DETERMINATION OF THE KINETIC PARAMETERS OF THERMOLUMINESCENT GLOW CURVES OF SINTERED AL_2O_3 PILLS BY THREE POINTS METHOD

DETERMINACIÓN DE LOS PARÁMETROS CINÉTICOS EN CURVAS DE BRILLO TERMOLUMINISCENTES DE PASTILLAS SINTERIZADAS DE AL_2O_3 POR EL MÉTODO DE LOS TRES PUNTOS

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ABSTRACT

Pérez Díaz M. E.*, R. R. Cogollo Pitalúa, O. D. Gutiérrez Flórez: Determination of the Kinetic Parameters of Thermoluminescent Glow Curves of Sintered Al_2O_3 Pills by Three Points Method. Rev. Acad. Colomb. Cienc., 37 (1): 85-89, 2013. ISSN 0370-3908.

The three points analysis method, proposed by Rasheedy, was applied to separate a complex thermoluminescence (TL) glow curve into its individual components and determine, for each component, the kinetic parameters. These are the order of kinetics b, the activation energy E (eV), and the pre-exponential factor S´´(s-1) associated with the TL glow peaks in sintered pure Al_2O_3 pills in response to gamma irradiation. The three points analysis method indicated that the glow curve of this material is the superposition of three general-order components, in which, the recombination processes predominates over retrapping processes.

Key words: alumina dosimeters, kinetic parameters determination, three points method.

RESUMEN

En este trabajo se aplicó el método de los tres puntos, propuesto por **Rasheedy**, para separar una curva de brillo termoluminiscente (TL) compleja en sus componentes individuales y determinar, para cada componente, los parámetros cinéticos. Estos parámetros son el orden cinético *b*, la energía de activación *E* (eV) y el factor pre-exponencial *S´´*(s^{-1}), asociados con las curvas de brillo TL en pastillas puras sinterizadas de Al_2O_3 expuestas a radiación gamma. El análisis con el método de los tres puntos indicó que la curva de brillo de este material se debe a la superposición de tres componentes TL de orden general, en los cuales, los procesos de recombinación predominan sobre los procesos de reatrapamiento.

Palabras clave: dosímetros de alúmina, determinación de parámetros cinéticos, método de los tres puntos.

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1. Introduction

Thermoluminescence dosimetry has found a very important use in clinical, personal and environmental monitoring of ionizing radiation [McLaughlin et al., 1989; Daniels et al., 1953; Vaijapurkar, Bhatnagar, 1993; Mckeever et al., 1995; Rasheedy et al., 2007; Kortov, 2007; Pérez, 2010]. Aluminum oxide is a promising alternative to the thermoluminescent materials currently used for in vivo dosimetry in quality control programs. The interest in alumina increased with the development of new materials on the basis of its structure, like α-Al_2O_3:C, which contain oxygen vacancies and provide a high TL sensitivity [Pérez, 2010; Rocha et al., 2003].

In the TL materials, the kinetic analysis of TL glow curves allows to study its dosimetric properties [Daniels, 1953; Mckeever, 1995; Pérez, 2010]. Additionally, a TL glow curve usually corresponds to a superposition of one or more curves (complex curve), and this disables to apply the conventional methods for isolated TL glow peaks. In order to analyze complex TL glow curves, **Rasheedy** has introduced the three points method for separating a complex curve into its TL individual components and to evaluate the kinetic parameters for each component [Rasheedy, 2007; Pérez, 2010; Rasheedy, 2005].

In this paper we determine, employing the three points method (TPM), the kinetic parameters in the TL glow curves exhibited by the alumina studied. The glow curve of this material includes three overlapped glow peaks.

2. Experimental

2.a. Processing

Commercial Alumina (W. R. Grace & Co-Conn) was used to prepare sintered pure Al_2O_3 pills of 2.5 mm of radius and 1 mm of thickness. The powder was initially cold-pressed (2 ton) and then sintered at 1000°C in air for 3 h; later the pills were milled, compacted and sintered again at the same conditions.

2.b. Thermoluminescence tests

Irradiations of samples, using absorption dose of 10 Gys, were carried out in air at room temperature using a Theratron 780C-^{60}Co unit at a distance of 80 cm relative to the source, in a radiation field of 10 x 10 cm^2. The samples were placed between two acrylic plates of 5 mm of thickness, with the purpose of reaching the conditions of electronic equilibrium. Thermoluminescence measurements were performed using a commercial Harshaw TLD 4500 dosimeter manufactured by Bicron®, using a linear heating rate of 5 Ks^{-1} from 50 °C up to 360 °C. The readings were carried out in a N_2 atmosphere in order to eliminate the infrared contribution due to the heating and to reduce the moisture effects. In order to reduce the residual signal of the material before each irradiation, allowing their re-utilization, samples were then annealed at 400 °C/1h (heating rate of 12.5 K/min), followed by cooling in air until to reach room temperature.

2.c. Structural and thermoluminescent analysis

Sinterized samples were characterized by means of X-ray diffraction (XRD). The diffractograms were obtained at room temperature by means of a X'Pert PRO (PANalytical) diffractometer using a copper source $K_{\alpha 1}$ λ=1.54056 Å to a sweeping rate of 0.026°/s.

Glow curves obtained were analyzed using the TPM proposed by **Rasheedy** [Pérez, 2010; Rasheedy, 2005], for obtaining the kinetic parameters of the individual glow peaks in a complex glow curve. These parameters include the order of kinetics b, the activation energy E (eV), the pre-exponential factor S'' (s^{-1}) and the initial concentration of trapped electrons n_0 (cm^{-3}).

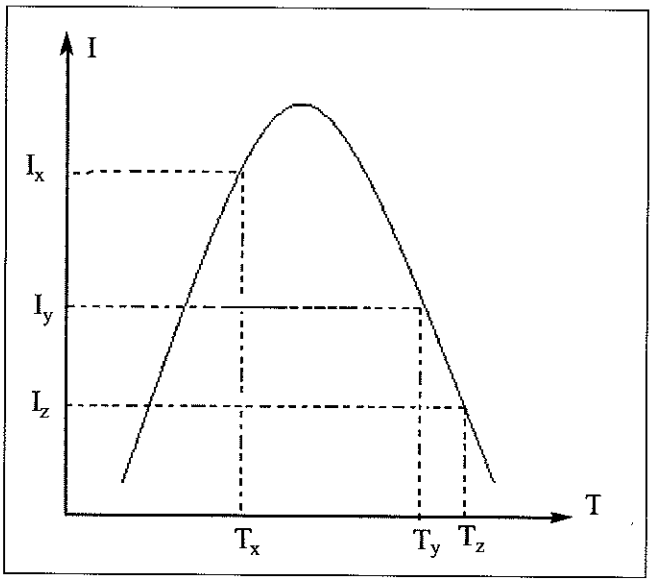

Figure1. Parameters I_x, I_y, I_z, T_x, T_y y T_z, in an isolated TL glow peak [Rasheedy, 2007].

This technique is applicable in TL curves consisting of multiple peaks and determines, by a general equation, the order b based on a set of three data points in an experimental TL glow curve (see Fig. 1) , considering that for general order kinetics, the behavior of TL intensity of a phosphor is governed by the following equation [Rasheedy, 2007; Rasheedy, 2005]:

$$I = -\frac{dn}{dt} = \frac{n^b}{N^{b-1}} S \exp\left(\frac{-E}{kT}\right) \quad (1)$$

Where I (in arbitrary units) is the TL intensity, n (cm^{-3}) the electron concentration trapped at time t (s), N (cm^{-3}) the traps concentration and k (eV/K) is the Boltzmann's constant. The solution of Eq. (1) for $b \neq 1$ is given by:

$$I = \frac{n_o S'' exp(-E/kT)}{\left[1+\left[((b-1)S'')/\beta\right]\int_{To}^{T} exp(-E/kT')dT'\right]^{b/(b-1)}} \quad (2)$$

Where β (Ks^{-1}) is the linear heating rate and n_0 (cm^{-3}) is the concentration of traps populated at the starting heating temperature T_0 (K). The pre-exponential factor S'' (s^{-1}), which is defined as $S''=S(n_0/N)^{b-1}$ is constant for a given dose, but it varies with changing the absorbed dose, i.e., with n_0. With equation (2) and the parameters b, E and S'', it will be possible to simulate the TL response in the alumina matrices studied.

From the TPM, the order of kinetics b is given by:

$$b = \frac{T_y[T_x - T_z]ln(y) - T_z[T_x - T_y]ln(z)}{T_y[T_x - T_z]ln\left[\frac{A_x}{A_y}\right] - T_z[T_x - T_y]ln\left[\frac{A_x}{A_z}\right]} \quad (3)$$

Where A_x, A_y and A_z indicate the areas under the glow peak from the temperatures T_x to T_f, T_y to T_f and T_z to T_f, respectively. There are not any relations between the intensities at which T_x, T_y and T_z exist. Also, T_x can antecede T_y (and/or T_z) or vice versa. The values of y and z are given by $y = I_x/I_y$ and $z = I_x/I_z$. The activation energy E is given either by

$$E = \left\{(\ln y) - b\ln[A_x/A_y]\right\}\left\{\frac{kT_xT_y}{T_x - T_y}\right\} \quad (4)$$

Or by

$$E = \left\{(lnz) - bln[A_x/A_z]\right\}\left\{\frac{kT_xT_z}{T_x - T_z}\right\} \quad (5)$$

Now, with b and E parameters the pre-exponential factor S'' is given by:

$$S'' = \frac{\beta E exp(E/kT_m)}{[bkT_m^2] - (b-1)E\varnothing exp(E/kT_m)} \quad (6)$$

Where T_m (K) is the temperature corresponding to the maximum intensity, I_m, of the glow peak and,

$$\varnothing = \int_{To}^{Tm} exp\left(\frac{-E}{kT'}\right)dT' \quad (7)$$

Finally, inserting (6) into (2) can be obtained an analytical expression for n_0:

$$n_o = \frac{I_m exp(E/kT_m)}{S''}\left(\frac{bkT_m^2 S''}{\beta E exp(E/kT_m)}\right)^{b/(b-1)} \quad (8)$$

In equation (8), the parameters b, E, S'' y β are known, and the values of I_m and T_m can be obtained from experimental glow curve.

The quality of **Rasheedy**'s fit has been tested with the figure of merit (FOM) [Bos et al., 1994], where FOM is given by

$$FOM = \sum_p \frac{100\,|\,y_{experimental} - y_{fit}\,|}{Area_{fit}} \quad (9)$$

Where $y_{experimental}$ and y_{fit} represent the experimental data and the values of the fitting function correspondingly. The summation extends over all the available points and $Area_{fit}$ represents the integral of the fitted glow curve. Glow curves with FOM values in excess of 5%, must be examined by another technique of deconvolution, because in these cases the fit is not as accurate.

3. Results

3.a. Structural and thermoluminescent analysis

Crystalline phase analysis (Fig.2) by means of Rietveld refinement [Pérez, 2010], revealed the presence of the α-alumina with rhombohedric structure and lattice parameters a=b= 4.75793 Å, c =12.989945 Å; and approximate crystal size of 2038.9 Å.

3.b. Kinetic analysis

Figure 3 shows the whole experimental TL glow curve obtained for the alumina samples.

Let us start with obtaining the kinetic parameters of the higher temperature peak, labelled peak 1. The value of b for this peak is calculated according to Eq. (3) at randomly selected Tx, Ty and Tz points of the rising and descending part of this peak, since the peaks 1 and 2 don't exhibit important overlapping. The activation energy E is determined according to

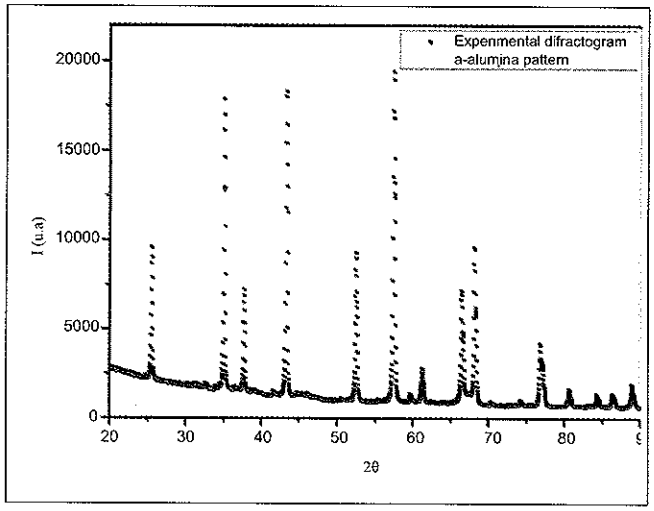

Figure 2. XRD pattern of the phase present into alumina samples.

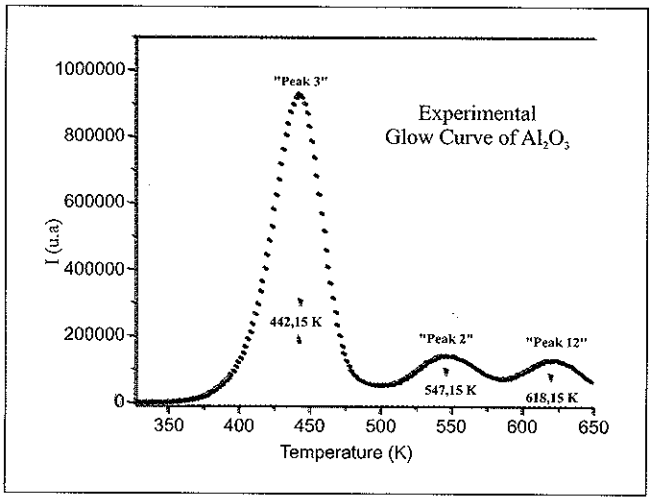

Figure 3. Experimental TL Glow Curve of alumina samples.

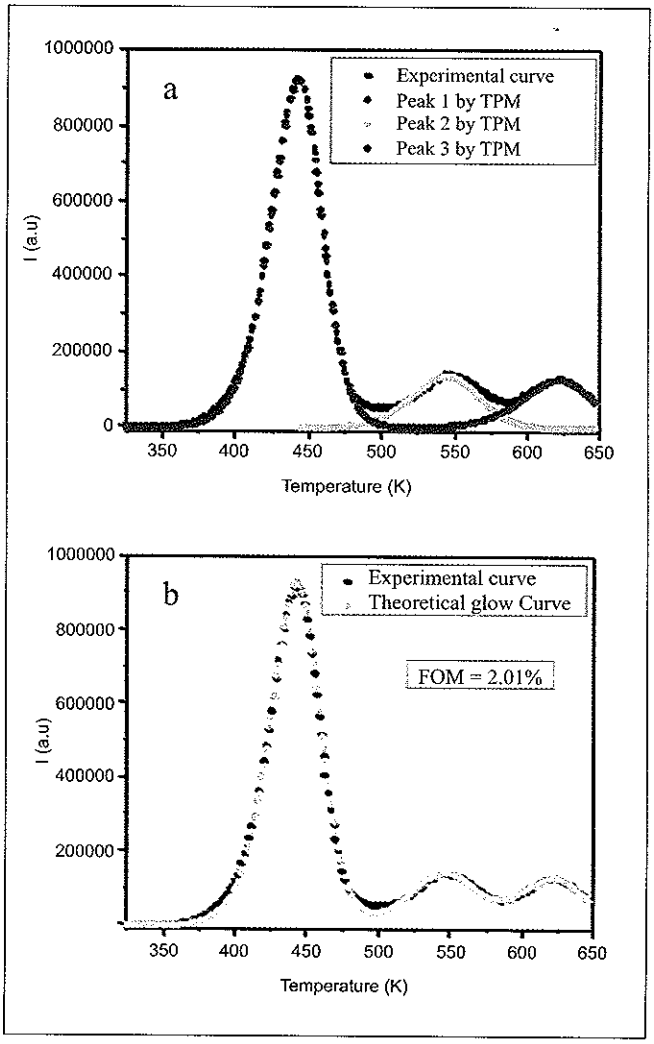

Figure 4. (a) Theoretical peaks obtained by TPM. (b) Experimental and fitted (summation of the theoretical peaks 1-3) curves.

Eqs. (4) or (5), while the pre-exponential factor S'' is estimated according to Eq. (6). Finally, the relative value of n_o is estimated according to Eq. (8). Later, we used the resulting parameters, β, b, E, S'' and n_o in Eq. (2) to fit the experimental glow peak 1 into a theoretical one. Then, the theoretical peak 1 was subtracted from the experimental glow curve and, over the remaining experimental glow curve, the mentioned procedures were repeated to obtain the kinetic parameters for peak 2 (employing in this case only the points of the descending part) and, once again, to obtain these parameters for the last peak 3. It is worth mentioning that, first, twenty runs of the TPM were executed in order to obtain average values of the kinetic parameters to generate each theoretical peak; and second, three theoretical peaks were enough to fit and to describe the whole experimental TL glow curve.

Fig. 4(a) shows the three theoretical peaks and the whole experimental glow curve. As shown in Fig. 4(b), the summation of theoretical peaks, fits well to the experimental glow curve (FOM value < 5%).

In the table 1 the kinetic parameters of each theoretical peak are listed. From the kinetic order b, it can be seen that recombination processes prevails over retrapping processes for peak 1 and 3, while for the peak 2 both processes occur.

On the other hand, the values of the activation energy for each peak are in agreement with the experimental observation since $E_{peak1} > E_{peak2} > E_{peak3}$. Similarly, the values of the initial concentration of trapped electrons n_o, show an agreement between their increment and the intensity of each peak,

Table 1. Experimental and kinetic (by TPM) parameters for peaks 1-3

Parameters	Peak 3	Peak 2	Peak 1
Tm (K)	442	543	622
Im (a.u)	9.28E+05	1.41E+05	1.29E+05
T0 (K)	323	444	544
b (K/s)	5	5	5
b	1.45	1.52	1.32
E (eV)	1.15431	1.3757	1.62579
S" (s-1)	4.86E+12	1.46E+12	3.58E+12
no (cm-3)	8.46E+06	1.67E+06	1.56E+06
FOM (%)	2.01		

since this parameter is proportional to the maximum Intensity of the TL peak.

4. Conclusions

The FOM value indicates that the three point method is valid as deconvolution analysis for the alumina investigated.

The three points method shows that experimental TL glow curve of alumina, only consists of three types of energy traps, since the overlapping of the theoretical peaks doesn't reveal the appearance of another signals.

The kinetic order indicates that the recombination prevails on the retrapping in the three types of energy traps that compose the experimental TL glow curve of alumina samples. Although for the "Peak 2" the method proposes a mixed deactivation mechanism in which the recombination prevails on the retrapping (b~1.5).

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