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Spectroscopic properties of Tm:Bi₄Ge₃O₁₂ crystals grown by the micro-pulling-down method

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Abstract

Tm³⁺-doped bismuth germanate crystals (Tm:BGO) with various doping concentrations of 0.5, 0.75, 1.0, 1.5, and 2.0 at.% were grown by the micro-pulling-down method (μ -PD). The effect of thulium concentration on the **growth**, structure, absorption spectra, emission spectra and fluorescence lifetime of ³H₄ and ³F₄ state was studied. Under excitation of 792 nm, Tm:BGO crystals exhibit two fluorescence bands corresponding to the ³H₄ → ³F₄ and the ³F₄ → ³H₆ transitions. The fluorescence lifetime of ³H₄ state decreased strongly as the thulium concentration increased, while the lifetime of ³F₄ state are relatively constant for all thulium concentrations.

Keywords: Tm:Bi₄Ge₃O₁₂, Micro-pulling-down method, Spectroscopic property

1. Introduction

Tm³⁺-doped laser materials have attracted much attention due to their potential applications in medical surgery, tele-communication, remote sensing, and pumping sources of optical parametric oscillators [1-3]. During the last decade, different Tm doped crystalline host materials have been investigated for their favourable properties to obtain an efficient laser emission. Tm³⁺ ions can be efficiently excited by commercial AlGaAs laser diode around 800 nm (Tm³⁺, ³H₆→³H₄ transition) and emission spectral intervals are around 1.5 μm [4], 1.9 μm [5] and 2.3 μm [6]. Laser oscillation of Tm³⁺ has been demonstration in numerous hosts such as LiYF₄ [7,8], BaY₂F₈ [9], CaF₂ [10], MgWO₄ [11], CaGdAlO₄ [12], YAlO₃ [13], LuScO₃ [14], and Y₂O₃ [15].

Bismuth germanate crystal Bi₄Ge₃O₁₂ (BGO) belongs to cubic system with the space group of I43d [16]. It has been studied as a host for Er³⁺, Eu³⁺, Dy³⁺, Pr³⁺ and Nd³⁺ ions, etc., with applications as optical temperature sensors, scintillators and laser gain media [17-21]. In addition, as a host material, BGO possesses many qualities desirable for laser applications such as excellent physical and chemical properties [22]. In 1979, A.A. Kaminskii et al. reported the absorption and emission properties of Tm³⁺-doped BGO crystal grown by Czochralski method [23]. The micro-pulling-down (μ-PD) method was used to grow BGO crystals with high quality and transparency, where the crystals have low thermal strain compared to other growth methods [24-26]. Eu:BGO and Nd:BGO crystals have also been grown by the μ-PD method [27-29]. BGO melt congruently and relatively high rate of evaporation of Bi₂O₃ occurs during melt overheating [30-31].

In this work, Tm:BGO crystals with different doping concentration were successfully grown by the micro-pulling down method. Achievement of stationary conditions for the growth of uniformly shaped (constant diameter) fiber crystals was considered as final goal and positive outcome of this paper. Spectral properties of the crystals were studied at room temperature.

2. Experimental

2.1 Crystal growth

Tm:Bi₄Ge₃O₁₂ crystals were grown by the μ-PD method [32]. The Tm₂O₃ (99.999%), Bi₂O₃ (99.999%) and GeO₂ (99.999%) powders were used as starting materials and weighed according to the formula Tm_{4x}Bi_{4(1-x)}Ge₃O₁₂ (x=0.005,0.0075,0.01,0.015,0.02). After thoroughly mixed in an agate mortar, they were pressed into bulks and sintered in the air at 750°C for 24h. The polycrystalline Tm:BGO was melted in a platinum crucible, and then the melt was pulled down through a capillary channel at the bottom of the crucible. The Tm:BGO crystals were grown with constant pulling rate of 0.3 mm/min by pulling down a <210> oriented BGO seed in the air atmosphere. Whatever the starting composition prepared in this work (Tm≤2at%), we had not seen any evolution of growth Kinetic. As shown in Fig. 1(a)-(e), five crack-free Tm:BGO single

crystals with dimensions of $\Phi 2 \times 44\text{-}68 \text{ mm}^3$ were obtained and present a light yellow color. The crystals produced from the crucibles were very uniform in shape according to the measurements performed directly from the fibers with accuracy of about $\pm 20 \text{ }\mu\text{m}$. The crystals have a rough appearance on the outside, but the inner part of the crystals was transparent and free of visible defects. It is important to note that, once the melt becomes Bi-poor there is no way to establish constant properties (solidification temperature and following shape of the meniscus) of the melt. Thus, for all Ge-rich systems evaporation of the bismuth oxide will only increase dissolution of the melt and its transformation from melt to flux system.

Fig.1. Photographs of the as-grown Tm:BGO crystals, (a) 0.5 at.%, (b) 0.75 at.%, (c) 1.0 at.%, (d) 1.5 at.% and (e) 2.0 at.%.

2.2 X-ray powder diffraction

In order to investigate the structure of Tm:BGO crystals, small section of the samples were cut from the as-grown crystals and grounded into powder in an agate mortar. And then the structure was examined by X-ray diffraction method (XRD, Bruker-D2, Germany) at a scan width of 0.05° with a range $5^\circ\text{-}90^\circ$.

2.3. Spectra measurements

For spectroscopic measurements, the Tm:BGO samples were cut from the as-grown crystals

and then optically polished to flat and parallel faces with the size of $\Phi 2 \times 2 \text{ mm}^3$. The absorption spectra were measured from 400 to 2000 nm by a UV-VIS-NIR spectrophotometer (Lambda 1050, Perkins Elmer, U.S.A.) at room temperature. The fluorescence spectrum as well as the decay time were recorded by a fluorescence spectrometer (Edinburg Instrument, FLS1000, U.K.) under the excitation 792 nm. All the measurements were carried out at room temperature.

3. Results and discussion

3.1 Crystal structure

The room temperature XRD patterns of Tm:BGO crystals are shown in Fig. 2. The crystal structure of undoped and Tm-doped BGO belongs to the cubic space group $\Gamma 43d$. The diffraction peaks of Tm:BGO crystals are in agreement with JCPDS 84-0505 of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. No additional impurity phases were found in the patterns. Due to the different doping concentration of Tm^{3+} ions, the relative intensity of each diffraction peak is different and the diffraction peaks of the XRD patterns were slightly offset to the right compared to the JCPDS 84-0505 of BGO. The lattice constants of Tm:BGO crystals are listed in Table 1. With the increasing of doping concentration x , the calculated lattice constant decreased, which is attributed to the smaller radius of Tm^{3+} ion ($0.869 \text{ \AA}$) compared with that of Bi^{3+} ion ($0.96 \text{ \AA}$) [33]. The results reveal that a small amount of Tm^{3+} ions did not change the structure of BGO crystal without any composition evolution resulting in a second-phase formation.

Fig.2. Room temperature XRD patterns of Tm:BGO crystals with a standard reference of undoped BGO (JCPD 84-0505)

Table 1. Lattice parameters of Tm:BGO crystals as a function of Tm concentration

x at.% Tm:BGO	a(Å)
0	10.497 ^[34]
0.5	10.453
0.75	10.451
1.0	10.445
1.5	10.428
2.0	10.419

3.2 Absorption spectra

The room temperature absorption spectra of BGO crystals doped with 0.5, 0.75, 1.0, 1.5, and 2.0 at.% of Tm³⁺ ions in the wavelength region of 400-2000 nm are displayed in Fig. 3. We note that all the samples have the same absorption spectra. Five absorption bands are located at approximately 474, 680, 792, 1211 and 1737 nm, which are attributed to the transitions from the ³H₆ ground state to ¹G₄, ³F₂+³F₃, ³H₄, ³H₅ and ³F₄ excited states, respectively. Among five main peaks, the peak at 792 nm (³H₆ → ³H₄) matches well with the emission of the commercial AlGaAs LD pumping. As the doping concentration increases from 0.5 at.% to 2.0 at.%, the absorption coefficient at 792 nm increases from 0.17 cm⁻¹ to 0.62 cm⁻¹. For 2.0 at.% Tm:BGO crystal, the full width at half-maximum (FWHM) of the absorption band at 792 nm is about 3.3 nm. The value is smaller than that of Tm:YAG (4 nm at 780 nm [35]), but larger than that of Tm:KY₃F₁₀ (2.8 nm at 778.6 nm [36]), which is suitable for LD pumping.

Fig.3. Absorption spectra of Tm:BGO crystals as a function of Tm concentration.

3.3 Fluorescence spectra

Under excitation at 792 nm, two fluorescence bands corresponding to the ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transitions within the measuring range are shown in Fig. 4. At thulium concentrations from 0.5 at.% to 2 at.%, no distinct change in the shape and position of the emission bands was observed in Tm:BGO crystals. We found that the intensity of emissions of the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition increases with the increase of thulium concentration. The upper level ${}^3\text{F}_4$ can be populated by a cross-relaxation process (${}^3\text{H}_4 + {}^3\text{H}_6 \rightarrow {}^3\text{F}_4 + {}^3\text{F}_4$) and the effectivity of this process increases with higher thulium concentrations. For 2.0 at.% Tm:BGO crystal, the FWHM of the emission band at 1452 nm was calculated to be 3.9 nm and the FWHM of the emission band at 1879 nm is about 44.6 nm. The FWHM of ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition is larger than the value of Tm:YAG (31.37 nm [37]). We did not register the emission around 2.3 μm . The energy gap between ${}^3\text{H}_4$ and ${}^3\text{H}_5$ energy level is about 4100 cm^{-1} and the Tm^{3+} ions at the ${}^3\text{H}_4$ level can relax nonradiatively to the ${}^3\text{H}_5$ level due to the larger phonon energy ($\approx 900 \text{ cm}^{-1}$) of BGO crystal [21].

Fig.4. Fluorescence spectra of Tm:BiBO crystals with different Tm doping concentration in (a) 1350-1550 nm and (b) 1700-2150 nm.

3.4 Fluorescence lifetime

Fig. 5(a) presents the fluorescence decay curves of Tm:BGO crystals in correspondence with the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition at 1452 nm at room temperature. The fluorescence lifetime was calculated to be 352 μs , 318 μs , 313 μs , 267 μs and 218 μs for the doping concentration of 0.5, 0.75, 1.0, 1.5 and 2.0 at.%, respectively, by a single exponential fitting. The lifetime of the $^3\text{H}_4$ state decreased strongly as the thulium concentration increased, which is due to the concentration quenching effect caused by the energy transfer between thulium ions at higher thulium concentration [38]. The fluorescence lifetime at 1452 nm of 1 at.% Tm:BGO is much longer than that of 1% Tm:KGd(WO₄)₂ (175 μs [38]) and 1% Tm:YVO₄ (100 μs [39]).

The fluorescence decay curves of Tm:BGO crystals corresponding to the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition at 1879 nm are shown in Fig. 5(b). The measured decay curves showed a single exponential decaying behavior, and the fluorescence lifetime was measured to be 5.43, 5.16, 5.36, 5.69 and 5.64 ms, respectively. In contrast to the lifetime of the $^3\text{H}_4$ state, the fluorescence lifetimes of $^3\text{F}_4$ state are relatively constant for all thulium concentrations. This can be explained by two different mechanisms: the reabsorption effect between $^3\text{F}_4 \rightarrow ^3\text{H}_6$ resonant transitions and repopulation of the $^3\text{H}_4$ state via the $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{F}_4 + ^3\text{F}_4$ cross-relaxation process [38]. The fluorescence lifetime at 1879 nm of 1 at.% Tm:BGO is much longer than that of 1% Tm:KGd(WO₄)₂ (1.71 ms [38]) and 1% Tm:YVO₄ (1.03 ms [39]). The results indicated that Tm:BGO single crystal may be a promising laser gain medium.

For 1.45 μm emission, the lifetime of the terminal $^3\text{F}_4$ level is much longer than that of the initial $^3\text{H}_4$ level, making the $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition self-terminating. The sensitive co-doping ions like Pr³⁺, Ho³⁺ and Tb³⁺ ions were proposed to depopulate $^3\text{F}_4$ state efficiently [40-42], which will be our next investigation in the near future.

Fig.5. Fluorescence decay curves of the ${}^3\text{H}_4$ and ${}^3\text{F}_4$ level of Tm:BGO crystals with different doping concentration.

4. Conclusion

Tm-doped BGO crystals with different doping concentration were successfully grown by the μ -PD method and uniformly single crystals fibers of constant diameter was reported. The room temperature XRD revealed that the cell parameter decreased with the increasing of doping concentration in good agreement with Vegard Low [43]. The absorption spectra, emission spectra and fluorescence lifetimes of Tm:BGO crystals were measured at room temperature. The absorption peak at 792 nm matches well with the emission of the commercial AlGaAs LD pumping. The intensity of emissions of the $^3F_4 \rightarrow ^3H_6$ transition increases with the increase of thulium concentration. The fluorescence lifetime of 3H_4 state decreased strongly as the thulium concentration increased, while the lifetime of 3F_4 state are relatively constant for all thulium concentrations. The results indicate that Tm:BGO crystal could be a promising laser gain medium.

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