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Tin as reducing agent in Eu^{2+} doped alkali-earth fluorophosphates

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Abstract. The blue europium band in alkali-earth fluorophosphates, determining the $4f^65d \rightarrow 8S_{7/2}$ allowed electric-dipole transitions in the Eu^{2+} ion, is studied. The simultaneous doping with Sn^{2+} provides a possibility of the realization of $\text{Sn} \rightarrow \text{Eu}$ transitions and of formation of Eu^{2+} ions as blue emission centres of high intensity. The M_I position is assumed for the Eu^{2+} ions in the apatite structure of the matrix.

1. Introduction

Calcium halophosphates are well known for their wide application as fluorescent lamp phosphors [1, 2], and some of them have recently been used as biocompatible materials [3]. Eu^{2+} activated alkali-earth chloroapatites are quite important as the blue component in the three-colour fluorescent lamps. J Yiping *et al* [4] have studied Eu^{2+} doped solid solutions based on Ca–Mg–Ba chlorofluorophosphates and has established three broad emission peaks at 460, 473 and 508 nm. Alkali-earth chloroapatites, activated with Eu^{2+} ions, are reported in [5] and it is suggested by M Kottaisamy that $\lambda_{\text{max}} = 453$ nm of the characteristic blue europium band depends on the type of M^{2+} ion in the lattice. The present paper reports an investigation of the Eu^{2+} emission in alkali-earth fluorophosphates prepared by coprecipitation. Sn^{2+} ions are used as a reducing agent in europium doped alkali-earth fluorophosphates.

2. Experiment

Halophosphate luminophores are characterized by the general formula $\text{Ca}_5\text{X}(\text{PO}_4)_3\cdot\text{A}, \text{B}$, where X denotes F^- or Cl^- ions, and A and B are the respective activators and sensitizers. According to well known techniques [1, 5], halophosphates are prepared by a high-temperature synthesis from a starting multicomponent charge.

The halophosphates of calcium fluorophosphates were prepared by a coprecipitation method described in previous studies [6, 7]. It is based on the coprecipitation of ions from solution, resulting in the preparation of a starting charge for the synthesis of the luminophores. Solutions (0.5 mol l^{-1}) of Ca^{2+} , Sr^{2+} , Ba^{2+} and NH_4^+ are used, while the F^- , Sn^{2+} and Eu^{3+} ions are in a concentration of 0.1 mol l^{-1} . A mixture is prepared, containing calcium, strontium, barium and activator ions in appropriate amounts, and, after heating to 80°C with continuous stirring, an ammonium hydrogen phosphate solution containing

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fluoride ions is added. Precipitation is performed at pH 5.5–6, the pH value being adjusted, when necessary, with ammonia. A white suspension of alkali-earth fluorophosphates is obtained under these conditions; this is the starting charge. After filtration, washing and drying of the precipitate, the resulting white polycrystalline powder is subjected to thermal activation at 1000 °C in a reductive or inert atmosphere. Following this thermal treatment, the synthesized halophosphate luminophores show a bright luminescence upon irradiation at 254 nm. Small screens prepared from these luminophores are studied in standard optical devices. The spectral distribution of the emission is recorded by means of a Zeiss mirror SPR-1 monochromator and detected using a photomultiplier, connected to a highly accurate digital millivoltmeter. Data processing is performed by means of a computer program. The excitation source is a 254 nm Hg line. The resolution of the spectral apparatus is about 1 nm. All spectra are taken at room temperature. During the coprecipitation of the dissolved ions, an apatite precipitate is formed, its structure being confirmed by x-ray diffraction (XRD) and differential thermal analysis [7, 8]. The high-temperature treatment of the starting charge resulted in recrystallization, i.e., the activator ions are built into the crystal lattice of the matrix.

3. Results and discussion

A reductive atmosphere is required to obtain Eu^{2+} ions, hydrogen being normally used as a reducing agent. In the present case, the reductive atmosphere consisted of Ar with 10% H_2 . The specimens obtained by thermal activation in this atmosphere possess an emission in the short wavelength spectral region, related to the blue Eu^{2+} luminescence. With these alkali-earth fluorophosphates the europium emission is found at 430–450 nm. Figure 1(a) shows spectra of the Eu^{2+} doped specimens of Ca, Ca–Sr and Ca–Ba fluorophosphates. The specimen based on Ca fluorophosphate (spectrum 1) reveals the lowest intensity. The partial substitution of Ca^{2+} by 5% Ba^{2+} in the matrix enhances the emission intensity by about 30%, as seen in curve 3, figure 1. Spectrum 2 is taken from a specimen containing 5% Sr^{2+} in the luminophore basis; in this case the intensity of the blue europium band is the highest, and a fivefold increase is observed, compared to spectrum 1. Simultaneously with the rise of $I_{\text{max}} = 1425$, the emission shifts to longer wavelengths. Figure 1(b) shows normalized luminescence spectra of the three types of alkali-earth fluorophosphate. The substitution of Ca^{2+} by Sr^{2+} or Ba^{2+} in the matrix results in a shift by 20 nm of λ_{max} to the longer wavelength region. The I_{max} and λ_{max} values found with the three types of alkali-earth fluorophosphate are given in table 1.

Table 1. Spectral data on the luminescence of Eu^{2+} in alkali-earth fluorophosphates.

<i>N</i>	Basis	Atmosphere	I_{max} (au)	λ_{max} (nm)
1	Ca fluorophosphate	Ar + 10% H_2	1425	430
2	Ca–Sr fluorophosphate	Ar + 10% H_2	9844	440
3	Ca–Ba fluorophosphate	Ar + 10% H_2	5644	451

Europium is introduced in the initial charge as Eu^{3+} ions. The transition of Eu^{3+} into Eu^{2+} is related to the reductive atmosphere during activation. The percentage of H_2 in the reducing atmosphere during the thermal treatment of the specimens affects the intensity of the blue europium band, which is clearly related to the amount of Eu^{2+} ions in the matrix.

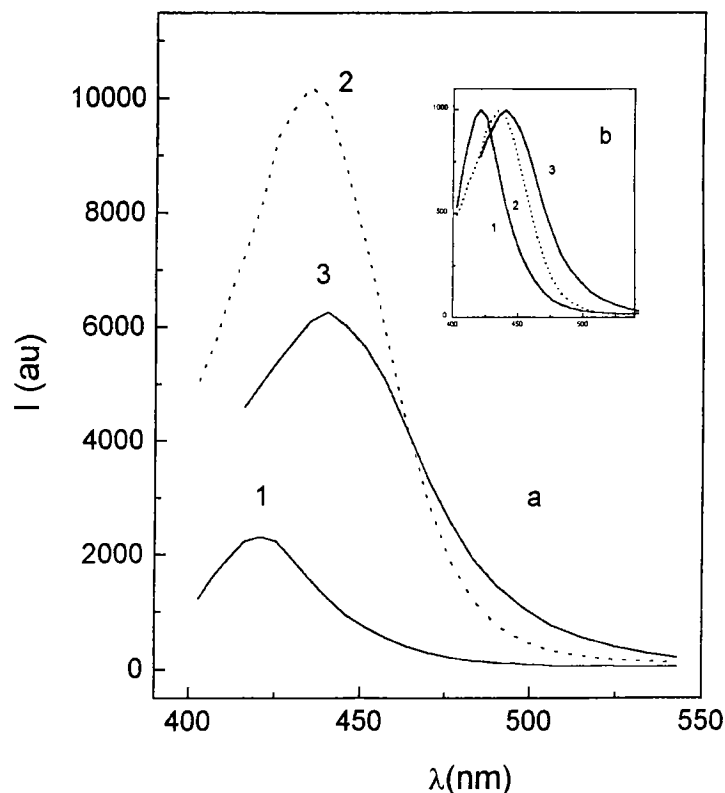


Figure 1. Luminescent spectra of Eu²⁺ doped with: 1, Ca fluorophosphate; 2, Ca-Sr fluorophosphate; 3, Ca-Ba fluorophosphate.

The emission spectra presented in figure 2 are recorded with specimens activated in an atmosphere containing 5%, 10% or 20% H₂. The highest intensity of the blue europium band is observed at 10% H₂ (curve 2, figure 2). A decrease of the luminescence intensity in curve 3, figure 2 is observed at 20% H₂ in the reductive atmosphere. The high hydrogen concentration probably leads to partial reduction of europium in the matrix, i.e., to a decrease of the Eu²⁺ luminescence centres, leading to a drop of the intensity.

Bivalent europium in the fluorophosphates studied determines an emission in the blue spectral region with λ_{max} of 430–450 nm, considerable intensity and relatively narrow emission band. This europium band can be attributed to the $4f^65d \rightarrow 8S_{7/2}$ allowed electric dipole transitions in the Eu²⁺ ion, in agreement with published data [5, 10]. However, the position of λ_{max} depends on the position of Eu²⁺ in the crystal lattice. The crystallography of alkali-earth apatites has been extensively studied [1, 9], and two types (M_I and M_{II}) of cationic position were established in the crystal lattice. We assume an M_I position of Eu²⁺, in a symmetry of point group C₃, surrounded by six oxygen atoms. The partial substitution of Ca²⁺ by Sr²⁺ or Ba²⁺ in apatite shifts the emission peak of Eu²⁺ to longer wavelengths. This shift could be explained by Eu²⁺ taking also some M_{II} positions in the Ca apatite lattice. We reported similar results [6, 7] for Mn²⁺, used as activator in Ca fluorophosphates; the manganese band shifted to longer wavelengths due to occupation of M_{II} positions in the lattice. M Kottaisamy *et al* [5] suggested that the longer wavelength emission of Eu²⁺ in

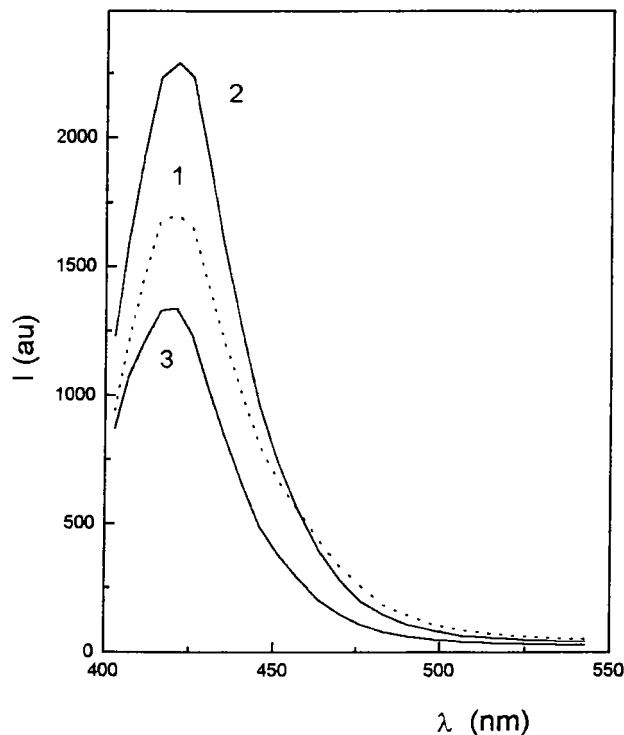


Figure 2. Emission spectra of $\text{Ca}_5\text{F}(\text{PO}_4)_3:\text{Eu}^{2+}$ in different reductive atmospheres:

	I_{max} (au)	λ_{max} (nm)
1. Ar + 5% H_2	1700	419
2. Ar + 10% H_2	2315	420
3. Ar + 20% H_2	1350	416

Ba apatite could be related to the occupation of M_{II} positions by Eu^{2+} in the basis, which is in agreement with our assumption. For the apatites studied here, it is also established that Ba^{2+} , partially substituting Ca^{2+} in the matrix, causes a substantial increase of the blue europium band intensity. This could be explained by the larger ionic radius of Ba^{2+} which is closer to that of Eu^{2+} , compared to the case of the Ca^{2+} ion. Thus barium probably favours the building up of more Eu^{2+} ions at M_{II} positions in Ca–Ba fluorophosphates.

The use of Sn^{2+} as a reducing agent of Eu^{3+} ions in the Ca fluorophosphate was then explored. An attempt was made to simultaneously introduce Eu^{3+} and Sn^{2+} ions in the matrix, the activation being effected in two atmospheres—an inert and a reductive one. Figure 3 shows the spectra of the two samples, while table 2 contains the spectral data of the luminescence. In the present case, the spectral data are obtained in the range of 5 nm only. Three europium bands are observed under these synthetic conditions—a blue one with $\lambda_{\text{max}} = 425$ nm, attributed to Eu^{2+} , and two longer wavelength bands in the region about 600 and 700 nm, related to Eu^{3+} . The longer wavelength emissions correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions (for the orange region) and to $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions (for the red one), the respective levels belonging to the $4f^6$ configuration of Eu^{3+} . The longer wavelength emissions are of much lower intensity compared with the blue emission

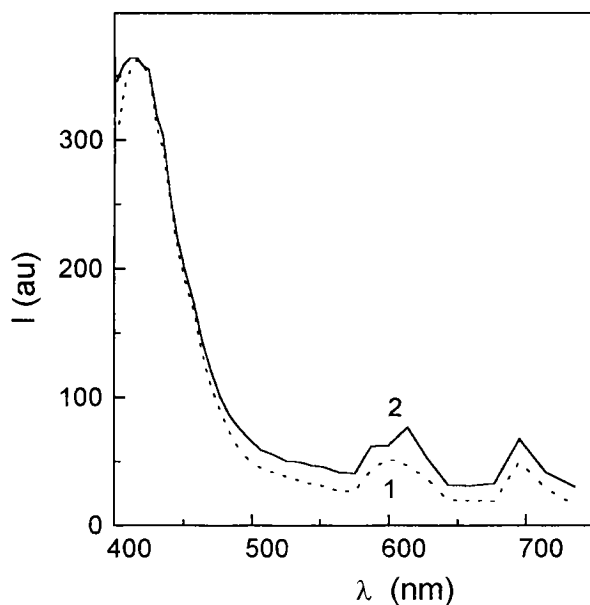
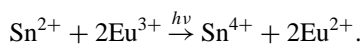


Figure 3. Luminescent spectra of europium and Sn²⁺ doped Ca fluorophosphate: 1, inert atmosphere (Ar); 2, reductive atmosphere (Ar + 5% H₂).

Table 2. Spectral data on the luminescence of Ca fluorophosphate doped with tin and europium.

N	Basis	Atmosphere	Reducing agent	Eu ²⁺		Eu ³⁺			
				I _{max}	λ _{max}	I _{max}	λ _{max}	I _{max}	λ _{max}
1	Ca ₅ F(PO ₄) ₃	Ar	Sn ²⁺	360	425	76	65	613	695
2	Ca ₅ F(PO ₄) ₃	Ar + H ₂	Sn ²⁺	350	420	52	50	600	695

attributed to europium and the emission intensities remain almost unaffected by the activation atmosphere. The almost identical intensity values of the blue Eu²⁺ bands suggest that the same Eu³⁺ concentration transforms into Eu²⁺ ions regardless of the activation atmosphere. This fact could be explained solely by the presence of Sn²⁺ ions in the matrix. Electron transitions with the participation of Sn²⁺ and Eu³⁺ ions are probably taking place according to the scheme:



This leads to the formation of Eu²⁺ due to the presence of Sn²⁺; tin ions prove to be an appropriate reducing agent, transforming the major portion of Eu³⁺ into Eu²⁺ ions. The small amount of Eu³⁺ ions remaining in the matrix is the reason for the low emission in the red spectral region. This is an experimental proof of the transformation of Eu³⁺ into Eu²⁺, i.e., the appearance of blue emission related to Eu²⁺ ions. It follows that the tin and europium amounts introduced into the matrix under our synthetic conditions are correctly chosen for obtaining a bright, blue Eu²⁺ luminescence in Ca fluorophosphate.

The spectrum of red europium luminescence in calcium fluorophosphate, without tin in the matrix, is shown in figure 4. One can see the structure of the europium bands appearing

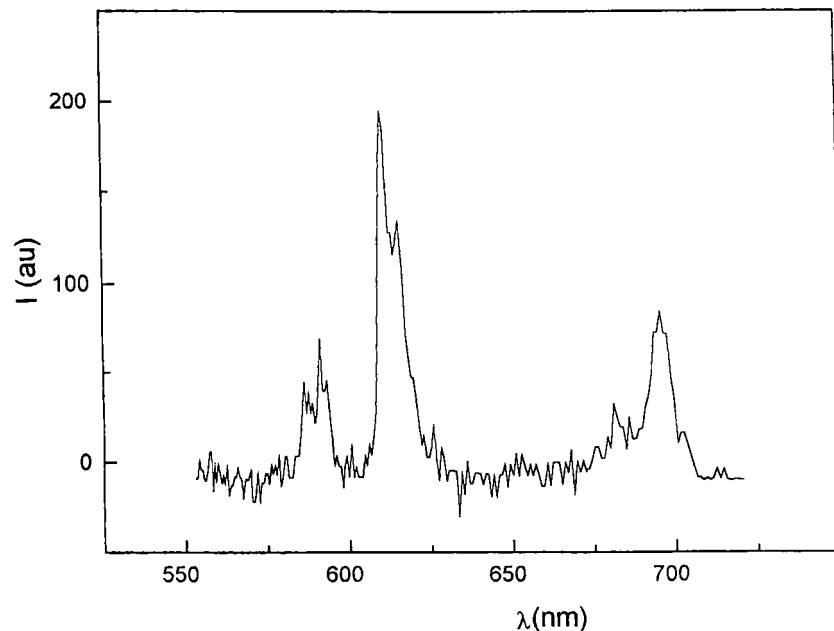


Figure 4. Emission spectra of Eu^{3+} in Ca fluorophosphate ($\lambda_{\text{exc}} = 254$ nm).

at 587, 610 and 620 nm, which correspond to transitions from the excited $^5\text{D}_0$ level of the $^7\text{F}_2$ levels of the Eu^{3+} ion, for the emission in the orange region. The emission at 695 nm is attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions between the levels mentioned above. These assumed transitions are in good agreement with published data [11] for Eu^{3+} in silicate matrices.

On the assumption that Eu^{2+} ions take M_I positions in the lattice, Sn^{2+} ions should occupy M_II sites in the crystal lattice of Ca fluoroapatite. That is, it is the M_II position which would facilitate Sn^{2+} ions to realize electron transitions between Sn^{2+} and Eu^{3+} , the latter ions also occupying M_II sites. We believe that we have established for the first time this reductive effect of Sn^{2+} ions in the matrix of Ca fluorophosphates doped with Eu^{3+} ions. Our results provide the possibility of elimination of the H_2 reductive atmosphere during the thermal treatment by the simple addition of Sn^{2+} ions in the matrix. This would undoubtedly facilitate the technological preparation of alkali-earth halophosphate luminophores with blue emission caused by the presence of Eu^{2+} ions. Halophosphate materials are at present the most widely applied lamp luminophores and the blue component in their emission is seldom encountered and is sought for this very reason.

4. Conclusion

The present studies lead to the assumption that Sn^{2+} and Eu^{3+} ions take M_II positions in fluoroapatites, while Eu^{2+} occupy M_I sites. The presence of Sn^{2+} ions facilitates the reduction of Eu^{3+} to Eu^{2+} ions in alkali-earth fluorophosphate matrices. Bivalent europium is characterized by a high-intensity narrow blue band with $\lambda_{\text{max}} = 430\text{--}450$ nm in the fluoroapatites studied.

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