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EVALUATION OF KINETICS PARAMETERS OF CaF_2:Tm (TLD - 300)TL DOSIMETERS

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ABSTRACT

Kinetics parameters of the 1st, 3rd and 5th peak of CaF_2:Tm TL dosimeters were studied by several methods.

INTRODUCTION

During the last few years CaF_2:Tm(TLD-300) has been extensively used for thermoluminescence dosimetry of ionizing radiation. In using TL dosimeters one of the main difficulties remains in the evaluation of the time occurence of an anomalous exposure superposed to a normal one. This problem has been studied by using $CaSO_4$ and CaF_2.[1] The simultaneous estimation of dose and elapsed time since exposure are based upon different behaviours of peaks in the glow curve.[2] For this purpose it is important to have a good knowledge on some kinetics parameters. There is a number of papers on determination of kinetics parameters of $CaSO_4$[3-5], but none on CaF_2 yet. The aim of this work is to determine experimentally the kinetics parameters of the 1st, 3rd and 5th peak of CaF_2:Tm TL dosimeters by the methods based on initial rise, peak's shape, different heating rates, isothermal decay and numerical fitting method comparing the results obtained among them.

EXPERIMENTAL

Materials used in this research were CaF_2:Tm (TLD-300) ribbons (1x3x3mm; 20 ± 2 mg) Harshaw.

Samples were annealed during 30 min at 573 K before use. The irradiations with ^{60}Co gamma radiation were made in the calibration center of ININ and in the Physics Department, University of Rome, at absorbed doses ranging from 100-150 mGy.

The measurements were made in a Harshaw 2000 A TL analyser connected to a

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picoprocessor Harshaw 2080. The heating rate used was 2.02 K s^{-1} except in the case when the different heating rate method was applied.

Methods used to determine the kinetic parameters were[6]:

Initial Rise.

The initial rise method was applied by fitting the rising part of a glow peak to an exponential function and plotting ln I against 1/T. This method was applied for first and third peak.

Starting from a full glow curve, Fig. 1, the intensity of the left hand side of the first peak must be an exponential function of T up to 1-2% of the full glow peak intensity at the maximum. So, a plot of ln I against 1/T must be linear; Fig. 2 shows this plot, from which the slope is equal to -E/k.

For the third peak a partial annealing has been used to erase the first peak only and to put into evidence the rise of the third peak (see Fig. 3). The slope procedure has been used to find out E from the plot ln I vs 1/T.

For fifth peak it was impossible to find the best annealing without any influence on the peak itself.

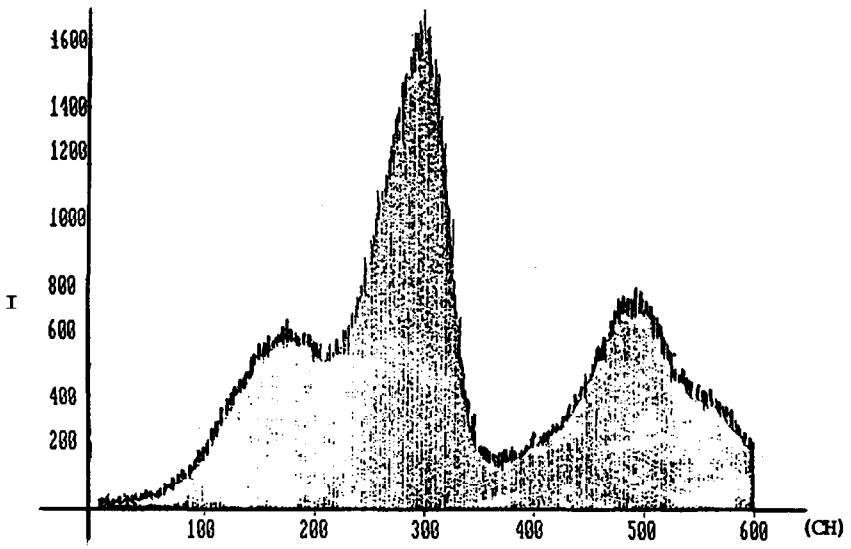

Fig.1. TLD-300 full glow-curve.

Peak's shape methods

Methods based on peak shape used in this study were those of Lushchick, of Halperin and Braner and of Chen. The order of the kinetics for each peak was estimated by means of Chen's method based on the value of the symmetry factor, μ_g. The value of μ_g puts into evidence a first order kinetics for first and third peak and second order for fifth peak. Glow peak parameters

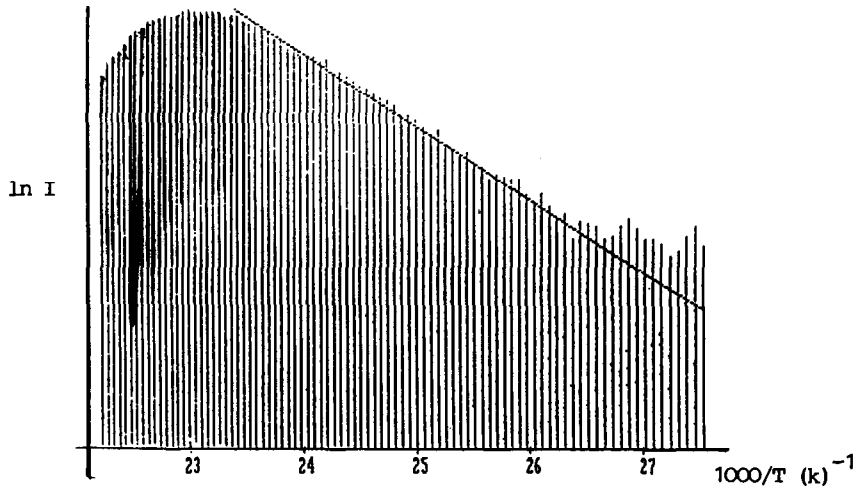

Fig.2. Initial rise fit.

required to apply these methods (see Fig. 4) are: $\delta = T_2 - Tm$; $\tau = Tm - T_1$; $\omega = T_2 - T_1$; $\mu_g = \frac{\delta}{\omega}$.

Evaluation of E by the method of Lushchick has been done for the three peaks using the following equations, corrected by Chen:

$E = 0.976\ k\ Tm^2/\delta$ 1st order kinetics

$E = 1.71\ k\ Tm^2/\ \delta$ 2nd order kinetics

The Halperin-Braner's equations (corrected by Chen) have been used for the left half side of first peak

$E = 1.52\ (kTm^2/\tau) - 3.16\ kTm$ first order

For the third and fifth peaks the equation of Chen has been used.

$E_\alpha = C_\alpha\ (kTm^2/\alpha) - b_\alpha(2\ kTm)$

where α stands for δ, τ or ω and the values of C_α and b_α for the three methods are:

$C_\tau = 1.51 + 3\ (\mu_g - 0.42)$; $b_\tau = 1.58 + 4.2\ (\mu_g - 0.42)$

$C_\delta = 0.976 + 7.3\ (\mu_g - 0.42)$; $b_\delta = 0$

$C_\omega = 2.52 + 10.2\ (\mu_g - 0.42)$; $b_\omega = 1$

Different heating rates

The Booth-Bohun method was applied for peaks first, third and fifth using two different heating rates: $\beta = 2.02\ K{\cdot}s^{-1}$ and $\beta = 6.1\ K{\cdot}s^{-1}$. The value of E was then obtained from the equation:

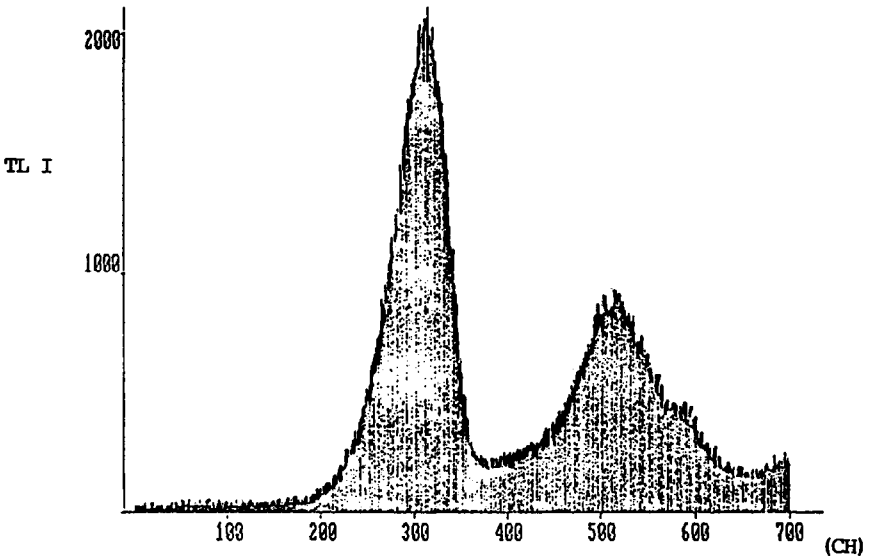

Fig.3. TLD-300 after partial annealing.

$$E = \frac{kTm_1 \; Tm_2}{Tm_1 - Tm_2} \ln \frac{\beta_1}{\beta_2}(Tm_2/Tm_1)^2$$

The Hoogenstraaten method was also applied for the three peaks using the following heating rates: 2.02, 3.0, 5.2, 6.1 and 10.3 $K \cdot s^{-1}$. The value of E was determined by plotting $\ln (Tm^2/\beta)$ against $1/Tm$ to obtain a linear relation. Fig. 5 shows these plots for the three peaks, from which the slope is equal to E/k.

Isothermal decay

Isothermal decay of the irradiated dosemeters was accomplished by submitting them to 473 ± 1 K and 483 ± 1 K for different times between 10 and 120 s measuring the phosphorescence decay at these temperatures. The plots of ln I against t shown in Fig. 6 were fitted to the linear relation which slope is equal to:

$$m_i = - s \exp (-E/kT_i) \qquad i = 1.2$$

from which

$$\ln m_i = \ln (-s) - E/kT_i$$

The slopes m_1 and m_2 at the given temperatures were taken obtaining:

$$\ln \frac{m_1}{m_2} = \frac{1}{T_1} \frac{1}{T_2} (-E/k)$$

Then, the value of E was calculated for the three peaks from this equation.

Numerical fitting method

Numerical curve fitting of glow peaks was used for 1st, 3rd and 5th peaks considering first order for 1st and 3rd peak and second order for 5th peak.

We consider the approximation proposed by Mohan and Chen[7] for first and second order kinetics.

$$I(T)=A \exp\left(-E/kT - s/\beta \int_{T_0}^{T} \exp(-E/kT')\, dT'\right) \qquad \text{first order}$$

$$I'(Ti) = \frac{\exp(-E/kTi)}{\exp(-E/kTm)} \cdot \frac{1 + (s'n/\beta) \int_{To}^{Tm} \exp(-E/kT)\, dT}{1 + (s'n/\beta) \int_{To}^{Ti} \exp(-E/kT)\, dT}^{2} \qquad \text{second order}$$

where A is a constant which is adjusted so that the intensity maxima of the experimental and theoretical curves coincide, E the activation energy in eV, k the Boltzmann constant in $eV \cdot K^{-1}$, T the temperature in K, To the initial temperature in K, Tm the temperature at maximum intensity in K, s the frequency factor in s^{-1}, s' a constant and n_0 the initial concentration of trapped carrier such that s'n has the dimensions $(time)^{-1}$ as the frequency factor.

The integral $\int_{To}^{T} \exp(-E/kT)dT$ was evaluated by means of the asymptotic series given by Haake.

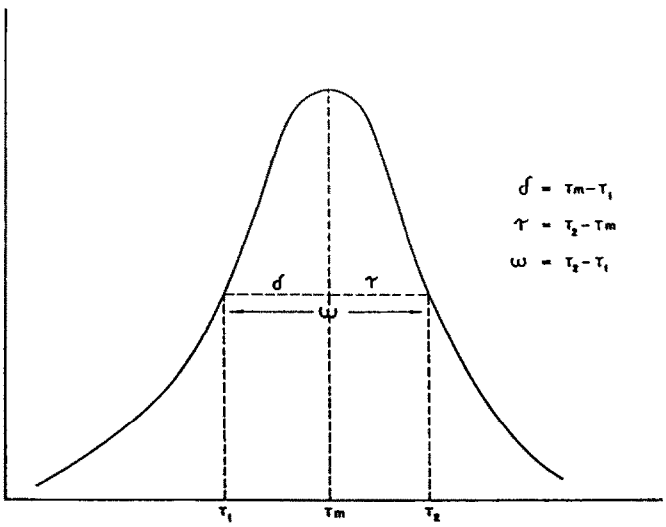

Fig.4. Glow-curve parameters.

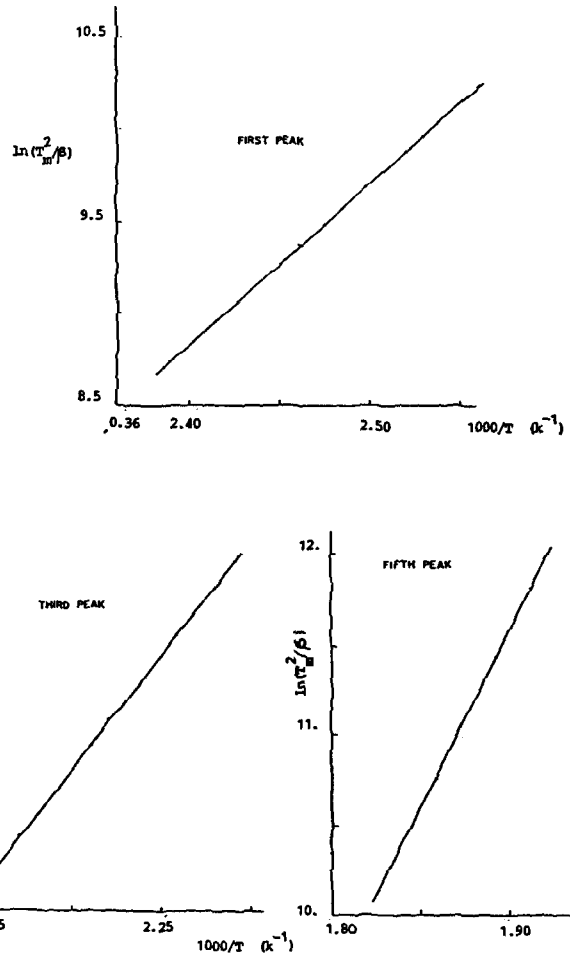

Fig.5. Different heating rates method.

$$\int_{To}^{T} \exp(-E/kT')dT' \cong T \exp(-E/kT) \sum_{n=1} \frac{kT}{E}^{n} (-1)^{n-1} n!$$

From the experimental curve, the intensities Ii corresponding to 20 temperatures, Ti, in the range of about 0.9 Tm to 1.1 Tm were taken. The peak was normalized by dividing each Ii by Im to give the intensities I_i. A value of E obtained by using another method was used as a "guess".

The sum S_1 of the differences between corresponding intensities was calculated from

$$S_1 = \sum_{i=1}^{N} (I'(Ti) - Ii) /N$$

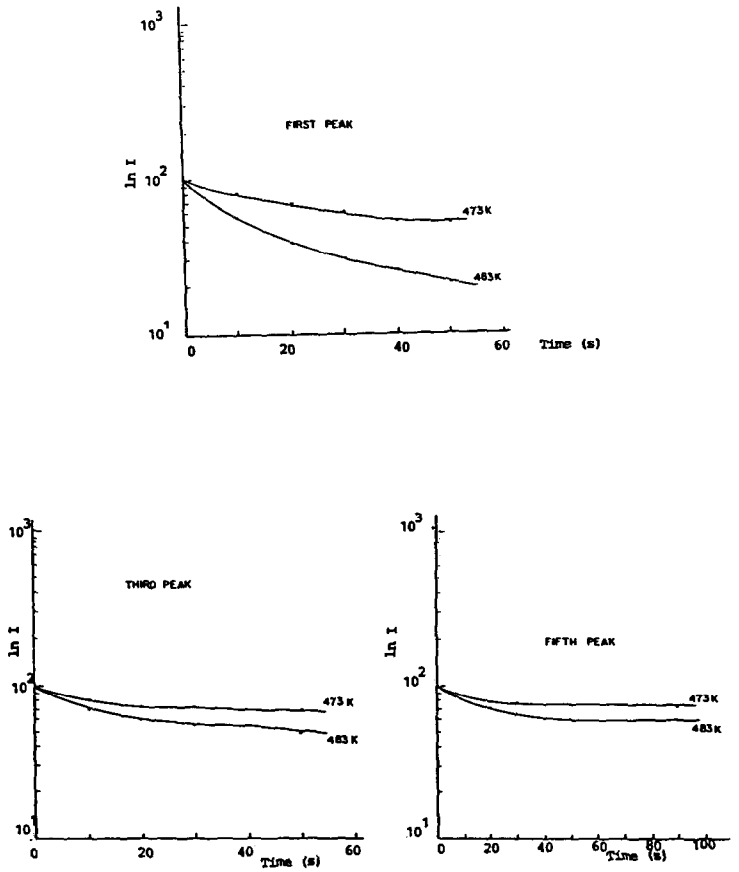

Fig.6. Isothermal decay.

If S_1 is positive, E is increased by 10%, and if S_1 is negative, E is decreased by 10% of its original value repeating the procedure until S_1 changes sign. At this point, the percentage of variation of E is reduced to 5% in addition to the direction of correction of E. From this point on, the percentage of correction of E is reduced to half its previous value in each step while the direction is still dictated by the sign of S_1.

This procedure was stopped when the last correction of E was smaller than 0.1%.

RESULTS AND CONCLUSIONS

Figure 2 shows the linear relation obtained by plotting ln(I) against 1/T for the rising part of the first and third peak of the glow curve of CaF_2 :Tm. From the slope of this plot we obtained an E value equal to 0.7125 $\pm$ 0.0054 eV and 1.1029 $\pm$ 0.0069 eV for first and third peaks, respectively.

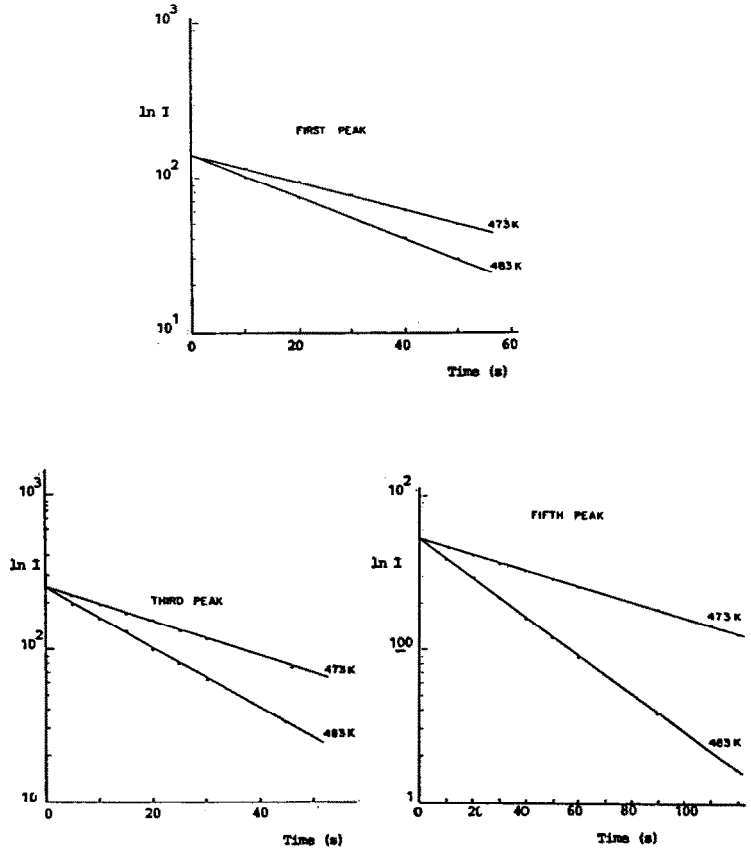

Fig.7. Isothermal decay.

The values of the symmetry factor, μ_g, obtained for the three peaks, 0.42 $\pm$ 0.07, 0.40 $\pm$ 0.09 and 0.54 $\pm$ 0.09 gave us a definitive indication of first order for first and third peak and of second order for fifth peak.

Values of glow peak parameters used to apply the methods based on glow peak shape are shown in Table 1. This table also shows the values of E obtained by using these methods.

Figure 5 shows the linear relation between ln (Tm^2/β) and 1/Tm obtained for the three peaks using different heating rates. From the slope of this plot E values shown in Table 1 were obtained. The values of E obtained by means of Both-Bohun method using two different heating rates are also shown in Table 1.

Isothermal decay of first, third and fifth peak of CaF_2:Tm at temperatures of 473 and 483 K is shown in Figure 6 for different times between 10 and 120 s.

TABLE 1

	FIRST PEAK	THIRD PEAK	FIFTH PEAK
Temperature of the maximum (K)	390.2 ± 3.3	437.8 ± 1.9	523.0 ± 3.2
Order of kinetics	first	first	second
Symmetry factor (μ_g)	0.42 ± 0.07	0.40 ± 0.09	0.54 ± 0.09
E value (eV): Initial rise	0.7125 ± 0.0054	1.1029 ± 0.0069	- - - - - -
Halperin-Braner	0.72 ± 0.07	- - - - - - - -	- - - - - -
Chen (δ)	- - - - - - - -	1.20 ± 0.03	1.90 ± 0.04
Chen (τ)	- - - - - - - -	1.10 ± 0.03	1.70 ± 0.02
Chen (ω)	- - - - - - - -	1.10 ± 0.03	1.80 ± 0.03
Hoogenstraaten	0.74 ± 0.07	1.11 ± 0.02	1.69 ± 0.02
Both-Bohun	0.74 ± 0.06	1.19 ± 0.03	1.75 ± 0.03
Isothermal decay	0.69 ± 0.06	1.07 ± 0.06	1.76 ± 0.05
Numerical Fitting	0.7423 ± 0.0018	1.3196 ± 0.0023	1.8417 ± 0.0025

Figure 7 shows the linear relations obtained plotting ln (I) against t at these temperatures. From the slopes of these plots the following E values were obtained: 0.69 ± 0.06 eV, 1.07 ± 0.06 eV and 1.76 ± 0.05 eV for first, third and fifth peaks, respectively.

Table 1 resumes the results obtained applying the diverses methods discussed in these paper to determine the E value.

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