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Redox reactions and thermoluminescence in some europium-doped phosphates

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Abstract. Rare earth (RE) ions in solids can exist in different valencies. Exposure to ionizing radiations and/or thermal treatment can change the valence state of the RE ions. $\text{RE}^{3+} \leftrightarrow \text{RE}^{2+}$ conversion has been assumed to play an important role in thermoluminescence (TL) processes. Experiments have been performed on TL and photoluminescence for several Eu-doped phosphates. It was found that there is no correlation between glow peaks and $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion. These findings place in doubt whether the accepted models for TL in RE-doped solids can be applied to phosphates.

1. Introduction

The luminescence of rare earth (RE) impurities in solids has been studied quite extensively (Blasse 1987, 1989, 1991, 1992). Several RE-doped phosphors such as $\text{CaSO}_4:\text{Dy}$, $\text{CaSO}_4:\text{Tm}$ (Yamashita *et al* 1971), $\text{Y}_2\text{O}_3:\text{Eu}$ (Wickershima and Lefever 1964), $\text{CaF}_2:\text{Dy}$ (Binder and Cameron 1969), $\text{CaF}_2:\text{Tm}$ (Lucas and Kaspar 1977), $\text{Mg}_2\text{SiO}_4:\text{Tb}$ (Hashizume *et al* 1971), $\text{LaPO}_4:\text{Ce,Tb}$ (Hashimoto *et al* 1991 and YAG:Nd (Penzkofer 1988) find important applications in various fields.

RE ions can exist in different valence states. Radiation-induced valence changes have also been studied since the early days. Eu and Sm ions exhibit characteristically different luminescences in different valence states (Blasse and Brill 1970) and are thus particularly suitable for studying radiation-induced valence changes. In several phosphors used in thermoluminescence (TL) dosimetry of ionizing radiations, radiation-induced $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$ conversion and the back conversion during heating (called 'redox reactions', a term borrowed from chemistry) has been claimed to play an important role. Merz and Pershan (1967) proposed a mechanism of TL for $\text{CaF}_2:\text{RE}$ phosphors which involves such redox reactions. A similar mechanism was proposed by Nambi *et al* (1974) for the $\text{CaSO}_4:\text{RE}$ system. Conclusive evidence for this mechanism has not been obtained, although the proposed theories have received quite general acceptance.

We have studied $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion, TL and photoluminescence (PL) in several phosphates doped with Eu^{3+} , with the aim of verifying the generality of the correlation between $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion and TL. These results are presented and discussed in this paper.

2. Experimental details

A number of efficient Eu^{2+} phosphors have been reported (Jenkins and McKeag 1950, Jaffe and Banks 1955, Wanmaker and ter Vrugt 1968, Pallila and O'Reilly 1968, Wachtel 1969,

Peters and Baglio 1970, Stevels 1978, Kobayashi *et al* 1980, Smets and Verlijdsdonk 1986, Smets *et al* 1989, Systema and Blasse 1991). In previous work, 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 become Eu^{3+} , and such phosphors would be most suitable for $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion studies. This, indeed, was the case with phosphates. Eu-doped phosphates (Hoffman 1968, Lagos 1968, Bril *et al* 1968, Blasse *et al* 1969, Waite 1974) $\text{Sr}_2\text{P}_2\text{O}_7$, SrMgP_2O_7 , $\text{Sr}_3(\text{PO}_4)_2$, BaMgP_2O_7 , KBaPO_4 , KSrPO_4 and NaBaPO_4 were prepared by the methods described in the references cited. The Eu concentration was 0.2 mol%. Characteristic Eu^{3+} emission was observed in all the as-prepared compounds except BaMgP_2O_7 .

TL glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931 B), DC amplifier and a millivolt recorder. 5 mg of phosphor were heated every time at the rate of 150 K min^{-1} .

Exposure to γ -rays was performed using a Co_{60} source. The fluorescence from various irradiated and unirradiated samples was studied using 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.

TL emission spectra were recorded by inserting the monochromator between the heater plate and the PMT. The monochromator (central electronics) used a 25 cm grating having $1200 \text{ grooves mm}^{-1}$, providing a resolution of 3 nm. Heavily irradiated (43.2 C kg^{-1}) samples were used to record the emission spectra. 50 mg of sample were heated at a rate of 300 K min^{-1} to the desired temperature and then held constant. A Hamamatsu R-955 PMT having a flat response over a wide spectral range was used.

3. Results and discussion

3.1. Photoluminescence emission

Eu^{3+} can be easily identified from its characteristic line emission (Blasse and Bril 1970) in the red region of the spectrum (around 595 and 610 nm). Eu^{2+} emission, on the other hand, is in form of a band the position of which differs from host to host (Blasse 1978). Using the PL technique the following general facts could be established.

In all the compounds studied except BaMgP_2O_7 , Eu was found to be in Eu^{3+} form. Irradiation by γ -rays converted a small fraction of Eu^{3+} to Eu^{2+} . There was no change in the Eu^{2+} emission intensity when the irradiated samples were annealed after irradiation at temperatures up to 675 K and cooled to RT and then the PL was recorded. For higher annealing temperatures, there was a reduction in Eu^{2+} luminescence and finally, for annealing temperatures exceeding 975 K, there was no trace of Eu^{2+} . For BaMgP_2O_7 , the Eu^{2+} emission did not decrease even after a 975 K anneal. Typical results for KBaPO_4 are presented in figure 1. It can be seen that for the as-prepared sample the luminescence is characteristic of Eu^{3+} , i.e. in the form of narrow lines around 595 and 610 nm. After irradiation, an additional emission is observed as a narrow band at around 420 nm. This can be assigned to Eu^{2+} emission arising from transitions of the $4f^65d$ configuration to the $^8\text{S}_{7/2}$ level of the $4f^7$ configuration. When the irradiated sample was annealed at 975 K for 15 min, the Eu^{2+} emission vanished. Figure 2 shows that the fraction of Eu^{2+} goes on increasing with increasing exposure in the range $0.4\text{--}63.7 \text{ C kg}^{-1}$.

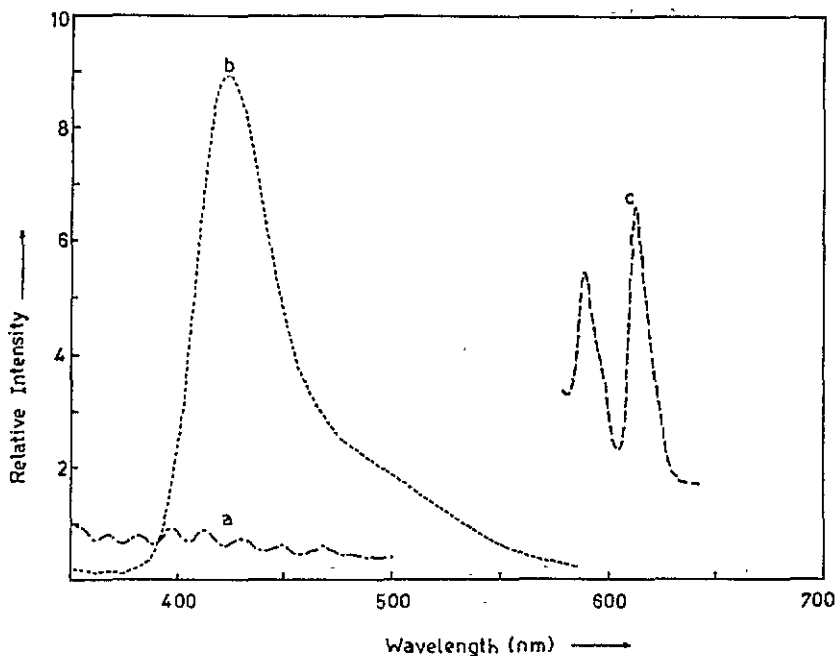


Figure 1. PL emission of $\text{K}_2\text{BaPO}_4:\text{Eu}$ samples: curve a, excitation at 320 nm, as-prepared sample; curve b, excitation at 320 nm, sample exposed to γ -rays; curve c, excitation at 250 nm, as-prepared sample and γ -irradiated sample.

3.2. Thermoluminescence glow curves

Figures 3 and 4 show the typical glow curves of various phosphors exposed to γ -rays (0.40 C kg^{-1}). The glow curve of $\text{CaSO}_4:\text{Dy}$, a material used in TLD, is also shown for the comparison. In all the phosphors there is a glow peak present at a temperature as low as around 375 K. For KSrPO_4 and SrMgP_2O_7 there is a prominent glow peak at higher temperatures. TL intensities comparable with that for $\text{CaSO}_4:\text{Dy}$ are observed for BaMgP_2O_7 and $\text{Sr}_2\text{P}_2\text{O}_7$. Intensities are much weaker for the other phosphors. The most relevant fact for the present study is that the glow peaks are observed at temperatures much below 675 K whereas $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion takes place only above this temperature.

3.3. Thermoluminescence emission spectra

TL emission spectra (figure 5) could be recorded for several samples which showed TL sufficiently intense for this purpose. In all the cases the TL emission spectra contained a peak similar to that observed for Eu^{2+} PL emission (table 1). There was also an emission band in the red region of the spectrum.

It may be surmised from the above results that Eu^{2+} , but not Eu^{3+} , plays an important role in emission processes. Since the Eu^{2+} PL is observed for annealing temperatures up to 675 K, it is clear that the Eu^{2+} ion does not change its valence state during the emission process. $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion takes place only above 675 K but there is no TL in this temperature range (glow curves were recorded up to 725 K, but only the relevant portions containing glow peaks are shown in figures 3 and 4).

A model for TL in the phosphors studied can now be outlined. The irradiation creates trapped holes and electrons (the exact trapping sites cannot yet be elucidated). During

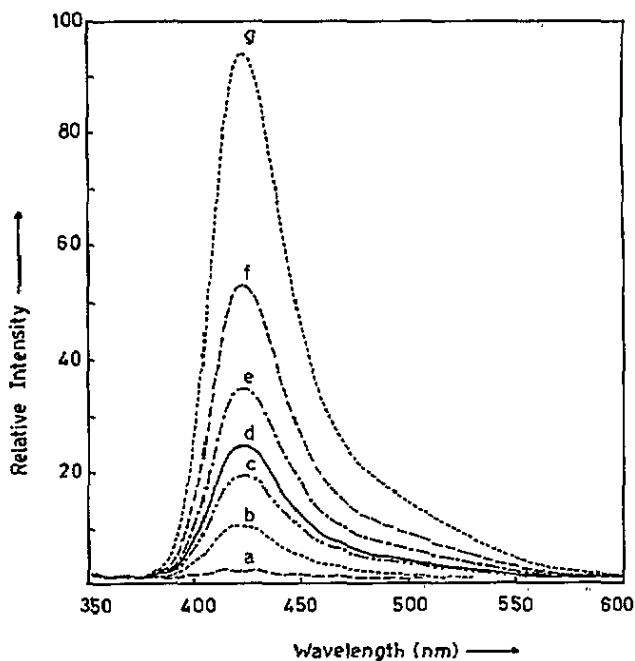


Figure 2. Eu^{2+} emission in $\text{KBaPO}_4:\text{Eu}$ exposed to γ -rays: curve a, 0.40 C kg^{-1} ; curve b, 2.51 C kg^{-1} ; curve c, 4.62 C kg^{-1} ; curve d, 6.73 C kg^{-1} ; curve e, 10.95 C kg^{-1} ; curve f, 21.5 C kg^{-1} ; curve g, 63.7 C kg^{-1} .

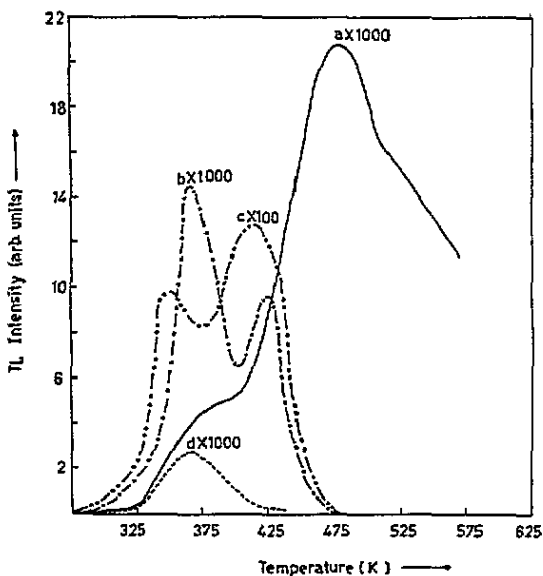


Figure 3. Glow curves of Eu-doped phosphates exposed to γ -rays (0.40 C kg^{-1}): curve a, $\text{CaSO}_4:\text{Dy}$; curve b, BaMgP_2O_7 ; curve c, SrMgP_2O_7 ; curve d, $\text{Sr}_2\text{P}_2\text{O}_7$.

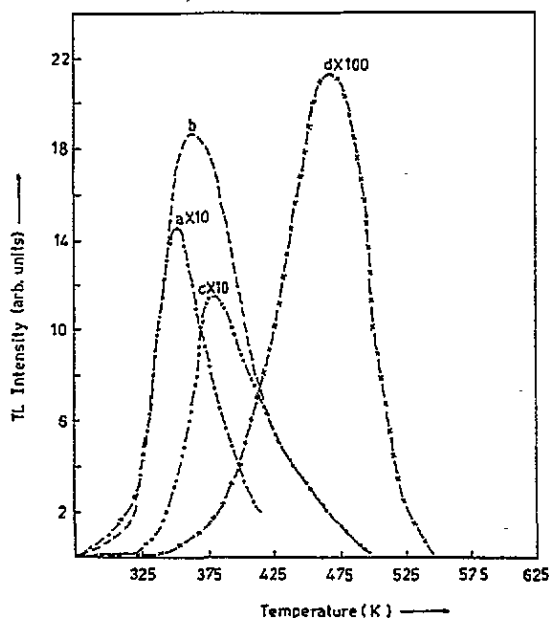


Figure 4. Glow curves of Eu-doped phosphates exposed to γ -rays (0.40 C kg^{-1}): curve a, $\text{Sr}_3(\text{PO}_4)_2$; curve b, NaBaPO_4 ; curve c, KBaPO_4 ; curve d, KSrPO_4 .

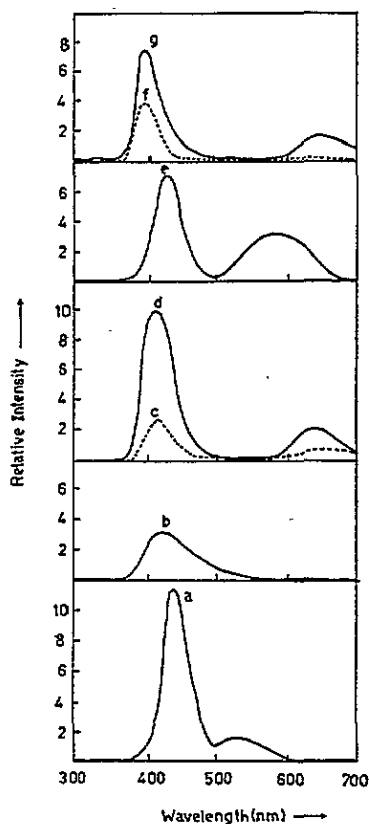


Figure 5. TL emission spectra of Eu-doped phosphates: curve a, KSrPO_4 (470 K); curve b, KBaPO_4 (385 K); curve c, BaMgP_2O_7 (364 K); curve d, BaMgP_2O_7 (425 K); curve e, $\text{Sr}_2\text{P}_2\text{O}_7$ (364 K); curve f, SrMgP_2O_7 (350 K); curve g, SrMgP_2O_7 (414 K). The temperatures at which the spectra were recorded are given in parentheses.

Table I. Data for TL and PL in some Eu-doped phosphates.

Compound	PL emission (nm)	TL emission (nm)	Glow peak temperature (K)
$\text{Sr}_2\text{P}_2\text{O}_7$	418	428	364
SrMgP_2O_7	390	400	350, 414
BaMgP_2O_7	402	412	364, 425
$\text{Sr}_3(\text{PO}_4)_2$	420	—	365
KBaPO_4	420	419	385
KSrPO_4	424	433	470
NaBaPO_4	450	—	375

heating, the electrons and holes recombine. The radiative recombinations are responsible for the TL emission in the red region. At some sites the energy of recombination is transferred to neighbouring Eu^{2+} ions which become excited and exhibit characteristic luminescence

during the return to the ground state.

The above mechanism is different from that proposed by Merz and Pershan (1967) for the $\text{CaF}_2:\text{RE}$ system and that by Nambi *et al* (1974) for the $\text{CaSO}_4:\text{RE}$ system. Merz and Pershan did not study $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion and TL emission as Eu was not present in trivalent form in their samples and the TL was very weak. For $\text{CaSO}_4:\text{Eu}$, both Eu^{3+} and Eu^{2+} emissions were observed. In our recent paper (Upadeo *et al* 1994) we have shown that, even for these phosphors, the experimental results can be more satisfactorily explained by a model similar to the model proposed here. It may be mentioned here that, from an independent argument, Matthews and Stoebe (1982) and Morgon and Stoebe (1989) found that a model based on energy transfer was more suitable than a model based on the redox reactions for explaining the TL processes in $\text{CaSO}_4:\text{Dy}$. In any case, the model of Merz and Pershan (1967) based on redox reactions is definitely not applicable to the Eu-doped phosphates studied in the present work, notwithstanding its validity for $\text{CaF}_2:\text{RE}$ and $\text{CaSO}_4:\text{RE}$ phosphors.

4. Conclusions

It can be concluded that redox reactions ($\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion) are observed in the Eu^{3+} -doped phosphates studied in the present work. These phosphors also exhibit TL. However, $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ back conversion does not seem to be related to any of the glow peaks. Eu^{3+} also does not play any role in TL emission. The TL emission spectra, on the other hand, contain strong Eu^{2+} emission. These facts suggest that the transfer of energy of electron-hole recombination to the Eu^{2+} ion is involved in the TL emission processes.

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