



Synthesis and luminescent properties of Eu^{3+} -doped phosphate-sulfate fluorapatites $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_6-x(\text{SO}_4)_x\text{F}_2$



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ABSTRACT

A series of phosphate-sulfate fluorapatites $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_6-x(\text{SO}_4)_x\text{F}_2:\text{Eu}^{3+}$ (2%) ($x = 0, 3, 6$) has been synthesized by the solid-state reaction at high temperature. The samples were characterized by X-ray diffraction, Infrared spectroscopy and Raman scattering spectroscopy. Eu^{3+} luminescence properties were investigated at 77 K using site selective and time-resolved spectroscopy. Lifetimes and the color points were calculated. The emission spectra and luminescence decays of Eu^{3+} ions indicate that there is an energy transfer between different sites occupied by Eu^{3+} .

1. Introduction

Apatites with the general formula $\text{Me}_{10}(\text{XO}_4)_6\text{A}_2$ form a large family of inorganic compounds, they crystallize in the hexagonal system with the space group $P6_3/m$ [1,2]. The apatite structure provides a great capacity to form solid solutions and, particularly, to accept several substitutes [3,4]. The monovalent A ion can be OH^- , F^- , O^{2-} , CO_3^{2-} ..., the trivalent anion XO_4 can be AsO_4^{3-} , VO_4^{3-} , CrO_4^{3-} , HPO_4^{2-} , CO_3^{2-} , SO_4^{2-} , SiO_4^{4-} . There is no literature information showing that vacancies could exist on the (XO_4) site. Me cations may be divalent (Ca^{2+} , Ba^{2+} , Pb^{2+}), monovalent (Na^+) or even trivalent (Rare-Earth Element REE^{3+}). The apatite-like structure is characterized by the presence of two types of tunnels permitting the location of two cationic sites labeled Me(I) and Me(II). Four Me(I) are at the center of narrow tunnels (4f sites), six Me(II) are situated around large tunnels (6h sites). The coordination number of Me(I) and Me(II) sites are nine and seven, with the local symmetry C_3 and C_s , respectively [5].

Over the last few decades, optical properties of rare-earth elements (REE) doped into various host materials have been extensively studied, mainly with respect to potential application in solid state lighting, displays, lasers, optical amplifiers, sensors, etc [6–10]. Among the various REE, europium is traditionally occupying a dominant role. The electronic configuration of Eu is $[\text{Xe}] 4f^7 6s^2$. In oxide matrices, it could be incorporated under its trivalent state Eu^{3+} . The Eu^{3+} ion has been recognized as an excellent red activator in the phosphors due to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) emission.

Having a relatively simple energy level scheme and a non-

degenerated $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, the trivalent europium Eu^{3+} is widely used to probe the crystallographic sites occupied by rare earth ions in the apatitic matrix. Since the $^5\text{D}_0$ state is non-degenerate, the structure of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ emission is only determined by the splitting of the terminal levels caused by the local crystal field. Moreover, as the $^7\text{F}_0$ level is also non-degenerate, site-selective excitation within the inhomogeneous broadened $^7\text{F}_0 \rightarrow ^5\text{D}_0$ absorption band can be performed by using the fluorescence line narrowing (FLN) technique to distinguish among different local environments around the rare-earth ions [11,12]. Several papers have reported the Eu^{3+} luminescence in phosphate apatites [12–15] or sulfate apatites [16].

In this study, Eu^{3+} activator ion is used as a structural probe in three Eu^{3+} -doped phosphate-sulfate fluorapatites with the theoretical chemical formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}(2\%)$, $\text{Ca}_7\text{Na}_3(\text{PO}_4)_3(\text{SO}_4)_3\text{F}_2:\text{Eu}(2\%)$ and $\text{Ca}_4\text{Na}_6(\text{SO}_4)_6\text{F}_2:\text{Eu}(2\%)$. It is a worthwhile goal to develop spectroscopic investigations of these Eu^{3+} doped compounds in order to enhance the application of these phosphates to visible light (red) emitting phosphors.

2. Experimental procedure

The samples with formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}(2\%)$, $\text{Ca}_7\text{Na}_3(\text{PO}_4)_3(\text{SO}_4)_3\text{F}_2:\text{Eu}(2\%)$ and $\text{Ca}_4\text{Na}_6(\text{SO}_4)_6\text{F}_2:\text{Eu}(2\%)$ symbolized by FSOP6:Eu(2%), FS3P3:Eu(2%) and FS6P0:Eu(2%), respectively, have been synthesized by solid-state reaction. The temperature varies between 773 K, 823 K and 1173 K depending on the S/P ratio. The pure phosphate apatite FSOP6:Eu(2%) is obtained at higher temperature

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(1173 K) than that of FS3P3:Eu(2%) (823 K) and of pure sulfate apatite FS6P0:Eu(2%) (773 K).

For example, the FS3P3:Eu(2%) was prepared by an initial mixture of sodium sulfate Na_2SO_4 , calcium carbonate CaCO_3 , calcium fluoride CaF_2 , di-ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$, di-ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and europium oxide Eu_2O_3 with the atomic ratio $\text{Ca} + \text{Na}/\text{S} + \text{P}$ fixed at 1.667. Stoichiometric amounts of reactants have been ground and heated in covered platinum crucible at 823 K for 24 h, the temperature rise is 10 K per minute. The heat treatment was accompanied by several grindings in order to get well-crystallized products. The three samples of phosphate-sulfates were prepared with the Eu^{3+} doping percentage ($\text{Eu}^{3+}/\text{Eu}^{3+} + \text{Ca}^{2+} + \text{Na}^+$) fixed at 0.02.

The purity of the resulting powders was checked by X-ray diffraction, IR spectroscopy and Raman scattering spectroscopy.

The X-ray diffraction (XRD) patterns have been recorded with a Bruker D8-advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54004 \text{ \AA}$). X-ray diffraction data have been collected over the $10\text{--}55^\circ$ 2θ range with a 0.021 step and at regular intervals of 12 s. The crystalline phases have been identified using the International Center for Diffraction Data (ICDD) powder diffraction files. The cell parameters were calculated by using a program “FullProf”.

The steady-state emission spectra were obtained using a Spectra Pro 750 monochromator, equipped with a Hamamatsu R928 photomultiplier and a 1200 l mm^{-1} grating blazed at 500 nm. A 450W xenon arc lamp was used as the excitation source. It was coupled with a monochromator, which used a 1800 l mm^{-1} grating blazed at 250 nm. The measurements were obtained at room temperature. Site selective excitation (or Fluorescence Line Narrowing) was performed at 77 K in a nitrogen cryostat. A tunable laser (EKSPLA OPO NT342B, 7 ns, 10 Hz) was used for scanning the excitation wavelength in the range of the lowest excited $^5\text{D}_0$ level of Eu^{3+} near 570–590 nm. The fluorescence was collected with an optical fiber and analyzed with the help of a spectrometer equipped with a 1200 l mm^{-1} grating blazed at 500 nm coupled to an intensified charge coupled device (ICCD) camera.

The luminescence decay curves were recorded under pulsed laser excitation (OPO laser, EKSPLA NT342, 10 Hz, 7 ns) and using an R1767 Hamamatsu photomultiplier through a HRS1 Jobin-Yvon monochromatic coupled with a LECROY LT 342 digital oscilloscope. The luminescence decay curves were recorded at RT and 77 K.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the X-ray diffraction patterns of the synthesized samples

$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2:\text{Eu}(2\%)$, $\text{Ca}_7\text{Na}_3(\text{PO}_4)_3(\text{SO}_4)_3\text{F}_2:\text{Eu}(2\%)$ and $\text{Ca}_4\text{Na}_6(\text{SO}_4)_6\text{F}_2:\text{Eu}(2\%)$.

The X-ray diagrams confirm that the three are formed by an apatitic phase; all the lines were indexed in the hexagonal system (space group $P6_3/m$). The unit-cell parameter values of these compounds are reported in Table 1.

The purity of the three compounds was then confirmed by the IR absorption spectroscopy and Raman scattering spectroscopy. The IR and Raman spectra are given in our recent work on undoped phosphate-sulfate fluorapatites $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{SO}_4)_x\text{F}_2$ [17]. In 2% Eu^{3+} -doped fluorapatites, the IR and Raman spectra are similar to those of undoped fluorapatites.

3.2. Photoluminescence

3.2.1. Emission under non-selective excitation

The emission spectra of the Eu^{3+} doped samples under non-selective excitation ($\lambda_{\text{exc.}} = 266 \text{ nm}$) recorded at 77 K are shown in Fig. 2. Emission peaks in the range 560–720 nm are attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0\text{--}4$) transitions of Eu^{3+} . The $^5\text{D}_0 \rightarrow ^7\text{F}_{1-4}$ transition lines are

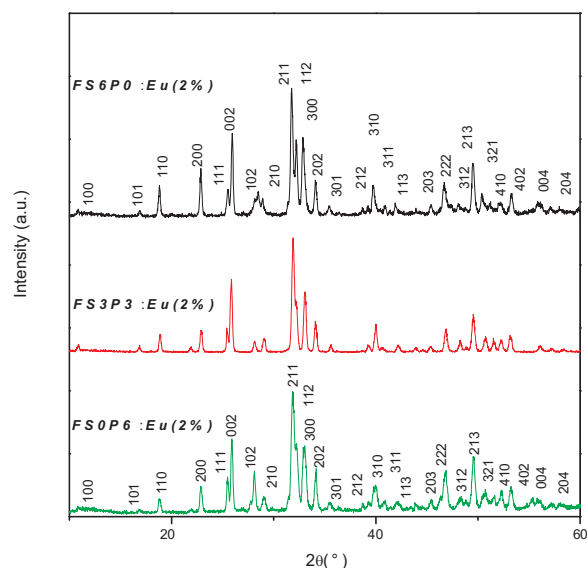


Fig. 1. X-ray diffraction patterns of $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{SO}_4)_x\text{F}_2:\text{Eu}(2\%)$ fluorapatites.

Table 1
Unit-cell parameters of $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{SO}_4)_x\text{F}_2:\text{Eu}(2\%)$ fluorapatites.

	FS0P6: Eu (2%)	FS3P3: Eu (2%)	FS6P0: Eu (2%)
a (Å)	9.414(1)	9.393(4)	9.369(9)
c (Å)	6.897(6)	6.874(2)	6.867(0)
Crystal system	Hexagonal		
Space group	$P6_3/m$		

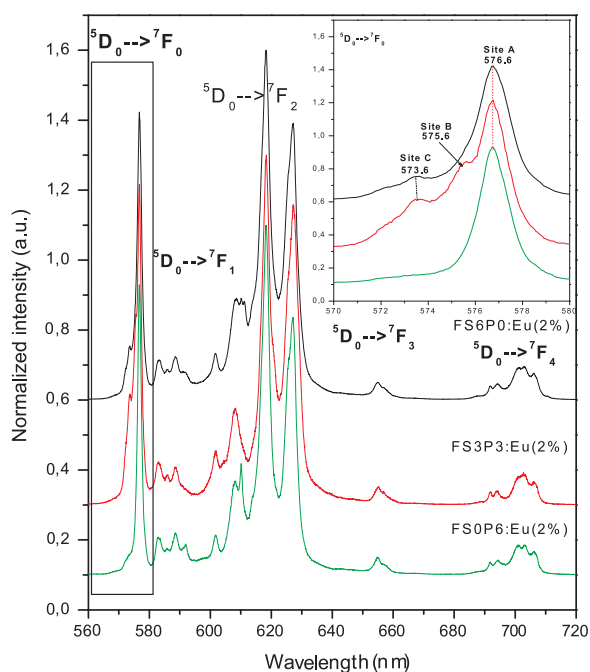


Fig. 2. Emission spectra under non-selective excitation of $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{SO}_4)_x\text{F}_2:\text{Eu}(2\%)$ fluorapatites at $T = 77 \text{ K}$ ($\lambda_{\text{exc.}} = 266 \text{ nm}$).

assigned by analogy to several apatites reported elsewhere [8,15,18–21].

The non-degenerate $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission line acquires special importance because it will reveal the presence of crystallographic sites in a given host matrix, so the analysis of this transition is very important to understand the Eu^{3+} environment.

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