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Site-selective upconversion excitation of $\text{Er}^{3+}:\text{KYF}_4$

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Abstract. A spectroscopic study of the green ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and blue ($^2\text{P}_{3/2} \rightarrow ^4\text{I}_{11/2}$) emissions from $\text{Er}^{3+}:\text{KYF}_4$ induced by a red tunable laser excitation is realized at liquid nitrogen temperature, for two Er^{3+} concentrations: 0.1 and 5 at.%. The emission spectrum can only be accurately interpreted by considering that it is due to two sites, whose contributions are successfully isolated using a two-step absorption process via $^4\text{I}_{13/2}$ for the green emission and a three-step absorption process via $^4\text{I}_{13/2}$ and $^4\text{S}_{3/2}$, for the blue emission. The excited-state energy transfer prevails over the excited-state absorption at high concentration (5 at.%).

1. Introduction

In the KYF_4 structure there are six crystallographic yttrium sites which can be substituted by trivalent erbium ions [1]. However, it is assumed that the erbium ions are distributed among only three of six sites in the KYF_4 crystal doped with 5 at.% Er^{3+} [2]. The same situation is observed for KYF_4 crystals doped with Eu^{3+} where four optical centres are detected [3]. On the other hand, the $\text{Er}^{3+}:\text{KYF}_4$ system is attractive from the viewpoint of upconversion-pumped solid-state lasers [4].

In this paper, we achieve a spectroscopic analysis of the laser-induced luminescence of Er^{3+} ions in KYF_4 , for Er^{3+} concentrations of 0.1 and 5 at.%. We separate the excitation and emission spectra arising from two different crystallographic sites. Red to green and red to blue upconversions are investigated with the aim of better understanding of the multiphoton excitation mechanisms. In the last ten years, the potentialities of such mechanisms gave rise to a strong interest [5, 6]. It will also be noted that to date no study of site-selective laser spectroscopy has been reported for the $\text{Er}^{3+}:\text{KYF}_4$ system.

2. Experiment

The single KYF_4 crystals doped with Er^{3+} ions (0.1 and 5 at.%) were grown under hydrothermal conditions [2]. The crystals were synthesized by a direct temperature-gradient method as a result of the reaction of aqueous solutions of KF (26–32 mol%) with appropriate mixtures of oxides Y_2O_3 and Er_2O_3 (99.995% pure) at a temperature of about 750 K, a temperature gradient of about 2 K cm^{-1} and pressures of 100–150 MPa. For the hydrothermal experiments autoclaves with copper liners having volume of about 40 cm^3 were utilized. Under these conditions isometrical hexagonal crystals up to 0.5 cm^3 in size were grown in the upper region

of the autoclave. The phase homogeneity of the synthesized crystals and the perfection of the crystal lattice were tested by the x-ray powder diffraction method [7]. For spectroscopic investigations, unoriented platelets of the crystals were used.

Excitation methods similar to those described in [8] were used. The crystals were cooled to liquid nitrogen temperature. The Er^{3+} ions were excited in the red spectral range with a tunable dye laser (Spectra Physics 375) pumped by a CW argon ion laser. The laser wavenumber was adjusted to obtain the maximum signal. The luminescence was dispersed by a Coderg monochromator and detected by an EMI 9558 QB photomultiplier.

The luminescence decays were measured using an electrooptic modulator (Gsänger, model LM0202) and a Metrix oscillograph (OX 750-2) interfaced with a microcomputer.

The absorption spectra were recorded at room temperature with a Perkin-Elmer lambda 9 spectrophotometer, and at low temperature (6 K) with a Cary 2300 spectrophotometer, at the University Claude Bernard Lyon 1.

The excitation spectra obtained by monitoring the luminescence intensity as a function of the laser wavenumber give clear information on the upconversion mechanism. These spectra consist of different sets of lines corresponding to ground state absorptions (GSA) and excited state absorptions (ESA) involved in the filling process of the emitting levels.

3. Results and discussion

The GSA spectrum of Er^{3+} in KYF_4 at 6 K (figure 1) corresponding to the transition $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ extends from 15 270 to 15 550 cm^{-1} . In this range, seven lines are visible, each of them being related to one sublevel of $^4\text{F}_{9/2}$.

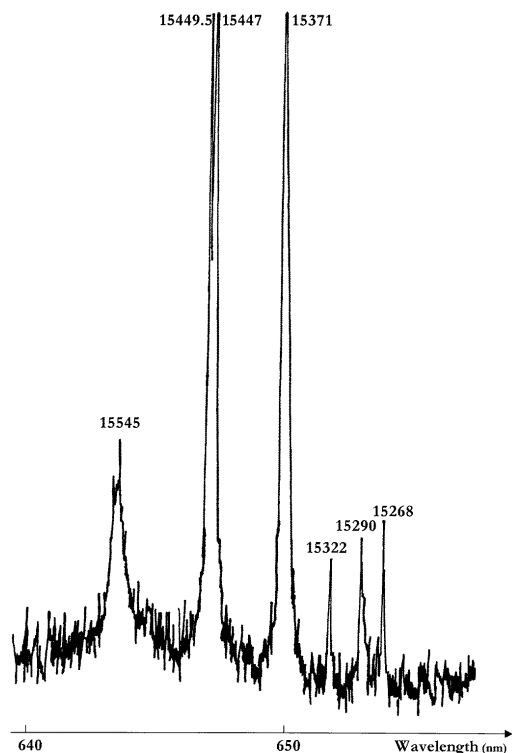
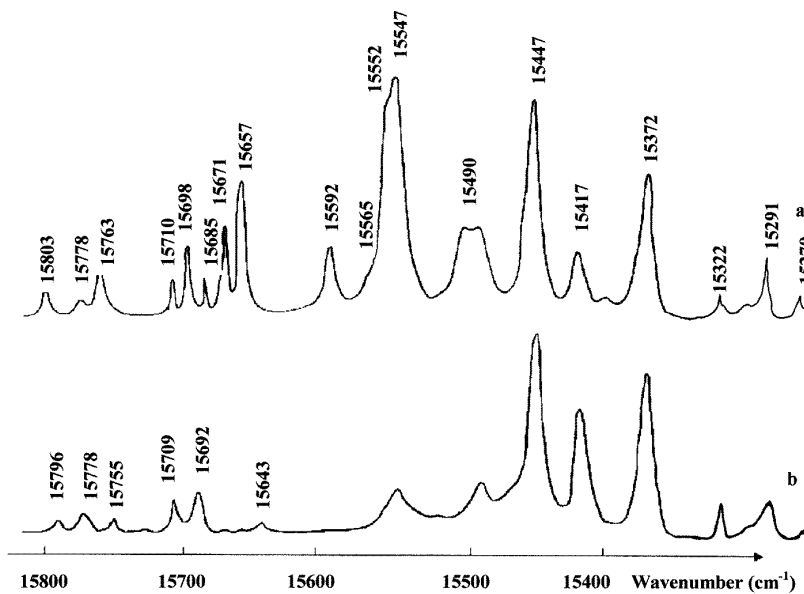


Figure 1. $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ absorption spectrum of Er^{3+} (5 at.%) KYF_4 at 6 K (the line positions are given in cm^{-1}).

Table 1. ${}^4\text{S}_{3/2}(\text{E}_i) \rightarrow {}^4\text{I}_{15/2}(\text{Z}_i)$ luminescence lines (in cm^{-1}) observed in the spectra of figure 3.

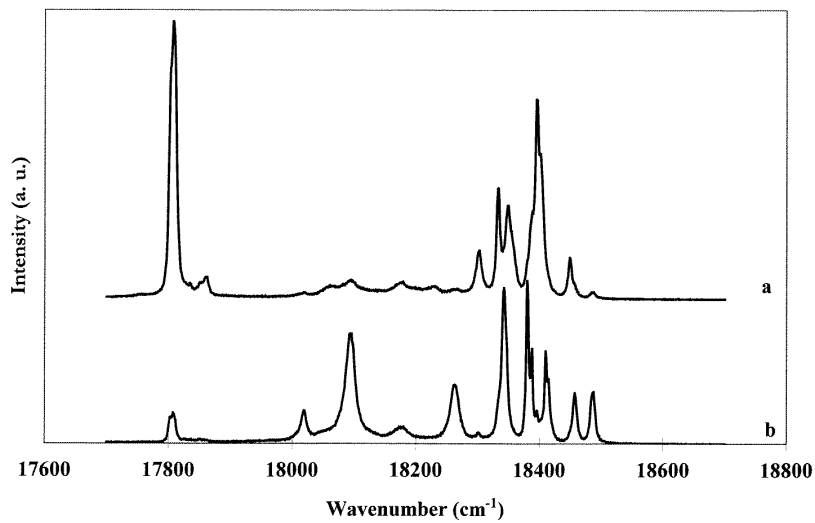
Line (cm^{-1})	Site	Transition
17 808	A	$\text{E}_1 \rightarrow \text{Z}_8$
17 861	A	$\text{E}_2 \rightarrow \text{Z}_8$
18 020	B	$\text{E}_1 \rightarrow \text{Z}_8$
18 095	B	$\text{E}_2 \rightarrow \text{Z}_8$
18 263	B	$\text{E}_1 \rightarrow \text{Z}_5$
18 302	A	$\text{E}_1 \rightarrow \text{Z}_5$
18 333	A	$\text{E}_1 \rightarrow \text{Z}_4$
18 342	B	$\text{E}_1 \rightarrow \text{Z}_4, \text{E}_2 \rightarrow \text{Z}_5$
18 349	A	$\text{E}_1 \rightarrow \text{Z}_3$
18 380	B	$\text{E}_1 \rightarrow \text{Z}_3$
18 388	B	$\text{E}_1 \rightarrow \text{Z}_2$
18 395	A	$\text{E}_1 \rightarrow \text{Z}_2$
18 410	B	$\text{E}_1 \rightarrow \text{Z}_1$
18 415	B	$\text{E}_2 \rightarrow \text{Z}_4$
18 449	A	$\text{E}_1 \rightarrow \text{Z}_1$
18 458	B	$\text{E}_2 \rightarrow \text{Z}_3$
18 487	B	$\text{E}_2 \rightarrow \text{Z}_1$

**Figure 2.** Excitation spectra of the green luminescence from Er^{3+} (0.1 at. %): KYF_4 at 77 K. The luminescence is detected at (a) $17\,808\text{ cm}^{-1}$ (A site) and (b) $18\,095\text{ cm}^{-1}$ (B site).

First, we present the results relative to $\text{Er}(0.1\%):\text{KYF}_4$. The spectrum of the green luminescence (${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions), induced by the laser tuned on $15\,447\text{ cm}^{-1}$, is composed of 17 major lines listed in table 1. This spectrum can be only accurately interpreted by considering that it is due to two distinct sites (called A and B), whose contributions are separated by a two-step absorption process (figure 1 of [8]). The same conclusion is inferred from the analysis of the blue and red luminescences, respectively attributed to the ${}^2\text{P}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transitions.

Table 2. ${}^4I_{13/2}(Y_i) \rightarrow {}^4F_{5/2}(H_i)$ excitation lines (in cm^{-1}) observed in the spectra of the figure 2.

Line (cm^{-1})	Site	Transition
15 803	A	$Y_1 \rightarrow H_3$
15 796	B	$Y_1 \rightarrow H_3$
15 778	A, B	$Y_2 \rightarrow H_3, Y_1 \rightarrow H_2$
15 763	A	$Y_3 \rightarrow H_3$
15 755	B	$Y_2 \rightarrow H_3$
15 710	A	$Y_1 \rightarrow H_2$
15 709	B	$Y_3 \rightarrow H_3$
15 698	A	$Y_1 \rightarrow H_2$
15 692	B	$Y_2 \rightarrow H_1, Y_3 \rightarrow H_2$
15 685	A	$Y_2 \rightarrow H_2$
15 671	A	$Y_2 \rightarrow H_2, Y_3 \rightarrow H_2$
15 657	A	$Y_3 \rightarrow H_2$
15 645	B	$Y_3 \rightarrow H_1$
15 592	A	$Y_1 \rightarrow H_1$
15 565	A	$Y_2 \rightarrow H_1$
15 552	A	$Y_3 \rightarrow H_1$

**Figure 3.** ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ luminescence spectra of Er^{3+} (0.1 at.%) $:\text{KYF}_4$ at 77 K. The laser wavenumber is tuned on (a) $15\,657\text{ cm}^{-1}$ (A site), (b) $15\,692\text{ cm}^{-1}$ (B site). The green luminescence is generated by a two-step absorption process via ${}^4I_{13/2}$.

The excitation spectrum of the green luminescence (detected at $17\,808\text{ cm}^{-1}$ for the A site or at $18\,095\text{ cm}^{-1}$ for the B site) consists of two sets of lines (figure 2): the ESA lines corresponding to the ${}^4I_{13/2} \rightarrow {}^4F_{5/2}$ transitions (table 2) are located on the high-energy side, the GSA lines corresponding to the ${}^4I_{15/2} \rightarrow {}^4F_{9/2}$ transitions on the low-energy side. An overlap between ESA ($15\,552\text{ cm}^{-1}$) and GSA ($15\,547\text{ cm}^{-1}$) is observed for A but not for B. The selective excitation of each site is achieved with an ESA line (figure 3): $15\,657\text{ cm}^{-1}$ (A), $15\,692\text{ cm}^{-1}$ (B). The three minor lines which appear clearly in figure 3 around $18\,050$, $18\,175$

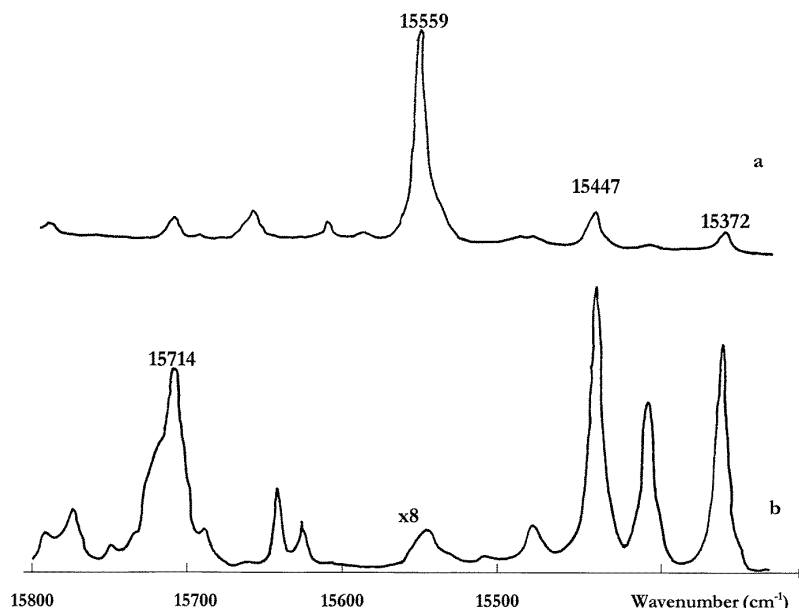


Figure 4. Excitation spectra of the blue luminescence from Er^{3+} (0.1 at.%) KYF_4 at 77 K. The luminescence is detected at (a) $21\,095\text{ cm}^{-1}$ (A site) and (b) $21\,339\text{ cm}^{-1}$ (B site).

and $18\,235\text{ cm}^{-1}$ have not been attributed in the absence of evidence. We have detected a third site (called A') whose spectra are identical to within 1 cm^{-1} to those of A, except for two further ESA lines ($15\,676$, $15\,687\text{ cm}^{-1}$) and a specific emission line located at $17\,082\text{ cm}^{-1}$, instead of $17\,808\text{ cm}^{-1}$ for the A site.

The excitation spectrum of the blue luminescence (detected at $21\,095\text{ cm}^{-1}$ for the A site, (figure 4(a)) reveals only one main peak located at $15\,559\text{ cm}^{-1}$ attributed to a second ESA transition (${}^4\text{S}_{3/2} \rightarrow {}^4\text{G}_{7/2}$). Notice the small mismatch between GSA ($15\,547\text{ cm}^{-1}$), ESA1 ($15\,552\text{ cm}^{-1}$) and ESA2 ($15\,559\text{ cm}^{-1}$). A three-photon absorption process (figure 3 of [9]), via ${}^4\text{I}_{13/2}$ and ${}^4\text{S}_{3/2}$, is, thus, clearly identified. No discontinuity has been observed at $15\,559\text{ cm}^{-1}$ in the excitation spectrum of the green luminescence for site A (figure 2(a)). Similar results are obtained for the B site (blue luminescence detected at $21\,339\text{ cm}^{-1}$, figure 4(b)) with an ESA line located at $15\,714\text{ cm}^{-1}$, greatly shifted relative to the GSA lines so that the three-step absorption process is less efficient than for the A site. The selective excitation of each site is achieved with an ESA line (figure 5): $15\,559\text{ cm}^{-1}$ (A), $15\,714\text{ cm}^{-1}$ (B). We give, in table 3, the Stark sublevel energies of Er^{3+} multiplets involved in the two- and three-step absorption processes, for the A and B sites. Notice that four Stark sublevels have been found for ${}^4\text{F}_{5/2}$ (A site) instead of three sublevels predicted by the theory for only one site. We believe that this discrepancy is due to the A' site.

In comparison with Er (0.1%): KYF_4 , no new lines appear in the spectrum of the blue emission from Er (5%): KYF_4 excited under $15\,447\text{ cm}^{-1}$. This spectrum is due to A and B sites (table 4). At 77 K, the blue emission is almost as intense as the green one but, by increasing the temperature from 77 to 300 K, the blue luminescence intensity decreases by a factor of 10^2 and the green one by a factor of 10. Several factors tend to explain the strong decrease of the luminescence as the temperature increases from 77 to 300 K: excitation line broadening, nonradiative transitions and cross-relaxations more efficient at room temperature.

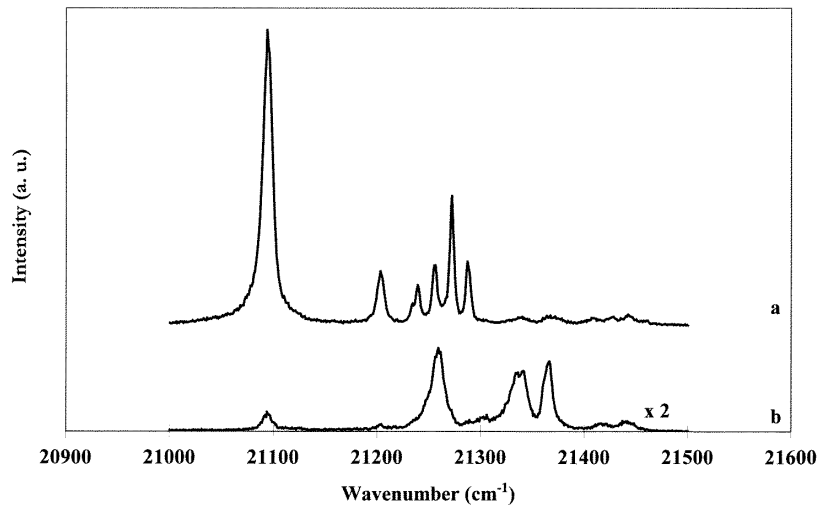


Figure 5. ${}^2P_{3/2} \rightarrow {}^4I_{11/2}$ luminescence spectra of Er^{3+} (0.1 at.%) KYF_4 at 77 K. The laser wavenumber is tuned on (a) $15\,559\text{ cm}^{-1}$ (A site) and (b) $15\,714\text{ cm}^{-1}$ (B site). The blue luminescence is generated by a three-step absorption process via ${}^4I_{13/2}$ and ${}^4S_{3/2}$.

Table 3. Stark sublevel energies (in cm^{-1}) of Er^{3+} multiplets involved in the multi-step excitation process.

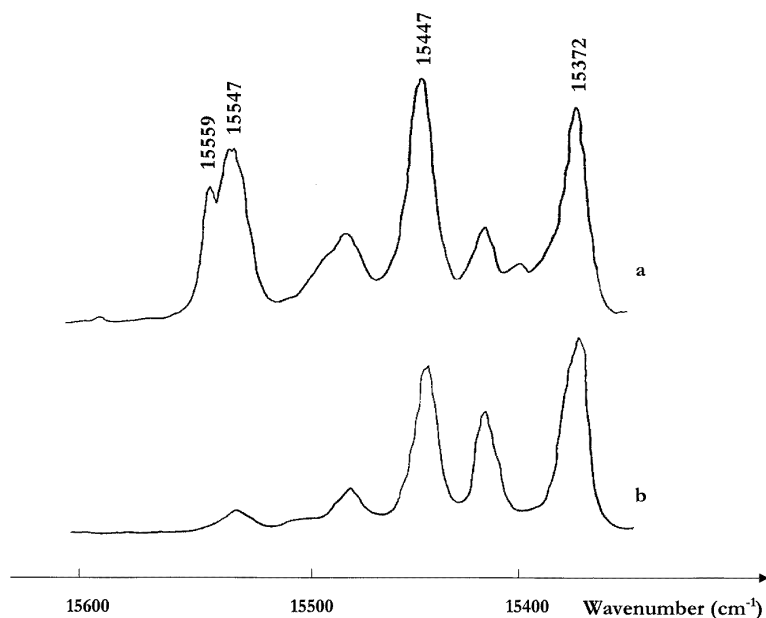
Multiplet	A centre	B centre
${}^4I_{15/2}$	0, 54, 100, 116, 147, 641	0, 30, 68, 147, 390
${}^4I_{13/2}$	6516, 6541, 6556	6532, 6574, 6620
${}^4I_{11/2}$	10 169, 10 187, 10 221, 10 256, 10 346	10 178, 10 203, 10 284
${}^4F_{9/2}$	15 323, 15 345, 15 547	15 291, 15 321, 15 373, 15 447, 15 520
${}^4S_{3/2}$	18 449, 18 502	18 410, 18 487
${}^4F_{5/2}$	22 108, 22 213, 22 226, 22 319	22 265, 22 310, 22 329
${}^2P_{3/2}$	31 441, 31 457	31 544, 31 618
${}^4G_{7/2}$	34 008	34 124

If the blue emitting level ${}^2P_{3/2}$ is populated through excited-state transfer from ${}^4S_{3/2}$ and ${}^4F_{9/2}$, the blue luminescence intensity will be proportional to the product of the populations of ${}^4S_{3/2}$ and ${}^4F_{9/2}$. Just like the green one, we have observed that the red fluorescence decreases by a factor of 10 between 77 and 300 K, which explains, assuming that the transfer coefficient does not depend upon the temperature, the decrease by a factor of 100 for the blue one.

In the excitation spectra of Er (5%) KYF_4 (figure 6) on the scale used for the recording, all the ESA lines disappear, except $15\,559\text{ cm}^{-1}$, while the GSA lines enhance strongly, signs of a higher activity of energy transfer upconversion [10]. The ESA probabilities from ${}^4I_{13/2}$ become negligible compared with the transfer (${}^4I_{13/2}, {}^4I_{13/2} \rightarrow {}^4I_{15/2}, {}^4I_{9/2}$). This is not the case of ESA from ${}^4S_{3/2}$ because this level is certainly less populated than ${}^4I_{13/2}$, which protects the ESA against the excited-state transfers. Though the Er^{3+} concentration is high (5 at.%), the blue luminescence from each site is still selectively excited by tuning the laser wavenumber on an ESA line starting from ${}^4S_{3/2}$ (figure 7): $15\,559\text{ cm}^{-1}$ (A), $15\,714\text{ cm}^{-1}$ (B). In the same conditions, the ${}^4S_{3/2}$ level is itself populated by an energy transfer involving Er^{3+} ions excited

Table 4. $^4\text{P}_{3/2}(\text{P}_i) \rightarrow 4\text{I}_{11/2}(\text{A}_i)$ luminescence lines observed in the spectra of figures 5 and 7.

Line (cm^{-1})	Site	Transition
21 095	A	$\text{P}_1 \rightarrow \text{A}_5$
21 203	A	$\text{P}_2 \rightarrow \text{A}_4$
21 240	A	$\text{P}_2 \rightarrow \text{A}_3$
21 255	A	$\text{P}_1 \rightarrow \text{A}_2$
21 259	B	$\text{P}_1 \rightarrow \text{A}_3$
21 272	A	$\text{P}_1 \rightarrow \text{A}_1, \text{P}_2 \rightarrow \text{A}_2$
21 288	A	$\text{P}_2 \rightarrow \text{A}_1$
21 334	B	$\text{P}_2 \rightarrow \text{A}_3$
21 341	B	$\text{P}_1 \rightarrow \text{A}_2$
21 366	B	$\text{P}_1 \rightarrow \text{A}_1$
21 417	B	$\text{P}_2 \rightarrow \text{A}_2$
21 440	B	$\text{P}_2 \rightarrow \text{A}_1$

**Figure 6.** Excitation spectra of the blue luminescence from Er^{3+} (5 at.%) KYF_4 at 77 K. The luminescence is detected at (a) $21\,095\text{ cm}^{-1}$ (A site) and (b) $21\,339\text{ cm}^{-1}$ (B site).

either on $^4\text{I}_{11/2}$ or on $^4\text{F}_{9/2}$. Thus, the green luminescence of two sites simultaneously occurs while the blue spectra are well separated.

A dynamic study is undertaken to try to specify the starting levels for the energy transfer leading to the blue emission. After a pulsed excitation into $^4\text{F}_{9/2}$ (pulse width $500\ \mu\text{s}$), the red emission exponentially decays with a time constant of $270\ \mu\text{s}$ (B), the green emission in $820\ \mu\text{s}$ (A) and $910\ \mu\text{s}$ (B) and the blue emission in $125\ \mu\text{s}$ (A) and $270\ \mu\text{s}$ (B). The shape of the decays is almost exponential. The lifetime measurements suggest that the blue emitting level is populated by an energy transfer between one Er^{3+} ion in $^4\text{S}_{3/2}$ and another in $^4\text{F}_{9/2}$.

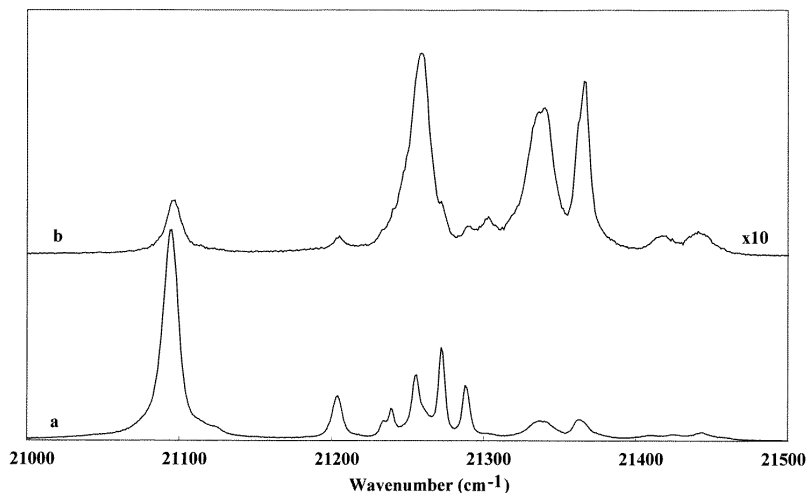


Figure 7. ${}^2P_{3/2} \rightarrow {}^4I_{11/2}$ luminescence spectra of Er^{3+} (5 at.%) KYF_4 at 77 K. The laser wavenumber is tuned on (a) $15\,559\text{ cm}^{-1}$ (A site) and (b) $15\,714\text{ cm}^{-1}$ (B site).

4. Conclusion

We have found two sites in $\text{Er}^{3+}:\text{KYF}_4$; either of them gives green and blue luminescences under red laser excitation. We have established the Stark sublevel energies and have clearly identified, at low concentration (0.1 at.%), a two-step absorption process which generates the green luminescence and a three-step absorption process which generates the blue luminescence. The sequential transfers predominate at high concentration (5 at.%).

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