

A novel magneto-optical crystal Yb:TbVO₄

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ABSTRACT

Highly transparent Yb:TbVO₄ single crystal with dimensions of Ø27 × 41 mm³ almost without scattering defects has been successfully grown by Czochralski technique. The spectra, thermal properties and laser-induced damage threshold were investigated in detailed. The Faraday rotation (FR) measurement was carried out by means of extinction method. The Verdet constant comes up to 80 rad m⁻¹ T⁻¹ at 1064 nm, significantly larger than TbVO₄ (58 rad m⁻¹ T⁻¹) and TGG (40 rad m⁻¹ T⁻¹) reported. Meanwhile, the as-grown crystal presents lower absorption coefficient and higher magneto-optical figure of merit at measured wavelength in comparison with TGG. Moreover, the crystal exhibits a substantially improved extinction ratio (42 dB) in contrast with TbVO₄ (29 dB), and exceeds the highest value of TGG (40 dB). These advantages make Yb:TbVO₄ a highly promising magneto-optical material candidate for optical isolators in the visible-near infrared region.

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1. Introduction

Optical isolators (OIs) based on the non-reciprocity of the Faraday effects play an increasingly important role in optic communication and optical measurement system [1–4]. They have been widely utilized to prevent optical feedback from reaching and damaging the laser so as to guaranty an unidirectional light propagation in the laser systems [5,6]. With the rapid advance in high-power lasers and high-power fiber lasers, the demand for OIs operated in the visible-near infrared region has greatly increased [7–9]. For such devices, large Faraday rotation and high transmittance of the magneto-optical material are equally crucial. However, the conventional Y₃Fe₅O₁₂ (YIG) crystals are not applicable in 400–1100 nm owing to their poor transparency [10]. Tb₃Al₅O₁₂ (TAG) single crystal is thought to be a good candidate for such requirements because of its superior magneto-optical properties, while the practically applicable TAG crystal has not been grown by Czochralski method due to its incongruent melting nature [9]. Currently, the most commonly used magneto-optical crystal for OIs in the VIS–NIR is Tb₃Ga₅O₁₂ (TGG) crystal, which has been extensively investigated owing to its relatively large Verdet constant as well as good transmittance and high thermal conductivity [11]. Unfortunately, it is not easy to grow high quality TGG due to the component deviation induced by the comparatively high decomposition and evaporation of Ga₂O₃ during crystal growth [12,13].

Among the rare earth (RE) ions, Tb³⁺ ion exhibits the best magneto-optical properties [14,15]. Therefore, considerable research for exploring novel terbium-based magneto-optical materials has been conducted [1–4,16,17]. Additionally, previous studies have found that some paramagnetic RE (RE = Ce³⁺, Pr³⁺, Nd³⁺, Yb³⁺ and so on) ions doped magneto-optical crystals, such as doped TGG, TAG and YIG, remarkably enhancing the magneto-optical performance because of the crystal field interaction and quantum-based super-exchange interaction between Tb³⁺ and other paramagnetic RE ions [18,19]. For instance, Ce³⁺, Pr³⁺ and Nd³⁺ doped TGG exhibits 20–30% larger Verdet constant in comparison with that of TGG [4,18,19]. Tb₃[Sc_{1.95}Lu_{0.05}](Al₃)O₁₂ garnet single crystals give rise to an increment of 20% of Verdet constant compared with TGG by doping Sc³⁺ and Lu³⁺ [20]. Besides, (YbBi)₃Fe₅O₁₂ crystals possess larger Faraday rotation and smaller temperature derivative of Faraday rotation by substituting Bi³⁺ and Yb³⁺ [21–23].

TbVO₄ single crystal appeared very recently, it could be grown by Czochralski method and the bulk crystal growth is easier than TGG. Some researchers have successfully grown pure TbVO₄ crystal with 50% larger Verdet constant compared to TGG [24,25]. However, RE ions doped TbVO₄ has not been reported yet. Both Tb³⁺ and Yb³⁺ belong to paramagnetic RE ions, Tb³⁺ has a larger ionic radius than Yb³⁺ so Yb³⁺ could be incorporated into Tb³⁺ site, and we expect that Yb³⁺ doped TbVO₄ with larger Verdet constants at some wavelengths can be obtained due to super-exchange interaction. Accordingly, the present study aimed at enhancing the Faraday effect of TbVO₄ by substituting Yb³⁺ for Tb³⁺ and growing high quality crystal

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without scattering defects simultaneously. In this article, we firstly report the growth of Yb:TbVO₄ crystal by Czochralski method, the crystal quality, spectrum, thermal properties, LIDT and magneto-optical properties were analyzed in detailed.

2. Experimental procedure

2.1. Crystal growth

Polycrystalline materials TbVO₄ and YbVO₄ used were synthesized by the liquid-phase reaction method. These compounds were weighted accurately according to the following ratios: Yb_{0.1}Tb_{0.9}VO₄ (10-at.% Yb doping concentration). Yb:TbVO₄ single crystal was grown by Czochralski method in a Ø65 × 40 mm³ iridium crucible under the protect of high purify nitrogen atmosphere. In our experiments, all crystals were grown along the [001] direction using a pure TbVO₄ crystal sample as the seed crystal at a pulling rate of 1–1.5 mm/h and a rotation rate of 6–12 rpm. After growth, the crystal was drawn out of the melt surface and cooled down to room temperature at an appropriate cooling rate.

2.2. Characteristics

The powder X-ray diffraction (XRD) measurement was examined by a computer-automated diffractometer (Bruker D8 Focus) equipped with Cu K_α radiation ($\lambda = 1.54,056 \text{ \AA}$) at room temperature. A step size of 0.02 and counting time of 0.1 s/step were applied in the 2θ range of 10–90°.

The concentration of Yb³⁺ ion in the crystal was analyzed using the inductively coupled plasma and optical emission spectrometry (ICP-OES) method. The sample was cut from the middle part of the as-grown crystal. The effective Yb³⁺ segregation coefficient K_{eff} can be calculated by the following equation: $K_{\text{eff}} = C_s/C_l$, where C_s is the Yb³⁺ concentration in the crystal, and C_l is the initial Yb³⁺ concentration in the melt.

The as-grown crystal was cut along (001) plane oriented by XRD, then ground and polished carefully to about 1 mm thickness

for spectra measurement. The transmission spectrum was measured using a Perkin-Elmer Lambda 900 UV–Vis–NIR Spectrophotometer at wavelength of 400–3000 nm. A rectangular prism with an angle of 15° was cut to determine the refractive index of as-grown crystal by a SpectroMaster UV–Vis–IR.

The thermal expansion coefficient was determined employing a thermo-mechanical analyzer (Perkin-Elmer TMA) in the temperature range of 25–500 °C at a heating rate of 10 °C/min. The thermal diffusion coefficient and specific heat were performed between 20 and 300 °C using a laser flash apparatus (NETZSCH LFA 447 Nano-flash) and a differential scanning calorimeter (Diamond DSC-ZC), respectively. The Laser-induced damage threshold (LIDT) testing was carried out using Nd:YAG laser system at 1064 nm with a pulse repetition rate of 1 kHz and the pulse duration of 5 ns. The (001) surfaces of 5 × 5 mm² were optically polished for LIDT measurement.

The optical weak absorption of as-grown crystal along c axis was measured at 1064 nm by photothermal common-path interferometer (PCI) technique [26]. The size of the sample used for the measurement was 5 × 5 × 5 mm³.

The X-ray photoelectron spectroscopy (XPS) was recorded using Thermo Scientific ESCALAB 250Xi for valence state analysis of elements.

The Faraday rotation (FR) measurement of the Yb:TbVO₄ crystal along c axis was carried out by extinction method [27] and the magnetic field intensity ranged from 0 to 1.2 T. Lasers of 532, 633 and 1064 nm were used as the sources of the probe beam. A sample with dimensions of 3 × 3 × 15 mm³ was employed and two 3 × 3 mm² faces were optically polished.

3. Results and discussion

3.1. The influence of cooling rate on optical quality

The as-grown Yb:TbVO₄ single crystals, shown in Fig. 1, are transparent and inclusions free with a slight yellow. Detailed growth results are listed in Table 1.

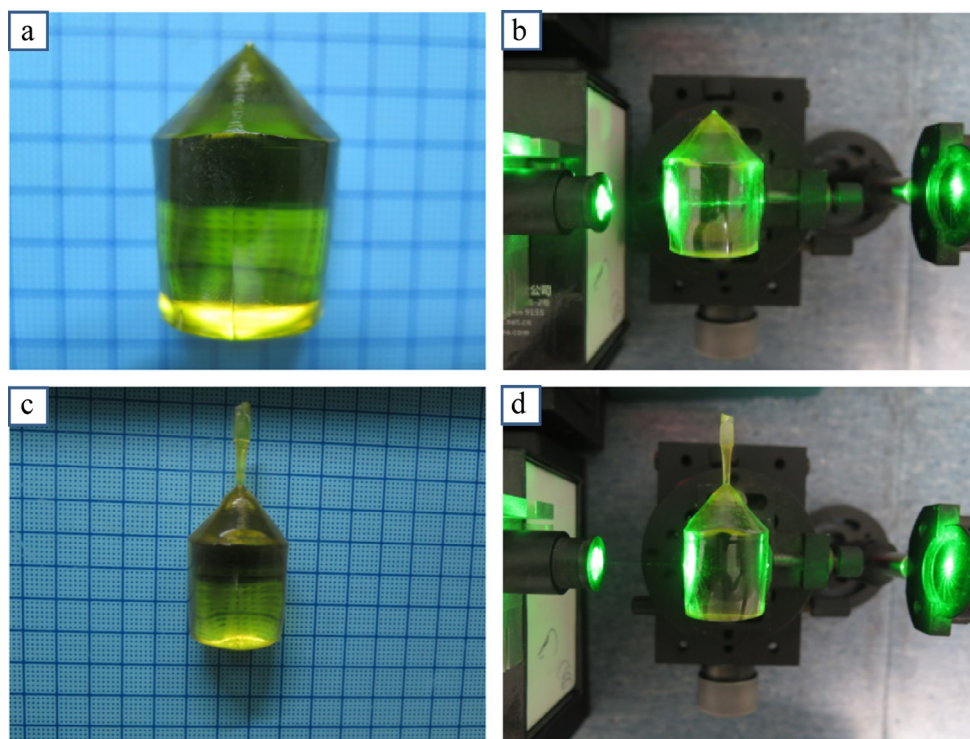


Fig. 1. Photos of as-grown Yb:TbVO₄ crystals: (a) and (b) numerous scattering defects, (c) and (d) almost without scattering defects.

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