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The spectra and sensitisation of laser self-frequency-doubling $Nd_xY_{1-x}Al_3(BO_3)_4$ crystal

Heng-fu Pan, Ming-guo Liu, Jing Xue and Bao-sheng Lu
Institute of Crystal Materials, Shandong University, Jinan, People's Republic of China

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Abstract. This paper reports on the absorption and luminescence spectra of a laser non-linear self-frequency-doubling $Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB) crystal at room temperature. Following the Judd–Ofelt theory, we have obtained the oscillator strength for seven bands and three intensity parameters Ω_2, Ω_4, Ω_6. The radiative lifetime τ of the metastable state $^4F_{3/2}$ and a series of laser coefficients of $^4F_{3/2} \rightarrow {}^4I_{J/2}$ transitions are also calculated. The primary results on the Cr–Nd sensitisation effect on Nd : Cr : YAB crystals are also reported.

1. Introduction

Recently, considerable attention has been paid to investigation of the laser self-frequency-doubling properties in neodymium yttrium aluminium tetraborate, $Nd_xY_{1-x}Al_3(BO_3)_4$ (NYAB), crystal [1, 2]. It has been found that NYAB crystal can realise laser self-frequency-doubling at 1.06 μm [3]. Because of its high Nd^{3+} ion concentration, large non-linear coefficient and stable physical and chemical properties, this crystal is expected to be an ideal multifunctional material for miniature lasers. Our results, based on calculations and measurements, suggest that the NYAB crystal will have many applications in a variety of fields.

2. Theory

We have measured the oscillator strength at room temperature according to the Kravetz formula [4]

$$f = 4.318 \times 10^{-9} \int \varepsilon(\sigma)\, \mathrm{d}\sigma \tag{1}$$

here $\varepsilon(\sigma)$ is the molar absorptivity and σ is the wavenumber.

In 1962, Judd [5] and Ofelt [6] (JO) presented a theory of rare earth ion spectra, providing quantitative calculations. According to JO theory, the electric dipole transition oscillator strength can be written as

$$f = \frac{8\pi^2 mc\sigma}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda(2,4,6)} \Omega_\lambda |\langle 4f^N(SL)J \| U^{(\lambda)} \| 4f^N(S'L')J' \rangle|^2. \tag{2}$$

Here, σ is the wavenumber, n is the refractive index and $\langle \| u^{(\lambda)} \| \rangle$ is the reduced matrix element of the unit tensor.

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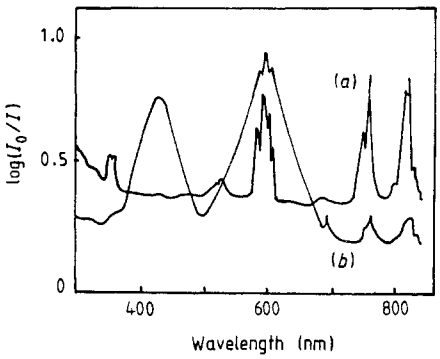

Figure 1. The absorption coefficient, $\log(I_0/I)$, of Nd:YAB and Cr:Nd:YAB at room temperature: (*a*) Nd:YAB (10 at.% Nd) (*b*) Cr:Nd:YAB (0.6 at.% Cr; 10 at.% Nd).

The data listed in [4] show that the reduced matrix element of the unit tensor is only related to the free ion parameters. These values do not change with the environment in which the free ions exist. We calculated related parameters in terms of the matrix element given in [4].

We now calculate the spontaneous radiative coefficient A, radiative lifetime τ, luminescence branch ratio β_c and integrating emitting cross section Σ.

(i) The spontaneous radiative coefficient A:

$$A[(SL)J, (S'L')J'] = (8\pi^2 e^2 n^2 \sigma^2/mc)f \tag{3}$$

where f is the emitting oscillator strength, from $|4f(SL)J\rangle$ to $|4f(S'L')J'\rangle$.

(ii) The radiative lifetime τ:

$$\tau = \left(\sum_{S'L'J'} A[(SL)J, (S'L')J']\right)^{-1}. \tag{4}$$

(iii) The luminescence branch ratio β_c:

$$\beta_c = A[(SL)]J, (S'L')J'] \Big/ \sum_{S'L'J'} A[(SL)J, (S'L')J']. \tag{5}$$

(iv) The integrating emitting cross section Σ:

$$\Sigma[(SL)J, (S'L')J'] = (1/8\pi^2 n^2 c\sigma^2)A[(SL)J,(S'L')J']. \tag{6}$$

3. The spectra of the NYAB crystal and the calculations

The absorption spectrum of the NYAB crystal (10 at.% Nd) in the type I phase matching direction is shown in figure 1(*a*). We have measured the experimental values by using equation (1), and obtained the three strength parameters in equation (2) using the least squares method. The oscillator strengths have also been calculated, and the results are

Table 1. The oscillator strength and intensity parameters in the laser self-frequency-doubling direction.

Transition	Wavenumber (cm^{-1})	$f_{exp} \times 10^6$	$f_{cal} \times 10^6$
$^4I_{9/2} \rightarrow {}^4F_{5/2}$ $^2H_{9/2}$	12 390	5.22	4.85
$\rightarrow {}^4F_{7/2}$ $^4S_{3/2}$	13 351	4.98	5.16
$\rightarrow {}^4F_{9/2}$	14 760	0.304	0.404
$\rightarrow {}^4G_{5/2}$ $^2G_{7/2}$	17 033	9.99	9.96
$\rightarrow {}^2K_{13/2}$ $^4G_{7/2}$ $^4G_{9/2}$ $^2K_{15/2}$	18 691	3.13	3.46
$\rightarrow {}^2G_{9/2}$ $(^2D, {}^2P)_{3/2}$ $^4G_{11/2}$	21 039	0.841	0.608
$\rightarrow {}^2P_{1/2}$	23 140	0.296	0.355

RMS = 3.2×10^{-7}
$\Omega_2 = 1.79 \times 10^{-20}$ $\Omega_4 = 2.44 \times 10^{-20}$
$\Omega_6 = 3.25 \times 10^{-20}$

Table 2. The spectrum parameters of the $^4F_{3/2} \rightarrow {}^4I_{J/2}$ transition for the Nd^{3+} ion.

Terminal state	Wavenumber (cm^{-1})	$f \times 10^6$	$A(s^{-1})$	β_c	Σ (10^{-18} cm)
$^4I_{9/2}$	11 530	3.68	963.8	0.395	3.255
$^4I_{11/2}$	9508	6.82	1217.7	0.499	6.033
$^4I_{13/2}$	7520	2.22	247.3	0.101	1.964
$^4I_{15/2}$	5450	0.21	12.29	0.005	0.186

$\tau = 409.6\ \mu s$

listed in table 1. From the error of the mean square root, it can be seen that the accuracy of the fitting is high.

We have also calculated the spontaneous radiative coefficient A, radiative lifetime τ, the luminescence branch ratio β_c, and the integrating emitting cross section Σ by using equations (3)–(6). The results obtained are shown in table 2.

From the spectrum and the luminescence linewidth $\Delta\gamma_{eff}$ (cm^{-1}) of the NYAB crystal, we obtained the peak value of the emitting cross section:

$$\Sigma = \int \sigma(\gamma)\, d\gamma = \sigma(\gamma_0)\, \Delta\gamma_{eff} = (1/8\pi cn^2\sigma^2)A.$$

The quantum efficiency is calculated according to the luminescence lifetime τ_{lum} of the metastable state $^4F_{3/2}$ and the radiative lifetime τ. They are listed in table 3.

Table 3. Some luminescence parameters of $Nd_xY_{1-x}Al_3(BO_3)_4$ ($x = 0.1$) crystal.

Parameters	Values
$^4F_{3/2} \rightarrow {}^4I_{11/2}$ linewidth	30 cm^{-1}
$^4F_{3/2} \rightarrow {}^4I_{11/2}$ emitting cross section	2.01×10^{-19} cm^2
$^4F_{3/2}$ luminescence lifetime	60 μs
$^4F_{3/2}$ quantum efficiency	14.6%

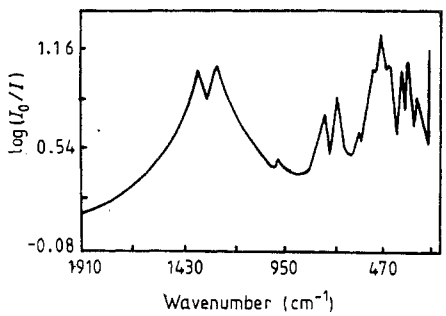

Figure 2. The infrared absorption coefficient of NYAB crystal powders.

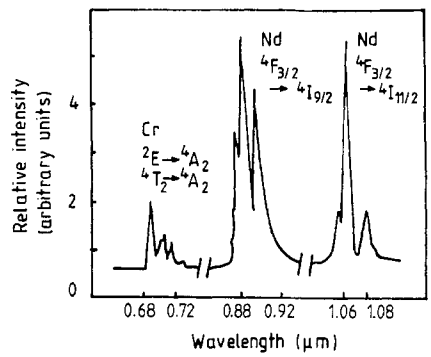

Figure 3. The luminescence spectrum of Cr:Nd:YAB at room temperature (0.6 at.% Cr; 10 at.% Nd).

From the data listed above, we can see that the quantum efficiency (14.6%) of the metastable state $^4F_{3/2}$ of Nd^{3+} ions in the NYAB crystal is rather lower than that of Nd:YAG (88–100%) and Nd:YAP (88%) [7]. This is caused by the cross relaxation and the non-radiative transition. In the NYAB crystal, the Nd^{3+} ions are shielded by the B–O–Al triangular prism and are separated from each other. The Nd–Nd interaction is very weak. This effect has already been confirmed [8]. Therefore, the low quantum efficiency must have resulted from the non-radiative transition process in which the phonon participated.

Figure 2 shows the infrared absorption spectrum of NYAB crystal powders. From figure 2 we can see that the phonon spectrum of the NYAB crystal lattice extends to 1346 cm^{-1}, while that of the YAP crystal only extends to 750 cm^{-1} [9] and of the YAG crystal to 857 cm^{-1} [10]. It is obvious that the phonon spectrum of the NYAB crystal lattice is much wider than those of the YAP and YAG crystals. The number of effective phonons participating in the non-radiative transition is very small. This will naturally lead to a large probability for the non-radiative transition. Furthermore, the largest phonon energy in a NYAB crystal matches the energy gap ΔE very well (ΔE = 5052–5634 cm^{-1}). It is exactly four times higher than the largest phonon energy 1346 cm^{-1}.

Therefore, the low quantum efficiency of the NYAB crystal can be attributed to the fact that the $^4F_{3/2}$ state jumps with high probability to the $^4I_{15/2}$ state non-radiatively by emitting four 1346 cm^{-1} phonons.

Table 4. The spectrum parameters for NYAB, Nd : YAG and Nd : YAP crystals, for comparison.

Parameter	Nd : YAG	Nd : YAP	NYAB
σ (cm^2)	3×10^{-19}	$(4–8) \times 10^{-19}$	2.01×10^{-19}
Concentration	1.2×10^{20}	2×10^{20}	$(5–10) \times 10^{20}$
$\tau_{lum}(^4F_{3/2})$	200 μs	150 μs	60 μs
$\beta_c(^4F_{3/2} \rightarrow {}^4I_{11/2})$	0.55	0.58	0.50

4. The sensitisation of Nd^{3+} luminescence by Cr^{3+} in Cr : Nd : YAB crystal

Figure 1(*b*) shows the absorption spectrum of Cr : Nd : YAB (0.6 at.% Cr; 10 at.% Nd). It shows that the absorption band of Cr : Nd : YAB is wider than that of NYAB. The highest peaks are at 420 nm and 580 nm, covering most of the visible light region. This is beneficial to the pumping efficiency of the xenon lamp. Furthermore, the absorption in the visible light region matches the sunlight spectra very well, making it possible to use the sun's energy as a pumping source.

Figure 3 shows the luminescence spectrum of Cr : Nd : YAB (0.6 at.% Cr; 10 at.% Nd) at room temperature. It is known from the shape of the Cr^{3+} ion line that the wide luminescence band for $^4T_2 \rightarrow {}^4A_2$ and the sharp peak for $^2E \rightarrow {}^4A_2$ were obtained at the same time. We have measured the lifetimes of the ^2E state in Cr : YAB (0.6 at.% Cr) and Cr : Nd : YAB (0.6 at.% Cr; 10 at.% Nd) from the $^2E \rightarrow {}^4A_2$ line decay (685 nm). The results obtained are

$$\tau_1 = 180.5\ \mu s \qquad \tau_2 = 56.6\ \mu s.$$

The transfer probability is

$$P = [(\tau_1 - \tau_2)/\tau_1] \times 100\% = 68.6\%.$$

5. Results and primary conclusions

The spectrum data for NYAB, Nd : YAG and Nd : YAP are listed in table 3 for comparison. Based on these results, we draw the following primary conclusions.

(i) The emitting cross section for wavelength 1.06 μm in the NYAB crystal is less than that for Nd : YAG and Nd : YAP. However, the activated ion concentration in NYAB is larger than that of Nd : YAG and Nd : YAP. Therefore, the gain of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in NYAB crystal is also larger. The structure of NYAB belongs to space group R32. Its non-linear coefficient is $d_{11}^{NYAB} = 3.9 d_{36}^{KDP}$ [11]. This shows that the NYAB crystal has good non-linear optical properties and should be an excellent multifunctional laser crystal yielding 0.53 μm green light directly. This is confirmed by the results of recent laser experiments [1–3].

(ii) Table 3 shows that the laser quantum efficiency of 14.6% for the metastable state $^4F_{3/2}$ of the Nd^{3+} ions resulted from the non-radiative transition of the extended phonon spectrum. We predict that a series of laser materials whose host is a YAB crystal will not have large quantum efficiency. Their laser properties will be much improved if the extending effect of the phonon spectrum is overcome and their existing structures are kept constant.

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References

[1] Lu Bao-sheng, Wang Jun, Pan Heng-fu, Jiang Min-hua, Liu En-quan and Hou Xue-yuan 1986 *Chinese Phys. Lett.* **3** 414–6
[2] *CLEO '88 Review: Laser Focus* 1988 (April) p 100
[3] Liu En-quan, Hou Xue-yuan, Lu Bao-sheng, Wang Jun, Pan Heng-fu and Jiang Min-hua 1987 *Acta Opt. Sinica* **7** 139–43 (in Chinese)
[4] Kaminskii A A 1981 *Laser Crystals* ed H F Ivey (Berlin: Springer)
[5] Judd B R 1962 *Phys. Rev.* **127** 750
[6] Ofelt G S 1962 *J. Çhem. Phys.* **37** 511
[7] Zhang Hong, Luo Zun-du, Zheng An, Wu Cheng-mei and Li Gan-sheng 1988 *Infrared Res.* A **7** 297–300 (in Chinese)
[8] Hong H Y-P and Dwight K *Laser* **11** 208–10
[9] Weber M J 1973 *Phys. Rev.* B **8** 54
[10] Hurrel J P 1968 *Phys. Rev.* **73** 851
[11] Lu Bao-sheng, Wang Jun, Pan Heng-fu and Jiang Min-hua 1987 *J. Synth. Cryst.* **16** 195–200 (in Chinese)