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Synthesis and dosimetry features of novel sensitive thermoluminescent phosphor of LiF doped with Mg and Dy impurities

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HIGHLIGHTS

- Lithium fluoride doped with Mg and Dy was fabricated for the first time using melting method.
- This dosimeter exhibits proper thermoluminescence properties.
- TL sensitivity of the fabricated phosphor is close to that of TLD-100 powder.
- TL properties such as fading, linearity of dose response and reusability are investigated.

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ABSTRACT

Lithium fluoride doped with Mg and Dy was fabricated for the first time using melting method. The optimum concentrations of impurities and thermal treatment were studied to achieve high thermoluminescence (TL) sensitivity. TL sensitivity of the fabricated phosphor is close to that of TLD-100 powder. T_m-T_{stop} technique was used to identify the number of overlapped TL glow peaks. Initial rise, isothermal decay and computerized glow curve deconvolution (CGCD) methods were applied to obtain kinetic parameters of the prepared TL material. Three component glow peaks were distinguished at temperatures 395, 448 and 510 K. Other TL properties such as fading, linearity of dose response and reusability are also presented and discussed.

1. Introduction

TL phenomenon in insulator materials can occur when the solids are exposed to ionizing radiation and then thermally stimulated (Bos, 2007). The peak intensity and the area underneath the TL glow peak are related to the absorbed dose. LiF-based TL materials are extensively used in personal monitoring because of chemical stability, low energy dependence and near tissue equivalence. These phosphors have effective atomic number of 8.14 which is close to that of biological tissue, 7.4 (Chen and Mckeever, 1997). It was found that TL intensity, sensitivity and emission of LiF crystal are intensely modified by type and amount of dopant and also the preparation method (Kim et al., 2004). Magnesium is reported to be one of the most effective dopants in increasing the TL response. Mg-related defects act as electron traps by forming impurity- vacancy dipoles in LiF (McKeever et al., 1995). Other dopants like copper, phosphorus and titanium are immensely studied. LiF:Mg,Ti, processed in the form of TLD-100, has proven to be a useful phosphor for TL dosimetry and LiF:Mg, Cu,P as GR-200, has become a popular TL dosimeter for clinical applications (Horowitz, 1993; Azorin et al., 2015). Today, materials doped with rare earth ions are widely used because of their special characteristics due to their atomic structures (the incomplete 4f shell) (Zahedifar et al., 2013; Jiang et al., 2008).

In this study a new phosphor, LiF:Mg, Dy, is introduced and compared to TLD-100 powder. The optimized concentrations of Mg and Dy dopants and the best annealing regime which provides the highest TL response were obtained. Other dosimetry features such as dose response, fading and reusability are studied and discussed. Number of peaks and kinetic parameters such as the activation energy and kinetics order were investigated by isothermal decay, initial rise and computerized glow curve deconvolution (CGCD) methods. The number of glow peak components in the complex glow curve of the produced phosphor were identified by T_m-T_{stop} analysis and the results were used as input parameters in CGCD procedure. Good agreement was found between CGCD and other mentioned methods.

This paper deals with successful development of LiF:Mg,Dy TL material using melting method. In previous works on characteristics of LiF:Mg,Dy, this phosphor has been prepared by edge defined film fed

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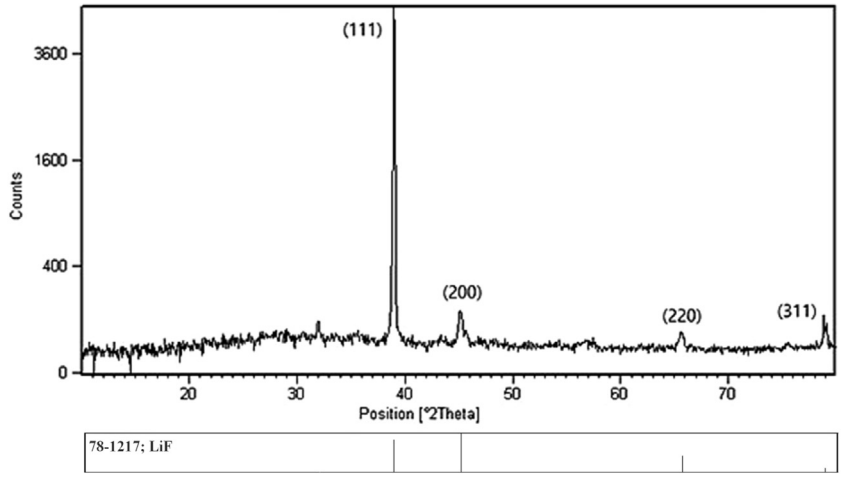

Fig. 1. XRD pattern of the fabricated LiF:Mg,Dy powder. Reference pattern of lithium fluoride is also shown.

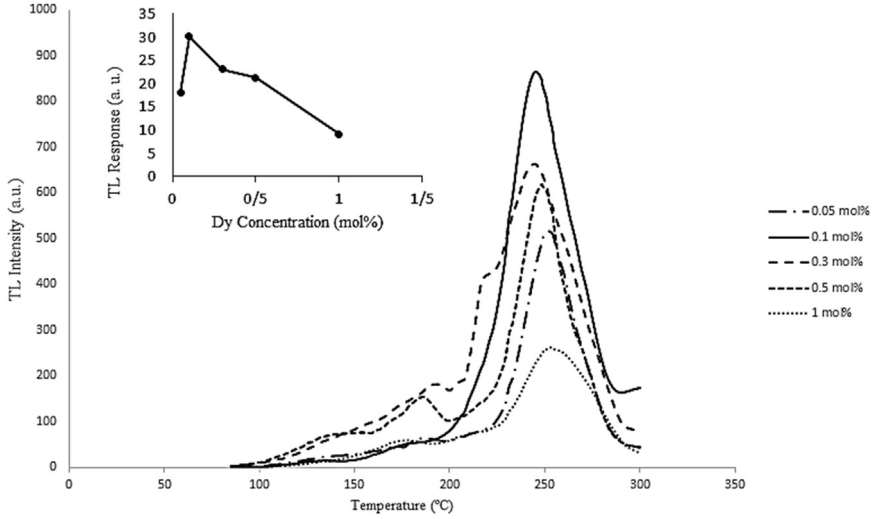

Fig. 2. TL Glow curves of LiF:Mg,Dy with different Dy concentrations and a fixed Mg concentration of 0.2 mol% at 500 mGy gamma dose from ^{60}Co. TL responses of different Dy concentrations are shown as insert.

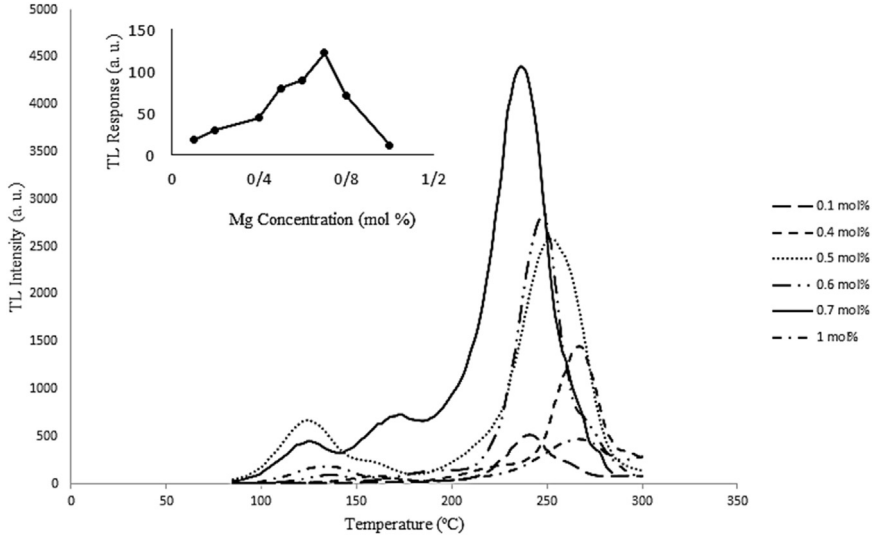

Fig. 3. Some TL glow curves with different Mg concentrations and optimized Dy concentration of 0.1 mol% and an administrated gamma dose of 500 mGy from ^{60}Co. TL responses of different Mg concentrations are shown as insert.

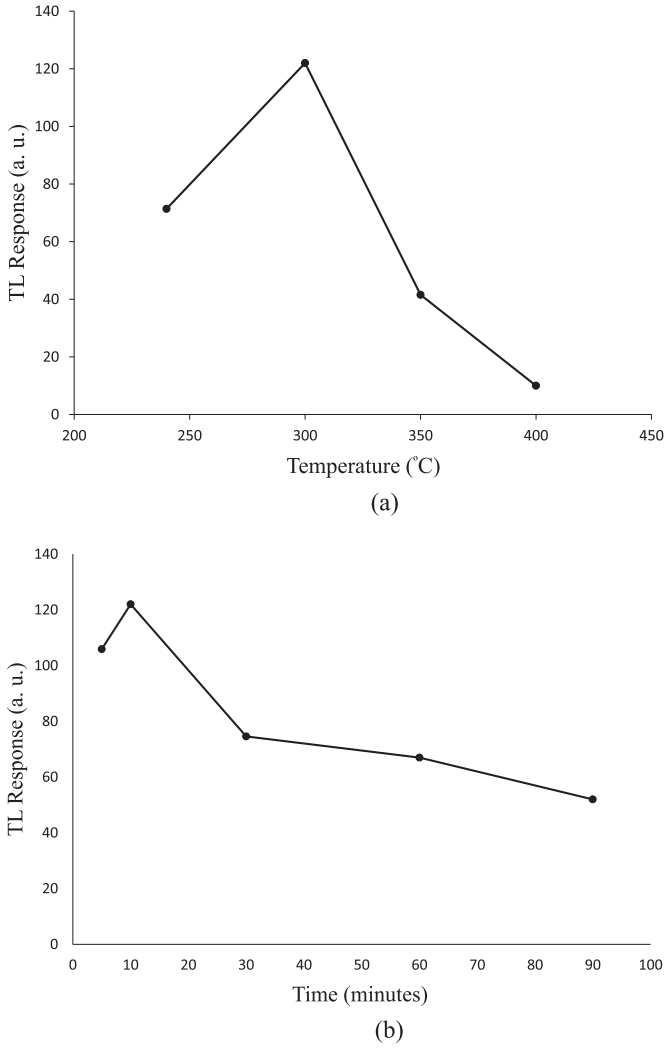

Fig. 4. (a): TL responses of prepared LiF:Mg,Dy under different annealing regimes of 240, 300, 350 and 400 °C for 10 min. (b) TL response of prepared LiF:Mg,Dy for different annealing times of 5, 10, 30, 60 and 90 min at 300 °C.

crystal growth (EFG) (Seth et al., 2012) and Bridgman technique (Ayyapan et al., 1981).

2. Materials and methods

TL properties of a material depend essentially on its preparation methods. Melting and granulation procedures are usual processes to prepare LiF-based TL materials (Lee et al., 2004). In this work, the melting method was used. The raw materials used are: LiF (of 99.99% purity), $MgCl_2$ (anhydrous of 98% purity) both purchased from Merck, and $Dy(NO_3)_3$. $5H_2O$ (of 99.9% purity) provided by Sigma-Aldrich. All materials were mixed and put in a platinum crucible to avoid undesirable effects during melting. The platinum crucible was placed in a special reactor so that the melting and cooling procedures were carried out under a controlled nitrogen atmosphere (with purity of 99.9995%). Since the heating temperature should not be lower than the melting point of LiF, 847 °C, doping was completed by melting LiF at 1050 °C in presence of activators in a nitrogen atmosphere for 30 min (Zha et al., 1993; Shoushan, 1988) in a furnace with accuracy of ± 1 °C. The nitrogen flow continued in both heating and cooling stages to insure nonappearance of oxygen in the crystalline structure. The cooled material was ground in a mortar to achieve homogeneous sample. The produced powder was annealed for 10 min in a programmable oven at 300 °C with precision of 1 °C and then cooled to room temperature with

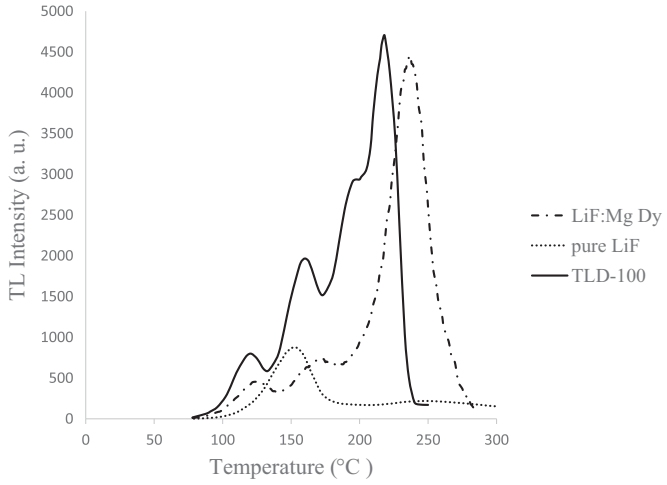

Fig. 5. Comparison of TL glow curves of pure LiF, TLD-100 powder and fabricated LiF:Mg,Dy irradiated to 500 mGy dose from ^{60}Co gamma source.

the rate of 75 °C/min in a dark environment.

All the irradiations were made using a ^{60}Co gamma source with the dose rate of 74.25 mGy/min. TL glow curves were recorded using a commercial TLD reader, Harshaw model 4500 by which the samples were heated on a heater strip (planchet) with a heating rate of 2 °C/s from 50 to 300 °C with accuracy of 1 °C. Since TL response depends directly on mass of the sample, the constant mass were kept at 0.007 g with precision of 0.01 mg. X-ray diffraction pattern was taken on a Rigaku D-maxcIII diffractometer with CuK_α radiations to confirm the formation of desired lattice structure.

3. Results

3.1. XRD pattern

Fig. 1 illustrates the typical XRD pattern of LiF:Mg,Dy. A cubic lattice structure was identified in accordance with ICSD collection code no. 062361, reference pattern code no. 78–1217. Crystalline planes of (111), (200), (220) and (311) cause diffractions through angles of 38.98, 45.15, 65.67 and 78.91 respectively.

3.2. TL characteristics

In order to examine the dependence of TL sensitivity on impurity concentration, firstly the samples were produced with different Dy concentrations of 0.05, 0.1, 0.3, 0.5, 1 mol% and a fixed Mg concentration of 0.2 mol%. The corresponding TL glow curves are shown in Fig. 2 and the TL responses as insert. As can be seen, the TL response is optimized at 0.1 mol% of Dy concentration.

Secondly, various Mg concentrations of 0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8 and 1 mol% with optimum amount of 0.1 mol% for Dy was studied. Some of TL glow curves are presented in Fig. 3 and the TL responses as insert. Results assert that the amount of 0.7 mol% of Mg tends to increase TL response. As can be seen, the change of Mg concentration substantially affects the height and area of the main peak, while the lower temperature peaks less impresses by changing Mg concentration. This behavior has been reported for other LiF based TLDs which confirms that Mg impurity essentially controls the intensity of TL glow peaks (Tang et al., 2008; Bilski et al., 1997).

Thermal treatment has significant effect on TL sensitivity and glow curve structure and maintaining the defect equilibrium and stabilization of traps. So it is important to acquire optimum pre-irradiation anneal. Thereby four annealing regimes were applied including: 240, 300, 350 and 400 °C all for 10 min. As can be seen in Fig. 4(a), incremental effect of the second regime of 300 °C on intensity of TL response

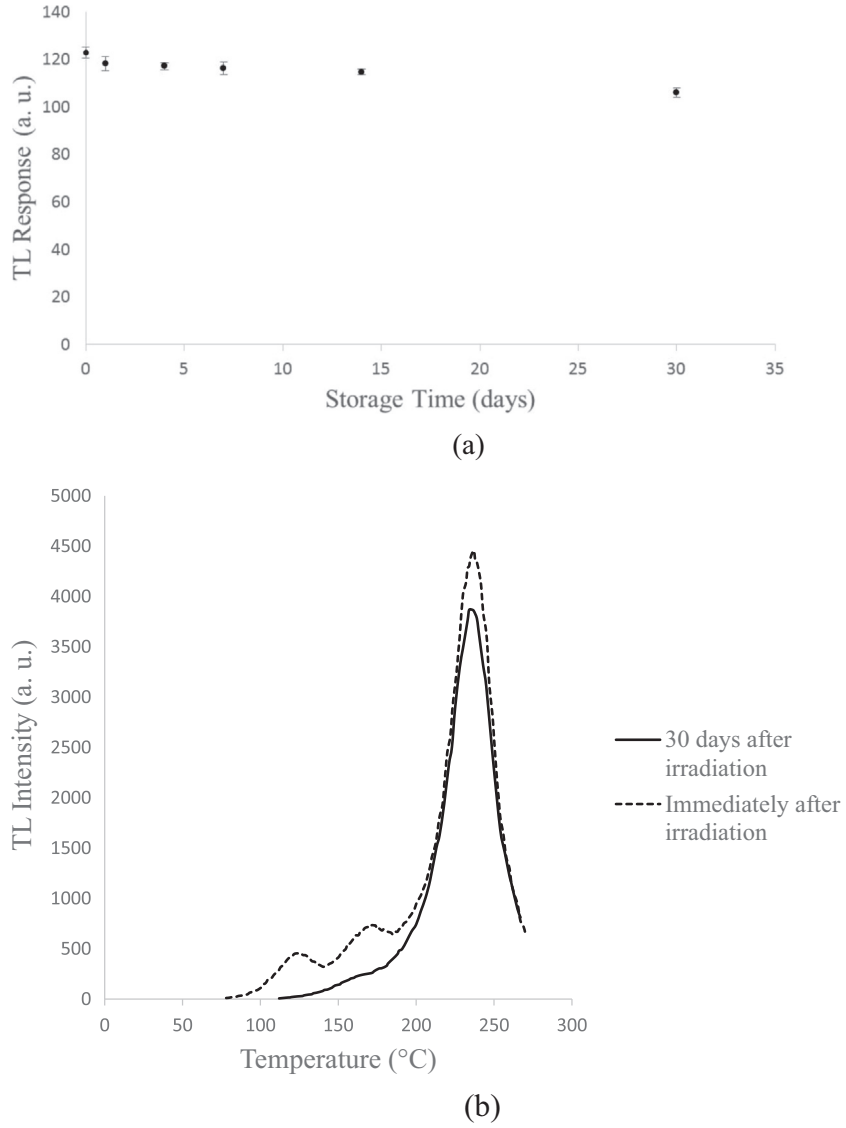

Fig. 6. (a): Fading of LiF:Mg,Dy powder immediately after gamma exposure and 1, 4, 7, 14 and 30 days after 500 mGy gamma irradiation. (b) TL response of the prepared sample immediately and 30 days after irradiation.

is obvious. Also in Fig. 4(b) the role of annealing time is illustrated. The sample was annealed at the optimum temperature of 300 °C for 5, 10, 30, 60 and 90 min. It is shown that duration of 10 min is sufficient to achieve more sensitivity. So the regime of 300 °C for 10 min was achieved as optimum pre-irradiation annealing process.

TL response of the prepared LiF:Mg,Dy at optimum conditions was compared to pure LiF and commercial TLD-100 powder with the same masses. The results are shown in Fig. 5. Considerable growth of the main peak in LiF:Mg,Dy compared to pure LiF is explicitly due to the presence of dopants. Also according to Fig. 5, TL sensitivity of the new TLD is near to TLD-100 powder. So LiF:Mg,Dy by fulfillment of required dosimetry criteria, can be useful in routine applications of personal and environmental dosimetry.

TL sensitivity of the sample with and without imposing nitrogen flow during melting and cooling procedures was investigated and the extra decrement in TL response was observed in the absence of nitrogen flow.

The stability of TL signal by storing the TL material at room temperature is an important point in choice of a TLD. To evaluate the fading of TL signal of LiF:Mg,Dy powder, the samples with the same mass of 0.007 g, undergone the pre-irradiation anneal of 300 °C for 10 min were exposed to the same gamma dose of 500 mGy and stored in a dark environment before readout. Then their TL signals were registered after 0, 1, 4, 7, 14 and 30 days after irradiation. The TL responses versus the storage time are represented in Fig. 6(a). First peak was faded completely after 30 days. Second and main (third) peak were faded about 60% and 10% respectively after a period of 30 days. For better comparison, glow curves recorded immediately after irradiation followed by storing for 30 days at room temperature are drawn in Fig. 6(b). Explicit intensity reduction of low temperature peaks is clear in this figure.

Then, the linearity of TL dose response of prepared phosphor was tested. For this purpose, samples with same masses were prepared and exposed to doses up to 100 Gy with ^{60}Co gamma rays. Fig. 7(a) shows the dose response in a log-log scale. A dose response line with the slope 1 in a log-log scale points to the linearity of dose response. As represented, Fig. 7(a) confirms the linearity of TL dose response in the range of 1 mGy to 10 Gy. Some of the selected TL glow curves (divide with the corresponding dose) at different dose levels are shown in Fig. 7(b). For testing the reusability of produced phosphor, the samples were annealed at 300 °C for 10 min, exposed to 500 mGy gamma dose and were readout with the heating rate of 2 °C/s. This process was repeated for 5 times. TL glow curves after 1, 3 and 5 cycles of reuse are illustrated in Fig. 8 and TL responses for 5 successive cycles of

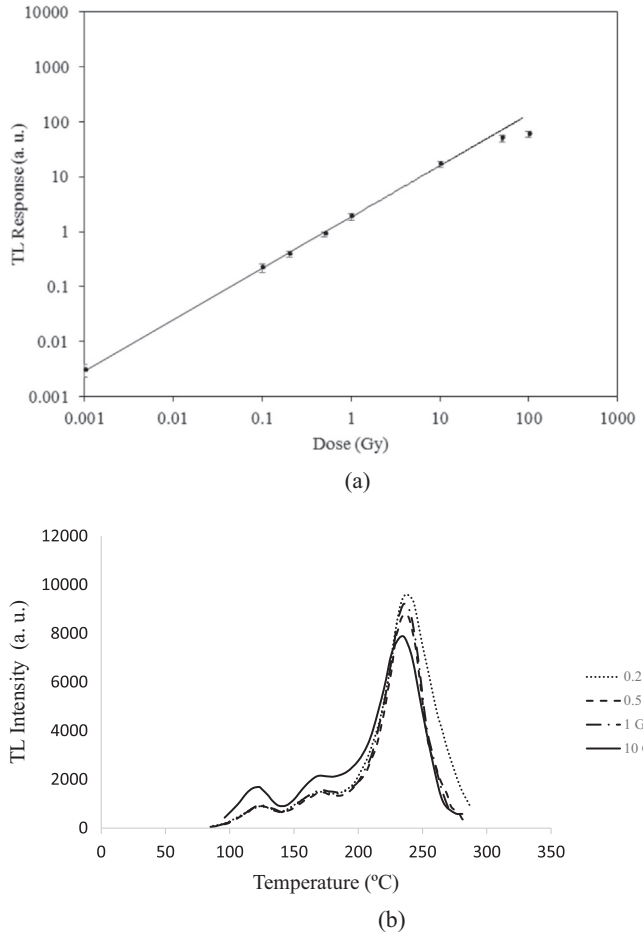

Fig. 7. (a): Dose response of the sample in log-log scale from 1 mGy to 100 Gy. Linearity in the dose range of 1 mGy to 10 Gy is clear. (b) Some of the selected TL glow curves after dose response experiment. The glow curves are divided with the corresponding dose for more clarity.

annealing, irradiation and readout are shown as insert. As is evident, the TL responses after 5 successive cycles of reuse does not change appreciably.

3.3. TL glow curve

To obtain trapping parameters and determine the shape of component TL glow peaks, the glow curve of LiF:Mg,Dy was de-convoluted using the computerized de-convolution program based on Levenberg-Marquart algorithm. The computer program has been written in our laboratory using non-linear least square method. Curve fitting procedure was done based on the solution of the general order kinetics equation given by (Kitis et al., 1998):

$$I(T) = I_m b^{\frac{b}{b-1}} \exp\left(\frac{E(T-T_m)}{kTT_m}\right) \times \left\{\frac{T^2}{T_m{}^2}(b-1)\left(1-\frac{2kT}{E}\right)\exp\left(\frac{E(T-T_m)}{kTT_m}\right) + 1 + (b-1)\frac{2kT_m}{E}\right\}^{\frac{-b}{b-1}} \quad (1)$$

In the above equation, I_m, T_m (K), E (eV) and T (K) refer to maximum peak intensity, maximum peak temperature, activation energy and absolute temperature, respectively. Parameter b is the kinetic order and k (eV/K) is the Boltzman's constant. The figure of merit (FOM) was utilized to test the validity of fitting (Balian and Eddy, 1997):

$$FOM = \sum_{j_1}^{j_f} \frac{100[y_i - y(x_i)]}{A} \quad (2)$$

Where A is the total area of the fitted glow peak between j_l and j_f, j_l and j_f are the numbers of the first and last temperature intervals used to curve fitting process, y_i is the intensity in the ith interval obtained from experiment and $y(x_i)$ the intensity given by Eq. (1). A good fit to the experimental glow curve is achieved when the FOM value is lower than 2.5%. The results of deconvolution procedure are shown in Fig. 9. The peak temperatures of LiF:Mg,Dy occur at 395 K, 448 K and 510 K. Kinetic parameters extracted from CGCD procedure are observed in Table 1.

TL kinetic parameters such as activation energy (E) and order of kinetics (b) were also measured by initial rise (IR) and isothermal decay (ID) methods. The kinetic parameters are reliable when the estimated values by different methods are in accordance with each other.

The basis of initial rise (IR) method is that the population of charge carriers in the active trap responsible for a definite glow peak remains unchanged in the initial rise part of the glow peak. It is established at the low temperatures (T is about 10% of the temperature of maximum intensity T_m) (Singh et al., 1988). The following equation shows the changes of the intensity with temperature at initial portion of TL glow

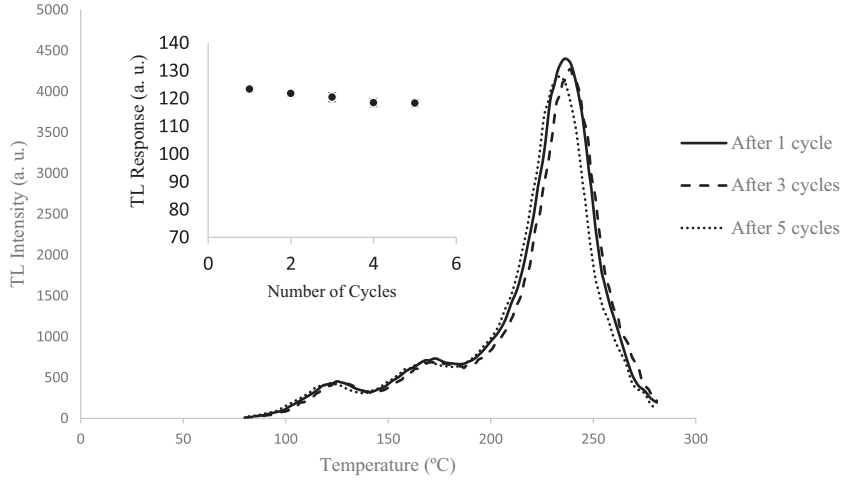

Fig. 8. TL Glow curves of the sample after 1, 3 and 5 cycles of reuse. TL responses for 5 successive cycles of annealing, irradiation and readout are shown as insert. Good stability is observed for the fabricated sample.

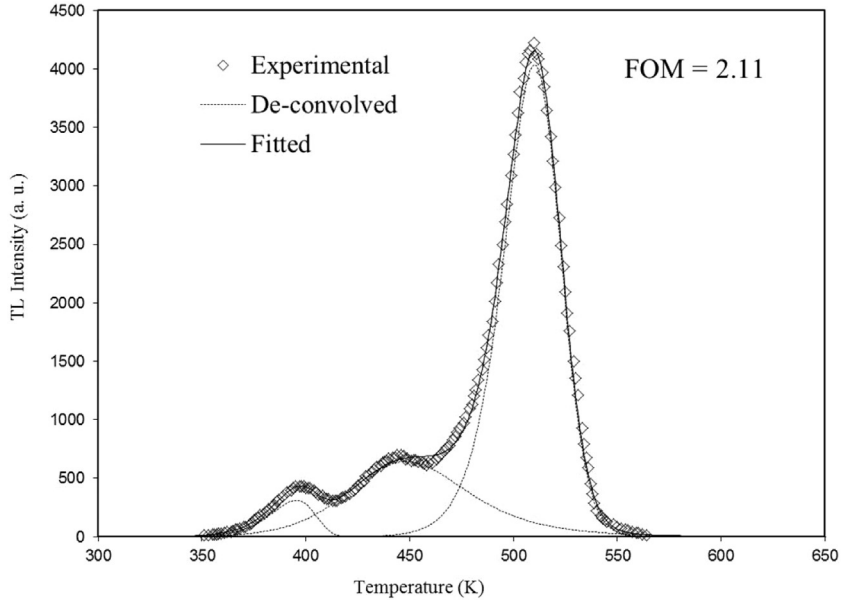

Fig. 9. De-convolved and experimental glow curve of LiF:Mg,Dy with FOM of 2.11. Three separated peaks can be seen in the figure.

Table 1
The obtained kinetic parameters of LiF:Mg,Dy by CGCD, IR and ID methods.

Peak Method	b CGCD	b ID	E (eV) CGCD	E (eV) IR	I_m (a.u.) CGCD	T_m (K) CGCD
1	1.01	1.15	1.24	1.28	339	395
2	2.00	1.89	0.83	0.89	707	448
3	1.38	1.47	1.91	1.97	4453	510

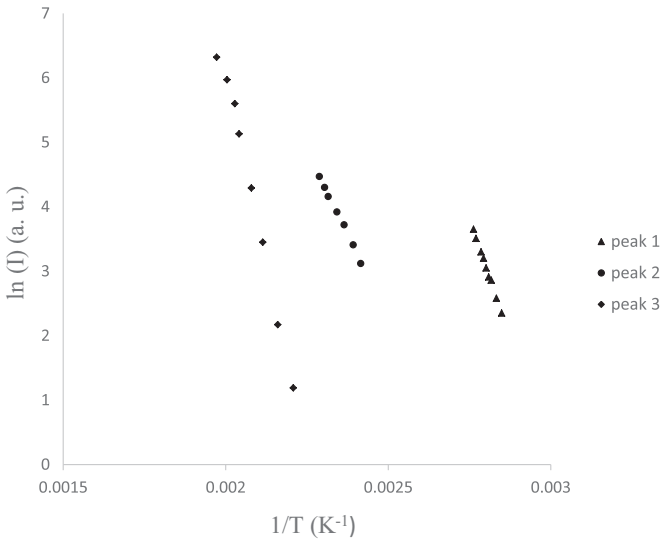

Fig. 10. Plot of ln (I) versus 1/T for three glow peaks of LiF:Mg,Dy. The slope of each straight line is equal to (-E/k).

curve:

$$I(T) = \text{const.}\ \exp(-E/kT)$$

According to this equation, plotting ln (I) as a function of 1/T would yield a straight line with the slope of (-E/k), so activation energy can be evaluated (Furetta and Weng, 1998).

In the case of overlapped peaks of the TL glow curve, a cleaning procedure should be applied. In evaluation of activation energy of peak 2, a thermal cleaning was used to clean peak 1. For this mean, the sample was heated up to 150 °C (temperature of the end point of peak 1) and then activation energy of peak 2 was evaluated using the initial part of remaining curve. In evaluation of activation energy of peak 3, thermal cleaning was done by heating up to 237° C (temperature of the maximum point of peak 3 (T_{m3})). Additionally, intensity of peak 2 at 510 K temperature (T_{m3}) is near 3% relative to intensity of peak 3 which cause to low error in calculation of activation energy of peak 3. The results are drawn in Fig. 10 for three TL peaks.

The order of kinetics of TL glow peaks were also calculated by isothermal decay (ID) method. The kinetics of the thermoluminescence can be expressed by May and Partridge equation:

$$I = -c\, dn/dt = cs'\, n^b \exp[-E/kT] \quad (3)$$

Where I is the TL intensity, c a proportionality constant, s′ pre-exponential factor, n the concentration of filled traps at time t, E the activation energy, T the absolute temperature, b kinetic order and k Boltzmann constant. Differentiation of Eq. (3) at constant T (ID temperature), and some mathematical calculations yield the desired equation:

$$\log(dI/dt) = (2 - 1/b)\log(I) - \beta \log(\gamma) \quad (4)$$

Where β and γ are constants (May and Partridge, 1964).

In this method, to remove overlap influence, prior peak was cleaned by thermal quenching and TL intensity was recorded as a function of time (t) at ID temperatures of 70 °C, 125 °C and 200 °C for peak1, peak 2 and peak 3, respectively. Using ID curves and drawing log (dI/dt) versus log (I) lead to a straight line with slope equal to (2–1/b) according to Eq. (4). So, the kinetic parameter b can be evaluated. The isothermal decay curves and straight lines of peak 1, peak 2 and peak 3 are shown in Fig. 11(a) and (b), respectively. The obtained values are presented in Table 1. A good coincidence can be observed between the obtained results of CGCD and IR and ID techniques.

4. Conclusions

TL dosimetry features of novel highly sensitive LiF:Mg,Dy phosphor were studied. The optimum concentrations of dopants were obtained at 0.7 mol% of Mg and 0.1 mol% of Dy. LiF:Mg,Dy exhibits a sharp dosimetry peak at 510 K and lower temperature peaks at 395 K and 448 K. Both the shape of glow curve and intensity of isolated glow peaks depend on Mg impurity rigorously. The best thermal treatment for

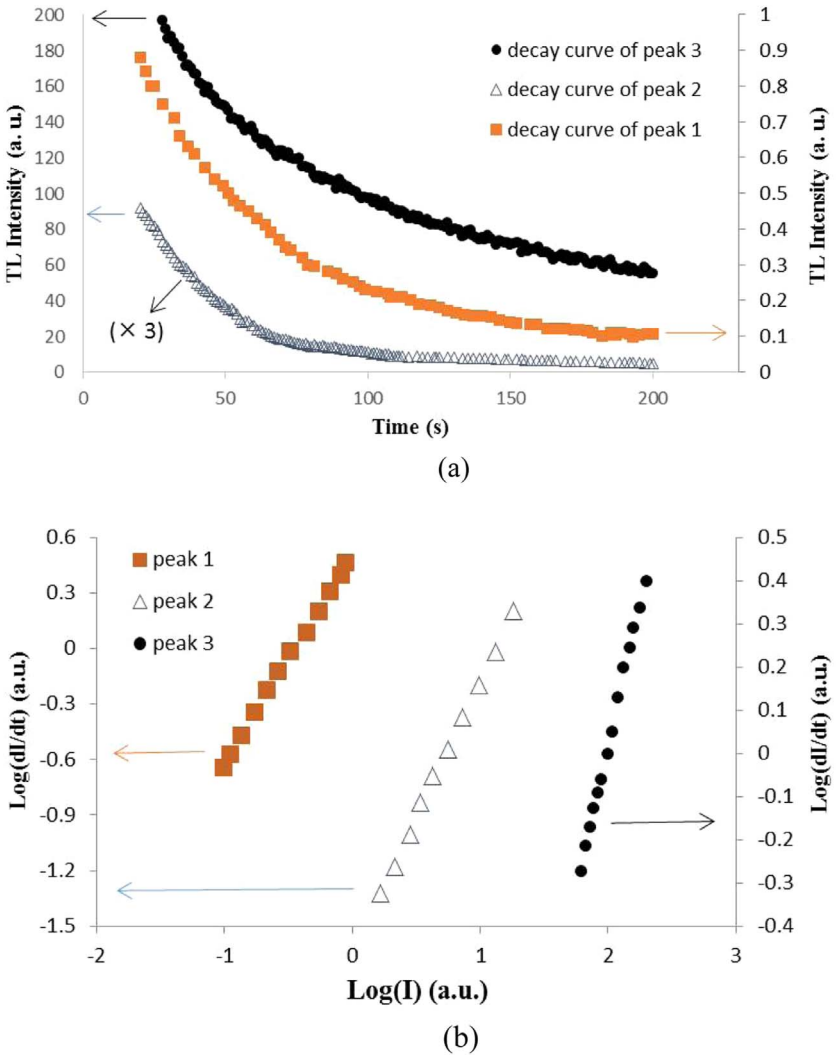

Fig. 11. (a): The isothermal decay curves of peak 1 (at ID temperature of 70 °C), peak 2 (at ID temperature of 125 °C) and peak 3 (at ID temperature of 200 °C) of synthesized dosimeter. The decay curve of peak 2 is multiplied by factor of 3 for more clarity. (b) The straight line log (dI/dt) vs log (I) related to peak 1, peak 2 and peak 3.

annealing regime, 300 °C for 10 min, results in remarkable increasing in TL sensitivity. Because of proper TL sensitivity, low fading, good re-usability and tissue-equivalence, the prepared phosphor is quite hopeful for environmental and personal dosimetry.

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