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Growth and Spectral Properties of Nd³⁺:NaLa(WO₄)₂ Crystals

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Nd³⁺:NaLa(WO₄)₂ crystals with a dimension up to 7 mm were grown from a high temperature solution using a double-crucible method. Scanning electron microscopy observations of the crystals showed that there were no small cracks on the surface of the crystals although they underwent two phase transitions when cooling down from high temperatures. X-ray diffraction studies indicated that the as-obtained product is pure low-temperature tetragonal Nd³⁺:NaLa(WO₄)₂. The absorption and fluorescence spectra for Nd³⁺:NaLa(WO₄)₂ were measured at room temperature. The absorption band at 804 nm has a wide full-width half maximum of 23 nm whose origin is discussed. The absorption and emission cross sections were calculated to be 7.24×10^{-20} cm² at 804 nm and 6.54×10^{-20} cm² at 1057 nm, respectively.

Key words: Crystal growth, Double-crucible method, Tungstates, Optical properties

I. INTRODUCTION

Diode pumped solid-state lasers have attracted increasing attention in recent years due to the rapid development of high power diode lasers. There are several Nd³⁺ doped crystals in common use as effective laser media, such as Nd:YAG and Nd:YVO₄ [1,2]. However, the output power of these lasers is quite sensitive to the pump wavelength owing to the narrow absorption band near 808 nm. Therefore, it is important to explore more efficient crystal materials with a wide absorption band for diode pumped solid-state lasers. Alkali metal-rare earth-double tungstates with a formula of MRe(WO₄)₂ have been reported to be a promising host material for solid-state lasers [3-18]. Highly efficient laser operations for the Nd³⁺ doped KLa(WO₄)₂ [19], NaY(WO₄)₂ [20], KLu(WO₄)₂ [21], Nd:KGd(WO₄)₂ [22,23] and LiLa(WO₄)₂ crystals [24] have already been demonstrated.

NaLa(WO₄)₂, which is one of the alkali metal-rare earth-double tungstates, belongs to the tetragonal system at room temperature with cell parameters: $a=0.5349$ and $c=1.162$ nm, $z=4$. There are two phase transitions for NaLa(WO₄)₂ at about 390 and 730 °C, respectively [25], which makes it difficult to grow large single crystals from high temperatures.

Several groups have reported the growth of NaLa(WO₄)₂ crystals using different techniques. Oishi *et al.* grew NaLa(WO₄)₂ crystals from high-temperature solutions [26] but the quality of the crystals was poor due to a fast growth rate and quick evaporation of the flux. NaLa(WO₄)₂ crystals were also grown via a hydrothermal method [25], but the

growth conditions, such as the temperature, the pH, and the pressure, were very strict. In this study, crack-free Nd³⁺:NaLa(WO₄)₂ crystals were grown from a high-temperature solution using a double-crucible method to prevent evaporation of the flux during crystal growth. The absorption and emission spectra for Nd³⁺:NaLa(WO₄)₂ were measured and some spectral parameters were calculated.

II. EXPERIMENTS

The initial materials used in this work were La₂O₃ (99.9%), Nd₂O₃ (99.9%), WO₃ (99%), Na₂CO₃ (99%) and Na₂WO₄ (99%). Na₂WO₄ was selected as flux for crystal growth. An appropriate amount (about 30 g) of the raw materials was weighed according to the molar ratio of La₂O₃:Nd₂O₃:WO₃:Na₂CO₃=4.75:0.25:65:30 and well mixed in an agate mortar. The mixture was preheated at 850 °C for 24 h and then ground thoroughly to make the composition homogenous.

Crystal growth was performed using a double-crucible method to prevent evaporation of the flux during growth. Figure 1 presents the experimental setup schematically. The pre-prepared mixture was put into the inner Al₂O₃ crucible which was located in the outer crucible containing about 40 g of Na₂WO₄. To avoid the evaporation of Na₂WO₄ at high temperatures efficiently, the inner crucible was covered with an alumina lid and another alumina crucible as shown in Fig.1. The double-crucible set was then put into a vertical furnace and a programmable temperature controller (AI-708P) was used to control the temperature. At first, the temperature was kept at 1150 °C for 4 h for homogenization of the molten salt and the flux and then slowly decreased to 850 °C in 10 days followed by a descending rate of 10 °C/h. The as-grown crystals were separated from the solidified flux with hot water.

X-ray diffraction (XRD) of the as-obtained prod-

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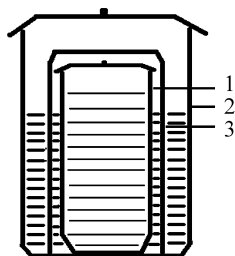


FIG. 1 Schematic double-crucible setup. 1: Inner Al_2O_3 crucible for crystal growth. 2: Outer Al_2O_3 crucible. 3: Middle Al_2O_3 crucible as a cover.

uct was carried out using an X-ray diffractometer (Rigaku, D/max- γ A) with Cu $K\alpha$ radiation in the range of $10^\circ \leq 2\theta \leq 70^\circ$. A scanning electron microscope (SEM, H-850) was used to investigate the morphology of the $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals. Absorption spectrum for $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ in the wavelength range from 300 nm to 900 nm was measured at room temperature using a spectrophotometer (UV-365). An X-ray fluorescence spectrometer (XRF-1800) was also employed to estimate the Nd^{3+} concentration in the $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals. Photoluminescence (PL) spectrum from 850 nm to 1700 nm for $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ was recorded at room temperature on a steady-state/lifetime fluorescence spectrometer (FLUOROLOG-3-TAU) under excitation at 804 nm.

III. RESULTS AND DISCUSSION

Figure 2(a) is a typical photograph of the as-obtained $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals with well developed and regular shapes. A transparent single $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystal with a size of about 7 mm \times 4 mm \times 4 mm is shown in Fig.2(b).

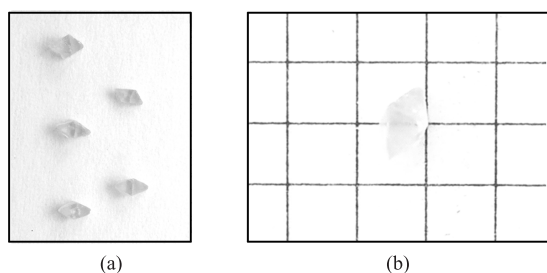


FIG. 2 Photographs of $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals. (a) $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals. (b) A single $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystal.

Figure 3 presents an SEM image of a $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystal. A smooth surface with some growth strips on it can be seen in Fig.3, and no small cracks are observed, which indicates that the crystal is crack-free although it underwent two phase transitions when cooling down from high tempera-

tures. A fast cooling (100 $^\circ\text{C}/\text{min}$) experiment of the $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals after growth was also carried out to investigate the effect of the phase transitions on the quality of the crystals. The SEM observations show that no small cracks are found on the surface of the crystal, which means that the phase transitions have little effect on the quality of the crystals. In addition, the $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals observed under a microscope look transparent and clear. Consequently, the $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystals can be grown from high-temperature solutions.

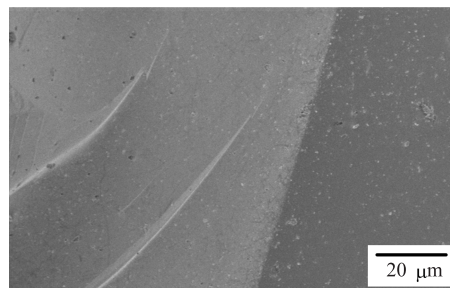


FIG. 3 The SEM image of a single $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ crystal.

The XRD pattern for the as-obtained product is given in Fig.4. The diffraction peaks in Fig.4 can be indexed according to the tetragonal $\text{NaLa}(\text{WO}_4)_2$ with lattice constants of $a=0.534$ and $c=1.161$ nm, which is quite consistent with the data in JCPDS 79-1118. No significant diffraction peaks coming from the high-temperature phase of $\text{NaLa}(\text{WO}_4)_2$ can be identified.

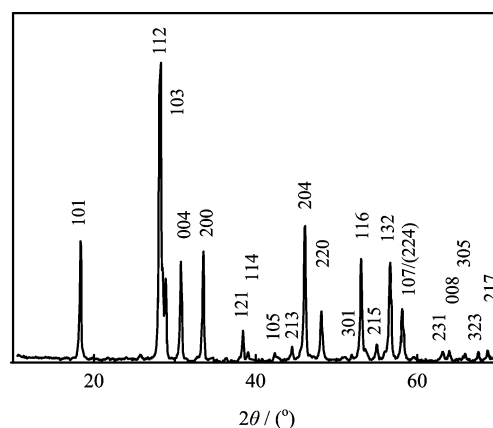


FIG. 4 XRD pattern of as-obtained $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$.

Figure 5 displays the absorption spectrum for $\text{Nd}^{3+}:\text{NaLa}(\text{WO}_4)_2$ at room temperature. It can be seen from Fig.5 that strong absorption bands are located at 356, 528, 585, 751, 804 and 872 nm, respectively, which originate from the $4f^n-4f^n$ electron transition in the Nd^{3+} . The most interesting for us is the broad absorption band at 804 nm with a full-width half maximum (FWHM) of 23 nm which is wider

than that for Nd³⁺:KY(WO₄)₂ (only 4 nm) [27] and Nd³⁺:LiLa(WO₄)₂ (18 nm) [24] at about 808 nm. The broad absorption band at 804 nm can be attributed to the crystal structure of Nd³⁺:NaLa(WO₄)₂. In contrast to the ordered configuration of K⁺ and R³⁺ in KR(WO₄)₂, the Na⁺ and R³⁺ including the active D³⁺ in the tetragonal Nd³⁺:NaR(WO₄)₂ are randomly distributed [28]. Therefore, the localized crystal fields around the active D³⁺ are different from each other resulting in the band-width of the electronic transition for the rare earth ions in NaR(WO₄)₂ being broader than that in KR(WO₄)₂.

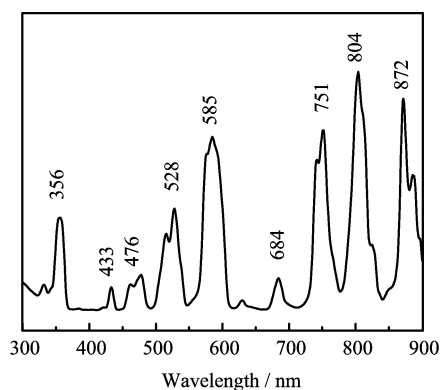


FIG. 5 Absorption spectrum of Nd³⁺:NaLa(WO₄)₂ at the room temperature.

The absorption coefficient of the Nd³⁺:NaLa(WO₄)₂ crystal at about 800 nm was measured to be 11 cm⁻¹ using a diode laser. In order to calculate the absorption cross section of the Nd³⁺:NaLa(WO₄)₂ crystal, the Nd³⁺ concentration in the Nd³⁺:NaLa(WO₄)₂ crystal was determined to be 1.52×10²⁰ cm⁻³ from XRF measurement, which indicates that the Nd³⁺ concentration in the Nd³⁺:NaLa(WO₄)₂ crystal is lower than the original doping concentration. Thus, the segregation coefficient of Nd³⁺ in NaNd_xLa_{1-x}(WO₄)₂ is also estimated to be 0.502. Therefore, the absorption cross section at 804 nm can be determined to be $\sigma_a = 7.24 \times 10^{-20}$ cm² using the following expression:

$$\sigma_a = \alpha / N_0 \quad (1)$$

where α is the absorption coefficient at 804 nm and N_0 is the Nd³⁺ concentration in Nd³⁺:NaLa(WO₄)₂.

Figure 6 presents the PL spectrum for Nd³⁺:NaLa(WO₄)₂ excited at a wavelength of 804 nm at room temperature. There are three emission bands in Fig.6 located at 860-922, 1034-1100 and 1314-1400 nm, corresponding to the electron transition from the ⁴F_{3/2} state to the ⁴I_{9/2}, ⁴I_{11/2} and ⁴I_{13/2} state in Nd³⁺, respectively. It can be seen from Fig.6 that the intensity of the PL band at 1057 nm is much higher than that of the others, which means the emission band has a high branch ratio. The branch ratio β at 1057 nm is calcu-

lated to be 0.72 by the following expression:

$$\beta = \frac{\int_{1034}^{1100} I(\lambda) d\lambda}{\int_0^{\infty} I(\lambda) d\lambda} \quad (2)$$

The emission cross section σ_{em} at 1057 nm is also obtained from the following formula:

$$\sigma_{em} = \beta \frac{\lambda^2}{4\pi^2 \tau_f n^2 \Delta\nu} \quad (3)$$

where λ is the emission wavelength, τ_f is the fluorescence lifetime which has been determined to be 182 μ s, $\Delta\nu$ is the half-band frequency, and n is the refractive index which is roughly 2.0. The calculated emission cross section σ_{em} at 1057 nm is 6.54×10⁻²⁰ cm². Table I lists some spectral parameters of several Nd³⁺ doped tungstate crystals. It can be seen from Table I that the FWHM of Nd³⁺:NaLa(WO₄)₂ is the broadest among them, and the luminescence efficiency at about 1060 nm for Nd³⁺:NaLa(WO₄)₂ is higher than that for Nd³⁺:KY(WO₄)₂ and Nd³⁺:KLa(WO₄)₂.

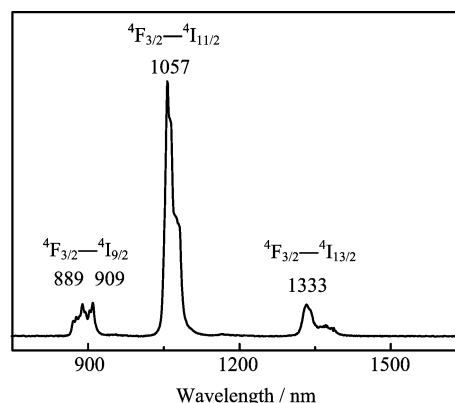


FIG. 6 PL spectrum of Nd³⁺:NaLa(WO₄)₂ excited at 804 nm.

IV. CONCLUSION

Crack-free Nd³⁺:NaLa(WO₄)₂ crystals with a dimension of up to 7 mm were grown from a high-temperature solution using a double-crucible method to avoid evaporation of the flux. No cracked sections on the surface of the crystals were found, which indicates that the phase transitions have little effect on the quality of the crystals. Therefore, Nd³⁺:NaLa(WO₄)₂ crystals can be grown from high temperature solutions. The broad absorption band at 804 nm is attributed to the random distribution of Na⁺ and R³⁺ in the tetragonal Nd³⁺:NaLa(WO₄)₂. The excellent spectral properties, e.g. the broad absorption band at 804 nm, the strong emission band at 1057 nm, and the large

TABLE I Spectral parameters of several Nd³⁺-doped tungstate crystals

Crystal	FWHM(~ 810 nm)	$\sigma_a(\sim 810$ nm)/ 10^{-20} cm ²	τ_f/μ s	$\sigma_{em}(\sim 1060$ nm)/ 10^{-19} cm ²	Ref.
Nd ³⁺ :NaLa(WO ₄) ₂	23	7.24	182	0.654	This work
Nd ³⁺ :KLa(WO ₄) ₂	12	7.6	157	0.50	[19]
Nd ³⁺ :KGd(WO ₄) ₂	12	—	120	3.50	[29-31]
Nd ³⁺ :KLu(WO ₄) ₂	3	7.93	79	2.41	[21]
Nd ³⁺ :KY(WO ₄) ₂	4	5.8	154	0.54	[27]

emission cross section at room temperature, make the Nd³⁺:NaLa(WO₄)₂ crystal a promising material for diode-pumped lasers.

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