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The Analysis of Main Dosimetric Glow Peaks in CaF_2:Tm (TLD-300)

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The thermoluminescence properties of CaF_2:Tm (TLD-300) are examined in detail after β-irradiation at room temperature. The glow curve of the sample shows two main dosimetric glow peaks: P3 (at ∼150°C) and P5 (at ∼250°C). The additive dose, variable heating rate, computer glow curve deconvolution, peak shape and three points methods are used to evaluate the trapping parameters, namely the order of kinetics (b), activation energy (E) and frequency factor (s) associated with the dosimetric thermoluminescent glow peaks (P3 and P5) of CaF_2:Tm (TLD-300) after different dose levels with β-irradiation.

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Thulium-doped calcium fluoride, CaF_2:Tm, dosimeters may be obtained as single crystals in the form of extruded rods or hot chips. The most available sizes of hot chips are the same as those of the other popular CaF_2 materials (viz. $0.32 \times 0.32 \times 0.9\,\text{mm}^3$). Tm-doped CaF_2 TL dosimeters were first introduced in 1977[1] and are sold commercially by Bicron-NE (Harshaw) as TLD-300. Dosimetric-quality material contains about 0.35 mol% Tm. TLD-300 is known to be particularly useful for the dosimetry of densely ionizing radiation. The glow curve of these dosimeters consists of two well-separated glow peaks (called peaks 3 and 5), each exhibiting a different dependence on the ionization density of the radiation (linear energy transfer, LET).[2] The ease with which peaks 3 and 5 can be separated in the glow curve and their good stability make these TL dosimeters particularly useful in certain applications, such as the estimation of radiation quality or dose measurements in mixed radiation fields in spite of its high $Z_{\text{eff}} = 16.3$. CaF_2:Tm, first mentioned by Lukas and Kapsar (1977), has been receiving considerable attention ever since.[2]

Bos and Dielhof[3] reported that the main peaks (3 and 5) have activation energies of 1.15 eV and 1.54 eV, respectively, with the corresponding frequency values of s being $4 \times 10^{12}\,\text{s}^{-1}$ and $1 \times 10^{14}\,\text{s}^{-1}$. They also demonstrated that the kinetics of all the peaks are first order. Unlike LiF:Mg, Ti (TLD-100), the trapping parameters for the TL peaks in CaF_2:Tm are found to be invariant with the heating rate. This suggests that the complex defect interactions during heating that are found in TLD-100 dosimeters are not active in this material. This is consistent with what is known about the thermal stability of the rare earth defects (aggregates) in alkaline earth fluorides.[4] The main emission peaks of TLD-300 are at 360 nm, 450 nm, 465 nm and 650 nm in the visible region corresponding to internal Tm transitions. In addition to these visible emission bands, strong luminescence in the infrared, at 795 nm, is also observed.[5]

The mechanisms for TL production in Tm-doped CaF_2 are suggested to be similar to those for the Dy-doped CaF_2 material, with the emission steaming from Tm^{+3} ions.[6] Phototransfer studies by Lakshman and Tiwari[7] indicate that the peak 5 complex near 270°C is caused by the release of electrons (from unknown sites), with the emission of Tm^{+3} stimulated by energy transfer. Hole release rather than F^o interstitial movement is preferred by these authors as the source of the TL emission at lower temperatures, i.e. up to and including peak 3. Clearly, the actual mechanisms are far from determined and, with most dosimetric forms of CaF_2, not enough detailed studies have been performed to obtain a clear picture.

The dosimetric characteristics of any TL material mainly depend on the sensitivity, energy response and the kinetic parameters quantitatively describing the trapping-emitting centers responsible for the TL emission. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. For example, the simultaneous estimation of the dose rate and the time elapsed since exposure are closely related to the position of the trapping levels within the band gap, and therefore it is necessary to have a good knowledge of these parameters. There are various methods for evaluating the trapping parameters (the order of kinetics (b), activation energy (E_a) and the frequency factor (s)) from the TL glow curves. When one of the glow peaks is highly isolated from the others, experimental methods such as the initial rise, various heating rates and peak shape methods can be used to determine them. Therefore, in this Letter, the additive dose (AD), variable heating rate (VHR), peak shape (PS), three points method (TPM), and computerized glow deconvolution (CGCD) methods are used to determine the kinetic parameters, namely the order of kinetics (b), activation energy (E_a) and the frequency factor (s) associated with the dosimetric thermoluminescent (TL) glow peaks (P3 and P5) of TLD-300 after different dose levels with β-irradiation.

The samples used in this study are CaF_2:Tm (TLD-300) crystal chips ($3.2 \times 3.2 \times 0.89\,\text{mm}^3$) obtained from our stock of TLDs produced earlier from the former company known as Harshaw Chemical Company, Ohio, USA. Before the subsequent irradi-

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ation, the samples are first annealed at 400 ± 1℃ for one hour to erase any residual information and then quickly cooled in air to room temperature at 75℃/min. All annealing treatments are carried out with a specially designed microprocessor-controlled electrical oven, which is able to control the temperature within ±1.0℃. The samples are irradiated at room temperature with beta rays from a calibrated ^{90}Sr-^{90}Y source. The activity of the β-source was calibrated by the manufacturer on March 10, 1994, and it is found to be about 100 mCi. Stronium-90 emits high-energy beta particles from their daughter products (^{90}Sr β-0.546 MeV together with ^{90}Y β-2.27 MeV).

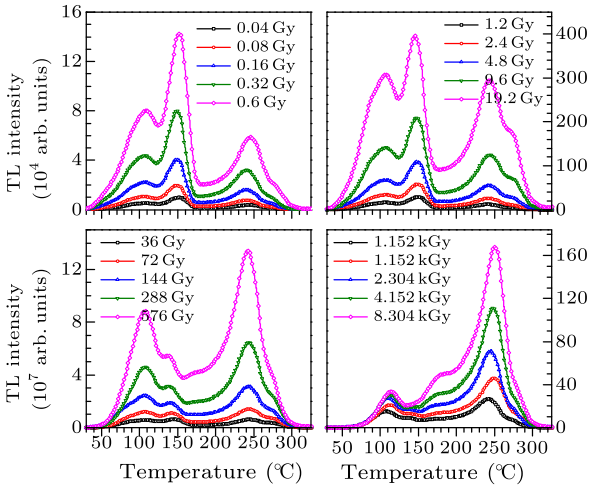


Fig. 1. The glow curves of TLD-300 measured after an annealing procedure of 400℃ for one hour by irradiation at room temperature on exposure to beta rays from 0.04 Gy up to 8.304 kGy and readout at a linear heating rate of $\beta = 1$℃/s

The evaluation of the kinetic parameters, i.e. the activation energy E_a of the traps involved in the TL emission, the kinetic order b, and the frequency factor s associated with the glow peaks of thermally stimulated luminescence, is one of the most studied subjects in the field of condensed matter physics. Thus, a reliable dosimetric study of a thermoluminescent material should be based on a good knowledge of its kinetic parameters. To form an opinion about the number of glow peaks and kinetic orders (b) of all the individual glow peaks in the glow curve structure of TLD-300, the additive dose (AD) method is utilized first in the current study. The samples are irradiated at different doses between ∼0.04 and ∼8.3 kGy to check the dose dependence effect on the peak positions. In TL theory,[8] the peak temperatures of the glow peaks are expected to change only with the heating rate for $b = 1$. Hence, for a constant heating rate, the peak maximum should not be affected by other experimental parameters and should thus be fairly constant within the limit of experimental uncertainties. However, for $b \neq 1$ and below the trap saturation points [n_o (concentration of trapped electrons) $< N_t$ (concentration of traps)], it is generally received that the peak temperatures are shifted to the lower temperature side with the increasing dose levels. The experimental observations have clearly shown that there are no significant changes in the shape of the glow curves of TLD-300 with the increasing dose level (Fig. 1). The positions of the peak temperatures of all glow peaks in the glow curve of TLD-300 are within the experimental error ±2℃ for all the doses. This result indicates that all the glow peaks in the glow curve of TLD-300 between room temperature and 400℃ can have first-order kinetics.

The recorded glow curves after the AD experiments are also used to determine the kinetic parameters by the peak shape method. This method is based on the shape and full width at half maximum (FWHM=$T_2 - T_1$) of a single glow peak, and the values of E_a are determined by the modified PS method of Chen.[9] According to this method, the kinetic order b of a single peak is easily obtained by means of the geometric factor $\{\mu_g = (T_2 - T_m)/(T_2 - T_1)\}$ and μ_g changes with the order of kinetics b from ∼0.42 to ∼0.52, where these two limits correspond to the first- and second-order kinetics, respectively. In addition to Chen's peak shape method, the kinetic parameters are also determined using Gartia, Singh & Mazumdar's[10] peak shape method, which requires prior knowledge of the kinetics order. In the present case, the symmetry factor (μ_g) of the isolated glow peaks, P3 and P5, of TLD-300 has been found to be 0.42±0.01, which gives a kinetic order of about 1. The method uses any points of a peak (i.e, $x = I_m/2$, or $2I_m/3$, or $4I_m/5$, where I_m is the maximum peak intensity). According to this method, it is possible to calculate the activation energy as follows:

$$E_a = \frac{(C_0 + C_1 b + C_2 b^2) k T_m^2}{|T_x - T_y|} + (D_0 + D_1 b + D_2 b^2) k T_m, \tag{1}$$

where k (eV·K^{-1}) is Boltzmann's constant, $|T_x - T_y| = \tau$, δ, ω, and C_0, C_1, C_2, D_0, D_1 and D_2 are the coefficients found by using the method of least squares for different orders of kinetics b in the range from 0.7 to 2.5 for different values of x.[10] Gartia *et al.* claimed that the E_a values obtained using Eq. (1) for $x = 1/2$ give more accurate results than Chen's peak shape equations.[10] As a result, the trapping parameters of the P3 and P5 calculated by this method are given in Table 1.

Recently, Rasheedy[11] improved the three points analysis method (TPM) for separating a composite TL glow curve into its individual components of glow peaks to evaluate the trap parameters of these peaks. According to this method, the order of kinetics b is given by

$$b = \frac{T_y[T_x - T_z]\ln(y) - T_z[T_x - T_y]\ln(z)}{T_y[T_x - T_z]\ln[A_x/A_y] - T_z[T_x - T_y]\ln[A_x/A_z]}, \tag{2}$$

where A_x, A_y and A_z are the areas under the glow peak from the temperatures T_x to T_f, T_y to T_f and T_z to T_f, respectively. The values of y and z are given by $y = I_x/I_y$ and $z = I_x/I_z$, respectively. The activa-

tion energy E_a is given either by

$$E_a = \{\ln y - b\ln[A_x/A_y]\}\left\{\frac{kT_xT_y}{T_x - T_y}\right\}, \quad (3)$$

or by

$$E_a = \{\ln z - b\ln[A_x/A_z]\}\left\{\frac{kT_xT_z}{T_x - T_z}\right\}. \quad (4)$$

Also, the frequency factor s in the first-order case is given by

$$s = (\beta E_a/kT_m^2)\exp(E_a/kT_m). \quad (5)$$

In the present study, the trapping parameters evaluated from the three points method are the results of calculations from the maximum intensity at temperature ~150℃ (P3) and ~245℃ (P5) up to 10% of the maximum intensities. The average values of the trapping parameters associated with P3 and P5 are given in Table 1.

All the glow curves are also analyzed by the CGCD method to obtain the number of glow peaks. This method has become very popular in obtaining the number of glow peaks in the complex glow curves and their kinetic parameters for the last three decades.[12] In this study, the first-order kinetics are approximated for all CGCD evaluations by the expression[13,14]

$$I(T) = n_0 s\exp\left(-\frac{E}{kT}\right)\exp\left[-\frac{s}{\beta}\frac{kT^2}{E}\exp\left(-\frac{E}{kT}\right)\cdot\left(0.992 - 1.620\frac{kT}{E}\right)\right], \quad (6)$$

and the general-order kinetics are approximated by the expression

$$I(T) = n_0 s\exp\left(-\frac{E}{kT}\right)\left[1+\frac{(b-1)s}{\beta}\frac{kT^2}{E}\exp\left(-\frac{E}{kT}\right)\cdot\left(0.992 - 1.620\frac{kT}{E}\right)\right]^{\frac{b}{1-b}}. \quad (7)$$

The number of glow peaks is not a free fitting parameter during the deconvolution of the measured glow curve into individual components in the CGCD programs. If the number of peaks is not known, it can be found by fitting the glow curve several times with a different number of components up to obtaining the best-fit result. Therefore, the real number of glow peaks in the glow curve of CaF_2:Tm is investigated by using different numbers of glow peaks in the CGCD program. In previously published studies,[15–20] it was observed that there are some conflicts regarding the number of glow peaks and therefore there has been no consensus on this parameter up to now. In the present study, it is observed that it is not possible to fit the glow curve of CaF_2:Tm by five components with first and/or general-order kinetics. In this case, there are large differences between the experimental and fitted glow curves when five first-order components are assumed in the CGCD program. After many treatments with different numbers of glow peaks, it is observed that the glow curve structure of CaF_2:Tm is well described by a linear combination of at least six first-order glow peaks. In this case, a reasonably good fit is always obtained. Therefore, the dosimetric peak of CaF_2:Tm is always fitted with six first-order components. One of the CGCD analyzed TL glow curves of CaF_2:Tm is shown in Fig. 2.

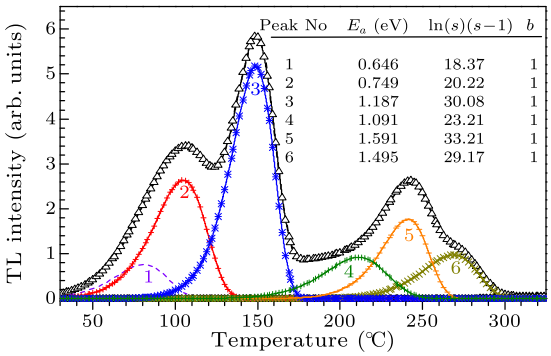


Fig. 2. The CGCD analyzed glow curves of Tm-doped CaF_2 measured after 12 Gy beta-ray irradiation at room temperature after an annealing procedure of one hour at 400℃.

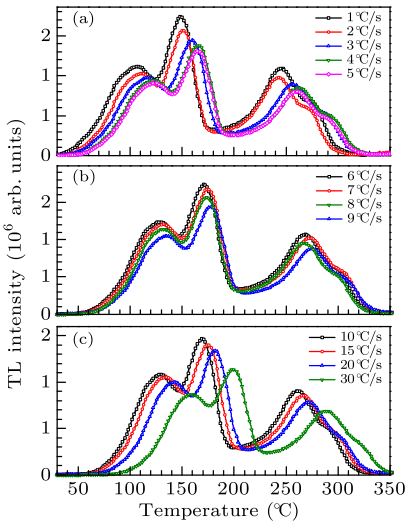


Fig. 3. The glow curves of TLD-300 crystals irradiated with a ^{90}Sr-^{90}Y beta source at linear heating rates between 1℃/s and 30℃/s ($D = 12$ Gy).

Another method used to determine the kinetic parameters in this study is the variable heating rate (VHR) method. This method is based on the shift position of the temperature (T_m) at the maximum point of intensity (I_m) to higher temperatures when the heating rate is increased. In the absence of a distribution of activation energies, a plotting of $\ln(T_m^2/\beta)$ against $1/(kT_m)$ should give a straight line of slope E_a/k and intercept $\ln(sk/E_a)$. The major advantage of this method is that the required data is to be taken at a peak maximum (I_m, T_m) which, in the case of a large peak surrounded by smaller satellites, can be reasonably accurately determined from the glow curve. For the variable heating rate method, different linear

heating rates between 1℃/s and 30℃/s are applied. The measured and then normalized glow curves after different heating rates are shown in Fig. 3. It is clearly seen that the peak temperatures of all glow peaks increase with the increasing heating rate. On the other hand, both the peak intensities and the total area of the dosimetric glow peak continuously decrease with the increasing heating rate in the investigated heating rate region. As a result, the calculated kinetic parameters from the slopes and intercepts by the variable heating rate method are also given in Table 1.

Table 1. The values of the activation energy E_a (eV) and frequency factor s (s^{-1}) of the main dosimetric peaks of TLD-300 determined by different methods.

P3 ∼150℃					P5 ∼245℃				
Method	b	E_a (eV)		ln s	Method	b	E_a (eV)		ln s
TPM	1	1.29		34.03	TPM	1	1.543		37.72
Peak shape(Chen)	1	E_τ	1.26	37.80	Peak shape(Chen)	1	E_τ	1.605	38.90
		E_δ	1.23				E_δ	1.571	
		E_ω	1.26				E_ω	1.605	
Gartia (1/2 ratio)	1	E_τ	1.231	34.66	Gartia (1/2 ratio)	1	E_τ	1.563	38.8
		E_δ	1.149				E_δ	1.592	
		E_ω	1.194				E_ω	1.575	
Gartia (2/3 ratio)	1	E_τ	1.277	33.50	Gartia (2/3 ratio)	1	E_τ	1.635	37.8
		E_δ	1.108				E_δ	1.467	
		E_ω	1.036				E_ω	1.556	
Gartia (4/5 ratio)	1	E_τ	1.387	34.50	Gartia (4/5 ratio)	1	E_τ	1.653	36.78
		E_δ	1.146				E_δ	1.367	
		E_ω	1.247				E_ω	1.487	
CGCD	1	1.187		30.08	CGCD	1	1.591		33.21
Heating rate	1	1.129		38.50	Heating rate	1	1.595		37.25

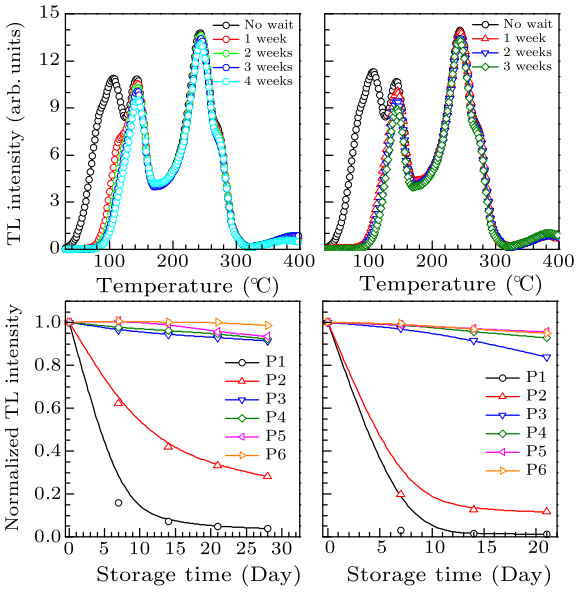


Fig. 4. A set of TL glow curves for a TLD-300 crystal measured after different storage times at room temperature and normalized TL intensity for (a) dark fading, and (b) optical fading. All the glow curves are read out at 1℃/s after exposed to 72 Gy irradiation.

For the storage time experiment the samples were firstly irradiated at temperature up to 400 ± 1℃ with 72 Gy exposed and then they were stored in the dark room at room temperature for different time periods. The storage time experiments are performed for different time periods from one day to four weeks for dark fading, and from one to three weeks for light fading. The measured glow curves of CaF_2:Tm at the end of the planned storage periods are shown in Fig. 4. As can be seen, P1 reduced to 95% and P2 to 70% of their original values. P3, P4 and P5 are reduced to almost 5% of their original values, while P6 is not affected by the planned storage time period of four weeks, performed in the dark. In the optical fading experiment, P1 reduces to 98% and P2 to 85% of their original values. P3 reduces to 10% and P4 reduces to 3% of their original value. P5 and P6 are barely affected by the storage time period of three weeks.

The results indicate that the glow curve CaF_2:Tm (TLD-300) after beta-irradiation between ∼0.04 Gy up to 8.3 kGy, and readout at a linear heating rate of $\beta = 1$℃/s in the temperature range from room temperature to 400℃, is the superposition of at least six glow peaks. The kinetic order (b), activation energy (E_a), and the frequency factor (s) of dosimetric peaks (P3 and P5) are calculated by applying different experimental methods. The results are listed in Table 1. It can be seen that the average values of the E_a values of P3 and P5 obtained by the TP, CGCD, VHR and PS methods of Chen and Gartia, Singh & Mazumdar give very close results. The recommended values given in this study are also in good agreement with those of Bos and Dilhof,[21] Azorin *et al.*,[22] Bacci *et al.*[23] and Jaferizadeh *et al.*[24]

In summary, an important feature of a thermoluminescence (TL) peak for its application in TL dosimetry and, even more, in TL dating is its stability with time. For the storage time experiments, a TLD-300 crystal is annealed at 400 ± 1℃ for one hour and irradiated up to 72 Gy. The storage time experiments are performed for different time periods in a dark room. Optical fading at room temperature was also investigated. The measured glow curves of CaF_2:Tm at the end of the planned storage periods are shown in Fig. 4. It can be seen that P1 reduces to

95% and P2 to 70% of their original values. P3, P4 and P5 reduce to almost 5% of their original values, while P6 is not affected by the planned storage time period of four weeks, performed in the dark. In the optical fading experiment, P1 reduces to 98% and P2 to 85% of their original values. P3 reduces to 10% and P4 reduces to 3% of their original value. P5 and P6 are barely affected by the storage time period of three weeks. In the simplest case of first-order kinetics, by using the equation, the lifetime for decay at room temperature can be found easily. Combining the trap parameters with this equation, the expected lifetime for the P3 is about 1.46×10^{7} s (1.4 years) and for the P5 is about 1.7×10^{13} s (5.3×105 years). These values are very promising for this crystal when used in TL dosimetry and even in TL dating.

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