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Trap parameters of dosimetric glow peaks of the CaF_2:Tm compounds (TLD-300)

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HIGHLIGHTS

- Dosimetric peaks of the CaF_2:Tm compounds (TLD-300).
- Trap parameters found by glow curve deconvolution.
- Employed kinetics derived without resorting to the quasi-equilibrium approximation.

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ABSTRACT

The kinetic parameters of dosimetric peaks of CaF_2:Tm (TLD-300) were found by employing a kinetics model derived from differential equations describing the carriers traffic but without resorting to the quasi-equilibrium approximation. Since both shape and position of glow peaks were observed not to change with dose, retrapping rates have been assumed negligible compared to rates of thermal release of electrons. The reported results show that the quasi-equilibrium approximation does not hold, an approximation used for derivation of first order kinetics, which is the kinetics employed so far for analyzing glow curves of the TLD-300.

1. Introduction

CaF_2:Tm is a well established dosimeter. It is produced by BICRON-NE (Harshaw), and sold as TLD-300 dosimeter. Its thermoluminescence peaks are stable up to pre-irradiation temperatures of 873 K, a temperature well above the highest temperature employed for recording its glow curve, namely, 623 K (Hsu and Li, 1990). Because of the dependence of the shape of the glow peaks on the linear energy transfer (LET), TLD-300 dosimeters are appropriate for dosimetry in mixed fields (Hajek et al., 2008; Massillon-JL et al., 2008; Skopec et al., 2008). Recently an article reported that TLD-300 can be used as an indicator of beam quality for low energy photon beams (Muñoz et al., 2015).

The dosimetric characteristics of any TL material mainly depend on the kinetic parameters quantitatively describing the trap and recombination centers involved in the thermoluminescent emission of light. Analysis of glow curves is a widely employed procedure to investigate the kinetics involved in the thermolumine scence of materials. Basically it relies on choosing a model, which is in accordance with experimental results at hand, and deriving a theoretical expression for the emitted light $I_{th}(T,\alpha)$ from the set of differential equations describing the carrier traffic among traps and recombination centers. α stands for the set of parameters characterizing traps and recombination centers and T is for the temperature.

As pointed out by Lewandowski et al. in practice the system of coupled differential equation describing correctly the thermoluminescent kinetics usually become intractable, so that exact analytical solutions are unobtainable for even the simplest of systems (Lewandowski et al., 1994).

Resorting to approximations and to the model shown in Fig. 1

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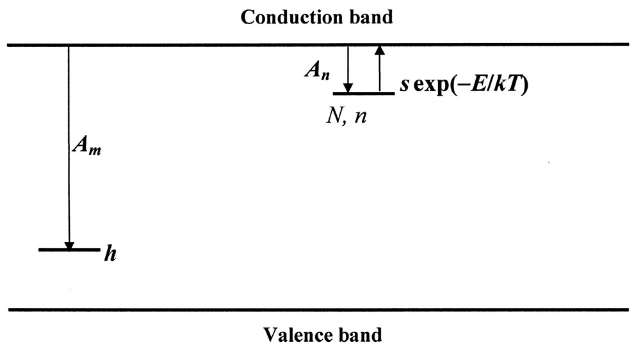

Fig. 1. OTOR model. A_m is the recombination probability, h is the concentration of holes in the recombination center, A_n is the retrapping probability, N is the concentration of traps, n is the concentration of trapped electrons, s is the frequency factor, E the activation energy, and k is the Boltzmann constant.

closed expressions for the TL intensity were derived, which are known as first order (FO) and second order (SO) kinetics (Chen and Mckeever, 1997). The model consists of a trap center and a recombination center (OTOR model).

For the OTOR model a closed expression for $I_{th}(T,\alpha)$ can be obtained when retrapping is negligible against recombination, and by resorting to the quasi-equilibrium approximation (QE) (Chen and Mckeever, 1997):

$$I_{th}(T,s,E,n0) = n0.s\,\exp\left(-\frac{E}{k.T}\right)\exp\left\{-\frac{s}{\beta}\int_{T0}^{T}\exp\left(-\frac{E}{k.u}\right)\mathrm{d}u\right\} \tag{1}$$

where $n0$ stands for the initial concentration of trapped electrons, s is the frequency factor, E the activation energy, and k is the Boltzmann constant. The heating rate is indicated with β. $T0$ is the temperature at which the recording of a glow curve starts.

The QE approximation assumes that $dn_c/dt \cong 0$ and $n_c \ll n$, where, n_c stands for the concentration of electrons in the conduction band. The kinetics described by Eq. (1) is the aforementioned FO kinetics. The main characteristic of the FO kinetics is that both the position and the shape of a peak do not change with dose if the same heating rate β is employed for obtaining glow curves for different doses. Thus, when experiments show that both the shape and position of a peak do not change with dose, the FO kinetics is usually employed in analyzing the glow curves. Because the peaks of the TLD-300 dosimeters show these characteristics, the glow curves were analyzed by resorting to FO kinetics (Bos and Dielhof, 1991; Bacci et al., 1990; Kafadar et al., 2013).

The validity of the QE approximation was questioned by Kelly et al. (Kelly et al., 1971) and several articles are concerned with this issue (Lewandowski et al., 1994; Opanowicz and Przybyszewski, 1994; Sunta et al., 1999a, 1999b; Chen and Pagonis, 2013; Marcazzo et al., 2007; Sunta, 2015).

The QE approximation is not a necessary requirement for the independence of the shape of a peak on dose. The requirement is that the retrapping rate by a trap be negligible in comparison to the release rate of electrons.

Recently an expression for the TL intensity has been derived from the differential equations for negligible retrapping rates compared to the electrons release rate, and without resorting to the QE approximation for a model, of which the OTOR model is a particular case (Molina et al., 2014). The model results by adding to the OTOR model a concentration of deep traps M, i. e., traps that retain the trapped electrons (or holes) for the temperatures a sample is subjected to. The thermally disconnected traps are supposed to be fully occupied, otherwise the shape of glow peaks might change after each irradiation. Charge neutrality requires $h{=}n+n_c+M$ if the deep traps are electron traps, and $h+M{=}n+n_c$ if the deep traps are hole traps. If both types of traps are present in a compound, as is the case for Al_2O_3: C compounds (Yukihara et al., 2003), M stands for net concentration of deep traps.

This model is known as the non interactive multi-trap system (NMTS) (Sadek et al., 2015). Since this model is more realistic than those employed so far for analyzing the glow curve of TLD-300, we used it to find the parameters characterizing the traps of these dosimeters.

2. Kinetics

As shown in Fig. 2 below, the shape of the glow peaks does not change with dose. This result indicates that retrapping of electrons by a trap is negligible compared to the release of electrons. As explained below, in section 3, the appropriate model for TLD-300 is made up of one recombination center and six traps.

For a model having one recombination center and several traps the kinetics derived for negligible retrapping compared to the release of electrons, and without resorting to the QE approximation reads (Molina et al., 2014):

$$I_{th}(T,\alpha) = A_m\left(N0 - \sum_{i=1}^{L} n0_i\,\exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)\mathrm{d}u\right\} - \frac{F(T)}{\beta}\right).\left(N0 + M - \frac{F(T)}{\beta}\right) \tag{2}$$

$N0 = \sum_{i=1}^{L} n0_i$, and $n0_i$ stands for the initial concentration of electrons in trap #i. E_i is the activation energy of trap #i, M is the concentration of thermally disconnected traps, A_m is the recombination probability, s_i is the frequency factor, and β stands as before for the heating rate. $I_{th}(T,\alpha)$ stands for the theoretical glow curve, which depends on the set α of parameters A_m, $n0_i$, s_i, E_i, and M. L stands for the number of traps. $F(T)$ is given by:

$$F(T) = \int_{T0}^{T} I(T)\mathrm{d}T \tag{3}$$

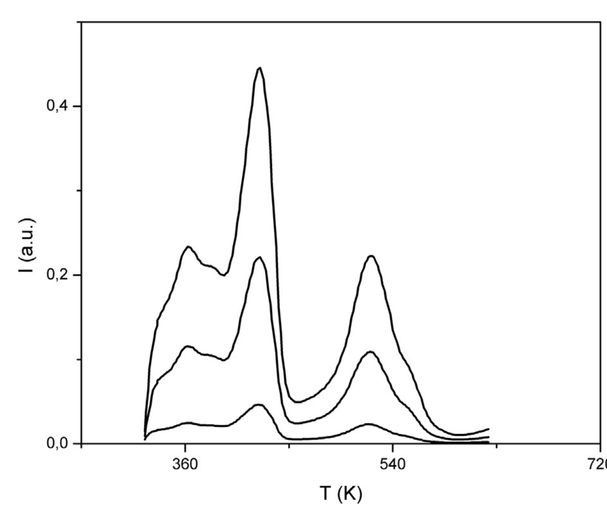

Fig. 2. Glow curves for irradiation times amounting to 1, 5 and 10 min with an Sr-90 β-source. The heating rate amounted to 1 K/s.

In Eq. (2) $M > 0$ if the deep traps are electrons traps, and $M<0$ if they are hole traps.

The first parenthesis in Eq. (2) is the concentration of electrons in the conduction band, and the second one is the concentration of holes in the recombination center.

A remark should be made about how Eq. (2) has been employed to find the set of parameters. Eq. (2) gives the intensity in counts per second. To perform a fitting it should be written

$$I_{th}(T,\alpha) = C.A_m\left(N0 - \sum_{i=1}^{L} n0_i \exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)\mathrm{d}u\right\} - \frac{F(T)}{\beta}\right).\left(N0 + M - \frac{F(T)}{\beta}\right) \quad (4)$$

The constant C takes into account the proportionality between the intensity given by counts/second and the recorded intensity given in a graph, such as Fig. 3.

Eq. (4) can be written:

$$I_{th}(T,\alpha) = \lambda\left(C.N0 - \sum_{i=1}^{L} C.n0_i \exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)\mathrm{d}u\right\} - \frac{C.F(T)}{\beta}\right).\left(C.N0 + C.M - \frac{C.F(T)}{\beta}\right) \quad (5)$$

where $\lambda = A_m/C$

C can be chosen so that $C.N0$ is the concentration of trapped electrons just before the recording of a glow curve given in units of area. Thus $C.N0$ is the area under the glow curve. By the same token $C.n0i$ is the initial concentration of trapped electrons in trap #i also given in units of area. Because of this change of units the concentration of deep traps is also given in units of area. This metric for giving the concentration of carriers is not new. It has been reported in ref. (Rasheedy, 1996).

The parameters sought were found by requiring for the set α that

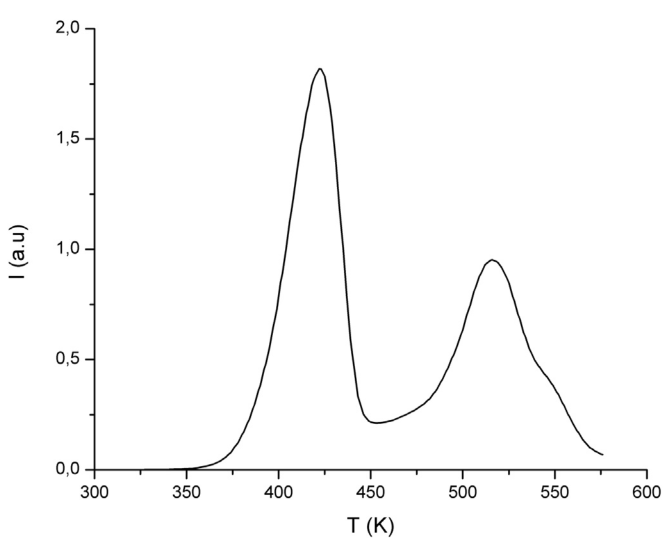

Fig. 3. Glow curve recorded after a post-irradiation annealing at 353 K for 10 min. The heating rate is 1 K/s.

$$I_{th}(T,\alpha) \simeq I_{\exp}(T) \quad (6)$$

$I_{exp}(T)$ stands for the experimental glow curve.

The Levenberg–Marquardt algorithm (L–M algorithm) was employed to find the parameters that yield the best fit between the theoretical and the experimental glow curve (Horowitz and Yossian, 1995). The goodness of the fit was evaluated by means of the figure of merit (FOM) given by

$$FOM = \frac{\sum_{j=1}^{N}\left|I_{th}(t_j,\alpha) - I_{\exp}(t_j)\right|}{\sum_{j=1}^{N}\left|I_{\exp}(t_j)\right|}.100\% \quad (7)$$

$I_{exp}(T)$ stands for the recorded glow curve. A set of parameters is acceptable if the FOM is less than 5% (Horowitz and Yossian, 1995).

3. Experiments

The probes were irradiated with a Sr-90 source for 1, 5 and 10 min. At the position of the probe the dose rate amounted to 22 mGy/min. The heating rate β was 1 K/s. Prior to each irradiation the samples were annealed at 673 K for 1 h in order to erase any residual information. The glow curves were recorded with a Harshaw 3500 reader.

The normalized curves for the three doses shown in Fig. 2 are difficult to distinguish visually from each other, a similar result as that shown in Fig. 2 of reference 8. This is why the peaks have been analyzed with FO kinetics as aforementioned (Bos and Dielhof, 1991; Bacci et al., 1990; Kafadar et al., 2013).

Glow curves of CaF_2:Tm (TLD-300) samples recorded between room temperature and 620 K originate from six traps, as concluded from T_M-T_{stop} measurements (Bos and Dielhof, 1991), and fitting algorithms (Kafadar et al., 2013). In previous publications the peaks have been identified from the lowest temperature peak to the highest temperature one with the numbers 1 to 6, as is done in reference 8.

The TL emission spectrum of the TLD-300 shows peaks at 357, 455, 475 and 650 nm. These peaks correspond to internal Tm transitions (Bos et al., 1995). This result indicates that the Tm ions are the only recombination centers.

On account of these findings the chosen model consists of one recombination center and six traps. We added to the model a concentration M of deep traps. If no deep traps are present, then the fitting algorithm should give $M=0$.

The two lowest temperature peaks fade much faster than the highest temperature peaks: the intensity of peak 1 decreases to 5% of its original value, and peak 2–30% of its original value in four weeks (Kafadar et al., 2013). In the same period peaks 3, 4 and 5 decreased little, namely, to almost 95% of their original values, while peak 6 is not affected (Kafadar et al., 2013). Thus peaks 3, 4, 5, and 6 can be employed as dosimetric peaks. In order to analyze these peaks probes were subjected to a post-irradiation annealing at 373 K for 15 min (Bos et al., 1995). In doing so the two peaks affected by the faster fading are eliminated. Fig. 3 shows the glow curve recorded after the post-irradiation annealing.

4. Glow curve analysis

Glow curve analyses were performed by employing Eq. (5) and by resorting to the Levenberg–Marquardt (LM) algorithm. In Eq. (5) $C.N0$ is the area under the recorded glow curve and$C.F(T) = \int_{T0}^{T} I_{rec}(u)\mathrm{d}u$, where $I_{rec}(T)$ stands for the recorded glow curve. Fig. 4 depicts $C.F(T)$.

The LM algorithm requires an analytical expression for$C.F(T)$.

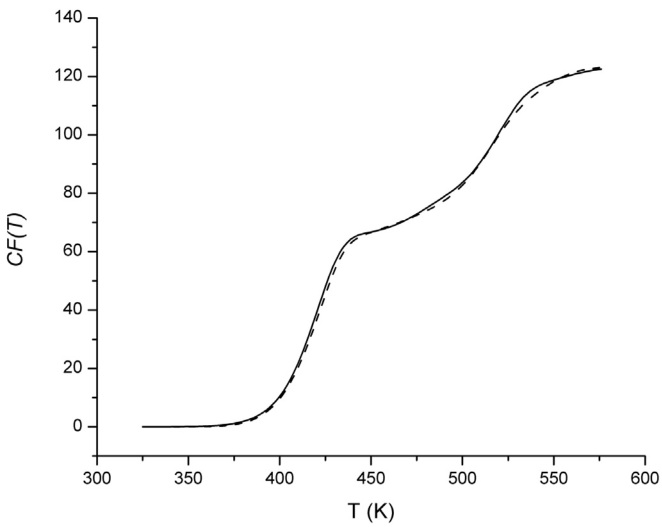

Fig. 4. *C.F*(*T*) computed from the glow curve (solid line), and found from the fitting of Eq. (10) (dashed line). FOM 1.5%.

Table 1
Parameters employed in Eq. (7).

i	a_i	b_i	c_i
1	65.97	1.861 10^{12}	12 980
2	10.158	5.123 10^{12}	15 160
3	37.544	53.36 10^{12}	17 030
4	10.234	0.00183 10^{12}	13 480

The following expression

$$F_{fit}(T) = A - \sum_{i=1}^{4} a_i \exp\left(- b_i \int_{T0}^{T} e^{-c_i/u} \mathrm{d}u \right) \quad (8)$$

was fitted to the curve obtained by integrating $I_{rec}(T)$.

In Table 1 the parameters a_i, b_i and c_i resulting from the fitting are listed. The FOM of the fitting is 1.5%.

Summarizing, the glow curve analysis is performed as follows: 1) a model of traps and recombination centers is chosen in accordance with findings at hand, 2) if the shape of a glow peaks does not change with dose Eq. (5) is employed, 3) from the sampling of $I_{exp}(T)$ $C.F(T)$ is computed, and later an analytical expression for $C.F(T)$ is found by fitting an appropriate function to the computed values, and 4) Eq. (5) is fitted to the glow curve by employing the L–M algorithm.

5. Results

Glow curve analyses employing different set of guess values yield FOM values around 4.7% for M equal or greater than 2000. The values of the energies for different M differ by less than 0.001 eV, and the frequencies by less than 0.5%. Table 2 depicts the parameters for $M = 2000$ along with the parameters reported in previous articles. The FOM of our fitting is 4.7% and, as it was mentioned above, a set of parameters is acceptable if the FOM is less than 5% (Horowitz and Yossian, 1995).

The errors indicated for the new kinetics were computed with the inverse of the Hessian matrix of the sum of the squares of the deviations S, namely, with the Hessian matrix of

$$S = \sum_{i=1}^{200} \left(I_{th}(T_i, \alpha) - I_{\exp}(T_i) \right)^2$$

200 is the number of sampling points delivered by the TL reader.

The comparison of the sets of parameters reported in Table 2 shows that they differ from each other. The most striking feature of the previously reported sets is the significant difference among them because they were determined by resorting to the same kinetics, namely, FO kinetics. A possible explanation for this may be that the result of a fitting procedure depends on the chosen guess values required by methods such as the LM-method (Chen and Mckeever, 1997).

Fig. 5 shows the experimental glow curve (dose 22 mGy), and the theoretical glow curve, which results by employing the parameters listed in Table 2.

Individual peaks are not included in Fig. 5 because it is incorrect to assume beforehand that each peak is related to a particular trap (Marcazzo et al., 2007). As shown in this reference some of the electron trapped in a given trap might be captured by other trap instead of recombining after being released.

The concentration n_c of electrons in the conduction band is given by:

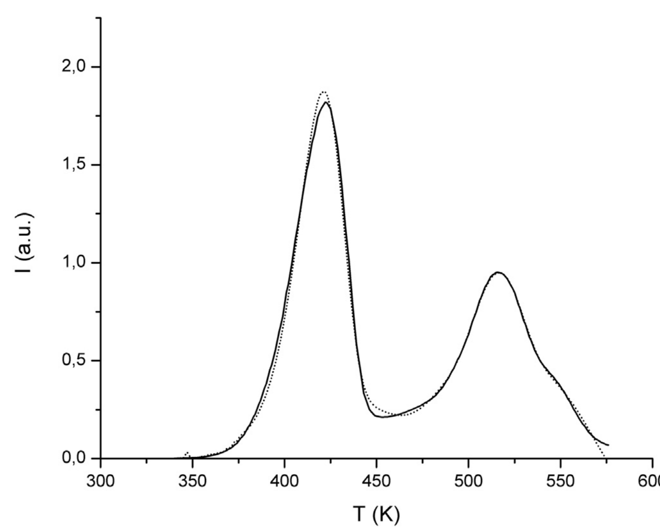

Fig. 5. Solid line: experimental glow curve, dash line: theoretical glow curve.

Table 2
Parameters obtained with the new kinetics and reported in previous articles. On the left the references are indicated.

	Peak 3		Peak4		Peak 5		Peak 6	
	E (eV)	s (10^9 s^{-1})	E (eV)	s(10^9 s^{-1})	E (eV)	s(10^9 s^{-1})	E (eV)	s(10^9 s^{-1})
Ref. (Bos and Dielhof, 1991)	1.15 ± 0.02	3000	1.30 ± 0.19	9000	1.51 ± 0.01	60 000	1.15 ± 0.04	4.0
Ref. (Bacci et al., 1990)	1.21 ± 0.01		0.89 ± 0.06		1.50 ± 0.03		1.01 ± 0.06	
Ref. (Kafadar et al., 2013)	1.187	11 000	1.091	12	1.591	260 000	1.495	4600
New Kinetics	1.149 ± 0.001	6089 ± 4	1.372 ± 0.001	1508 ± 0.2	1.501 ± 0.016	695 000 ± 8000	1.458 ± 0.010	1425 ± 9

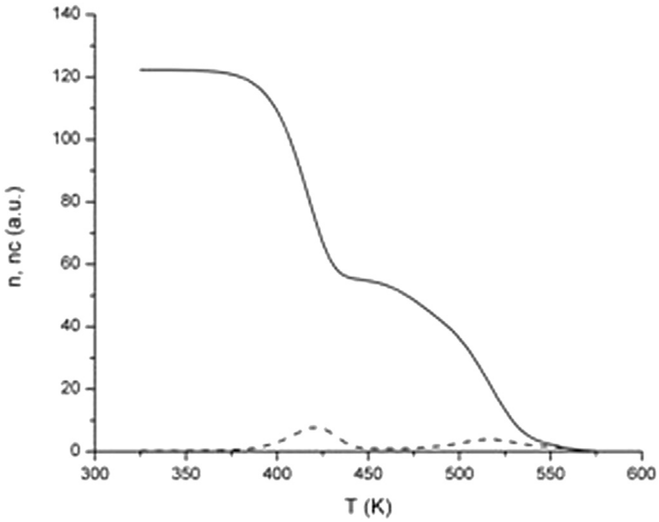

Fig. 6. Concentration of electrons in the conduction band (dash line), and the concentration of trapped electrons (solid line).

$$n_c = N0 - \sum_{i=1}^{L} n0_i \exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)du\right\} - \frac{F(T)}{\beta} \quad (10)$$

or by changing the metrics as above

$$C.n_c = C.N0 - \sum_{i=1}^{L} C.n0_i \exp\left\{-\frac{s_i}{\beta}\int_{T0}^{T}\exp\left(-\frac{E_i}{ku}\right)du\right\} - \frac{F(T)}{\beta} \quad (11)$$

Both, the concentration of trapped electrons and the concentration of electrons in the conduction band are depicted in Fig. 6.

From Fig. 6 it is clear that between 400 and 450 K, and as of 475 K electrons accumulate in the conduction band (the QE approximation does not hold). This means that electrons released from a trap at a given temperature could stay for a while in the conduction band and recombine later at a higher temperature. This is the reason why in Eq. (5) the theoretical intensity is not equal to the sum of peaks, each one related to a trap, as is the case for the FO and GO kinetics.

6. Conclusion

The set of parameters characterizing the traps involved in the dosimetric peaks of the TLD-300 dosimeter were found employing a model derived without resorting to the QE approximation. As shown in Fig. 6 the QE does not hold, so that the FO kinetics employed so far to analyze the glow curves of the TLD-300 may not be the appropriate kinetics. Since the FO kinetics is a particular case of the new kinetics, and it is not known before performing an analysis whether or not the QE approximation holds, it is advisable to employ Eq. (5) instead of FO kinetics.

References

Bacci, C., Bernardini, P., DI Domenico, A., Furetta, C., Rispoli, B., 1990. Analysis of the thermoluminescence kinetics of CaF_2(Tm) peaks with glow curve deconvolution. Nucl. Instr. Meth. Phys. Res. A 286, 295–300.

Bos, A.J.J., Dielhof, B., 1991. The analysis of the thermoluminescent glow peaks in CaF_2:Tm (TLD-300). Radiat. Prot. Dosim. 37 (4), 231–239.

Bos, A.J.J., De Jong, R.W., Meijvogel, K., 1995. Effects of type of radiation on glow curve and thermoluminescence emission spectrum of CaF_2:Tm. Radiatr. Meas. 24, 401–405.

Chen, R., Mckeever, W.S., 1997. Theory of Thermoluminescence and Related Phenomena. World Scientific.

Chen, R., Pagonis, V., 2013. On the quasi-equilibrium assumptions in the theory of thermoluminescence (TL). J. Lumin. 143, 734–740.

Hajek, M., Berger, T., Bergmann, R., Vana, N., Uchiori, Y., Yasuda, N., Kitamura, H., 2008. LET dependence of thermoluminescent efficiency and peak height ratio of CaF_2:Tm. Radiat. Meas. 43, 1135–1139.

Horowitz, Y.S., Yossian, D., 1995. Computerized glow curve deconvolution: application to thermoluminescence dosimtery. Radiat. Prot. Dosim. 60, 1–114.

Hsu, P.C., Li, S.H., 1990. Influence of high temperature annealing on TL response of CaF_2:Tm. Radiat. Prot. Dosim. 33, 189–191.

Kafadar, V.E., Bedir, M., Necmeddin Yazıcı, A., Günal, T., 2013. The analysis of main dosimetric peaks of CaF_2:Tm (TLD-300). Chin. Phys. Lett. 30 (5), 057802.

Kelly, P., Laubitz, M.J., Bräunlich, P., 1971. Exact solutions of the kinetic equations governing thermally stimulated luminescence and conductivity. Phys. Rev. B 4, 1960–1968.

Lewandowski, A.C., Markey, B.G., McKeever, S.W.S., 1994. Analytical description of thermally stimulated luminescence and conductivity without the quasiequilibrium approximation. Phys. Rev. B 49, 8029–8047.

Marcazzo, J., Santiago, M., Spano, F., Lester, M., Ortega, F., Molina, P., Caselli, E., 2007. On the quasi-equilibrium assumptions in the theory of thermoluminescence (TL). J. Lumin. 126, 245–250.

Massillon-JL, G., gamboa-de Buen, I., Buenfil, A.E., Monroy-Rodriguez, M.A., Brandan, M.E., 2008. CaF_2:Tm (TLD-300) thermoluminescent response and glow curve induced by γ-rays and ions. Nucl. Instr. Meth. Phys. Res. B 266, 772–7803.

Molina, P., Sommer, M., Marcazzó, J., Santiago, M., Henniger, J., Caselli, E., 2014. Thermoluminescent kinetics for negligible retrapping: its application to the analysis of the glow curve of Y_2O_3:Eu^{+3}. Radiat. Phys. Chem. 97, 81–84.

Muñoz, D., Avila, O., Gamboa-de Buen, I., Brandan, M.E., 2015. Evolution of the CaF_2:Tm (TLD-300) glow curve as an indicator of beam quality for low energy photon beams. Phys. Med. Biol. 60, 2135–2144.

Opanowicz, A., Przybyszewski, K., 1994. Is the quasi-equilibrium approximation in description of thermally stimulated luminescence and conductivity valid?. In: Proceedings SPIE 2373, Solid State Crystals: Materials Science and Applications, pp. 236–240.

Rasheedy, M.S., 1996. A new method for obtaining the trap parameters of complex thermoluminescence glow peaks. J. Phys. D Appl. Phys. 29, 1340–1344.

Sadek, A.M., Meissa, H.M., Basha, A.M., Kitis, G., 2005. Properties of the thermoluminescence glow peaks simulated by the interactive multi-trap system (IMTS) model. Phys. Status Solidi B 252 (4), 721–729.

Skopec, M., Loew, M., Price, J., Moskovich, M., 2008. Classification of mixed- radiation fields using the vector representation of thermoluminescent glow curves. Radiat. Meas. 43, 410–413.

Sunta, C.M., 2015. Unraveling Thermoluminescence, Springer Series in Materials Science, vol. 202, pp. 103–132.

Sunta, C.M., Feria Ayta, W.E., Kulkarni, R.N., Chubaci, J.F.D., Watanabe, S., 1999. J. Phys. D Appl. Phys. 32, 717–725.

Sunta, C.M., Feria Ayta, W.E., Chubaci, J.F.D., Watanabe, S., 1999. The quasi-equilibrium approximation and its validity for the thermoluminescence of inorganic phosphors. Radiat. Prot. Dosim. 84 (1–4), 51–54.

Yukihara, E.G., Whitley, V.H., Polf, J.C., Klein, D.M., McKeever, S.W.S., Akselrod, A.E., Akselrod, M.S., 2003. The effects of deep trap population on the thermoluminescence of Al_2O_3:C. Radiat. Meas. 37, 627–638.