Ba$_3$Tb(PO$_4$)$_3$: Crystal growth, structure, magnetic and magneto-optical properties

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ABSTRACT

Ba$_3$Tb(PO$_4$)$_3$ crystals have been grown by the slow-cooling method and the Czochralski technique for the first time for magneto-optical applications. The single-crystal X-ray diffraction confirms that the compound crystallizes in the cubic system $I\bar{4}3d$, with eulytite structure with $a = 10.4484(12)$ Å, $V = 1140.6(2)$ Å^3 and $Z = 4$. The hardness of Ba$_3$Tb(PO$_4$)$_3$ crystal is about 5.5 Moh. The temperature dependence of the magnetic susceptibility indicated that the Ba$_3$Tb(PO$_4$)$_3$ crystal exhibits paramagnetic behavior over the experimental temperature-range 2–300 K. Transmittance spectra and the Faraday rotation have been investigated, which demonstrate that Ba$_3$Tb(PO$_4$)$_3$ crystal shows a higher visible transparency than Tb$_3$Ga$_5$O$_{12}$ crystal and yields a Faraday rotation comparable to that of Sr$_3$Tb(BO$_3$)$_3$ crystal. Ba$_3$Tb(PO$_4$)$_3$ is therefore a promising material in particular for new magneto-optical applications in the visible region.

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1. Introduction

Since the demonstration of the first laser in 1960, magneto-optic materials have attracted a great deal of attention due to their potential applications in high-precision laser measurements, advanced display systems, etc. [1,2]. Faraday isolators (FIs) are fundamental components used in advanced optical communications system to prevent harmful back-reflections from reaching a laser equipped with such an isolator, and to eliminate parasitic oscillations in amplifier systems or frequency instabilities in laser diodes [2]. As the central part of the FIs, the 45° Faraday rotator obtained by magneto-optic materials primarily determines the performance of FIs [3]. Yttrium iron garnet, Y$_3$Fe$_5$O$_{12}$ (YIG), characterized by a high transparency in the IR region (1.2–5.0 μm) [4], a low saturation magnetization and a large Faraday rotation angle, are so far the most commonly used materials in FIs.

However, as the rapid development of visible light communications [5–7], the demand of FIs operated at visible region are rapidly increasing, while the conventional YIG crystals are not practical due to their very poor transparency in this spectral region [8]. Therefore, an intensive search for new magneto-optic materials with a low optical absorption loss in the visible spectral region began and led to numerous new rare earth (RE)-based materials, which exhibit Curie–Weiss paramagnetic behavior, due to the

4f → 4f5d transition of RE^{3+} ions [9]. Tb^{3+} yields to the largest Faraday rotation, so that electric dipole contribution of Tb^{3+} dominates even over that of Fe^{3+} in magnetic terbium–iron garnet [10], and hence show the best magneto-optical properties [11,12].

Terbium–gallium garnet, Tb$_3$Ga$_5$O$_{12}$ (TGG), a commonly used crystalline magneto-optic material, with a broader transparency range and a high Verdet constant [13] is mainly applied in the near IR region. Moreover, although TGG melts congruently at approximately 1825 °C, its Czochralski growth is not exempt of difficulties. The decomposition and evaporation of Ga$_2$O$_3$ from the TGG melt, which is easy to over flow the container during the crystal growth process due to its large infiltration, lead to a serious component deviation from the congruent melting [14,15].

Terbium-doped glasses [16–18], which have often been used in large diameter glass laser systems, due to superior size scalability, are so far the most commonly used magneto-optic materials for the visible regions. However, this amorphous glass material cannot be used in high average power lasers because of its low thermal conductivity and low relatively stability.

Taking into account the requirements for a magneto-optic material applied in the visible spectral region, the family of eulytite-type rare-earth phosphates M$_3$R(PO$_4$)$_3$ (where M = alkaline-earth metal, and R = lanthanide), which demonstrate great potential for applications in laser host materials [19–21], and phosphors [22,23], have come to draw more and more attention from our research group. Ba$_3$Tb(PO$_4$)$_3$ (BTP), a member of the eulytite phosphates, crystallize in the cubic system with space group $I\bar{4}3d$ (PDF 43-0640). It is an

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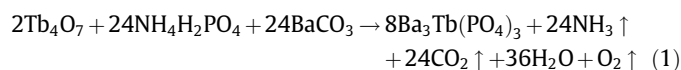 *E-mail addresses:* gfylaser@sina.com (F. Guo), j.z.chen@fzu.edu.cn (J. Chen).

isotropic medium, with strong crystallizability, low cost of materials, and no special absorption at the visible–near IR region. These features are advantages for a magneto-optical material candidate.

In this investigation, we attempt to employ the slow-cooling method and the Czochralski technique to grow BTP single crystal. The structure, spectral, magnetic and magneto-optical properties were discussed as well.

2. Experimental

2.1. Synthesis and crystal growth

The starting materials used for the crystal growth were prepared by the conventional solid-state reaction method from stoichiometric mixtures of analar grade $BaCO_3$, $NH_4H_2PO_4$, and Tb_4O_7 powders according to the following chemical reaction equation:

$$2Tb_4O_7 + 24NH_4H_2PO_4 + 24BaCO_3 \rightarrow 8Ba_3Tb(PO_4)_3 + 24NH_3 \uparrow \\ + 24CO_2 \uparrow + 36H_2O + O_2 \uparrow \quad (1)$$

The stoichiometric amount of raw materials was weighed with the excess amount 1.5 mol% of P_2O_5 to compensate for its volatilization loss during the process of crystal growth, and then ground homogeneously in an alumina mortar with the ethanol. The uniformly mixed raw materials were pressed into tablets and then sintered at 900 °C for 12 h in air. They were then cooled to room temperature, reground, extruded into pieces and sintered again at 980 °C in air for 23 h. The purity of the sample was checked by X-ray powder diffraction. A single eulytite phase of BTP was obtained when repeated heat treatment caused no further changes in the X-ray powder diffraction.

The single crystals BTP were grown from a melt system by the slow-cooling method. The polycrystalline pieces were heated to melt at about 1650 °C in an iridium crucible (56 mm in diameter and 43 mm in height) by a radiofrequency furnace under a nitrogen atmosphere, and then maintained at this temperature for 2 h to homogenize the melt. After 2 h, the temperature was slowly cooled to about 1390 °C at a rate of 2–10 °C/h (2 °C/h for 20 h, 5 °C/h for 20 h and 10 °C/h for 12 h). After the mixture was annealed at a rate of 60 °C/h to room temperature, only a single eulytite phase, which was proved by X-ray powder diffraction, was obtained. The as-grown BTP-1 single crystal, shown in Fig. 1(a), is transparent and crack free with a very slight yellowish coloration.

Since only a single eulytite phase was obtained from the melt, BTP is a congruently melting material, and the crystals also can be grown by the Czochralski technique. The starting materials were melted in an iridium crucible, heated by a radiofrequency furnace under a protective atmosphere of N_2. A seed crystal of $\langle 0\,0\,1 \rangle$ orientation, cut from the initial BTP crystal which obtained by the slow-cooling method, was dipped into the melt and then slowly

withdrawn, so that the crystal began to grow along the c-axis with 1.0–2.0 mm/h pulling rate and 12–16 r/min rotating velocity. After crystallization, the crystal was pulled out of the melt and cooled down to room temperature at a rate of 5–30 °C/h.

The as-grown BTP-2 single crystal, shown in Fig. 1(b), is transparent with dimensions of Ø20 × 25 mm with a very slight yellowish coloration. After oriented accurately by X-ray diffraction, the as-grown crystals were cut along the (0 0 1) crystal plane, and then wafers were ground and polished carefully for the following measurement, as shown in Fig. 1(c).

2.2. Structure determination

A single crystal of BTP with approximate dimensions of $0.50 \times 0.40 \times 0.20 \text{ mm}^3$ was selected for the single-crystal X-ray diffraction (XRD) analysis. The diffraction data were collected using the $\omega/2\theta$ scan technique on a Rigaku Saturn CCD diffractometer equipped with a graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The. The diffraction intensity data were corrected for Lorentz polarization factors. The structure was solved by direct methods with SHELXS-97 [24] and refined by the full-matrix least-squares technique with SHELXL-97 [25]. The final refinement of the structure was achieved using a fixed site occupancy ratio 3:1 for Ba and Tb equal to the ideal values in accordance with the chemical formula $Ba_3Tb(PO_4)_3$. The experimental parameters for data collection and refinement are summarized in Table 1. The final refined atomic coordinates and displacement parameters are given in Table 2. The selected inter-atomic distances and angles are listed in Table 3.

2.3. Hardness measurement

The hardness of as-grown BTP crystal, determined by using a 401MVA™ Vickers-microhardometer, is about 717.5 VDH, and is equal to about 5.5 Moh, which is close to that of siliceous glass, and hence is favorable for crystal machining.

2.4. Transmission spectrum

The transmission spectrum of as-grown crystal BTP was measured by using a Perkin-Elmer Lambda UV–Vis–NIR spectrophotometer, over the wavelength range from 400 to 1500 nm with a 2 nm resolution at room temperature. In order to evaluate the transparency of as-grown crystal, a commercial device-quality TGG sample, supplied by Physcience Opto-electronic Co. Ltd. Beijing, was also used for the spectral measurement with the same test conditions.

2.5. Variable-temperature magnetic susceptibility

The temperature dependence of the magnetic susceptibility was measured under both zero-field-cooled (ZFC) and field-cooled (FC)
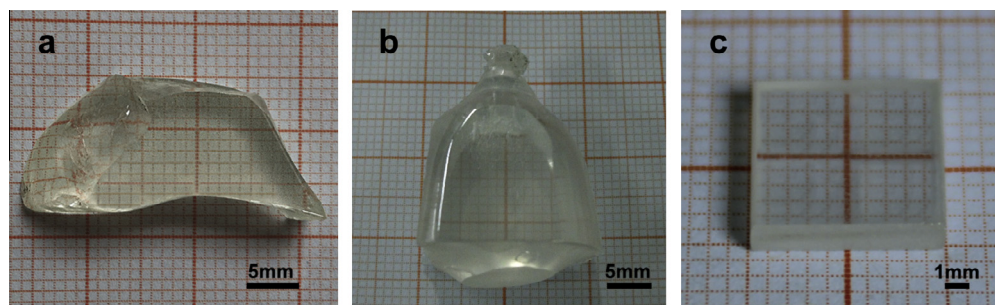

Fig. 1. Photographs of as-grown crystals (a) BTP-1 (slow cooling method), (b) BTP-2 (Czochralski technique), and polished wafer (c).