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Mechanism of thermoluminescence in $\text{CaF}_2:\text{Eu}$ and $\text{CaSO}_4:\text{Eu}$ phosphors

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Abstract. $\text{CaF}_2:\text{RE}$ and $\text{CaSO}_4:\text{RE}$ are important phosphors. The phosphors corresponding to $\text{RE} \equiv \text{Dy}$ and Tm find applications in thermoluminescence dosimetry using ionizing radiations. Although these phosphors have been in use for several years, the mechanism of thermoluminescence in these phosphors is not well understood. The role of RE ions in emission has been clearly indicated. Two types of model have been proposed. In model 1 it is assumed that a hole recombines with a RE^{2+} ion to convert it into RE^{3+} . Model 2 proposes that the energy of electron–hole recombination is transferred to the RE ion. Experimental results on $\text{CaSO}_4:\text{Eu}$ and $\text{CaF}_2:\text{Eu}$ are presented which show that model 2 is closer to reality.

1. Introduction

$\text{CaF}_2:\text{Sm}$ was the earliest solid state laser after ruby (Sorokin and Stevenson 1961). This generated interest in the $\text{CaF}_2:\text{RE}$ system. Methods were devised to incorporate RE ions in the divalent state. It was found that irradiation with electrons, γ -rays, etc, causes partial $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$ conversion (McClure and Kiss 1963). Thermoluminescence (TL) was one of several tools used to understand the mechanism of such conversion. Through such studies it was discovered that $\text{CaF}_2:\text{Dy}$ (Binder and Cameron 1968, 1969) and $\text{CaF}_2:\text{Tm}$ (Lucas *et al* 1977) are highly sensitive phosphors which can be used in thermoluminescence dosimetry (TLD) of the ionizing radiations. These phosphors are commercially used as TLD materials under the trade names TLD-200 and TLD-300, respectively. Strong TL was observed in $\text{CaSO}_4:\text{RE}$ also (Yamashita *et al* 1968, 1971). $\text{CaSO}_4:\text{Dy}$ and $\text{CaSO}_4:\text{Tm}$ are efficient TLD phosphors.

A large number of papers have been published on the dosimetric aspects of $\text{CaF}_2:\text{RE}$ and $\text{CaSO}_4:\text{RE}$ phosphors (Driscoll *et al* 1986, Da Rosa and Nette 1988, Fox *et al* 1988, Azorin *et al* 1993), but there are very few studies which discuss the mechanism of TL. Merz and Pershan (1967a) correlated $\text{RE}^{3+} \leftrightarrow \text{RE}^{2+}$ conversion with several glow peaks in $\text{CaF}_2:\text{RE}$ phosphors. They also observed that the TL emission spectra consisted of characteristic RE^{3+} emission (Merz and Pershan 1967b). On the basis of these facts they proposed that irradiation produces RE^{2+} and trapped hole centres. During heating, holes are thermally released and they combine with RE^{2+} to convert it into RE^{3+} in the excited state. A radiative transition to the ground state results in TL emission. The TL emission spectra of all glow peaks were in the form of characteristic RE^{3+} emission. This mechanism proposed by Merz and Pershan will be referred to as model 1.

Most of the subsequent studies have accepted this model. The model was also extended to $\text{CaSO}_4:\text{RE}$ by Nambi *et al* (1974) who obtained similar results for this system. They

also suggested another possibility that irradiation produces electron and hole centres and during the read-out the thermally released hole recombines with electron. The energy of recombination is transferred to a RE^{3+} ion which finally emits light. This mechanism will be referred to as model 2. In support of model 1, Bapat (1977) showed, from PL measurements, $Eu^{3+} \leftrightarrow Eu^{2+}$ conversion following irradiation, and back conversion after the TL run, in $CaSO_4:Eu$. Similar results could not be obtained for $CaF_2:Eu$ as, in the studies of both Merz and Pershan (1967a) and Nambi *et al* (1979), samples containing trivalent Eu were not used.

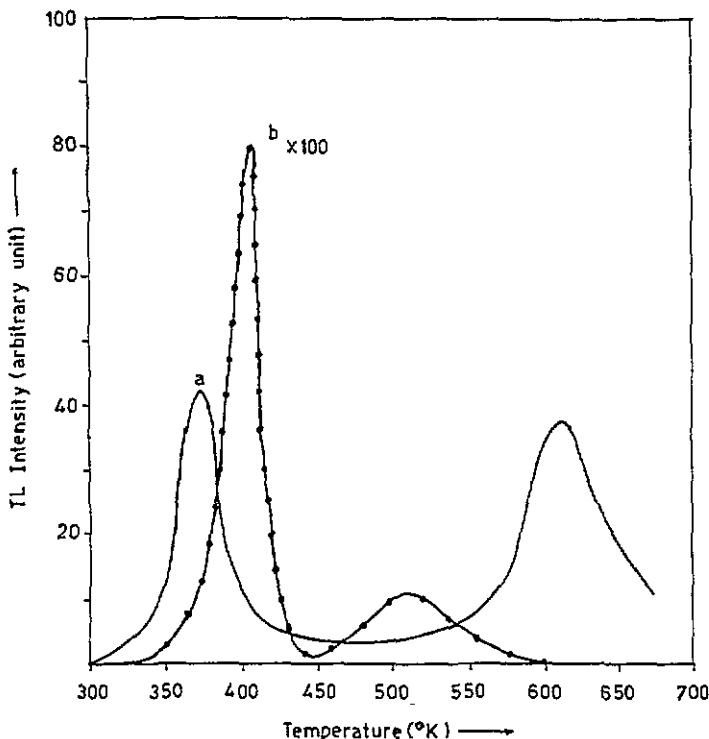


Figure 1. Glow curves for samples exposed to γ -rays (6.4 C kg^{-1}): curve a, $CaF_2:Eu$; curve b, $CaSO_4:Eu$ (samples D-400 and V-925).

We synthesized $CaSO_4$ and CaF_2 samples containing Eu in exclusively trivalent form. In our previous papers (Dhopte *et al* 1991, 1992) we have discussed several shortcomings of model 1. However, most papers discussing the mechanism of TL in the dosimetry phosphors accept model 1, forgetting that it was proposed for TL below room temperature in oxygen-free crystals. In dosimetry, one is dealing with high-temperature TL and it is not known whether the crystals are oxygen free. No systematic efforts have been made to establish the correlation between $RE^{3+} \leftrightarrow RE^{2+}$ conversion and the glow peaks above RT in the dosimetry phosphors. It is also known (McClure and Kiss 1963) that even for the highest exposures the amount of RE^{3+} converted to RE^{2+} is about 5%. This fraction is too small to allow study of the $RE^{3+} \leftrightarrow RE^{2+}$ conversion by monitoring the RE^{3+} concentration. RE^{2+} can be monitored by measuring the characteristic absorption. However, in irradiated samples, there can be confusion in identifying radiation-induced absorption and the absorption of RE^{2+} . RE^{2+} ions may be identified by their characteristic PL. The PL of only Eu, Sm and Yb ions in divalent states have been studied in detail. In crystals containing these ions, it may in principle be possible to study $RE^{3+} \leftrightarrow RE^{2+}$ conversion by monitoring the RE^{2+} emission.

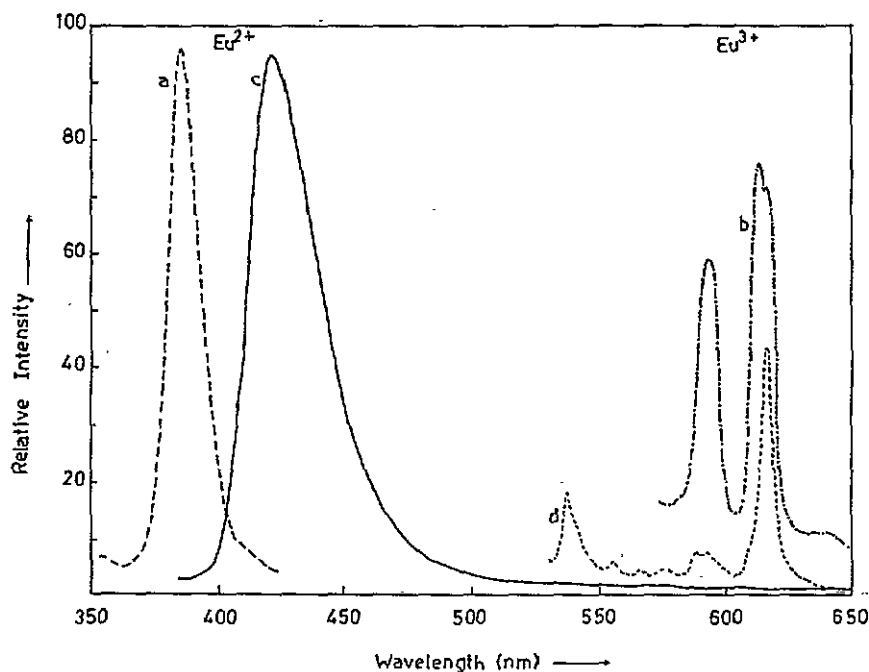


Figure 2. PL emission spectra of irradiated samples: curve a, $\text{CaSO}_4:\text{Eu}$, $\lambda_{\text{ex}} = 320$ nm; curve b, $\text{CaSO}_4:\text{Eu}$, $\lambda_{\text{ex}} = 250$ nm; curve c, $\text{CaF}_2:\text{Eu}$, $\lambda_{\text{ex}} = 335$ nm; curve d, $\text{CaF}_2:\text{Eu}$, $\lambda_{\text{ex}} = 250$ nm. The $\text{CaSO}_4:\text{Eu}$ samples are D-400 (see text).

We have carried out measurements on $\text{CaF}_2:\text{Eu}$ and $\text{CaSO}_4:\text{Eu}$ phosphors using TL, PL and ESR techniques. The results are presented and the implications for the models used to explain TL in $\text{CaF}_2:\text{RE}$ and $\text{CaSO}_4:\text{RE}$ phosphors are discussed in this paper.

2. Experimental details

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (7.35 g Analar grade) was dissolved in triply distilled deionized water. EuCl_2 (11.4 mg) was added to the solution. $\text{CaSO}_4:\text{Eu}$ was precipitated by the addition of H_2SO_4 (GR grade, Merck). The precipitate was collected and dried in an oven at 373 K and then annealed in vacuum at 1200 K. These samples will be denoted V-925.

In the other method, the procedure used by Danby *et al* (1982) was adopted. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.36 g) and Eu_2O_3 (3.5 mg) were dissolved in about 50 ml of concentrated H_2SO_4 . The acid was distilled out in a closed system similar to that used for the preparation of the dosimetry phosphor $\text{CaSO}_4:\text{Dy}$ (Rao *et al* 1980). $\text{CaSO}_4:\text{Eu}$ thus prepared was repeatedly washed with distilled water to remove the traces of acid and dried in an oven at 373 K. The samples were annealed at 673 K for 2 h following this preparation. These samples will be denoted D-400.

$\text{CaF}_2:\text{Eu}$ was prepared in a similar way by precipitation from CaCl_2 solution; the details have been described elsewhere (Dhopte *et al* 1992).

Subsequent PL measurements showed that, in $\text{CaF}_2:\text{Eu}$ and $\text{CaSO}_4:\text{Eu}$ (samples D-400), Eu was present in exclusively trivalent form and, in $\text{CaSO}_4:\text{Eu}$ (samples V-925), it was present in predominantly divalent form.

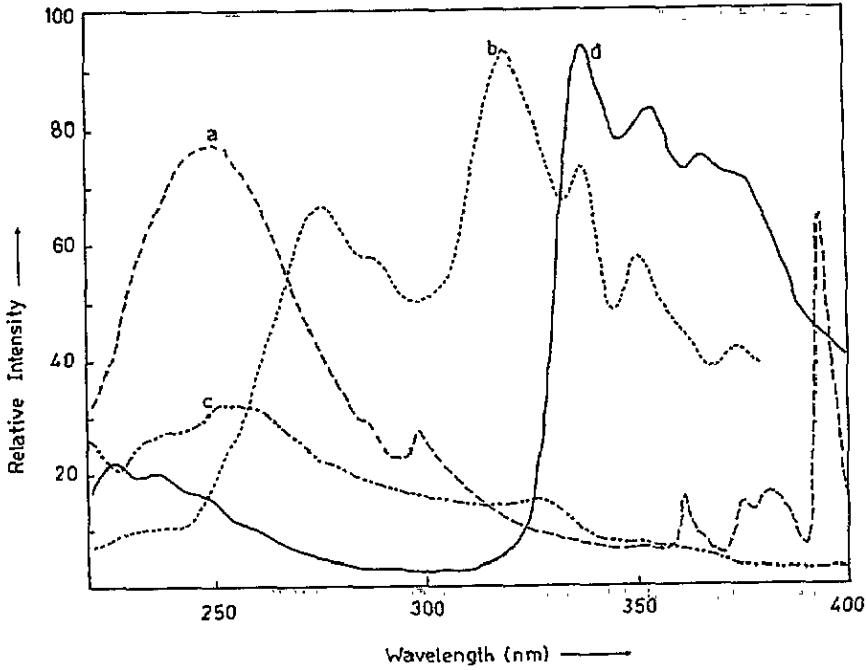


Figure 3. PL excitation spectra of irradiated samples: curve a, $\text{CaSO}_4:\text{Eu}$, $\lambda_{\text{em}} = 610$ nm; curve b, $\text{CaSO}_4:\text{Eu}$, $\lambda_{\text{em}} = 385$ nm; curve c, $\text{CaF}_2:\text{Eu}$, $\lambda_{\text{em}} = 610$ nm; curve d, $\text{CaF}_2:\text{Eu}$, $\lambda_{\text{em}} = 424$ nm. The $\text{CaSO}_4:\text{Eu}$ samples are D-400 (see text).

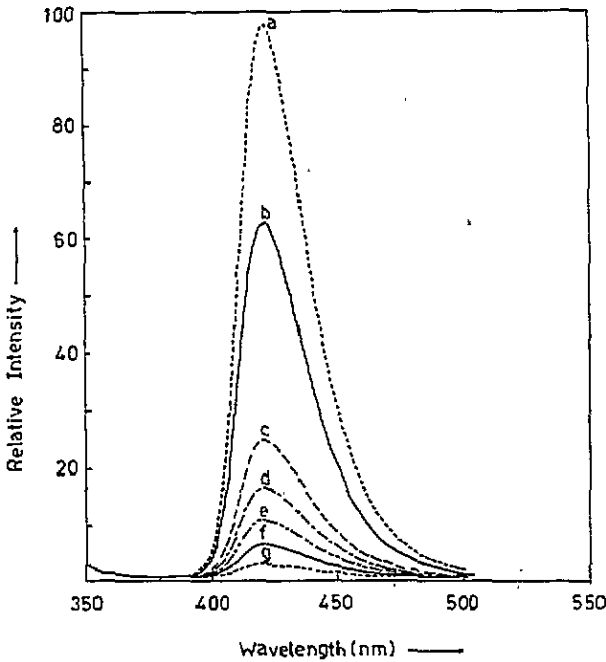


Figure 4. Eu^{2+} emission for $\text{CaF}_2:\text{Eu}$ exposed to 63.7 C kg^{-1} and then heated to various temperatures T_p (excitation wavelength, 335 nm): curve a, 413 K; curve b, 453 K; curve c, 493 K; curve d, 533 K; curve e, 573 K; curve f, 613 K; and curve g 653 K.

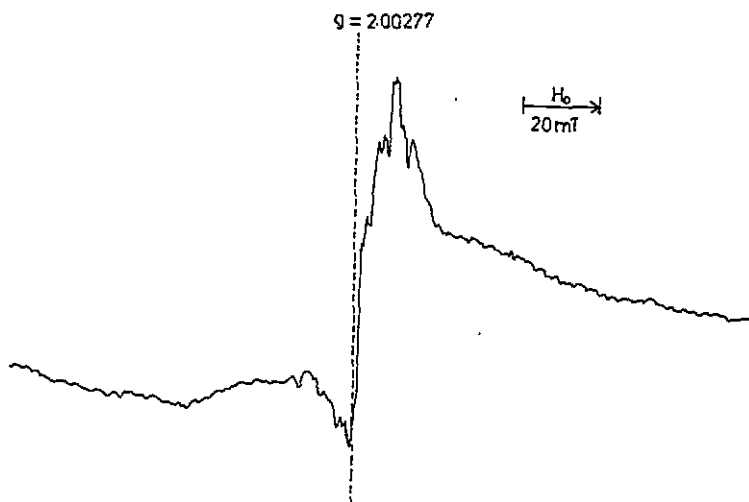


Figure 5. ESR of Eu^{2+} in $\text{CaF}_2:\text{Eu}$ exposed to 63.7 C kg^{-1} .

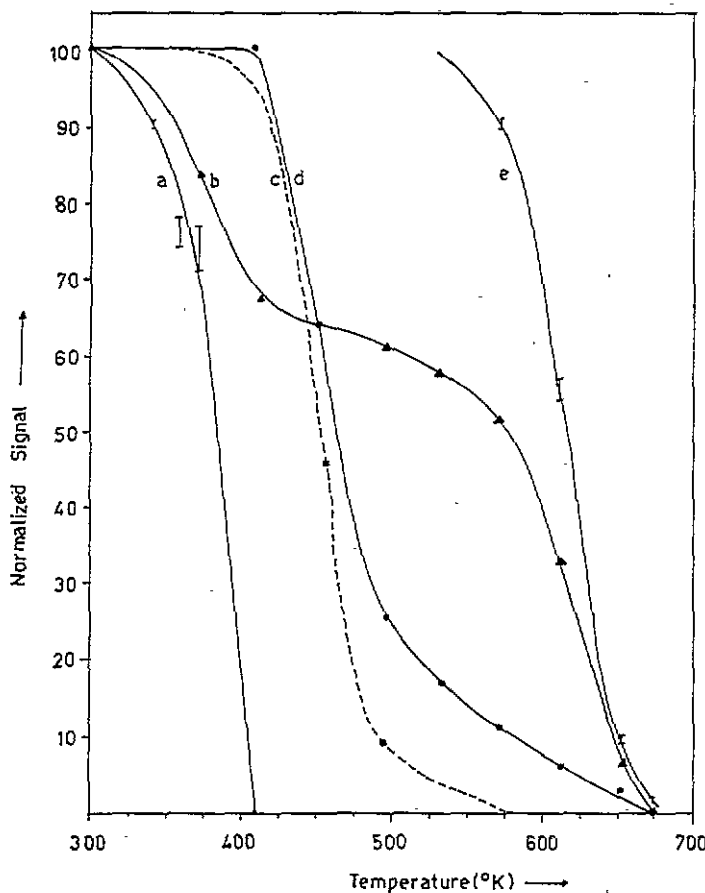


Figure 6. Temperature dependence of various experimentally measured quantities for $\text{CaF}_2:\text{Eu}$ exposed to 63.7 C kg^{-1} , normalized to the measurement at $RT \equiv 100$: curve a, remaining area under the 375 K glow peak; curve b, remaining area under the entire glow curve; curve c, strength of ESR signal corresponding to Eu^{2+} ; curve d, intensity of PL emission corresponding to Eu^{2+} ; curve e, remaining area under the 610 K glow peak.

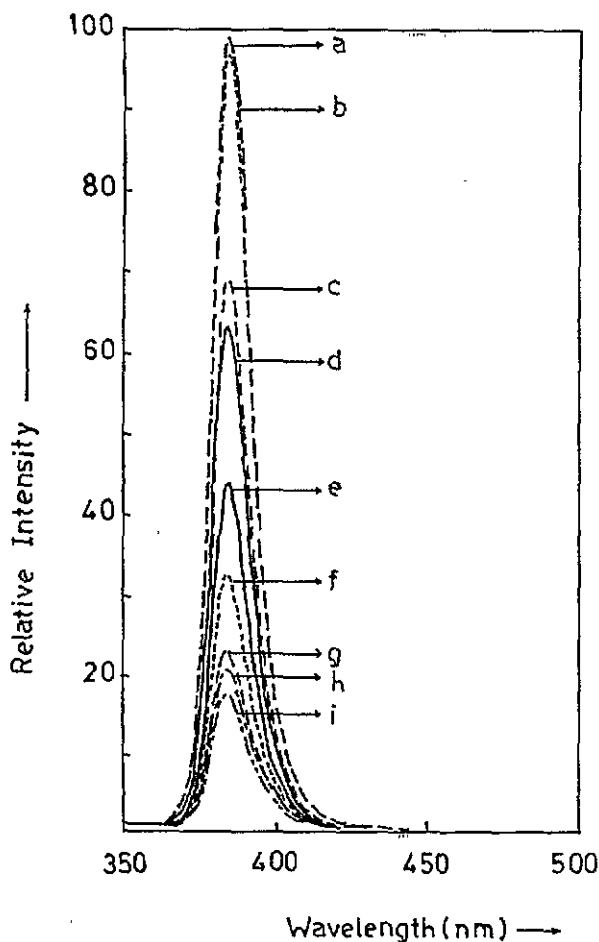


Figure 7. Eu^{2+} emission in $\text{CaSO}_4:\text{Eu}$ (sample D-400) exposed to 63.7 C kg^{-1} and then heated to various temperatures T_p (excitation wavelength, 320 nm): curve a, 425 K; curve b, 450 K; curve c, 475 K; curve d, 525 K; curve e, 550 K; curve f, 575 K; curve g, 600 K; curve h, 625 K; curve i, 650 K.

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

TL emission spectra and the monochromatic glow curves 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. Irradiated (63.7 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} up to the desired temperature at which it was then held constant. A Hamamatsu R-955 PMT having a flat response over a wide spectral range was used and no corrections for detector response were applied.

Exposure to γ -rays was achieved using a ^{60}Co source. Fluorescence from various irradiated and unirradiated 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.

ESR measurements were carried out on a Varian E-112, E-line Century Series, X-band ESR spectrometer which utilizes 100 kHz field modulation. TCNE ($g = 2.00277$) was used as a standard for g -factor measurements.

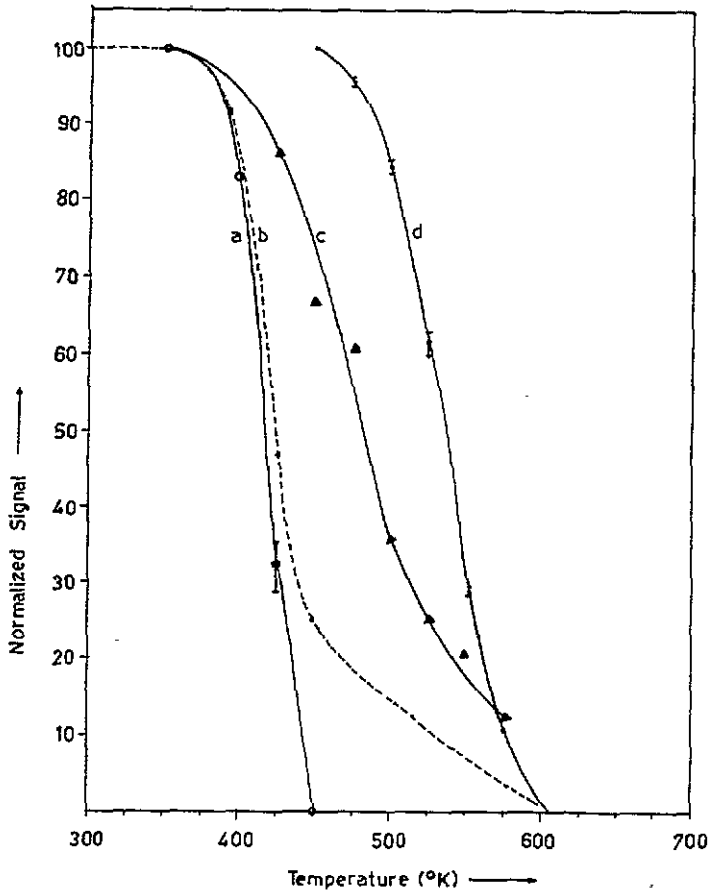


Figure 8. Temperature dependence of various experimentally measured quantities for $\text{CaSO}_4:\text{Eu}$ (sample D-400) exposed to 63.7 C kg^{-1} , normalized to the measurement at $\text{RT} \equiv 100$: curve a, remaining area under the 412 K glow peak; curve b, remaining area under the entire glow curve; curve c, intensity of PL emission corresponding to Eu^{2+} ; curve d, remaining area under the 508 K glow peak.

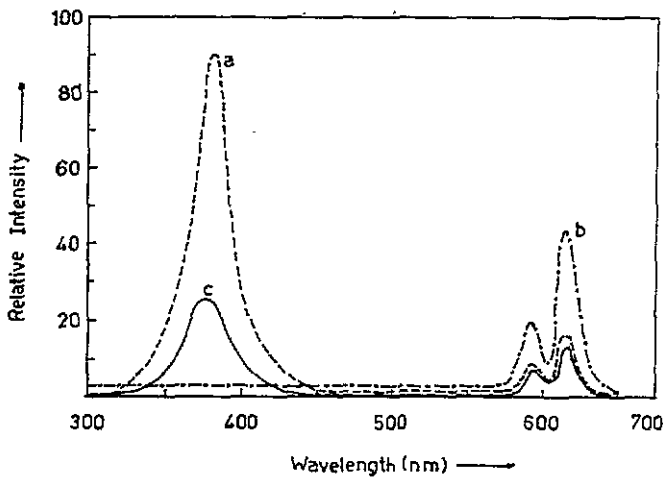


Figure 9. TL emission spectra for $\text{CaSO}_4:\text{Eu}$; curve a, sample D-400, 412 K peak; curve b, sample D-400, 508 K peak; curve c, sample V-925, 508 K peak.

3. Results and discussion

Figure 1 shows the TL glow curves for $\text{CaF}_2:\text{Eu}$ and $\text{CaSO}_4:\text{Eu}$ samples. In $\text{CaF}_2:\text{Eu}$, two prominent glow peaks can be seen at around 375 and 610 K. For $\text{CaSO}_4:\text{Eu}$, the glow peaks

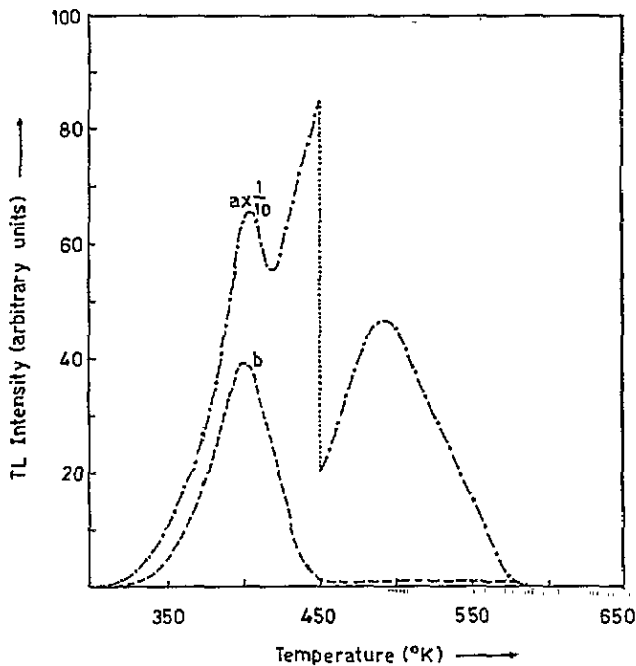


Figure 10. Monochromatic glow curve for $\text{CaSO}_4:\text{Eu}$ (sample D-400) for emission wavelengths of 610 nm (curve a) and 385 nm (curve b).

are at 412 and 508 K. If the TL is due to $\text{RE}^{2+} \rightarrow \text{RE}^{3+}$ conversion, then the intensity of Eu^{2+} luminescence should decrease with increasing temperature in much the same way as the light sum. The following experiment was done to test this. Samples were heated to a certain temperature T_p and then cooled to RT; the Eu^{2+} emission was measured. T_p was varied over a temperature range covering the entire glow curve.

Figure 2 shows typical Eu^{2+} and Eu^{3+} emissions for $\text{CaF}_2:\text{Eu}$ and $\text{CaSO}_4:\text{Eu}$. Figure 3 shows the corresponding excitation spectra. Eu^{2+} emission for $\text{CaSO}_4:\text{Eu}$ peaks at 385 nm and can be excited by 320 nm, while that for $\text{CaF}_2:\text{Eu}$ has a maximum at 424 nm and can be efficiently excited by 337 nm light. Figure 4 shows Eu^{2+} luminescence for $\text{CaF}_2:\text{Eu}$ samples annealed to various temperatures T_p .

Eu^{2+} can also be monitored by measuring ESR. Figure 5 shows a typical ESR signal for $\text{CaF}_2:\text{Eu}$ samples exposed to γ -rays. The observed spectrum arises from Eu^{2+} ions. Not all the fine-structure lines are seen, possibly owing to the low concentration of Eu^{2+} . Only one principal g -value could be calculated from the spectrum, namely $g = 1.9966$, and is in reasonable agreement with the g -factors expected for Eu^{2+} ions (Danby 1983). It should be mentioned that no ESR lines were observed in unirradiated $\text{CaF}_2:\text{Eu}$, indicating that all the Eu ions are probably in the trivalent state.

Figure 6 shows the relation between the intensity of Eu^{2+} luminescence and the area under the glow curve remaining after T_p , for $\text{CaF}_2:\text{Eu}$. The remaining area is proportional to the population of the filled trap at that instant. The area under the entire glow curve, as well as those under the 350 and 610 K peaks, evaluated separately are plotted as a function of T_p , in figure 6. It is seen that, up to 410 K, the remaining area decreases but there is no fall in the Eu^{2+} concentration. Thus up to the first glow peak there is no $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion. At around 425 K, the Eu^{2+} luminescence intensity starts to decrease. The decrease is very fast in the region 425–500 K, and a slow decrease in PL intensity is seen in the range 500–675 K, which is in the region of the 610 K glow peak. Figure 6 clearly shows that there is no correlation between the 410 K glow peak and $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion.

In the temperature region 410–500 K, there is a sharp decline in Eu^{2+} luminescence, but there is no TL in this region. Thus, there seems to be a total lack of correlation between $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion and TL in $\text{CaF}_2:\text{Eu}$. The ESR signal corresponding to Eu^{2+} also shows the same temperature dependence as shown by Eu^{2+} PL.

Similar results for $\text{CaSO}_4:\text{Eu}$ are plotted in figures 7 and 8. Again we see no correlation between TL and $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion. However, if only the area under the 508 K peak is considered, then there is some correlation between $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion and TL. On irradiation with γ -rays, no ESR lines which could be attributed to Eu^{2+} were observed. The PL emission spectrum of the same sample, on the other hand, shows bands which are characteristic of Eu^{2+} , thus indicating definite $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion following γ irradiation. On the basis of these observations, it may be concluded that the fraction of Eu^{3+} ions converted to Eu^{2+} is very small. This explains the absence of the ESR signal in the irradiated samples. The low concentration of Eu^{2+} ions gives rise to reasonable PL emission owing to the high luminescence efficiency.

The above results show that the 350 K peak in $\text{CaF}_2:\text{Eu}$ and the 425 K peak in $\text{CaSO}_4:\text{Eu}$ are definitely not related to $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion. The higher-temperature peak in $\text{CaSO}_4:\text{Eu}$ may be assigned to such redox reactions, or the observed correlation may be a coincidence. To test this, the following experiment was performed. In sample V-925, Eu^{3+} is present only in traces, and one should not obtain 508 K peak, if it originates in $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion. The glow curve for the sample V-925 is the same as that for the sample D-400, and the 508 K peak can be clearly seen.

The results on TL emission are also quite interesting. For sample D-400, we observed that TL emission was different for the 412 and 508 K peaks (figure 9). The emission corresponding to 412 K peak consists of both Eu^{2+} (385 nm) and Eu^{3+} (595 and 610 nm) luminescence. For the 508 K peak in sample D-400, there is no Eu^{2+} emission observed. The difference between the natures of the two peaks is also demonstrated by the monochromatic glow curves (figure 10). For the emission wavelength of 385 nm, the glow curve shows only the 412 K peak, while for 613 nm emission the 508 K peak is more prominent and the 412 K peak is seen only as a shoulder.

In sample V-925, Eu is present in a predominantly divalent form, and Eu^{3+} exists only in trace amounts. The TL emission for the 412 K peak is similar to that observed for sample D-400. The TL emissions corresponding to the 508 K peak, however, are different for the two samples in that, for sample V-925, it contains prominent Eu^{2+} emission and weak Eu^{3+} emission while, for sample D-400, no Eu^{2+} emission is observed for the 508 K peak.

TL in $\text{CaF}_2:\text{Eu}$ was very weak and the TL emission spectra could not be studied.

The results on TL emission show that for $\text{CaSO}_4:\text{Eu}$ the 412 K peak cannot be assigned to processes described by model 1, as the associated TL emission consists of dominant Eu^{2+} luminescence. The 508 K peak for sample D-400 can be explained by model 1, as the emission is in the form of characteristic Eu^{3+} luminescence. On the other hand, for sample V-925, there is little Eu^{3+} emission and yet the same glow peak at 508 K is observed. These facts go against model 1 which attributes TL to $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ conversion. The results can be explained by model 2. According to this model, the TL arises because of transfer of energy of electron-hole recombination to a RE ion followed by characteristic RE ion emission. The traps are thus characteristic of the host lattice while the TL emission is characteristic of the RE ions present. In sample D-400, both Eu^{2+} and Eu^{3+} are present in the as-irradiated sample. Both Eu^{3+} and Eu^{2+} emissions are observed in the 412 K peak. At higher temperatures, Eu^{2+} ions become converted to Eu^{3+} and hence TL emission corresponding to the 508 K peak for sample D-400 is in the form of characteristic Eu^{3+}

luminescence. In sample V-925, Eu is present in a predominantly divalent state and hence the major TL emission comes from Eu^{2+} at all temperatures.

4. Conclusions

It can be concluded from the results presented and discussed here that there is no correlation between the TL glow peaks above room temperature and $\text{Eu}^{3+} \leftrightarrow \text{Eu}^{2+}$ conversion in $\text{CaSO}_4:\text{Eu}$ and $\text{CaF}_2:\text{Eu}$ samples. The lack of correlation can be explained by model 2 which attributes TL to the transfer of electron-hole recombination energy to the RE ion followed by characteristic RE ion emission. Model 2 may also be valid for $\text{CaSO}_4:\text{RE}$ and $\text{CaF}_2:\text{RE}$ systems in general.

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