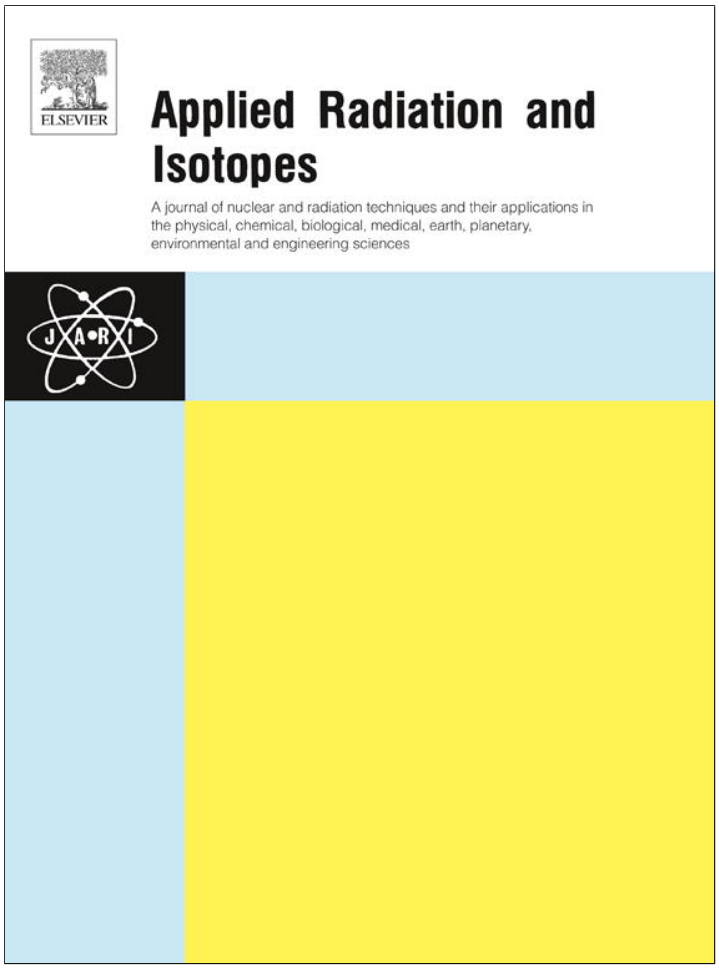

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Determination of kinetics parameters of the main glow peaks for $KMgF_3$:Lu and LiF:Mg phosphors after long-term high temperature storage

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HIGHLIGHTS

- Validation of modified isothermal decay expression is given.
- The maximum TL intensity, I_M, decreases with post-irradiation thermal treatment.
- Because of overlapped glow peaks a variation on the E values as the doses was obtained.
- The activation energy of TL glow peaks, $KMgF_3$:Lu and LiF:Mg, was calculated.
- The kinetics parameters obtained are in agreement by GOK and SQPGCD deconvolution.

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ABSTRACT

The isothermal decay method is useful for determining the trap activation energy in thermoluminescent material for dosimetry purposes. Recently we proposed new modified expressions for isothermal decay method. As validation of the modified expressions, after long-term (4 h) high temperature storage, the activation energy of experimental TL glow peaks, $KMgF_3$:Lu (0.17 and 0.34 mol%) and LiF:Mg (0.04 mol%), in the framework of the general-order kinetic was calculated. The results of the kinetics parameters were compared with those obtained by the other methods like Initial Rise (IR), Sequential Quadratic Programming Glow Curve Deconvolution (SQPGCD), deconvolution of the TL glow curves by assuming the General Order Kinetic (GOK), and Chen General-Order Kinetics method. It seems that both SQPGCD and GOK deconvolution methods give more accurate kinetics parameters values for the experimental glow curves.

1. Introduction.

It is known that several methods have been proposed in order to determine the kinetic parameters of the thermoluminescence (TL) glow curves. Most of these methods are based on an isolated peak in the glow curve i.e. peak shape methods. However, in most cases related with TL materials, the glow curves involve several overlapping glow peaks (Chen and McKeever, 1997; Horowitz, et al., 1998; Kitis, et al., 1998) resulting in the impossibility of using the various peak shape methods. The isothermal decay (ID) method is useful for determining the trap activation energy in TL phosphor (Taylor and Lilley, 1978; Delgado and Gomez Ros, 1988; Satinger, et al., 1999; Kitis, et al., 1996). This method consists in measuring the intensity of the light emitted by an irradiated sample when it is kept at a constant temperature. Afterward, the kinetics parameters are obtained by analyzing the shape of the decay curve. In a previous work, a full mathematical description of the kinetics expressions used in TL isothermal decay experiment has been presented (González et al., 2011). These equations have been slightly modified considering the peak intensity at the maximum (I_M) instead of the peak total area (Φ) (Furetta et al., 2007) as proportional to the absorbed dose. The expressions for the isothermal decay method were applied to the principal glow peaks of the LiF:Mg,Cu,P+PTFE and BaSO4:Eu+PTFE using first- and second-order kinetics, respectively. On the other hand, this method was not applied to a general order kinetic glow peak. The aim of this work is to use the modified expressions for the isothermal decay method in the general order case (González et al., 2011) to obtain the activation energy, after high temperature

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storage, of both $KMgF_3$:Lu and LiF:Mg experimental TL glow peaks. Therefore, the kinetic parameters values were compared with those obtained by other methods like Initial Rise (IR) Method (Furetta, 2003), Sequential Quadratic Programming Glow Curve Deconvolution (SQPGCD) (López, 1994), deconvolution of the TL glow curves by assuming the General Order Kinetic (GOK) (May and Partridge, 1964, Rasheddy, 1993) and Chen General-Order Kinetics method (Chen, 1969).

2. Mathematical analysis

2.1. Isothermal decay equations

According to a previous work (González et al., 2011), the first, second and general order kinetics the isothermal decay equations can be written as follows, considering the maximum intensity of the glow peaks and their maximum temperature:

First-order decay

$$E = k\frac{T_2T_1}{T_1-T_2}\ln\left(\frac{F_C I_{MT1}-D_0}{F_C I_{MT2}-D_0}\right) \tag{1}$$

Second-order decay

$$E = k\left[\frac{T_2T_1}{T_1-T_2}\right]\ln\left[\frac{I_{MT2}(I_{M0}-I_{MT1})}{I_{MT1}(I_{M0}-I_{MT2})}\right] \tag{2}$$

General-order decay

$$E = k\frac{T_1T_2}{T_1-T_2}\ln\frac{\left(\frac{I_{MT1}}{I_{M0}}\right)^{1-b}-1}{\left(\frac{I_{MT2}}{I_{M0}}\right)^{1-b}-1} \tag{3}$$

where I_{MT1} is the TL intensity at the maximum of the peak, I_M, at the storage temperature T_1. I_{MT2} is the TL intensity at the maximum of the peak, I_M, at the storage temperature T_2 and I_{M0} is the peak intensity at the maximum, I_M, measured immediately after irradiation.

In all the previous cases the "kinetics order parameter", b, is not known; then, it was necessary to use the geometrical factors of the peak, τ, δ, ω and $\mu=\delta/\omega$, where $\tau=T_M-T_1$, $\delta=T_2-T_M$ and $\omega=T_2-T_1$. It must be taken into account that the geometrical factors do not differ too much from each other when I_{M0}, I_{MT1} and I_{MT2} are considered.

2.2. Initial Rise Method

One of the main characteristics of the Initial Rise Method is that, at the low temperature tail of a peak the amount of trapped electrons can be assumed as a constant, and the dependence on temperature can be neglected. In fact, by increasing temperature up to $T_C < T_M$ (the corresponding intensity I_C should not be larger than 15% of I_M for the full TL glow peak under evaluation) the first exponential of Eq. (4) increases whereas the second term may still be unity.

$$I(T) = n_0 s\exp\left(-\frac{E}{kT}\right)\exp\left[-\frac{s}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right] \tag{4}$$

A further increase in temperature ($T > T_C$) makes the second term decrease: the competition of both terms results in the maximum of the intensity I. In this assumption, as long as the second term is unity, the thermoluminescent emission can be described by

$$I(T) \propto \exp(-\frac{E}{kT}) \tag{5}$$

The $\ln(I)$ on the function of $1/T$ plot is then made and a straight line should be obtained. From the slope, $-E/k$, E is evaluated without any knowledge of the frequency factor s as well as of the kinetic order.

2.3. Chen general-order kinetics method

In the case of the Chen general-order kinetics method (Chen, 1969), it considered a general-order kinetics ranging from 1 to 2, giving the possibility of non-integer values for the kinetics order with the general expression

$$E_\alpha = c_\alpha\left(\frac{kT_M^2}{\alpha}\right) - b_\alpha(2kT_M) \tag{6}$$

where α is τ, δ or ω. The values of c_α and b_α are summarized as below.

$c_\tau = 1.51 + 3.0(\mu-0.42)$ $b_\tau = 1.58 + 4.2(\mu-0.42)$

$c_\delta = 0.976 + 7.3(\mu-0.42)$ $b_\delta = 0$

$c_\omega = 2.52 + 10.2(\mu-0.42)$ $b_\omega = 1$

with

$$\mu = \frac{\delta}{\omega} = \frac{T_2-T_M}{T_2-T_1}$$

being $\mu=0.42$ for a first-order kinetics and $\mu=0.52$ for a second-order kinetics.

Finally, considering a linear heating rate of 2 K/s, the pre-exponential factor s for general-order kinetics was calculated with the following equation for general order (Furetta, 2003):

$$s = \left[\frac{kT_M^2\exp\left(-\frac{E}{kT_M}\right)}{\beta E}\left(1+\frac{2kT_M(b-1)}{E}\right)\right]^{-1} \tag{7}$$

which is expressed now in sec^{-1}.

2.4. Deconvolution procedures

According to the experimental results, the glow curves for both materials seem to be complex, in the sense that the TL emission may be originated by a distribution of traps instead of a single trap level. As a consequence, it seems to be correct the use of the deconvolution procedure for determining the activation energy related to the trap levels.

The General Order Kinetic (GOK) model (May and Partridge, 1964) was assumed and the glow curves deconvolution was carried out considering the GOK model modified by Rasheddy (Rasheddy, 1993). The new equation of intensity includes the ratio n_0/N which takes into account the fraction of occupied traps. Then, the equation describing TL intensity is given by

$$I = n_0^b s\exp\left(\frac{-E}{kT}\right)/N^{b-1}\left[1+\frac{s(b-1)(n_0/N)^{(b-1)}}{R}\int_{T_0}^{T}\exp\left(\frac{-E}{kT}\right)dT'\right]^{1/(b-1)} \tag{8}$$

where n_0 stands for the initial concentration of electrons in traps, N for the corresponding concentrations of traps and R is the heating rate. Besides, E is the activation energy of the trap, s stands for the frequency factor, b the order of kinetics, k for the Boltzmann constant and T is the temperature in Kelvin. The goodness of fit was evaluated by using the figure of merit (FOM) (Balian and Eddy, 1977) which is given as

$$FOM = 100\sum_{i=1}^{m}\frac{\left|I_{exp}(T_i)-I_{fit}(T_i)\right|}{A} \tag{9}$$

where $I_{exp}(T)$ and $I_{fit}(T)$ are the experimental and fitted glow curves, respectively; A is the area under curve $I_{exp}(T)$ and m is the number of experimental points.

In order to obtain the kinetics parameter values of the glow curves, another deconvolution procedure taken into account based on the Sequential Quadratic Programming Glow Curve Deconvolution (SQPGCD) developed at the National Institute of Nuclear Research—Mexico (ININ) (López, 1994) was used. The deconvolution is based on the following general equation (May and Partridge, 1964):

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right)\left[1+\frac{s(b-1)}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\frac{b}{b-1}} \quad (10)$$

where n_0 is the initial concentration of the trapped charges, s is the frequency factor (s^{-1}), b is the kinetics order, ranging from 1 to 2, and β is the heating rate (2 K/s). Eq. (10) could be rewritten as follows (López, 1994):

$$I(T) = \frac{I_m \exp(W(T-T_m))}{\left[\frac{1}{b}+\left(1-\frac{1}{b}\right)\exp(W(T-T_m))\right]^{\frac{b}{(b-1)}}} \quad (11)$$

where

$$W = \frac{E}{kT_m^2}$$

and the best fitting was calculated by the corresponding figure of merit (FOM) and it was less than 5% which means that it is a good fitting (Horowitz and Yossian, 1995).

3. Experimental and methodology

$KMgF_3$:Lu monocrystal phosphor was made at the Physics Department of Rome University "La Sapienza" (Furetta, et al.,1990). Samples of perovskite have been obtained from the melt of KF and MgF_2 in the stoichiometric ratio by the Kyropoulos method (Patterson, 1962). Doped crystals were obtained by adding a proper amount of the Lu impurity to the melt. The crystals of $KMgF_3$, with a Lu concentration of 0.17 mol% had a mass of 43.93 mg and dimensions of $4\times2\times1$ mm; the 0.34 mol% concentration had a mass of 133 mg with dimensions of $5\times5\times2$ mm.

The LiF:Mg powder phosphor was made at the National Institute of Nuclear Research (ININ) of Mexico. For preparing the TL material, 10 g of commercial LiF powder analytical grade (Aldrich) was placed in a platinum crucible to be dried and the dopant was added in aqueous solution ($MgCl_2$) at 0.02, 0.04, 0.08, 0.12 mol%. The powder dried was submitted to a thermal treatment at 673 K for 30 min, followed by heating at 1123 K for 30 min, finally obtaining the LiF:Mg phosphor. All thermal treatments were performed in a nitrogen atmosphere. The material obtained was then crushed and sieved choosing the polycrystalline powder with size in the range of 74–177 μm. This powder was heated at 673 K for 1 h before any irradiation. The LiF:Mg with 0.04 mol% of dopant showed better sensitivity.

Before irradiation the $KMgF_3$:Lu samples were annealed at 573 K for a period of 30 min (González et al., 2004) and LiF:Mg at 673 K for a period of 1 h. After being cooled down at room temperature, all the samples were irradiated with a test dose of 1 Gy. Immediately after irradiation, all the TL samples were read out to select those having the same sensitivity and the same glow curve shape. The TL readout has been made with an average mass of 15 ± 1 mg for LiF:Mg. A TL reading system Harshaw Model 4000 was used, with a linear heating rate of 2 K/s under continuous nitrogen gas to avoid spurious TL signals. All TL glow curves were integrated from 333 to 573 K, for both $KMgF_3$:Lu and LiF:Mg phosphors. The selected samples were annealed and irradiated at different gamma doses (1–100 Gy) to record their glow curves and to measure the peak intensity at the maximum, I_{M0}. Finally, to obtain I_{MT1} and I_{MT2} at the end of the storage, a new annealing and a new irradiation at the same doses as before, stored at 353 and 373 K for 4 h to $KMgF_3$:Lu and 373 and 383 K to LiF:Mg. After these periods a last readout of the samples was made. The deconvolution by the SQPGCD method (López, 1994) was applied to the glow curves obtained at 1, 5, 10, and 25 Gy gamma doses, in the linear range of the dose–TL response, in order to test if the maximum temperature T_M and E values were changing as a function of the delivered dose; $KMgF_3$:Lu shows a more complex structure glow curve than that of LiF:Mg, i.e., it is possible that some overlapped TL peaks exist. The T_M–T_{STOP} measurement (McKeever, 1980) was carried out between 305 and 623 K range temperature to determine the TL peaks under the experimental glow curves.

4. Results and discussion

4.1. The case $KMgF_3$:Lu

The two different preparations of $KMgF_3$ with 0.17 mol% and 0.34 mol% of Lu impurity were compared in order to check the effect of impurity concentration on the TL intensities and their kinetics parameters. The samples were irradiated at 1 Gy and kept at high temperature (353 and 373 K) storage during 4 h. The TL sensitivity was higher for $KMgF_3$:Lu with 0.34 mol% than that of the 0.17 mol% sample, but the same glow curve structure was observed. For the main glow peak (435 K) of the $KMgF_3$:Lu (0.17 mol%) the geometrical factor μ was equal to 0.45 and the order kinetics b was 1.78 by using Chen General-Order Kinetics (Eq. (6)) (Table 1). These factors values were similar to those obtained for the $KMgF_3$:Lu (0.34 mol%) sample (Table 1). Using Eq. (3) for general-order decay an activation energy value equal to 1.45 ± 0.03 eV was found.

Table 1
Kinetics parameters for general-order kinetics evaluated with different methods.

Method and kinetic parameters	$KMgF_3$:Lu [0.17 mol%]	$KMgF_3$:Lu [0.34 mol%]	LiF:Mg [0.04 mol%]
General Order Decay, Eq.(3)			
E (eV)	1.45	0.92	2.15
s (s^{-1})	3.18*E*+15	2.86*E*+09	1.90*E*+20
Initial Rise			
E (eV)	0.89	0.76	1.63
s (s^{-1})	1.24*E*+09	4.03*E*+07	1.22*E*+15
GOK			
b	1.55	1.47	1.88
E (eV)	1.02	1.04	1.83
s (s^{-1})	8.2*E*+11	1.05*E*+12	9.9*E*+20
FOM	2.10	1.60	1.90
SQPGCD			
b	1.78	1.37	1.79
E (eV)	1.22	1.07	2.06
s (s^{-1})	1.47*E*+13	2.88*E*+11	2.28*E*+19
FOM	0.71	0.65	0.24
Chen General-Order Kinetics, Eq.(5)			
τ	27.02	24.57	19.29
Δ	22.03	19.80	17.96
Ω	49.05	44.36	37.25
μ	0.45	0.45	0.48
b	1.78	1.37	1.79
E_τ (eV)	0.81	0.89	1.66
E_δ (eV)	0.73	0.80	1.25
E_ω (eV)	0.77	0.85	1.46
s_τ (s^{-1})	1.39*E*+08	1.29*E*+09	7.34*E*+14
s_δ (s^{-1})	1.68*E*+07	1.17*E*+08	7.38*E*+10
s_ω (s^{-1})	4.83*E*+07	4.43*E*+08	8.22*E*+12

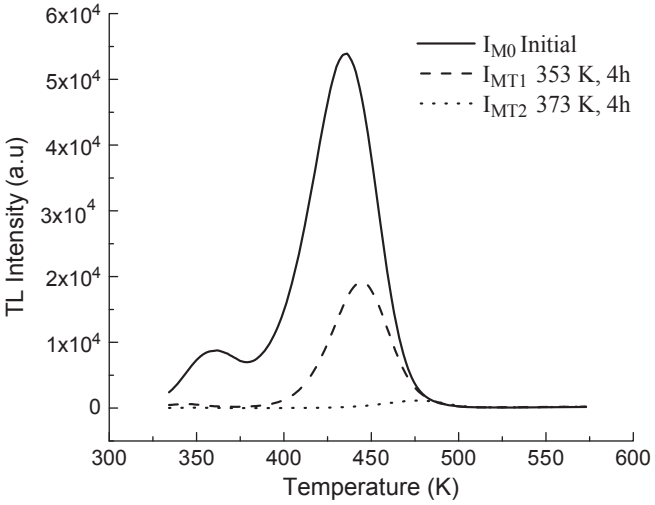

Fig. 1. Glow curves from $KMgF_3$:Lu (0.34 mol%) irradiated at 1 Gy (solid line) and stored at 353 (dashed line) and 373 K (dotted line) for 4 h.

Table 2
E values calculated by Chen General-Order Kinetics, Eq. (6), for KMgF3:Lu (0.34 mol%).

Temperature (K)	T_M (K)	μ	$(Ec)_\tau$	$(Ec)_\delta$	$(Ec)_\omega$
I_{TM0}	436	0.45	0.89	0.80	0.85
I_{TM1}, 353	445	0.47	1.16	0.92	1.05
I_{TM2}, 373	476	0.47	1.24	0.98	1.11

Fig. 1 shows the glow curves for $KMgF_3$:Lu (0.34 mol%); a similar structure has also been observed for $KMgF_3$:Lu (0.17 mol%). The maximum TL intensity (I_M) decreases as a function of post-irradiation thermal treatment (353 and 373 K), and the maximum temperature (T_M) of the main peak was shifted to the high temperature side of the glow curve. The kinetics parameters for both samples are reported in Table 1. Table 2 contains the activation energy *E* values obtained by using Chen General-Order Kinetics (Eq. (6)). After long-term (4 h) high temperature storage (353 K) of the perovskite sample, the T_M value of the main glow peak was shifted from 436 K to 445 K, while at the other storage temperature (373 K) the T_M peaked from 436 to 476 K. It is observed that a small TL glow peak at 342 K (69 °C) (Fig. 2) can influence the main peak at 444 K (171 °C) obtained with 10 Gy. In the inset of Fig. 2, measurement of the T_M–T_{STOP} method shows that the main glow peak, shifted after long-term high temperature (Fig. 1), is composed of distribution of overlapped peaks. The storage temperature erases the peaks on the low temperatures sides of the main dominant peak causing the shift of T_M toward the right side. Because overlapped glow peaks exist, inset of Fig. 2, the T_M values shift as a function of storage temperature, and the higher temperature of TL single glow peaks becomes dominant. However, the kinetic values ($\mu = 0.45 \pm 0.01$) remain unchanged, and the activation energy *E* given by Eq. (6) has a slight variation in the values: $E_\tau = 0.89 \pm 0.18$, $E_\delta = 0.80 \pm 0.08$, $E_\omega = 0.85 \pm 0.13$ eV (Table 1). In this case, those values of the kinetic parameters are like an average of the mixed parameters instead of one single peak.

A new set of measurements have been done as a function of different levels of dose. At first the dose–response was measured between 1 and 100 Gy (inset of the Fig. 3). The corresponding glow curves obtained at 5, 10, and 25 Gy (Fig. 3) were considered in order to analyze the possible dependence of the kinetics parameters on the irradiation dose. By using the SQPGCD deconvolution method, Eq. (11), the main peak was fitted considering three peaks when the doses were 5 and 10 Gy. At 25 Gy dose the main peak was fitted using four peaks (Table 3). The activation energy *E* values of the

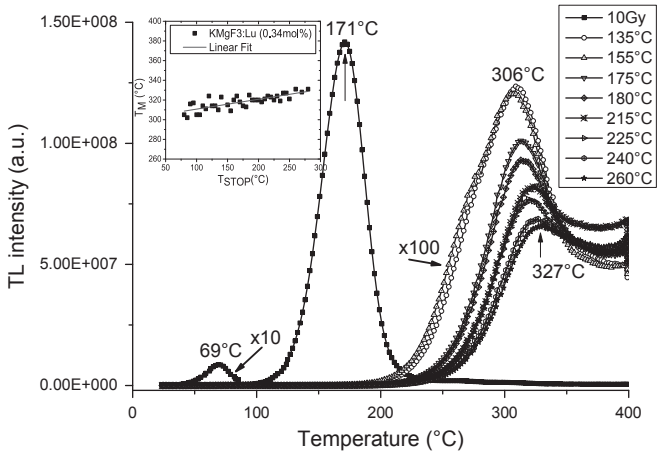

Fig. 2. T_M–T_{STOP} result of $KMgF_3$:Lu (0.34 mol%) exposed to 10 Gy. A small first glow peak at 69 °C (342 K) is observed; it was magnified by a 10 factor. The main glow peak is located at 171 °C (444 K). The remaining glow curves, at high temperature side, show that the glow peaks shifted from 306 to 327 °C (579–600 K). In the inset is the T_M–T_{STOP} result; an increased T_M (306–327 °C) was observed because the main peak (171 °C) is influenced by the first glow peak (69 °C).

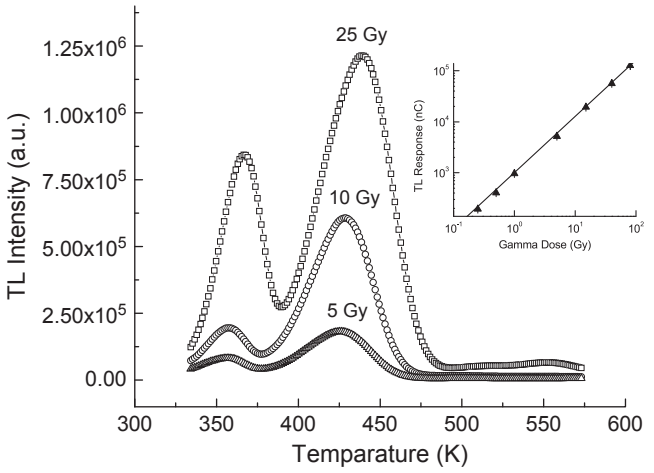

Fig. 3. Glow curves of $KMgF_3$:Lu (0.34 mol%) irradiated at different doses. In the inset is the linear dose–response up to 100 Gy.

main glow peak (peak number 2) were between 0.92 and 1.07 eV. The variation on the *E* values as a function of the dose is due to the overlapped peaks that influenced the shift of T_M toward higher temperature, and it seems that T_M increases at high dose. T_M and *b* values, 426–437 K and 1.30–1.51, respectively, were similar to those obtained by using Eq. (3) for general-order decay (Table 3).

4.2. The case LiF:Mg

The glow curve of LiF:Mg (Fig. 4), at 1 Gy, exhibits three glow peaks occurring at 424, 462, and 516 K (main peak). The first two small peaks (424 and 462 K) disappeared after high temperature storage. The LiF:Mg samples were stored at 423 and 443 K for 4 h after irradiation with 1 Gy (Fig. 4). In this case, the kinetic parameters obtained were $\mu = 0.48$, $b = 1.79$ and $E = 2.15 \pm 0.03$ eV (Table 1). Fig. 4 shows that the maximum TL intensity, I_M, slowly decreases with post-irradiation thermal treatment. The maximum temperature, T_M, of the main peak (peak number 3) shifted at higher temperature of the glow curve. *E* values were obtained by the Chen General-Order method, Eq. (6), (Table 4). It was observed that T_M of the main glow peak shifted at higher temperatures (516–524 K) when the LiF:Mg was heating at 423 K during 4 h. Another measurement, at 443 K during the same time (4 h), shows

Table 3
Kinetics parameters obtained by deconvolution using SQPGCD, Eq. (11), for $KMgF_3$:Lu (0.34 mol%).

Dose (Gy)	Peak	T_M (K)	I_M (a.u.)	b	E (eV)	s (s^{-1})	FOM
	1	359	9581	1.40	0.87	2.16E+11	0.65
1	**2**	435	58,245	1.37	1.07	2.88E+11	
	3	488	1231	2.00	1.38	2.40E+13	
	1	354	71,059	1.05	0.72	2.58E+09	0.04
5	**2**	426	181,573	1.30	0.92	9.69E+09	
	3	502	3030	2.00	1.65	5.67E+15	
	1	356	164,963	1.05	0.80	3.30E+10	0.03
10	**2**	428	606,706	1.33	1.00	7.76E+10	
	3	501	10,084	2.00	1.20	1.32E+11	
	1	367	730,880	1.05	0.84	5.28E+10	0.02
25	**2**	437	1214,126	1.51	1.04	1.28E+11	
	3	536	40,949	2.00	1.32	2.61E+24	

Peak **2** is the main peak.

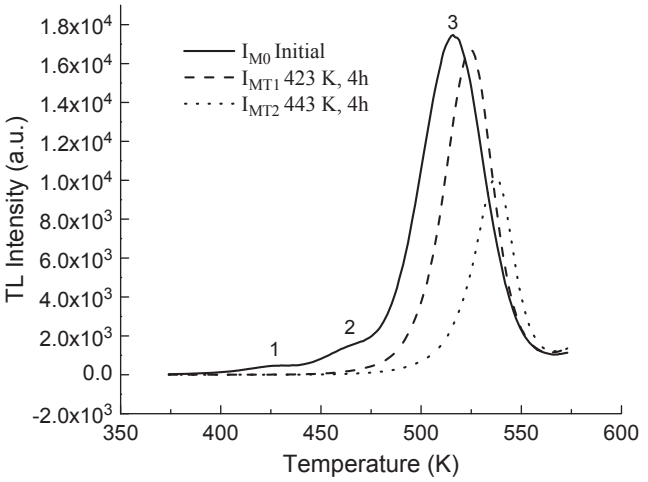

Fig. 4. Glow curves from LiF:Mg (0.04 mol%) irradiated at 1 Gy (solid line), and stored at 423 (dashed line) and 443 K (dotted line) for 4 h.

Table 4
E values calculated by Chen General-Order Kinetics, Eq. (6), for LiF:Mg (0.04 mol%).

Temperature (K)	T_M (K)	μ	$(Ec)_\tau$	$(Ec)_\delta$	$(Ec)_\omega$
I_{TM0}	516	0.48	1.66	1.25	1.46
I_{TM1}, 423	524	0.49	2.34	1.66	2.02
I_{TM2}, 443	537	0.46	2.82	2.21	2.56

that the T_M parameter shifted from 516 K to 537 K. Again, the maximum temperature T_M of the main glow peak (peak number 3) is strongly influenced by the post-irradiation thermal treatment. In this case, the kinetic order has no important change ($\mu = 0.48 \pm 0.01$), while the E values were different, as shown in Table 4. Fig. 5 shows the glow curves of LiF:Mg and in the inset figure is the linear dose–response. The kinetics parameters at different gamma doses (1, 5, 10, and 25 Gy) were obtained by using the SQPGCD method, Eq. (11), and three peaks were taken into account for the best Figure of Merit. The glow curve's structure for LiF:Mg was not very complex as in the case of perovskite phosphor; however the first two small glow peaks do not strongly influence the main glow peak which was shifted from 516 to 520 K when the samples were irradiated at different gamma doses (1–25 Gy) (Table 5). The average of the activation energy (E)

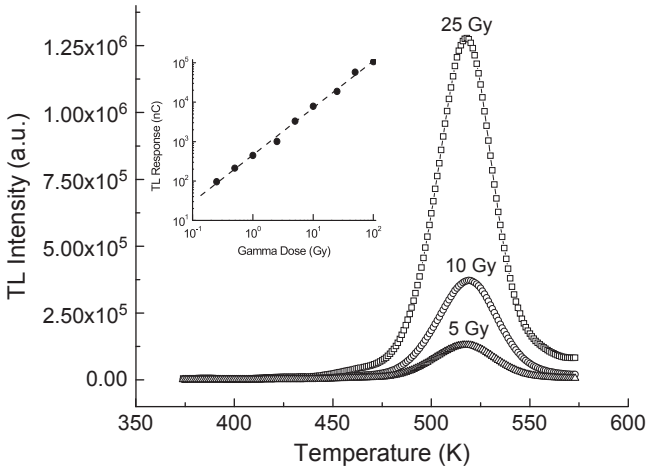

Fig. 5. Glow curves of LiF:Mg (0.04 mol%) irradiated at different doses. In the inset is the linear dose–response up to 100 Gy.

Table 5
Kinetics parameters obtained by deconvolution using SQPGCD, Eq. (11), for LiF:Mg (0.04 mol%).

Dose (Gy)	Peak	T_M (K)	I_M (a.u.)	b	E (eV)	s (s^{-1})	FOM
	1	424	310	1.05	1.21	3.24E+13	0.24
1	2	462	902	1.05	1.57	2.07E+16	
	3	516	17474	1.79	2.06	2.28E+19	
	1	427	1069	1.19	1.71	2.92E+19	0.13
5	2	461	3555	1.05	1.91	1.37E+20	
	3	519	128474	1.83	2.11	4.80E+19	
	1	425	3036	1.61	1.59	1.36E+18	0.04
10	2	462	8723	1.05	1.79	6.63E+18	
	3	520	355318	1.82	2.19	3.28E+20	
	1	428	4663	1.09	1.72	4.18E+19	0.01
25	2	463	17822	1.05	1.92	1.72E+20	
	3	520	1167922	1.93	2.40	3.70E+22	

Peak **3** is the main peak.

parameter for the main glow peak (peak number 3) of LiF:Mg was about 2.20 ± 0.15 eV at different gamma doses (Table 5), while, the average values of the maximum temperature (T_M) and the kinetic order (b) were 519 ± 2 K and 1.84 ± 0.06, respectively. At the lowest dose (1 Gy) the main glow peak temperature, T_M, was 516 K and the activation energy E, calculated by the SQPGCD method, was 2.06 eV (Table 5); the E value obtained by using the General Order Decay (Eq. (3)) was 2.15 eV (Table 1). It seems that the different values obtained by Eq. (3) are a consequence of the overlapped glow peaks that influence the main one when the phosphor was subjected to the high temperature of thermal treatment during long-term storage. A similar situation was also observed for the perovskite phosphor (Table 3). Table 1 shows the values of kinetics parameters for $KMgF_3$:Lu and LiF:Mg phosphors. As it can be expected, low values of the kinetics parameters (E) and (s) were obtained using both the Initial Rise (IR) and the Chen General-Order Kinetics (Eq. 6) method. For both $KMgF_3$:Lu and LiF:Mg phosphors, acceptable values of kinetics parameters were obtained by using the modified equations of the isothermal decay method. The values obtained by using this method were better than those obtained by IR and Chen-GOK methods because the experimental glow curves cannot be considered as single peaks. In the first case, i.e. for the IR method, at the low temperature of the

glow curve, there is at least one other peak which limits the reliability of this method. In the second case, the results obtained by using the Chen-GOK method are not reliable because of the presence of at least two unfolded peaks. On the contrary the glow curves can be fitted very well by using a deconvolution procedure. The kinetics parameters values aforementioned (see Table 1) were more accurate by using the GOK and SQPGCD deconvolution methods for the glow curves and good FOM values, 1.6–2.10 and 0.24–0.71, respectively, were obtained. The differences among the kinetics parameters (E, s, b) values (Table 1) may be related to the physical model based on the discrete trap distribution and the other important factor is the fact ascribed to the overlapped glow peaks that influenced the main glow peak of $KMgF_3$:Lu and LiF:Mg phosphors. Further works on trap structure and their recombination mechanism of point defects in these phosphors are necessary.

5. Conclusions

Modified thermal decay expressions given as a function of the peak intensity (I_M) at the maximum temperature (T_M) were used. For evaluation of those equations, the principal TL glow peaks of $KMgF_3$:Lu and LiF:Mg phosphors were considered. After long-term (4 h) high temperature storage the modified equations were valid when a general-order kinetics has been considered. The kinetic parameters values obtained by using the modified equations are in agreement with those obtained by IR and Chen-GOK methods. On the other hand, it seems that both GOK and SQPGCD deconvolution methods give more accurate kinetics parameters values for the glow curves and good FOM values were obtained. Activation energies (E) and pre-exponential factors (s) values obtained by using the modified equations for thermal decay can be useful as guess values in the aforementioned deconvolution methods.

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