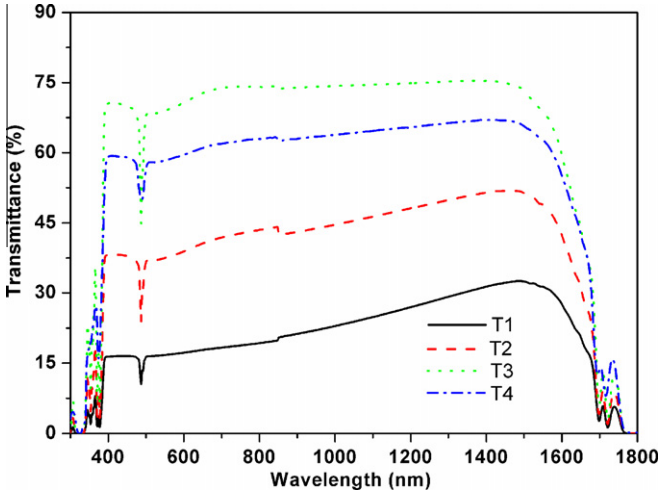

Fig. 3. Optical transmittance of the mirror polished transparent ceramic samples.

The four ceramic samples were thermally etched at 1400 °C for 10 h, then the microstructure could be observed by SEM (presented in Fig. 4a–d, respectively). An obvious trend is that the average grain size grew larger with higher sintering temperatures. The average grain size was about 14.2 μm for T1, 16.3 μm for T2, 18.3 μm for T3, and 26.4 μm for T4. For T1, many pores could be seen between the grain boundaries or enclosed in the grains. In addition, the low optical transmittance of T1 might be caused by the discrepancy of the refractive index of TAP and TAG. In accordance with the optical transmittance measurement, the amount of pores in T3 was the fewest. The white dashed lines might be the mechanical scribe during the polishing process. Pores turned more again in T4, which could illustrate the reduction of the optical transmittance of T4. It is clear that overheating can cause abnormal grain growth (or call it "re-crystallization of the grains"). Under this condition, the gain boundary migration rate is too high, which tends to enclose pores into the abnormally growing grains.

Since thermal management is a very important point in high power lasers, thermal conductivity of T3 was measured and provided in Fig. 5 as a function of the temperature. The thermal conductivity of T3 at room temperature was 6.5 W m^{-1} K^{-1}, which was lower than that of TGG single crystal (7.4 W m^{-1} K^{-1}). The