

# SrAl<sub>4</sub>O<sub>7</sub> : Eu<sup>2+</sup> nanocrystals: synthesis and fluorescence properties

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## Abstract

Divalent europium doped strontium di-aluminate (SrAl<sub>4</sub>O<sub>7</sub> : Eu<sup>2+</sup>) nanocrystals have been synthesized using a facile sol–gel polymer thermolysis method. The photoluminescence characteristics of smaller particles ( $\phi \sim 15$  nm) show a significant difference with respect to their bulk counterpart. In this nanocrystalline system, the electronic structure of the Eu<sup>2+</sup> excited state seems to undergo considerable modification induced by the surface states involved in slow relaxation kinetics that mimic phosphorescence like features.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Doped nanocrystals, broadly classified into semiconductor and insulator types, attract a great deal of interest both from the application and fundamental points of view. The literature on semiconductor nanocrystals eventually leading to a quantum-dot structure is very extensive [1, 2]. On the other hand, information on insulator type luminescent nanoceramics seems to be limited. This is probably because the constituents are disparate in nature and in their chemical properties.

Divalent europium doped alkaline earth aluminate based phosphors, having an average particle size of a few microns, are extensively used in luminescent lighting and photocopying lamps [3, 4]. As far as we know, reports on the study of Eu<sup>2+</sup> luminescence in nanocrystalline aluminates seem to be very few [5, 6]. Hence we are motivated to synthesize a nanocrystalline analogue of strontium di-aluminate doped with divalent europium (DEDA) and study its luminescent properties. Since luminescence transitions are regulated by an electronic transition mechanism, it would be worthwhile seeing if the electronic structure of the dopant ion undergoes

any modification on account of a decrease in particle size. The results of the present investigation have revealed the involvement of surface states (SS) of nanocrystals in modifying the electronic structure of the relaxed excited 5d state of the dopant Eu<sup>2+</sup> ion.

## 2. Experimental

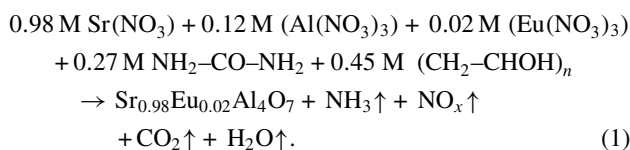
The starting materials, represented by chemical formulae such as SrCO<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, HNO<sub>3</sub>, Eu(NO<sub>3</sub>)<sub>3</sub>, NH<sub>2</sub>–CO–NH<sub>2</sub> (urea), and (CH<sub>2</sub>–CHOH)<sub>n</sub> (polyvinyl alcohol (PVA), *n* being the degree of polymerization), used for the synthesis were either analysed reagents (BDH Chemicals, India) or of 99.9% (Indian Rare Earths) purity. Polycrystalline samples of divalent europium doped strontium di-aluminate (Sr<sub>1–x</sub>Al<sub>4</sub>O<sub>7</sub> : Eu<sub>x</sub><sup>2+</sup>; Eu<sup>2+</sup>, concentration *x* = 2 mol%) were prepared by the conventional solid state reaction method using alumina crucibles in a reducing atmosphere created by burning activated charcoal at 1200°C. The nanocrystalline analogue of these luminescent ceramics was synthesized using a self-propagating high temperature combustion synthesis method [7] employing PVA and urea [8] as a polymeric dispersion matrix and fuel, respectively. The chemical stoichiometry

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**Table 1.** Least squares refined crystallographic cell parameters for bulk and nano  $\text{SrAl}_4\text{O}_7 : \text{Eu}^{2+}$  (space group  $C_{2/c}$ ) samples.

Sample	Particle size, $\phi$ (nm)	Refined cell parameters				
		$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	Cell volume (Å <sup>3</sup> )
A	14	12.93	8.98	5.55	106	620.164
B	34	13.02	9.00	5.53	106	622.69
JCPDS #25-1208	—	13.04	9.01	5.54	106	624.867

of the reactants and organic fuel(s) taken in concentrations (made up to 10 ml of aqueous medium) correspond to the equation

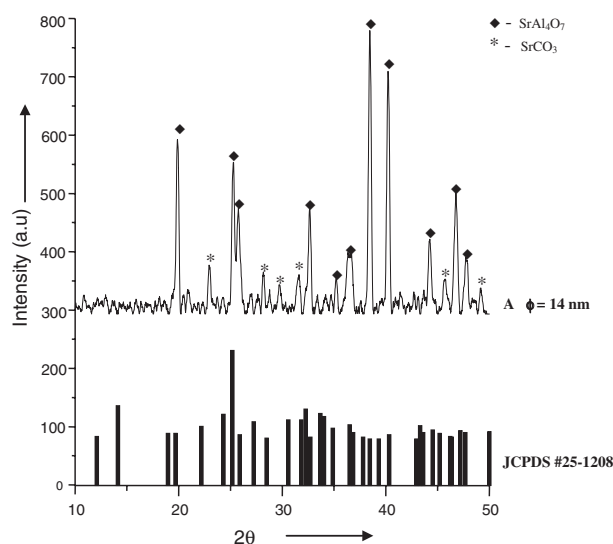
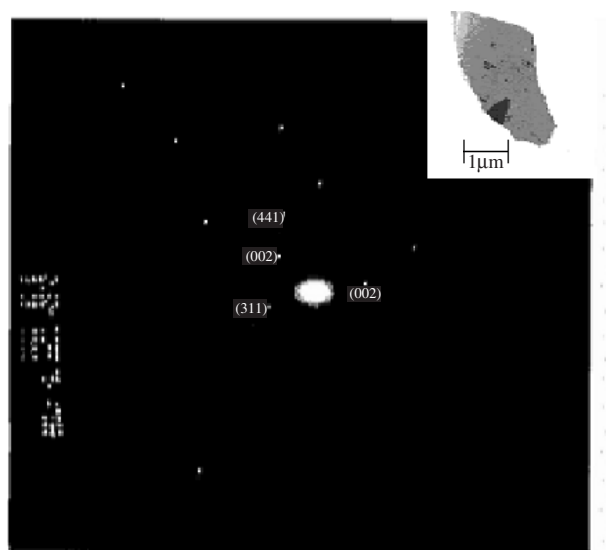


In this study two types of nano-aluminate sample were prepared using sol–gel thermolysis at 400°C and 800°C for 2 h and were labelled as A and B, respectively. The products obtained thus were found to be chemically pure, as checked using the MAC Science MXP3 powder x-ray diffraction (XRD) system. Crystallographic unit cell parameters were refined using a standard least squares fitting procedure, and the cell parameters obtained were in good agreement with standard values (table 1). A selected area electron diffraction (SAED) pattern and bright field image of the nanoparticles were obtained using a Hitachi H-7100 transmission electron microscope (TEM). Optical characterization (fluorescence and phosphorescence emission, excitation, spectra, and lifetime measurements, limited to the milliseconds range) of the materials synthesized were carried out using a Varian Cary-Eclipse fluorescence spectrophotometer employing a 15 W Xe pulsed flash lamp and planar–concave diffraction gratings having a groove density of 1200 lines per millimetre. Diffuse reflectance spectra and the corresponding Kubelka–Munk plot were obtained using a Varian Cary 500 double beam UV–Vis spectrophotometer.

### 3. Results and discussion

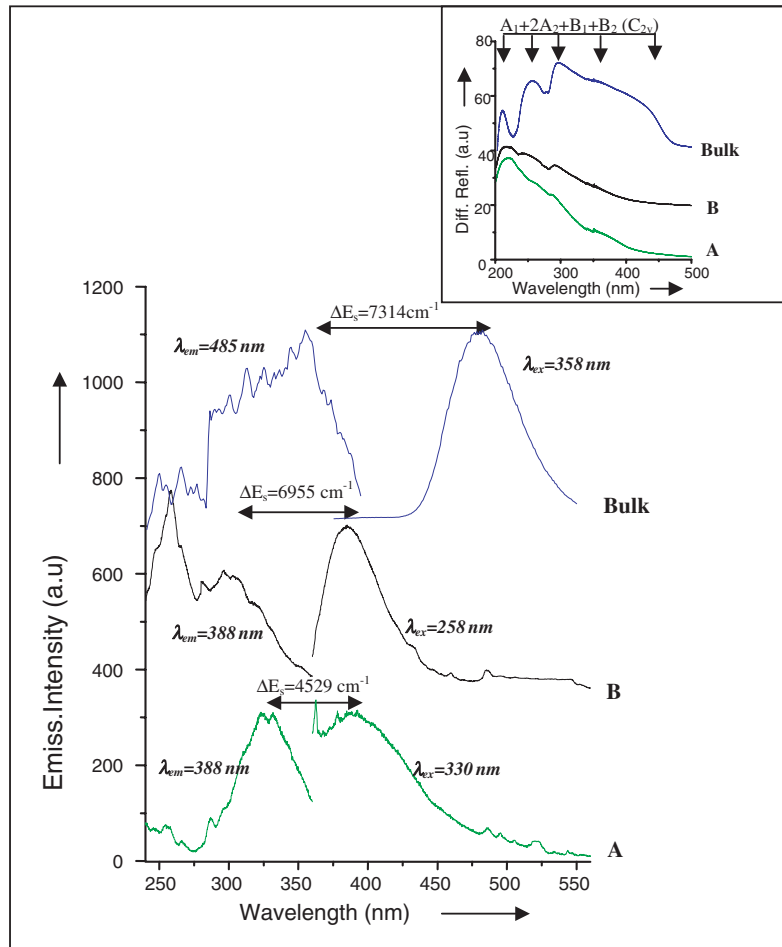
#### 3.1. Material properties

XRD patterns obtained for these samples matched well with the standard JCPDS file # 25-1208 corresponding to the strontium di-aluminate ( $\text{SrAl}_4\text{O}_7$ ) system. In figure 1 we present the XRD pattern corresponding to strontium di-aluminate nanocrystalline sample A, synthesized through thermolysis at 400°C. The XRD pattern also indicates some weak lines corresponding to  $\text{SrCO}_3$  as a secondary phase in trace levels. Gases evolved from the burning of hydrocarbons such as  $\text{CO}_2$  during the course of thermolysis may react with  $\text{SrO}$  to form a  $\text{SrCO}_3$  phase in trace levels. This is not expected to interfere with the luminescent properties. It should be noted that in the SAED pattern (figure 2), apart from the diffraction spots corresponding to the  $\text{SrAl}_4\text{O}_7$  target phase, there are also weak spots with lower  $d$  values  $\leq 1$  Å. These are not readily indexable

**Figure 1.** XRD pattern of the nanocrystalline  $\text{SrAl}_4\text{O}_7 : \text{Eu}^{2+}$  (A) sample compared with JCPDS#25-1208 corresponding to the  $\text{SrAl}_4\text{O}_7$  system. The particle size ( $\phi$ ) of the nanocrystalline sample, calculated using the Scherrer formula, is indicated.**Figure 2.** SAED pattern of nanocrystalline  $\text{SrAl}_4\text{O}_7 : \text{Eu}^{2+}$  sample A. Diffraction spots corresponding to the Sr di-aluminate phase are indicated. The corresponding TEM bright field image is shown in the inset.

under any of the possible unreacted reactants or intermediate phases.

The crystallite size of the nanoparticles could be increased in a limited way by increasing the pyrolysis temperature from 400°C to 800°C. Using XRD line-broadening studies, it has been found that sample A yielded particles of size 14 nm while sample B yielded particles of an average size of 34 nm. It is significant to note that the adiabatic flame temperature ( $T_f$ ) generated during the combustion reaction is determined only by the combination of the organic precursors, the starting materials, and the target phase rather than the temperature of thermolysis. In the present combination of reactants, organic precursors, and target phase, the flame temperature ( $T_f$ ) can be expected to be around 1850°C [9, 10].



**Figure 3.** Photoluminescence emission and excitation spectra of bulk and nanocrystalline (A and B)  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples. Inset: diffuse reflectance spectra (Kubelka–Munk plot) of the  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples. The Stark structure in the  $\text{Eu}^{2+}$  excited state corresponding to  $C_{2v}$  local symmetry is also indicated.

**Table 2.** Comparison of fluorescence and phosphorescence characteristics of bulk and nanocrystalline  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples.

Sample	Photoluminescence data						Phosphorescence data		
	Emission (max.), $\lambda_{\text{em}}$ (nm)	Excitation (max.), $\lambda_{\text{ex}}$ (nm)	Stokes shift, $\Delta E_{\text{s}}$ ( $\text{cm}^{-1}$ )	Red-shift calculation			Emission (max.), $\lambda_{\text{em}}$ (nm)	Excitation (max.), $\lambda_{\text{ex}}$ (nm)	Phosphorescence decay time, $\tau$ (ms)
				$\varepsilon_{\text{c}}$ ( $\text{cm}^{-1}$ )	$\varepsilon_{\text{cfs}}$ ( $\text{cm}^{-1}$ )	$D$ ( $\text{cm}^{-1}$ )			
A	388	330	4348	2211	5981	326	472	310	113
B	388	258	6955	2289	7136	404	515	330	27
Bulk	485	358	7314	3618	11593	1733	485	235	25

### 3.2. Fluorescence properties

Photoluminescence emission, excitation spectra for the bulk and nanocrystalline  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples, and also corresponding diffuse reflectance spectra (Kubelka–Munk plot) are presented in figure 3. Furthermore, related spectral data for the bulk and nanosamples are given in table 2. Upon UV excitation,  $\text{Eu}^{2+}$  in strontium di-aluminate yields a narrow band emission in the blue–bluish green region ( $\sim 400\text{--}500\text{ nm}$ ), which can be ascribed to an allowed  $4f^65d \rightarrow 8S_{7/2}(4f^7)$  electric dipole transition. It is important to note that the excitation and emission maxima for the nanosample show a significant blue-shift ( $\sim 2000\text{ cm}^{-1}$ ) with respect to that of the bulk system. It is possible that the excited state configuration

of  $\text{Eu}^{2+}$  undergoes considerable modification on account of the size miniaturization. Also it is important to observe that a clear Stark splitting pattern is absent in the excitation spectrum corresponding to the nanosample, in particular for sample A.

Strontium di-aluminate crystallizes under monoclinic  $C_{2/c}$  lattice symmetry [11]. Correspondingly, this may suggest a maximum local symmetry of  $C_{2v}$  for the  $\text{Eu}^{2+}$  luminescent centre(s) occupying cationic site(s) due to  $\text{Sr}^{2+}$  ion(s). This orthorhombic local symmetry will lift all the orbital degeneracy of the lone 5d electron of the dopant  $\text{Eu}^{2+}$  ion. This will enforce a Stark splitting structure something like  $A_1 + 2A_2 + B_1 + B_2$ . It has been found that the XRD patterns obtained for the bulk samples and nanosamples are quite comparable. This may suggest nearly identical (or at least comparable)

lattice symmetries for the bulk and the nano-aluminate system. This in turn implies nearly comparable local site symmetries for the  $\text{Eu}^{2+}$  site(s) for both the bulk systems and nanosystems. As a consequence, any significant difference in the Stark splitting structure of the 5d excited orbital(s) between the bulk samples and nanosamples cannot be expected. Some Stark splitting pattern is decipherable from the excitation spectrum corresponding to the bulk sample given in figure 3. However, for the nanosystem, in particular for sample A, such a Stark structure is missing. Furthermore, in the diffuse reflectance spectra, which are the complementary images of the excitation spectra, a clear Stark structure consistent with  $C_{2v}$  local site symmetry is obvious for the bulk sample, while such a structure is missing for the nanosample (figure 3 inset).

It is known that in a nanocrystalline system, the crystallographic unit cell of the host lattice tends to contract due to the increased surface area [12]. This may lead to a decrease in the lattice constant as is observed (table 1). On account of the size miniaturization, innumerable SS are generated from broken chemical bonds, leading to a lattice lacking long range periodicity. These SS will be located near the band-edge region of the host matrix. This means that there is an increased propensity for interaction between the excited 5d state of the dopant  $\text{Eu}^{2+}$  ion and the SS, which may eventually wash away the Stark structure of the excited 5d state of  $\text{Eu}^{2+}$ . This should be reflected in the relaxation kinetics of the  $\text{Eu}^{2+}$  excited state.

It is more important to note that the photoluminescence emission and excitation maxima of the nanocrystals showed a considerable blue-shift with respect to that corresponding to the bulk system. From the pioneering work of Dorenbos [13] on the f–d transition of  $\text{Eu}^{2+}$  in several inorganic compounds, we can estimate the red-shift,  $D$ , using the relation

$$D = \varepsilon_c + \frac{\varepsilon_{\text{cfs}}}{r(A)} - 1890 \text{ (in cm}^{-1}\text{)} \quad (2)$$

with  $\varepsilon_c$ ,  $\varepsilon_{\text{cfs}}$ , and  $r(A)$  being the shift in the 5d state of  $\text{Eu}^{2+}$  in the system with respect to the free ion value, the crystal field splitting in the 5d state, and the fraction of  $\varepsilon_{\text{cfs}}$  contributing to the shift determined by the local symmetry of the  $\text{Eu}^{2+}$  site in the system, respectively. It has been found that the nanosamples show a blue-shift ( $\sim 1400 \text{ cm}^{-1}$ ) in the excited 5d level with respect to the bulk sample. This is because in the case of the nanosystem the value of  $D$  is around  $300 \text{ cm}^{-1}$ , as compared with a value of  $1700 \text{ cm}^{-1}$  for the bulk system, which is about five-fold lower than for the bulk sample (table 2). This means that in the nanosample, the excited 5d Stark state(s) will move closer to the fundamental absorption edge of the nanocrystalline host matrix, which in turn may lead to a larger scope for interaction with SS.

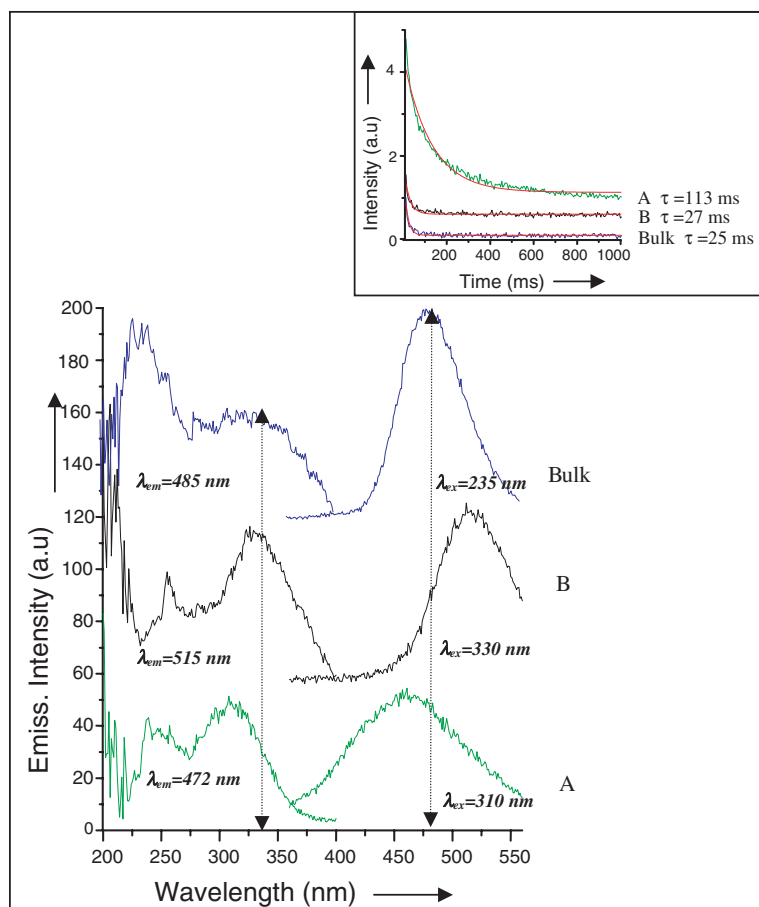
### 3.3. Is the relaxation kinetics of $\text{Eu}^{2+}$ excited state(s) delayed?

Under UV excitation,  $\text{Eu}^{2+}$  doped Sr di-aluminate nanocrystals showed afterglow luminescence resembling phosphorescence features. In order to identify the possible origin of  $\text{Eu}^{2+}$  emission showing slow kinetics, the phosphorescence emission and excitation spectra were recorded (figure 4). The bulk sample showed a phosphorescence emission maximum at 485 nm, which is at the same spectral position as the

photoluminescence emission of the bulk sample. It is known that the photoluminescence emission maximum of polycrystalline Sr di-aluminate:  $\text{Eu}^{2+}$  lies at around 485 nm [14]. In contrast, for the nanosample the phosphorescence emission maxima are quite different from that of the photoluminescence emission maxima, showing a considerable red-shift in the former case. On the other hand, phosphorescence excitation spectra for both bulk samples and nanosamples showed some similarity, with two broad bands having maxima around 250 nm and 320 nm, respectively. It is possible that the excitation band in the region of 250 nm gaining considerable intensity may correspond to the vicinity of the fundamental absorption edge of the host matrix.  $\text{Eu}^{2+}$  emission occurring due to an allowed f–d electric dipole transition mechanism will have a large radiative transition probability ( $\sim 10^6 \text{ s}^{-1}$ ) because the decay time of the  $\text{Eu}^{2+}$  excited state will usually be in the microsecond regime [15]. In the present investigation, using kinetic studies limited to the millisecond regime, it has been found that the phosphorescence emission of  $\text{Eu}^{2+}$  in Sr di-aluminate nanocrystals shows a low radiative transition probability. This is because the phosphorescence decay profile showed a lifetime value of  $\tau = 113 \text{ ms}$  at  $\lambda_{\text{em}} = 472 \text{ nm}$  when fitted under single-exponential decay (figure 4 inset). This value is too low for an allowed f–d transition of  $\text{Eu}^{2+}$ . Surprisingly the bulk sample also showed a slow component with  $\tau = 25 \text{ ms}$  phosphorescence, but with much lower emission intensity, which is at least one order lower than that for the nanocrystalline sample. For reasons of simplicity and comparison we employed a single exponential fit in all cases. Significantly, the fitting of a decay profile under a single exponential was not perfect, especially in the case of sample A. This suggests the presence of multiple processes in the kinetics of phosphorescence decay for sample A. These may come from several types of pronounced interactions such as an impurity ( $\text{Eu}^{2+}$ ) Stark state versus crystallite size interaction, SS versus impurity interaction, and so on.

Recently Chang *et al* [16] have reported afterglow luminescence from a  $\text{Eu}^{2+}$  doped Sr di-aluminate bulk system lasting several minutes. In  $\text{Eu}^{2+}$  doped strontium aluminate bulk samples, only mono-aluminate ( $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}$ ) is known to show a long phosphorescence at 515 nm lasting several minutes–hours and, this is attributed to a hole-trapping mechanism based on a conventional lattice-defect model [17, 18]. Hence it looks highly probable that the millisecond component observed for the bulk sample in this study may have a different origin related to lattice defects or impurities in the chemicals used and can be ignored in view of its low intensity.

On the other hand, for the nanocrystalline Sr di-aluminate:  $\text{Eu}^{2+}$  system, the slow kinetics observed appears to come from a totally different mechanism. This is because for the nanosystem the trap depth, which can be estimated from  $\text{Eu}^{2+}$  phosphorescence lifetime data, indicates a nearly two-fold higher value. Furthermore, a clear Stark structure characterizing the excited  $\text{Eu}^{2+}$  level is absent. Modification of the  $\text{Eu}^{2+}$  excited state configuration can be attributed to the presence of SS generated from broken chemical bonds, the lattice lacking long range periodicity, and so on. The absence of any Stark structure in the diffuse reflectance spectra for the nanosample given in the inset of figure 3 confirms this point.

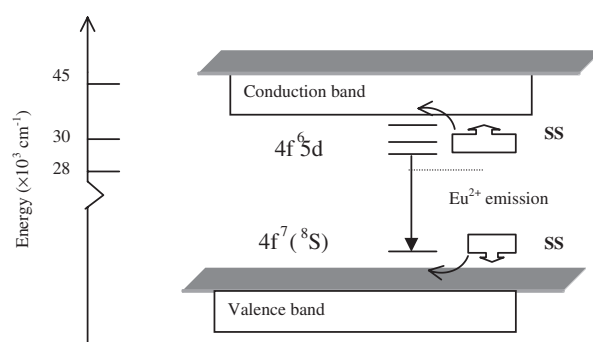


**Figure 4.** Photoluminescence emission and excitation spectra of bulk and nanocrystalline (A and B)  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples. Inset: corresponding decay time pattern of  $\text{SrAl}_4\text{O}_7:\text{Eu}^{2+}$  samples. For nanosample A, the decay time  $\tau = 113$  ms under 310 nm excitation, and it shows intense phosphorescence afterglow.

It can be seen from the photoluminescence emission and excitation spectra of nanocrystalline samples that only the latter undergoes considerable modification. This means that  $\text{Eu}^{2+}$  excited state(s) undergo significant modification on account of  $\text{Eu}^{2+}$  Stark level *vis a vis* SS interaction in the proximity of the fundamental absorption edge of the host matrix. A long decay time of the order of 100 ms seems to indicate a thermal process activated from shallow traps. This can occur in the proximity of conduction and valence band edges for the reason that broken chemical bonds and slightly off-stoichiometric (cation/anion deficient) compositions can create traps near valence and conduction band edges as shown schematically in figure 5.

#### 4. Conclusions

In summary, using a facile sol-gel pyrolysis method,  $\text{Eu}^{2+}$  doped luminescent strontium di-aluminate nanocrystals with size in the range of 15–35 nm have been synthesized. In this preliminary study on DEDA nanocrystals, it has been found that for smaller particles the  $\text{Eu}^{2+}$  luminescence decay time observed ( $\sim 100$  ms) is too slow to be fitted for an f-d allowed transition. Alternatively this can be explained by considering a complex 5d excited state of  $\text{Eu}^{2+}$  generated from the impurity versus surface state interaction in the vicinity of the absorption



**Figure 5.** Schematics of the blue-shifted 5d excited Stark level of  $\text{Eu}^{2+}$  dopant in nano-strontium di-aluminate interacting with surface states (SS). In the dopant  $\text{Eu}^{2+}$  Stark structure, the solid and dashed lines, respectively, indicate the positions corresponding to nano- and bulk-systems.

edge of the host nanocrystalline system. A more detailed study is needed to have deeper insight into the interaction mechanism, and this is our future goal.

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