Spectroscopic study of Eu^{3+} in the fluorapatite $Sr_{10}F_2(PO_4)_6$

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Abstract

The luminescence of the Eu^{3+} ion in the fluorapatite $Sr_{10}F_2(PO_4)_6$, prepared by solid state reaction and by co-precipitation, is reported. For low amounts of Eu^{3+}, the ion is incorporated into the C_s site of the structure. Some extra emissions are also observed, due to the substitution of O^{2-} and OH^- for F^-. Due to this fact, five sites for Eu^{3+} are thus optically detected and chemically characterized.

1. Introduction

The Eu^{3+} ion is known as an active element for red-emitting phosphors. It is moreover a very useful structural and optical probe. The optical properties of Eu^{3+} have thus been investigated in many matrices. In a first paper, some preliminary spectroscopic studies about Eu^{3+} doped $Sr_{10}F_2(PO_4)_6$ were presented [1]. It was observed that the presence of O^{2-} or OH^- ions in the F^- site induced some extra emission bands, due to the sensitivity of Eu^{3+} to its environment.

This paper deals with a more complete characterization of the Eu^{3+} ion sites in $Sr_{10}F_2(PO_4)$ based on the chemical synthesis of the doped compounds.

2. Experimental details

The doped samples were prepared using both solid state and co-precipitation methods.

2.1. Solid state

The fluorapatites $Sr_{10-2x}Eu_xNa_xF_2(PO_4)_6$ ($0 \leqslant x \leqslant 2$) were prepared by weighing out stoichiometric amounts of $Sr_3(PO_4)_2$, $EuPO_4$, Na_3PO_4 and SrF_2. The mixtures were put in a closed though not sealed platinum tube and heated up to 1100 °C for 2–20 h, depending on the x value. The samples were then air-quenched.

Another compound, with formula $Sr_{8.67}Eu_{0.67}Na_{0.67}F_2(PO_4)_6$ ($x = 0.67$) was made under the same experimental conditions; the starting materials were $Sr_3(PO_4)_2$, EuF_3 and Na_3PO_4 (SrF_2 was not used for this synthesis).

2.2. Co-precipitation

A solution containing $Sr(NO_3)_2$ and $Eu(NO_3)_3 \cdot 6H_2O$ was added at 25 °C into a solution containing 0.15 M H_3PO_4 and NH_4F, which was first basified with 1 M NH_{3aq} (pH = 10). During the addition, pH was maintained around 10 with 0.45 M NH_{3aq}. The precipitate was then filtered, washed with distilled water, dried at 110 °C and heated up to 1100 °C during 2 h. It was then air-quenched. This preparation was supposed to lead to a fluorohydroxyapatite.

A 0.1% Eu^{3+} doped strontium hydroxyapatite was also prepared for further optical studies, under identical experimental conditions, but without NH_4F. One part of the precipitate was heated up to 800 °C for 4 h, the other one up to 1100 °C during 4 h.

2.3. Characterization

The samples were characterized by X-ray diffraction; they showed a pure apatitic structure. The formula of the compounds prepared by co-precipitation was determined by chemical analysis. The supposed fluorohydroxyapatite was in fact a fluoroxyhydroxyapatite with formula: $Sr_{10-x}Eu_{2x/3}\Box_{x/3}F_\epsilon(OH)_{0.7}O_{(1.3-\epsilon)/2}\Box_{(1.3-\epsilon)/2}$ $(PO_4)_6$ ($0 \leqslant x \leqslant 2$) with $\epsilon = 0.157$ ($\Box$ = anionic or cationic vacancies). Infrared spectroscopy and thermogravimetric analysis showed that the "hydroxy" part came from the basic conditions and the "oxy" part from the following reaction:

$$2F^- + H_2O \longrightarrow O^{2-} + \Box + 2HF \qquad (1)$$
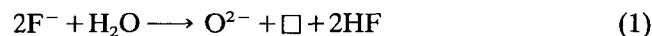
The doped hydroxyapatite prepared at 800 °C is $Sr_{9.985}Eu_{0.01}\Box_{0.005}(OH)_2(PO_4)_6$, whereas at 1100 °C an oxyhydroxyapatite is obtained, according to

$$2OH^- \longrightarrow O^{2-} + \Box + H_2O \qquad (2)$$
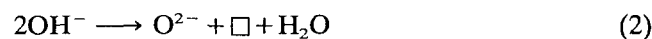
A fluorination test was also achieved by mixing a doped apatite with NH_4HF_2 and heating this mixture at 100 °C for 2 h and then at 400 °C for 1 h. A fluoroxyhydroxyapatite (with $x = 1.5$) and pure hydroxyapatite were treated this way. The IR spectra revealed that for the former, the OH^- band at 3570 cm^{-1} was increased; on the contrary no modification of the OH^- band intensity could be noticed for the latter.

3. Optical results

The apparatus for optical measurements was presented elsewhere [1]. The emission spectra of $Sr_{10-2x}Eu_xNa_xF_2(PO_4)_6$ prepared in solid state were recorded at 300 and 77 K under excitation at 337.1 nm. Figure 1 shows the spectrum obtained for $Sr_8EuNaF_2(PO_4)_6$. The luminescence arises quasi-exclusively from the $^5D_0$ level. Selective excitations into the $^5L_6$ and ^5D_J ($J > 0$) levels gave the same result; this indicates that the charge transfer band is relatively low. Nevertheless, this spectrum shows a very complex structure, indicating that there is more than one site occupied by Eu^{3+}. Figure 2 shows an expansion of the emission spectrum in the 565–580 nm wavelength range ($^5D_0 \rightarrow {}^7F_0$ transitions). Five transitions are present; this means that Eu^{3+} is incorporated into five different sites. The
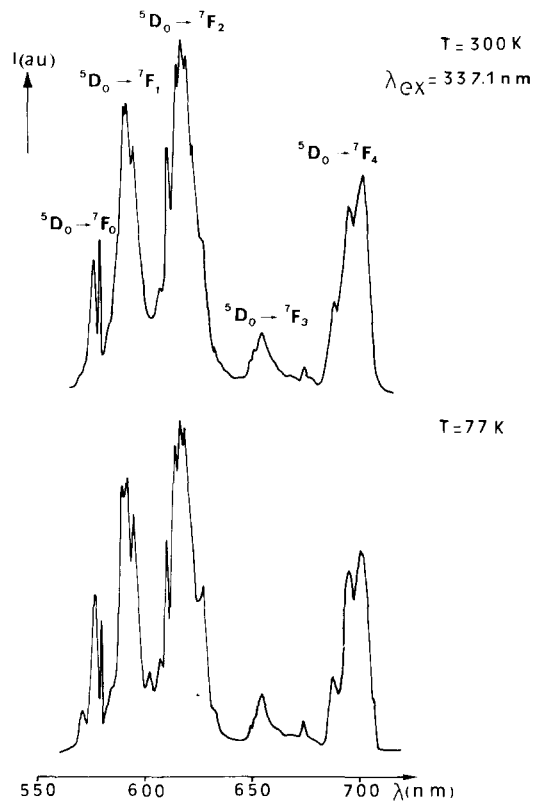

Fig. 1. Emission spectrum of Eu^{3+} in $Sr_8EuNaF_2(PO_4)_6$ prepared by the solid state reaction, at 300 and 77 K ($\lambda_{exc} = 337.1$ nm).
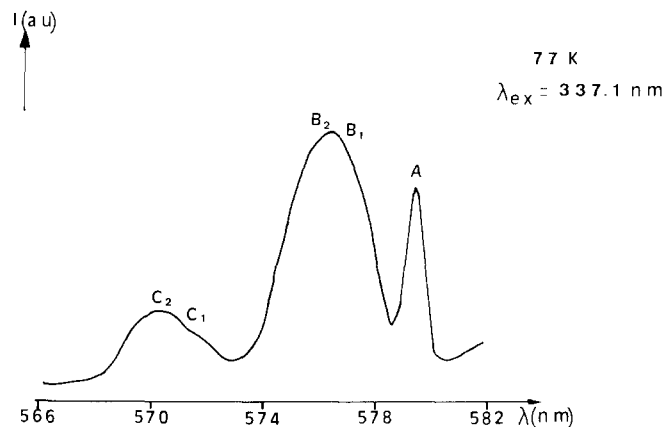

Fig. 2. Expansion of the emission spectrum of Eu^{3+} in $Sr_8EuNaF_2(PO_4)_6$ in the 565–580 nm wavelength range, at 77 K ($\lambda_{exc} = 337.1$ nm).
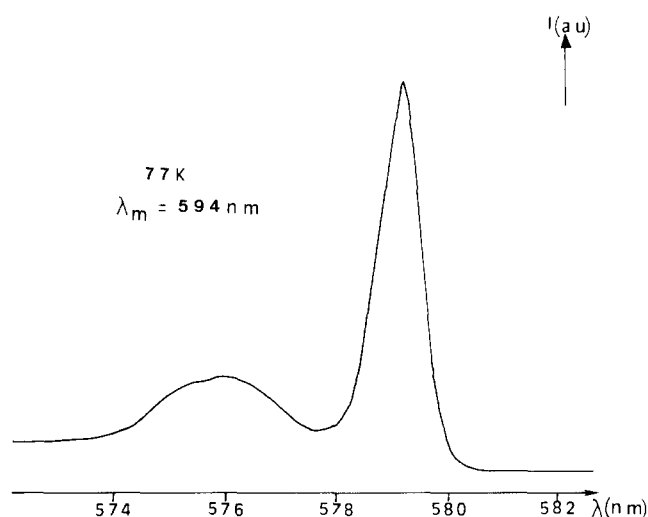

Fig. 3. Excitation spectrum of Eu^{3+} emission (site A) in $Sr_8EuNaF_2(PO_4)_6$ in the $^7F_0 \rightarrow {}^5D_0$ range, at 77 K.

wavelengths are: 579.2 (site A), 577.5 (site B_1), 576.0 (site B_2), 572.0 (site C_1) and 570.3 nm (site C_2). The band lying at 579.2 nm is very narrow. At 300 K, the emission corresponding to the sites C_1 and C_2 disappeared.

The excitation spectrum of the $^5D_0 \rightarrow {}^7F_1$ emission lying at 594 nm (site A) is shown in Fig. 3, in the $^7F_0 \rightarrow {}^5D_0$ wavelength range. The excitation bands corresponding to the sites A, B_1 and B_2 are observed, indicating that an energy transfer from Eu^{3+} in sites B_1 and B_2 to Eu^{3+} in site A exists.

The Eu^{3+} emission spectrum achieved at 77 K for $Sr_8EuNaF_2(PO_4)_6$ under excitation at 579.2 nm is shown in Fig. 4. This spectrum corresponds to Eu^{3+} ions incorporated into the C_s site of the fluorapatite, for which F^- is a part of the environment. Some time resolved spectroscopy measurements achieved for different gate and delay times gave the same spectra with the same intensity ratio between the different emission
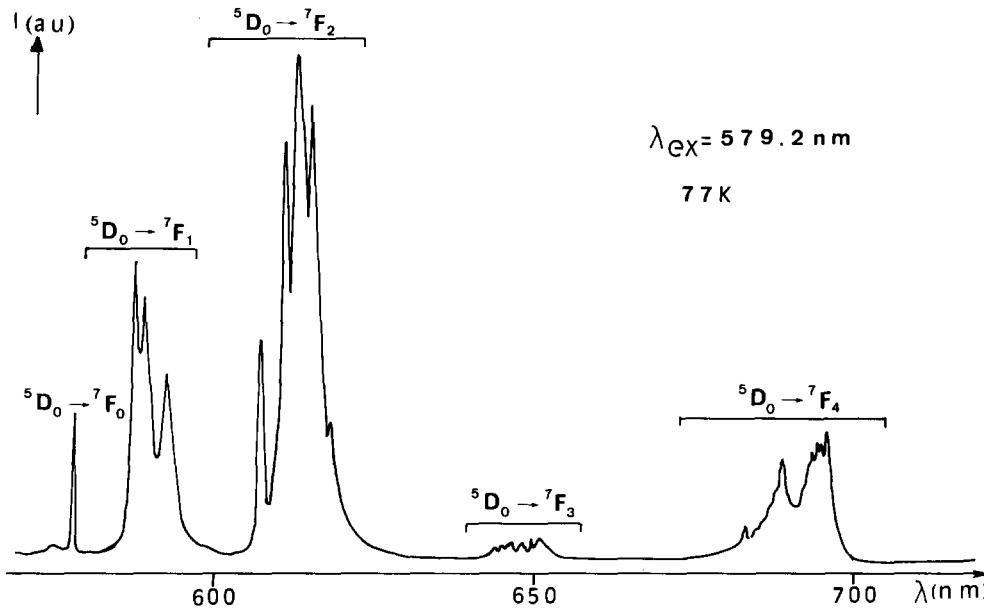
Fig. 4. Emission spectrum of Eu^{3+} in $Sr_8EuNaF_2(PO_4)_6$ prepared by the solid state reaction, at 77 K (λ_{exc} = 579.2 nm).

bands; this indicates that Fig. 4 is characteristic of the unicity of this C_s site. The wavelengths and energies of the observed emission bands are given in Table 1. It should be noted that the spectrum recorded for the compound $Sr_{8.67}Eu_{0.67}Na_{0.67}F_2(PO_4)_6$ prepared without SrF_2 is the same than that given in Fig. 4, whatever the excitation wavelength.

The emission spectrum achieved for $Sr_{8.5}Eu\square_{0.05}F_{0.16}(OH)_{0.7}O_{0.57}\square_{0.57}(PO_4)_6$ (x = 1.5) prepared by co-precipitation is given in Fig. 5. This spectrum is similar to that shown in Fig. 1. However, intensity for the emission belonging to site A decreased, whereas an increase was observed for the emissions corresponding to sites B_1, B_2, C_1 and C_2.

The emission spectra recorded for the hydroxyapatite $Sr_{9.985}Eu_{0.01}(OH)_2(PO_4)_6$ and the oxyhydroxyapatite $Sr_{9.985}Eu_{0.01}(OH)_{2-y}O_{y/2}(PO_4)_6$ (x = 0.015) are shown in Figs. 6(a) and (b), respectively. In Fig. 6(a), a $^5D_0 \rightarrow {}^7F_0$ emission at 571.4 nm is observed with a high intensity;

TABLE 1. Wavelengths and energies of the $^5D_0 \rightarrow {}^7F_J$ transitions for site A

λ (nm)	Energy (cm^{-1})	I/I_0 (%)	Assignment
579.2	17265	100	$^5D_0 \rightarrow {}^7F_0$
589.5	16963	100	$^5D_0 \rightarrow {}^7F_1$
590.1	16946	88	
694.4	16824	79	
609.7	16401	44	$^5D_0 \rightarrow {}^7F_2$
613.8	16291	82	
615.3	16253	100	
618.0	16181	90	
620.9	16106	27	

this emission is quenched for doping above 1% (x = 0.15). In Fig. 6(b), two bands appear, lying at 570.0 and 571.8 nm; no emission in the 575–577 nm wavelength range is observed.

Finally, after fluorination of the compound $Sr_{8.5}Eu\square_{0.05}F_{0.16}(OH)_{0.7}O_{0.57}\square_{0.57}(PO_4)_6$, the Eu^{3+} emission spectrum shows a decrease in intensity for the bands corresponding to the sites B_1, B_2, C_1 and C_2.

4. Discussion

In apatite-like phosphates, the Eu^{3+} ion is exclusively located in the C_s site and only for higher Eu^{3+} amounts would the C_3 site be occupied [2]. The Eu^{3+} ion located into the C_s site is hepta-coordinated: Eu^{3+} is surrounded by 6 oxygen atoms and the fluorine. It is thus clear that the luminescence shown in Fig. 4 is due to this Eu^{3+} ion, whereas the other bands are due to Eu^{3+} ions for which environment is modified by a partial substitution of O^{2-} and OH^- for F^-, depending on the synthesis. According to Fig. 6(a), it seems that the $^5D_0 \rightarrow {}^7F_0$ transition lying at 571.4 nm is due to a Eu^{3+}–OH^- ion-coupling, whereas in oxyhydroxyapatite (Fig. 6(b)) this emission is displaced to 570.0 nm, the band at 571.8 nm being due to a Eu^{3+}–O^{2-} ion-coupling. These two ion-couplings are observed for both fluoroxyhydroxyapatites prepared in the solid state or by co-precipitation; these Eu^{3+} sites were called C_1 and C_2. The existence of these transitions at 77 K only (Fig. 1) confirms such a hypothesis. Similarly, the bands appearing at 576.0 and 577.5 nm in the fluoroxyhydroxyapatite (Figs. 1 and 5) could be attributed to

Fig. 5. Emission spectrum of Eu^{3+} in $Sr_8Eu\square_{0.05}F_{0.16}(OH)_{0.7}O_{0.57}(PO_4)_6$ prepared by co-precipitation at 77 K (λ_{exc}=337.1 nm).

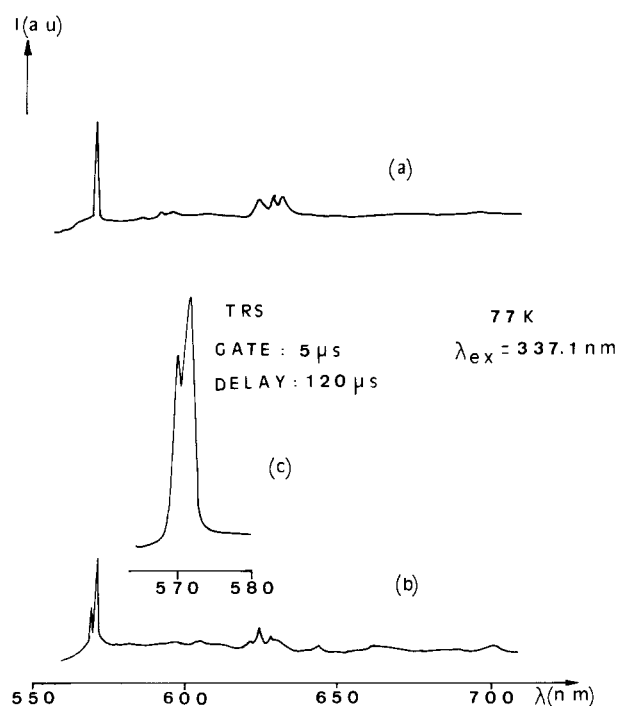Fig. 6. Emission spectrum of Eu^{3+} in $Sr_{9.985}Eu_{0.01}(OH)_2(PO_4)_6$ (a) and $Sr_{9.985}Eu_{0.01}(OH)_{2-y}O_{y/2}(PO_4)_6$ (b), at 77 K (λ_{exc}= 337.1 nm). TRS measurement of the emission in the oxyhydroxy-apatite (c).

$Eu^{3+}-F^--OH^-$ and $Eu^{3+}-F^--O^{2-}$ ion-couplings [3]. These two other Eu^{3+} sites were called B_1 and B_2. This hypothesis is supported by the fact that, after

fluorination of the fluoroxyhydroxyapatite with $x=1.5$, the bands near 576–578 nm disappeared, due to the following reaction, confirmed by IR spectroscopy:

$$O^{2-} + \square + NH_4HF_2 \longrightarrow F^- + OH^- + NH_4F \qquad (3)$$
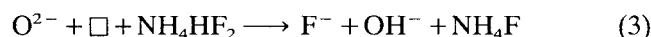
Anionic vacancies are involved in the fluorination (reaction (3)); this explains why the fluorination of the pure hydroxyapatite had no effect on Eu^{3+} lumines-cence. It is obvious that bands corresponding to the sites B_1, B_2, C_1 and C_2 are much more intense for compounds prepared in aqueous solution (Fig. 5). Their existence in solid state compounds (Fig. 1) seems to be due to commercial SrF_2 which is able to incorporate OH^- and O^{2-} [4]. Indeed, these emissions did not appear for the compound prepared without SrF_2.

Some preliminary luminescence dynamics showed that a transfer occurs between Eu^{3+} located in sites B_1, B_2, C_1 and C_2 and Eu^{3+} in site A. This is the reason why it was not possible to make selective excitation in each site. Apart from the $^5D_0 \rightarrow {}^7F_0$ transition, the other emissions attributed to the sites B_1, B_2, C_1 and C_2 were thus not assigned.

5. Conclusion

The luminescence of Eu^{3+} in strontium fluorapatite indicated that the active ion is located in the C_s site

of the apatitic structure, for low concentrations. Modification of the Eu^{3+} environment by substitution of O^{2-} and OH^- for F^- created four other sites for the active ion. These sites were characterized on the basis of the experimental preparation.

Our purpose is now to analyze the luminescence dynamics in order to understand the energy transfer processes that occur in the matrix.

References

1 A. Zounani, D. Zambon and J.C. Cousseins, *J. Alloys Comp.*, *188* (1992) 82.
2 G. Blasse, *J. Solid State Chem.*, *14* (1975) 181.
3 D. Zakaria, *Thesis*, Clermont-Ferrand, France, 1991.
4 J.I. Pena, P.J. Alonso and R. Alcala, *Mater. Res. Bull.*, *25* (1990) 757.