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Optical spectroscopy of $\text{BaY}_2\text{F}_8:\text{Dy}^{3+}$

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Abstract

The optical spectra of the $\text{BaY}_2\text{F}_8:\text{Dy}^{3+}$ laser crystal have been investigated in the 5000–30 000 cm^{-1} range. The Judd–Ofelt parametrization scheme has been applied to the analysis of the room temperature absorption spectra. The calculated radiative lifetime of the $^4\text{F}_{9/2}$ state is 1.48 ms. Decay curves of the visible emission have been measured as a function of the temperature for two different Dy^{3+} concentrations (0.5 and 4.4%). In the case of the diluted crystal the emission profiles are single exponential with decay times consistent with the radiative lifetime. The decay curves of the concentrated crystal are not exponential and they obey the Inokuti–Hirayama model for energy transfer for an electric dipole–dipole interaction in the absence of diffusion among the donors. The emission cross section at 575 nm has been estimated using the integral β – τ method in order to assess the potentialities of this compound as a solid state laser material in the yellow region.

1. Introduction

Recent studies have raised some interest on optical materials based on the Dy^{3+} ion in the perspective of developing new laser media for the near-infrared (NIR) and visible regions [1, 2] or NIR saturable absorbers for Q -switch devices [3]. In particular, fluoride hosts have been demonstrated to be suitable for laser operation in the 2–4 μm range thanks to their low multiphonon relaxation rate [4]. Actually, there are rather few active media having efficient emission in this region, which is very interesting for applications in spectroscopy and medicine. The most important among them is certainly $\text{BaY}_2\text{F}_8:\text{Dy}^{3+}$ (BYF: Dy^{3+}), whose stimulated emission at 3 μm was reported for the first time by Johnson and Guggenheim [5]. They pointed out that these laser properties are a consequence of a particular combination

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of properties such as long fluorescence lifetimes of the intermediate states and low phonon energies of the host. However, despite its technological interest, this material has never been completely characterized from the spectroscopic point of view, to the best of our knowledge. Recently Toncelli *et al* [6] studied the temperature dependence of the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ emission transition involved in the laser action, whereas the structure of the lowest energy levels was analysed by Magnani *et al* [7] using Newman's superposition model. We are carrying out a systematic study of the optical spectra of Dy^{3+} in insulating crystals in order to evaluate their perspectives of application and to investigate some aspects of the excited state dynamics of this ion which are yet to be fully understood. In this work we have measured the absorption and emission properties of BYF:Dy^{3+} at various temperatures for two different crystal concentrations. The room temperature absorption spectrum has been analysed in the frame of the Judd–Ofelt (JO) approach, and the intensity parameters have been evaluated from a least squares fit of the experimental oscillator strengths. These parameters have been used to calculate the spontaneous emission probabilities, the branching ratios and the radiative lifetimes of the most important emitting levels, which have been compared with the experimental values. The visible luminescence decay curves have been measured as a function of the temperature and analysed using suitable models in order to obtain information on the excited state dynamics in this material.

2. Experimental details

Single crystals of BYF containing 0.5% and 4.4% of Dy^{3+} were grown by means of the Czochralski method. The structure is monoclinic, space group $C2/m$ with cell parameters $a = 6.983 \text{ \AA}$, $b = 10.519 \text{ \AA}$, $c = 4.264 \text{ \AA}$ and $\beta = 99.7^\circ$ [8]. Rare earths enter substitutionally into the Y^{3+} site having C_2 point symmetry.

The absorption spectra were measured with a spectroscopic system equipped with a 300 W halogen lamp fitted with a 0.25 m Spex monochromator as source, and a 1.26 m Spex monochromator with a RCA C31034 photomultiplier or a PbS NEP cell to analyse and detect the output radiation. The luminescence spectra in the visible region (440–830 nm) were measured using the same set-up with the optical pathway properly modified and a 450 W xenon lamp instead of the halogen lamp. For the measurement of the luminescence decay curves, the sample was excited at 355 nm using a pulsed Nd:YAG laser (Quanta System model SYL 202); the emission was isolated by means of a Hilger–Watts Model D330 double monochromator and detected with a Hamamatsu R943-022 photomultiplier connected to a LeCroy 9410 transient digitizer. The samples were cooled by means of an Air Products Displex DE 202 or a Galileo Vacuum Tech Model K1 closed-cycle cryostat.

3. Optical spectra and laser parameters

The low temperature absorption spectra and the Stark levels structure of the Dy^{3+} ion in BYF have already been reported and discussed [5, 7]. We have measured the room temperature absorption spectrum of the crystal under investigation in order to carry out the Judd–Ofelt (JO) analysis and to obtain information on the excitation wavelengths. The result is shown in figure 1: the observed transitions have been assigned on the basis of the energy level scheme of the Dy^{3+} ion reported in the literature (2, 7). Their intensities have been analysed in the framework of the JO theory. Ten bands were considered to calculate the intensity parameters Ω_N ($N = 2, 4, 6$); we did not take into account the ${}^6\text{F}_{1/2} \leftarrow {}^6\text{H}_{15/2}$ transition because its intensity is negligible. The oscillator strengths of the transitions were carefully determined

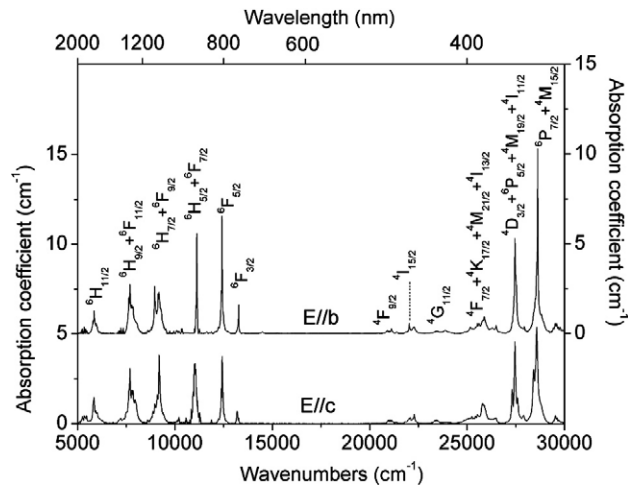


Figure 1. Polarized room temperature absorption spectrum of BYF:Dy³⁺.

Table 1. Experimental and calculated oscillator strengths (P) of Dy³⁺ in BYF. The Judd–Ofelt parameters, Ω_λ , the RMS and the percentage error are also tabulated.

Excited state	Barycentre (cm ⁻¹)	P_{exp} (10 ⁶)	P_{calc} (10 ⁶)
⁶ H _{11/2}	5 888	1.40	1.56
⁶ H _{9/2} + ⁶ F _{11/2}	7 742	3.48	3.48
⁶ H _{7/2} + ⁶ F _{9/2}	9 120	3.48	3.47
⁶ F _{7/2}	11 150	2.96	3.02
⁶ F _{5/2}	12 417	1.52	1.45
⁶ F _{3/2}	13 227	0.29	0.27
⁴ F _{9/2}	21 002	0.23	0.23
⁴ I _{15/2}	22 242	0.52	0.52

$\Omega_2 = 1.52 \times 10^{-20}$ cm², $\Omega_4 = 2.33 \times 10^{-20}$ cm², $\Omega_6 = 3.67 \times 10^{-20}$ cm²
RMS = 4.44×10^{-8} ; error 2.6%

by taking into consideration the polarizations of the bands, and the experimental data were fitted on the basis of the JO parametrization scheme after subtraction of the magnetic dipole contribution for the ⁴I_{15/2} ← ⁶H_{15/2} transition. This contribution is small and is not reported here. The reduced matrix elements were taken from Jayasankar and Rukmini [9], and the value of the refractive index was assumed to be $n = 1.51$ according to [10]. The evaluated intensity parameters are reported in table 1, together with the observed and calculated oscillator strengths, the root mean square deviation (RMS), and the percentage error. The calculated spontaneous emission probabilities and the radiative branching ratios for the transitions from the ⁴F_{9/2} state to the lower ones are reported in table 2, together with the radiative lifetime of the emitting level. They were estimated using the calculated intensity parameters and correcting for the refractive index. The radiative lifetime of the ⁶H_{13/2} lasing level has been also calculated: its value, 51 ms, is in reasonable agreement with that estimated by Toncelli *et al* [6], 44 ms. The JO analysis of the room temperature absorption spectra allows us to compare the efficiencies of different crystals activated with the same rare earth ion. In the present case, the comparison between the intensity parameters obtained for BYF:Dy³⁺ and those listed by Görller-Wallrand and Binnemans [11] evidences quite low values for Ω_2 and Ω_4 .

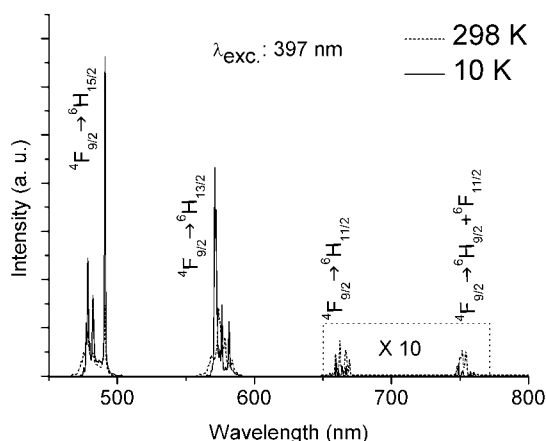


Figure 2. 10 and 298 K emission spectrum of BYF:Dy³⁺.

Table 2. Calculated spontaneous emission probabilities A and radiative branching ratios β for the ${}^4F_{9/2}$ emitting level. (Calculated radiative lifetime $\tau = 1.48$ ms.)

Final state	A (s ⁻¹)	β
${}^6F_{5/2}$	2	0.003
${}^6F_{7/2}$	5	0.007
${}^6H_{5/2}$	4	0.004
${}^6H_{7/2}$	0	0.000
${}^6F_{9/2}$	6	0.009
${}^6F_{11/2}$	11	0.016
${}^6H_{9/2}$	11	0.016
${}^6H_{11/2}$	24	0.035
${}^6H_{13/2}$	380	0.561
${}^6H_{15/2}$	236	0.348

Considering the reduced matrix elements involved in the JO calculations [9], it can be noted that the value of the Ω_2 parameter exclusively depends on the intensity of the hypersensitive ${}^6F_{11/2} \leftarrow {}^6H_{15/2}$ absorption manifold [12] and that also the Ω_4 value is strongly related to this transition. As a consequence, the radiative lifetime of the ${}^4F_{9/2}$ emitting level is 1.48 ms, quite long with respect to the values reported for other crystals activated with Dy³⁺, such as, for example, CaMoO₄:Dy (152 μ s) and YAB:Dy (344 μ s) [13, 14]. The relationship between the intensity of the hypersensitive transition (and then the Ω_2 parameter) and the visible fluorescence dynamics of these materials, as well as their dependence on the structural characteristics of the host matrix, constitutes a particularly intriguing topic deserving to be better understood. We are collecting experimental data in order to have more information on this matter.

The visible luminescence of BYF:Dy³⁺ has not yet been investigated in detail to our knowledge, maybe because it has never been considered suitable for technological applications. This point of view is rapidly changing after the discovery of laser action of Dy³⁺-doped tungstates in two novel laser channels in the yellow (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition) and red (${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition) regions [2]. Since then, interest in the visible emission properties of Dy³⁺-doped crystals is considerably increasing. The 10 and 298 K emission spectra of BYF:Dy were measured after excitation at 397 nm. They are shown in figure 2. The spectra

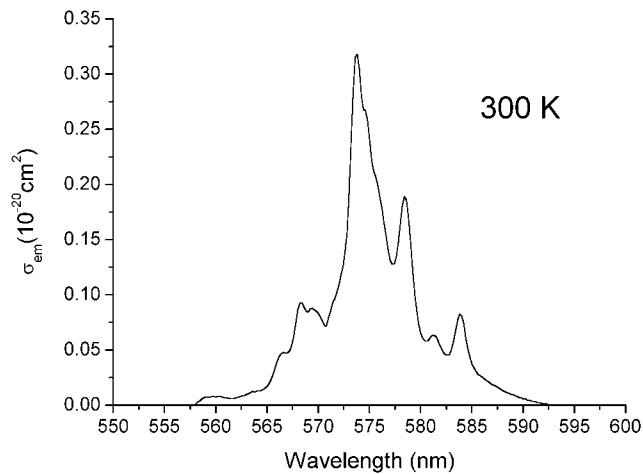


Figure 3. ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission cross section at 300 K for BYF:Dy³⁺, derived by the integral β - τ method.

present four band systems centred at about 486, 575, 664, and 752 nm. They can be assigned to the transitions from the ${}^4F_{9/2}$ level to the ${}^6H_{15/2}$, ${}^6H_{13/2}$, ${}^6H_{11/2}$, and ${}^6H_{9/2} + {}^6F_{11/2}$ states, respectively. The structures of the low temperature manifolds reflect the composition of the terminal levels reported in the literature [5, 7]. An extremely weak band, located at 831.5 nm and assigned to the ${}^4F_{9/2} \rightarrow {}^6H_{7/2} + {}^6F_{9/2}$ transition, is not shown. The ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is attractive for laser operation in the yellow region at about 575 nm, i.e. a region for which very few solid state active media have been reported. The emission cross section σ_{em} provides interesting information about the potential laser performance of a material, and it can be easily evaluated from the luminescence spectrum using the integral β - τ method [15]:

$$\sigma_{em}(\lambda) = \frac{\beta \lambda^5 I(\lambda)}{8\pi n^2 c \tau_{rad} \int \lambda I(\lambda) d\lambda} \quad (1)$$

where $I(\lambda)$ is the experimental emission spectrum, c is the velocity of light, n is the refractive index and β and τ_{rad} are the branching ratio and radiative lifetime of the ${}^4F_{9/2}$ multiplet, respectively, as taken from the Judd–Ofelt calculation. The result of the calculation is shown in figure 3. The peak cross sections are $0.32 \times 10^{-20} \text{ cm}^2$ at 574 nm and $0.19 \times 10^{-20} \text{ cm}^2$ at 578 nm, of the same order of magnitude of those reported for other Dy³⁺-doped oxide crystals and glasses (see [16] and references therein). These values do not take polarization into account, and therefore have to be considered as an estimate. Moreover, some nonlinear processes might take part in determining the actual laser efficiency of the system (for example excited state absorption); nevertheless, these results indicate that BYF:Dy³⁺ is a potential candidate for laser operation in the yellow region and deserves further investigations in this direction.

4. Fluorescence dynamics and laser parameters

The decay curves of the luminescence from the ${}^4F_{9/2}$ level of Dy³⁺ both in 0.5% and 4.4% doped crystals were measured as a function of the temperature after pulsed excitation at 355 nm. In the case of the diluted crystal, the decay profiles were nearly single exponential at all temperatures, as shown in figure 4 for the low temperature emission. The lifetimes range from 1.06 ms at

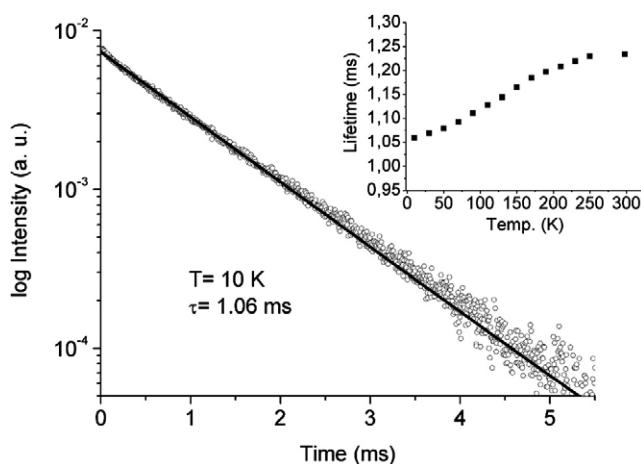


Figure 4. Decay profile of the 10 K emission from the ${}^4F_{9/2}$ level of 0.5% BYF:Dy $^{3+}$. Inset: temperature behaviour of the lifetimes.

10 K to 1.24 ms at 298 K (see the inset of figure 4). The comparison with the radiative lifetime calculated from the JO analysis indicates that the non-radiative processes are not negligible. It is worth pointing out that the measured lifetime increases with increasing temperature, as usually observed for Dy $^{3+}$ -doped oxide crystals [13, 16] and glasses [17]. The thermalization of the ${}^4F_{9/2}$ and ${}^4I_{15/2}$ levels has been demonstrated to be not sufficient to account for this particular phenomenon [16]. Recently, Kaminskii *et al* [2] and Dominiak-Dzik *et al* [18] have reproduced the temperature behaviour of the lifetimes using a model based on the hypothesis that the Stark components of the ${}^4F_{9/2}$ emitting level have different transition rates. This mechanism is certainly reasonable in our opinion, even if it needs further experimental confirmations. Other possibilities, like for example the reabsorption of the emitted radiation, cannot yet be excluded. The decay curves of the concentrated crystal are not exponential. They can be fitted by the Inokuti–Hirayama model, in the assumption that the donor–acceptor transfer is much faster than migration [19]. In the case of electric multipolar interaction the time evolution of the emission intensity from the donor is given by the following equation:

$$\phi(t) = A \exp \left[-\frac{t}{\tau} - \alpha \left(\frac{t}{\tau} \right)^{3/s} \right] \quad (2)$$

where $\phi(t)$ is the emission intensity after pulsed excitation, A is the intensity of the emission at $t = 0$, τ is the lifetime of the isolated donor, α is a parameter containing the energy transfer probability, and $s = 6$ for dipole–dipole (DD), 8 for dipole–quadrupole (DQ), and 10 for quadrupole–quadrupole (QQ) interactions. We have fitted the decay curves by means of equation (2) considering A , τ , and α as adjustable parameters. The three possible interaction mechanisms were taken into consideration, and the final result was that the analysis carried out with $s = 6$ has been revealed to be significantly better than those with $s = 8$ or 10. As an example, the Inokuti–Hirayama fit of the 10 K decay curve is shown in figure 5. The experimental lifetime increases with temperature from 1.34 ms at 10 K to 1.54 ms at 298 K, and is in good agreement with the estimated radiative lifetime, 1.48 ms, especially in consideration of the intrinsic error ($\pm 20\%$) affecting the JO calculations. The parameter α provides information on the probability of the energy transfer process:

$$\alpha = \frac{4}{3} \pi \cdot \Gamma \left(1 - \frac{3}{s} \right) N_a R_0^3 \quad (3)$$

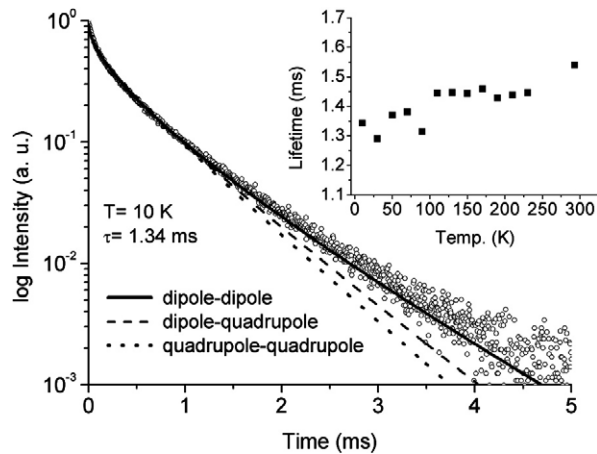
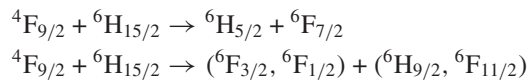


Figure 5. Decay profile of the 10 K emission from the ${}^4F_{9/2}$ level of 4.4% BYF:Dy³⁺. Inset: temperature behaviour of the lifetimes.

where Γ is the gamma function, N_a the concentration of acceptors and R_0 is the critical distance. In the present case, the calculated R_0 -value ranges from 8.9 to 9.2 Å, a reasonable value for energy transfer processes involving rare-earth ions especially if compared to the average nearest neighbour distance for a 4.4% Dy³⁺-doped BYF crystal which is 12.6 Å. With these data we can estimate the donor-acceptor interaction parameter by means of the relation

$$C_{DA} = \frac{R_0^6}{\tau_0}. \quad (4)$$

The obtained value, $0.4 \times 10^{-51} \text{ m}^6 \text{ s}^{-1}$, is quite similar to that reported for YAB:Dy³⁺ [16]. Different resonant or nearly resonant cross relaxation processes can account for this energy transfer process. For example,



and so on. The available data do not allow us to discriminate between the possible mechanisms. As a conclusion, it can be inferred that the excited state dynamics of the Dy³⁺-doped crystals still present interesting aspects to be clarified, for which further experimental work is necessary.

5. Concluding remarks

The optical absorption and emission properties of BYF:Dy³⁺ have been investigated with a twofold purpose:

- (1) the spectroscopic characterization of this important 3 μm laser material;
- (2) the evaluation of its potentialities as an active medium for visible laser operation at 575 nm.

The JO analysis gives evidence of relatively low values of the Ω_2 and Ω_4 parameters as a consequence of the low intensity of the hypersensitive ${}^6F_{11/2} \leftarrow {}^6H_{15/2}$ absorption transition. This results in a relatively long radiative lifetime of the ${}^4F_{9/2}$ emitting level, that strongly affects the excited states dynamics of this material. The decay profiles of the visible luminescence have been measured as function of the temperature for two different crystal concentrations. Their analysis indicates that the emission decay time increases with temperature as in the cases

of Dy³⁺-doped oxide crystals and glasses. Moreover, energy transfer processes take place in the more concentrated crystal: these have been reliably characterized using the Inokuti–Hirayama model, and some hypotheses have been proposed about the cross relaxation mechanisms which could be at the origin of these processes. We are extending our investigations to other Dy³⁺-based systems in order to obtain more information on this topic.

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