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Observations on a high temperature peak in the thermoluminescence of fluorites

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Abstract. A new peak at about 650°C has been observed in the thermoluminescence emission of gamma irradiated natural fluorites containing significant quantities of lanthanide rare-earth (RE) elements as impurities. Thermal activation energy of the corresponding trap has been evaluated to be 2·99 eV with a frequency factor of 10^{16} sec^{-1}. The optical activation energy, as deduced from photo-transfer-induced-TL from this trap, is 5·36 eV. Many types of natural fluorites as well as synthetically grown CaF_2 crystals doped with single and pairs of rare earth elements have been studied and the results indicate that the high temperature peak is associated with Sm impurity coexisting with Y, La or Ce in CaF_2. There are indications that this newly observed TL peak can be gainfully employed in ultraviolet dosimetry and geological dating of fluorite deposits.

Keywords. Thermoluminescence; CaF_2 crystals; frequency factor; rare earth elements; dosimentry; geological dating.

1. Introduction

Fluorite is one of the few minerals whose thermoluminescence (TL) characteristics have been studied in detail because of its high TL sensitivity and possible applications in radiation dosimetry and geology (Przibram 1956; Kaufhold and Herr 1968 and Nambi *et al* 1968). It was generally known that the TL emission is due to rare earth (RE) impurities present in fluorites and this had led to TL researches with artificially grown CaF_2 phosphors doped with known RE elements (Merz and Pershan 1967; Fong 1967). So far the highest temperature at which a TL peak has been detected in fluorites and CaF_2 (RE) phosphors stands at about 510°C (Sunta *et al* 1970 and Rao 1975). Studies on the presence, if any, of still higher temperature peaks in minerals and TL phosphors is quite an important aspect of TL investigations for better understanding of TL mechanisms (Sunta *et al* 1971) as well as for applications in geology (Bonfiglioli 1968) and UV radiation dosimetry (Sunta *et al* 1970).

2. Experimental details

2.1. *TL glow curve recording*

The reader used in the present study has been described in detail in Samant *et al* (1974); however, a heating rate of 1020°C/min coupled with a chart speed of 20 cm/min was employed to record the particular high temperature TL peak under investigation.

In order to record the peak without the overlap of lower temperature peaks, the TL glow curve was always recorded in two steps; in the first run, TL glow curve was recorded only upto 575°C and the sample allowed to cool to room temperature immediately (this yields glow curves with the well-known TL peaks I to V, the last appearing at 510°C); in the second run, starting from room temperature, the heating was taken to 750°C, thus recording only the hitherto unexplored, highest temperature peak (figure 1).

Usually 5 mg of the sample powder (75 to 200 μ size) was used in the tiny heating tray of the TL reader to record TL glow curves.

2.2. *TL spectra recording*

The TL emission spectra were recorded using a 0·25 m Jarrel Ash grating monochromator and an EMI 9558 QB or ASCOP 541E photomultiplier. To record the emission spectrum of any TL glow peak, a powder sample of about 20 $\sim$ 30 mg was maintained at a temperature some 50–70° lower than the particular glow peak temperature and the TL light was successively scanned for its spectral quality a number of times.

In samples with very low TL output, spectra were constructed from monochromatic glow curves recorded by using either narrow band pass filters or a wide slit monochromator instead of the filter combination in the TL reader described earlier. Details regarding such TL spectral measurements can be found in published literature (Nambi *et al* 1974; Nambi 1975).

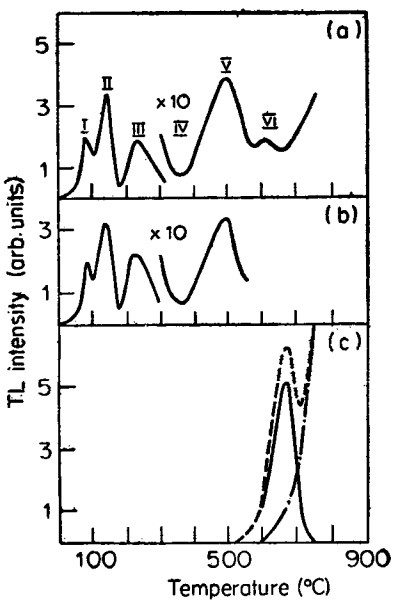

Figure 1. TL glow curve of natural CaF_2. **a.** Full glow curve. **b.** glow curve interrupted at 575° and **c.** glow curve rerun after step **b** (the background subtracted glow peak is indicated by the continuous curve). Sample No. 13 in table 1. Gamma exposure : 3×10^5 R.

2.3. *Preparation, annealing and irradiation of samples*

Thirteen different samples of natural CaF_2 were tested, twleve of which were of Indian origin and one was procured from France (table 1). The French sample has TL characteristics very much similar to the famous CaF_2 TLD powder marketed by MBLE, Belgium.

Numerous artificial crystals of CaF_2 grown with single or pairs of RE dopants by an improved Stockbarger technique in our laboratory (Rao 1975) were also tested.

The crystals that gave significant intensities for the high temperature TL peak under investigation, were grown at least thrice independently to check the reproducibility of the TL quality.

Thermal annealing studies were carried out using the same crystal growing furnace, whenever vacuum annealing at fairly high temperature was required. Otherwise, a muffle furnace was used.

Gamma irradiations of the samples were carried out in a gamma cell where the exposure rate at sample location was 5620 R min^{-1}; ultraviolet irradiations were done using a deuterium lamp for $\lambda < 250$ nm and a Jarrel Ash mercury lamp for irradiations at its well-known emission wavelengths; visible light irradiations at desired wavelengths were obtained from a quartz-iodine tungsten lamp and a grating monochromator.

Impurity analysis especially for Y and RE in flourites were done by atomic absorption spectroscopy and/or neutron activation.

3. Results and discussion

3.1. *TL peak VI in natural fluorites*

Of the 13 natural CaF_2 samples checked for their TL output both in the natural state (NTL) as well as after artificial gamma irradiation (ATL), only the French sample

Table 1. Descriptions of natural fluorite samples and comparison of the TL peak VI intensities.

Sample No./Description	Location/source obtained	TL peak VI (arb. units)*
1. Golden yellow crystal	Amba Dungar—Gujarat	4·4
2. White and violet layers opaque	Geological specimens—India	13·0
3. Yellow crystals	Poona—Maharashtra	2·4
4. Dark green crystal	Amba-Dungar—Gujarat	3·8
5. White crystal	Amba-Dungar—Gujarat	3·8
6. Light green clear colour	University of Baroda	7·8
7. Dull transparent crystal	Geological specimens—India	—
8. Crystal aggregate	Amba—Dungar, Gujarat	7·5
9. Faint purple transparent crystal	Geological specimens—India	—
10. Violet opaque rock	Mandwa-Ki-Pal Rajastan	—
11. Bluish violet crystal	Geological specimens—India	—
12. Green fluorite vein in quartz	Mandwa-Ki-Pal Rajasthan	—
13. Light green powder	Nuclear grade CaF_2 obtained from Products Mineraux et Chemiques D'aubusson, France	11·0

*Vacuum annealed at 850°C for 1 hr and given a gamma irradiation of 10^6R.

gave an easily discernible high temperature peak in the region of 625–650°C (the exact peak temperatures were dependent upon the gamma dose given (cf. § 3.4d). TL glow curves in figure 1 correspond to the French sample. This sample was subjected to various annealing temperatures in air and vacuum and the results obtained are shown in figure 2. The decrease in TL sensitivity with increase of temperature of annealing in air is similar to the observations of Kaufhold and Herr (1968) on the lower temperature glow peaks. The interesting result however is the vacuum annealing curve which shows a maximum TL output for annealing at 850°C, a temperature at which Ar annealing removes almost completely the TL sensitivity of the sample. Although the decrease in TL sensitivity due to air heating can be explained in terms of O or OH poisoning of the phosphors (Nakajima 1971), the sensitisation produced due to vacuum annealing is not yet understood.

Prompted by the results obtained for sample 13 as shown in figure 2, all the 12 Indian fluorites were also vacuum-annealed at 850°C for an hour and the glow curves recorded after gamma irradiation. Seven samples exhibited the high temperature peak in the region of 650°C and at least one of them was as sensitive as the French sample (table 1).

3.2 *TL peak VI in synthetic CaF_2 crystals*

The single crystals grown for this study were CaF_2 crystals doped with (i) single RE dopant; (ii) pairs of RE dopants; and (iii) a pair with one dopant being always yttrium and the other rare earth. The total concentration of dopants in any particular crystal was uniformly chosen to be 0·05 % by weight which is about the optimum concentration for maximum TL output in CaF_2 lattice (EL-Kolaly 1977). TL glow

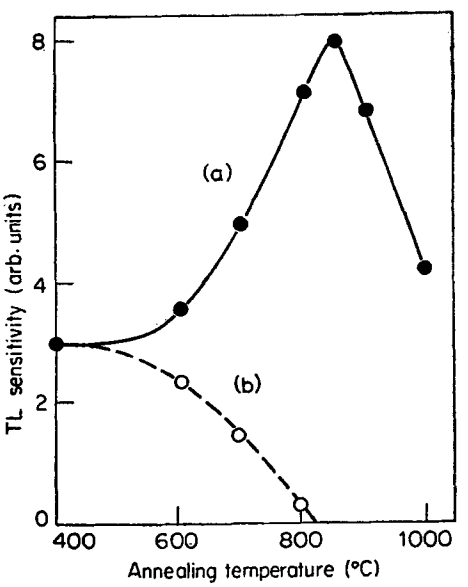

Figure 2. Effect of thermal annealing on TL peak VI of gamma irradiated Nat. CaF_2 (sample 13). **a.** Annealed in vacuum for 1 hr prior to irradiation. **b.** Annealed in air for 1 hr prior to irradiation.

Table 2. Characteristics of TL peak VI in natural CaF_2 and various synthetic CaF_2 phosphors.

Dopant in synthetic CaF_2	Peak temperature (0°C)	Relative intensity	Peak width at half maximum intensity, °C
Undoped	615	2·1	ND
La (0·05%)	605	8·0	76
Y (0·05%)	610	56	71
Sm (0·05%)	638	110	82
Y (0·05%) & Nd (0·05%)	610	1·0	ND
Y (0·05%) & Dy (0·05%)	638	1·0	ND
Y (0·05%) & Eu (0·05%)	610	1·5	ND
Y (0·05%) & Tb (0·05%)	610	3·0	88
Y (0·03%) & Sm (0·02%)	625	73	74
La (0·03%) & Sm (0·02%)	630	110	76
Ce (0·03%) & Sm (0·02%)	615	340	58
Nat. CaF_2 (all RE present)	625	30·0	80

ND — not discernible; in any case, > 100°C.

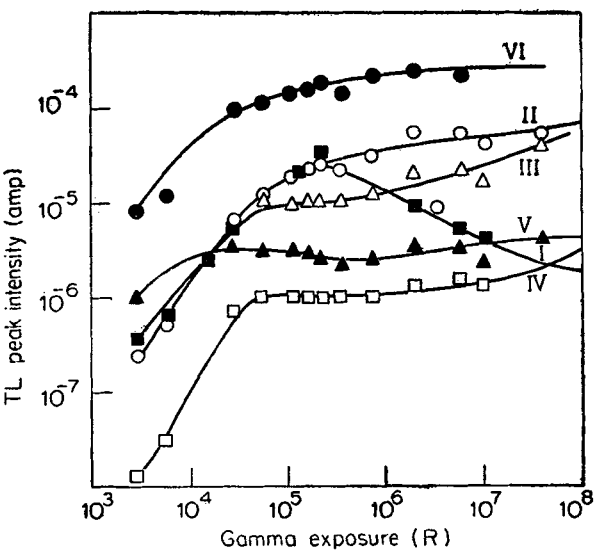

Figure 3. Dose dependence of natural CaF_2 TL peaks (peak VI was recorded with OX_1 filter whereas all other peaks were recorded with neutral filters.)

curves of all samples after gamma irradiation were recorded both with and without OX_1 band pass filter. The results obtained are presented in table 2 which shows that a sixth TL peak occurring at temperatures between 605 and 638°C with varying halfwidths was detected in eleven crystals.

3.3 *Characteristics of the peak VI and possible applications*

3.3a *Build-up and saturation characteristics for gamma irradiation.* Build-up of peak intensity with increasing irradiation shows saturation tendencies beyond about 10^5R (figure 3). It should be noted that peak V at $\sim$ 510°C used in geological applications saturates at $> 10^4$ R. Thus peak VI offers an extended dose range in these applications.

3.3b *Thermal activation energy and mean life time.* The thermal activation energy of the TL peak VI was determined by three different techniques and the results are presented in table 3. The mean value of 2·99 eV for the activation energy (E) seems to bear the same relationship with peak temperature (T_m) as the other peaks in this phosphor (Sunta 1971; Merz and Persham 1967).

$$E = 3{\cdot}7 \times 10^{-3} T_m - 0{\cdot}22 \text{ eV}.$$

This leads to a frequency factor of $\sim 10^{16}$ sec^{-1} and a mean life (at room temperature) of $\sim 10^{30}$ year. Such a large life-time for the trap is of great advantage in applications of geological dating.

3.3c *Photo-transferred thermoluminescence characteristics of* 650°C *TL Peak.* The nature of studies conducted is very similar to those followed for the 510°C peak in the same sample (Sunta *et al* 1970). A sample having only the 650°C peak as the residual thermoluminescence (RTL) obtained from a 850°C vacuum annealed powder exposed to a gamma irradiation $> 10^4$ R and annealed at 550°C for 15 min was exposed to UV radiation from a mercury lamp and then heated to record the TL glow curve. It was found that all the lower temperature TL peaks are regenerated with a slight bleaching of RTL (figure 4). It is well-known (Sunta *et al* 1970) that UV irradiation bleaches the RTL to an extent depending on wavelength and the released charge carriers are distributed among the available empty traps of all types. This explains the observation shown in figure 4. The photo-transferred thermoluminescence (PTTL) sensitivity variations in terms of the height of the dosimetry peak III with wavelength of UV irradiation is shown in figure 5, the peak at 230 nm indicates an optical activation energy of about 5·36 eV for the peak VI. Thus there seems to be a E_{opt}/E_{th} ratio of about 1·79 compared to 1·66 reported for peak V in the same phosphor (Sunta 1971). The PTTL behaviour of peak VI shows promises for applications in UV dosimetry.

3.3d *Energy distribution inside the trap corresponding to peak VI.* An important feature of the TL peak VI is the shift in the peak temperature depending upon the

Table 3. Evaluation of the activation energy for the 650°C peak.

Method	Reference	E (eV)
Initial rise method	Garlick and Gibson (1948)	2·92
Isothermal decay method	Townsend *et al* (1967)	2·99
Geometrical shape factor method	Halperin & Braner (1960)	3·05

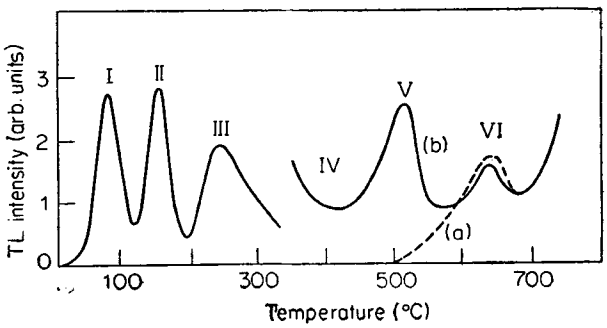

Figure 4. PTTL glow curve obtained from glow peak VI in natural CaF_2. **a.** RTL glow curve. **b.** PTTL glow curve after UV exposure. Sample No. 13 (table 1), 10^6R irradiated and annealed at 550°C for 15 min. UV source: 253·6 nm Hg light.

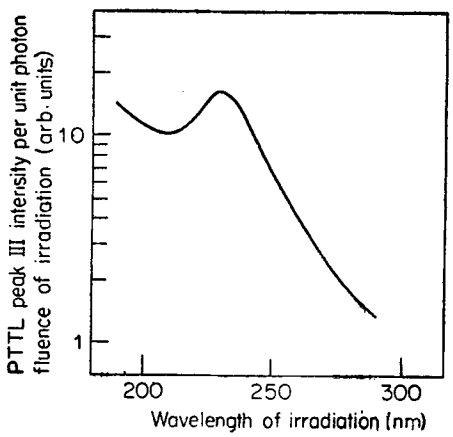

Figure 5. Wavelength dependence of PTTL response from TL peak VI in natural CaF_2. Sample No. 13 (table 1), 10^6R irradiated and annealed at 550°C for 15 min. UV source: Light from deuterium lamp through a monochromator.

gamma dose or the level of bleaching of the peak intensity. These results are presented in figures 6(a) and 6(b). It is seen that the temperature of the sixth peak lies anywhere in the region of 625–700°C. Such a trend in the shifting of peak temperature is thought to be due to a continuous distribution of energy levels around a single value of thermal activation energy corresponding to an apparent single peak.

3.3e *Spectral emission characteristics of the* 650°C *TL peak.* TL emission spectrum of the sixth peak has been scanned by maintaining an irradiated sample at about 550°C (i.e. after erasing all the earlier TL peaks). The emission spectrum consists of a single broad band around 325 nm (figure 7). The spectra obtained at lower temperatures corresponding to the lower temperature peaks are also shown in the same figure for comparison. In order to ascertain if any TL emission in the visible region had been missed owing to the abnormally high thermal background at 550°C, peak VI was recorded using band pass filters in the visible region and no TL output could be actually obtained.

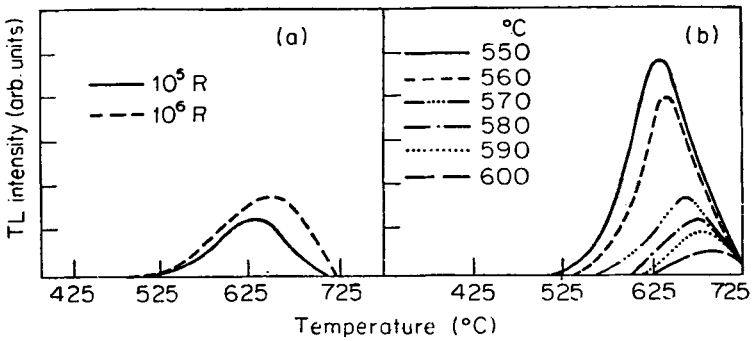

Figure 6. Shift in peak temperature of TL peak VI in natural CaF_2. **a.** Increasing gamma exposures on virgin sample. **b.** Increased bleaching after 10^5R exposure on 850°C vacuum annealed sample. Bleached for 2 min.

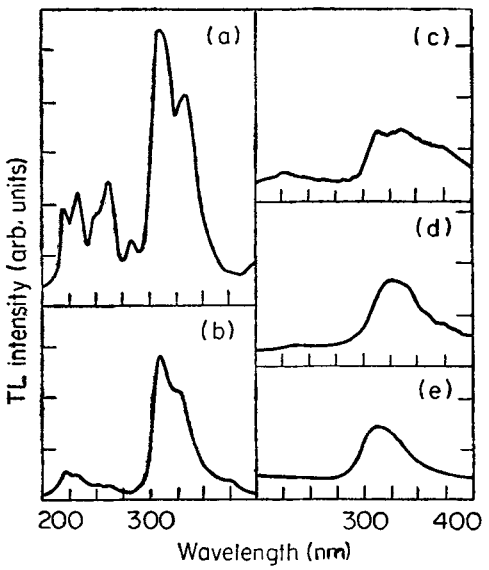

Figure 7. TL emission spectrum in the UV region of natural CaF_2 at various temperatures. **a.** 70°C. **b.** 200°C. **c.** 300°C. **d.** 400°C and **e.** 550°C. Sample: No. 13 (table 1) vacuum annealed at 850°C for 1 hr and gamma irradiated to 10^5R.

4. Conclusions

Of the synthetic samples, the significant emission intensities for the sixth peak with comparable halfwidths have been obtained in CaF_2(Sm), CaF_2(La,Sm) and CaF_2 (Y,Sm); CaF_2 (Ce,Sm) gives an intense sixth peak but much sharper than that found in natural samples (table 2). Thus, Sm seems to be an important requirement for the occurrence of high temperature TL peak in CaF_2 phosphors. Observation of a fairly strong VI peak in CaF_2(Y) and weakly intense peak VI in samples in which Sm was not explicitly added as dopant should be attributed to tracer quantities of Sm in the undoped CaF_2 samples (analysed to be 0·6 ppm$\pm$50%).

Doping CaF_2 with Sm alone has yielded an intense sixth peak at 640°C while doping with Y alone has yielded a peak at 610°C with less intensity. Doping with La alone has yielded a peak at 605°C with still less intensity. In the undoped sample, La/Y are present in much higher concentration than Sm and hence these observations. Yttrium is known to replace Ca in fluorites very efficiently (Pringsheim 1949) and concentration of Y in our samples (both natural and synthetic) ranged between 20–300 ppm. Hence the combined presence of Y and Sm impurities can be considered as responsible for TL peak VI in natural fluorites. The optimum concentrations for the combination is experimentally found to be 0·03% and 0·02% by weight respectively for Y and Sm dopants.

The elements Dy, Eu, Nd and Tb when codoped with Y have yielded almost the same intensities as the undoped sample but much less than that of the sample doped with Y alone. This is thought to be due to interference quenching between Y and these rare earths.

The 325 nm band in the TL spectrum is a characteristic emission of Y in CaF_2 lattice and this could be well recorded at lower temperatures too for the CaF_2(Y) samples. In CaF_2(Ce, Sm) samples which gave the maximum TL intensities at 615°C for the peak VI, a possibility exists that the 325 nm band emission is the thermal broadening effect on the well-known 317 nm and 338 nm emissions of Ce^{3+} (Sunta 1971).

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