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Thermoluminescence (TL) characterization of the perovskite-like $KMgF_3$, activated by Lu impurity

P. R. GONZÁLEZ
Instituto Nacional de Investigaciones Nucleares, A.P. 18-1027, México, D.F., Mexico
C. FURETTA, J. AZORÍN, T. RIVERA
Dept de Física, Universidad Autónoma Metropolitana-Iztapalapa, 0934 México, D.F., Mexico
E-mail: furt@xanum.uam.mx
G. KITIS
Nuclear Physics Laboratory, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece
F. SEPÚLVEDA
Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, 07738 México, D.F., Mexico
C. SANIPOLI
Department of Physics, Rome University, La Sapienza, Italy

This paper reports the thermoluminescent characteristics of a new production of perovskite $KMgF_3$ activated by Lu ions. Linearity, reproducibility, fading and other properties have been investigated. Because of the presence of ^{40}K in the compound, the self dose effect has been investigated. Furthermore, the Sequential Quadratic Programming Glow Curve Deconvolution (SQPGCD) technique has been used for the determination of the kinetic parameters, i.e., activation energy, frequency and pre-exponential factors of the trapping centers, and the kinetic order of the recombination process. © *2004 Kluwer Academic Publishers*

1. Introduction

The study on the perovskite compound $KMgF_3$ as a thermoluminescent phosphor started some years ago. Indeed, this phosphor was proposed since 1990 as a promising thermoluminescent material with good dosimetric performances for environmental and clinical dosimetry [1–11].

Ternary compounds belonging to the fluoroperovskites have the general formula ABF_3, where A and B stand for an alkali metal, K in the present case, and an alkaline earth metal, i.e., Mg, respectively.

During the past years, $KMgF_3$ containing various kinds of activating impurities showed to give a series of phosphors with very attractive thermoluminescent properties. The interest in this particular compound is caused by its very low hygroscopicity, which is of great importance to long-term use in different environmental conditions, its relatively high melting point, 1343 K, which allows for thorough annealing treatments of the samples. Furthermore, its effective atomic number Z_{eff} is 13.4 that is an intermediate value between tissue equivalent and high atomic number phosphors.

The aim of the present work is to report a detailled thermoluminescent characterization of $KMgF_3$ activated by Lu ions.

2. Materials and methods

Samples of $KMgF_3$ have been obtained from the melt using the Kyropoulos technique. The molten mass was formed by heating at 1335 K, in a platinum crucible and under nitrogen atmosphere, the starting powder, consisting of a finely ground stoichiometric mixture (mole ratio 1:1) of pure and dried KF and MgF_2. The growth of crystals was obtained with the pulling method from the above melt, starting the process with an air-cooled platinum finger or with the aid of a crystal seed. In the former case polycrystalline ingots were obtained, in the latter single crystals were grown with typical dimensions of 2–3 cm in diameter and 2–3 cm in length. All samples were optically transparent.

Doped crystals were obtained with the same technique by adding a proper amount of the desired impurity to the melt. For this work, three different dopant concentrations were used: 0.17 (preparation A), 0.34 (preparation B) and 0.66 (preparation C) mol% of LuF_3 respectively.

As segregation and evaporation phenomena of the impurity occurred during the growth, the final dopant concentration in the crystal cannot be exactly controlled and the dopant turns out to be inhomogeneous in the crystal boule. For this reason, the sample was reduced to powder and the powder was mixed with PTFE resin

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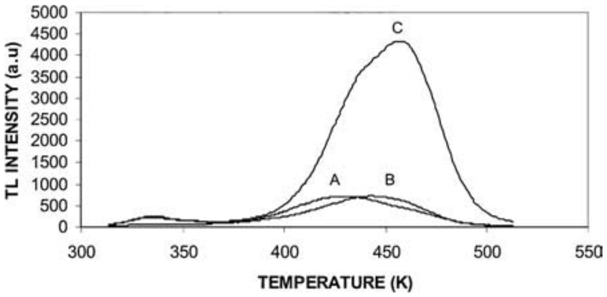

Figure 1 Glow curves of the three different preparations of $KMgF_3$:Lu: (A) 0.17 mol%, (B) 0.34 mol%, and (C) 0.66 mol%.

powder in the ratio 2(PTFE):1($KMgF_3$:Lu). Aliquots of the obtained mixture were placed in stainless steel dies and pressed at about 100 MPa, at room temperature. The pellets so obtained were thermally treated for synterization, for a period longer than five hours in an oven, with nitrogen atmosphere, increasing the temperature step by step from RT up to 673 K, just below the melting temperature of PTFE. After synterization, the samples cooled down slowly to RT.

The syntered pellets had an average mass of (20 ± 3) mg, a diameter of 5 mm and a thickness of 0.6 mm.

To obtain a homogeneous batch, all pellets were annealed at 573 K for 30 min; after cooling, the annealed samples were read out for the intrinsic background determination, according to the readout procedure given below. The background readings were always subtracted to the readings of the irradiated samples. The pellets received a γ-test dose of 1 mGy and then all samples were read-out in only one session to avoid any interferring fading effect. The reading system was a Harshaw TL reader (Mod.4000), with a constant heating rate of 10 K/s; nitrogen gas was allowed to flow into the reader during read-out to avoid any spurious signals; the TL emission was integrated from 313 to 573 K and all samples having a TL response outside ±5% from the average were rejected. A second read out was performed for the background which was subtracted from the first reading. A PC connected with the TL reader allowed to record and analyse the received glow curves. Fig. 1 shows the glow curves of $KMgF_3$:Lu for the three different concentrations. A heating rate of 2 K/s was used only for deconvolution, to minimize the temperature lag between TL samples and heating planchet.

3. Experimental results

3.1. Self-dose measurement

A drawback of $KMgF_3$:Lu is the presence of the natural isotope ^{40}K, which induces a TL signal superimposed to the TL signal due to the external irradiation [10, 12, 13]. To take this effect into account, an accurate measurement of the self-dose irradiation has been carried out over a period of one month at room temperature and in dark condition. No special care was taken in shielding the annealed samples because the well known local background (81.7 nGy/h). Fig. 2 shows the increase of the dose in the perovskite samples, owing to the self-dose as well as the external background dose, as a function of the storage time. The TL readings were transformed into dose by extrapolation of the calibration curve (see next paragraph). The net contribution of ^{40}K to the total dose results to be about 0.22 mGy/month.

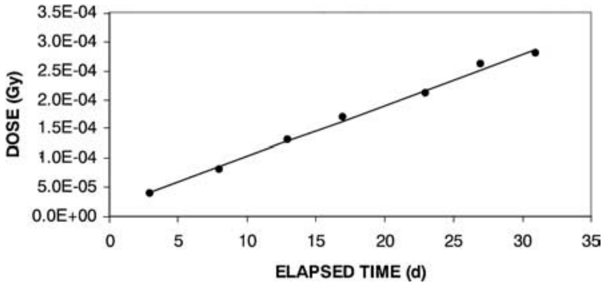

Figure 2 Self-dose increase as a function of the exposure time.

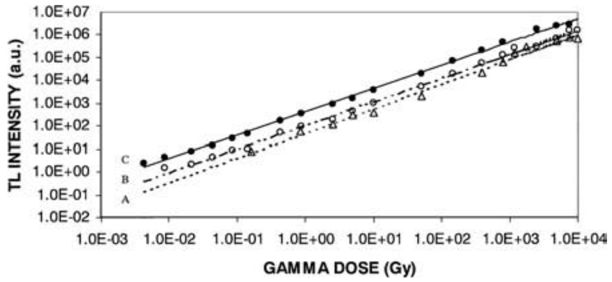

Figure 3 TL response as a function of the given doses.

3.2. TL response versus dose

The TL response as a function of the given dose was obtained using two different ^{60}Co sources: (i) an irradiator Vickrad 220, having a dose rate of 0.9 mGy/s, (ii) a Gammacell 2000 with a dose rate of 68 mGy/s. Lu doped $KMgF_3$ samples were exposed, under build up condition, to different doses. Five samples were used for each point of dose and for each concentration: the average values are plotted in Fig. 3. The dose range was from about 1 mGy, for B and C preparations, to 1 kGy. Preparations B and C show a good linear behaviour in the whole range of given doses. Preparation A, with the lowest concentration of dopant, shows a short zone of superlinearity after 100 Gy, followed by a saturation region. A further discussion is given below in this paper. The most doped samples, preparation C, seem to show a slight saturation effect very near to the maximum delivered dose.

3.3. Precision of the dose evaluation

The variation of the TL response of several pellets, previously exposed to the same dose, allows to estimate the precision which can be obtained in the evaluation of a given dose. The following relation can be used for this test (ANSI, 1975):

$$\frac{D_{\max} - D_{\min}}{D_{\min}}\% < 30\% \qquad (1)$$

where $D_{\max}$ and $D_{\min}$ are respectively the maximum and minimum TL readings, expressed in dose units.

After annealing, 12 pellets of preparation C received a test dose of 0.5 Gy. After read out, the maximum and minimum values, expressed in dose, were respectively 0.54 and 0.46 Gy. Using these data, the previous relation gives a value of 17.4%, which is lower than the maximum permissible limit.

TABLE I Sensitivities of the various sample preparations compared to LiF

Sample	Lu (mol%)	Weight (mg)	TL material (mg)	TL integral	Sensitivity TL/(mg · dose)	Relative sensitivity
A	0.17	22.17	7.38	362.59	49.07	0.91
B	0.34	26.7	8.89	961.97	108.09	2.01
C	0.66	27.34	9.11	1497.24	164.3	3.06
TLD-100		22.77	22.77	1221.52	53.64	1

3.4. Relative sensitivity

The sensitivities of the three preparations have been compared to the sensitivity of LiF (TLD-100). After annealing, a gamma dose of 100 mGy was given to few selected samples. Table I shows the obtained results.

3.5. Lower detection limit (LDL)

The LDL, at 95% confidence level, was determined for the preparations B and C. The LDL resulted to be 71 and 218 μGy for preparation C and B respectively.

3.6. Reproducibility of the TL measurements

For this test, 10 pellets for each doping concentration received a test dose of 120 mGy after annealing. After read-out, the samples were annealed again, irradiated with the same dose and read-out. The procedure was repeated over five cycles. The standard deviation in percentage, taken as the reproducibility parameter, was better than 5%, with respect to the average over the five readings obtained from the same sample, and less than 1% over the average of the 10 average values.

3.7. Fading

The fading effect was studied over a period of 30 days. Several selected samples of preparations B and C were annealed and irradiated with a test gamma dose of 100 mGy and then stored in a black box at RT and read out at different times over one month. The data were then corrected by the self-dose contribution as well as by the local background and normalized to the zero elapsed time from irradiation. Fig. 4 shows the results over the period of one month: it can be noted that the fading rate is negligible over one month.

3.8. Analysis of the TL response vs. dose

This analysis was carried out on samples having a dopant concentration of 0.17 mol% (preparation A), which present an evident superlinearity zone followed by saturation. The TL response as a function of dose for this preparation is shown in Fig. 5.

The dose response can be analysed by using two universal indices proposed by Chen and McKeever [14].

The first of these indices is called superlinearity index $g(D)$ and gives an indication of the change in the slope of the dose response. The second index is the supralinearity index $f(D)$ and it is used to quantify the size of correction required for extrapolation of the linear dose region.

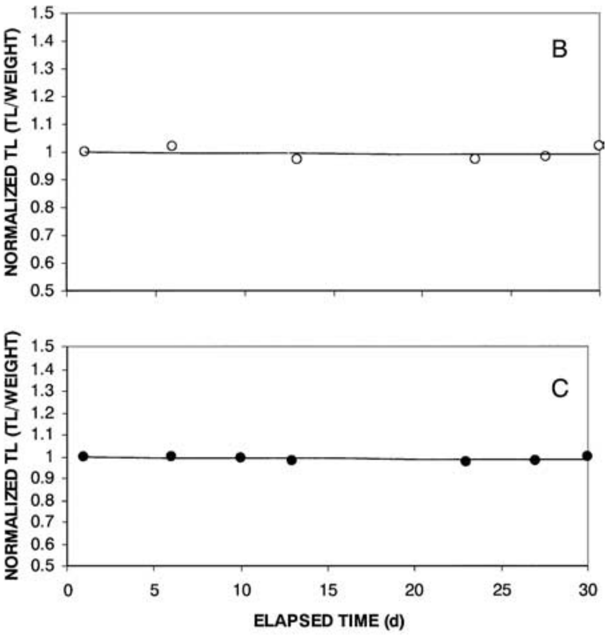

Figure 4 Fading as a function of the elapsed time from irradiation, for samples B and C.

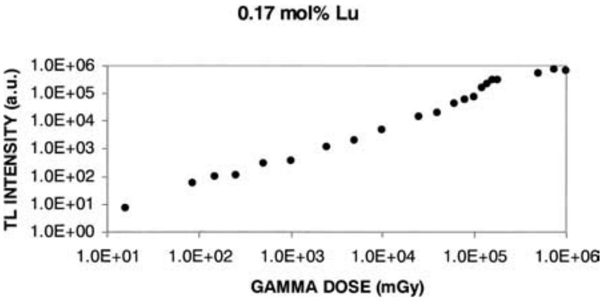

Figure 5 TL response vs. dose for sample A.

The $g(D)$ function is defined as

$$g(D) = \left[\frac{D \cdot \mathrm{TL}''(D)}{\mathrm{TL}'(D)}\right] + 1 \qquad (2)$$

where $\mathrm{TL}'(D)$ is the first derivative of the fitting function TL vs. dose, and $\mathrm{TL}''(D)$ is its second derivative.

The $f(D)$ function is given by the following expression:

$$f(D) = \frac{\frac{\mathrm{TL}(D)-\mathrm{TL}_0}{D}}{\frac{\mathrm{TL}(D_{\mathrm{lin}})-\mathrm{TL}_0}{D_{\mathrm{lin}}}} \qquad (3)$$

where D_{lin} is the normalization dose in the linear region and TL_0 is the intercept on the TL axis.

The first step is then to find a fitting equation for the experimental TL vs. dose plot given in Fig. 5. In the present case, two different equations have been used for the fit. The first equation is based on the superlinearity theory by Mische and McKeever (M-McK) [15].

The model presented by Mische and McKeever considers that the supralinearity is due to a competition mechanism taking place during the heating in order to record the TL glow-curve, as well as a spatial association between traps and centers. The equation which gives the TL intensity when a competition during heating take place is:

$$\mathrm{TL} = \eta \cdot n \left\{ \frac{KS}{4\pi s^2} + \left(1 - \frac{KS}{4\pi s^2}\right) \frac{S}{S_c} \frac{m}{n_c} \right\} \tag{4}$$

where η is the intrinsic luminescence efficiency ($0 < \eta \leq 1$) usually assumed equal to 1, S is the capture cross section of a trapped hole, S_c the capture cross section of the competing centre, K a certain fraction of electron and hole traps which exists in pairs and s the separation distance of electron and hole within the pairs fraction K. n, concentration of electron traps, and m, concentration of recombination centers, are dose dependent and can be expressed in the form:

$$n(D) = N[1 - \exp(-\alpha \cdot D/N)]$$

$$m(D) = M[1 - \exp(-\beta \cdot D/M)]$$

The neutrality condition $(N_c - n_c) + n = m$ has been used to determine $n_c(D)$. $N_c - n_c$ is the concentration of competing electron traps, that are filled, n_c is the concentration of empty competing electron traps, N, N_c and M are the concentrations of total available electron competing electron and hole traps, and α and β are the 'dose constants'.

For the needs of the present study the above equation can be simplified in order to evaluate the first and second derivative and make a fit to the experimental data. The simplified form is:

$$\mathrm{TL} = (F6 \cdot n) + \frac{F7 \cdot (n \cdot m)}{F3 + n - m} \tag{5}$$

where

$$F3 = N_c \quad F4 = \frac{\alpha}{N} \quad F5 = \frac{\beta}{M} \quad F6 = \frac{KS}{4\pi s^2}$$

$$F7 = (1 - F6)\frac{S}{S_c}$$

The fitting parameters are given in Table II. Fig. 6 gives the fit of the experimental data, $n(D)$, as well as $m(D)$ and $n_c(D)$.

TABLE II Parameters of the fitting Equation 5

Parameters	Values
$F1 = N$	0.547
$F2 = M$	2.71
$F3 = N_c$	2.69
F4	0.00146
F5	0.0187
F6	0.89
F7	0.221

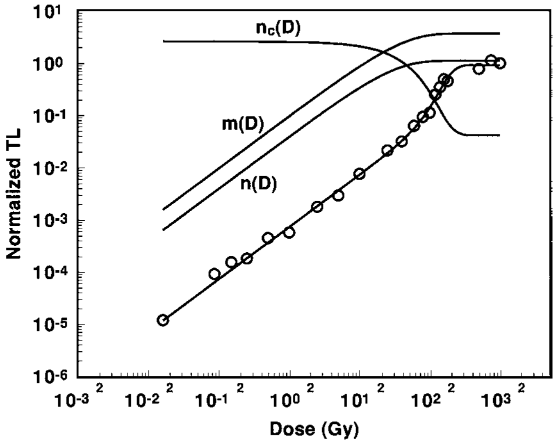

Figure 6 Fit of the TL response vs. dose (sample A) using Equation 5.

The other equation is based on the Waligorski and Katz (W-K) theory [16, 17], where the superlinearity is considered as an effect of competition during irradiation.

This equation is based on the Katz track structure theory. According to the track theory the superlinearity is due to pre-existing 1-hit and 2-hit trap structures. The equation describing the superlinear TL dose response curve is:

$$\mathrm{TL} = M\left[1 - \exp\left(-\frac{D}{E01}\right)\right] + (1 - M) \cdot \left[1 - \left(1 + \frac{D}{E02}\right)\exp\left(-\frac{D}{E02}\right)\right] \tag{6}$$

Since in the present work the primary interest is to obtain the first and second derivatives in order to evaluate $g(D)$, for the sake of simplicity and to avoid the normalisation over the value of saturation region, the equation is rewritten in the following simplified form.

$$\mathrm{TL} = AM\left[1 - \exp\left(-\frac{D}{E01}\right)\right] + BM\left[1 - \left(1 + \frac{D}{E02}\right)\exp\left(-\frac{D}{E02}\right)\right] \tag{7}$$

where D is the dose, $E01$ the characteristic dose for the 1-hit component, $E02$ the characteristic dose for the 2-hit component and M a mixing parameters.

The fitting parameters are given in Table III and Fig. 7 gives the fitting plot.

TABLE III Parameters of the fitting Equation 7

Parameters	Values
AM	3.015×10^3
E01	6.095
BM	6.567×10^5
E02	150

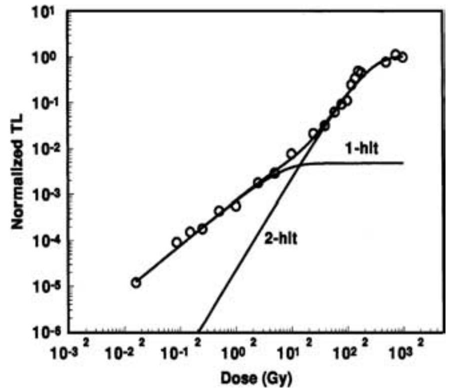

Figure 7 Fit of the TL response vs. dose (sample A) using Equation 7.

The 1-hit is given by the term

$$AM\left[1 - \exp\left(-\frac{D}{E01}\right)\right]$$

and the 2-hit by the term

$$BM\left[1 - \left(1 + \frac{D}{E02}\right)\exp\left(-\frac{D}{E02}\right)\right]$$

Fig. 8 gives the plot of both indices $g(D)$ and $f(D)$ as a function of dose, as they have been evaluated from the fit line through the experimental points, using the fitting Equation 5.

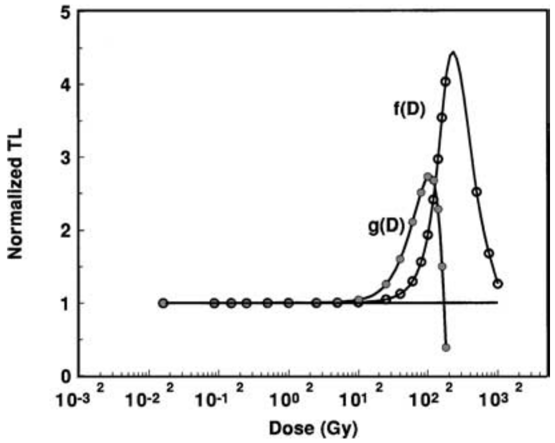

Figure 8 $g(D)$ and $f(D)$ indices according to the fit in Fig. 6.

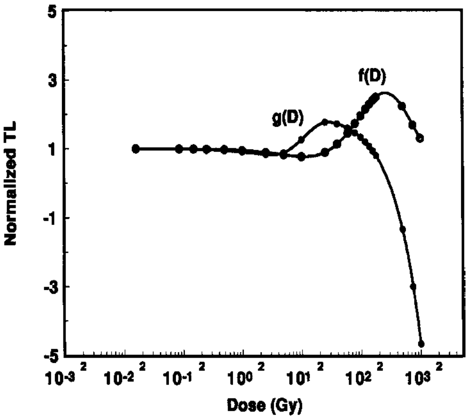

Figure 9 $g(D)$ and $f(D)$ indices according to the fit in Fig. 7.

Fig. 9 gives the behaviour of the same indices, according to the fitting Equation 7.

From Figs 8 and 9 some observations can be obtained.

The TL response results to be linear up to about 4 Gy because both indices $g(D)$ and $f(D)$ are equal to one. From 4 Gy to about 180 Gy, both $g(D)$ and $f(D)$ are greater than unity meaning that the TL response is superlinear and also supralinear. At around 180 Gy, $g(D) = 1$ and $f(D) > 1$: in this case saturation of the TL response starts. In the region from 180 Gy to 10^3 Gy, $g(D)$ is less than 1 and $f(D)$ still remains positive and greater than 1: the TL response is then sublinear.

4. Kinetic parameters

A complete description of the thermoluminescent characteristics of a new material cannot leave out some indications concerning the kinetic parameters, i.e. the activation energy E of the traps involved in TL emission, the order of the kinetics b and, finally, the frequency factor s and the pre-exponential factor s^*. All these parameters are necessary for a complete characterization of the material, being related to the trap stability.

To obtain these parameters, the Sequential Quadratic Programming Glow Curve Deconvolution (SQPGCD) developed at ININ [18] was used. Several samples of preparation C received a gamma dose of 100 mGy after annealing and were then read out. The resulting glow curves were stored in a on line computer and then analysed by SQPGCD program. Fig. 10 shows that the best deconvolution is obtained with three intense peaks and two very little, the last two located on the ascending and descending sides of the experimental glow peak. The figure of merit (FOM) [19] of the fit was 0.40%. Table IV lists the glow curve parameters obtained for each deconvoluted peak.

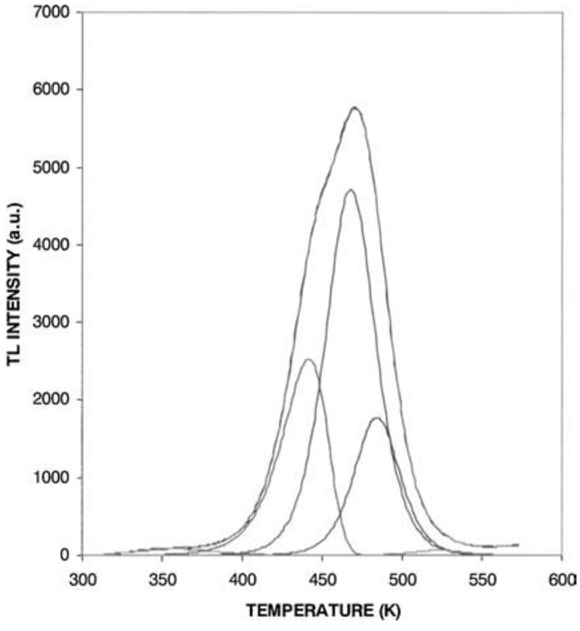

Figure 10 Deconvolution of the glow curve of sample C.

TABLE IV Kinetics parameters as obtained by deconvolution

Peak no.	T_M (K)	b	E (eV)	s (s^{-1})	n_0 (m^{-3})	s^* ($^{m3(b-1)}$) s^{-1}
1	359	2.0	0.71		2.28×10^3	5.40×10^5
2	442	1.0	1.26	3.24×10^{13}	4.44×10^4	
3	468	2.0	1.81		9.39×10^4	6.47×10^{13}
4	484	2.0	2.13		3.24×10^4	8.52×10^{16}
5	523	2.0	2.33		1.26×10^4	4.07×10^{18}

5. Discussion

Concerning the TL response vs. dose, basically there are two models which describe the origin of superlinearity in thermoluminescent materials. The first model has been proposed by W-K [16, 17]. In their model the superlinearity is due to competition processes taking place during the absorption stage, i.e., during the irradiation of the sample. The second model has been proposed by M-McK [15] and it considers the superlinearity as a consequence of competition effects taking place during the thermal excitation of the sample, i.e., during readout.

The two models are totally different and they have been chosen for fitting the experimental data according to the following reasons:

- To use the analytical relations of the TL dose response curve, provided by both models, for the evaluation of the $g(D)$ index. Although the $g(D)$ index describes superlinearity much better than the $f(D)$ index, it is not frequently used in the scienctific works. For example, the superlinearity index $f(D)$ can be only used when the TL dose response curve at low dose is linear. The reason of the lack in the use of the $g(D)$ index is the need of an analytical relation for the TL dose response curve which, in general, is not a trivial problem.
- To look at the potentiality of the analytical relations provided by the two models for fitting real experimental data. At our best knowledge, this has been done only for LiF:Mg, Ti, using the W-K equation. Furthermore, using the fitting results some arguments about the origin of superlinearity phenomena in the material under investigation can be arisen.

Concerning the two models, some observations can be done.

The W-K model can predict a superlinearity index in a large range of TL dose response curve but fails when $g(D)$ assumes high values. On the contrary, the M-McK model can predict even very high values of $g(D)$. In the present case the expression given by M-McK model seems to describe better the TL dose response curve. Indeed, the fitting obtained by the M-McK equation, which has never done before at our best knowledge, gives the opportunity to go insight to some details of the recombination during thermal excitation.

Fig. 6 is a clear indication of the argument suggested by M-McK: i.e., the superlinearity behaviour should not be considered as an-over response at high doses, but it should be seen as an under-response at low doses. So, looking at Fig. 6, the actual number of trapped electrons is given by the curve $n(D)$. At low doses the number of empty competitors $n_c(D)$ is extremely high, so that a very large number of electrons liberated during heating goes to competitors and not to the recombination centers. So, the experimentally recorded response is decreasing respect to $n(D)$ which means an under-response at low doses. However, as the dose increases more and more competitors are filled so that the competition becomes more weak. The result is that the number of thermally liberated electrons going now to the recombination centers is increasing and, in turn, the TL response increase too. Finally, when the number of empty competitors ceases all the liberated electrons go to the recombination centers. In this case the experimental TL dose response curve and the $n(D)$ curve coincide.

Any way the difference between the two models does not influence the practical application of the studied material to dosimetry. The differences become important when, for instance, one deals with radiation damage. If one considers that the TL dose response curve is an indication of radiation damage in the material, then this indication is directly deduced from the shape of the curve in the case of competition during irradiation which is not the case for the competition during heating.

Looking now at Fig. 6, the actual degree of the radiation damage is not show by the experimental TL dose response curve but from $n(D)$. This means that the actual degree of radiation damage can be only found by the best selection of the function $n(D)$ for fitting the experimental data.

6. Conclusions

$KMgF_3$:Lu presents many attractive properties for its use as dosimeter in some applications. Having an intermediate effective atomic number, its sensitivity, at least for preparation C, is 3 times higher than the LiF sensitivity and it only needs an accurate calibration in the radiation field of use, i.e., a calibration for each X energy used, to eliminate the possibility of over-estimating the delivered dose. Furthermore, the linear range of dose, from 1 mGy to 1 kGy for preparation B and C, covers many kinds of applications. Comparing the properties of $KMgF_3$:Lu to the properties of other compounds of the same family, i.e., $KMgF_3$:Eu, $KMgF_3$:Ce, $KMgF_3$:Tl and $KMgF_3$:La, it has to stress the very large linear dose response for $KMgF_3$:Lu and the absence of fading over one month for B and C preparations.

The main drawback could be caused by the presence of ^{40}K in the compound: any way, the effect of self-dose can be easily handled for practical needs. A self-dose irradiation of 0.22 mGy/month should not be a serious problem in dosimetric applications where high dose levels have to be monitored, as in the case of clinical dosimetry.

The annealing procedure is very simple and no post-irradiation annealing is necessary.

Finally, another important characteristics is the simple glow curve structure, which allows a simple setting of the TL reader parameters.

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