*Appl. Radiat. Isot.* Vol. 39, No. 3, pp. 233–236, 1988
*Int. J. Radiat. Appl. Instrum. Part A*
Printed in Great Britain. 

0883-2889/88 $3.00 + 0.00


# Determination of TL Parameters of $CaSO_4$:Dy Produced at Instituto de Pesquisas Energéticas e Nucleares (IPEN)

L. L. CAMPOS

Departamento de Proteção Radiológica–NP, Instituto de Pesquisas Energéticas e Nucleares–IPEN, Comissão Nacional de Energia Nuclear–CNEN/SP, C.P. 11049, 05499 São Paulo, Brazil

(*Received* 20 *August* 1987)

Two important parameters to be determined in a thermoluminescence study are the frequency factor ($s$) and the trap depth ($E$). The $E$ and $s$ determinations are based on glow curve analysis. Results of experiments made with $CaSO_4$:Dy prepared in the Dosimetric Materials Production Laboratory of Instituto de Pesquisas Energéticas e Nucleares (IPEN) are presented in this paper.

## 1. Introduction

Various kinds of thermoluminescent (TL) phosphors have been used as dosimeters in the field of solid state radiation dosimetry. Anhydrous calcium sulphate, $CaSO_4$, is a wide band gap material that has been shown to be a highly versatile TL dosimeter material with high sensitivity and simple glow curve structure. $CaSO_4$, when activated by dysprosium ($CaSO_4$:Dy), has possible applications in: $\beta$-ray dosimetry;[1] thermal and fast neutron dosimetry;[2,3] mixed $\gamma$-neutron field dosimetry;[4] high exposure dosimetry[5] and it is increasingly used for low dose measurements in x and $\gamma$ radiation fields.[6]

The Dosimetric Material Production Laboratory of IPEN developed a dosimetric grade $CaSO_4$:Dy crystal[7] which, in the form of pellets ($CaSO_4$:Dy + Teflon), has been used in personnel and environmental monitoring.

Glow curves are characterized by phenomenological parameters, such as: activation energy or trap depth ($E$); and frequency factor ($s$), that determine the observed shape. These parameters reflect properties of the TL material that are important in TL dosimetry; for example the stability and temperature of the TL emission. These parameters were determined for the $CaSO_4$:Dy produced at IPEN and are shown in the present work.

## 2. Sample Preparation

Thermoluminescence dosimetry (TLD) grade $CaSO_4$:Dy (0.1 mol % Dy) phosphor was prepared using the method of evaporation in a sealed system[7] developed at IPEN. The starting materials are: commercially available $CaCO_3$ (Baker Analysed Reagent), "specpure" $Dy_2O_3$ (99.999%) from Johnson Matthey Chemicals; and concentrated sulphuric acid from Merck.

Single crystals were obtained and analysed by the x-ray diffraction method that confirmed the monocrystallinity of the samples. This material was crushed and sieved to select grains between 85 and 185 $\mu$m. Freshly prepared samples were heated at 600°C for 1 h. This treatment gives optimum TL sensitivity for the phosphor samples.[8]

The TL response was determined using the Harshaw TL Reader Model 2000 A + B. Light emission was integrated in the temperature interval between 175 and 310°C.

Figure 1 shows the typical TL glow curve of $CaSO_4$:Dy. The main glow peak appears at 200°C. A low temperature peak can be observed at about 140°C. These temperatures were measured in the reader pan. The average sensitivity expressed as the magnitude of the electrical signal in the photomultiplier tube produced by $2.58 \times 10^{-4}$ C kg$^{-1}$ (1 R) of exposure on 1 mg of the sample is 6.95 nC R$^{-1}$ mg$^{-1}$, and the ratio of the main dosimetric peak height to the 140°C peak height is about 4.5.

## 3. Method

The methods used to determine the trap parameters were: various heating rates; initial rise; and peak shape method.

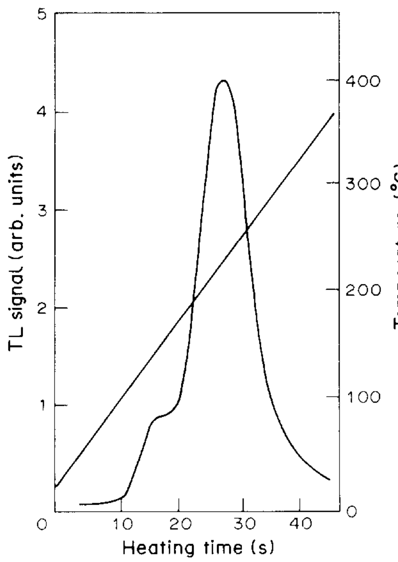


Fig. 1. TL glow curve of $CaSO_4$:Dy.

*3.1. Various heating rates*

This method was suggested by Hoogenstraaten.[9] He proposed to use different heating rates to evaluate $E$ based on the variation of the peak temperature $T_m$ with the heating rate $\beta$. The plot of $\ln(\beta/T_m^2)$ vs $1/T_m$ yields a linear relation:

$$\ln(\beta/T_m^2) = \ln(sk/E) - E/kT_m \qquad (1)$$

the straight line resulting has a slope $-E/k$, where $k$ is Boltzmann's constant and hence $E$ can be found. Extrapolation to $1/T_m = 0$ gives the value of $\ln(sk/E)$ from which $s$ can be calculated by the insertion of $E/k$ found from the slope.

*3.2. Initial rise*

This method, proposed by Garlick and Gibson,[10] is the simplest procedure to obtain an estimate of the trap depth and is independent of the order of kinetics involved. The method basically assumes the following: (i) in the early rising range of temperatures, i.e. $T \ll T_m$, the rate of change of trapped carrier population is negligible (and hence the intensity is strictly proportional to $\exp(-E/kT)$); (ii) the frequency factor essentially remains the same at all temperatures; (iii) there is no overlap of glow peaks belonging to different trapping levels. Thus this method requires solving:

$$\ln I = c - E/kT \qquad (2)$$

where $c$ is a constant.

A plot of $\ln I(T)$ vs $1/T$ for this leading part of the glow curve therefore yields a straight line of slope $-E/k$ from which $E$ can be calculated.

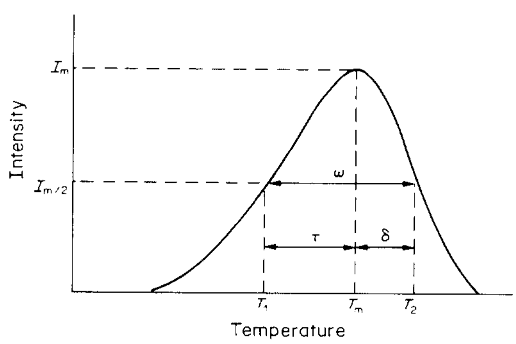


Fig. 2. A schematic glow peak showing the parameters $\omega = T_2 - T_1$; $\tau = T_m - T_1$; $\delta = T_2 - T_m$.

*3.3. Glow curve shape*

$T_m$, $T_1$ and $T_2$ which are respectively the peak temperature and temperatures on either side of $T_m$ corresponding to half the peak intensity (Fig. 2), are dependent upon the shape of the glow peak and there are several equations developed to relate $E$ with all or with some of these temperatures. Three methods based on the glow curve shape were used in this study:

*3.3.1. Lushchik.*[11] This method makes use of the descending part of the glow peak assuming that the area of the half peak equals the area of the triangle having identical height and half width. For second order kinetics the expression to evaluate $E$ is:

$$E = 2kT_m^2/\delta \qquad (3)$$

where $\delta = T_2 - T_m$.

*3.3.2. Halperin–Braner.*[12] This method assumes that the area of the half peak at the rising part is the same as the area of a triangle, and for second order kinetics the expression to evaluate $E$ is:

$$E = \frac{2kT_m^2}{\tau}(1 - 3\Delta) \qquad (4)$$

where $\Delta = 2kT_m/E$ and $\tau = T_m - T_1$.

*3.3.3. Chen.*[13] This method uses both $T_1$ and $T_2$ and assumes $e^{\Delta} \simeq 1 + \Delta$, then:

$$E = 2kT_m \frac{1.76\,T_m}{\omega - 1} \qquad (5)$$

where $\omega = T_2 - T_1$.

In all cases the frequency factor can be evaluated by means of the question:

$$\frac{\beta E}{kT_m^2} = s\exp(-E/kT) \qquad (6)$$

derived from the Randall–Wilkins[14] equation.

## 4. Experimental Procedure

Before use, freshly prepared $CaSO_4$:Dy was annealed for 1 h at 400°C. Irradiations were performed using a $^{60}Co$ source (20 mCi) under electronic equilibrium conditions to an exposure of $2.58 \times 10^{-4}$ C kg$^{-1}$. The measurements were always carried out about 24 h after irradiation. A linear heating rate of 9.7 K s$^{-1}$ was used in all cases of thermoluminescence read-out, except when the method based on different heating rates was applied.

Table 1. Values of heating rates, $T_m$ and glow curve shape parameters of $CaSO_4$:Dy determined by the different heating rates method

| $\beta$ $(K\ s^{-1})$ | $T_m$ $(K)$ | $\frac{1000}{T_m}$ $(K^{-1})$ | $\frac{\beta}{T_m^2}$ $(K^{-1}s^{-1})$ | $\delta$ $(K)$ | $\omega$ $(K)$ | $\mu$ |
|---|---|---|---|---|---|---|
| 4.38 | 451.47 | 2.225 | $2.15 \times 10^{-5}$ | 50.37 | 98.55 | 0.51 |
| 7.27 | 462.02 | 2.164 | $3.41 \times 10^{-5}$ | 47.25 | 90.87 | 0.52 |
| 9.66 | 466.20 | 2.145 | $4.44 \times 10^{-5}$ | 40.57 | 80.18 | 0.51 |
| 12.73 | 470.32 | 2.126 | $5.75 \times 10^{-5}$ | 43.28 | 82.74 | 0.52 |
| 16.47 | 475.58 | 2.103 | $7.28 \times 10^{-5}$ | 41.18 | 82.35 | 0.50 |
| 19.30 | 479.51 | 2.085 | $8.39 \times 10^{-5}$ | 48.25 | 86.85 | 0.53 |

Each reported value corresponds to the average of five measurements.

In this work only parameters corresponding to the main glow peak shown in Fig. 1 were determined.

The following linear heating rates were used in the different heating rates method: 4.38, 7.27; 9.66; 12.73; 16.47 and 19.30 K $s^{-1}$, obtaining the glow curves for each case.

In order to apply the initial rise method and the method based on glow curve shape, the dosimetric peak was isolated by means of the Hoogenstraaten method.[9] This consists in erasing all peaks preceding the one to be studied by one thermal treatment. For the $CaSO_4$:Dy, this treatment is 100°C for 15 min.

The initial rise method was applied fitting the rising part of the glow curve to an exponential function and plotting $\ln I(T)$ vs $1/T$.

To apply the methods based on the glow curve shape, the paramaters $\tau = T_m - T_1$, $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$ (Fig. 2) were determined. The kinetics order was estimated by means of the Chen method,[13] which is based on the value of the symmetry factor $\mu_g = \delta/\omega$. These values were substituted in equations corresponding to the used methods.

All fittings were effected by means of the least squares method evaluating $E$ with an uncertainly of $\pm\ \sigma$(standard deviation of the mean value) and $s$ values in a range between two extreme values.

## 5. Results and Conclusions

The variation of $T_m$ with the heating rate is shown in Table 1 and the plot of $\ln(\beta/T_m^2)$ vs $1/T_m$, obtaining a linear relation, is shown in Fig. 3, from which $E$ and $s$ values were obtained by applying equation (1).

The linear relation obtained by plotting $\ln I(T)$ vs

Table 2. Values of $I(T)$ and $T$ for $CaSO_4$:Dy determined by the initial rise method

| $I(T)$ (arb. units) | $T$ $(K)$ | $\frac{1000}{T}$ $(K^{-1})$ |
|---|---|---|
| 20 | 312.89 | 3.196 |
| 30 | 316.45 | 3.160 |
| 40 | 318.87 | 3.136 |
| 50 | 320.95 | 3.116 |
| 60 | 321.91 | 3.106 |
| 70 | 322.78 | 3.088 |

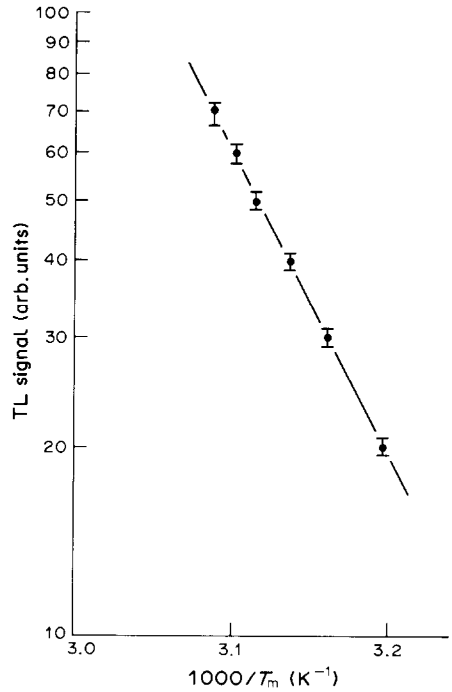


Fig. 3. Linear relation $\beta/T_m^2$ against $1000/T_m$ obtained using different heating rates.

$1/T_m$ (Table 2) in the initial rise method is shown in Fig. 4. From this linear relation the value of $E$ was obtained applying equation (2).

The symmetry factor was found to have a value of $0.51 \pm 0.01$. This symmetry value corresponds to a kinetic order of two.

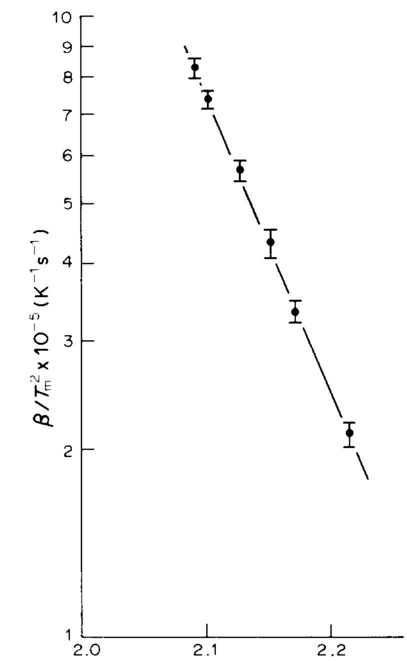


Fig. 4. Linear relation between $\ln I$ and $1000/T$ obtained applying the initial rise method.

Table 3. Values of activation energy and frequency factor of $CaSO_4$:Dy TL dosimeter determined by different methods

| Method | $E$ (eV) | $s$ ($s^{-1}$) |
|---|---|---|
| Different heating rates | $0.95 \pm 0.05$ | $10^9$–$10^{11}$ |
| Initial raise | $1.00 \pm 0.08$ | $10^9$–$10^{11}$ |
| Glow curve shape: | | |
| Lushchik | $0.87 \pm 0.07$ | $10^8$–$10^{10}$ |
| Halperin–Braner | $0.85 \pm 0.07$ | $10^8$–$10^9$ |
| Chen | $0.80 \pm 0.06$ | $10^7$–$10^9$ |

The values of $E$ were obtained by glow curve shape methods substituting the values of the glow peak parameters in equations (3), (4) and (5). These parameters are listed in Table 1.

The values of $s$ were obtained applying equation (6).

In Table 3 values of the activation energy and frequency factor of $CaSO_4$:Dy TL material determined by different methods are shown.

In conclusion, the values of $E$ and $s$ obtained show good agreement using the different methods of calculation.

These results are in reasonable agreement with those obtained by others[15,16] for $CaSO_4$:Dy.

## References

1. Rosa L. A. R., Caldas L. V. E. and Cunha P. G. *Radiat. Prot. Dosim.* **14,** 329 (1986).
2. Gordon A. M. P. L. and Muccillo R. *Int. J. Appl. Radiat. Isot.* **30,** 571 (1978).
3. Pradhan A. S., Bhatt R. C., Lakshmanan A. R., Chandra B. and Shindi S. S. *Phys. Med. Biol.* **23,** 723 (1978).
4. Ayyangar K., Chandra B. and Lakshmanan A. R. *Phys. Med. Biol.* **19,** 656 (1974).
5. Caldas L. V. E. and Mayhugh M. R. *Health Phys.* **31,** 451 (1976).
6. Campos L. L. and Lima M. F. *Radiat. Prot. Dosim.* **14,** 333 (1986).
7. Campos L. L. *J. Lum.* **28,** 481 (1983).
8. Morato S. P., Gordon A. M. P. L., Santos E. N., Gomes L., Campos L. L., Prado L., Vieira M. M. F. and Bapat V. N. *Nucl. Instrum. Methods* **200,** 449 (1982).
9. Hoogenstraaten W., *Philips Res. Rep.* **13,** 515 (1958).
10. Garlick G. F. J. and Gibson A. F. *Proc. Phys. Soc.* **60,** 574 (1948).
11. Lushchik C. B. *Soviet Phys. JEPT* **3,** 390 (1956).
12. Halperin A. and Braner A. A. *Phys. Rev.* **117,** 408 (1960).
13. Chen R. *J. Appl. Phys.* **40,** 570 (1969).
14. Randall J. T. and Wilkins H. M. F. *Proc. Roy. Soc. (London) A* **184,** 347 (1945).
15. Azorín J., Gutiérrez A. C. and Martínez C. G. A. *Radiat. Eff.* **84,** 263 (1983).
16. Furetta C. and Gennai P. *Radiat. Eff.* **55,** 23 (1981).