

Thermally stimulated luminescence and electron paramagnetic resonance studies of actinide doped calcium chloro phosphate

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Abstract. Electron paramagnetic resonance [EPR] and thermally stimulated luminescence [TSL] studies were conducted on self [α]-irradiated ^{239}Pu doped calcium chloro phosphate and γ -irradiated $^{239}\text{Pu}/^{238}\text{UO}_2^{2+}$ doped calcium chloro phosphate to elucidate the role of the electron/hole traps in thermally stimulated reactions and to obtain trap parameters from both TSL and EPR data. TSL glow peaks around 135 K (# peak 1), 190 K (# peak 2), 435 K (# peak 5) and 490 K (# peak 7) were observed and their spectral characteristics have shown that Pu^{3+} and UO_6^{6-} act as luminescent centres in calcium chloro phosphate with respective dopants. EPR studies have shown the formation of the radical ions H^0 , PO_4^{3-} , O^- , O_2^- and $[\text{ClO}]^{2-}$ under different conditions. Whereas the $[\text{ClO}]^{2-}$ radical being stable up to 700 K, was not found to have any role in TSL processes, the thermal destruction of other centres was found to be primarily responsible for the TSL peaks observed. The trap depth values were determined both by using the TSL data and also the temperature variation of EPR spectra of these centres.

Keywords. Thermally stimulated luminescence; electron paramagnetic resonance.

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1. Introduction

The apatites form a large number of naturally occurring compounds with the general formula $\text{M}_{10}(\text{YO}_4)_6\text{X}_2$ where M represents the positive divalent ions, YO_4 are groups such as PO_4^{3-} and VO_4^{3-} and X are the halide or hydroxide ions. They are reported to be extensively used as fluorescent lamp phosphors and as potential hosts for laser materials (Prener 1967; Budin *et al* 1979; Pappalardo *et al* 1983). Thermally stimulated luminescence [TSL] of the irradiated samples of chlorapatite has been reported (Lapraz and Baumer 1981; Fukuda *et al* 1987) with dopants such as Mn^{2+} , Ce^{3+} , Ag^+ , Sb^{3+} and Pb^{3+} . However, no detailed investigations are reported on the luminescence properties, the role of impurities as activators of luminescence and the electron/hole recombination processes that might stimulate the luminescence in these compounds exposed to ionizing radiation. Among the possible dopants which can activate the luminescence, the actinide elements are unique due to their electronic and nuclear properties. As mentioned in our earlier studies (Dalvi *et al* 1984; Seshagiri *et al* 1988; Natarajan *et al* 1986, 1988; Mithlesh Kumar *et al* 1988) trap level spectroscopic studies of actinide-doped phosphors are of special interest due to their inherent α -activity, thereby facilitating the study of radiation damage processes due to internal α -irradiation with higher linear energy transfer than X- or γ -rays. The present study deals with the TSL and EPR investigation of calcium chloro phosphate (i.e. calcium

chlorapatite abbreviated as CaCIAP) doped with ^{239}Pu and ^{238}U . Of these only ^{239}Pu has appreciable specific activity, to produce internal damage over short periods of time and hence can be effectively used for investigating the α -radiation induced defects. Among the actinides, uranyl ion, known for strong fluorescence, was chosen with a view to enhancing the TSL efficiency. Further, we have used the temperature dependence of EPR, not only for correlation with TSL peaks to identify the thermally stimulated reactions but also for obtaining activation energies wherever possible. This has given another method of obtaining the trap depth values which in turn can be used as a confirmation of the TSL mechanism by EPR–TSL correlations.

2. Experimental details

2.1 Apparatus

The TSL studies were conducted on a unit, the details of which have been described elsewhere (Dalvi *et al* 1980). Electron paramagnetic resonance [EPR] studies were conducted on a varian V-4502 and a Bruker ESP-300 spectrometer with a variable temperature accessory. A ^{60}Co source (dose rate = 0.2 Mrad/hr) was used for γ -irradiation of the samples.

2.2 Phosphor preparation and characterization

Samples of undoped CaCIAP were synthesized in powder form by high temperature solid state reaction. Stoichiometric quantities of CaCO_3 (A.R. grade), anhydrous CaCl_2 and $(\text{NH}_4)_2\text{HPO}_4$ were fired in a platinum crucible at 1250 K in air for 4–5 hr. A part of the sample was mixed with U_3O_8 (spec pure) and heated at 1250 K for 3 hr. Pu doped samples were prepared in an analogous manner using spec pure/high purity oxides of the respective elements. The dopant concentration in all the samples was 0.5% by weight. The X-ray diffraction pattern of all the samples agreed well with those reported for chlorapatites by Fukuda *et al* (1987). These results have shown that the compounds prepared are of single phase apatites. The samples were also analysed for their trace metallic constituents by emission spectroscopic methods. All the elements (other than the dopants) were found to be below the detection limits (typically at 1–10 ppm level). The incorporation of ^{239}Pu in the samples were ascertained by radiometric methods.

3. Results and discussion

3.1 Thermally stimulated luminescence

The TSL glow pattern obtained in the 300–650 K range on self [α]-irradiated samples of Pu doped CaCIAP (stored for about 10 days) is shown in figure 1. The TSL was not observable in freshly prepared Pu doped samples and had built up with time of storage due to cumulative radiation dose. The build up of the TSL peak at 490 K with storage time is shown in figure 2. Experiments were also conducted after γ -irradiation of freshly quenched samples. It was found that the TSL glow pattern remained essentially same (with a single peak at 490 K).

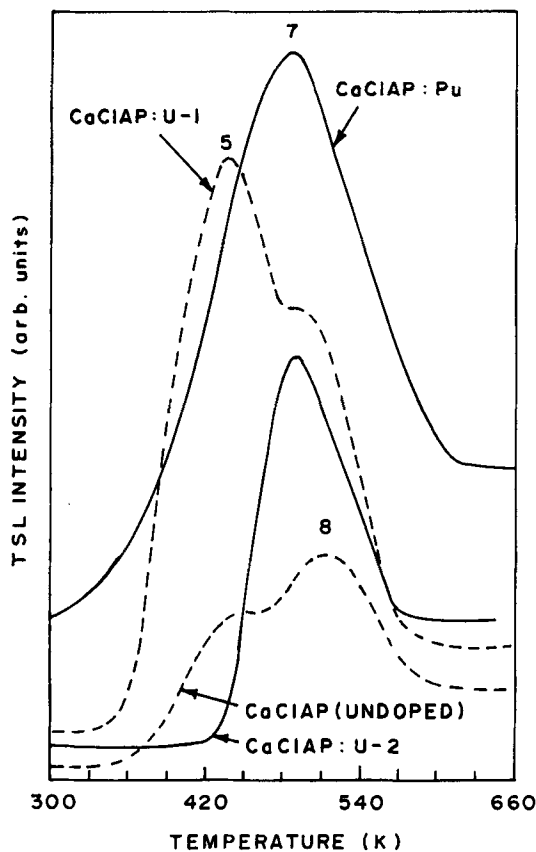


Figure 1. The TSL glow curves of γ -irradiated undoped CaClAP, UO_2^{2+} doped CaClAP (U-1) (γ -dose = 0.2 Mrad) and purely self-irradiated Pu doped CaClAP (stored for about 10 days after preparation of the sample, (α -dose = 0.85 Mrad) obtained in the high temperature region. CaClAP U-2 refers to the glow curve obtained after thermal treatment of the gamma irradiated sample at 425 K. A heating rate of 2.5° K/s was used.

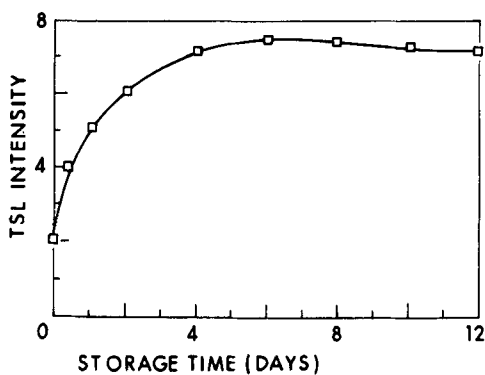


Figure 2. α -dose dependence of the TSL peak at 490 K in freshly quenched CaClAP: ^{239}Pu (α -dose rate = 36×10^{-4} Mrad/h).

The TSL glow curve of γ -irradiated samples of UO_2^{2+} doped CaCIAP, however, has shown peaks around 435 and 490 K (heating rate = 2.5 K/sec). For obtaining accurate trap parameters for 490 K peak, the 435 K peak was "removed" by thermal treatment [heating to 425 K] (Jimenez de Castro and Alvarez Rivas 1979). The TSL glow curves obtained for these samples along with those for undoped CaCIAP are also included in figure 1 for comparison. Systematic gamma dose dependence studies have shown the prominent peaks at 490 K and 435 K in Pu and UO_2^{2+} doped samples to saturate after a gamma dose of 0.24 Mrad.

The TSL glow curves were also recorded in the sub-room temperature region [130–300 K] after γ -irradiation of the samples at 77 K for 2 hr (dose = 0.40 Mrad). All the samples showed a prominent TSL glow around 130–140 K; in addition glow peaks at 185/190 K were also observed (heating rate = 1 K/sec). Figure 3 shows the TSL glow curve of undoped and doped samples of $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ in the 130–300 K region. The prominent glow peaks in the sub-room temperature region are numbered as 1 and 2 in order of increasing T_m whereas the glow peaks in high temperature region are numbered as 5 to 8 (Refer to table 3 and figures 1 and 3). All the prominent TSL glow peaks in the high temperature region (300–700 K) were found to obey first order kinetics as seen from isothermal decay studies.

The trap parameters, trap depth (E) and frequency factor (s) were calculated using different heating rates method (Hoogenstraaten 1958), initial rise method (Garlick and Gibson 1948) and non-equilibrium phase transition model (Dalvi *et al* 1983). Figure 4 shows the plots of $\ln(T_m^2/\beta)$ vs. $1/T_m$ (where β refers to the heating rate employed and T_m is the peak temperature observed) obtained using the different heating rates method for the 435 K peak in U doped sample and 490 K in Pu doped sample. The values of transition temperature (T_c) used in the NEPT model (Dalvi *et al* 1983) was determined experimentally by following the temperature dependence

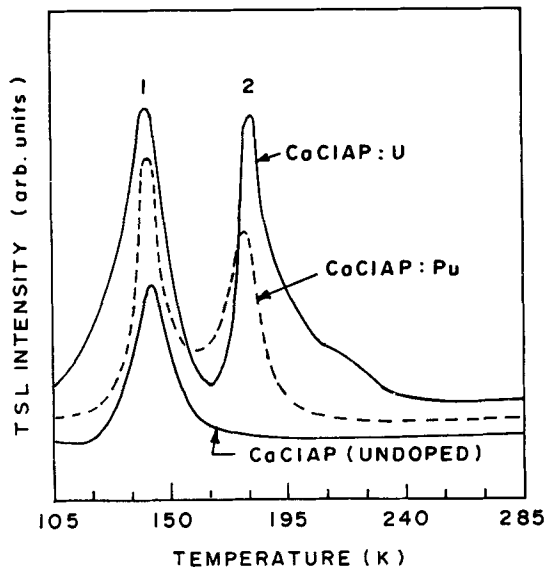


Figure 3. The TSL glow curves of undoped CaCIAP, UO_2^{2+} doped CaCIAP, and ^{239}Pu doped CaCIAP in the sub-room temperature region after γ -irradiation at 77 K (dose = 0.4 Mrad). A heating rate of 1 K/s was employed.

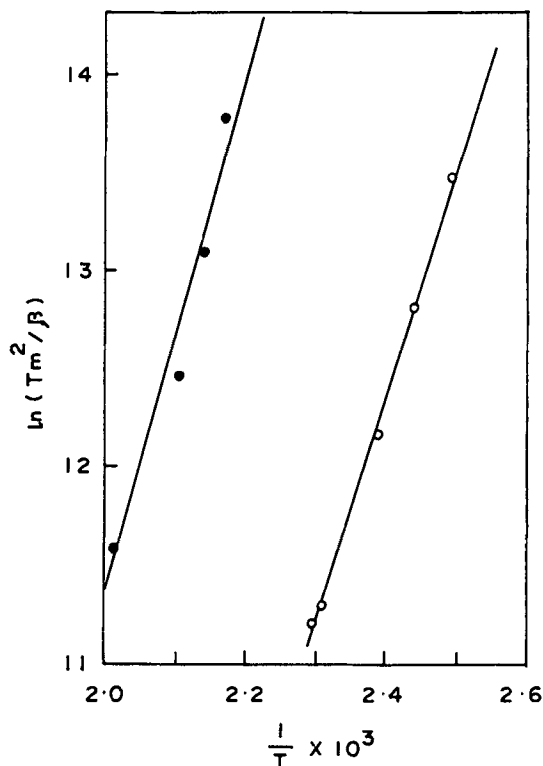


Figure 4. Plot of $\ln(T_m^2/\beta)$ vs $1/T_m$ obtained from different heating rate methods; ● glow peak at 490 K in Pu doped CaClAP and ○ glow peak at 435 K in UO_2^+ doped CaClAP.

of the EPR signals responsible for the different TSL peaks. For the sub-room temperature peaks Booth's method (Booth 1954) was used to calculate the trap depth. In this case, since only two heating rates were employed Arrhenius plots could not be obtained for these peaks. The trap depth values were also determined using the temperature dependence of EPR spectra, wherever possible. For all the Arrhenius plots obtained in TSL/EPR methods for obtaining E, a least square fit program was employed to obtain the best fit of $\ln(T_m^2/\beta)/\ln I$ values. Table 1 gives the trap parameters obtained in CaClAP lattices with different dopants.

The intensities of the TSL glow peaks were not strong enough to record the emission spectrum for any of the undoped/doped samples using the 0.25 M scanning monochromator. Hence spectral studies were carried out using narrow band interference filters. The prominent peaks observed with various dopants and their spectral characteristics are given in table 2. The intensities of the TSL peaks in the sub-room temperature were too weak to record the emission spectrum even with the use of interference filters. However, in UO_2^+ doped samples emission in the yellowish orange region could be visually observed, as the samples were warmed to room temperature from 77 K suggesting that UO_6^{2+} acts as the luminescent centre (Blasse and Van Den Heuvel 1974; Jong *et al* 1979) for the sub-room temperature peaks.

Table 3 gives the peak temperatures of the prominent TSL glows observed in the present studies for both doped and undoped samples of calcium chlorapatite with a heating rate of 0.5 K/sec. The data obtained for Mn/Ce doped and undoped CaClAP

Table 1. TSL peak temperature and trap parameters observed in CaClAP matrix with various dopants.

Peak temp. (K)		Trap depth (eV)			Frequency factor (sec ⁻¹)	
T_m	T_c	DHR	IR	EPR	^s DHR	^s NEPT
CaClAP:UO ₂ ²⁺						
135*	130	—	—	0.11 ± 0.01	—	3.6 × 10 ⁴
190*	176	0.31*	—	0.25 ± 0.04	1.6 × 10 ⁷	3.0 × 10 ⁹
435	418	0.99 ± 0.04	1.01 ± 0.02	0.85 ± 0.06	6.6 × 10 ¹⁰	2.4 × 10 ¹²
492	—	1.15 ± 0.19	—	—	3.4 × 10 ¹¹	—
CaClAP:Pu						
138*	136	—	—	0.10 ± 0.02	—	6.1 × 10 ⁴
185*	170	0.32*	—	0.33 ± 0.04	1.8 × 10 ⁸	6.0 × 10 ⁹
490	466	1.25 ± 0.07	1.19 ± 0.13	—	1.6 × 10 ¹³	7.7 × 10 ¹⁴

*Heating rate = 1 K/sec. DHR = Different heating rates method. IR = Initial rise method. T_c is the transition temperature determined from EPR using non-equilibrium phase transition model (Dalvi *et al* 1983).

^sValue determined using Booth's method (Booth 1954).

Table 2. Luminescent centres and their spectral character for the prominent glow peaks observed in doped CaClAP matrix.

Dopant	Peak temp. T_m (K)	Spectral groups (nm)	Luminescent centre	Reference
Pu ⁴⁺	490	580 and 480	Pu ³⁺	McLaughlin <i>et al</i> 1968; Stacy <i>et al</i> 1972
UO ₂ ²⁺	435	598, 630 and 660	UO ₆ ⁶⁻	Blasse and Van Den Heuvel 1974; Jong <i>et al</i> 1979

by Lapraz and Baumer (1981) and for Ag doped CaClAP by Fukuda *et al* (1987) are also included in the table 3 for comparison. The trap depth values for the respective peaks are given in table 4. It is clear from table 3, that all the peaks except the peak nos # 2, # 4 and # 7 are characteristic of the host lattice. The spread in peak temperatures in unodoped/doped samples may be associated with the differences involved in the preparation of the samples and annealing behavior.

3.2 Electron paramagnetic resonance studies

3.2.1 *Above room temperature:* Undoped CaClAP and UO₂²⁺ doped CaClAP did not show the presence of any paramagnetic species prior to γ -irradiation. The EPR signals

Table 3. Prominent peak temperatures of glow curves in CaClAP lattices (Heating rate = 0.5 K/sec; Peak temperatures in °K.).

Sample	Ref.	Peak nos							
		1	2	3	4	5	6	7	8
Undoped	^(a)	118 ± 4	—	—	—	418	445	—	500
Mn doped	^(a)	118 ± 4	—	—	—	—	445	—	500
Ce doped	^(a)	118 ± 4	—	—	370	—	—	—	—
Ag doped	^(b)	—	—	338	—	—	448	—	—
Undoped	^(b)	—	—	338	—	—	443	—	—
Undoped	^(c)	137 ± 3	—	—	—	415 ± 2	—	—	490 ± 2
Sm doped	^(c)	135 ± 3	183 ± 3	—	—	408 ± 2	—	462 ± 2	—
U doped	^(c)	135 ± 3	190 ± 3	—	—	410 ± 2	—	460 ± 2	—
Pu doped	^(c)	138 ± 3	185 ± 3	—	—	—	—	467 ± 2	—
Th [#] doped	^(c)	140 ± 3	183 ± 3	—	373 ± 2	—	—	465 ± 2	—

[#]The TSL/EPR results on Th/Sm doped CaClAP are not included in the paper, only the glow peak temperatures are given for comparison. Peak nos # 3 and 6 are not observed in the present studies.

^(a)Lapraz D *et al* 1981 *Phys. Status Solidi (a)* **68** 309

^(b)Fukuda N *et al* 1987 *Radiation protection dosimetry* **70** 93

^(c)Present work. Peak temperature corresponding to a heating rate of 1 K/sec for peaks 1 and 2.

Table 4. Trap depth values of prominent TSL glow peaks observed in CaClAP lattices (eV).

Sample	Ref.	Peak nos							
		1	2	3	4	5	6	7	8
Mn doped crystal	^(a)	0.16	—	—	—	0.87	1.08	—	1.20
Mn doped powder	^(a)	0.10	—	—	—	—	0.60	—	—
Ce doped	^(a)	0.16	—	—	0.91	—	—	—	—
Undoped	^(c)	0.12*	—	—	—	0.92	—	—	1.30
Sm [#] doped	^(c)	0.12*	0.27	—	—	0.97	—	1.11	—
U doped	^(c)	0.11*	0.28	—	—	1.00	—	1.15	—
Pu doped	^(c)	0.10*	0.33	—	—	—	—	1.22	—
Th [#] doped	^(c)	N.D	0.28	—	0.76	—	—	1.20	—

[#]The TSL/EPR results on Th/Sm doped CaClAP are not included in the paper, only the trap depth values are given for comparison, *Trap depth value determined using EPR data.

^(a)Lapraz and Baumer 1981; trap depth value determined by initial rise or Chen's method.

^(c)Present work. Trap depth values were determined by different heating rates and initial rise method; the average value is given in the table. For sub-room temperature glow peaks Booth's method (Booth 1954) and EPR method were used to calculate the trap depth, the average value is given in the table. N.D. = Not Determined.

observed in self [α]-irradiated ²³⁹Pu doped CaClAP (recorded after 2 hrs of storage of freshly prepared sample) were very weak; however the EPR spectra recorded at 300 K after two weeks of storage at room temperature (figure 5) clearly showed a quartet with $g_{\parallel} = 2.0034$, $A_{\parallel} = 30$ G; $g_{\perp} = 2.0273$, $A_{\perp} = 13$ G for ³⁵Cl nuclei; weak H⁰ ($A_{av} = 495$ G, $g_{av} = 2.0070$, shown in figure 7) and two other centres with $g_{\parallel} = 2.0034$, $g_{\perp} = 2.0386$; and $g_{\parallel} = 2.0459$, $g_{\perp} = 1.9997$). Earlier Roufosse *et al* (1974) have detected

two trapped hole like centres in CaClAP after x-irradiation of the crystals that were flux grown in air. On the basis of their work, the radical with $g_{\parallel} = 2.0034$; $g_{\perp} = 2.0273$ having quartet hyperfine structure is assigned to $[\text{ClO}]^{2-}$ molecular ion and the centre with $g_{\parallel} = 2.0034$ and $g_{\perp} = 2.0386$ to O^- radical. The centre with $g_{\parallel} = 2.0459$ and $g_{\perp} = 1.9997$ is assigned to O_2^- radical (Marfunin 1979). It has been reported in literature that crystals grown in air atmosphere are likely to incorporate amount of oxygen impurity ions at Cl^- sites concomitant with the introduction of corresponding number of charge compensating Cl^- ion vacancies. On the other hand crystals grown in HCl atmosphere were reported to yield purer stoichiometric crystals (Roufousse *et al* 1974; Knottnerus *et al* 1972; Knottnerus and Den Hartog 1975). The samples used in the present study are essentially similar to the crystals grown in air atmosphere and hence oxygen centered radical were observed.

No marked changes in the EPR spectra are observed on further gamma irradiation of the CaClAP:Pu sample. These spectra are also shown in figure 5. Same type of centres are observed on samples of UO_2^{2+} and undoped CaClAP γ -irradiated at 300 K except that H^0 intensity is stronger as compared to ^{239}Pu doped samples. The origin of H^0 centres can be probably due to OH^- ions, which is known to be a common impurity in alkaline earth halides (CaCl_2 in this case) used in the preparation of the halophosphate samples. It is also possible that OH^- may have been doped in to the samples while heating in air at 1250 K.

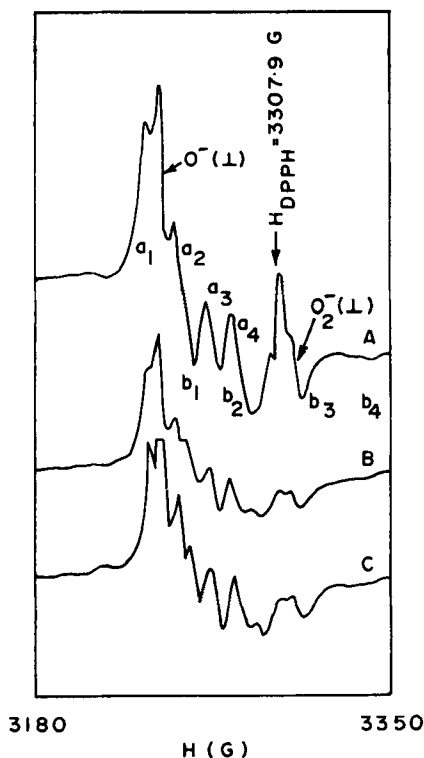


Figure 5. The EPR spectra obtained at 300 K in (A) ^{239}Pu doped CaClAP stored for about 2 weeks after preparation of the sample (α -dose rate = 3.6 Krad/h). (B) Undoped CaClAP and (C) UO_2^{2+} doped CaClAP (γ -dose = 0.4 Mrad). a_1, a_2, a_3, a_4 (\perp components) and b_1, b_2, b_3, b_4 (\parallel components) are quartets due to $^{35,37}\text{Cl}$ hyperfine interaction in $(\text{ClO})^{2-}$ radical.

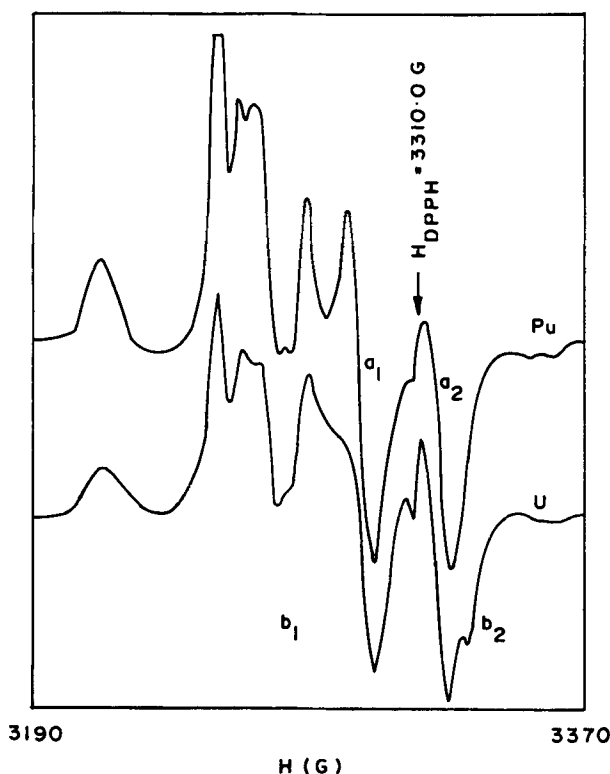


Figure 6. The EPR spectrum obtained at 77 K on samples of ^{239}Pu and UO_2^{2+} (U) doped CaClAP after γ -irradiation at 77 K (dose = 0.4 Mrad). a_1 , a_2 and b_1 , b_2 are doublet lines associated with PO_4^{2-} radical.

3.2.2 Low temperature region: Figure 6 shows the EPR spectrum of Pu/ UO_2^{2+} doped samples of CaClAP γ -irradiated at 77 K for 2 hrs. No resonance due to Pu^{3+} or UO_2^+ could be observed either at 300 K or 77 K up to a magnetic field of 12.5 kG the highest that can be achieved with our magnet. The EPR spectra showed the presence of a doublet with $g_{\parallel} = 2.0089$, $A_{\parallel} = 49$ G; $g_{\perp} = 2.0077$ and $A_{\perp} = 26$ G ($g_{\text{av}} = 2.0081$, $A_{\text{av}} = 34$ G) and this is identified as the PO_4^{2-} centre as reported in hydroxy apatites (Cevc *et al* 1972). Apart from this the main radical ion $[\text{ClO}]^{2-}$ and O^- are also observed as in room temperature γ -irradiated samples (discussed earlier). The quartet structure of Cl however, becomes more clear after the thermal destruction of the PO_4^{2-} centre at around 175 K. The thermal destruction of PO_4^{2-} is responsible for the intense TSL glow observed around 185 K in Pu doped CaClAP and 190 K in UO_2^{2+} doped CaClAP.

3.3 Thermal stabilities of the radical ions and correlation of TSL and EPR

To correlate the TSL peaks observed in the CaClAP lattice EPR temperature variation experiments were carried out on all the samples (doped as well as undoped). It was found that the centres H^0 , O_2^- and PO_4^{2-} show a sharp fall in intensity at different temperatures and these seem to be related to some of the TSL peaks observed in CaClAP lattices. The thermal activation energies for these centres were determined

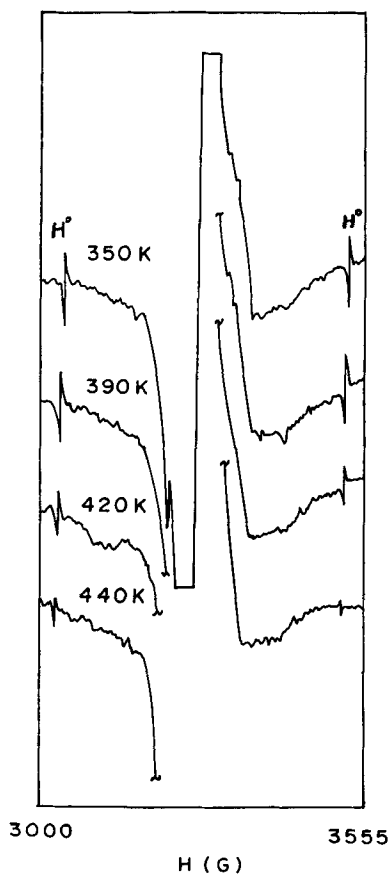


Figure 7. The EPR spectra obtained at different temperatures on samples of UO_2^{2+} doped CaClAP after γ -irradiation at room temperature (dose = 2 Mrad).

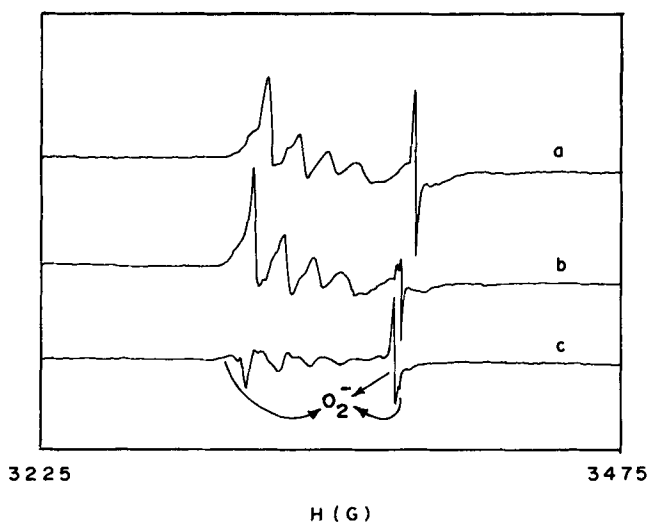


Figure 8. EPR spectra of gamma irradiated CaClAP:Pu (dose = 2.0 Mrad) (a) at room temperature; (b) after heating to 480 K and cooling back to room temperature and (c) difference spectrum obtained by subtracting spectrum (b) from spectrum (a).

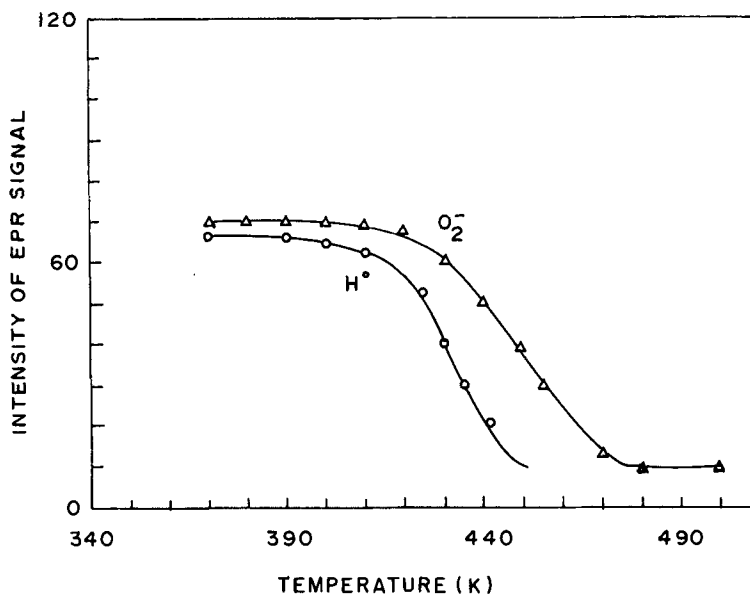


Figure 9. The temperature dependence of intensities of EPR signals due to H[•] (○), in UO₂²⁺ doped CaClAP and O₂^{•-} (Δ) in ²³⁹Pu doped CaClAP in the high temperature range.

using the equation $\ln[-\ln(1 - \Delta I/I)] = \text{constant} - E/kT$ (Huzimura *et al* 1980), where I is the intensity of the EPR signal and ΔI is the amount of the decrease in signal at each temperature. A least square fit programme was employed here to obtain the best fit of the data. The EPR spectra of room temperature γ -irradiated UO₂²⁺ doped CaClAP recorded at different temperatures are shown in figure 7. Figure 8 shows the EPR spectra of γ -irradiated CaClAP:Pu at room temperature and also the spectra taken at room temperature on a sample heated to 480 K. Further the difference spectrum obtained by subtracting the latter spectrum from the former spectrum (using the software available with Bruker ESP-300 spectrometer) is also shown in figure 8. It can be seen from the difference spectra that O₂^{•-} radical with orthorhombic symmetry and with $g_1 = 2.0459$, $g_2 = 2.001$ and $g_3 = 1.999$ disappears on heating the sample up to 480 K and there is an increase in the intensity of ClO²⁻ ion (spectra which is out of phase compared to that of O₂^{•-}). This phase difference arises due to enhancement of ClO²⁻, following the destruction of O₂^{•-}. This fact is taken into account in proposing the mechanism for the glow peak around 490 K. The temperature dependence of the intensities of the radical ions (as seen by EPR) are shown in figures 9 and 10 respectively. The probable mechanisms for various peaks (wherever possible) proposed by correlating the TSL glows to thermal stability of paramagnetic radical ions are summarized in § 3.4.

3.4 Mechanisms proposed for the TSL glow peaks observed in CaClAP lattices

(1) Peaks #1 and #2: The EPR data suggest that for peaks #1 and #2 thermal destruction of PO₄²⁻ is responsible (see figure 10). For the lower temperature peak, PO₄²⁻ is expected to be a recombination centre whereas the higher temperature peak

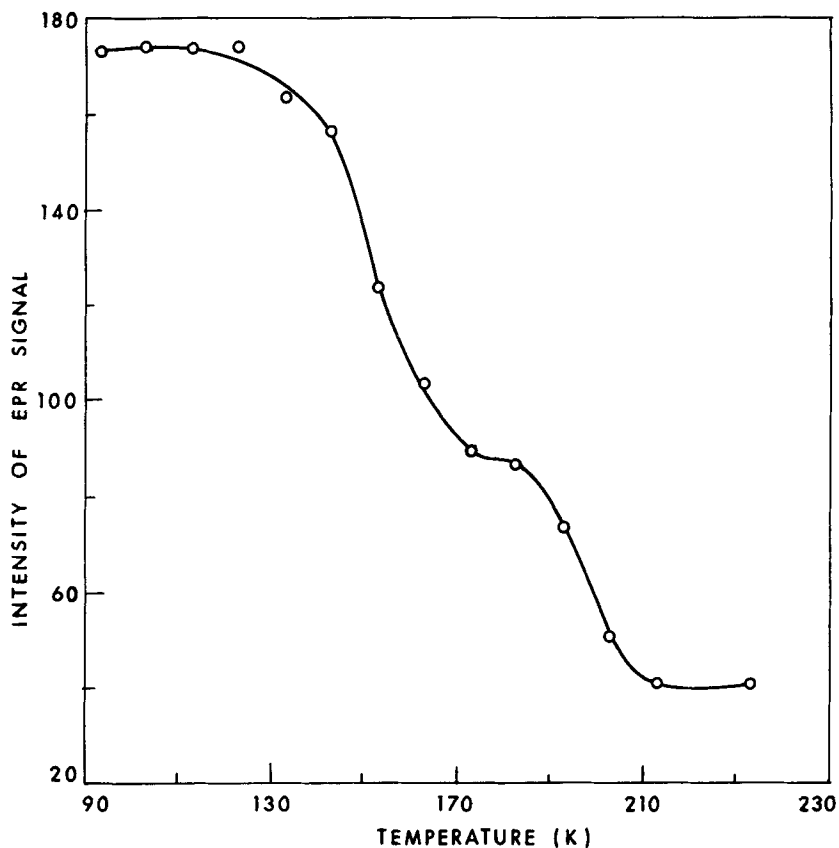
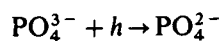


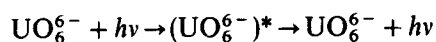
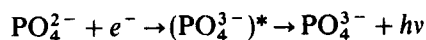
Figure 10. The temperature dependence of the intensity of the PO_4^{2-} radical in ^{239}Pu doped CaClAP in the sub-room temperature range.

corresponds to the thermal ionization of PO_4^{2-} to PO_4^{3-} . The proposed mechanisms are:

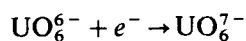
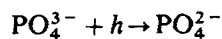
Peak 1: On γ -irradiation at 77 K,



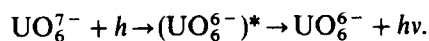
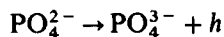
On heating to 135 K,



Peak 2: On γ -irradiation at 77 K,



On heating to 170 K,

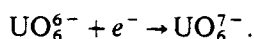
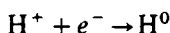
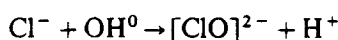
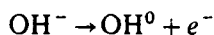


The trap depth value as determined from temperature dependence of EPR for the PO_4^{2-} radical ion has been observed to be 0.25 ± 0.04 eV in uranium doped CaClAP.

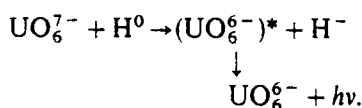
(3) 435 K peak

This is associated with the thermal destruction of H^0 .

On γ -irradiation at 300 K,



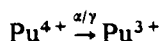
On heating at 435 K,



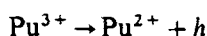
The activation energy as found out from the thermal stability plot for H^0 is of the order of 0.85 ± 0.06 eV.

(4) Peak at 490 K

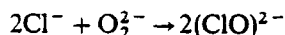
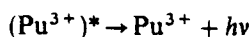
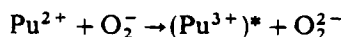
This is associated with the thermal destruction of O_2^- radical.



On gamma irradiation at 300 K,



On heating at 490 K,



The TSL properties of α -irradiated CaClAP and Ag doped CaClAP have been earlier studied by Lapraz and Baumer 1981 and Fukuda *et al* 1987. They conclude that the main trapping centres are specific of the crystal lattice as in the case of hydroxy apatites (OHAP) or fluorapatites (FAP), (Lapraz *et al* 1979, 1985; Lapraz 1980). No TSL peak was attributed by them to the thermal bleaching of the main radiation induced paramagnetic centres that are observed in apatites. Instead they had attributed the TSL peaks essentially due to vacancies and O^{2-} defects in halide sites. The photoluminescence and thermoluminescence properties of Eu^{2+} doped $\text{Ca}_2\text{PO}_4\text{Cl}$ have been studied by Meijerink and Blasse (1990). Their results have suggested that TSL is due to centre-to-centre recombination for the two major peaks in the thermoluminescent spectrum. Fukuda *et al* (1987) further report the thermal destruction of H^0 around 373 K. In their case the EPR spectra were recorded at 77 K, after heating the samples to 373 K and maintaining there for 10 minutes. In the present

work, EPR temperature variation experiments clearly showed that thermal destruction of H^0 occurs only around 420 K in undoped and UO_2^{2+} doped samples. The PO_4^{2-} radical ion and O_2^- radical ion also show sharp fall in intensity around 170–180 K and 450–460 K respectively. These features were used in suggesting the probable mechanism of the TSL glows.

4. Conclusion

The paramagnetic radical ions produced in halophosphate lattices (doped/undoped) under different irradiation conditions and their role in thermally stimulated electron transfer reactions have been identified. The prominent TSL glow peaks are associated with the thermal destruction of H^0 , O_2^- and a two stage destruction of PO_4^{2-} radical. The trap depth values were determined using the TSL data as well as the temperature variation of the EPR spectra.

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