

# Luminescence of $\text{Eu}^{2+}$ in some fluorides prepared by reactive atmosphere processing

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## Abstract

When phosphors are prepared by conventional solid-state route by heating in air, usually unwanted impurities like  $\text{OH}^-$ ,  $\text{O}_2^-$ , etc., get incorporated. Such impurities can be quite harmful to the luminescence processes. Especially, fluorides are highly susceptible to hydrolysis. It is necessary to use highly sophisticated procedures like high vacuum and HF or  $\text{CF}_4$  atmosphere for preparation of fluoride based phosphors. It is shown that using a simple wet chemical process and a modified reactive atmosphere processing (RAP) technique, fluorides showing intense  $\text{Eu}^{2+}$  photoluminescence can be prepared.

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## 1. Introduction

When phosphors are prepared by conventional solid-state route by heating in air, usually unwanted impurities like  $\text{OH}^-$ ,  $\text{O}_2^-$ , etc., get incorporated. Such impurities can be quite harmful to the luminescence processes. Especially, fluorides are highly susceptible to hydrolysis. To get over this difficulty, phosphors are prepared in inert atmosphere of  $\text{N}_2$ , Argon, etc. Scavengers like  $\text{PbF}_2$  have also been used to get rid of  $\text{OH}^-$ . Even such phosphors may show inefficient luminescence, possibly due to deviation from stoichiometry. The stoichiometry can be preserved by preparing the crystals in 'reactive' atmosphere instead of the inert atmosphere. For example preparation of fluoride crystals in fluorine atmosphere will prohibit the substitution of  $\text{F}^-$  by other impurity ions. The reactive atmosphere processing (RAP) was successfully used by Pastor and co-workers [1–5] for preparation of optical/laser quality crystals. We have adopted and modified this technique for preparation of  $\text{Cu}^+$  doped phosphors [6–8]. In the simplified, modified RAP, the

phosphor/ingredients are heated with an appropriate RAP agent like Teflon,  $\text{NH}_4\text{F}\cdot\text{HF}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CCl}_4$ , etc., in a closed glass tube at about 450 C for 1 h. It is then transferred to a graphite crucible pre-heated to a suitable temperature. The molten phosphor/reacted ingredients are then quickly quenched to room temperature. The procedure eliminates the need for vacuum and yet produces suitable phosphors which are as good as those produced by more sophisticated techniques. The procedure was found suitable for producing  $\text{Cu}^+$  doped phosphors which could not be prepared by preparation in air or inert atmosphere. We have prepared some  $\text{Eu}^{2+}$  activated fluorides using this technique. Very intense photoluminescence (PL) was found in these phosphors which are reported here.

## 2. Experimental

Fluorides were freshly prepared by neutralization of HF with metal carbonates. Freshly prepared fluorides were thoroughly mixed with europium salts in the required stoichiometry.  $\text{Eu}^{2+}$  concentration refers to the amount added during the synthesis. The powders were transferred to a glass tube and about 2.5 wt.% RAP agent was added. The tube was closed with a tight stopper and slowly heated to 450 C for 1 h. The stopper was removed and the powders were transferred to a graphite crucible pre-heated to a suitable temperature. After heating in the graphite crucible for 1 h the resulting phosphor was rapidly quenched to room

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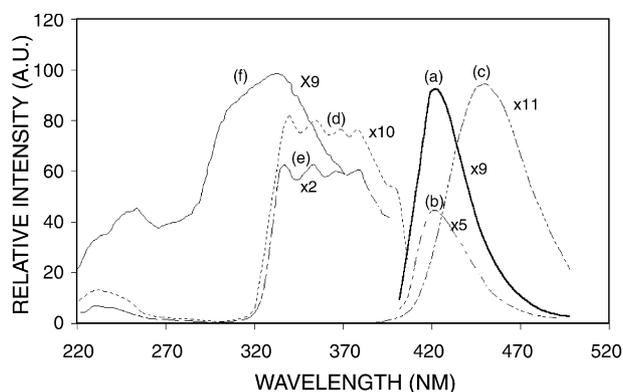


Fig. 1. Photoluminescence of  $\text{CaF}_2:\text{Eu}^{2+}$  phosphor: (a) emission of sample prepared by RAP, (b) emission of sample prepared without RAP. Excitation wavelength is 337 nm. Emission spectrum for the commercial lamps phosphor  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  is also shown for the comparison (curve c, excitation by 254 nm). (d) Excitation spectrum of sample prepared by RAP for 424 nm emission, (e) excitation spectrum of sample prepared without RAP for 424 nm emission, (f) excitation spectrum for commercial lamps phosphor  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  RAP for 450 nm emission. Numbers on the curves are the multipliers of the ordinate for obtaining relative intensities.

temperature by pouring on the metal block. Formation of compounds was confirmed by matching the XRD data with JCPDS/ICDD files ( $\text{CaF}_2$  ICDD 75-0363,  $\text{KMgF}_3$  ICDD 75-0307,  $\text{LiCaAlF}_6$  ICDD 73-2441). PL measurements at room temperature were performed using a Hitachi F-4000 spectro-fluorimeter in the range 220–700 nm with spectral slit width of 1.5 nm. Fine powders (40–65  $\mu\text{m}$ ) were used for PL measurements.  $\text{LiCaAlF}_6$  completely melted during the heat treatment. The quenched samples were crushed to fine powders and sieved. Particles in the range 72–210  $\mu\text{m}$  were used for PL as well as TL experiments.

Theratron 780 E therapy machine employing  $\text{Co}^{60}$  source was used for gamma exposures. Exposure rate was  $2.32 \times 10^{-2} \text{ } ^\circ\text{C/kg/min}$ . Thermoluminescence glow curves were recorded on Nucleonix, Hyderabad (India) TL Reader (Model no. TL 10091) with a heating rate of  $2 \text{ } ^\circ\text{C/s}$  using Hamamatsu R.6095 PMT.

### 3. Results and discussions

#### 3.1. $\text{CaF}_2:\text{Eu}^{2+}$

$\text{CaF}_2:\text{RE}$  phosphors have received attention of several research workers.  $\text{CaF}_2:\text{Sm}^{2+}$  is one of the earliest solid-state laser materials [9].  $\text{CaF}_2:\text{Dy}^{3+}$  is a phosphor for dosimetry of ionizing radiations using thermoluminescence [10]. Use of  $\text{CaF}_2:\text{Eu}^{3+}$  for dosimetry using radio-photoluminescence (RPL) has also been suggested [11].

Fig. 1 shows PL results for  $\text{CaF}_2:\text{Eu}^{2+}$  phosphor. An intense emission peaking at 424 nm is obtained in the sample prepared by RAP (curve a). This is in good agreement with the reported value for  $\text{CaF}_2:\text{Eu}^{2+}$  [11]. Emission arises from transition from levels of  $4f^65d^1$  configuration to the ground state ( $^8\text{S}_{7/2}$ ) of  $4f^7$  configuration. The intensity is an order of magnitude smaller for the sample prepared without RAP (curve b). Moreover, the results for samples prepared without RAP are not consistent. The PL intensities vary a great deal for different batches. The highest intensity obtained is shown in Fig. 1. For RAP samples, on the other hand, PL intensities were within 10% of each other for 10 batches. It is worth mentioning that without use of any reducing agent, europium is incorporated in divalent state. The

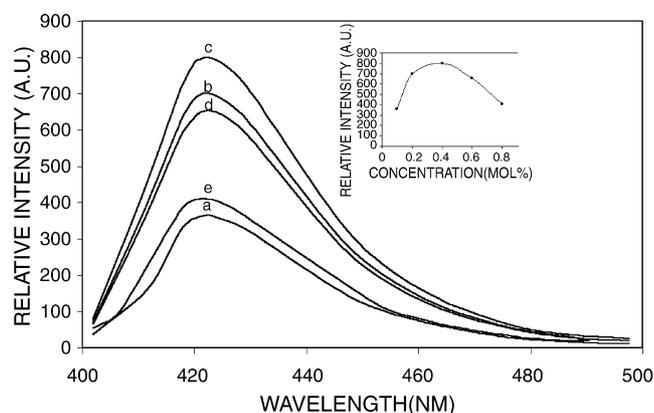


Fig. 2. Effect of  $\text{Eu}^{2+}$  concentration on photoluminescence of  $\text{CaF}_2:\text{Eu}^{2+}$  phosphor. Excitation wavelength was 337 nm. (a)  $\text{Ca}_{0.999}\text{Eu}_{0.001}\text{F}_2$ , (b)  $\text{Ca}_{0.998}\text{Eu}_{0.002}\text{F}_2$ , (c)  $\text{Ca}_{0.996}\text{Eu}_{0.004}\text{F}_2$ , (d)  $\text{Ca}_{0.994}\text{Eu}_{0.006}\text{F}_2$ , (e)  $\text{Ca}_{0.992}\text{Eu}_{0.008}\text{F}_2$ .

PL intensity of the RAP prepared sample is comparable to that of a commercial lamp phosphor. For comparison, emission of the commercial  $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$  phosphor (sylvania 2466 blue) is shown (curve c). Fig. 2 shows the effect of  $\text{Eu}^{2+}$  concentration on PL intensity. Maximum intensity is obtained for 0.4 mol%, corresponding to the composition  $\text{Ca}_{0.996}\text{Eu}_{0.004}\text{F}_2$ . Concentration quenching is observed for higher concentrations.

#### 3.2. $\text{KMgF}_3:\text{Eu}^{2+}$

$\text{KMgF}_3$  has the cubic perovskite crystal structure.  $\text{K}^+$  ions are at the center of a cube, with  $\text{Mg}^{2+}$  ions at the corners. Fluorine ions are located on the midst of each of the sides of the cube. It is useful as optical window material in VUV region [12]. It has been studied more frequently with 3d activators [13]. It has also been studied as UV scintillator and radiation dosimetry phosphor [14–16].  $\text{KMgF}_3:\text{Eu}^{2+}$  has also been studied earlier [17–25].

XRD pattern of  $\text{KMgF}_3$  synthesized matched very well with ICDD 75-0307. There are no indications of formation of the other phase  $\text{K}_2\text{MgF}_4$ . As per ICDD records, diffraction lines around  $d=2.81$  and 1.99 are observable in patterns of both  $\text{KMgF}_3$  and  $\text{K}_2\text{MgF}_4$  (ICDD 76-0038). Lines at  $d=2.949$  and 2.1399 distinguishes  $\text{K}_2\text{MgF}_4$  from  $\text{KMgF}_3$ . There were no diffraction lines at these positions in our sample. There were no indications of the unreacted constituents as well. KF (ICDD 36-1458) can be identified by the diffraction lines at 2.674 and 1.891. No such lines were observed. Similarly, absence of lines at 3.267 ( $\text{TMgF}_2$  ICDD 72-2231), 2.143 and 1.694 ( $\text{CMgF}_2$  ICDD 38-0882) indicated that there was no unreacted  $\text{MgF}_2$  present. Thus the  $\text{KMgF}_3$  synthesized is phase pure.

Fig. 3 shows PL spectra for  $\text{KMgF}_3:\text{Eu}^{2+}$  samples. In RAP processed sample, very intense emission is observed around 358 nm (curve a). Line emissions due to f–f transitions are superposed on the band emission due to transition from levels of  $4f^65d^1$  configuration to the ground state ( $^8\text{S}_{7/2}$ ) of  $4f^7$  configuration. This is close to the reported value [17]. PL results for the sample not subjected to RAP are again inconsistent. Large batch to batch variations were observed in the PL intensity. The excitation spectrum has a pronounced maximum around 250 nm

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