Rare earth crystal field spectra as a probe of librational motions in BaY$_2$F$_8$ solid state laser crystals

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Abstract. The fine structure (FS) accompanying a few lines, originated by crystal field (CF) transitions of rare earths (RE), as Er$^{3+}$ and Tm$^{3+}$, in BaY$_2$F$_8$ single crystals, is analyzed as a function of the RE$^{3+}$ concentration (0.5÷20 at%) and temperature (9-300 K), by using high resolution (as fine as 0.02 cm$^{-1}$) Fourier transform spectroscopy and linear dichroism measurements. The 9 K absorption spectra show that FS includes weak, narrow, and closely spaced (0.4÷0.8 cm$^{-1}$) lines, covering a few cm$^{-1}$ range on both sides of the narrowest among the CF lines. The FS increases by increasing the RE$^{3+}$ concentration and vanishes at rather low temperature (40 and 60 K for Er$^{3+}$ and Tm$^{3+}$, respectively). The polarized light spectra confirm the association of a given set of FS lines to a specific CF line. The FS is ascribed to the simultaneous excitation of an electronic CF transition and of a local librational (or hindered rotation) mode of the RE$^{3+}$-F$^-$ group. The attribution is supported 1) by specific features of the host matrix and guest rare earths, which allow some mobility of F$^-$ ions, and 2) by the spacing of the FS lines, which is in excellent agreement with the calculated RE$^{3+}$-F$^-$ group rotational constant.

1. Introduction

The spectroscopic evidence for molecular group rotations (both free and hindered) in condensed matter comes mostly from rotovibrational spectra where such modes are simultaneously excited together with the stretching ones. The pioneering works dealt, for example, with diatomic molecular groups, as cyanide and hydroxyl ions, substituting for the halogen in alkali halides [1-2] and more recently with HD molecular groups in silicon [3]. The stretching mode absorption line, falling in the mid-infrared region, is accompanied by side lines: their separation from the central line supplies information about the rotational (or librational) mode energy. At low temperatures barriers separating different energy minima restrict the molecular group motion allowing only librations (or hindered rotations): tunneling across the barriers may occur as well. By increasing the temperature, thermally activated free rotations may take place. IR spectroscopy allowed monitoring even rotations of polyatomic molecular groups in condensed matter, e.g. NO$_2$ and NO$_1$ in alkali halide crystals [4], OCS and SF$_6$ in liquid He clusters [5-6]. A number of narrow, rotationally resolved side lines, spaced only
by ~0.02 cm$^{-1}$ and grouped into P and R branches, were detected around the v$_3$ vibrational absorption of the SF$_6$ group [6].

Much less is known about rotational or librational lines accompanying electronic transitions, very likely due to the broadness of lines arising from such transitions, which may hide the finely spaced rotational spectrum. However, a nice example is provided by optical measurements performed on benzoic acid doped with pentacene: the absorption and emission spectra show two line progressions, spaced by 12.2 and 16.7 cm$^{-1}$, which were attributed to the lowest frequency libration modes of pentacene in the electronic ground and excited state, respectively [7]. The width of the electronic absorption line (a few cm$^{-1}$) is much smaller than the libration mode frequency, thus allowing the detection of the side lines.

In the present work the remarkable sharpness of absorption lines (as narrow as 0.13 cm$^{-1}$) originated by electronic transitions of rare earths (RE), as Er$^{3+}$ and Tm$^{3+}$, in monoclinic BaY$_2$F$_8$ single crystals [8-9], is exploited to probe possible librational or rotational modes. Such crystals are also of technological interest being good rare earth hosts for laser applications [10]. More in detail, the fine structure (FS) accompanying a few lines, induced by the f-f electronic transitions of both RE$^{3+}$, is analyzed as a function of the RE$^{3+}$ concentration and temperature, by taking advantage of both high resolution Fourier transform spectroscopy and linear dichroism measurements. The attribution to fluorine libration with respect to the RE$^{3+}$ is discussed on the basis of BaY$_2$F$_8$ crystal structure [11], rotational constants of RE$^{3+}$-F complexes, and spacing between the FS lines.

2. Experimental Details

The BaY$_2$F$_8$ single crystals were grown by a computer-controlled Czochralski technique under a purified argon atmosphere [12]. The investigated samples were doped with 0.5, 2, 12, and 20 Er$^{3+}$ at% and with 1 Tm$^{3+}$ at% [8]. A nominally pure sample was also analyzed as a reference.

The optical absorption spectra were monitored by means of a Fourier Transform (FT) spectrometer Bomem DA8, operating in the 2000-24000 cm$^{-1}$ range and capable of a nonapodized resolution as fine as 0.01 cm$^{-1}$. The sample temperature was controlled in the 9-300 K range by means of a CTI Cryogenics model 22 Cryodine Refrigerator equipped with KRS5 and fused silica windows. Measurements with linearly polarized light in the IR region (4000-10000 cm$^{-1}$) were performed by using a gold grid polarizer deposited onto a KRS5 substrate.

3. Results and discussion

Figure 1 displays the fine structure, which accompanies the line peaking at 6530.2 cm$^{-1}$ (A1 line), originated by the Er$^{3+}$ zero phonon crystal field (CF) transition from the lowest sublevel of the $^4I_{15/2}$ ground manifold to the lowest sublevel of the $^4I_{13/2}$ excited manifold [8], in two BaY$_2$F$_8$ samples doped with different Er$^{3+}$ amounts, i.e. 0.5 and 2 at% (see curves a and b, respectively). The absorption spectrum, measured at 9 K with an apodized resolution as fine as 0.04 cm$^{-1}$, shows on both sides of the stronger A1 line (indicated by an arrow) the FS, consisting in other weaker, narrow lines laying very close to the A1 and a progression (spanning over a few cm$^{-1}$) of much weaker ones. A magnification of the weakest lines is provided by the inset of Fig. 1, where the spectra in the 6524.1-6529.5 cm$^{-1}$ range are compared for two Er$^{3+}$ concentrations: the line pattern and position are the same for both samples, while their amplitude increases by increasing the Er$^{3+}$ doping level. At the highest concentrations (12 and 20 at%), the FS grows accordingly (as the A1 line does), but it is partially blurred due to line inhomogeneous broadening and overlapping of absorptions induced by RE$^{3+}$ clusters [8]. These results, joined to the absence of FS in pure samples, support that such a structure is closely related to the presence of Er$^{3+}$. FS lines have been detected to ‘decorate’ other among the narrowest lines induced by Er$^{3+}$ CF transitions.

Similar FS patterns accompany the narrowest CF lines induced by Tm$^{3+}$ doping (1 at%) in BaY$_2$F$_8$ as, for example, the A1 and A2 lines at 5681.85 and 5683.46 cm$^{-1}$, respectively, see figure 2(a). The two Tm$^{3+}$ CF lines originate from two transitions reaching the same final state within the excited $^2F_4$ manifold and starting from the first two sublevels (separated only by 1.61 cm$^{-1}$) of the ground $^2H_6$
The spectra were measured at 9 K by light propagating along the c axis [11] and with the electric field orthogonal and parallel to the a axis (curve a and b, respectively): they prove the strong optical anisotropy of the Tm$^{3+}$ CF transitions. The A1 and A2 lines show an opposite dependence on the polarization angle. The weak FS lines, indicated by arrows in figure 2(a), exhibit the same polarization dependence as the CF A1 and A2 lines do (solid red and dashed blue arrows, respectively), supporting the hypothesis that a group of FS lines is associated with a well defined CF line. Detailed analysis of the FS and CF line amplitudes vs. the polarization angle for both Er$^{3+}$ and Tm$^{3+}$ transitions confirms such close association.

![Figure 1](image_url)

**Figure 1.** Optical absorption spectra of BaY$_2$F$_8$ samples doped with different Er$^{3+}$ concentrations (curves a: 0.5 at%, res. 0.02 cm$^{-1}$; curve b: 2 at%, res. 0.04 cm$^{-1}$) measured at 9 K in the region of the $^4$I$_{15/2} \rightarrow ^4$I$_{13/2}$ transition. The inset shows a magnification of the 6524.1-6529.5 cm$^{-1}$ range. Arrows indicate some lines of the FS pattern.

The fine structure vanishes at rather low temperatures: the FS lines are no longer distinguishable from the CF ones they are associated with, already at 40 and 60 K for Er$^{3+}$ and Tm$^{3+}$ doping, respectively. Their amplitude shows a much faster thermally induced decrease than the CF lines due either to isolated RE$^{3+}$ or to RE$^{3+}$ clusters (the a lines in Ref. 8).

As shown by figures 1 and 2(a) the separation of the closest FS lines from the related CF one may be as small as $\sim$0.4 cm$^{-1}$ (i.e. $\sim$5×10$^{-5}$ eV) and the spacing between neighbor FS lines is in the $\sim$0.2-0.8 cm$^{-1}$ range.

In principle the FS lines might be attributed to 1) hyperfine splitting due to $^{167}$Er (22.94% natural abundance) and $^{169}$Tm (100% natural abundance) nuclear spins (I=7/2 and 1/2, respectively) interaction with the 4f-electron total angular momenta; 2) isotopic effects due to the presence, in addition to $^{167}$Er, of $^{166}$Er, $^{168}$Er, and $^{170}$Er of comparable natural abundance (33.41, 27.07, and 14.88%, respectively); 3) vibronic transitions in which the incoming photon excites simultaneously a CF electronic transition and a BaY$_2$F$_8$ lattice mode; 4) simultaneous excitation of both an electronic transition and a low energy local mode (e.g. hindered rotations, librations) induced by the RE$^{3+}$ doping.
The FS shows a large number of lines of different amplitudes, see figures 1 and 2(a), which cannot be accounted for by the 2I+1 lines of comparable amplitudes expected on the basis of a possible hyperfine interaction for Er$^{3+}$ and Tm$^{3+}$ (eight and two, respectively). Furthermore hyperfine interaction should be excluded, because once the value of the coupling constant for a given RE and the CF eigenfunctions of that RE in the host crystals [8] are known, its associated features and their energy splittings should follow determinate quantitative and qualitative patterns [13-14] which are not compatible with the present observations. Even isotopic effects should be ruled out in the case of Er$^{3+}$ doped samples, because the number of lines expected is lower than that observed and the spacing among lines should be much smaller, i.e. $\sim 1 \times 10^{-3}$ cm$^{-1}$, as in the case of Er$^{3+}$ doped LiYF$_4$ tetragonal single crystals [15]. The FS lines cannot be induced by vibronic transitions [16-17], because the separation of the strongest among the FS lines from the CF lines is extremely small (of the order of a few tenths of cm$^{-1}$, i.e. $\sim 10^{-4}$ eV): the density of states for lattice modes of such low energies is negligible.

Figure 2. (a) Optical absorption spectra of a BaY$_2$F$_8$: Tm$^{3+}$ 1 at% sample in the region of the $^3$H$_6 \rightarrow ^3$F$_4$ transition measured at 9 K with linearly polarized light propagating along the c axis (res.=0.04 cm$^{-1}$). Curves a and b: electric field orthogonal and parallel to the a axis, respectively. Arrows indicate some of the FS lines associated with the A1 (solid red) and A2 (dashed blue) CF lines. (b) The FS line shifts from the related CF A1 (▼) and A2 (▲) lines as a function of a quantum number n. Solid line is the linear fit of the experimental data.

The last hypothesis, i.e. the simultaneous excitation of both electronic transition and local modes (e.g. hindered rotations, librations) is supported by 1) the BaY$_2$F$_8$ structure, 2) RE$^{3+}$ size, and 3) rotational constant B of RE$^{3+}$-F$_n$ groups (B=$\hbar^2/2M_l$, where $\hbar$ is the reduced Planck’s constant and $M_l$ is the RE$^{3+}$-F group moment of inertia). In monoclinic BaY$_2$F$_8$, Y$^{3+}$ ion is surrounded by eight F$^-$ anions: four are classified as F1, two as F2, and two as F3 [11]. The rather large thermal parameter suggests that the F3 may be slightly out of the binary axis and may benefit of some mobility. Furthermore, Er$^{3+}$ and Tm$^{3+}$ ionic radii (1.14 and 1.13 Å, respectively, for fluorides and coordination number=8, as in BaY$_2$F$_8$ [18]) are smaller than that of Y$^{3+}$ (1.16 Å), which they substitute for, thus providing additional
room for possible F motion. From the separation F3-Y3+-Y3+ (or F3-RE3+ in doped samples)=2.242 Å [11]
and the Er3+, Tm3+, and F masses, 2B for the F3-Er3+ and F3-Tm3+ complexes can be easily calculated as 2B_{calc}=0.39 cm⁻¹.

On the basis of the above premises the separations (shifts) of the FS lines from the related CF line were collected 1) for all the 'decorated' CF lines appearing in unpolarized spectra of Er3+ and Tm3+ doped samples and 2) for different Er3+ concentrations. The shifts of the lines, symmetrically located with respect to the related CF line, were selected and plotted vs. a quantum number n. The experimental data could be well fitted to straight lines, from whose slope the 2B parameter could be easily evaluated as 2B_{exp}=(0.36±0.006) cm⁻¹ for both Er3+ and Tm3+ FS line progressions. The average 2B_{exp} value, obtained for different transitions and concentrations, is in good agreement with the 2B_{calc} reported above for F3-RE3+ complexes. Slightly different 2B_{exp} values were obtained by considering, among the FS lines related to a given CF line, only the 'strongest' ones (i.e. those closest to the CF line), for example in the case of the FS accompanying A1 and A2 Tm3+ CF lines displayed in figure 2(a): the plot of the FS line shifts from the related CF A1 and A2 lines vs. quantum number n, portrayed in figure 2(b), supplies a value of 2B_{exp}=(0.41±0.01) cm⁻¹, which is anyway in excellent agreement with 2B_{calc}=0.39 cm⁻¹. Similar linear dependence of the lines belonging to P and R branches as a function of a rotational quantum number was found for OCS molecules embedded in liquid He droplets [5].

In spite of the overall self consistency of the description supplied, some criticisms and refinements may be put forth. 1) The description of F-RE3+ complex as a free-rotator is naïve: more likely the F-RE3+ complex mobility is restricted and characterized by hindered rotations and/or librations, and 2) a few of the FS lines actually monitored by the spectra do not fit in the linear plots. Beyeler [19] has calculated the vibration-rotation absorption spectra of 'rotator' hindered by fields of cubic symmetry for different energy barriers (separating potential minima) and temperatures. The simulation supplies line-rich spectra, which resemble closely those accompanying the RE3+ CF lines (originated by electronic transitions) in the present work. The lines are not equally spaced, unless the barrier vanishes and/or the temperature is high enough to allow 'free rotations'. At low temperatures the lines are fewer and are due to librations of the molecular group within the potential wells: in this case the librational absorption lines appear on the high energy side, well separated from the central line. For KT<<V_0, where V_0 is the energy barrier, the molecular group occupies levels below the top of the barrier and the energy levels are those of a harmonic oscillator of frequency ν_{libr} which depends on V_0 and on the rotational constant B as

\[ \nu_{\text{libr}} = 2 \left( \frac{V_0 B}{\nu_{\text{libr}}} \right)^{1/2} \]  (1)

where ν_{libr}, V_0, and B are expressed in cm⁻¹ [4]. Tunnelling across the energy barrier is also expected.

In the case of BaY2F8: Tm3+, in addition to the closely spaced FS lines overlapping the A2 and A1 CF lines at 5681.8 and 5683.45 cm⁻¹, respectively, there are two groups of much weaker FS lines on the higher energy side, separated from the A1 and A2 lines by about 4.5 and 4.7 cm⁻¹, respectively, see figure 2(a). The main lines of the two groups peak at 5686.27 and 5688.2 cm⁻¹, respectively, and exhibit the same polarization dependence as the A1 and A2 lines do, see figure 2(a): they may be regarded as librational lines associated to the A1 and A2 lines. Although Eq. (1) was written for a cubic potential, which is not necessarily that probed by the F: Tm3+ complex in BaY2F8, however V_0 may be roughly estimated by assuming librational frequencies ν_{libr}=4.5 and 4.7 cm⁻¹ and 2B_{exp}=0.41 cm⁻¹ (see above). The resulting values of V_0 are about 25 and 27 cm⁻¹, i.e. the energy barrier 'seen' by the librating F: Tm3+ molecular group, when the Tm3+ electronic transition starts from the first excited sublevel and from the lowest one within the ground 3H₉ manifold, respectively, to reach the first sublevel of the excited 3F₂ manifold (A2 and A1 lines). The low values of V_0 (of the order of 3×10⁻³ eV) explain why the FS lines are no longer detectable yet at T>60 K (see above), due also to the thermally induced line broadening. At high temperature the F: Tm3+ molecular group experiences a precession around a fixed axis: a thermally activated process makes it able to pass over the barrier which separates different angular positions, corresponding to the potential minima. However the typically free-rotator line spectrum cannot be detected due to the simultaneous line broadening. At low
temperatures the barrier can be crossed only by tunneling and the F-Tm\(^{3+}\) molecular group performs only small angular oscillations (librations) within the well.

In BaY\(_2\)F\(_8\): Er\(^{3+}\) spectra it is difficult to identify unequivocally a librational line, from whose position \(V_0\) might be, at least roughly, estimated according to Eq. 1. The Er\(^{3+}\) FS lines are no longer distinguishable at temperatures as low as 40 K (see above): this suggests that the energy barrier which separates different orientations of the F-Er\(^{3+}\) complex is still less than that estimated for the F-Tm\(^{3+}\) one. Thus 9 K can be regarded as a temperature high enough to forbid the librational line detection.

In conclusion, by taking advantage of high resolution spectroscopy applied at low temperatures and sharpness of CF lines, due to Er\(^{3+}\) and Tm\(^{3+}\), it was possible to detect in BaY\(_2\)F\(_8\) crystals a fine structure, composed by series of weak and closely spaced lines, accompanying the narrowest among the CF lines, which is ascribed to the simultaneous excitation of an electronic CF transition and of a local librational (or hindered rotation) mode of the RE\(^{3+}\)-F group. The attribution is supported by specific features of the host matrix and guest rare earths, which allow some mobility of F ions and by the spacing of the FS lines which is in excellent agreement with the calculated RE\(^{3+}\)-F group rotational constant. The energy barrier which separates different potential minima could be, at least roughly, evaluated as low as 3×10\(^{-3}\) eV in BaY\(_2\)F\(_8\): Tm\(^{3+}\). The FS lines can be regarded as a rot(electr)onic structure: its pattern resembles that displayed by the extensively studied rotovibrational spectra (anyway not well resolved in crystalline solids [1-2]), but, at variance of the latter, its detection is quite rare and difficult, especially in the case of low energy ‘rotational’ modes, as in the present work.

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