On Eu³⁺ luminescence in the hexagonal NaYF₄ phase

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Abstract

The luminescence of Eu^{3+} in $NaYF_4$ is reported. Analysis of the $^5D_0 \longrightarrow {}^7F_1$ emission allows one to distinguish between the luminescence of Eu^{3+} in each of the two Y^{3+} sites. The strong absorption band in the short wavelength range of the reflection spectra is ascribed to a charge transfer process due to Eu–O (an impurity) interactions.

1. Introduction

Recently, several papers have been published on the luminescence of the hexagonal $NaLnF_4$ (Ln $\equiv$ Y, Gd, Tb, Ce, Eu, Nd, Ho) phase concerning its crystal structure [1, 2] and energy transfer processes [3, 4]. The possibility of using these compounds as diode-pumped IR solid state lasers [5] or for up-conversion laser action [6] has also been studied.

In all cases (except for Ln $\equiv$ Y) this material shows high luminescence efficiency. The present paper deals with some results on the luminescence of Eu^{3+} in $NaYF_4$. A more detailed investigation concerning especially the site symmetry will be given in a subsequent paper.

2. Experimental details

The preparation of powder samples has been described previously [1, 7]. For the emission and excitation measurements, carried out in our laboratory, a tunable dye laser pumped with a nitrogen laser (Jobin–Yvon LA04) was used as an excitation source. The resolution of this equipment is better than 0.5 cm^{-1}. The emission was detected using a Jobin–Yvon HR 1000 monochromator in combination with a photomultiplier (Hamamatsu R 1104). A PAR model 162/164 boxcar averager was used to record the time-resolved spectra. The diffuse reflection spectrum was obtained using a Perkin–Elmer Lambda 9 spectrophotometer (wavelength range from 200 to 2500 nm).

3. Structure

The hexagonal $NaLnF_4$ phase exists for Ln $\equiv$ Y, La–Lu. There are three cations sites, one fully occupied by rare earth ions ($1a$ site), one randomly occupied by both rare earth and sodium ions ($1f$ site) and the third fully occupied by sodium ions. According to the literature, this phase crystallizes in the $P\bar{6}$ space group, both rare earth sites having C_{3h} [8, 9] or D_{3h} [3] symmetry.

4. Results and discussion

Figure 1 gives the diffuse reflection spectrum of $NaEuF_4$ at 300 K. It consists of several lines between 300 and 600 nm and a surprisingly strong wide band between 200 and 300 nm. The lines can be attributed to intraconfigurational 4f–4f transitions originating from the ground $^7F_0$ level (also from the $^7F_1$ and $^7F_2$ levels at 300 K), whereas the wide band originates from transitions to charge transfer states (CTSs) due to Eu–O (an impurity) interactions (the Eu–F CTS lies at about 180 nm).

Upon excitation at 396 nm ($^7F_0 \longrightarrow {}^5L_6$ transition) the samples show efficient orange luminescence at 300 and 77 K. Figure 2 presents the emission spectrum of Eu^{3+} in $NaYF_4:Eu^{3+}$ (0.25%) at 77 K. It consists of several lines corresponding to $^5D_J \longrightarrow {}^7F_{J'}$ transitions. The excitation spectrum of the $^5D_0 \longrightarrow {}^7F_2$ emission does not reveal any band corresponding to CTSs.

In Fig. 3 a part of the emission spectra recorded for $NaY_{0.95}Eu_{0.05}F_4$ and $NaEuF_4$ at 77 K is shown. For the diluted compund the Eu^{3+} $^5D_0 \longrightarrow {}^7F_1$ emission consists of at least six lines instead of the expected four lines for two Eu^{3+} ions located on sites with C_{3h} or D_{3h} symmetry. In $NaEuF_4$ the $^5D_0 \longrightarrow {}^7F_1$ emission shows
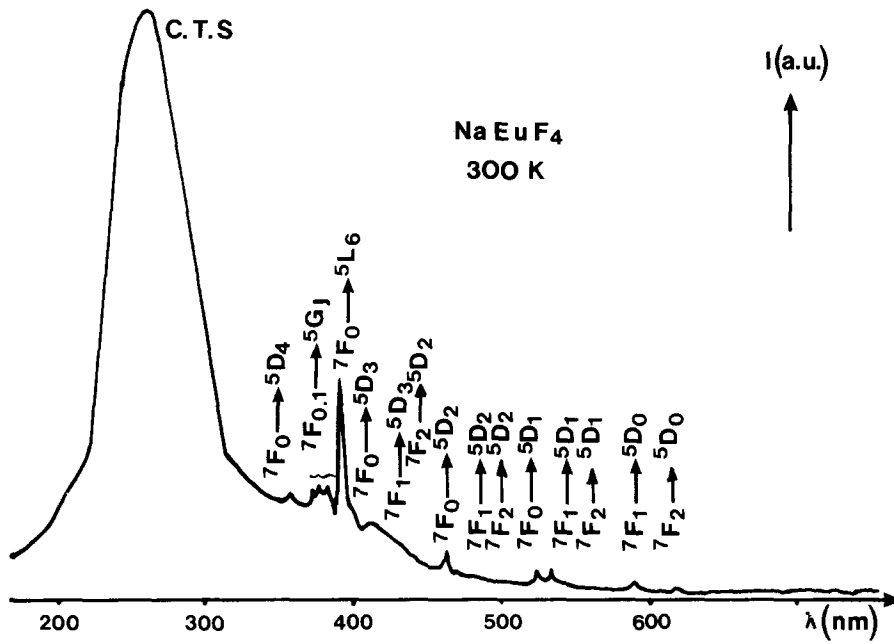
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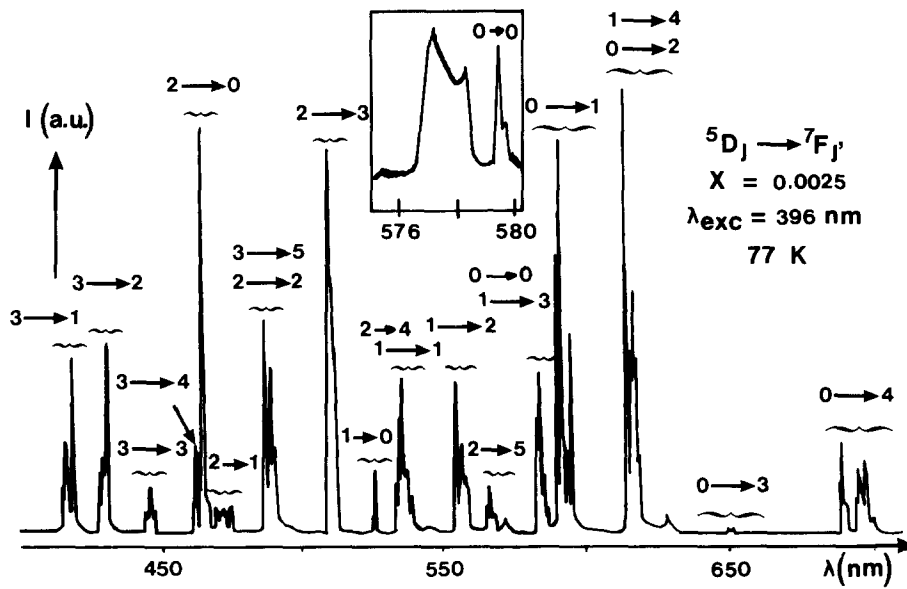
Fig. 1. Diffuse reflection spectrum of NaEuF₄ at 300 K.

Fig. 2. Emission spectrum of NaYF₄:Eu³⁺ (0.25%) at 77 K (excitation at 396 nm). The notation $J \longrightarrow J'$ refers to the transitions $^5D_J \longrightarrow {}^7F_{J'}$.

four lines, but the two labelled E2 and E3 are broader than those labelled E1 and E4. This observation indicates that the two emission lines E2 and E3 contain the two small emission lines marked with an asterisk on the Eu³⁺ $^5D_0 \longrightarrow {}^7F_1$ emission spectrum of the diluted sample (Fig. 3a). Ambiguities concerning the site symmetry exist based on the number of lines observed for

other transitions. Two (intrinsic) $^5D_0 \longrightarrow {}^7F_0$, and nine $^5D_0 \longrightarrow {}^7F_2$ transitions have been observed instead of zero and two for two Eu³⁺ ions respectively in sites with C_{3h} or D_{3h} symmetry. For the other transitions the number of observed lines is lower than the authorized number. This means that the real local symmetry of the Eu³⁺ ion is distorted from the ideal one proposed
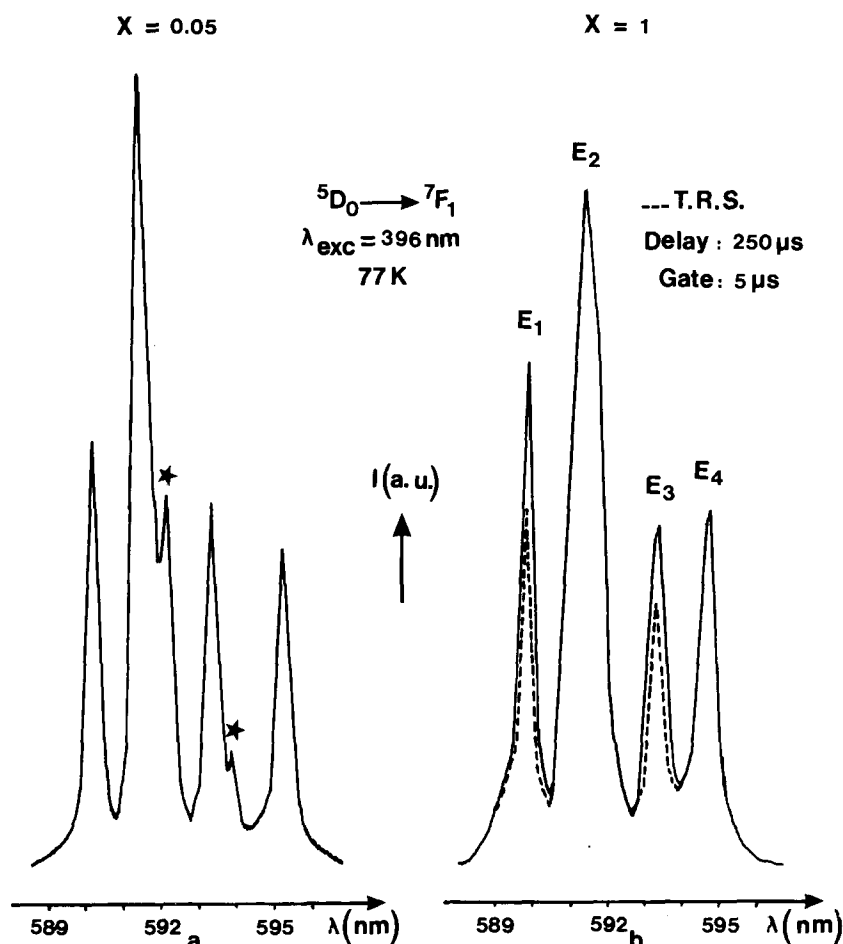
Fig. 3. Eu^{3+} $^5D_0 \longrightarrow {}^7F_1$ emission spectra at 77 K under 396 nm excitation in (a) NaYF$_4$:Eu^{3+} (5%) and (b) NaEuF$_4$: ——, integrated spectrum; ----, time-resolved spectrum (delay 250 μs, gate width 5 μs)

by Burns [8]. The number of observed lines is consistent with C_s point symmetry for the two rare earth sites [10].

Recording the fluorescence of NaEuF$_4$ a short time after the laser pulse (delay 250 μs and gate width 5 μs) (Fig. 3b) allows us to classify the lines of the $^5D_0 \longrightarrow {}^7F_1$ emission by pairs E1 + E3 and E2 + E4. These E1 + E3 and E2 + E4 pairs originate from the location of Eu^{3+} ions on the 1f and 1a sites respectively [3, 10].

The total splitting of both $^7F_1$ levels of the Eu^{3+} ions on the two sites as a function of concentration is reported in Fig. 4. The observed variations can be attributed to the existence of two different phases: a luminescent phase, the composition of which should be close to Na(Y$_{0.4}$Eu$_{0.6}$)F$_4$, and a non-luminescent phase, as suggested by the constant splittings of both $^7F_1$ levels between $X_{Eu} = 20\%$ and 60% and by the existence at high temperature of several homogeneity domains of variable composition in the NaF–LnF$_3$ system [9, 11]

with a cubic unit cell. This assumption is not consistent with the linear dependence of the volume of the unit cell on the concentration of Eu^{3+} ions in NaYF$_4$, as shown in the inset of Fig. 4. Moreover, the unit cell volume of the cubic phases mentioned above is always more important than the unit cell volume of the hexagonal phase.

The emission spectra of the weakly doped compounds, upon excitation at 337.1 nm (nitrogen laser radiation), showed satellite lines in the $^5D_0 \longrightarrow {}^7F_{0-2}$ wavelength range as mentioned in ref. 12. The attribution of the two most intense lines to the $^5D_0 \longrightarrow {}^7F_0$ (at 578 nm) and $^5D_0 \longrightarrow {}^7F_2$ (at 622 nm) emission transitions originating from an Eu^{3+} ion near an oxygen impurity was supported by the observation of the Eu–O CTS in the diffuse reflection spectra as mentioned above. Moreover, a similarity between the extra lines of the emission spectra and the emission spectra registered in rare earth (RE) oxysalts (see e.g. ref. 13), where the luminescent species is the (REO)$_n^{n+}$ complex
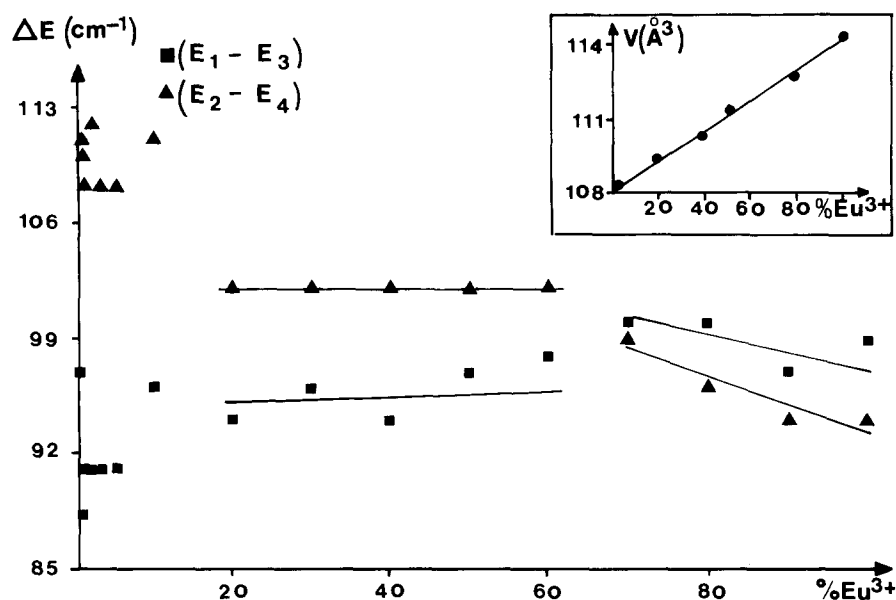
Fig. 4. Splitting of the $^7F_1$ levels as a function of the Eu^{3+} concentration in $NaYF_4:Eu^{3+}$ at 77 K. The inset indicates the evolution of the volume of the unit cell of $NaYF_4:Eu^{3+}$ as a function of concentration.
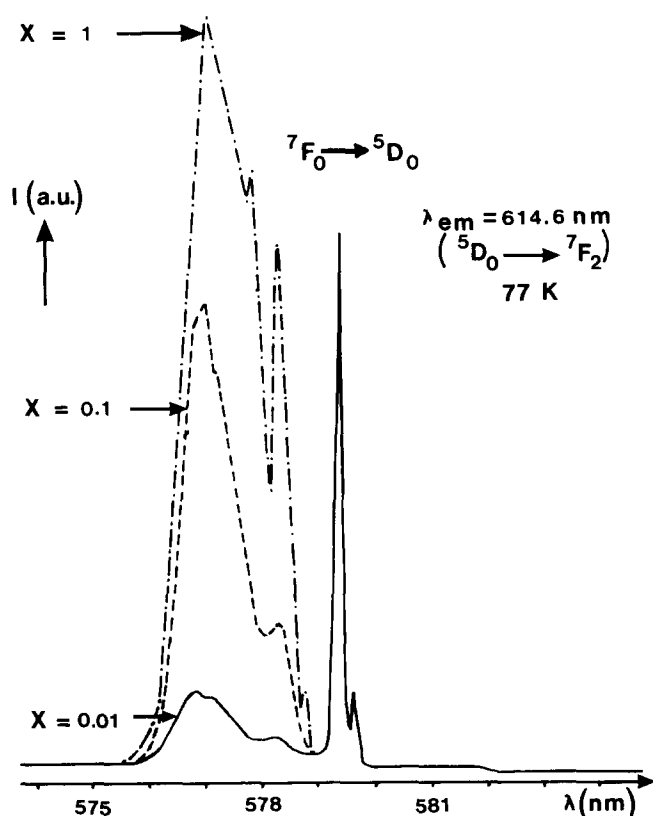

Fig. 5. $^7F_0 \longrightarrow {}^5D_0$ excitation spectra for the Eu^{3+} $^5D_0 \longrightarrow {}^7F_2$ emission in $NaY_{1-x}Eu_xF_4$ at 77 K.

cation, has been observed. On the other hand, resonant lines were found in the excitation spectra as shown in Fig. 5. In this figure the narrow lines at 579.4 and 579.7 nm correspond to the $^7F_0 \longrightarrow {}^5D_0$ absorption transitions of the two Eu^{3+} ions on $1a$ and $1f$ sites [10]. The excitation bands around 578 nm correspond to the $^7F_0 \longrightarrow {}^5D_0$ transitions of Eu^{3+} ions neighbouring an oxygen impurity in the form of an O^{2-} ion associated with a fluorine vacancy or incorporated in OH^- ions.

In conclusion, the spectroscopic results for $Eu:NaYF_4$ indicate that the two rare earth sites are distinguishable. An interesting feature is the observation of satellite lines in the excitation spectra as well as in the emission spectra of the diluted compounds. These lines have been attributed to the presence of oxygen impurities. Further investigations concerning the characterization of this host material with respect to the site symmetry of the rare earth and the attribution of the extra lines will be undertaken.

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