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Optical properties of $Nd:YbVO_4$ crystal

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Optical characteristics of a new laser crystal $Nd:YbVO_4$ were studied. The optical parameters of *a*-cut and *c*-cut $Nd:YbVO_4$ crystals were calculated by the Judd–Ofelt theory. The absorption cross-section of *a*-cut $Nd:YbVO_4$ crystal was 5.34×10^{-20} cm^2 at 808 nm, while it was 4.20×10^{-18} cm^2 of *c*-cut $Nd:YbVO_4$ crystal. The properties of energy transfer between Nd and Yb ions in $Nd:YbVO_4$ crystal were discussed. In the fluorescence spectra, a peak at 472 nm appeared, which resulted from the coupling interaction between two Yb ions.

Keywords: $Nd:YbVO_4$ crystal, Judd–Ofelt theory, energy transfer.

1. Introduction

Diode-pumped all solid-state lasers have been widely used in many areas, such as industry processing, medical treatment, military affairs and others. The development of solid-state lasers requires new and improved laser materials (higher absorption and emission cross-sections, high thermal conductivity and so on). Therefore, it is important to explore new laser materials.

Among laser crystals, Nd-doped crystals are the most frequently used to produce 0.9, 1.06 and 1.34 μm wavelength lasers. Nd-doped crystals with nonlinear crystals (for example, KTP) can produce red, green or blue lights with high conversion efficiencies and beam qualities. Now, $Nd:YbVO_4$ crystal, a new member of Nd-doped orthovanadate family, is studied by us. Yb ions are usually used as active ions to obtain 1 μm emission, but here they are used as lattice structure ions. Yb^{3+} only has two states, $^2F_{7/2}$ and $^2F_{5/2}$. Outer electrons of Yb^{3+} cannot well shield the electrons of *f* shell. Therefore, Yb^{3+} can easily interact with other nearby Yb and Nd ions. Energy transfers between Nd and Yb ions were found in our experiment. So the optical properties of $Nd:YbVO_4$ crystal are different from other Nd-doped crystals such as $Nd:YVO_4$, $Nd:GdVO_4$ [1, 2]. Nonradiative energy transfer from trivalent Nd to trivalent Yb is well-known in glasses and crystals already [3–6]. Now, energy transfer processes from

Nd to Yb ions still remain as an active area of investigation because they play a central role in designing laser and optoelectronic materials.

In this paper, the optical characteristics of Nd:$YbVO_4$ crystal were investigated. Absorption and emission cross-sections of Nd ions were calculated. Energy transfers between Nd and Yb ions were also studied.

2. Experimental set up

The Nd:$YbVO_4$ crystal has zircon structure belonging to the point group *D4h* and to the space group *I41/amd*. The Nd:$YbVO_4$ crystals were grown by the Czochralski method. The growth atmosphere was O_2 plus 2% of N_2. The pulling rate was from 1 to 2 mm/h. The crystal was rotated at a rate of 10–20 rpm during its growth. After growing, it was cooled at a speed of 30–50°C/h. The specific heat of Nd:$YbVO_4$ crystal was 0.49 J/g·K. The thermal conductivity along *a* axis and *c* axis was 3.9 and 5.1 W/mK, respectively. The thermal expansion coefficients along three directions were $\alpha_a = 2.5\times10^{-6}$ K^{-1}, $\alpha_b = 2.6\times10^{-6}$ K^{-1}, $\alpha_c = 8.7\times10^{-6}$ K^{-1} [7], respectively. The concentration of Nd ions is 1 at.% ($Nd_{0.1}$:$Yb_{0.99}VO_4$). The *a*-cut and *c*-cut Nd:$YbVO_4$ crystals with dimensions of 5×5×2 mm^3 were investigated. The absorption spectra were measured by using a Jasco V570 UV/VIS/NIR spectrophotometer. The fluorescence spectra were measured by TRIAX 550 and a fiber optical spectrometer (AvaSpec-3648).

3. Discussions and results

The absorption spectra of *a*-cut and *c*-cut Nd:$YbVO_4$ crystals are shown in Figs. 1**a** and 1**b**, respectively.

The optical parameters of *a*-cut and *c*-cut Nd:$YbVO_4$ crystals such as absorption and emission cross-sections, fluorescence branching ratio were calculated by Judd–Ofelt theory:

$$\int K(\lambda)\mathrm{d}\lambda = \frac{D(\lambda)\mathrm{d}\lambda}{lge \cdot L} \tag{1}$$

$$\int K(\lambda)\mathrm{d}\lambda = N_0 \frac{8\pi^3 e^2 \overline{\lambda}}{3hc} \frac{(n^2+2)^2}{9n} \frac{1}{2J+1} S_{\mathrm{exp}}(J \rightarrow J') \tag{2}$$

$$S_{\mathrm{cal}}(J'' \rightarrow J') = \sum_{t=2,4,6} \Omega_t \left| \langle 4f^n \psi'' J'' \| U^{(t)} \| 4f^n \psi' J' \rangle \right|^2 \tag{3}$$

where $K(\lambda)\mathrm{d}(\lambda)$ is the integrated absorption coefficient, $D(\lambda)\mathrm{d}(\lambda)$ – the integrated absorbance, equal to the area under the absorption curve, S_{exp} and S_{cal} – the transition-line intensity for the absorption and emission, respectively, $(J \rightarrow J')$ – the transition between the ground state J and final state J', and $(J'' \rightarrow J')$ – between the excited

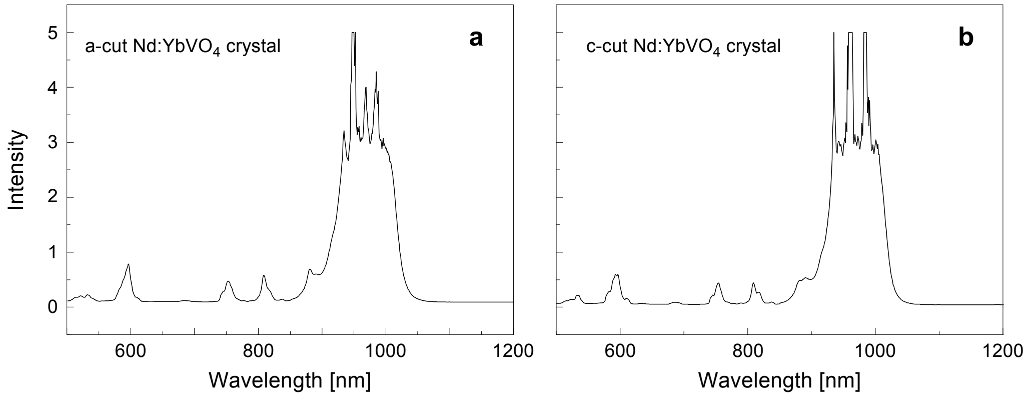

Fig. 1. Absorption spectrum of *a*-cut (**a**) and *c*-cut (**b**) Nd:YbVO$_4$ crystal.

level J'' and terminal level J'; L – the length of the crystal, N_0 – the average density of Nd^{3+} in the lattice structure, e – the electron charge, n – the refractive index of the crystal, h – Planck's constant, c – the speed of light, Ω_t ($t = 2, 4, 6$) – the three phenomenological intensity parameters arising from the static crystal field, $\langle 4f^n \psi'' J'' \| U^{(t)} \| 4f^n \psi' J' \rangle$ the reduced matrix elements.

The transition probability for the spontaneous emission per unit time $A(J'' \to J')$, and the absorption cross-sections of Nd^{3+} ions $\sigma_a(\lambda)$ were calculated by using the following equations:

$$A(J'' \to J') = \frac{64\pi^4 e^2}{3h\bar{\lambda}^3} \frac{n(n^2+2)^2}{9} \frac{1}{2J''+1} S_{\text{cal}}(J'' \to J') \tag{4}$$

$$\sigma_a(\lambda) = \frac{D(\lambda)}{N_0 L l g e} \tag{5}$$

The results were listed in the following tables. Tables 1 and 2 give the absorption and luminescence parameters of *a*-cut Nd:YbVO$_4$ crystal.

T a b l e 1. Absorption parameters of *a*-cut Nd:YbVO$_4$ crystal.

Transition final state $4f''\psi'j'$	Central wavelength $\bar{\lambda}$ [nm]	$S_{\text{exp}}(J \to J')$ [$\times 10^{-20}$ cm^2]	$\sigma_{\text{abs}}(\lambda)$ [$\times 10^{-20}$ cm^2]
$^2P_{1/2}$	436	0.159	1.38
$^4G_{11/2}$, $^2P_{3/2}$, $^2D_{3/2}$, $^2G_{9/2}$	475	0.630	1.36
$^4G_{9/2}$, $^4G_{7/2}$	532	2.085	2.10
$^4G_{5/2}$	596	8.406	7.24
$^4S_{3/2}$, $^4F_{7/2}$	753	3.400	4.32
$^2H_{9/2}$, $^2F_{5/2}$	808	3.165	5.34

Table 2. Luminescence parameters of *a*-cut $Nd:YbVO_4$ crystal.

Final state	Central wavelength $\bar{\lambda}$ [nm]	$S_{cal}(J \to J')$ [$\times 10^{-20}$ cm^2]	$A(J'' \to J')$ [s^{-1}]	τ_{rad} [μs]	$\beta_{J''J'}$ [%]	$\sum(J'' \to J')$ [$\times 10^{-18}$ cm^{-2}]
$^4I_{9/2}$	880	1.015	2027.30	202.0	40.95	5.39
$^4I_{11/2}$	1060	2.156	2423.67	202.0	48.95	9.43
$^4I_{13/2}$	1350	0.870	477.18	202.0	9.65	2.99
$^4I_{15/2}$	1880	0.115	22.42	202.0	0.45	0.28

The three phenomenological parameters Ω_2, Ω_4, Ω_6 are 7.51×10^{-20}, 2.93×10^{-20}, 3.53×10^{-20} cm^2, respectively. The root mean square (rms) error is 7.65×10^{-21} cm^2. Therefore, it is suitable for $Nd:YbVO_4$ crystal using the Judd–Ofelt theory to calculate the optical parameters.

As other Nd-doped crystals, the highest absorption cross-section of $Nd:YbVO_4$ is obtained at 593 nm of 7.24×10^{-20} cm^2. The second high absorption cross-section is at 809 nm wavelength, at which the absorption cross-section is 5.34×10^{-20} cm^2. Compared with the $Nd:LuVO_4$ crystal, which we have done before, the absorption cross--sections of $Nd:YbVO_4$ crystal are lower than those of $Nd:LuVO_4$ crystal [8].

The fluorescence branching ratio $\beta_{J''J'}$ at 1060 nm is 48.95, which is the highest in all emission lights. However, due to a strong wide absorption band around 950 nm of Yb ions, it is difficult to realize laser operation at 1060 nm. The fluorescence branching ratio $\beta_{J''J'}$ at 1350 nm is 9.65, which is almost the same as other usually used Nd-doped orthovanadate [1, 2]. The integral emission cross-section at 1.35 μm is 2.99×10^{-18} cm^{-2}. The emission life τ_{rad} of $^4F_{3/2}$ is calculated to be 202 μs, which is obviously higher than that of $Nd:GdVO_4$ and $Nd:LuVO_4$ crystals [2, 8]. Therefore, it is consistent with the law that the lower the emission cross-section is, the higher the emission life is.

Tables 3 and 4 give the optical parameters of *c*-cut $Nd:YbVO_4$ crystal.

Table 3. Absorption parameters of *c*-cut $Nd:YbVO_4$ crystal.

Transition final state $4f''\psi'j'$	Central wavelength $\bar{\lambda}$ [nm]	$S_{exp}(J \to J')$ [$\times 10^{-20}$ cm^2]	$\sigma_{abs}(\lambda)$ [$\times 10^{-20}$ cm^2]
$^2P_{1/2}$	436	0.052	0.88
$^4G_{11/2}$, $^2P_{3/2}$, $^2D_{3/2}$, $^2G_{9/2}$	466	0.458	0.85
$^4G_{9/2}$, $^4G_{7/2}$	535	2.103	2.04
$^4G_{5/2}$	593	7.978	5.51
$^4S_{3/2}$, $^4F_{7/2}$	754	3.042	4.10
$^2H_{9/2}$, $^2F_{5/2}$	809	2.509	4.20

Table 4. Luminescence parameters of *c*-cut Nd:YbVO$_4$ crystal.

Final state	Central wavelength $\bar{\lambda}$ [nm]	$S_{cal}(J \to J')$ [$\times 10^{-20}$ cm^2]	$A(J'' \to J')$ [s^{-1}]	τ_{rad} [μs]	$\beta_{J''J'}$ [%]	$\sum(J'' \to J')$ [$\times 10^{-18}$ cm^{-2}]
$^4I_{9/2}$	880	0.870	1738.20	235.4	40.92	4.62
$^4I_{11/2}$	1060	1.851	2080.84	235.4	48.98	8.81
$^4I_{13/2}$	1350	0.748	409.91	235.4	9.65	2.57
$^4I_{15/2}$	1880	0.099	19.261	235.4	0.45	0.24

The three phenomenological parameters of Ω_2, Ω_4, Ω_6 are 7.32×10^{-20}, 3.41×10^{-20}, 4.11×10^{-20} cm^2, respectively, and the rms error is 8.88×10^{-21} cm^2.

The absorption cross-sections of *c*-cut Nd:YbVO$_4$ crystal are correspondingly lower than those of *a*-cut Nd:YbVO$_4$ crystal. The absorption cross-section at 809 nm of *c*-cut Nd:YbVO$_4$ crystal is 4.20×10^{-18} cm^2. The emission cross-section at 1.35 μm is 2.57×10^{-18} cm^{-2}. The emission life of $^4F_{3/2}$ is 235 μs, lower than that of *a*-cut Nd:YbVO$_4$ crystal.

Using the following equation:

$$a = \ln 10^A / L \tag{6}$$

(where α is the absorption coefficient of the crystal, L is the length of the crystal, A is the absorption intensity of the crystal), the absorption coefficients of Nd:YbVO$_4$ crystal can be calculated. The absorption coefficients of *a*-cut and *c*-cut Nd:YbVO$_4$ crystals are 6.99 and 6.73 cm^{-1}, respectively, at 809 nm.

Otherwise, from Fig. 1, it can be seen that the strongest absorption takes place at about 950 nm with a wide absorption band. The full width at half maximum (FWHM) is 100 nm or so. This absorption band is attributed to Yb ions' absorption, which is

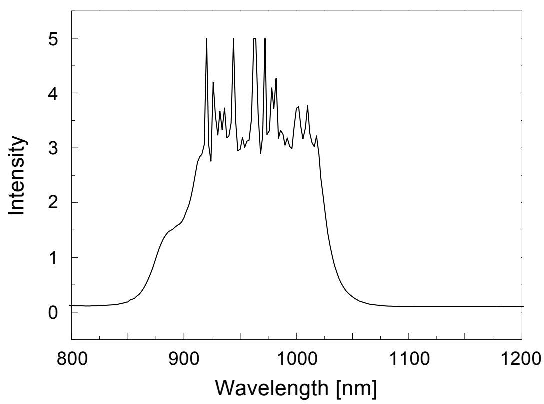

Fig. 2. Absorption spectrum of a pure YbVO$_4$ crystal.

different from other Nd-doped crystals, such as Nd:YVO_4 crystal. Absorption spectra of a pure $YbVO_4$ crystal were measured in order to compare with those of Nd:$YbVO_4$ crystal, which is shown in Fig. 2. The absorption intensity at 950 nm is almost the same for the two crystals, which indicates that all the Yb ions in Nd:$YbVO_4$ crystal take part in the absorption activity. The Yb ions here are not only as structural ions but also as active ions. Therefore, the characteristics of Yb ions are not the same as other rare earth ions such as Y and Gd ions.

Then the Nd:$YbVO_4$ crystal was pumped by a 808 nm laser diode. The spectrum is shown in Fig. 3 measured by AvaSpec-3648. The emission of 1020 nm was found. Figure 4 shows the energy levels of Nd and Yb ions. Nd ions absorb the 808 nm wavelength light and transit from the ground state $^4I_{9/2}$ to the excited state $^4F_{5/2}$. After a fast nonradiative relaxation to the $^4F_{3/2}$ state, the excitation energy is efficiently transferred to the $^2F_{5/2}$ state of Yb ions. Then the emission of 1020 nm wavelength of Yb ions from $^2F_{5/2}$ state to $^2F_{7/2}$ state is found, which can be seen from Fig. 3. This process is predicted as the dipole–dipole interaction [9]. At this process, phonons are required to fill the energy gap between the Nd^{3+} emission and Yb^{3+} absorption bands. The frequency

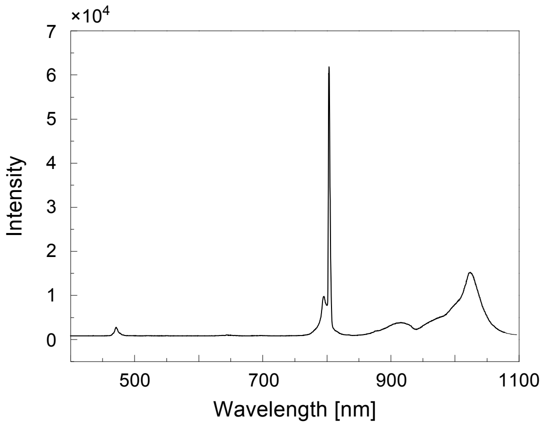

Fig. 3. The fluorescence spectrum of Nd:$YbVO_4$ crystal stimulated by 808 nm light.

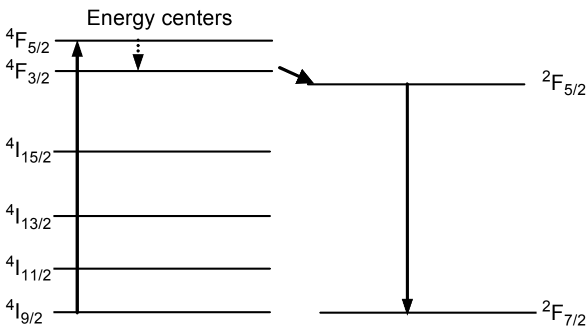

Fig. 4. The energy levels of Nd and Yb ions.

shift is about 1160 cm^{-1}. Therefore, the energy transfer between Nd and Yb ions takes place with emissions of one phonon at a frequency of 1160 cm^{-1} or multiple phonons at 580 or 387 cm^{-1}.

In addition, it was found out that the blue light appeared at a wavelength of 472 nm in the fluorescence spectrum. When the energy transferred from $^4F_{3/2}$ state of Nd ions to $^2F_{5/2}$ state of Yb ions, cooperated luminescence took place through coupling interactions of two excited state of Yb ions. The process can be written as

$$Y_b^*(^2F_{5/2}) + Y_b^*(^2F_{5/2}) = 2Y_b(^2F_{7/2}) + h\nu \tag{7}$$

In this process, the Yb ions of $4f^{13}$ electrons have strong coupling interaction with adjacent Yb ions and form the coupling electron pairs by Kulun interactions. Two Yb ions at the excited state annihilated, resulting in the cooperated emission. The two ions emit at the same time and a visible photon at 472 nm is achieved. This emission process involved two Yb photons so that the energy of the visible photon is two times of single Yb ion emission.

At the same time, the damage threshold of Nd:YVO$_4$ crystal was measured when it was pumped by a continuous 808 nm laser diode, and the damage threshold was found to be approximately 1.67 kw/cm^2.

Figure 5 gives the luminescence spectrum stimulated by 940 nm light measured by TRIAX 550. The emission peak of Yb ions is at 1029 nm. There is a small peak at 1065 nm, pointed by the arrow. The emission of 1065 nm wavelength is the transition from $^4F_{3/2}$ state to $^4I_{11/2}$ state of Nd ions. The appearance of 1065 nm wavelength in the luminescence spectrum indicated that there was an energy transfer from Yb ions to Nd ions. The energy transferred from $^2F_{5/2}$ state of Yb ions to $^4F_{3/2}$ state of Nd ions. The energy of Yb ions at $^2F_{5/2}$ state is lower than that of Nd ions at $^4F_{3/2}$ state. Therefore, in this process, one or more phonons need to be absorbed to fill the energy gap between Yb ions and Nd ions. So the energy transfer rate from Yb ions to Nd ions is low, and the intensity of the peak at 1065 nm is weak.

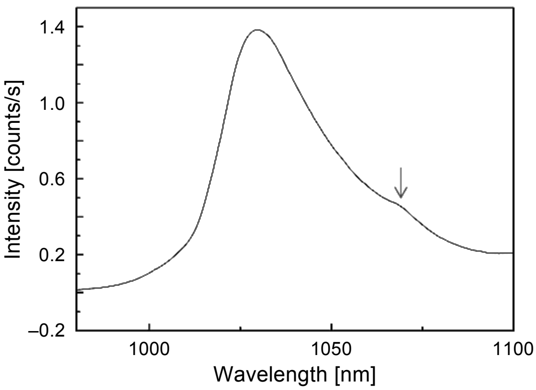

Fig. 5. The luminescence spectrum of Nd:YbVO$_4$ crystal stimulated by 940 nm light.

4. Conclusions

Optical characteristics of Nd:$YbVO_4$ crystal were investigated. The absorption and emission parameters were calculated by the Judd–Ofelt theory. The absorption and emission cross-sections of *a*-cut Nd:$YbVO_4$ crystal are higher than those of *c*-cut Nd:$YbVO_4$ crystal as usual Nd-doped orthovanadate crystals. The integral emission cross-section at 1.35 μm is 2.99×10^{-18} and 2.57×10^{-18} cm^{-2}, respectively for *a*-cut and *c*-cut Nd:$YbVO_4$ crystal. The two processes of Nd $\rightarrow$ Yb and Yb $\rightarrow$ Nd energy transfer were verified. The energy transfer from Nd ions to Yb ions can be used to create the new channels of Yb lasers by doping Nd ions. The laser properties of Nd:$YbVO_4$ crystal at 1.35 μm will be further studied.

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