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The role of F centres in the thermoluminescence of low-energy UV- and x-irradiated $KCl:Eu^{2+}$

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Abstract. The thermoluminescence of ultraviolet- (250 nm) and x-ray-irradiated $KCl:Eu^{2+}$ is investigated. The peaks are located in the same positions independent of the radiation used to excite the sample, with differences only in the peak intensity ratios. Thermal and optical bleaching methods allow us to relate the thermoluminescence peaks located in the low-temperature region (320–425 K) to F_z centres and those in a higher-temperature region (425–530 K) to F centres.

1. Introduction

Recently, Eu^{2+}-doped alkali halide single crystals have been the subject of intensive investigation, mainly due to their potential application in personal dosimetry for the actinic region (Aguirre de Cárcer *et al* 1991, Jaque *et al* 1991) as well as for ionizing radiation of the x-ray (Camacho *et al* 1988, Pérez Salas *et al* 1993), β, α (Aguirre de Cárcer *et al* 1993) and γ types (Buenfil and Brandan 1992). In the case of ionizing radiation, the damage induced is well understood and it is also well accepted that it involves a primary electron–hole pair formation process, giving rise to F and H centres in pure alkali halide crystals, and perturbed F centres (F_z centres) due to the presence of impurities in doped samples (Agulló-López *et al* 1982). In fact, two absorption bands located at 560 nm and at 596 nm x-irradiated $KCl:Eu^{2+}$ crystals have been attributed to F centres (Rubio *et al* 1982) and F_z centers (Agulló-López *et al* 1982) respectively. The thermoluminescence (TL) induced by this type of radiation in pure KCl crystals is related to a recombination process between the radiation-induced interstitial halogen atoms and F centres or F aggregates (Jiménez de Castro and Alvarez Rivas 1979, Brovetto *et al* 1991). However, this is not the case for non-ionizing radiation such as low-energy UV light. TL in UV-irradiated Eu-doped alkali halides has been explained by photoionization of the Eu^{2+} ions and the subsequent trapping of the freed electron (Aguirre de Cárcer *et al* 1988) according to the reaction

$$Eu^{2+} + (h\nu)_{UV} \rightarrow Eu^{3+} + e^-_{trapped}.$$

The trapped electrons can then be thermally released during the heating process producing the observed luminescence due to the electron–hole recombination process (Aguirre de Cárcer *et al* 1991):

$$Eu^{3+} + e^-_{trapped} \rightarrow (Eu^{2+})^* \rightarrow Eu^{2+} + (h\nu)$$

where $(Eu^{2+})^*$ denotes an Eu^{2+} excited state. Therefore, apparently the mechanisms behind the observed TL for ionizing and non-ionizing radiation are of different natures. However, TL experiments on NaCl:Eu^{2+} carried out at liquid-nitrogen temperature (López *et al* 1991) have shown that the TL glow peaks in x-ray- and UV-irradiated samples are essentially the same. This observation is in agreement with more recent findings involving the TL of NaCl:Eu^{2+} irradiated at room temperature with x-rays, α, β and UV light (Aguirre de Cárcer *et al* 1993); for any type of radiation used the TL glow curves are very similar, showing differences only in the intensity ratios of the TL peaks.

The similarity between the TL glow curves produced with ionizing and non-ionizing radiation might indicate that a common damage mechanism is behind both irradiation processes, although for the case of low-energy (around 250 nm) UV light a process involving F centres is difficult to accept, since low-energy UV radiation is not energetic enough to produce intrinsic damage in the crystal. In the present work we have investigated the relation between the TL in KCl:Eu^{2+} crystals induced with x-ray and UV light of 250 nm at room temperature (RT), showing that the TL glow curves have common features. It is important to notice that this wavelength of UV low-energy light has been chosen to excite the TL of these crystals, since the TL excitation spectrum is composed of a well defined band between 200 and 280 nm peaked around 230 nm. A thermal and optical bleaching process performed on x-ray- and UV-irradiated samples allowed us to relate the participation of F and F_z centres to the TL process.

2. Experimental details

The KCl:Eu^{2+} single crystals were grown by the Czochralski method under a controlled Ar atmosphere, and were kindly supplied by the Instituto de Física, Universidad Nacional Autónoma de México (IFUNAM). The Eu^{2+} ions were added to the melt of KCl as $EuCl_2$ previously reduced from $EuCl_3$ using H_2 gas at 1073 K. The crystals were $1 \times 2 \times 2$ mm^3 in size containing 0.1 wt% of Eu^{2+}. Prior to irradiation the samples were annealed at 773 K for 30 min followed by fast cooling through contact with a Cu block. For x-irradiation we used a soft x-ray source, Tel-X-Ometer system model 580M (Tel-Atomic), operating at 20 kV and 80 μA, with the beam filtered by a 1 mm thick Al sheet. Optical absorption measurements were done using a λ9 spectrophotometer (Perkin Elmer). The ultraviolet radiation was obtained from a 1000 W Oriel Hg–Xe high-pressure arc lamp operating at 250 W. The beam was focused through the entrance slit of a Kratos monochromator (Schoeffel Instruments), 0.25 m focal length; the outcoming monochromated beam was coupled to an optical fibre and directed to the planchet of a Harshaw 4000 TLD system. TL glow curves were obtained using a linear heating rate of 5 K s^{-1} from RT up to 673 K under a N_2 atmosphere. The same optical set-up provided us with light for optical bleaching. The irradiation and measurements were performed in the dark to avoid the unwanted effect of environmental light.

3. Results

Figure 1 shows the RT optical absorption spectrum of a 20 min x-irradiated KCl:Eu^{2+} crystal. It consists of three broad bands; the first two located around 243 and 343 nm correspond to the well known Eu^{2+} absorption bands. These bands have been attributed to the Eu^{2+} electronic transitions from the $4f^7$ state to the e_g and t_{2g} states of the $4f^6$ 5d configuration

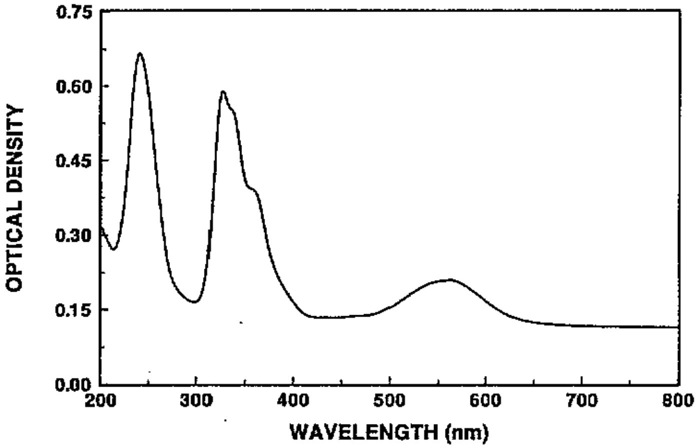

Figure 1. The RT optical absorption spectrum of a 20 min x-irradiated KCl:Eu^{2+} crystal. The bands at 243 and 343 nm are Eu^{2+} absorption bands; the band at 560 nm is due to F centres produced by irradiation.

respectively (Rubio *et al* 1982). The third absorption band at 560 nm is created by x-irradiation and it has been ascribed to F centres in KCl:Eu^{2+} crystals (Rubio *et al* 1982). Figure 2 shows the absorption spectrum obtained at 10 K, after RT photostimulation with F light (520 nm) of a previously x-irradiated crystal. Two absorption bands appear at 535 and 590 nm. Taking into account the well established temperature shift of the F absorption band in alkali halide crystals (Rodrígues-Mijangos *et al* 1993), we recognise that the band at 535 nm is due to F centres. On the other hand, the absorption band with a maximum at 590 nm has been associated with F_z centres in KCl:Eu^{2+} crystals (Agulló-López *et al* 1982). It is important to stress the fact that the F_z band is clearly resolved only after photostimulation with F light.

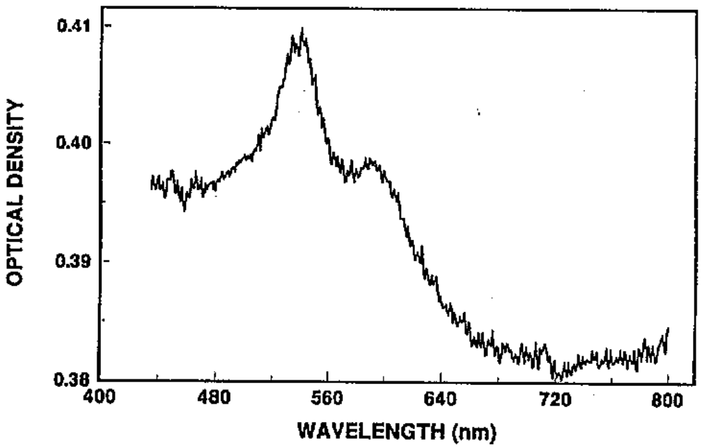

Figure 2. The absorption spectrum of KCl:Eu^{2+} taken at 10 K for a sample previously x-irradiated and subsequently photostimulated with F light at RT. The bands at 535 and 590 nm are ascribed to F and F_z centres, respectively.

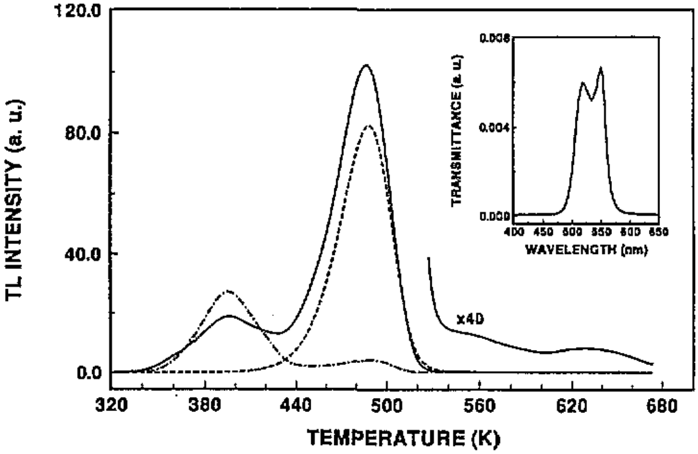

Figure 3. TL glow curves of a 5 s x-irradiated KCl:Eu^{2+} crystal: immediately after irradiation (full curve); thermally bleached up to 453 K (broken curve) and photostimulated for 1200 s with F light after thermal bleaching (chain curve). The F-light spectrum used is shown in the inset.

Figure 3 shows TL glow curves for 5 s x-ray-irradiated KCl:Eu^{2+} crystals. The full curve is for samples immediately after irradiation. From figure 3 we can see that the TL curve for x-irradiated samples consists of two main glow peaks, which are located at 395 and 487 K, and two sets of less intense ones, peaked at 563 and 644 K. The shape of the glow curve is similar to that reported by Camacho *et al* (1988) but with differences in the glow-peak positions, which might be due to differences in the heating rate used. For the sake of clarity we have selected three regions for TL peak classification: region **A** for glow peaks located in the 320–525 K temperature interval; region **B** for glow peaks between 425 and 530 K; region **C** includes those peaks in the 530–673 K range. To obtain further insight about the nature of the electron traps filled after irradiation, we have performed a thermal and optical bleaching process described below. After irradiation the sample was heated up to 453 K, causing the glow peaks of region A to disappear. The resulting TL curve after bleaching is depicted in figure 3 (broken curve). The thermally bleached sample was then photostimulated with F light in the 500–560 nm range using a filter whose transmittance curve is shown in the inset of figure 3. After photostimulation, the glow curve obtained showed a regeneration of the low-temperature glow peaks, initially removed by thermal bleaching, along with a strong intensity lowering of the glow peak originally located at 487 K. The photostimulated TL curve is also shown in figure 3 (chain curve). Figure 4 shows the characteristic thermal-annealing curve of the F centres. For comparison the TL glow curve of a sample irradiated for 5 s with x-rays (figure 3, full curve) is shown in the same figure.

On the other hand, figure 5 shows glow curves of a 250 nm UV- (broken curve) and x-ray-irradiated (full curve) KCl:Eu^{2+} crystal. For UV-irradiated samples we observe three sets of TL peaks: the first set includes peaks located at 353, 381 and 413 K, the second has a peak at 487 K and the third set is composed of several glow peaks in the 530–673 K temperature interval. We recall here that these sets of TL peaks are located in regions A, B and C respectively, previously defined on the TL of x-irradiated samples. For both radiation types, note that the positions of all peaks in regions A and B coincide, showing different relative intensities. The lower-temperature peaks observed in UV-irradiated samples appear

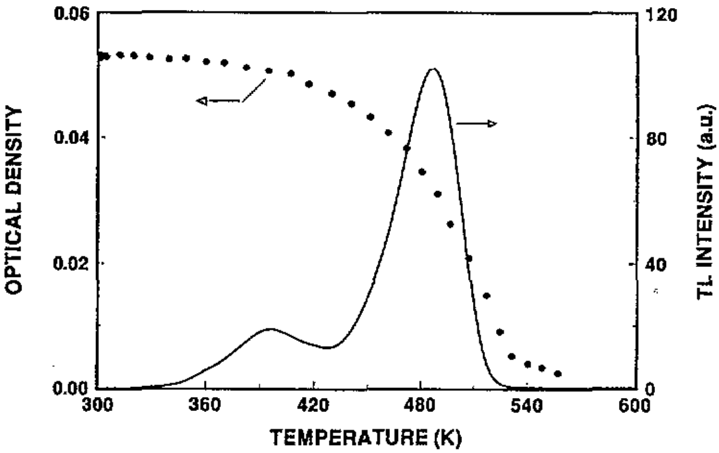

Figure 4. The TL glow curve (full curve) and thermal annealing of F centres (full circles) of $KCl:Eu^{2+}$ x-irradiated for 5 s and 10 min, respectively.

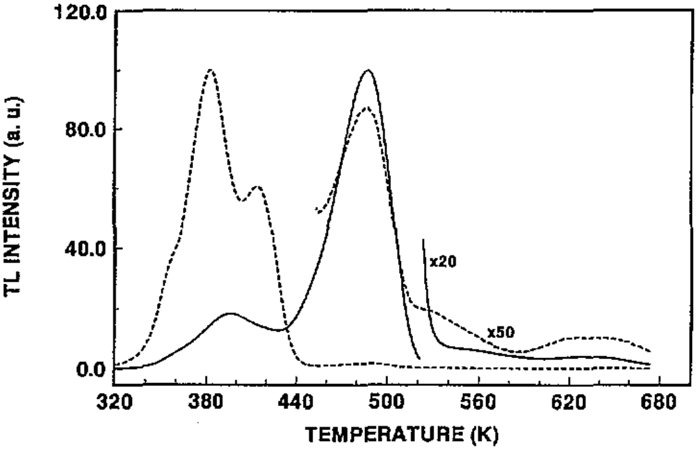

Figure 5. Normalized TL glow curves of $KCl:Eu^{2+}$ obtained immediately after 5 s x-irradiation (full curve) and after irradiation for 240 s with 250 nm light (broken curve).

also in x-irradiated samples but with weaker intensities.

The resemblance of the glow curves for x-ray- and UV-irradiated samples may lead us to believe that the participation of F centres in both processes take place in spite of the fact that in UV-irradiated samples no absorption band due to the presence of F centres has been detected. If F centres happen to exist, they are out of the detection limits of our spectroscopic equipment.

To obtain further insight into the problem we have performed a thermal and optical bleaching process, identical to the one used in x-irradiated samples, of the glow peaks located in region A for crystals irradiated with UV light. Figure 6 shows the glow curve obtained immediately after irradiation (full curve). Then, the sample was linearly heated from RT up to 453 K, causing the peaks of region A to disappear; the resulting TL glow curve after bleaching is depicted in the same figure (broken curve). The thermally bleached sample

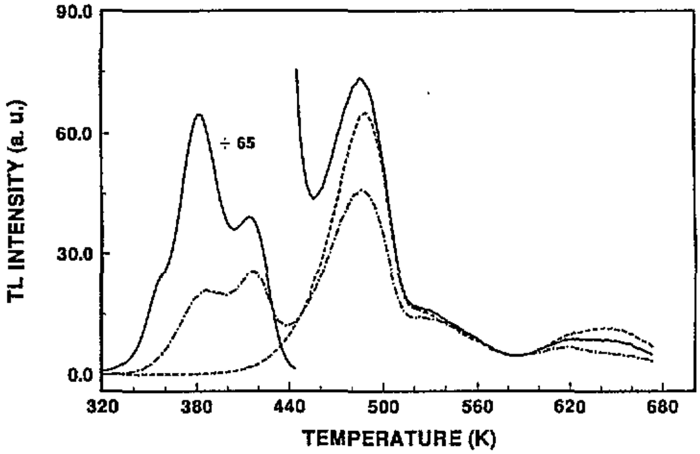

Figure 6. TL glow curves of a KCl:Eu^{2+} crystal irradiated with 250 nm light for 240 s: immediately after irradiation (full curve), thermally bleached up to 453 K (broken curve) and photostimulated for 120 s with F light after thermal bleaching (chain curve). The F-light spectrum used is shown in the inset in figure 1.

was then photostimulated for 120 s with F light in the 500–560 nm range (see the inset in figure 3); the glow curve obtained after photostimulation showed a regeneration of the glow peaks in region A initially removed by thermal bleaching; the photostimulated glow curve is also shown in figure 6 (chain curve). The thermal bleaching process, reaching temperatures up to 543 K, caused all peaks in regions A and B to disappear. Also, photostimulation with F light produced the regeneration of all glow peaks in these regions, the glow peaks in region A being more easily regenerated.

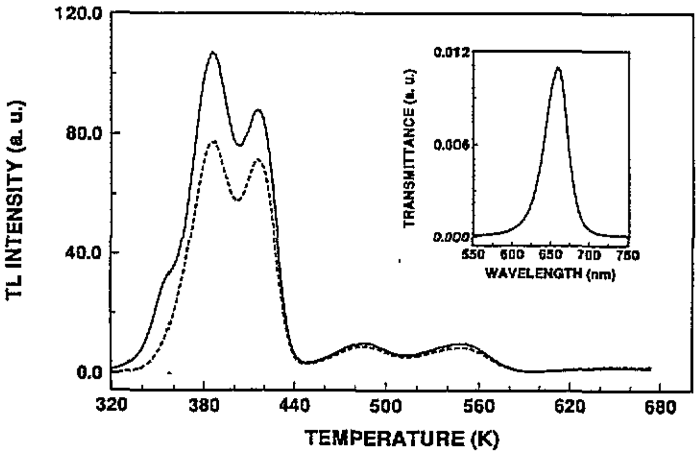

Figure 7. TL glow curves of a KCl:Eu^{2+} crystal irradiated with 250 nm light for 240 s: immediately after irradiation (full curve) and after being photostimulated for 15 min with F_z light (broken curve). The F_z-light spectrum used is shown in the inset.

Additional evidence about the F-type-centre participation in the low-temperature traps is obtained when a previously UV-irradiated sample is subjected to photostimulation with F_z light (650 nm). The results are displayed in figure 7. The F_z-light spectrum is shown in the inset of the same figure. The full curve is taken immediately after irradiation for 240 s with 250 nm light; glow peaks in all three regions are seen. The broken curve was obtained after photostimulation with F_z light for 15 min, without any thermal bleaching process. The photostimulation affects mainly the glow peaks in region A as compared to the effect on the glow peaks located in regions B and C. It is important to mention that the 353 K peak is not observed after photostimulation due to its characteristic fading.

4. Discussion and conclusions

The formation of F centres is evident in KCl:Eu^{2+} x-irradiated samples and they can be clearly observed through their optical absorption spectrum. However, in order to resolve the F_z-centre band one needs to photostimulate the previously x-irradiated sample with F light. This process enhances the F_z-centre population since it frees electrons, which are later trapped near a Eu^{2+}–vacancy (I–V) pair, forming the characteristic defect structure known as the F_z centre.

Thermal annealing analysis of the x-irradiation-induced F centres shows a strong correspondence between the F-centres annealing step and the glow peaks located in region B of the TL glow curve. Similar results have been observed by Opyrchal *et al* (1989) in γ-irradiated KCl:Eu^{2+} and by Rascón and Alvarez (1978) in KCl:Ca and KCl:Sr crystals. These results imply the participation of the F centres in the TL glow peaks located in region B. In fact, the glow peaks in this region coincide with the glow peaks in x-irradiated pure KCl in the 458–469 K temperature interval, which have been related to F centres by Brovetto *et al* (1991).

On the other hand, we have observed an F_z-centre formation, along with a regeneration of the TL glow peaks in region A, of a previously x-irradiated and F-light-stimulated sample, which was subjected to a thermal bleaching process to erase the TL glow peaks in region A. The recovery or increase in the TL intensity of the low-temperature glow peaks in region A takes place at the expense of an intensity decrease of the TL glow peaks in region B. Our results are in agreement with those already reported for γ-irradiated KCl:Sr^{2+} (Kamavisdar and Deshmukh 1981) and microcrystals of KCl:Ca^{2+} (Pode *et al* 1983), and also in x-irradiated RbCl:Eu^{2+} (Sastry and Sapru 1981). Therefore we conclude that the glow peaks in region A involve the annealing of F_z centres. A similar association has been made by Ohkura (1964) in x-irradiated KCl:Sr^{2+} crystals.

We recall that the conclusions stated above are related to x-irradiated samples. We shall now discuss the results obtained with UV irradiation (250 nm). The TL glow curve of UV-irradiated samples is similar to that of x-irradiated crystals but with different intensity ratios. That is, the intensities are higher for peaks in region A and lower in region B as compared to the TL glow curve of x-irradiated samples Aguirre de Cárcer *et al* (1993) have also reported similar TL glow-peak intensity ratios in UV-irradiated NaCl:Eu^{2+} as compared to TL glow curves of γ-, β- and x-ray-irradiated specimens. Application of the same thermal bleaching and F-light photostimulation procedure used in x-irradiated samples lead in UV-irradiated specimens also to the regeneration of TL glow peaks in region A. This gives an indication that the TL glow peaks in regions A and B, in UV- and x-irradiated samples, have the same thermoluminescent origin. Also the similarity of TL glow curves of UV- and x-irradiated samples indicates that UV-irradiation produces F and F_z centres in KCl:Eu^{2+} as x-irradiation does but with lower efficiency. It is important to call attention to the fact that the F centres in KCl:Eu^{2+} are formed with a very low efficiency, impeding their detection by optical absorption under the present UV-irradiation time exposure. However, we have been able to detect around 10^{14} (F centres) cm^{-3} when exposing a sample for 1 h to UV light of 200 nm. In fact, the F-centre production efficiency as a function of UV excitation wavelength has been obtained by Sever *et al* (1986) in pure KBr. Using their results as a guide to estimate the F-centre formation in KCl:Eu^{2+} (recalling that KCl is harder to colour than KBr using UV light (Brown 1967)) with UV light we may expect two to three orders of magnitude fewer F centres when exciting with 250 nm as compared with 190 nm light. This means that we would require about 100–1000 h to obtain F-centre concentrations detectable with our spectrophotometric equipment.

In summary, we may therefore conclude that the glow peaks in region B are related to trapped electrons in the form of F centres, and the glow peaks located in the region A to F_z centres. The present statement holds true for UV and x-irradiation, in spite of the general agreement that low-energy UV light is unable to produce colour centers. The optical bleaching of F centres by photostimulation with F light has results in the production of F_z centres. This means that an electron detrapped from a deep trap (a vacancy far away from a Eu^{2+}–cation vacancy dipole), in region B or C, is being retrapped at shallow traps (a vacancy in the neighbourhood of the I–V dipole) in region A, forming the F_z centers. The TL associated with this process is similar to a phototransferred thermoluminescence (PTTL) process (McKeever 1985). It should be mentioned that the phenomenon of TL excited with UV light needs further investigation in order to clarify the mechanisms, trapping and recombination centres, associated with the thermally stimulated light emission.

Finally, it is well known that the TL of KCl:Eu^{2+} is strongly dependent on the aggregation–precipitation state of the Eu^{2+} ion nucleated in the crystal. In fact we have observed that the glow peaks in region C show lower or higher glow-peak intensities depending on the annealing time of the sample. This may indicate that those traps are related to some kind of aggregates, perhaps defects trapped around some stable or metastable Eu^{2+} aggregates. However, this point needs further and more detailed investigation.

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