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Trap spectroscopy and thermoluminescence of CaF_2 based TLDs

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A comprehensive picture of trap-spectroscopy of CaF_2 based TLDs namely natural CaF_2, CaF_2:Dy (TLD-200), CaF_2:Tm (TLD-300) and CaF_2:Mn (TLD-400) has been presented in the paper. We demonstrate that all the CaF_2 based TLDs have some common characteristics in terms of trap-depths relevant to dosimetry. Unlike most of the studies, the role of the frequency factor (s) and the order of kinetics (b) that decide critically the stability of relevant glow peaks have been examined. This has been achieved by performing deconvolution of the entire glow curves of the systems and subjecting the criteria of acceptance of curve-fitting not only by considering 'Figure of Merit' (FOM) but rigorous statistical tests.

Keywords: Trapping parameters, CaF_2, TLD, FOM, Trap-spectroscopy

1 Introduction

Calcium fluoride (CaF_2) based TLDs belong to one of the various high Z thermoluminescent phosphors and have a long and rich history of its own[1]. Essentially four varieties of TLDs based on CaF_2 matrix have been extensively studied for their various practical applications. The four varieties are: natural fluorite of some specific origin containing suitable activities or synthetic CaF_2 with either manganese (Mn), dysprosium (Dy), or Thulium (Tm) as their dopants.

The suitability of a material for being considered as a TLD is based on various properties, one of them being the stability of the dosimetric glow peak. A detail account of this important aspect of applicability of six commonly used TLDs that include CaF_2:Dy, CaF_2:Tm and CaF_2:Mn has been presented by Harvey *et al*[2]. As a thumb rule the dosimetric glow peak must be strong and occur in the region[3] 200-250°C. The stability of a particular glow peak is dependent on the lifetime (τ) of a glow peak i.e. the lifetime of the associated electron / hole in the relevant trapping level. It is given by:

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

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 constant. Eq. (1) is strictly true for first order kinetics (b = 1) and for $1 \le b < 2$ the modified equation as derived by Lovedy and Gartia[4] is:

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

i.e. for non-first order ($b \neq 1$) glow peak, τ is significantly different depending upon the magnitude of b; when b = 2, τ is few order of magnitude more than that for b = 1. We note that for b = 2 we cannot evaluate τ. Assuming $b \approx 1.99$, τ for the most dominant TL peaks may be estimated to be multiple of ≈ 100 or more. Here lies the importance of the parameter b a point that will be examined in the present paper.

Thus, 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 on equal footing. This paper presents the following important points that provide the physical basis to the entire glow curve i.e. TL in CaF_2 based TLDs. These are:

(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?
(iii) Finally, reliability of the evaluated values of trapping parameters that determines the suitability of the material in terms of stability of the relevant TL peak.
(iv) Is there something unique in terms of trap-spectroscopy of CaF_2 based as TLDs?

In order to establish these points we analyze TL curves of natural fluorite of bluish-green shade of Indian origin as well as TLD-200, TLD-300 and TLD-400. The TL data of natural fluorite is measured in our own laboratory while for those of other TLDs we have used some of the published work of some other researchers. Two glow curves of TLD-200 and TLD-400 are from the work[2] of Harvey *et al*[2]. whereas those for TLD-300 are from the work of Olko[5] and Moyers and Nelson[6].

2 Experimental Details

The TL of natural fluorite of Indian origin (bluish-green shade) is gently hand crushed in an agate mortar to a uniform size of 90-100 µm. 10 mg of the reader annealed material is used in each measurement. The TL measurement is 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[7]. The samples are irradiated at room temperature with an inbuilt beta irradiation (^{90}Sr) source with a dose rate of (0.084 Gy s^{-1}). The irradiated samples are read out in flowing nitrogen atmosphere. Clean standard glass filters (combination of Schott UG-11 and BG-39) are always installed in the reader between the sample and the photomultiplier tube (EMI 9635). These filters permit the passage of light wavelength ranging from ~300 to ~400 nm and eliminate unwanted radiations emitted from the heater. The duration between irradiation and TL reading is always kept constant at about 10 min. All data is presented after subtraction of the background emission.

2.1 Theoretical techniques used for analysis

The theoretical technique used for the analysis of the glow curves has been given in detail in the recent paper[8]. The equation governing the TL process for general order kinetics ($1<b\leq 2$) following Pagonis *et al*[9]. can be written as:

$$I(T) = n_0 s'' \exp\left[-\frac{E}{kT}\right] \times \left[1 + \frac{s''(b-1)}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\left(\frac{b}{b-1}\right)} \quad \ldots(3)$$

where E is the 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 $\beta = \frac{dT}{dt}$ is heating rate, t the 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 so-called effective pre-exponential factor for general order kinetics ($m^{3(b-1)}s^{-1}$) and $s'' = s' n_0^{(b-1)}$, an empirical parameter acting as an "effective frequency factor" for general-order kinetics (in s^{-1}).

It is to be noted that Eq. (2) is not valid for b = 1 and hence for b = 1 we compute TL with b = 1.001. Eq. (2) is routinely used in Computerized Glow Curve Deconvolution (CGCD) of glow curves of dosimetric materials[10].

In CGCD, the criteria of goodness-of-fit is, generally, the low value (~ less than 1%) of Figure Of Merit (FOM)[11-12], defined as :

$$FOM = \sum_{j_{start}}^{j_{stop}} \frac{100\left|y_j - y(x_j)\right|}{A} \quad \ldots (4)$$

where j_{start} = 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, A is the integral of the fitted glow curve. In addition, we have used standard statistical tests like Kolmogorov-Smirnov (K-S)[13], Lilliefors[14], and Shapiro-Wilk (W)[15] to check the goodness-of-fit. These tests are built-in in STATISTICA.

3 Results and Discussion

The deconvolution of TL curves of fluorite of bluish-green shade of Indian origin recorded with heating rate (β) 1°s^{-1} and 5°s^{-1} are shown in Fig. 1(a and b) while the relevant TL parameters are presented in Table 1. The low value of FOM shows that the fitting is excellent.The deconvolution of three TL curves of TLD-300 are shown in Fig. 2(a, b and c). The curves are those excited by γ (Cs-137), α (Am-241) and iron-ion beams. The selection of these are based on the fact that TLD-300 response in terms of ratios of the high temperature TL peak (~250°C) and the low temperature peak (~150°C) are quite sensitive to the energy of the photon[1]. This provides us the opportunity to investigate a system that exhibits common TL peaks i.e. trapping levels

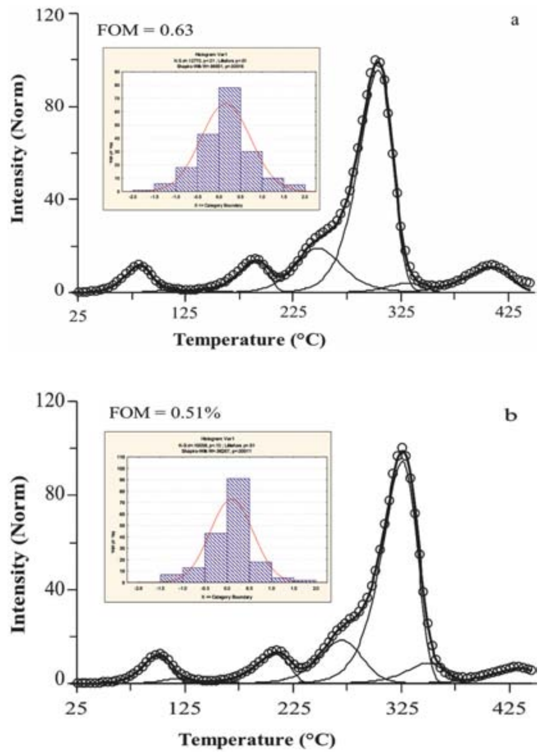

Fig. 1 — Deconvoluted TL curves of natural CaF_2 of bluish-green shade. (a) for $\beta = 1°s^{-1}$ and (b) for $\beta = 5°s^{-1}$.
○○○○ – experimental data; ── – best-fit component TL peaks; ━━ – sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

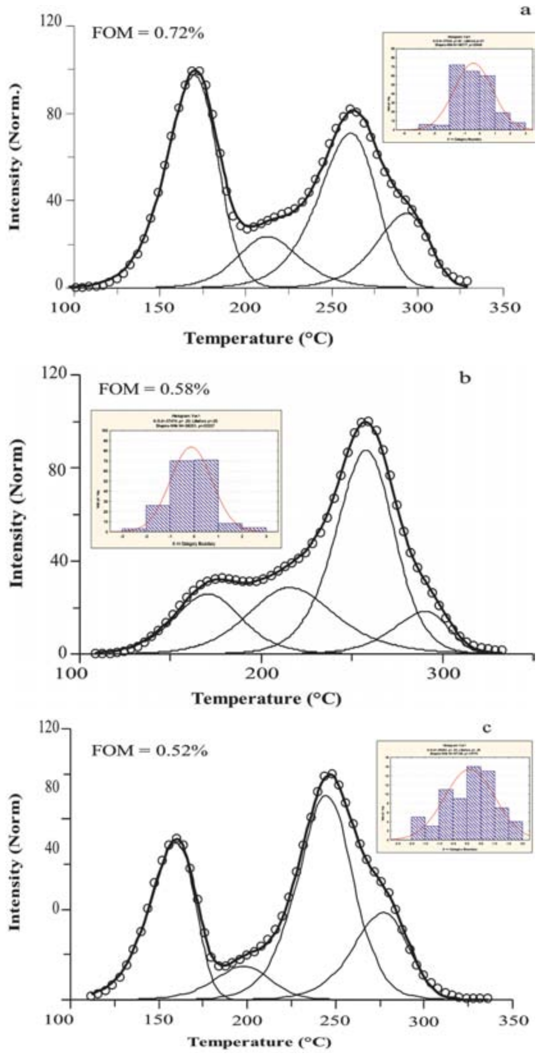

Fig. 2 — Deconvoluted TL curves of TLD-300. (a) γ (Cs-137) – irradiated Fig. 1 of Olko (1998), (b) α (Am-241) – irradiated Fig. 1 of Olko (1998) and (c) iron-ion beams irradiated Fig. 6 of Moyers and Nelson (2009).
○○○○ – digitized experimental data; ── - best-fit component TL peaks; ━━ - sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

Table 1 — TL parameters of Natural fluorite (bluish-green shade)

Heating rate, $\beta = 1°Cs^{-1}$						Heating rate, $\beta = 5°Cs^{-1}$					
T_m (°C)	I_m (relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)	T_m (K)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)
82.00	12.04	0.99	1.02×10^{13}	1.31	1.70h	100.00	12.17	0.99	9.75×10^{12}	1.14	1.42h
110.50	1.31	1.19	4.09×10^{14}	1.00	2.78d	118.00	2.12	1.19	9.73×10^{14}	1.25	1.56d
140.00	0.79	1.19	2.55×10^{13}	2.00	1.22×10^{01}y	148.00	0.69	1.19	6.50×10^{13}	2.00	4.79y
190.00	13.61	1.30	9.97×10^{12}	1.00	2.20×10^{01}y	208.50	13.23	1.30	1.32×10^{13}	1.00	1.66×10^{01}y
248.00	19.90	1.50	1.97×10^{13}	2.00	2.55×10^{06}y	270.00	19.58	1.50	2.41×10^{13}	1.40	3.47×10^{04}y
304.00	100.00	1.90	2.60×10^{15}	1.08	1.10×10^{09}y	326.00	100.00	1.90	2.98×10^{15}	1.00	8.85×10^{08}y
332.00	4.19	1.90	4.05×10^{14}	1.00	6.50×10^{09}y	350.00	9.21	1.90	6.67×10^{14}	1.00	3.95×10^{09}y
410.00	11.52	1.90	4.95×10^{12}	1.00	5.32×10^{11}y	434.00	6.88	1.90	7.73×10^{12}	1.00	3.41×10^{11}y

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

Table 2 — Thermoluminescence parameters of glow curves of TLD-300 (CaF_2:Tm)

Glow curves of TLD-300 (CaF_2:Tm)	T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)
Fig. 2(a)	170.00	100.00	1.30	9.33×10^{13}	1.30	3.36 y
	212.50	24.07	1.60	6.12×10^{15}	2.00	3.93×10^{05} y
	261.00	72.82	1.60	1.63×10^{14}	1.20	1.85×10^{05} y
	293.50	35.03	1.90	1.09×10^{16}	1.13	2.75×10^{08} y
Fig. 2(b)	170.50	29.52	1.20	5.89×10^{12}	1.74	2.94 y
	215.60	32.63	1.20	2.62×10^{11}	2.00	1.75×10^{03} y
	257.85	100.00	1.89	1.34×10^{17}	1.55	2.98×10^{07} y
	290.00	20.87	1.90	1.41×10^{16}	1.13	2.15×10^{08} y
Fig. 2(c)	159.50	76.82	1.30	2.26×10^{14}	1.10	1.08 y
	198.00	16.56	1.50	1.72×10^{15}	1.50	5.84×10^{02} y
	244.70	100.00	1.90	5.04×10^{17}	1.60	1.31×10^{07} y
	277.00	43.05	1.90	3.71×10^{16}	1.25	9.47×10^{07} y

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

Table 3 — Thermoluminescence parameters of glow curves of TLD-200 (CaF_2:Dy)

Glow curves of TLD-200 (CaF_2:Dy)	T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)
Fig. 3	150.50	23.44	1.30	3.71×10^{15}	1.10	23.96 d
	176.00	100.00	1.30	4.16×10^{14}	2.00	5.27×10^{01} y
	212.50	13.54	1.50	4.13×10^{15}	1.00	1.22×10^{02} y
	238.50	70.83	1.50	5.73×10^{14}	1.90	8.76×10^{03} y
	281.00	16.67	1.90	2.08×10^{17}	1.00	1.27×10^{07} y

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

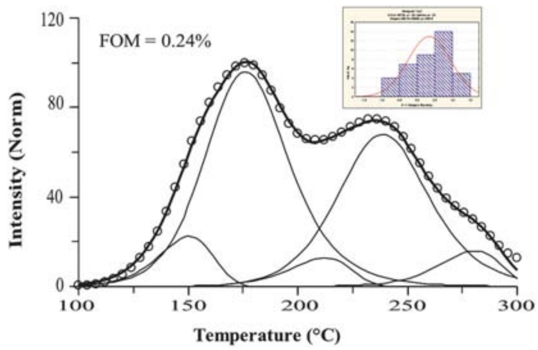

Fig. 3 — Deconvoluted TL curves of TLD-200. γ (Cs-137) – irradiated 28 days faded Fig. 6b of Harvey et al. (2010). ○○○○ – digitized experimental data; ── - best-fit component TL peaks; ━━ - sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

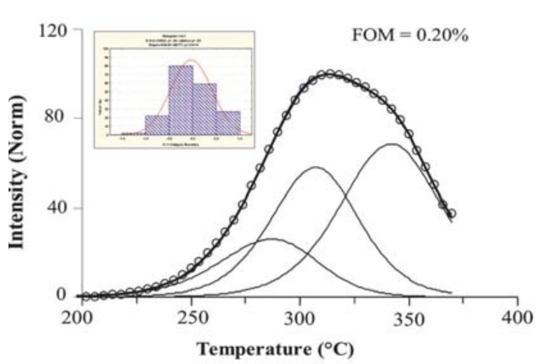

Fig. 4 — Deconvoluted TL curves of TLD-400. γ (Cs-137) – irradiated 1 day faded Fig. 12b of Harvey et al. (2010). ○○○○ – digitized experimental data; ── - best-fit component TL peaks; ━━ - sum of best-fit component TL peaks. (The histogram of deviation is shown in inset)

but of different intensities. This gives additional support to the acceptability of our data analysis. The relevant TL parameters are presented in Table 2 which shows that there is a fairly good agreement in terms of trap-depth of the so called peak 3 and peak 5. Trap-depth of peak 3 is ~1.20 to 1.30 eV while that for peak 5 is ~1.60 to 1.90 eV.

CGCD of a glow curve of TLD-200 (where the low temperature peaks are allowed for 28 days post-irradiation fading) reported[2] by Harvey *et al*[1]. is shown in Fig. 3 and the relevant CGCD output is presented in Table 3. It shows that the complex glow curve consists of five highly overlapped glow peaks but characterized by only three trapping levels of depth 1.30, 1.50 and 1.90 eV. That more than one TL peaks can have the same activated energy was argued by Gartia[16] and substantiated in subsequent works[17,18]. This concept of more than one TL peak having same trap-depth is true for natural fluorite as well as TLD-200 and TLD-300 as well as TLD-400 (Fig. 4 and Table 4). The statistical outputs of the best-fit

Table 4 — Thermoluminescence parameters of glow curves of TLD-400 (CaF_2:Mn)

Glow curves of TLD-400 (CaF_2:Mn)	T_m (°C)	I_m (Relative)	E (eV)	s (s^{-1})	b	τ_{300K} (b = b*)
Fig. 4	287.00	37.96	1.40	5.03×10^{12}	1.39	3.42×10^{03} y
	307.00	84.67	1.90	5.12×10^{16}	1.73	1.91×10^{08} y
	341.50	100.00	1.90	5.36×10^{15}	1.86	3.52×10^{09} y

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

Table 5 — Output of statistical tests

Glow curves of Figure Numbers	Kolmogorov-Smirnov (K-S) test	Lilliefors test	Shapiro-Wilk (W) test
Fig. 1a	d=0.12770, p<0.01	P<0.01	W=0.96651, p=0.00016
Fig. 1b	d=0.10058, p<0.10	P<0.01	W=0.96267, p=0.00011
Fig. 2a	d=0.07034, p<0.20	P<0.01	W=0.98177, p=0.00406
Fig. 2b	d=0.07474, p>0.20	P<0.05	W=0.98251, p=0.02227
Fig. 2c	d=0.08262, p>0.20	P>0.20	W=0.97128, p=0.10770
Fig. 3	d=0.09739, p>0.20	P>0.20	W=0.96685, p=0.29910
Fig. 4	d=0.04543, p>0.20	P>0.20	W=0.98177, p=0.01414

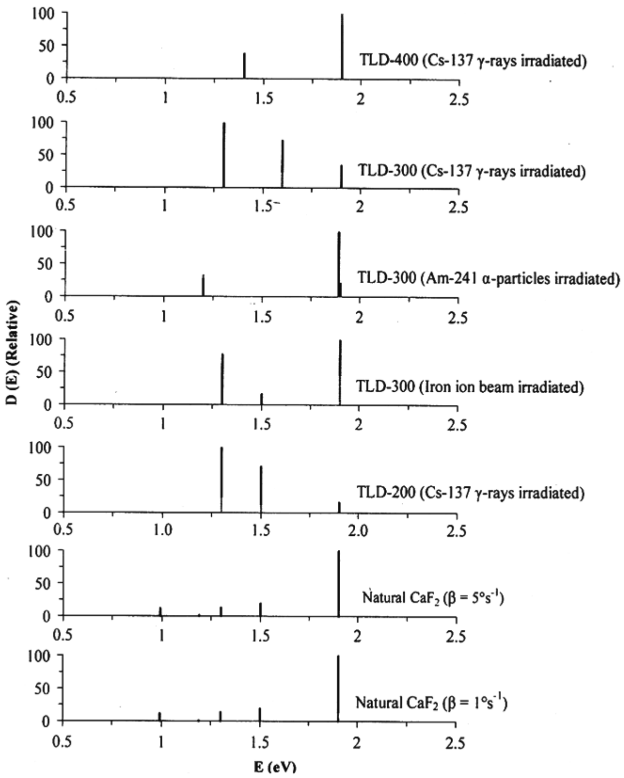

Fig. 5 — Plot of relative trap-density of different trapping levels in the seven glow curves of CaF_2 based TLDs

analysis of the present work are presented in Table 5. The spectroscopy of traps (plot of density of trapping levels in energy scale) as obtained by our analysis of seven glow curves of CaF_2 based TLDs is shown in Fig. 5. The data clearly shows the uniqueness of the common feature of the system.

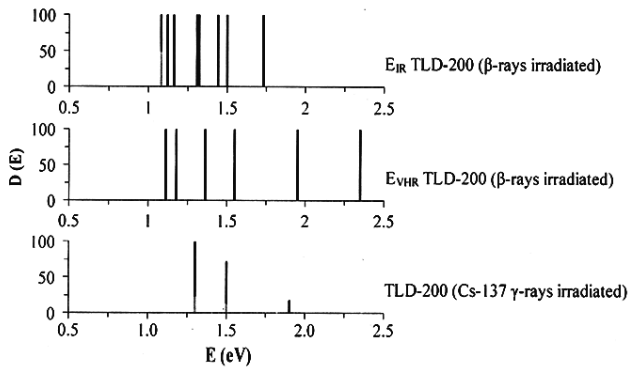

Fig. 6 — Trap spectroscopic comparison of TLD-200

For the sake of demonstration of the validity of our analysis, we shall discuss briefly a specific case of TLD-200 that has been critically examined by Yazici *et al*[19]. Their analysis has not led to any definite answer to the values of trap depths except that for a so called TL peak no. 4. The values of trap-depths obtained by initial rise (IR), various heating rates (VHR), peak shape (PS) and computerized glow curve deconvolution (CGCD) for other TL peaks could not be linked. Such failure is often encountered by various researchers leading to pessimistic view on TL data analysis. The typical recent one is that viewed by Aitsalo *et al*[20]., who opined that deconvolution is not a scientifically sound method of interpretation and analysis of TL curves. Our analysis clearly demonstrates that this is not true. Even under the extreme pessimistic view as observed in Table 3 of Yazici *et al*[19]., experienced researchers can use the table for meaningful interpretation. The table shows the existence of as many as nine peaks with trap-depths of 1.08, 1.08, 1.12, 1.16, 1.31, 1.32, 1.44, 1.73 and 1.50 eV, respectively as revealed by IR. These traps are very much present in TLD-200 as per our analysis (Table 3). We show the trap spectroscopy of TLD-200 based on our present result and that reported by Yazici *et al*[19]. where we compare E_{IR}, E_{VHR} of Yazici *et al*[19]. and our analysis. The comparison is shown in Fig. 6. The abnormal value of E_{CGCD} obtained by Yazici *et al*[19]. is probably because of misjudgment in accepting goodness-of-fit. This aspect we have already discussed.

Based on the entire data we would conclude the following:

(i) TL is an unique tool capable of establishing the spectroscopy of traps relevant to TLDs. 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, TLD-200, TLD-300 and TLD-400 are different. Sometimes a particular trap may totally be missing.

(ii) In TLD-200 (CaF_2: Dy), traps relevant to dosimetry as per our evaluation have depths 1.30, 1.50 and 1.90 eV that give rise to five TL peaks.

(iii) TLD-400 (CaF_2: Mn) is characterized by two traps of depths 1.40 and 1.90 eV but manifested in the form of three TL peaks.

(iv) Certainly, it is concluded that indiscriminate use of first order TL peaks for all the peaks is not correct.

(v) This study provides a solid physical basis for use of TLD-300 in mixed-field dosimetry; an area of high-end use of TLDs.

Acknowledgement

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