Thermal and optical properties of Tm$^{3+}$:NaLa(WO$_4$)$_2$ crystal

1 Fujian Institute of Research on the Structure of Matter, State Key Laboratory of Structural Chemistry, Chinese Academy of Sciences, Fuzhou, 350002 Fujian, P.R. China
2 Graduated School of Chinese Academy of Sciences, 100039 Beijing, P.R. China

ABSTRACT A Tm$^{3+}$-doped NaLa(WO$_4$)$_2$ single crystal with a dimension of $20 \text{mm} \times 40 \text{mm}$ was grown by the Czochralski method. Anisotropic thermal expansion coefficients of this crystal were investigated. Polarized absorption spectra, emission spectra and decay curve were recorded at room temperature. The absorption and emission cross-section were presented. Based on the Judd–Ofelt analysis, we obtained the three intensity parameters: $\Omega_2 = 10.21 \times 10^{-20}$, $\Omega_4 = 2.66 \times 10^{-20}$, and $\Omega_6 = 1.46 \times 10^{-20}$ cm$^2$. The radiative probabilities, radiative lifetimes, and branch ratios of Tm$^{3+}$:NaLa(WO$_4$)$_2$ were calculated, too. Luminescence lifetime of the $^3H_4$ level was measured to be 220 $\mu$s. The stimulated emission cross-section for the $^3F_4 \rightarrow ^3H_6$ transition were determined using the reciprocity method, potential laser gain for this transition were also investigated, the gain curves implied that the tunable range is up to 200 nm.

PACS 42.70.Hj; 78.20.-e

1 Introduction

Thulium lasers are of interest as sources of light in the near infrared eye-safe region, around 1.5 $\mu$m, on the $^3H_4 \rightarrow ^3F_4$ transition, and around 1.9 $\mu$m, on the $^3F_4 \rightarrow ^3H_6$ transition. The 1.9 $\mu$m emission transition has applications in medicine and remote sensing [1], and the laser operation is very efficient due to the cross-relaxation processes between Tm$^{3+}$ ions [2]. Thulium transition at 1.5 $\mu$m is very interesting for optical communications purpose due to the third optical transmission window of the silica fibers [3]. Laser action for this transition has been realized by sensitization with Yb in YLF fibres after excitation by diode and YAG:Nd$^{3+}$ pumping [3–5]. Interest in thulium-doped crystals is motivated by progress in powerful, well-developed AlGaAs laser diodes, which are well suited for optical pumping at around 800 nm into the $^3H_4$ energy level of thulium ions [6].

The NaLa(WO$_4$)$_2$ (NLW) single crystal belongs to the tetragonal system with the space group of $I4_1/a$. It has the scheelite (CaWO$_4$) structure. The cell parameters are as follows: $a = b = 5.349$ Å, $c = 11.628$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 332.70$ Å$^3$, $Z = 2$ [7]. NLW crystals have been reported to be good host lattices for Nd$^{3+}$ and Yb$^{3+}$ ions [8–12]. This crystal has a suitable hardness and good chemical stability and is moisture free. Furthermore, as it melts congruently, large size single crystal can be easily obtained by the Czochralski (CZ) method. In this paper, crystal growth, thermal expansion coefficients of Tm$^{3+}$ doped NLW were investigated. Polarized room temperature absorption spectra were applied to Judd–Ofelt (J–O) analysis [13] and [14] to calculate spectral parameters. We also present polarized room temperature fluorescence spectra and the luminescence decay curve. The results show that this crystal may be a preferable candidate for a laser media.

2 Experimental

2.1 Crystal growth

Tm$^{3+}$-doped NLW crystal (shown in Fig. 1) was grown by the Czochralski technique. Tm$^{3+}$:NLW polycrystalline material used for single crystal growth was obtained by using the method of solid-state reaction. The initial chemicals of analytical grade Na$_2$CO$_3$, WO$_3$, and spectral grade La$_2$O$_3$, Tm$_2$O$_3$ were mixed in the molar ratio in an agate mortar and then charged into a platinum crucible. These ma-

FIGURE 1 Grown crystal of Tm$^{3+}$:NaLa(WO$_4$)$_2$ crystal
terials were heated at 900°C for 4 days and then they were placed in a $\Phi 30 \times 50 \text{ mm}^2$ platinum crucible and heated in the DJL-400 furnace. They were heated up to a temperature 50°C higher than the crystallization temperature for about 1 h so as to melt them completely and homogeneously. With the [001]-cut seed, large Tm:NLW single crystal with high optical quality was obtained. During crystal growth, the Pt rod rotated at a rate of 12–20 rpm and the pulling rate was 0.8–1.2 mm/h. When the growth process was over, the crystal was drawn out of the molten and cooled down to room temperature at a rate of 10–30°C/h. The X-ray powder diffraction pattern of the crystal matches well with the standard file of NLW.

The concentration of thulium ions in the crystal was measured to be 0.2322 wt. % by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method; the corresponding ion concentration of Tm$^{3+}$ was determined to be $5.43 \times 10^{19}$ ions/cm$^3$.

2.2 Measurements of thermal expansion

Thermal expansion coefficients of Tm$^{3+}$:NaLa(WO$_4$)$_2$ along the crystallographic axes were measured by Diatometer 402 PC in the temperature range of 150–500°C. The as-grown crystal was oriented by YX-2 X-ray Crystal Orientation Unit produced by Dandong Radiative Instrument Co., LTD. and was cut into samples along the crystallographic axes. The lengths of samples along $a$- and $c$-axes were 6.71 and 7.55 mm, respectively. The sample was kept in a fused silica sample holder and heated at a rate of 5°C/min in the air atmosphere.

2.3 Spectroscopic measurements

Room temperature polarized absorption spectra were measured in the range from 280 to 2000 nm by using Perkin–Elmer UV-VIS-NIR Spectrometer (Lambda-900). The room temperature polarized fluorescence spectra and luminescent decay curve were excited near 795 nm by using Edinburgh Instruments FLS920 spectrophotometer. The sample used for spectroscopic measurements was optically polished to flat and parallel faces, and the dimension of the sample was $5 \times 5 \times 1.51 \text{ mm}^3$ ($c \times a \times b$).

3 Analysis and discussion

3.1 Thermal expansion coefficients

The thermal expansion data of a laser crystal are important factors for its growth and applications [15, 16]. It is related to the thermal stress and thermal stable coefficient. Crystals with large anisotropic thermal expansion coefficients are easily cracked during the course of crystal growth and process due to improper temperature gradient. Under laser operating conditions, improper temperature gradient caused by light absorption of the laser crystal may disturb the laser oscillation, and can also lead to crystal cracking.

The thermal expansion coefficients form a second rank tensor [17]. For a tetragonal crystal as Tm:NLW, there are only two independent principle thermal expansion components, $\alpha_1 = \alpha_2$ and $\alpha_3$. They can be obtained by measuring the thermal expansions of the $a$- and $c$-oriented crystal samples. The average linear thermal expansion can be defined as:

$$\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T}, \quad (1)$$

where $L_0$ is the initial length of the sample at room temperature and $\Delta L$ is the change in length when the temperature changes $\Delta T$. The figure of thermal expansion ratios versus temperature was shown in Fig. 2. From this figure, no abnormality within the measuring temperature range is observed. We can calculate the thermal expansion coefficient from the slope of the linear fitting of the linear relationship between $\Delta L/L_0$ and the temperature. In this case, the linear thermal expansion coefficients for $c$-and $a$-axes are $2.49 \times 10^{-5}$, $1.23 \times 10^{-5}$ K$^{-1}$, respectively. The anisotropic positive thermal expansion coefficients suggest that $c$-axis orientation seed, less temperature fluctuation, proper slow annealing program are crucial in the crystal growth procedure. Thermal expansion coefficients obtained in this work are comparable to those of other scheelite crystals, such as NaGd(MoO$_4$)$_2$ and SrWO$_4$ crystals, as shown in Table 1.

3.2 Absorption data and the Judd–Ofelt analysis

NLW crystal belongs to anisotropy uniaxial crystals. Figure 3 shows the polarized absorption spectra measured at room temperature with light polarized parallel ($\pi$ spectrum) and perpendicular ($\sigma$ spectrum) to the optical axis of NLW:Tm$^{3+}$ crystal. The spectra consist of six resolved bands associated with the transitions from the $^3H_6$ ground state to the $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3 + ^3F_2$, $^1G_4$ and $^1D_2$ excited states. The absorption system in the 770–820 nm range is important for laser diode pumping. For the $\pi$ polarization spectrum, the most intense absorption occurs at 794 nm with a 11 nm full width at half maximum (FWHM), while