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Optical properties of Dy^{3+} doped yttrium–aluminium borate

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Abstract

A Dy^{3+} doped yttrium–aluminium borate (Dy:YAB) crystal has been optically characterized. The refractive indices at seven different wavelengths, ranging from the visible to the near infrared (IR), have been measured and the Sellmeier curves have been calculated. The polarized optical absorption spectra have been obtained at room temperature, and the Judd–Ofelt parameters have been calculated. The lifetime of the upper laser level $^4F_{9/2}$ has been estimated and compared with the experimental value. Evidence of high luminescence quantum efficiency of the $^4F_{9/2}$ state in YAB is provided by measured lifetimes.

1. Introduction

Rare earth ion doped nonlinear crystals have received much attention because of their potential application in compact diode-pumped visible optical lasers [1, 2]. Usually blue–green–red solid state lasers based on nonlinear crystals are obtained by self-frequency doubling of the rare earth emissions in the infrared, but an effective solid state yellow laser is still needed. Dy^{3+} has previously demonstrated yellow emission in other crystal hosts [3] making it a promising ion in this sense. YAB crystals have shown excellent properties as laser hosts when doped with rare earths ions like Nd^{3+} [4] and Yb^{3+} [5]. In addition to the nonlinear properties, YAB crystals have good thermal and chemical stability [6] and high acceptance when doped with rare earths [7], which has provided laser systems emitting at different colours with a rather

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good efficiency. The combination of these host properties with those of the Dy^{3+} ion makes the system Dy:YAB promising for obtaining a solid state laser device with yellow emission.

The YAB crystal structure is rhombohedral, it is known to be isomorphous with huntite $CaMg_3(CO_3)_4$ [8] and the active rare earth dopant ion occupies the Y^{3+} ion site, with a local symmetry D^3. It is a negative uniaxial crystal presenting a moderate birefringence; its refractive indices have been previously obtained, in the visible range, when doped with Nd^{3+} and Yb^{3+} [9, 10].

Recent works in Dy:YAB spectroscopy [11, 12], applying Judd–Ofelt (JO) theory, gave two different groups of JO parameters and theoretical lifetime calculations with a poor agreement with the experimental values. Neither work takes into account either the birefringence of YAB or the dispersion of the refractive indices.

In the present work, refractive indices have been measured from the visible to the near infrared (NIR), and the Sellmeier curves have been established with an accuracy to the fourth decimal digit. The polarized optical absorption spectra, at room temperature, have been investigated. Judd–Ofelt theory has been applied to estimate the radiative lifetime of the $^4F_{9/2}$ state of Dy^{3+} in YAB, and a very good agreement with the experiments has been found.

2. Experiment

Dy^{3+} doped YAB crystals were grown by the closed crucible flux method as previously reported [13]. The dopant concentration was determined by means of total-reflection x-ray fluorescence (TRXRF) and turned out to be 1.67×10^{20} ions cm^{-3}.

Plate samples of Dy:YAB, thickness 0.11 cm, were cut from the grown crystals with the c-axis either parallel to the main faces, for σ ($E \perp c$) and π ($E \parallel c$) absorption spectra, or perpendicular, for the refractive index measurements.

The refractive indices were measured by the prism-coupling method [14], using a rutile prism with a base angle of about 30° and its optical axis perpendicular to the light incidence plane. Absorption spectra were obtained using a JASCO V-570 spectrophotometer.

The lifetime decay of the $^4F_{9/2}$ level was measured at 575 nm, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition, upon excitation at 458 nm from a Coumarine dye laser pumped by the third harmonic of a Q-switched Nd:YAG laser with a pulse width of 6 ns and a repetition rate of 10 Hz. The signal was selected by a double monochromator with a resolution of 3 cm^{-1} and detected by a photon counting system connected to a multi-channel digital analyser.

3. Results and discussion

To fully characterize the refractive indices of the Dy:YAB crystal, they were measured at seven different wavelengths ranging from the visible to the near infrared, as reported in table 1. The extent of the wavelength range to the near infrared was important for obtaining accurate values of the refractive indices in that region. In fact these are the values used when calculating the Judd–Ofelt parameters.

These data were fitted, by means of a least square (LS) method, to a four-parameter Sellmeier formula [10] and the equations obtained are

$$n_o = 3.126\,91 + \frac{0.009\,35}{\lambda^2 - 0.102\,34} - 0.028\,93\lambda^2 \tag{1}$$

$$n_e = 2.857\,17 + \frac{0.011\,97}{\lambda^2 - 0.058\,94} - 0.010\,91\lambda^2 \tag{2}$$

where n_o and n_e are the ordinary and extraordinary refractive indices and λ the vacuum

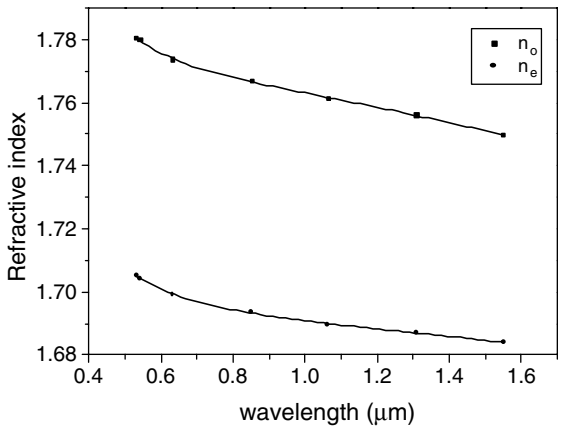

Figure 1. Dispersion curves of the refractive indices for Dy:YAB crystal.

Table 1. Wavelengths used and corresponding values of the measured ordinary (n_o) and extraordinary (n_e) refractive indices of Dy:YAB.

Wavelength (nm)	n_o	n_e
532	1.7804	1.7053
544	1.7798	1.7041
633	1.7737	1.6993
852	1.7669	1.6936
1064	1.7613	1.6895
1309	1.7560	1.6872
1550	1.7497	1.6840

wavelength in microns. Figure 1 shows the experimental points and the fitting curves; an agreement to the fourth decimal digit was obtained.

Figure 2 shows the σ and π absorption spectra of Dy:YAB; the band assignment is also indicated. The wavelength range between 500 and 700 nm was omitted as the material is completely transparent in that spectral region. The optical lines are not perfectly resolved due to the broadening originated by thermal population of the different levels within the ground state $^6H_{15/2}$. This is a necessary condition for the validity of JO theory [15, 16], which is based on the assumption of equal population for all the Stark levels.

The JO formalism for anisotropic crystals [17] can be applied to estimate the JO parameters Ω_t ($t = 2, 4, 6$). These parameters allow the calculation of the radiative transition probabilities and branching ratios between any two states of the system, and are quite useful when designing a laser device.

For uniaxial crystals the absorption oscillator strength $S(J \rightarrow J')$ from the ground state ($J = 15/2$) to a particular excited state J' is given by

$$S_{ED}(J \rightarrow J') = \frac{3hc(2J+1)}{8\pi^3 \rho \bar{\lambda} e^2} \frac{\Gamma_\pi + 2\Gamma_\sigma}{\chi_\pi + 2\chi_\sigma} \tag{3}$$

where ρ is the Dy^{3+} concentration in the host crystal; $\bar{\lambda}$ is the mean wavelength of the transition and $(2J + 1) = 16$ is the multiplicity of the ground state; $\Gamma_{\sigma,\pi}$ are the integrated absorbances and $\chi_{\sigma,\pi} = (n^+_{\sigma,\pi}2)^2/9n_{\sigma,\pi}$ makes allowance for the refractive index of the medium with $n_\sigma = n_o$ and $n_\pi = n_e$ taken from equations (1) and (2) respectively; c is the vacuum light velocity and h is Planck's constant.

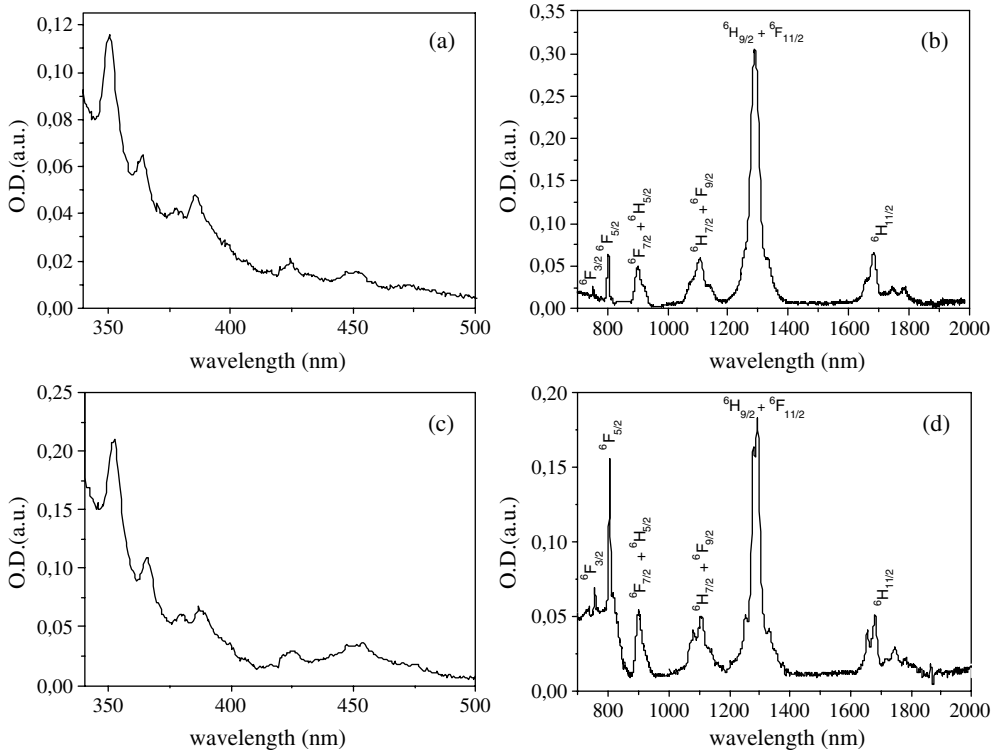

Figure 2. Room temperature polarized absorption spectra. (a) and (b) σ polarization; (c) and (d) π polarization.

According to the JO theory, the line oscillator strength of any electric dipole (ED) transition between two states J and J' can be written as

$$S_{\mathrm{ED}}(J \rightarrow J') = \sum_{t=2,4,6} \Omega_t |\langle J \| U^t \| J' \rangle|^2. \tag{4}$$

The elements of the reduced matrix U^t vary only slightly from medium to medium for a given lanthanide. Therefore they can be considered unchanged and for transitions from the ground state of Dy^{3+}, they could be taken from the tables of [17].

Making use of the absorption spectra of figure 2, the line oscillator strengths of ED transitions departing from the ground state to levels $^6H_{11/2}$, $^6H_{9/2}$, $^6F_{11/2}$, $^6H_{7/2}$, $^6F_{9/2}$, $^6H_{5/2}$, $^6F_{7/2}$, $^6F_{5/2}$ and $^6F_{3/2}$ were calculated. Then, using equations (3) and (4), by means of a LS method, the JO intensity parameters $\Omega_2 = 10.81 \times 10^{-20}$ cm^2, $\Omega_4 = 2.05 \times 10^{-20}$ cm^2, $\Omega_6 = 3.28 \times 10^{-20}$ cm^2 were obtained. Table 2 illustrates the seven experimental and calculated line strengths; the root mean square deviation is 3×10^{-21} cm^2. The JO parameters obtained here are in fairly good accordance with those recently reported by Dominiak-Dzik *et al* [11] but are in disagreement with those obtained by Cavalli *et al* [12].

The importance of Dy:YAB crystals resides in the possibility of exploiting them for the realization of yellow-emitting lasers. On the basis of the JO theory, the radiative lifetime of the upper laser level, $^4F_{9/2}$ [11], can be calculated from the radiative transition rates A_{rad} from this level to the less energetic ones. The expression for the radiative transition rate, between

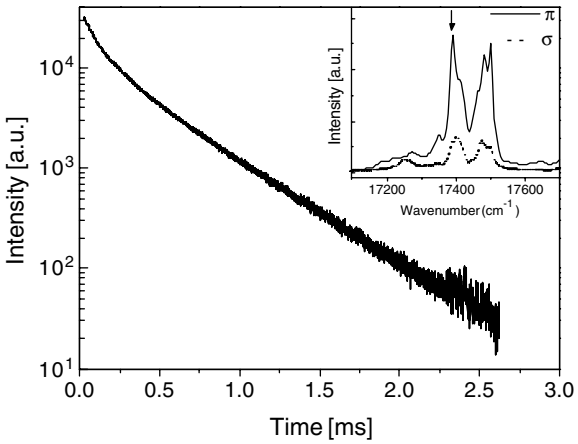

Figure 3. The room temperature decay curve of the $^4F_{9/2}$ dysprosium level. In the inset we show the emission spectrum of the $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition in σ and π polarizations. The arrow indicates the wavenumber chosen for the lifetime measurement.

Table 2. Absorption line strengths in Dy:YAB crystal.

	λ (nm)	S_{exp} (10^{-20} cm^2)	S_{cal} (10^{-20} cm^2)
$^6H_{11/2}$	1728	3.32	3.18
$^6H_{9/2}, {}^6F_{11/2}$	1291	13.19	13.21
$^6H_{7/2}, {}^6F_{9/2}$	1104	3.77	3.68
$^6H_{5/2}, {}^6F_{7/2}$	908	2.25	2.63
$^6F_{5/2}$	814	1.40	1.13
$^6F_{3/2}$	756	0.40	0.20

two states J and J', is

$$A_{(J\rightarrow J')} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3}\left(\frac{2}{3}n_\sigma^2\chi_\sigma + \frac{1}{3}n_\pi^2\chi_\pi\right)\sum_{t=2,4,6}\Omega_t U_t^2. \tag{5}$$

This expression is related to the radiative lifetime by the equation

$$\tau = \frac{1}{\sum A(J \rightarrow J')}. \tag{6}$$

Using the reduced matrix elements for Dy^{3+} ions presented in [18], and the wavelength values for each transition taken from [11], an estimated lifetime of $\tau = 460$ μs is obtained for the level under study.

To compare this value with the experimental one, we measured the fluorescence decay of the $^4F_{9/2}$ level, reported in figure 3. It was found that the decay does not fit a single exponential, but could be described as a double exponential. The fast decay, with a τ_1 lifetime of about 100 μs, is ascribed to the presence of a strong energy-transfer mechanism, due to the high doping level as already observed [12]. Moreover, the multiphonon relaxation is negligible, as the maximum phonon energy [19] is less than one fifth of the energy gap between the $^4F_{9/2}$ level and the next lower one, and so the slow lifetime, $\tau_2 = 400 \pm 10$ μs, can be considered representative of the radiative decay. It is also possible to distinguish the number of ions decaying according to the different lifetimes. In fact, as the intensity decay of the

luminescence is fitted by

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

the percentage of ions with a slow lifetime, τ_2,will be given by

$$N = \frac{A_2\tau_2}{A_1\tau_1 + A_2\tau_2} \cong 70\%.$$

This value demonstrates the high luminescence quantum efficiency of the $^4F_{9/2}$ state in YAB. It is worth noting that the estimated radiative lifetime obtained in the present work is the most accurate one as compared with the experimental value τ_2. The latter is in good agreement with the one reported in [11]. Moreover, the consistency of our optical characterization of Dy:YAB is an important result considering that the dopant concentration of our sample is similar to that used in laser devices.

4. Conclusions

Dy:YAB crystals have been optically characterized in terms of their refractive indices and their optical absorption. The Sellmeier curves for ordinary and extraordinary indices have been established from the experimental values obtained in the visible and in the near IR. The Judd–Ofelt intensity parameters have been calculated from the line strengths of the σ and π absorption spectra, taking into account YAB anisotropy. The radiative transition rates and the radiative lifetime from the $^4F_{9/2}$ level have been calculated, the latter being in good agreement with the experimental value. Evidence of high luminescence quantum efficiency of the $^4F_{9/2}$ state in YAB is provided by measured lifetimes. This work gives a consistent optical characterization of Dy:YAB crystals which is the first step towards the realization of a yellow solid state laser device.

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