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Glow peaks of Re (Re = Eu, Ce) doped CaF_2 relevant to dosimetry

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Glow peaks of Re-doped (Re = Eu, Ce) have been studied for their relevance to dosimetry. All the key parameters that are essential in predicting the stability of glow peaks are evaluated by Computerised Glow Curve Deconvolution (CGCD). Unlike most of the earlier works, in this study the importance of order of kinetics (b) is considered keeping the recent development in mind. Finally, the values of the parameters evaluated are examined, considering the solid-state aspect of defects in the material.

Keywords: CGCD, CaF_2, Dosimetry, Order of kinetics, Glow curve deconvolution

1 Introduction

CaF_2 is available as a commercial thermoluminescence dosimeter (TLD) in three different brands namely TLD-200, TLD-300 and TLD-400 (Harshaw Company Standard). In addition to these, natural fluorite[1] is also known to be an excellent TLD. CaF_2 based TLDs are more sensitive as compared to LiF based TLDs. This has fascinated researchers to study the materials for different applications[2] barring the regular use in personnel dosimetry where tissue-equivalence is a pre-requisite. In dosimetry amongst many other requirements two major concerns are:

(i) Stability of the signal i.e. the signal should not decay significantly with time.
(ii) It should be possible to integrate the signal with reasonable accuracy.

The first one can be tested by using the equation:

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right) \quad \ldots(1)$$

where, τ is the lifetime of charge in the trap, E the trap-depth, s the frequency factor, T the storage temperature ≈ 300 K and k is Boltzmann's constant.

Eq. (1) is strictly true for first order kinetics ($b = 1$). Recently, Singh and Gartia[3] have shown that for non-first order ($b \neq 1$) the modified equation is:

$$\tau = \frac{\exp\left(\frac{E}{kT}\right)}{s(2-b)} \quad \ldots(2)$$

Thus, for non-first order kinetics τ even for some value of E and s is significantly higher. For $b = 2$ in principle one cannot evaluate τ since denominator becomes zero. However, taking $b \approx 1.99$ or so one can say that for $b = 2$, stability is few order higher than that the case of $b = 1$. Thus, it is imperative to establish the kinetics of TL rigorously that can be achieved by computerized glow curve deconvolution (CGCD). It can also automatically enable one to integrate the signal accurately.

Rare-earths are accepted activators in most of the commercial phosphors; fluorides are no exception to this. They are mostly sought after in development of phosphors because their characteristic light emission covers the entire visible region. When rare-earth ions are added to CaF_2 they enter the lattice substitutionally for Ca^{2+} and in the case of europium usually are more stable in the divalent state. Qualitatively, rare-earth doped CaF_2 exhibits similar glow peaks[4] but quantitatively the relative intensities of the different TL peaks are dependant[4] on the specific rare-earth. We have studied the TL and also examine the stability aspect of TL peaks of CaF_2 (natural), $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$. The selection of $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$ is due to the fact that Eu^{2+} and Ce^{3+} are excellent activators enhancing the luminescent yield of many phosphors[5].

2 Experimental Details

Fluorites of bluish-green variety of Indian origin (obtained from M/S The Hindustan Minerals Natural

History Specimen Supply Co., Kolkata) were gently hand crushed in an agate mortar to a uniform size of 90-100μm. Preparation of CaF_2:Re (Re = Eu, Ce) usually have been employed by precipitation or other methods from various routes[6,7]. CaF_2:Eu is prepared by precipitation using $Ca(NO_3)_2$, Eu_2O_3 and NH_4F as starting materials. For CaF_2:Ce, the same procedure has been employed using $Ca(NO_3)_2$, $Ce_2(CO_3).H_2O$ and NH_4F, respectively as reactants. Samples were annealed at 700°C for 1 h.

The TL measurement of CaF_2 (natural) was performed using the commercial TL/OSL reader (model no. Risø TL/OSL reader TL-DA-15). The equipment is globally accepted as a standard TL reader[8]. The details are also presented in the earlier paper[9]. Glow curves of CaF_2:Re (Re = Eu, Ce) were measured by using Harshaw TLD reader (Model QS-3500) at IUAC, New Delhi.

2.1 Theoretical Techniques

The theoretical technique used for the analysis of the glow curves has been given in detail in the paper[10]. The equation governing the TL process for general order kinetics ($1<b\leq 2$) following Pagonis *et al*[11]. can be written as:

$$I(T) = n_0 s'' \exp\left[-\frac{E}{kT}\right] \times \left[1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\left(\frac{b}{b-1}\right)} \quad \ldots(2)$$

where E is the activation energy or trap depth (eV), k the Boltzmann's constant (eV K^{-1}), T the absolute temperature (K), $T = T_0 + \beta t$ where $\beta = \frac{dT}{dt}$, heating rate. t is time (s), T_0 the temperature at time t = 0 (K), n_0 the number of trapped electrons at time t = 0 (m^{-3}), b the kinetic order, a parameter with values typically between 1 and 2 s' the effective pre-exponential factor for general order kinetics ($m^{3(b-1)}s^{-1}$). $s'' = s' n_0^{(b-1)}$, an empirical parameter acting as an "effective frequency factor" for general-order kinetics (in s^{-1}).

Eq. (2) is not valid for b = 1 and hence for b = 1 we compute the TL with b = 1.001. Eq. (2) is routinely used in Computerized Glow Curve Deconvolution (CGCD) of glow curves of dosimetric materials[12]. In CGCD, the criteria of goodness-of-fit is, generally, the low value[13,14] (~ less than 1%) of Figure Of Merit (FOM) defined as:

$$\text{FOM} = \sum_{j_{\text{start}}}^{j_{\text{stop}}} \frac{100\left|y_j - y\left(x_j\right)\right|}{A} \quad \ldots(3)$$

where j_{start} is the initial temperature in the fit region, j_{stop} the final temperature in the fit region, y_j the experimental TL intensity at temperature j, $y(x_j)$ the value of the fit found at temperature j and A is the integral of the fitted glow curve.

In addition, the standard statistical tests like Kolmogorov-Smirnov (K-S)[15], Lilliefors[16], and Shapiro-Wilk[17] (W) have been used to check the goodness-of-fit. These tests are built-in in STATISTICA.

3 Results and Discussion

Glow curves of CaF_2 phosphors namely, natural CaF_2 (Bluish-Green), $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$ are shown in Fig. 1, respectively. Natural CaF_2 shows a complex glow curve having visible peaks around 75 to 110°C, 160 to 200°C, 200 to 270°C, 270 to 350°C and 375 to 430°C, respectively, whereas glow curves of $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$ are relatively less complex and exhibit an intense TL peak in the region 250-300°C depending upon heating rate; a region excellent for dosimetry in terms of stability of the signal. As a thumb rule, the dosimetric glow peak must be strong[18] and occur in the region 200-250°C. The stability of a particular glow peak can have several causes; thermal fading at ambient temperature being the most prevalent in TLDs. The stability of electron/hole in a trapping level relevant to dosimetry depends upon three key parameters i.e. E, s and b. Unfortunately in the investigation of trapping levels in most materials including TLDs most researchers have not considered the importance of E, s and b an equal footing. The following important points that will provide a physical basis to the entire glow curves of CaF_2 phosphors, have been studied in the present paper.

(i) The number of TL peaks that constitute the entire glow curve under consideration (RT–400°C).
(ii) Can we indiscriminately use first order kinetics (b = 1) for all the TL peaks as done by many researchers?

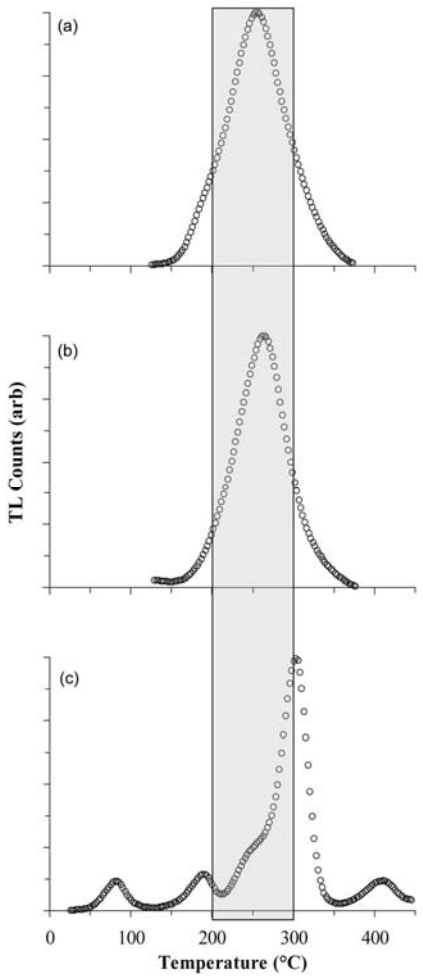

Fig. 1 — TL curves of CaF_2 phosphors. (a) $CaF_2:Ce^{3+}$, $CaF_2:Eu^{2+}$, (c) natural CaF_2 (bluish-green). (Heating rate used for all cases are $1°s^{-1}$. The range relevant to dosimetry is shaded)

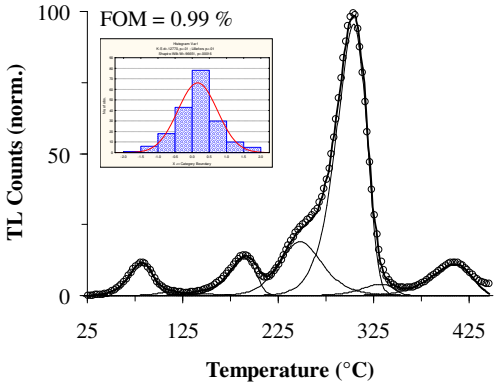

Fig. 2 — Deconvoluted TL curves of natural CaF_2 of bluish-green shade, (heating rate = $1°s^{-1}$ and 25 Gy β–irradiated) ○○○○ – experimental data; —— – best-fit component TL peaks; ▬▬ – sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

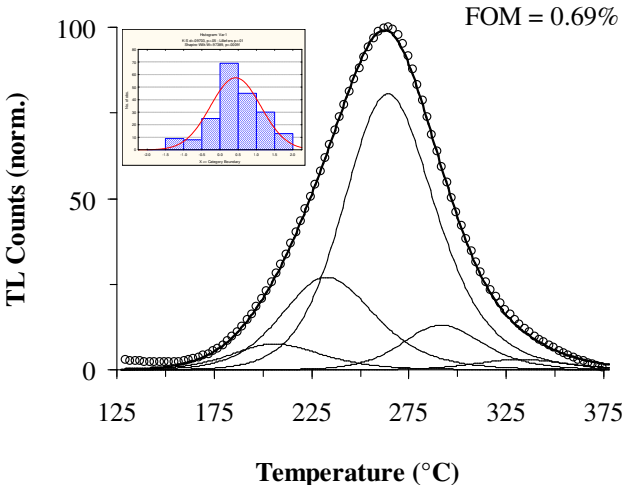

Fig. 3-Deconvoluted TL curves of natural CaF_2:Eu, (heating rate = $1°s^{-1}$ and 25 Gy γ –irradiated). ○○○○ – experimental data; —— – best-fit component TL peaks; ▬▬ – sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

Table 1 — Thermoluminescence parameters of glow curves of natural CaF_2

T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)
82.0	12.0	0.99	1.02×10^{13}	1.31	1.70×10^{00} y
110.5	1.3	1.19	4.09×10^{14}	1.00	2.78×10^{00} y
140.0	0.8	1.19	2.55×10^{13}	2.00	1.22×10^{01} y
190.0	13.6	1.30	9.97×10^{12}	1.00	2.20×10^{01} y
248.0	19.9	1.50	1.97×10^{13}	2.00	2.55×10^{06} y
304.0	100.0	1.90	2.60×10^{15}	1.08	1.10×10^{09} y
332.0	4.2	1.90	4.05×10^{14}	1.00	6.50×10^{09} y
410.0	11.5	1.90	4.95×10^{12}	1.00	5.32×10^{11} y

*For $b = 2$, we have approximated $b = 1.99$.

(iii) Finally, how realistic is the evaluated values of trapping parameters that determine the suitability of the material in terms of stability of the relevant TL peak.

(iv) Finally, as a material is there something unique in terms of trap-spectroscopy of CaF_2 based candidates used as TLDs?

Hence, TL curves of natural fluorite of bluish-green shade of Indian origin as well as $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+,}$ have been analyzed. The deconvolution of TL curves of natural CaF_2 is shown in Fig. 2 while the relevant TL parameters are presented in Table 1. The low value of FOM shows that the fitting is excellent. CGCD of a glow curves of $CaF_2:Eu^2$, $CaF_2:Ce^{3+}$ are shown in Figs 3 and 4, respectively. The relevant

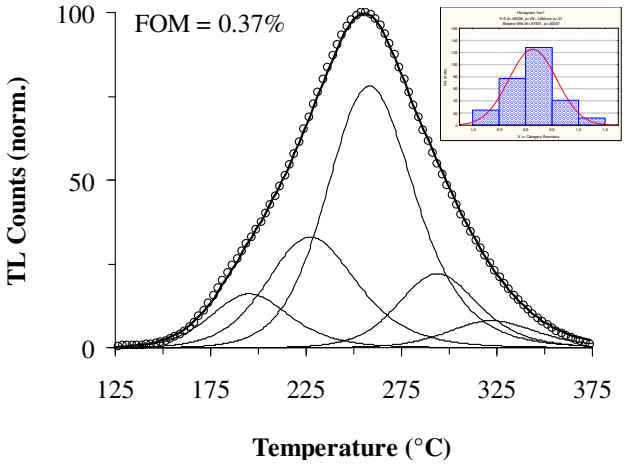

Fig. 4 — Deconvoluted TL curves of natural CaF_2:Ce. (heating rate = 1°s^{-1} and 25 Gy γ –irradiated), ○○○○ – experimental data; —— – best-fit component TL peaks; ▬▬ – sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

Table 2 — Thermoluminescence parameters of glow curves of natural $CaF_2:Eu^{2+}$

T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} ($b = b^*$)
206.0	9.3	1.2	2.42×10^{11}	2.00	1.90×10^{03} y
232.5	33.5	1.3	5.09×10^{11}	2.00	4.31×10^{04} y
264.0	100.0	1.5	6.84×10^{12}	2.00	7.35×10^{06} y
291.5	16.1	1.9	6.07×10^{15}	2.00	4.34×10^{10} y
332.0	3.7	1.9	3.86×10^{14}	2.00	6.83×10^{11} y

*For $b = 2$, we have approximated $b = 1.99$.

Table 3 — Thermoluminescence parameters of glow curves of natural $CaF_2:Ce^{3+}$

T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} ($b = b^*$)
195.0	20.5	1.3	6.52×10^{12}	2.00	3.37×10^{03} y
227.0	42.3	1.3	7.23×10^{11}	2.00	3.03×10^{04} y
258.0	100.0	1.5	1.01×10^{13}	2.00	4.98×10^{06} y
293.5	28.2	1.9	5.25×10^{15}	2.00	5.02×10^{10} y
322.0	10.3	1.9	7.37×10^{14}	2.00	3.58×10^{11} y

*For $b = 2$, we have approximated $b = 1.99$

CGCD outputs are presented in Tables 2 and 3. More or less single looking glow curves each consisting of five highly overlapped glow peaks but characterized by only three/four trapping levels of depth 1.20, 1.30, 1.50 and 1.90 eV. That more than one TL peaks can have the same activated energy was argued by Gartia[19] and substantiated in subsequent works[20,21]. This concept of more than one TL peak having same trap-depth is true for natural fluorite as well as $CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$ (Figs 3 and 4 and Tables 2 and 3). The statistical outputs of the best-fit analysis of the present work are presented in Table 4. The spectroscopy of traps (plot of density of trapping levels in energy scale) as obtained by our analysis of the three glow curves of CaF_2 phosphors is shown in Fig. 5. The data clearly shows the uniqueness of the common feature of the system.

Based on the entire data we would conclude the following:

(i) TL is a unique tool capable of establishing the spectroscopy of traps relevant to TL dosimetry. These trapping levels have trap-depths 1.20, 1.30, 1.50 and 1.90 eV in case of CaF_2 based TLD. The only difference being that the relative densities of traps occupancy for natural fluorite,

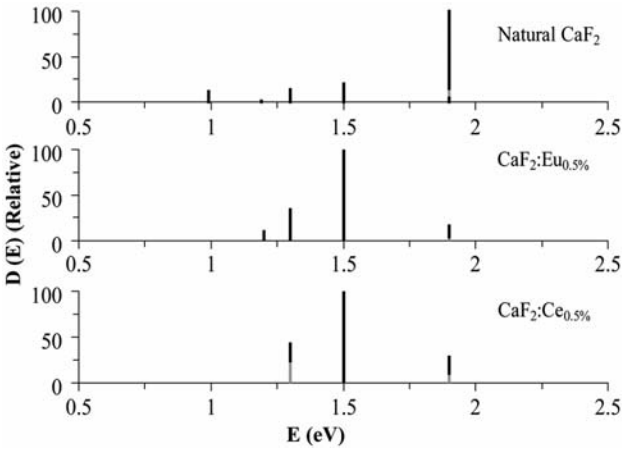

Fig. 5 — Plot of relative trap-density of different trapping levels in the three glow curves of CaF_2 based TLDs

Table 4 — Output of statistical Tests

Glow curves of Figure Numbers	Kolmogorov-Smirnov (K-S) test	Lilliefors test	Shapiro-Wilk (W) test
Fig. 2	d=0.12770, p<0.01	P<0.01	W=0.96651, p=0.00016
Fig. 3	d=0.09703, p<0.05	P<0.01	W=0.97389, p=0.00091
Fig. 4	d=0.09336, p<0.05	P<0.01	W=0.97501, p=0.00007

$CaF_2:Eu^{2+}$ and $CaF_2:Ce^{3+}$ are different. Sometimes a particular trap may totally be missing.

(ii) In all the cases, traps relevant to dosimetry as per our evaluation have depths 1.19/1.20, 1.30, 1.50 and 1.90 eV that give rise to five TL peaks.

(iii) The values of '*s*' are in the range ~ 10^{11}-10^{15} s^{-1}, a physically realistic range.

(iv) In all certainly we conclude that indiscriminate use of first order TL peaks for all the peaks is not correct. 2nd order kinetics certainly have increased the order of stability.

(v) In modeling, use of statistical criterion provides quality of the modeling.

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