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Research Article

Thermoluminescence Properties of Novel Self-Agglomerating $CaSO_4$:Eu Phosphors Obtained by an Environmentally Friendly Method

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In this work, we report the thermoluminescence (TL) properties of self-agglomerating $CaSO_4$:Eu samples obtained by an environmentally friendly coprecipitation technique. No binding material is needed to form solid $CaSO_4$:Eu samples. Samples exposed to beta particle irradiation exhibit a TL maximum at 473.15 K when a 5 K/s heating rate is used, they are two times more sensitive than the TLD-100 commercial dosimeter, and their lower detection limit was determined to be less than 0.69 mGy. The computerized glow curve deconvolution carried out fitting the residual glow curves from McKeever method revealed that the whole glow curve is composed of four individual TL peaks with intermediate-order kinetics. The main peak order kinetics is $b = 1.48$. This result agrees with that computed using Chen's formula.

1. Introduction

Since it was first proposed by Farrington Daniels as a useful tool for radiation dosimetry, the increasing use of the thermoluminescence (TL) technique was accompanied by a growing interest in the development of new phosphor materials with properties suitable to be used as TL dosimeters [1–3]. $CaSO_4$ has a long history as one of the most investigated thermoluminescent materials. It exhibits a high TL sensitivity for which it is attractive for dosimetry applications that involves low level doses, such as environmental radiation levels from natural sources [2–8].

In recent years, nano- and microstructure materials have been synthesized and their TL properties studied to evaluate their application in radiation dosimetry. LiF nanocubes doped with different elements are very sensitive under exposure to gamma rays and C^{6+} ions, the Eu and Tb doped samples being the most sensitive [9, 10]. The dosimetric capabilities of Al_2O_3 nanoparticles have also been investigated under exposure to gamma radiation and 85 MeV C^{6+} ions, showing a linear response as well as a low TL fading for Tb doped samples [11].

The synthesis of nano- and microsized $CaSO_4$has also been reported, as well as the effect of different dopants (Ag, Cu, Dy, Eu, and Tb) on their TL properties after exposure to gamma radiation [12, 13]. Eu and Tn doped samples exhibit a prominent TL peak in the temperature range 230–270°C and a linear response upon the radiation dose in the dose range from 10 Gy to 10 kGy, being attractive phosphors for high dose dosimetry, useful in food and seed irradiation [13].

Usually, the synthesis of $CaSO_4$:X (X = dopant) involves the use of sulfuric acid, so important health risks have to be taken into account. Moreover, it contributes to environmental

pollution. On the other hand, for practical convenience, it is preferred to have dosimeters in solid form rather than in powder form. In order to obtain handled solid samples, $CaSO_4$ is embedded in Teflon, glass as a binding material, which prevents having 100% $CaSO_4$ samples [6–8, 14–17].

We reported on the synthesis of novel self-agglomerating Eu doped $CaSO_4$ phosphors, using a cheap, easy, and environmental friendly aqueous solution based chemical route. Solid samples were obtained with no need of any binding material, nor the use of sulphuric acid [18]. Those are the two remarkable advantages of the reported coprecipitation technique over the conventional method used for dosimetric $CaSO_4$ preparation. Glow curves of beta particle irradiated samples exhibited a TL maximum located at 473.15 K using a 5 K/s heating rate.

Going on with the study of the TL properties of the self-agglomerating $CaSO_4$:Eu samples, in this article we report their TL characterization after being exposed to beta particle irradiation, such as TL versus dose response, sensitivity as a function of irradiation-TL readout cycle number, lower detection limit, and TL fading. Furthermore, the computerized glow curve deconvolution using a general order kinetics model reveals that the glow curves are composed of four individual peaks, the main with kinetics order $b = 1.48$.

2. Materials and Methods

$CaSO_4$:Eu powder was synthesized as follows: an Na_2SO_4 (Baker, 99.98%) aqueous solution was added to a $CaCl_2$ (Merck, 99.9%) and $EuCl_3$ (Alfa Aesar, 99.99%) aqueous solution. The reaction proceeded with stirring at room temperature (295 K). Then, 0.0836 g of the precipitated powder was weighed and placed in a 6.0 mm diameter cylindrical mold and compressed at 0.5 ton during 3.0 min using a hydraulic press to fabricate pellet-shaped samples. No binding material was needed to form the solid 100% $CaSO_4$:Eu samples. The obtained pellets were sintered at 973.15 K during 9 h under air atmosphere using a Thermolyne 4000 furnace. During the sintering process, the pellets lost *ca.* 30% of their mass. The thickness of the samples after being sintered is *ca.* 0.5 mm. The $EuCl_3$ weight added to the aqueous solution was calculated to have 0.05 mol% of dopant, considering this concentration in the initial solution. These obtained detectors are fully mechanically stable.

A Risø TL/OSL-DA-20 unit equipped with a ^{90}Sr beta source was used to perform beta particle irradiations and TL measurements. All irradiations were accomplished using a 5 Gy/min dose rate at room temperature (295 K), and the TL readouts were carried out under N_2 atmosphere using a 5°C/s heating rate, except for the McKeever method readouts, for which a 2 K/s heating rate was used. Photoluminescence data were collected in a spectrofluorometer brand SPEX, model FLUOROMAX. X-ray diffraction (XRD) patterns were obtained in a Rigaku Geigerflex diffractometer equipped with a graphite monochromator by using Cu-Kα radiation (λ = 1.542 Å).

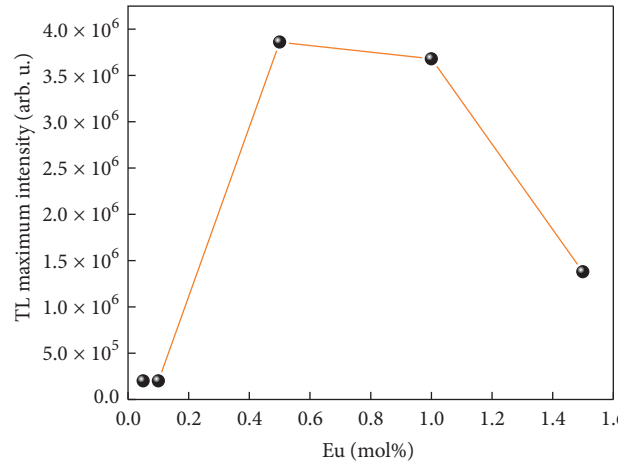

Figure 1: Intensity of the thermoluminescence emission maximum of $CaSO_4$:Eu samples, for 0.1, 0.5, 1.0, and 1.5 mol% Eu concentrations.

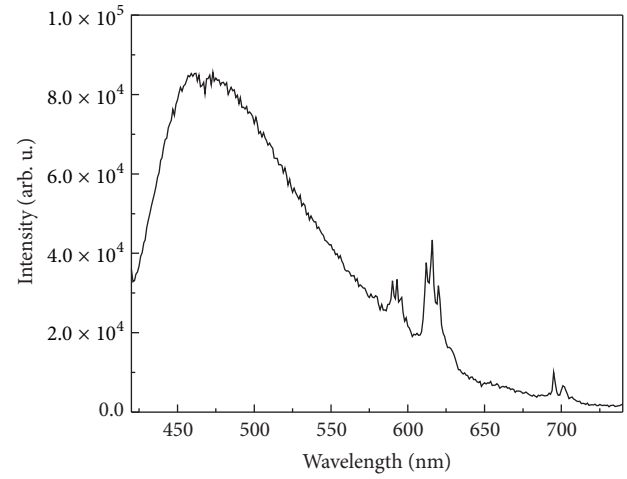

Figure 2: Photoluminescence emission spectrum of synthesized $CaSO_4$:Eu (Eu 0.5 mol%).

3. Results and Discussion

Figure 1 shows the intensity of the TL emission maximum of $CaSO_4$:Eu samples, for 0.1, 0.5, 1.0, and 1.5 mol% Eu concentrations. All samples were exposed to 2.5 Gy of beta particle irradiation. It can be seen that samples with 0.5 mol% exhibit the most intense TL emission, so, for the subsequent characterization, samples with that Eu concentration were used. In order to confirm the presence of Eu into the samples and to identify its valence state, the photoluminescence (PL) of the synthesized $CaSO_4$:Eu was obtained. Figure 2 shows the PL emission spectrum as obtained when exciting by 394 nm light. The presence of emissions with maximum at 590, 617, and 700 nm can be noted, revealing the presence of Eu^{3+} [19].

Figure 3 shows the X-ray diffraction (XD) pattern of synthesized $CaSO_4$:Eu samples. As can be seen, the diffraction peaks agree with those of $CaSO_4$ *anhydrite* (ICDD no. 37-1496), whose reference lines are included for comparison.

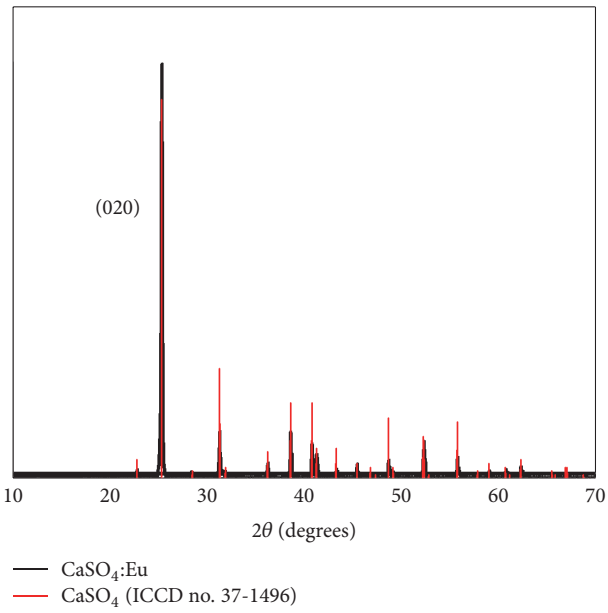

Figure 3: X-ray diffraction (XRD) pattern of synthesized $CaSO_4$:Eu, together with the reference XRD peaks of $CaSO_4$ *anhydrite* (ICDD 37-1496).

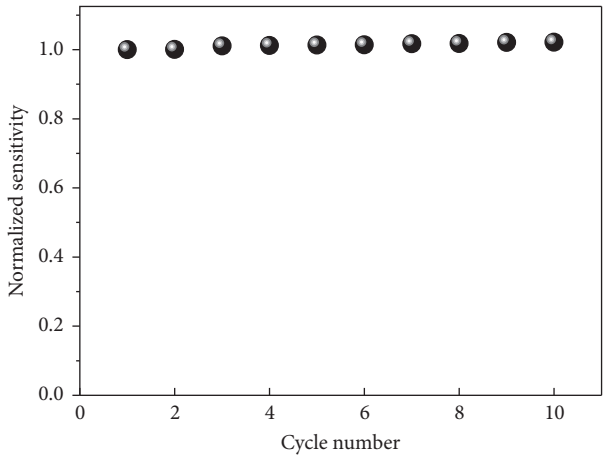

Figure 4: Normalized sensitivity as a function of the irradiation-TL readout cycle number.

Figure 4 shows the normalized sensitivity of a sample as a function of the irradiation-TL readout cycle number. All ten irradiations were carried out using a 1.0 Gy dose without preirradiation annealing. The first and the last readout differ as low as 3%. This result shows that the TL intensity of this phosphor was scarcely changed during the 10 cycles.

Figure 5 shows the glow curves of $CaSO_4$:Eu exposed to beta particle irradiation, in the dose range from 0.08 up to 1.0 Gy. A defined glow curve and the fact that the TL intensity increases for increasing doses can be seen. In fact, higher doses were also used (up to 170 Gy), as will be shown. No shift of the TL maximum was observed. The form factor computed taking the maximum of the glow curve as

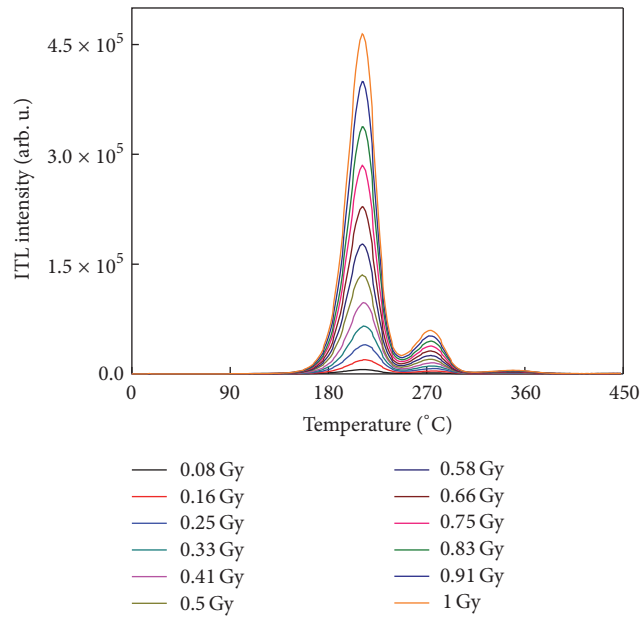

Figure 5: Thermoluminescence glow curves of pellet-shaped $CaSO_4$:Eu samples, after being exposed to beta particle irradiation in the 0.08–1.0 Gy dose range.

a peak is 0.44, close to the 0.42 value characteristic of first-order processes [20]. The lack of exact agreement with the theoretically ideal value 0.42 could indicate the superposition of more than one individual peak and/or that non-first-order kinetic order TL processes are involved. The TL maximum is located at around 473.15 K, considered suitable for dosimetry applications. Other less intense maxima are observed around 443.15 K and above 773.15 K, respectively.

Figure 6(a) shows the integrated TL (ITL) as a function of the irradiation dose, in the range from 0.08 to 10 Gy of beta particle irradiation. Figure 6(b) shows ITL for doses up to 150 Gy. For the lower doses, a superlinear behavior can be seen, while, for doses greater than 10 Gy, a sublinear dependence is observed, with saturation clues above 50 Gy. The lower detection limit (LDL) was determined to be 0.69 mGy [21]. The LDL depends on both the sample and upon the reading system. In spite of the LDL value and the fact that the linear dependence was found to lower investigated doses, the system used to irradiate samples does not allow delivering doses lower than 80 mGy, and so further investigations should be carried out in order to study the TL features of the synthesized $CaSO_4$ at lower dose levels.

Figure 7 shows the ITL as a function of the time interval elapsed between the irradiation and the corresponding TL readout. As can be seen, for the investigated time intervals the TL signal displays a very stable behavior with a 2.4% loss of the initial integrated TL (that recorded just after irradiation) after being stored in darkness at room temperature. In all cases, samples were exposed to 1.0 Gy of beta particle irradiation.

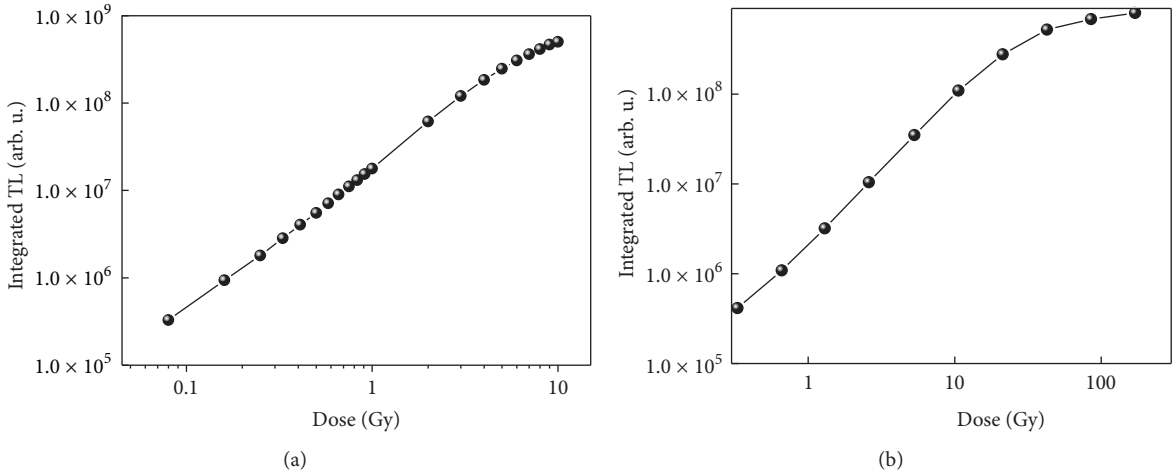

Figure 6: Integrated thermoluminescence as a function of irradiation dose, in the range from (a) 0.08 to 10 Gy and (b) up to 170 Gy.

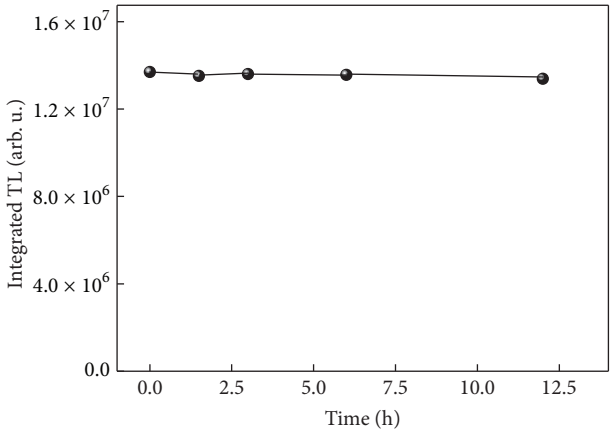

Figure 7: Integrated thermoluminescence (TL) as a function of the time interval elapsed between irradiation and the corresponding TL readout.

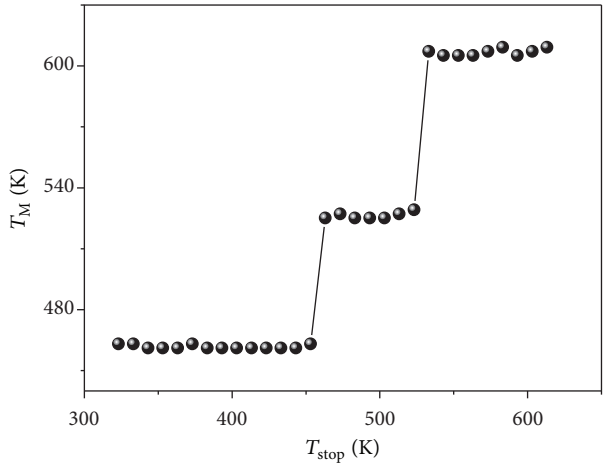

Figure 8: Position of the maximum emission temperature, T_M, arisen from the glow curves obtained after partial thermal cleaning up to temperature T_{stop}.

The glow curve deconvolution (GCD) was carried out using a general order expression for the individual TL peaks to be fit, such as [22]

$$I(T) = I_m b^{b/(b-1)} \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\left[Z_m + (b-1)(1-\Delta)\frac{T^2}{T_m^2}\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)\right]^{b/(1-b)}, \quad (1)$$

where b is the kinetics order, $Z_m = 1 + (b-1)\Delta_m$, $\Delta = 2kT/E$, and $\Delta_m = 2kT_m/E$. The experimental data for the GCD of the $CaSO_4$:Eu glow curve were collected according to the McKeever method: after irradiation of samples, a TL readout (partial thermal cleaning) up to a specific temperature T_{stop} is followed by a new readout of the sample up to 400°C in order to obtain the residual glow curve [23]. The latter glow curves were treated for the fitting from which the kinetics parameters were obtained.

Figure 8 shows the graph T_m-T_{stop} that is obtained by registering the first TL maximum corresponding to the glow curve that follows to partial cleaning up to a temperature T_{stop}. As can be seen, there are three well defined maxima, in accordance with the glow curves displayed in Figure 5. Although in Figure 5 the maxima do not exhibit shift when doses change, the steps in Figure 8 show curvature that indicate that non-first-order processes are involved.

The computational work started from the residual glow curve corresponding to the highest T_{stop} temperature that allows isolating the highest possible individual TL peak and in this way evaluating its trapping parameters with the best accuracy. Once these trapping parameters were computed, the next step is to proceed to the deconvolution of the residual glow curves corresponding to lower T_{stop} temperatures fixing the values of the evaluated kinetics parameters of the highest peak and that allows resolving the following individual peak. The process follows to deconvolute the whole glow curve.

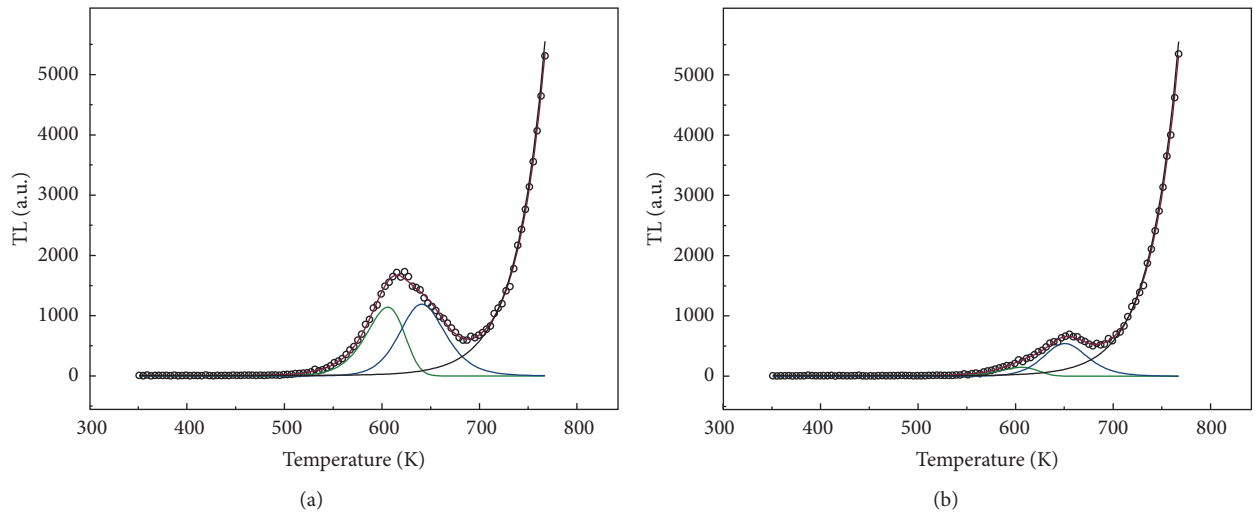

Figure 9: Examples of glow curve deconvolution (GCD) of $CaSO_4$:Eu glow curve, as obtained after partial thermal cleaning up to (a) 623 K and (b) 643 K.

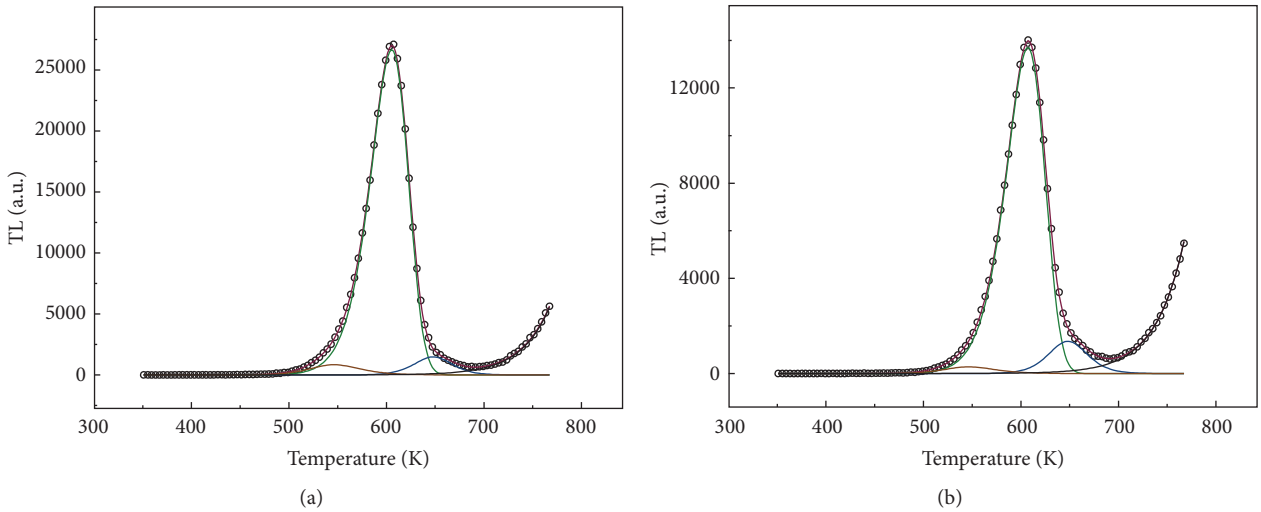

Figure 10: Examples of glow curve deconvolution (GCD) of $CaSO_4$:Eu glow curve, as obtained after partial thermal cleaning up to (a) 543 K and (b) 593 K.

The glow curves fitting was performed using the MINUIT program [24], where the goodness of the fit was tested by the figure of merit (FOM) [25], defined by

$$\text{FOM} = \sum_i \frac{\left|Y_{\text{Exper}} - Y_{\text{Fit}}\right|}{A} \quad (2)$$

with Y_{Exper} being the data of the experimental glow curve, Y_{Fit} being the fitted glow curve, and A being the area of the fitted glow curve.

Four steps of the procedure followed for the GCD are shown in Figure 9. The glow curve shapes after the partial thermal cleaning at temperatures above 623 K and 643 K are shown in Figures 9(a) and 9(b). At these high thermal cleaning temperatures, the highest TL peak can be studied. In the case of Figure 9(a), the low temperature TL peak is a residual of a higher intensity TL peak, which will be shown below. The glow curve shapes for T_{stop} = 543 and 593, respectively, are shown in Figures 10(a) and 10(b). These glow curves include the high temperature TL peak at 643 K shown in Figure 9, a main peak, and a satellite at its low temperature tail.

The complete GCD of the whole glow curve is shown in Figure 11. The vertical axis is displayed in logarithmic scale in order to observe the goodness of fit as well as the detailed resolution in the individual peaks. The kinetics parameters obtained from the GCD are summarized in Table 1. In this table, b is the kinetics order, T_{max} the maximum of the TL peak, E the activation energy of the trapping states associated with the peak, and s the preexponential factor. The main peak is peak 1 of Table 1 and the trapping parameters of the peak at lower temperature shown in Figure 11 are not included.

Table 1: Kinetics parameters obtained from the GCD analysis. In this table, b is kinetics order, T_{max} the maximum of the TL peak, E the activation energy of the trapping states associated with the peak, and s the preexponential factor.

Peak	b	T_{max} (K)	E (eV)	s (s^{-1})
1	1.48	461	1.82	$7.50 \pm 1.9 \times 10^{18}$
2	1.24	525	1.96	$6.48 \pm 0.55 \times 10^{17}$
3	1.15	606	1.68	$2.88 \pm 0.8 \times 10^{12}$
4	2	645	2.18	$4.4 \pm 2.9 \times 10^{16}$

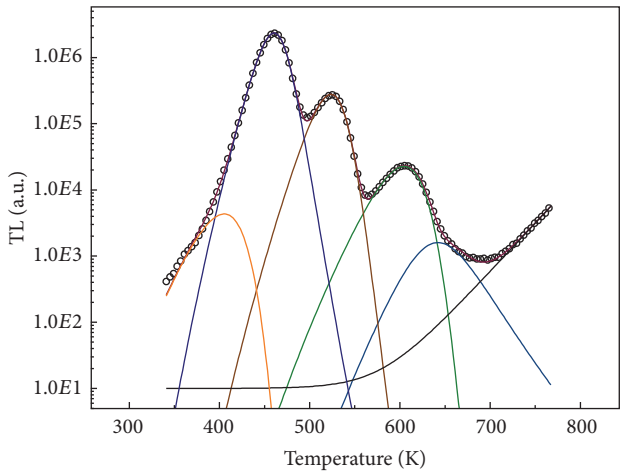

Figure 11: Glow curve of $CaSO_4$:Eu resolved into individual TL peaks by glow curve deconvolution (GCD) analysis.

The main TL peak predominates over the other ones. Taking this fact into account, Chen's formula

$$E_\alpha = c_\alpha \left(\frac{KT_m^2}{\alpha} \right) - b_\alpha \left(2KT_m \right) \tag{3}$$

was used to estimate the activation energy. In Chen's formula, $\alpha = \delta$ or τ or ω, and

$$\begin{aligned} c_\tau &= 1.51 + 3\left(\mu\text{-}0.42\right) \\ b_\tau &= 1.58 + 4.2\left(\mu\text{-}0.42\right) \\ c_\delta &= 0.976 + 7.3\left(\mu\text{-}0.42\right) \\ b_\delta &= 0 \\ c_\omega &= 2.52 + 10.2\left(\mu\text{-}0.42\right) \\ b_\omega &= 1. \end{aligned} \tag{4}$$

The activation energy value obtained using Chen's formula was 1.9 eV, which is in good agreement with the GCD results.

4. Conclusions

In this work, the thermoluminescence properties of beta particle irradiated self-agglomerating $CaSO_4$:Eu are reported. In addition to being a self-agglomerating phosphor (no binding material was needed to fabricate 100% $CaSO_4$:Eu solid samples), the synthesized $CaSO_4$ is obtained through an easy, cheap, and environmentally friendly chemical reaction. These pellet-shaped samples exhibit a TL maximum located at 200°C when a 5°C/s heating rate is used and are two times more sensitive than the commercially available dosimeter TLD-100, and their lower detection limit was determined to be less than 1.0 mGy. Although the synthesized samples were characterized after beta particle exposure, from previous reports (some cited in Section 1) it is known that other kinds of radiations also excite the TL in $CaSO_4$. The computerized glow curve deconvolution carried out fitting the residual glow curves from McKeever experiments revealed that the whole glow curve is composed of four individual peaks with intermediate-order kinetics. The main peak order kinetics is $b = 1.48$. This result agrees with that computed using Chen's formula, based on the shape of the glow curve. The method here reported can be used to synthesize $CaSO_4$ doped with other impurities different than those used in this work, opening new possibilities in the search of new high performance dosimetric $CaSO_4$ based phosphors.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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