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# Radiation-induced valence changes in Eu-doped phosphors

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Received 12 February 1996, in final form 17 September 1996

**Abstract.** Europium impurities can be incorporated in two forms: divalent and trivalent. Phosphors activated by  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$  find important applications. Exposure to ionizing radiations is known to cause  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion. This conversion is important in understanding thermoluminescence and radiophotoluminescence applications. However, there have been no systematic studies on  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion. Data on  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion in a large number of europium-doped phosphors are presented in this paper. It is concluded that efficient  $\text{Eu}^{2+}$  phosphors are suitable hosts for studying  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion.

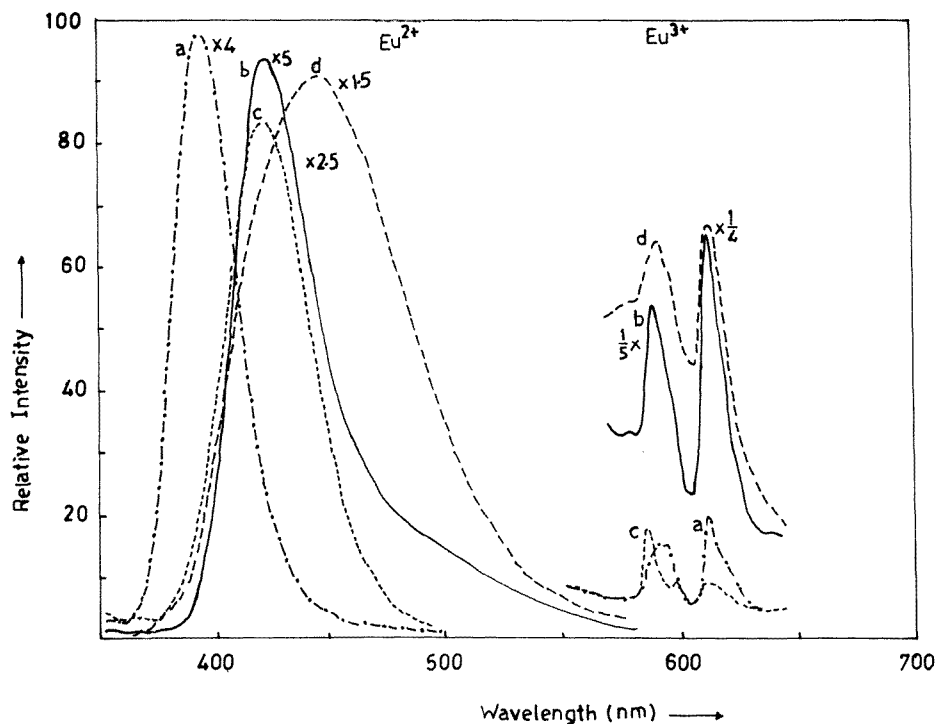
## 1. Introduction

Rare-earth ions are known to exist in various valence states although the trivalent state is the most prevalent. In particular, Sm and Eu ions are known to be stable in trivalent as well as divalent states. It is also known that exposure to ionizing radiation often results in  $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$  conversion (Merz and Pershan 1967). In fact in the two well known phosphors used in dosimetry of ionizing radiations using thermoluminescence (TL), namely  $\text{CaF}_2 : \text{Dy}$  and  $\text{CaSO}_4 : \text{Dy}$ , such conversion has been proposed to play a major role in the thermoluminescent processes (Merz and Pershan 1962, Nambi *et al* 1974).

$\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion may also be used in radiophotoluminescence (RPL) dosimetry of ionizing radiations.  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  are known to exhibit characteristically different photoluminescence (PL). Thus, in a solid exposed to ionizing radiation, characteristic  $\text{Eu}^{2+}$  luminescence will be observed. If the intensity of luminescence can be correlated with the amount of exposure, the latter can be estimated by studying the  $\text{Eu}^{2+}$  luminescence. It has already been suggested (Calvert and Danby 1984) that RPL in  $\text{CaSO}_4 : \text{Eu}$  can be used for this purpose.

Despite such interesting applications in the field of dosimetry of ionizing radiation, not much is known about the radiation-induced  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion. No efforts have been made to correlate quantitatively the efficiencies of such conversions and the TL sensitivities. Physicochemical factors which determine the efficiency of radiation-induced  $\text{RE}^{3+} \leftrightarrow \text{RE}^{2+}$  conversion have not been identified. There also do not seem to be any studies on Eu-doped phosphors which could be a suitable substitute for  $\text{CaSO}_4 : \text{Eu}$ . It has been mentioned that  $\text{Eu}^{3+}$  ions at cubic sites are more susceptible to radiation-induced conversion to  $\text{Eu}^{2+}$  (Baker *et al* 1958), and the maximum amount that can be converted to  $\text{Eu}^{2+}$  is about 1% of the total  $\text{Eu}^{3+}$  in the phosphor. There are no measurements available which would substantiate or refute these statements.

In this paper we present a first exhaustive report on the radiation-induced  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion in several well known Eu-doped phosphors.



**Figure 1.** Typical  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  emission in phosphates: (a)  $\text{Sr}_{0.8}\text{Mg}_{1.2}\text{P}_2\text{O}_7 : \text{Eu}$ ; (b)  $\text{KBaPO}_4 : \text{Eu}$ ; (c)  $\text{Sr}_3(\text{PO}_4)_2 : \text{Eu}$ ; (d)  $\text{NaBaPO}_4 : \text{Eu}$ . Unirradiated samples showed only  $\text{Eu}^{3+}$  emission, while irradiated ( $63.7 \text{ C kg}^{-1}$ ) samples exhibited strong  $\text{Eu}^{2+}$  emission besides the  $\text{Eu}^{3+}$  emission. The numbers on the curves are the multipliers of the ordinate for obtaining the relative PL intensity.

## 2. Experimental details

### 2.1. Materials

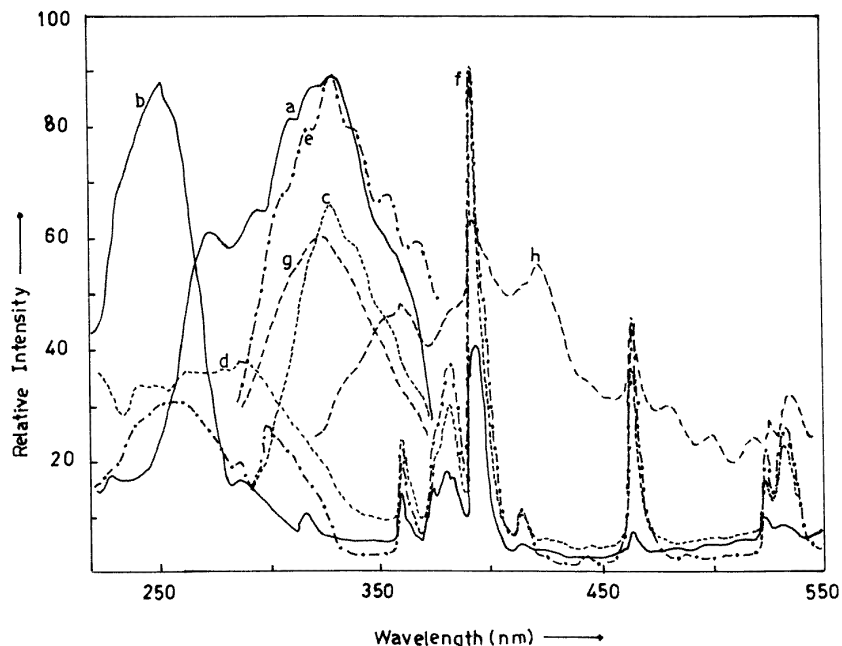
The following types of compound were considered suitable for studying  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion:

(a) compounds containing a high concentration of  $\text{Eu}^{3+}$ , so that total conversion to  $\text{Eu}^{2+}$  (which could be around 1% of the  $\text{Eu}^{3+}$  concentration) could be high by virtue of the abundance of  $\text{Eu}^{3+}$ ; stoichiometric  $\text{Eu}^{3+}$  compounds such as  $\text{KEuP}_4\text{O}_{12}$ ,  $\text{EuMgAl}_{11}\text{O}_{19}$ ,  $\text{K}_2\text{Eu}_2(\text{SO}_4)_4$ ,  $\text{SrEu}_2(\text{WO}_4)_4$ ,  $\text{CaEu}_2(\text{WO}_4)_4$ ,  $\text{Ca}_3\text{Eu}(\text{WO}_4)_3$ ,  $\text{Sr}_3\text{Eu}_2(\text{BO}_3)_4$ ,  $\text{SrEuBO}_4$ ,  $\text{K}_5\text{Eu}_2(\text{MoO}_4)_4$ ,  $\text{EuAlO}_3$  and  $\text{Sr}_3\text{Eu}(\text{PO}_4)_3$ ;

(b) compounds of Gd, Y and La in which the RE ion can be substituted by  $\text{Eu}^{3+}$  to a large extent: oxychlorides, sulphates, aluminates such as  $\text{GdAlO}_3$ , tungstates of the form  $\text{Y}_{2-x}\text{Eu}_x\text{WO}_6$ , oxides such as  $\text{NaGd}_{1-x}\text{Eu}_x\text{O}_2$ ,  $\text{La}_{1.96}\text{Y}_{0.02}\text{Eu}_{0.02}\text{O}_3$  and  $\text{SrY}_{1.9}\text{Eu}_{0.1}\text{O}_4$ , borates such as  $\text{CaY}_{0.98}\text{Eu}_{0.02}\text{BO}_4$  and phosphates such as  $\text{LaY}_{0.72}\text{Ba}_{0.14}\text{Eu}_{0.14}\text{LiPO}_4$ ;

(c) known  $\text{Eu}^{3+}$  phosphors such as  $\text{Y}_2\text{O}_3 : \text{Eu}$ ,  $\text{YVO}_4 : \text{Eu}$ ,  $\text{YPO}_4 : \text{Eu}$ ,  $\text{Gd}_2\text{O}_3 : \text{Eu}$  and  $\text{La}_2\text{O}_3 : \text{Eu}$  which contain as much as 5 mol%  $\text{Eu}^{3+}$  and exhibit efficient  $\text{Eu}^{3+}$  luminescence;

(d) known  $\text{Eu}^{2+}$  phosphors such as  $\text{Sr}_3(\text{PO}_4)_2 : \text{Eu}$ ,  $\text{Ba}_3(\text{PO}_4)_2 : \text{Eu}$ ,  $\text{Ba}(\text{PO}_3)_2 : \text{Eu}$ ,



**Figure 2.** Typical PL excitation spectra for various phosphates: (a)  $\text{Sr}_{0.8}\text{Mg}_{1.2}\text{P}_2\text{O}_7$  : Eu,  $\lambda_{em} = 390$  nm; (b)  $\text{Sr}_{0.8}\text{Mg}_{1.2}\text{P}_2\text{O}_7$  : Eu,  $\lambda_{em} = 590$  nm; (c)  $\text{KBaPO}_4$  : Eu,  $\lambda_{em} = 420$  nm; (d)  $\text{KBaPO}_4$  : Eu,  $\lambda_{em} = 610$  nm; (e)  $\text{Sr}_3(\text{PO}_4)_2$  : Eu,  $\lambda_{em} = 420$  nm; (f)  $\text{Sr}_3(\text{PO}_4)_2$  : Eu,  $\lambda_{em} = 610$  nm; (g)  $\text{NaBaPO}_4$  : Eu,  $\lambda_{em} = 450$  nm; (h)  $\text{NaBaPO}_4$  : Eu,  $\lambda_{em} = 592$  nm.

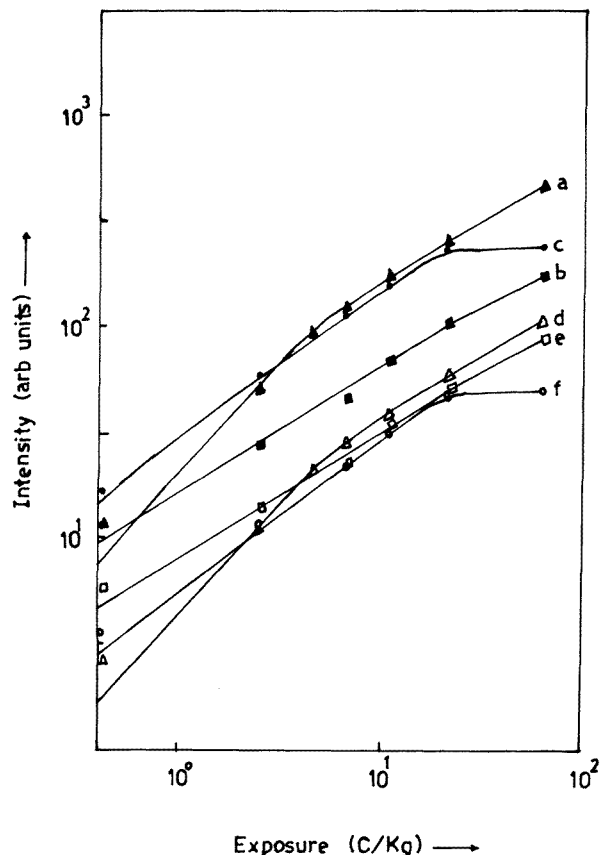
$\text{KBaPO}_4$  : Eu,  $\text{NaBaPO}_4$  : Eu,  $\text{KSrPO}_4$  : Eu,  $\text{Sr}_2\text{P}_2\text{O}_7$  : Eu,  $\text{SrMgP}_2\text{O}_7$  : Eu,  $\text{BaMgP}_2\text{O}_7$  : Eu,  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  : Eu,  $\text{BaB}_8\text{O}_{13}$  : Eu,  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  : Eu, alkaline-earth hexa-aluminates,  $\text{SrB}_2\text{O}_4$  : Eu,  $\text{SrB}_6\text{O}_{10}$  : Eu and alkaline-earth chlorides (these solids seem to be suitable for accommodating the  $\text{Eu}^{2+}$  ion in rather a high concentration; if somehow  $\text{Eu}^{3+}$  is incorporated in these solids, then it may be readily converted to  $\text{Eu}^{2+}$ , which will fluoresce with a high efficiency);

(e) compounds which are expected to resemble  $\text{CaSO}_4$  and  $\text{CaF}_2$  in their physiochemical properties: alkali and alkaline-earth sulphates and fluorides ( $\text{CaSO}_4$  : Eu (Dhopte *et al* 1991) and  $\text{CaF}_2$  : Eu (Dhopte *et al* 1992) were found to exhibit high  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion; the alkali and alkaline-earth sulphates, alkaline-earth fluorides and  $\text{PbF}_2$  also might exhibit this property).

The compounds were prepared using the well known methods of solid state chemistry. References giving more details of the preparation procedure will be cited at the appropriate places.

## 2.2. Methods

Exposures to  $\gamma$ -rays were made using a  $^{60}\text{Co}$  source. Fluorescence from various irradiated and unirradiated powder samples was studied on a Hitachi F-4000 fluorescence spectrophotometer. The same amount of sample was used every time. Emission and excitation spectra were recorded with a spectral slit width of 1.5 nm.



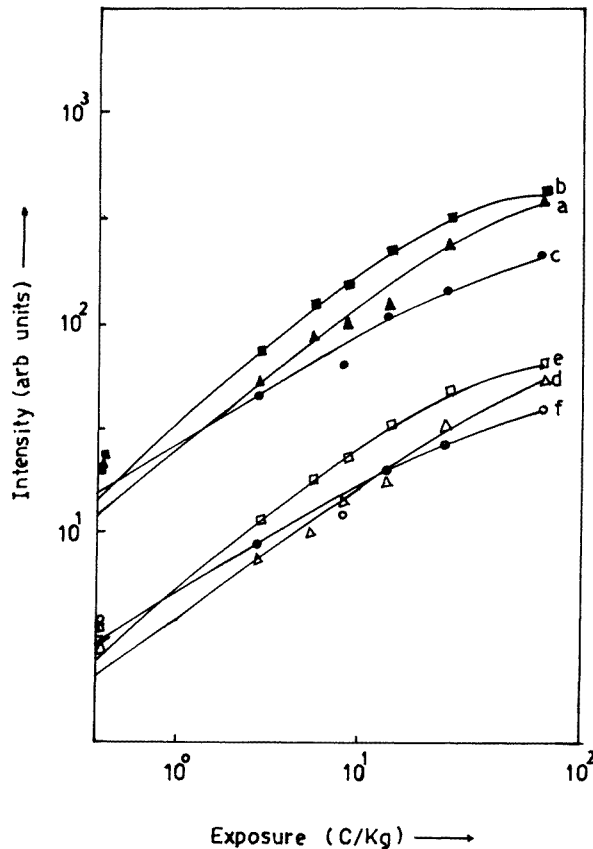
**Figure 3.** Response curves for europium-doped phosphates subjected to  $\gamma$  exposures, where the intensity of  $\text{Eu}^{2+}$  emission is plotted as a function of exposure: curves a and d,  $\text{KBaPO}_4 : \text{Eu}$ ; curves b and e,  $\text{NaBaPO}_4 : \text{Eu}$ ; curves c and f,  $\text{KSrPO}_4 : \text{Eu}$ . Curves a–c show peak height and curves d–f peak area.

### 3. Results and discussion

#### 3.1. Stoichiometric $\text{Eu}^{3+}$ compounds

$\text{KEuP}_4\text{O}_{12}$  (Mazurak and Graber 1992),  $\text{Sr}_3\text{Eu}_2(\text{BO}_3)_4$ ,  $\text{SrEuBO}_4$  (Blasse 1969),  $\text{K}_5\text{Eu}(\text{MoO}_4)_4$  (Blasse 1978) and  $\text{Sr}_3\text{Eu}(\text{PO}_4)_3$  (McCurthy *et al* 1982) were synthesized according to the methods given in the references cited.  $\text{EuMgAl}_{11}\text{O}_{19}$  was prepared by the combustion synthesis (Kingsley *et al* 1990). Tungstates were obtained by precipitation from aqueous solutions. The precipitates were dried and heated in air at  $1000^\circ\text{C}$  for 15 h.  $\text{K}_2\text{Eu}_2(\text{SO}_4)_4$  was prepared by boiling an aqueous solution containing the constituent sulphates in stoichiometric proportions. The aluminate  $\text{EuAlO}_3$  (Jaffe 1970) was synthesized by coprecipitation of hydroxides followed by heating at  $1000^\circ\text{C}$  for 12 h.

In all these compounds, strong  $\text{Eu}^{3+}$  luminescence was observed in the form of narrow bands at around 595 and 610 nm corresponding to transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ,  $^7\text{F}_2$ , respectively. The excitation is in form of a charge-transfer (CT) band in the region 230–320 nm and the lines corresponding to f–f transitions in the region 320–540 nm. Exposure to ionizing



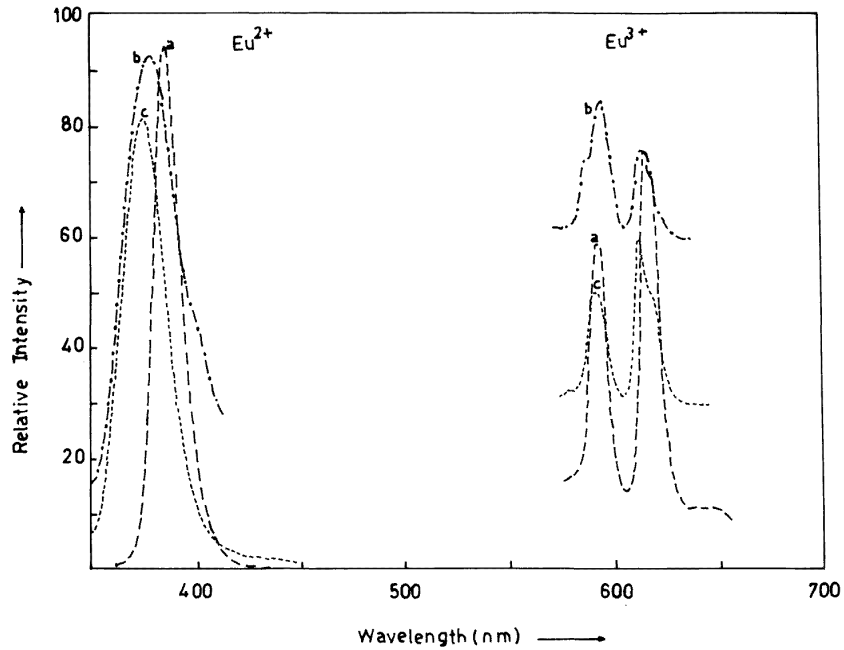
**Figure 4.** Response curves for europium-doped phosphates subjected to  $\gamma$  exposures, where the intensity of  $\text{Eu}^{2+}$  emission is plotted as a function of exposure: curves a and d,  $\text{Sr}_{0.8}\text{Mg}_{1.2}\text{P}_2\text{O}_7$  : Eu; curves b and e,  $\text{Sr}_2\text{P}_2\text{O}_7$  : Eu; curves c and f,  $\text{Sr}_3(\text{PO}_4)_2$  : Eu. Curves a–c show peak height, and curves d–f peak area.

radiations had little effect on the PL. No luminescence attributable to  $\text{Eu}^{2+}$  could be observed.

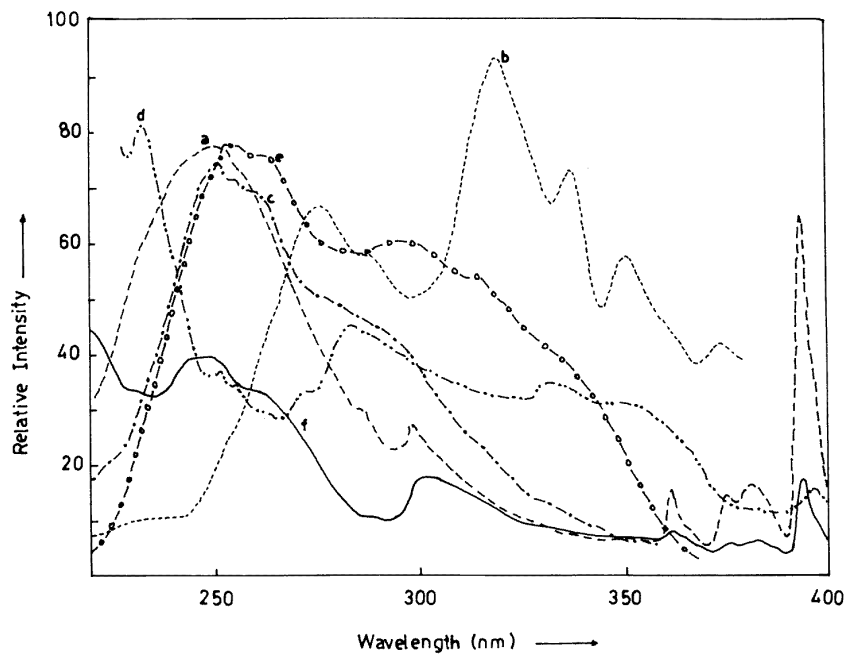
### 3.2. $\text{Eu}^{3+}$ phosphors

$\text{Gd}_2\text{O}_3$  : Eu (5 mol%),  $\text{La}_2\text{O}_3$  : Eu (5 mol%) and  $\text{Y}_2\text{O}_3$  : Eu (5 mol%) (Ropp 1965) were prepared by dissolving the RE oxides in nitric acid and then precipitating the mixed oxalate with oxalic acid, which was subsequently decomposed to give the desired mixed RE oxide.  $\text{YVO}_4$  : Eu (Burrus and Paulusz 1968) and  $\text{YPO}_4$  : Eu (Bril and Wanmaker 1964) were prepared by heating a mixture of the related oxides with  $\text{NH}_4\text{VO}_3$  or  $\text{NH}_4\text{H}_2\text{PO}_4$  at  $1100^\circ\text{C}$  for 10 h and then washing by  $\text{NH}_4\text{OH}$  solution followed by a second heating.

In all these compounds, the well known intense luminescence of  $\text{Eu}^{3+}$  was observed. The efficiency of luminescence in  $\text{Y}_2\text{O}_3$  : Eu and  $\text{YVO}_4$  : Eu was estimated, using an apparatus previously described (Alexander *et al* 1993) to be greater than 95%. However, no change in luminescence was observed following exposure to  $\gamma$ -rays as high as  $50 \text{ C kg}^{-1}$ .

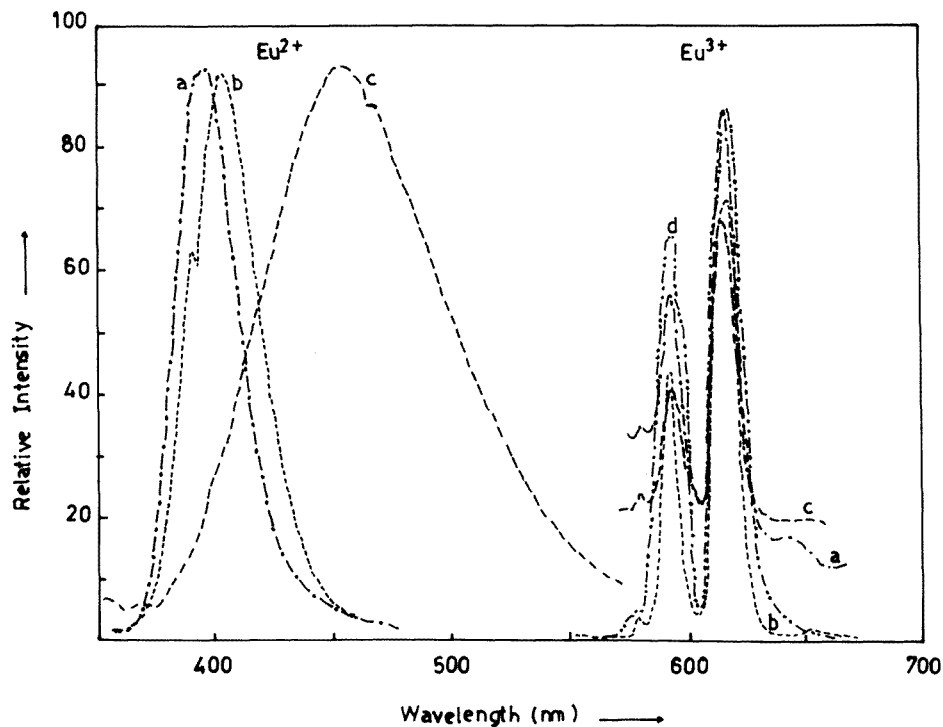


(A)



(B)

**Figure 5.** (A) Typical  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  PL emission in alkaline-earth sulphates: (a)  $\text{CaSO}_4 : \text{Eu}$ ; (b)  $\text{SrSO}_4 : \text{Eu}$ ; (c)  $\text{BaSO}_4 : \text{Eu}$ . (B) PL excitation spectra for alkaline-earth sulphates: (a)  $\text{CaSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 395 \text{ nm}$ ; (b)  $\text{CaSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 595 \text{ nm}$ ; (c)  $\text{SrSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 385 \text{ nm}$ ; (d)  $\text{SrSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 595 \text{ nm}$ ; (e)  $\text{BaSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 375 \text{ nm}$ ; (f)  $\text{BaSO}_4 : \text{Eu}$ ,  $\lambda_{em} = 595 \text{ nm}$ .



**Figure 6.** Typical  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  emission in alkali sulphates: (a)  $\text{Rb}_2\text{SO}_4$  : Eu; (b)  $\text{K}_2\text{SO}_4$  : Eu; (c)  $\text{Cs}_2\text{SO}_4$  : Eu; (d)  $\text{Na}_2\text{SO}_4$  : Eu.

### 3.3. Compounds of Y, Gd and Eu

Oxychlorides (Blasse and Brill 1967, Wolfert and Blasse 1984), oxides (Blasse 1964, Blasse and Brill 1969), tungstates (Blasse and Brill 1966), borates (Blasse 1969) and phosphates (McAlister 1968) were prepared by the methods described in the respective references.

Sulphates containing 0.1 or 5 mol% Eu were prepared by evaporating the aqueous solutions containing the constituent sulphates.

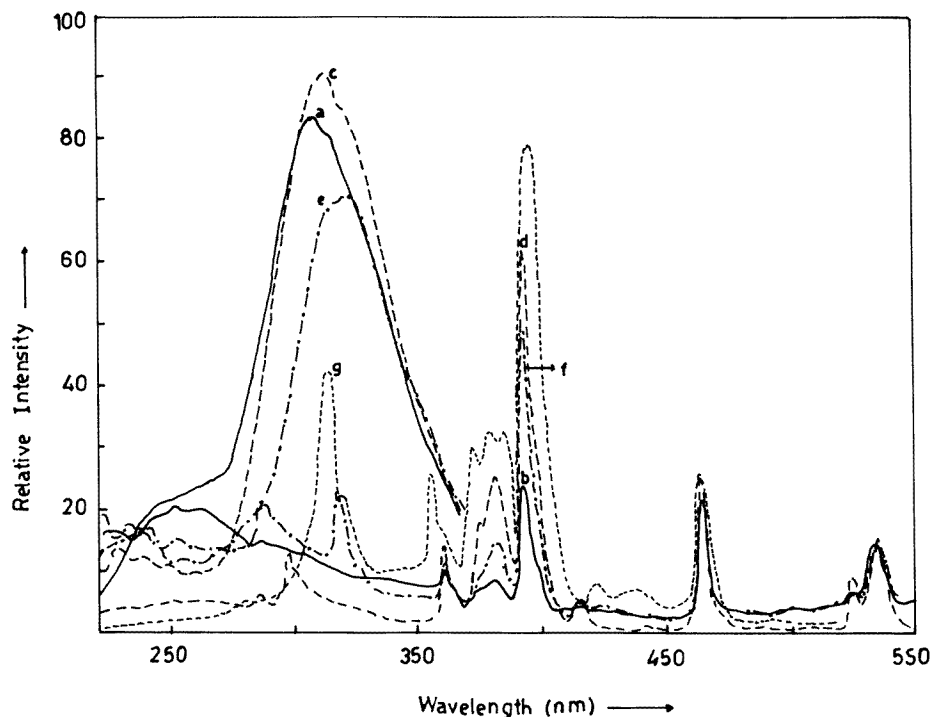
Aluminates were synthesized by coprecipitation of hydroxides followed by heating at  $1000^\circ\text{C}$  for 12 h.

In all these compounds,  $\text{Eu}^{3+}$  luminescence of moderate intensity was observed, but again there was no  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion following the  $\gamma$  irradiation.

### 3.4. Efficient $\text{Eu}^{2+}$ phosphor

A number of efficient  $\text{Eu}^{2+}$  phosphors have been reported (Wanmaker and ter Vrugt 1968, Smets *et al* 1989, Peters and Baglio 1970, Pallila and O'Reilly 1968, Jenkins and McKeag 1950, Wachtel 1969, Jaffe and Banks 1955, Smets and Verlijndonk 1986, Kobayashi *et al* 1980, Stevels 1978, Systma and Blasse 1991). Most of the reported phosphors were prepared in a reducing atmosphere so as to convert Eu to the divalent form. It was thought that, by preparing the phosphor in air, Eu may appear as  $\text{Eu}^{3+}$ . Phosphates (Hoffman 1968, Lagos 1968, Brill *et al* 1968, Waite 1974, Blasse *et al* 1969), borates (Wanmaker and Brill 1964), chloroborates (Peters and Baglio 1970), silicates (Blasse *et al* 1968) and

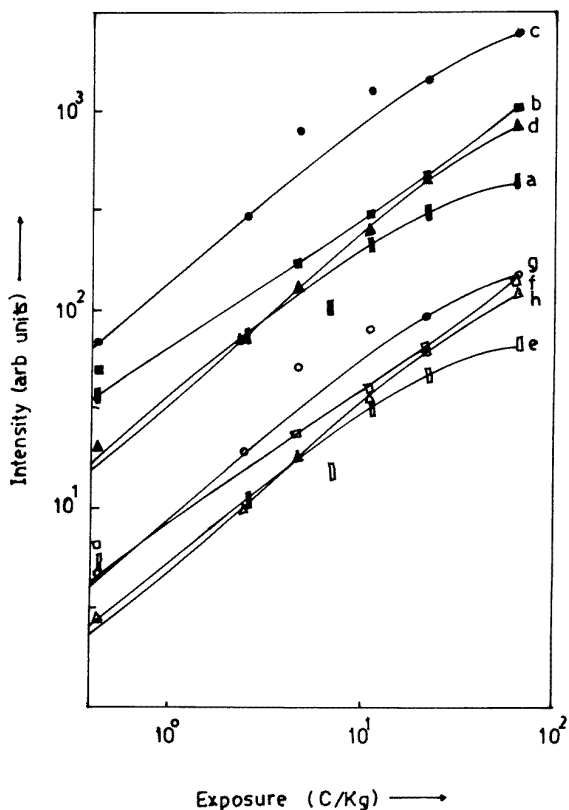




**Figure 7.** PL excitation spectra for alkali sulphates: (a)  $\text{Rb}_2\text{SO}_4 : \text{Eu}$ ;  $\lambda_{em} = 410$  nm; (b)  $\text{Rb}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 610$  nm; (c)  $\text{K}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 410$  nm; (d)  $\text{K}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 610$  nm; (e)  $\text{Cs}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 450$  nm; (f)  $\text{Cs}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 610$  nm; (g)  $\text{Na}_2\text{SO}_4 : \text{Eu}$ ,  $\lambda_{em} = 610$  nm.

$\text{BaFX}$  ( $X = \text{Cl}$  or  $\text{Br}$ ) (Gurvich *et al* 1990) were prepared by the methods described in the references cited with the difference that the reducing atmosphere was not used.  $\text{SrAl}_2\text{O}_4$  was made by decomposing the composite hydroxide, and the hexa-aluminates were prepared by combustion synthesis (Kingsley 1990). Characteristic  $\text{Eu}^{3+}$  emission and absence of  $\text{Eu}^{2+}$  were observed in the as-prepared compounds, namely, phosphates, silicates and aluminates. In alkaline-earth chlorides and chloroborates,  $\text{BaB}_8\text{O}_{13}$ ,  $\text{Ba}_3(\text{PO}_4)_2$ ,  $\text{K}_2\text{Sr}(\text{PO}_3)_4$  and  $\text{BaMgP}_2\text{O}_7$ , considerable  $\text{Eu}^{2+}$  emission was observed even when the samples were prepared in air, and for this reason these compounds were not found suitable for  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion studies.

Upon  $\gamma$  irradiation, conversion to  $\text{Eu}^{2+}$  was found only in phosphates except  $\text{Ba}(\text{PO}_3)_2$ , and not in aluminates and silicates (figure 1). The characteristic  $\text{Eu}^{2+}$  luminescence which could be excited by UV light in the spectral region 290–350 nm (figure 2) was observed for  $\text{KBaPO}_4$  (410 nm),  $\text{KSrPO}_4$  (424 nm),  $\text{NaBaPO}_4$  (450 nm),  $\text{Sr}_2\text{P}_2\text{O}_7$  (418 nm),  $\text{Sr}_{0.8}\text{Mg}_{1.2}\text{P}_2\text{O}_7$  (390 nm),  $\text{Sr}_3(\text{PO}_4)_2$  (420 nm) and  $\text{Ba}_2\text{MgP}_4\text{O}_{13}$  (402 nm).  $\text{Eu}^{2+}$  emission bands were at the positions indicated in parentheses. When the  $\text{Eu}^{3+}$  concentration was high (a few mole per cent), there was weak  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion. However, when the compounds were heated at  $700^\circ\text{C}$ , there was no back conversion ( $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ ). The  $\text{Eu}^{3+}$  concentration was varied over the range 0.1–0.2 mol%. It was found that for lower (0.2 mol%)  $\text{Eu}^{3+}$  concentrations there was excellent  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion following



**Figure 8.** Response curves for different samples subjected to  $\gamma$  exposure: curves a and e,  $\text{K}_2\text{SO}_4 : \text{Eu}$ ; curves b and f,  $\text{Rb}_2\text{SO}_4 : \text{Eu}$ ; curves c and g,  $\text{CaSO}_4 : \text{Eu}$ ; curves d and h,  $\text{CaF}_2 : \text{Eu}$ .

the  $\gamma$  irradiation. When the irradiated samples were annealed at  $700^\circ\text{C}$ , there was complete back conversion to  $\text{Eu}^{3+}$ , except for  $\text{BaBPO}_4$ . The response curves showing the intensity of  $\text{Eu}^{2+}$  luminescence as a function of  $\gamma$  exposures are presented in figures 3 and 4.

### 3.5. Alkali and alkaline-earth sulphates

Ca, Sr and Ba sulphates doped with Eu were prepared following the method of Yamashita *et al* (1972). Eu-doped alkali sulphates were prepared by simply dissolving the sulphates in the required proportions in distilled water, evaporating the solution to dryness and then quenching from  $700^\circ\text{C}$ . Excellent  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion was found for  $\text{CaSO}_4 : \text{Eu}$ , confirming the literature results (Dhopte *et al* 1992). Good conversion was also observed for  $\text{SrSO}_4 : \text{Eu}$ . The conversion could not be increased by increasing the  $\text{Eu}^{3+}$  concentration in excess of 0.1 mol%. For high concentrations, conversion was less, and  $\text{Eu}^{2+}$  was present even in unirradiated samples. In the case of  $\text{BaSO}_4 : \text{Eu}$ , samples free of  $\text{Eu}^{2+}$  could not be prepared and  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion was least among the alkaline-earth sulphates.  $\text{MgSO}_4$  was not prepared as it is highly hygroscopic.  $\text{Eu}^{2+}$  emission (figure 5(A)) was in the form of narrow bands around 375 nm ( $\text{BaSO}_4$ ) and 385 nm ( $\text{CaSO}_4$  and  $\text{SrSO}_4$ ). These positions are in agreement with the literature values (Yamashita *et al* 1985). Excitation

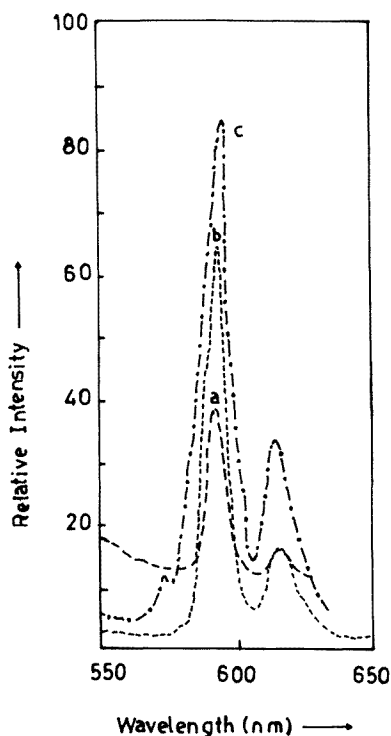


Figure 9. Typical  $\text{Eu}^{3+}$  emission in fluorides: (a)  $\text{CdF}_2$  : Eu; (b)  $\text{PbF}_4$  : Eu; (c)  $\text{BaF}_2$  : Eu.

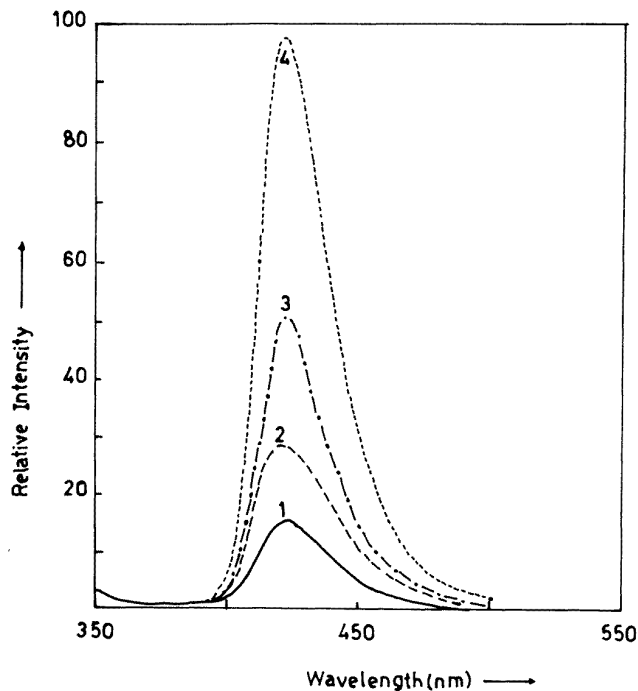
was achieved by UV light corresponding to several broad bands in the region 275–350 nm (figure 5(B)).

Among the alkali sulphates, lithium and sodium sulphate incorporated Eu in trivalent form. In  $\text{Na}_2\text{SO}_4$ , as much as 5 mol%  $\text{Eu}^{3+}$  could be doped. No  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion was observed. In the remaining alkali sulphates, Eu was found to enter as  $\text{Eu}^{2+}$ , when in a low concentration. The  $\text{Eu}^{2+}$  emission is in the form of a narrow band at around 410 nm for  $\text{Rb}_2\text{SO}_4$ , a band at around 410 nm with shoulders for  $\text{K}_2\text{SO}_4$ , and a broad band at around 450 nm for  $\text{Cs}_2\text{SO}_4$  (figure 6). Excitation could be achieved by UV light in the range 290–350 nm (figure 7). With increasing Eu concentration,  $\text{Eu}^{2+}$  luminescence decreased. For concentrations above 1 mol% in  $\text{Rb}_2\text{SO}_4$  and 5 mol% in  $\text{K}_2\text{SO}_4$ , no  $\text{Eu}^{2+}$  luminescence was detected. There was efficient  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion in these compounds. The response curves are shown in figure 8, together with those for  $\text{CaSO}_4$  and  $\text{CaF}_2$ .

### 3.6. Fluorides

Fluorides were prepared by precipitation from aqueous solution with  $\text{NH}_4\text{F}$  or by heating the metal nitrates with  $\text{NH}_4\text{F}$ .

Excellent  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion was found for  $\text{CaF}_2$  (figure 10).  $\text{Eu}^{3+}$ -doped  $\text{MgF}_2$  could be obtained when the precipitation was carried out from the sulphate solution. However, there was no  $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$  conversion. In  $\text{CdF}_2$  and  $\text{PbF}_4$ , most of the  $\text{Eu}^{3+}$  was at cubic sites, as could be seen by a dominant band at around 595 nm (figure 9). One



**Figure 10.**  $\text{Eu}^{2+}$  emission in  $\text{CaF}_2 : \text{Eu}$  exposed to  $\gamma$ -rays: curve 1,  $4.62 \text{ C kg}^{-1}$ ; curve 2,  $10.95 \text{ C kg}^{-1}$ ; curve 3,  $21.5 \text{ C kg}^{-1}$ ; curve 4,  $63.7 \text{ C kg}^{-1}$ .

may expect good conversion to  $\text{Eu}^{2+}$ . However, no such conversion was observed. No conversion was found for  $\text{SrF}_2$  and  $\text{BaF}_2$  either.

#### 4. Conclusions

From the results presented here the following conclusions can be drawn.

(1) No  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion is observed for compounds of La, Gd and Y. Thus, Eu seems to be highly stabilized in the trivalent form in these compounds.

(2) No  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion is observed in stoichiometric  $\text{Eu}^{3+}$  compounds and known  $\text{Eu}^{3+}$  activated phosphors. Even in the other compounds exhibiting  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion, the conversion is found to be greater for lower concentrations of Eu. The presence of a high  $\text{Eu}^{3+}$  concentration thus seems to be unfavourable for radiation-induced  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion.

(3)  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion has been found in several but not all phosphates, sulphates and halides. Many of these compounds exhibited efficient TL also. It might be tempting to suggest correlation between TL sensitivity and  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  conversion. However, recently (Upadeo *et al* 1994, Upadeo and Moharil 1995) we have shown that the TL glow peak temperatures do not correlate with  $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$  conversion. It may prove useful to search for a RPL phosphor using  $\text{Eu}^{2+}$  luminescence amongst these compounds.

## Acknowledgments

We are indebted to Professor P Khanna, Director, NEERI, for permitting us to undertake these investigations. One of us (SVU) wishes to thank the Council of Scientific and Industrial Research for the award of a fellowship.

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