

Internal irradiation effects in ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$: EPR, TSL and PAS investigations

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Abstract. The electron/hole trapped centres created during internal irradiation in ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ were investigated using electron paramagnetic resonance (EPR), thermally stimulated luminescence (TSL) and photoacoustic spectroscopic studies (PAS). These techniques were used to identify the defects and characterize the thermally induced relaxation processes. TSL studies of self (α)/ γ -irradiated ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ revealed two glow peaks around 400 and 433 K. Plutonium introduced as Pu^{4+} was partly reduced to Pu^{3+} due to self irradiation. This was ascertained from PAS studies. EPR studies carried out on these samples showed the formation of radical ions SO_4^- , SO_3^- , O_3^- , etc. The thermal destruction of SO_4^- ion was found to be associated with the prominent glow peak around 433 K. Pu^{3+} was found to act as luminescent centre for the observed TSL glow. The trap depth for the glow peak at 433 K has been determined from TSL and EPR data.

Keywords. Thermally stimulated luminescence; electron paramagnetic resonance; photo acoustic spectroscopy.

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1. Introduction

Rare earth doped mixed sulphate compounds such as $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$, $\text{K}_3\text{Na}(\text{SO}_4)_2$, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, etc. are of intense current interest due to their possible role as excellent dosimetric materials and also for their optical properties [1, 2]. In this connection actinide dopants incorporated in mixed sulphate lattices, have unique role due to their α -activity causing auto radiolytic effects thereby facilitating TSL. This role of actinides is besides the more common function as fluorescent activator. Furthermore the existence of actinide ions in multiple valence states facilitates the formation of point defects favourable for enhancing luminescence. The self irradiation effects in actinide doped solids can result in the formation of numerous types of colour centres/radical ions as well as stabilization of actinide ions in unusual valence states of actinide ions [3, 4]. EPR and TSL are two techniques that can be effectively used in tandem to get an insight to the radiation damage centres produced due to internal (α) irradiation. ^{238}U (specific activity 0·74 dpm/ μg) exists in oxidation states + 4, + 6 and + 3. The most common among these is UO_2^{2+} , which is known to be strongly fluorescing and is a good activator for intense TSL [5]. Plutonium on the other hand, is not known to give significant fluorescence in the visible region. It is well known that plutonium exists in oxidation states of + 4 and + 3 specially in solids. This is relevant in the formation of

local defect sites in the lattice. Conventionally optical absorption studies are normally used in similar investigations for identifying the metal ion impurities and/or colour centres. For powder samples PAS studies are better suited for the purpose. PAS is a versatile technique that can be used to probe the non-radiative relaxation processes even in weakly fluorescing samples. Thus in the present work on ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ we have combined EPR, TSL and PAS techniques to get an insight about the radiation damage centres produced due to internal (self- α) irradiation.

2. Experimental

Samples of Pu (0.5% by weight) doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ were prepared by the method similar to that reported earlier [5]. The incorporation of Pu in the sample has been ascertained by radiometric methods. TSL and PAS studies were carried out on home-built unit [6, 7]. EPR spectra were recorded on a Bruker ESP-300 Spectrometer at X-band frequency. A variable temperature accessory (V-4502) was used for EPR temperature variation experiments. A ^{60}Co gamma source with a dose rate of 2 kGy/h was used for gamma irradiation.

3. Results and discussion

In freshly prepared samples of $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$, no TSL could be observed. However, on samples stored for about 2 weeks (α -dose rate = 10 kGy/hr.), a weak TSL peak around 433 K was observed (heating rate = 150 K/min.). On gamma irradiation of freshly quenched samples, an intense peak around 433 K was observed with a shoulder around 400 K (figure 1). Systematic gamma dose dependence studies have shown the TSL peak at 433 K to saturate after a gamma dose of about 6 kGy. The spectral studies of the TSL glow carried out using narrow band interference filters revealed emission groups around 580 and 485 nm characteristic of Pu^{3+} ion [8, 9]. The intrinsic luminescence of SO_4^{2-} was reported to be around 360 nm in alkaline earth sulphate lattices [10]. Substantial reduction in the intensity of TSL glows were observed when filters transmitting below 380 nm were used. This suggest that SO_4^{2-} does not act as luminescent centre in the mixed sulphate lattices. The trap depth energy values for the

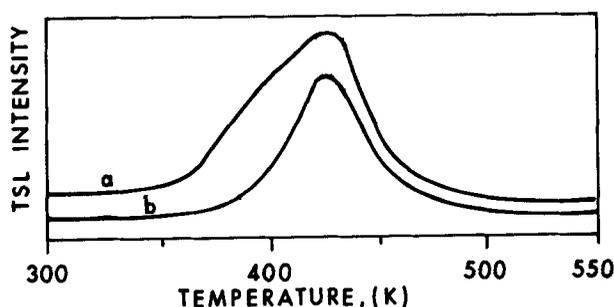


Figure 1. (a) TSL glow curve of γ -irradiated Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ in the 300–550 K temperature range (γ -dose = 3/kGy). (b) TSL glow curve of the γ -irradiated sample recorded after annealing at 400 K for 1 min. (The TSL glow curve of self (α)-irradiated sample was essentially similar to the γ -irradiated ones.)

peak at 433 K as determined from different heating rates method and initial rise method are given in table 1.

3.1 Photo acoustic spectroscopic studies

No absorption peaks were observed in unirradiated/gamma irradiated samples of undoped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$. However, on purely self (α) irradiated samples stored for about 24 h absorption bands around 445, 460, 560, 600, 680, 740, 780 and 820 nm are observed. The PAS of Pu doped sample was obtained after subtraction (in digital form) of the blank [$\text{undoped K}_2\text{Ca}_2(\text{SO}_4)_3$] spectrum. Both the sample and blank spectra were corrected for the source intensity variation and were stored in the computer. The difference spectra is shown in figure 2. The absorption peaks around 445, 460, 680, 740 and 820 nm are assigned to Pu^{4+} and those at 560, 600, 780 and 820 nm are assigned to Pu^{3+} on the basis of the absorption spectra reported for Pu ions in solutions in

Table 1. Trap parameters

TSL peak temp.* (K)	Trap depth (eV)			Frequency factor (sec^{-1})
	DHR	IR	EPR	
433	0.87	0.83	0.88	2.2×10^9

DHR = Different heating rates method; IR = Initial rise method;

* – heating rate = 150 K/min.

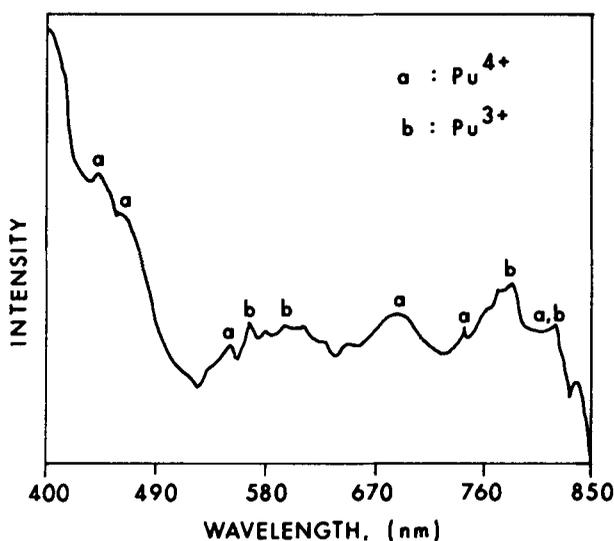


Figure 2. The photoacoustic absorption spectra (corrected for source intensity profile using a black body absorber) of Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ after γ -irradiation (γ -dose = 3 kGy). The spectrum was obtained after subtraction (in digital form) of the blank (undoped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$) spectrum.

literature [11]. Pu^{4+} complexes are also reported to have absorption below 440 nm ($5f^n \rightarrow 5f^{n-1}6d$). The high relative intensity in PAS spectrum below 440 nm can probably be due to predominant non-radiative relaxation. (The PAS intensities and absorption intensities can differ depending on the relative probability of radiative and non-radiative relaxation.) On gamma irradiation no change in the absorption maxima was observed.

3.2 EPR studies

The EPR spectrum of ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ recorded at room temperature three days after preparation is shown in figure 3. The spectrum contained signals due to SO_3^- ($g = 2.0030$), SO_4^- ($g_{\perp} = 2.0116$, $g_{\parallel} = 2.0160$) and O_3^- ($g = 2.0130$). These radical ions were found to build up in a period of 15 days and leveled off in intensity afterwards. The build up of the radical ions viz. SO_4^- and SO_3^- as a function of time of self-irradiation is shown in figure 4. In freshly quenched samples subjected to γ -irradiation from ^{60}Co source (dose = 2 kGy), the same radical ions were found to be present. No additional signal could be seen up to a γ -dose of 40 kGy. In uranium doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ reported earlier [5], EPR signals due to SO_2^- were found to overlap with that of SO_3^- line and SO_2^- disappeared around 400 K. In view of the intense SO_3^- signal observed in Pu doped sample, the presence of SO_2^- ion ($g_{\perp} \approx 2.004$) in smaller amounts could not be ruled out. No EPR signals due to Pu^{3+} could be obtained either at 77 K or at room temperature up to a magnetic field of 12.0 KG, the highest that can be achieved with our magnet. The EPR spectra of gamma irradiated samples recorded at different temperatures are given in figure 5. From the temperature dependence studies of the EPR spectra of irradiated samples carried out in the 300–600 K range, it was found that SO_4^- gets destroyed in the temperature range 410–420 K suggesting its role in the glow peak observed around 433 K. The radical ion O_3^- showed a reduction in intensity in the

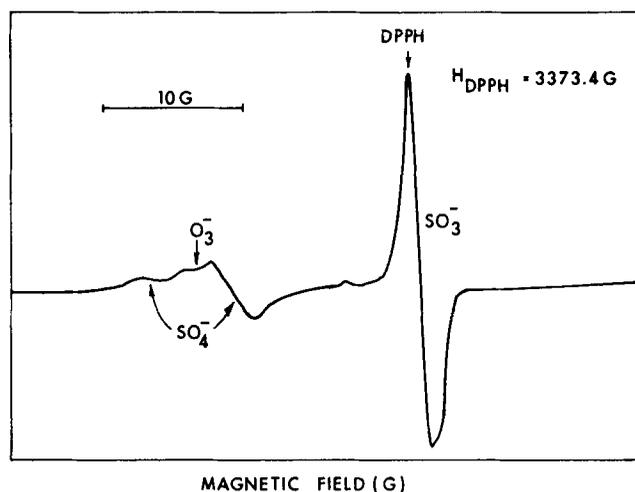


Figure 3. EPR spectrum of self (α)-irradiated Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ (recorded 24 h after preparation of sample) at 300 K (α -dose rate = 3.6 kGy/h).

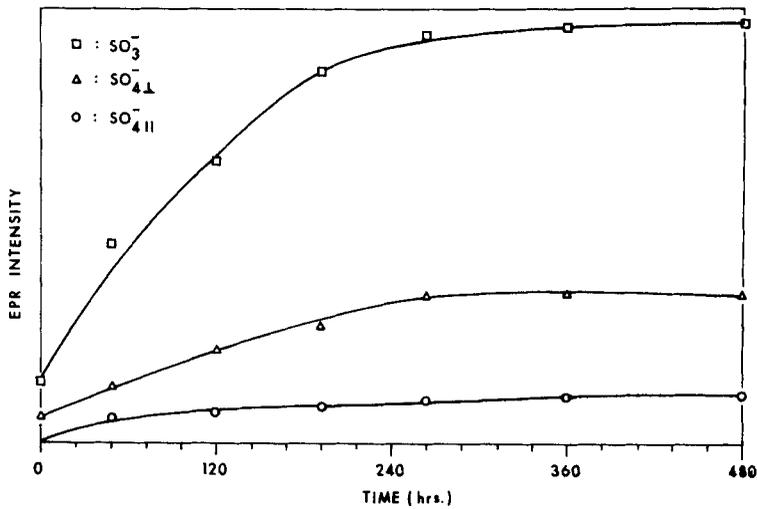
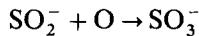
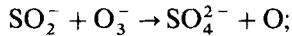


Figure 4. Build up of the radical ions SO_3^- and SO_4^- (as observed by EPR) as a function of period of self (α)-irradiation in ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$.

380–450 K temperature range while the SO_2^- radical was found to disappear around 400 K. This could probably account for the increase in SO_3^- intensity beyond 400 K.

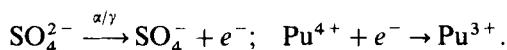


Essentially SO_3^- is generated out of SO_2^- and O_3^- in a two step process. An increase in SO_3^- signal intensity beyond 380 K was also observed in our studies on Am/Eu doped SrSO_4 [12]. The thermal stability plots for the radical ions are given in figure 6. The trap depth value was also determined from the temperature dependence of the EPR signal of the SO_4^- ion for the peak at 433 K by plotting $\ln[-\ln(1 - \Delta I/I)]$ vs. $1/T$, where I is the intensity of the EPR signal and ΔI is the amount of decrease of signal at each temperature [13]. The trap depth value, thus determined is included in Table 1.

3.3 Mechanism for the TSL glows

(i) *Peak at 400 K:* This peak could not be studied in detail due to its low intensity. It could probably be associated with the thermal destruction of SO_2^- as reported in uranium doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$.

(ii) *Peak at 433 K:* Plutonium was doped as Pu^{4+} . It is most likely that Pu^{4+} would go to Ca^{2+} site rather than K^+ site. A tetravalent ion at a divalent site would be a good electron trap. The detection of Pu^{3+} along with Pu^{4+} in PAS studies clearly shows that Pu^{4+} traps an electron purely by internal α/γ irradiation. This is essentially a radiation induced partial reduction of Pu^{4+} . EPR studies have shown the concomitant formation of SO_4^{2-} indicating that electron is released from SO_4^{2-} .



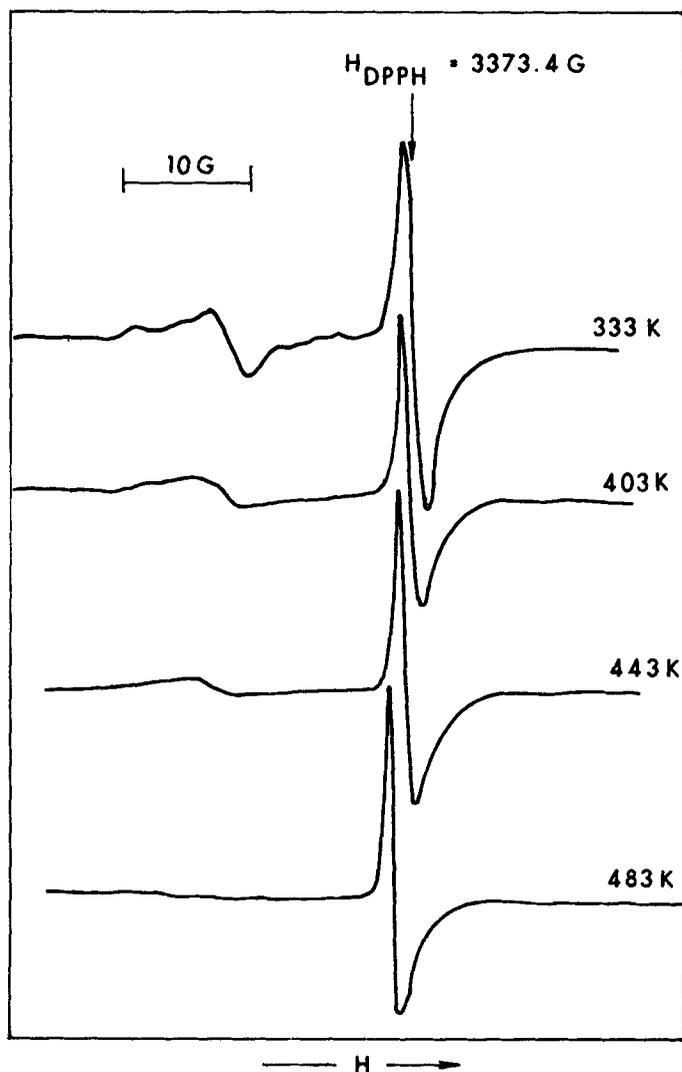
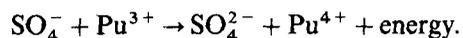


Figure 5. The EPR spectra of γ -irradiated ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ recorded at different temperatures (γ -dose = 3 kGy).

On heating to 433 K, the hole on SO_4^- becomes mobile i.e. SO_4^- takes an electron from adjacent SO_4^{2-} so that effectively SO_4^- appears to be mobile. When such an SO_4^- comes closer to Pu^{3+} then the electron transfer from Pu^{3+} to SO_4^- takes place and the reaction products would be SO_4^{2-} and Pu^{4+} with associated liberation of energy.



The liberated energy can go in to excitation of $\text{Pu}^{3+}/\text{SO}_4^{2-}$ or both. Pu^{4+} is reported to give fluorescence in the infrared region [8]. Therefore direct excitation of Pu^{4+}

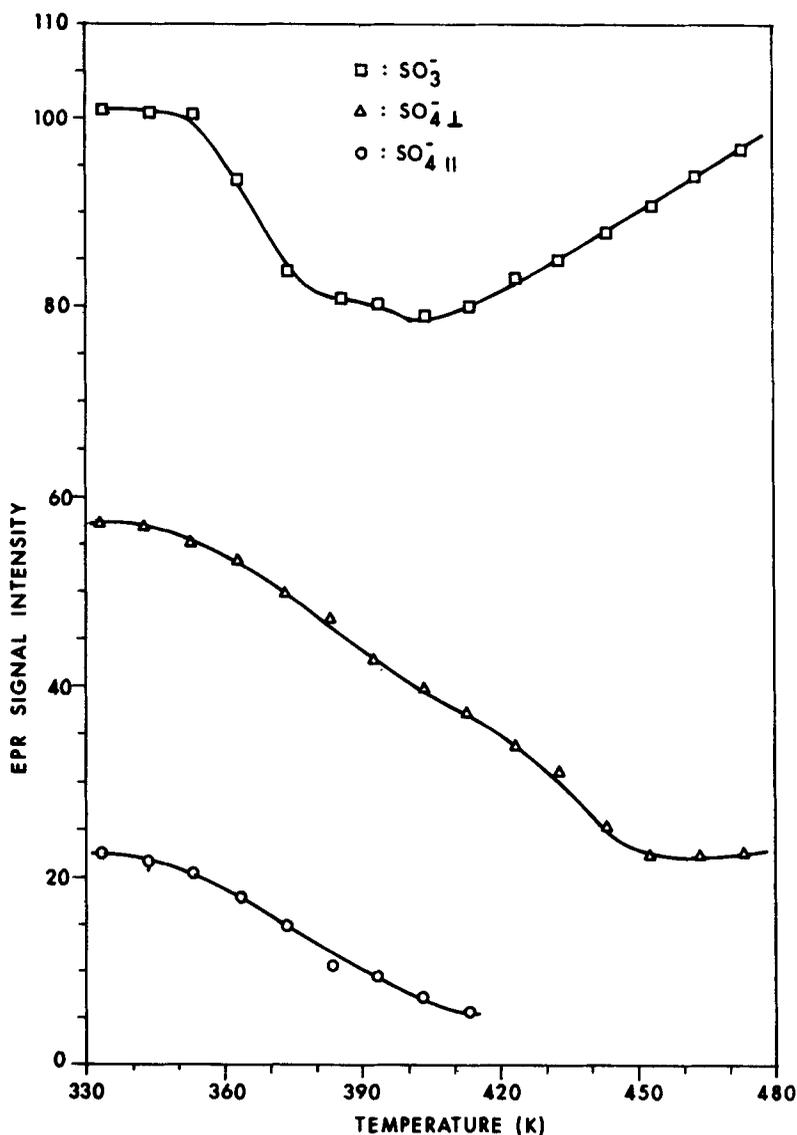
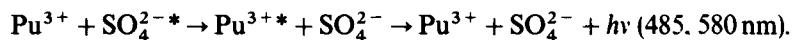


Figure 6. Temperature dependence of intensities of the radical ions SO_4^- and SO_3^- observed in ^{239}Pu doped $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$.

essentially relaxes through non-radiative mechanism. This would not show in TSL. The SO_4^{2-} ion is known to give emission around 360 nm [10]. This energy can be transferred to Pu^{3+} as it has a broad absorption band in that region, resulting in the formation of excited Pu^{3+} which on de-excitation gives Pu^{3+} emission around 485 and 580 nm as seen from TSL spectral studies.



4. Conclusion

The TSL glow peak at 433 K is associated with the thermal destruction of SO_4^- ion as observed from EPR. The presence of $\text{Pu}^{4+}/\text{Pu}^{3+}$ in the samples has been confirmed from PAS studies.

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