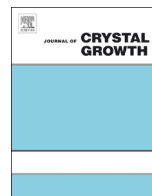




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Growth and spectroscopic properties of Tb³⁺-doped Na₃La₉O₃(BO₃)₈ crystal



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ABSTRACT

Tb³⁺ doped Na₃La₉O₃(BO₃)₈ (Tb:NLBO) crystals have been grown by the top-seeded solution growth (TSSG) method. X-ray powder diffraction results show that the introduction of Tb³⁺ does not change the structure of NLBO crystal. Tb³⁺ concentration was determined by inductively coupled plasma optical emission spectrometry to be 1.089 × 10²¹ ions/cm³. The absorption and emission spectra were measured at room temperature by using a (1 0 0) oriented crystal wafer. According to the Judd–Ofelt theory, the spontaneous transition probabilities, fluorescence branch ratio, and the radiation lifetime of ⁵D₄ state were calculated. The unpolarized and polarized emission properties under the 367 nm excitation were evaluated. The decay time of the 543 nm emission assigned to the ⁵D₄–⁷F₅ transition was also measured. All the results show that Tb:NLBO crystal would be a promising green laser material.

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1. Introduction

Rare earth (RE) and other element complex borates are of great interest because of their potential applications in nonlinear optics (NLO) and laser engineering. In the past few decades, many complex borate crystals have been developed, including YAl₃(BO₃)₄ [1], La₂CaB₁₀O₁₉ [2], Ca₄REO(BO₃)₃ (RE=Y, Gd) [3,4], etc. Since rare earth ions have a great similarity in their coordination structures and physicochemical properties, the crystal structure and properties do not dramatically change when the rare earth ions are replaced partly or completely by different rare earth ions. If the rare earth active ions are doped, these borates exhibit excellent luminescence properties, and can be used as the self-frequency doubling or luminescence materials, such as Nd:YAl₃(BO₃)₄ [5], Nd:Ca₄GdO(BO₃)₃ [6], and Nd:La₂CaB₁₀O₁₉ [7]. Among all rare earth active ions, only Eu³⁺ and Tb³⁺ could emit visible fluorescence strong enough for practical applications [8]. The recent study [9] has shown that Tb³⁺ has potential to provide a visible four-level laser system as its energy-level structure is

similar to that of Nd³⁺, and the spectroscopic characteristic of Tb³⁺ largely depends on host lattice [8]. However, there were very few reports on the spectroscopic properties of Tb³⁺ doped rare earth borates, except for some primary studies on Tb:Ca₄GdO(BO₃)₃ [10] and Tb:YAl₃(BO₃)₄ [11] crystals. Therefore it is of significance for investigating Tb³⁺ luminescence in other promising host materials.

Na₃La₉O₃(BO₃)₈ (NLBO) is a promising borate nonlinear optical crystal with excellent optical properties, such as a large nonlinear optical coefficient, a wide transparency range, and a high laser induced damage threshold. In addition, the crystal exhibits high chemical stability and good mechanical properties [12]. In contrast to the above host materials, NLBO possess a much higher concentration of rare earth ions ($N = 1.505 \times 10^{22}$ ions/cm³) [13]. Therefore its crystal structure can accommodate much larger amounts of Tb³⁺, which offers a very good opportunity to design a high-terbium-content luminescent system.

To our knowledge, Tb³⁺ doped NLBO single crystal are not available in previous literatures. In this work, we report on the growth of Tb:NLBO crystal by the top-seeded solution growth (TSSG) method. The spectral properties were characterized by absorption and emission spectra, and the spectroscopic parameters were calculated on the basis of the Judd–Ofelt theory

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[14,15]. The fluorescence decay time of the ${}^5D_4\text{--}{}^7F_5$ transition in Tb:NLBO crystal has also been reported.

2. Experimental

2.1. Crystal growth

Tb:NLBO crystals were grown by the top-seeded solution growth (TSSG) method in $\text{Na}_2\text{O}\text{--}\text{B}_2\text{O}_3\text{--}\text{NaF}$ flux system. The starting materials were 99.99% purity La_2O_3 and Tb_4O_7 , analytical grade Na_2CO_3 , H_3BO_3 and NaF. According to the formula $\text{Na}_3\text{Tb}_{9x}\text{La}_{(9-9x)}\text{B}_8\text{O}_{27}$ ($x=0\text{--}0.8$), the polycrystalline samples were synthesized by high-temperature solid-state reaction at $970\text{ }^\circ\text{C}$ for 72 h with several intermediate grindings. From the X-ray powder diffraction (XRPD) analysis of these samples, it can be concluded that the maximum doping concentration for Tb^{3+} in NLBO crystal is about 30%. In addition, Bai et al. [16] has reported that the quenching of $\text{Na}_3\text{Tb}_{9x}\text{La}_{(9-9x)}\text{B}_8\text{O}_{27}$ ($x=0.05\text{--}0.2$) polycrystalline samples occurs when the doping concentration is higher than 10%. Therefore the initial doping concentration 10% was adopted for single crystal growth. The polycrystalline samples of $\text{Na}_3\text{Tb}_{0.9}\text{La}_{8.1}\text{B}_8\text{O}_{27}$ were mixed with Na_2CO_3 , H_3BO_3 , and NaF in molar ratio of 1:7:6:9, and then the mixture were melted into a platinum crucible in several batches. The crucible was placed into a cylindrical resistance heated furnace with a Shimaden FP23 controller with an accuracy of $\pm 0.1\text{ }^\circ\text{C}$. The homogenization of the solution was achieved by stirring with a platinum stirrer at $1080\text{ }^\circ\text{C}$ for 48 h. A tentative seed was used to determine the saturation temperature ($1008\text{ }^\circ\text{C}$). After that, a seed crystal with [1 1 0] orientation was dipped into the solution at $1030\text{ }^\circ\text{C}$ and kept for 30 min to dissolve its rough surfaces. Then the temperature was quickly lowered to $1008\text{ }^\circ\text{C}$, and decreased at a rate of $0.1\text{--}0.3\text{ }^\circ\text{C}/\text{day}$ during the growth. The growing crystal was rotated at 4 rpm. When the growth was finished after about a month, the crystal was pulled out of the solution, and cooled to room temperature at a rate of $5\text{ }^\circ\text{C}/\text{h}$. The as-grown Tb:NLBO crystal with slightly cracking is shown in Fig. 1. The transparency was low due to the adhesion of flux on the crystal surface. From the size and cracking degree of crystals, it can be inferred that the growth of Tb^{3+} doped NLBO crystal is more difficult than that of undoped one [17].

2.2. X-ray powder diffraction analysis

High-temperature XRPD analysis of as-grown crystal was performed by using an automated Bruker D8 X-ray diffractometer in air atmosphere. The temperature was controlled by a furnace with an accuracy less than $2\text{ }^\circ\text{C}$ at 25, 300, 500, 700, 900, and $1000\text{ }^\circ\text{C}$, respectively. Powder diffraction data were collected in the 2θ range of $8\text{--}80^\circ$ with a scanning step width of 0.02° and a counting time of 0.2 s. Lattice parameters were calculated and refined with the software Jade [18].

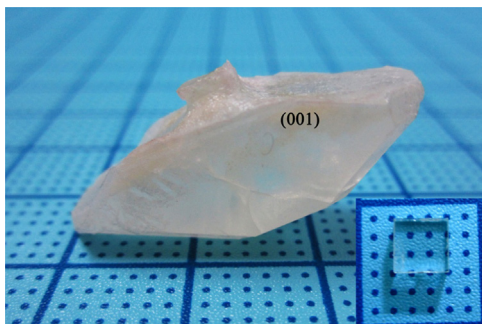


Fig. 1. As-grown Tb^{3+} doped NLBO crystal and polished wafer.

The Tb^{3+} concentration in Tb:NLBO crystal was determined by inductively coupled plasma optical emission spectrometry (Varian 710 ICP-OES). The sample was cut from the transparent part of the crystal.

2.3. Spectral measurement

A (1 0 0) oriented rectangular wafer with dimensions of $4 \times 4 \times 1.95\text{ mm}^3$ was cut from the as-grown crystal, and its two $4 \times 4\text{ mm}^2$ facets were polished (see Fig. 1). The absorption spectrum was measured at room temperature by using a Lambda 900 UV-vis-NIR spectrophotometer in the wavelength range of $280\text{--}600\text{ nm}$. The emission spectra excited by a Xenon lamp at 367 nm were recorded by a FLS920 spectrofluorimeter (Edinburg Instrument) at room temperature. The fluorescence decay time for ${}^5D_4\text{--}{}^7F_5$ transition monitored by 543 nm and excited by 367 nm was also measured with the above spectrofluorimeter at room temperature.

3. Results and discussion

3.1. XRPD analysis and components

The XRPD patterns of Tb:NLBO crystal in the range of $25\text{--}1000\text{ }^\circ\text{C}$ are shown in Fig. 2. These patterns at different temperatures are consistent with the calculated one from the single crystal crystallographic data of NLBO crystal [13]. No impurity phases were found. The unit-cell parameters of Tb:NLBO crystal were calculated to be $a=8.796\text{ \AA}$, $c=8.616\text{ \AA}$, and $V=577.3\text{ \AA}^3$, which were slightly less than those of NLBO crystal ($a=8.903\text{ \AA}$, $c=8.713\text{ \AA}$ and $V=598.1\text{ \AA}^3$) [13]. This difference in unit-cell parameters results from the one in the radius between Tb^{3+} (109.5 pm) and La^{3+} (121.6 pm) [19]. The different ionic radius might also bring thermal stress to the growing crystal. The thermal expansion coefficients along a and c axes were defined as: $\alpha_a(T)=(da/a)/dT$ and $\alpha_c(T)=(dc/c)/dT$ [20,21]. In the temperature range of $25\text{--}1000\text{ }^\circ\text{C}$, α_a and α_c were calculated to be 3.324×10^{-6} and $9.579 \times 10^{-6}\text{ }/^\circ\text{C}$, respectively. The value of α_c/α_a is up to 2.88, indicating the existence of large anisotropy of thermal expansion. The cracking of Tb:NLBO crystal in Fig. 1 probably results from large anisotropy of thermal expansion.

The content of Tb^{3+} in single crystal was determined to be $1.089 \times 10^{21}\text{ ions/cm}^3$ at the initial doping concentration of 10%. The segregation coefficient for Tb^{3+} was calculated to be 0.68 with the formula $k_{\text{eff}}=c_1/c_2$, where c_1 and c_2 are the concentration of Tb^{3+} in the single crystal and polycrystalline samples,

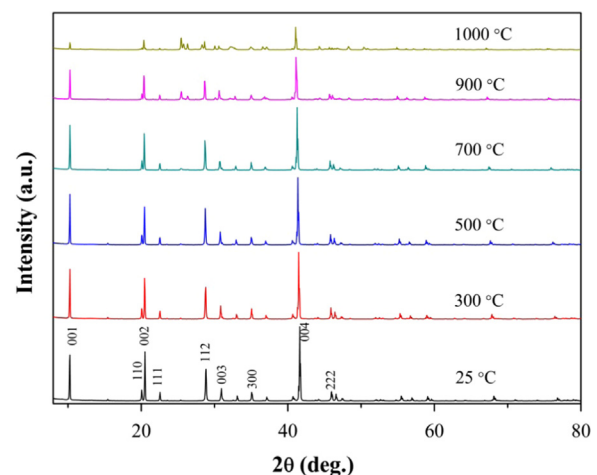


Fig. 2. High-temperature XRPD patterns of Tb:NLBO crystal in the range of $25\text{--}1000\text{ }^\circ\text{C}$.

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