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KINETICS PARAMETERS IN Mg_2SiO_4:Tb THERMOLUMINESCENT MATERIAL

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This paper reports a first approach on the kinetics parameters of terbium-activated magnesium orthosilicate using various methods. A deconvolution has also used for taking into account a more complex glow-curve structure.

Keywords: thermoluminescent material - kinetic parameters, terbium-activated magnesium orthosilicate

Introduction

Mg_2SiO_4:Tb thermoluminescente phosphor is well known [1] for its high gamma sensitivity (40–100 times that of LiF:Mg,Ti), with moderate photon energy dependence (at 30–40 KeV the response is about 5 times that one to Co-60), a simple annealing characteristics (500°C for half one hour) and excellent fading stability.

Its effective atomic number is approximately 11 so that it could be useful in environmental and personnel monitoring.

Several investigations have been carried out on this phosphor: i.e. optical and thermal effects on the TL response [1], sensitization and photo-transfer [2].

The aim of the present work is to investigate some phenomenological parameters such as activation energy (E), frequency factor (s) and kinetics order (l) which determine the peak shape and reflect TL properties of the phosphors that are important in dosimetric applications: i.e., TL temperature emission and TL stability at various storage temperatures.

The kinetics parameters have been investigated using various methods as, for instance, the deconvolution and the Chen's peak shape methods.

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Experiment

Terbium - activated magnesium orthosilicate used in the present investigation was in form of discs of 5.0 mm in diameter and 0.5 mm in thickness. After annealing at 500°C for half one hour, the samples were irradiated with a Sr-Y β-source and readout in a Vinten TL reader with a linear heating rate of 8.1 $K \cdot sec^{-1}$. The TL emission consists in a strong glow-peak at about 515 K. A little hint of a shoulder can be observed on the discending part of the experimental glow-curve (full line in Fig. 1). Each of experimental points represents an average value obtained from five dosimeters.

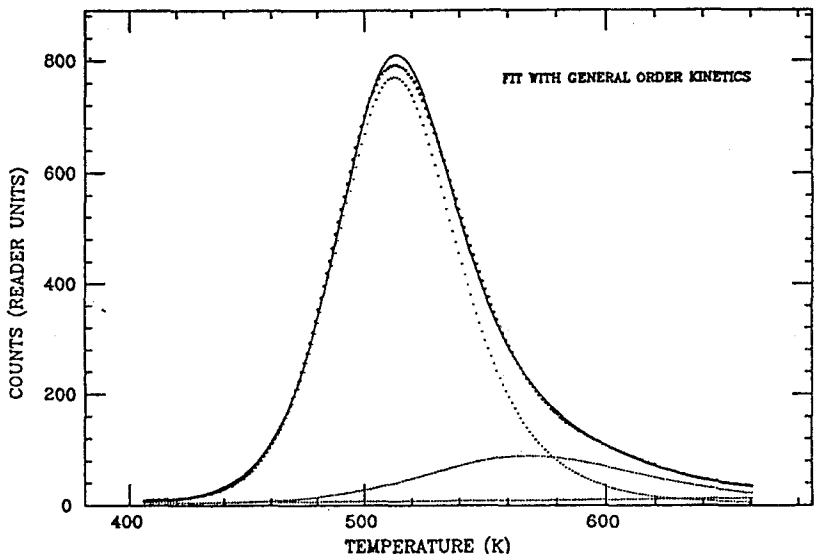

Fig. 1 Glow curve of Mg_2SiO_4:Tb; experimental glow-curve (—), fitted glow curve (• • •), deconvolution (...)

Methods of analysis

– Initial rise

The trap depth of the main peak was obtained at first by the initial rise method [3]. In the region where $T \ll T_m$, the rate of change of trapped electrons is negligible so that the TL intensity is proportional to $\exp(-E/kT)$ only.

Plotting ln (I) *vs.* $1/T$ a linear plot is obtained with slope equal to $-E/k$. Figure 2 shows this plot.

Table 1 reports the values of E.

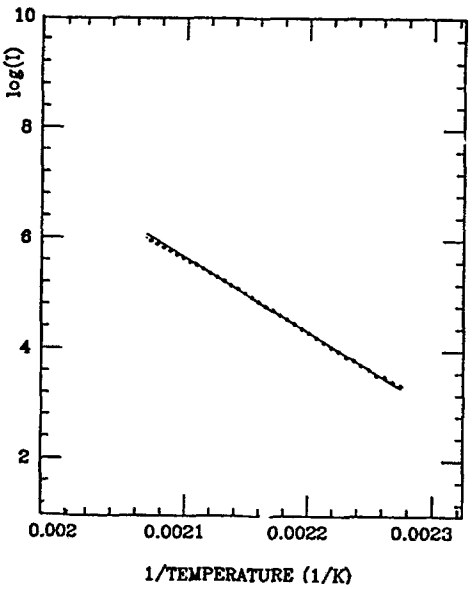

Fig. 2 Initial rise plot

– Peak shape methods

The order of the kinetics was first estimated by the value of the symmetry factor $\mu_g = \delta/\omega$ [4] where $\omega = \tau + \delta$ is the total half-width of the peak, τ the half-width at the low temperature side of the peak and δ the half-width towards the fall-off of the glow peak. Then, τ and δ can be obtained from the following temperatures: T_1, T_2 and T_m which are respectively the temperatures on either side of T_m. According to the previous quantities, a μ_g value of 0.55±0.02 has been obtained, indicating a second order kinetics.

After that the following formulas have been used:

Grosswiener [5]: $E_\tau = 1.68\,\mathrm{k}\,\frac{T_1 T_m}{\tau}$

Lushchik [6]: $E_\delta = 1.706\frac{kT_m^2}{\delta}$

Halperin & Braner [7]: $E_\tau = 1.813\frac{kT_m^2}{\tau} - 4kT_m$

Chen [8]: $E_\omega = 2kT_m\,(1.756\frac{T_m}{\omega} - 1)$

Chen (general method) [9]: $E_\alpha = c_\alpha\,(k\frac{T_m^2}{\alpha}) - b_\alpha\,(2kT_m)$

where α stands for δ, τ, or ω and c_α and b_α are respectively:

$c_\tau = 1.51 + 3\,(\mu_g - 0.42)$
$c_\delta = 0.976 + 7.3\,(\mu_g - 0.42)$
$c_\omega = 2.52 + 10.2\,(\mu_g - 0.42)$
$b_\tau = 1.58 + 4.2\,(\mu_g - 0.42)$
$b_\delta = 0$
$b_\omega = 1$

– Area methods

This method [10] is based on the measurement of the area subtended by the glow peak. Using the integration limits as T_i and T_f, where T_i is variable and T_f corresponds to the end of the glow peak, a value $S(T_i)$ is obtained for the area between T_i and T_f. The following expression is then obtained

$$\ln\left[\frac{I(T_i)}{S(T_i)^\alpha} = \frac{E}{kT_i} + c\right]$$

where α is a numerical value which linearizes the previous equation and corresponds to the kinetics order of the process.

Table 1 Kinetic parameters E values obtained using differential methods

Method		Main peak			Shoulder		
		E/eV	l	s/sec^{-1}	E/eV	l	s/sec^{-1}
Initial rise		1.12±0.03	–	–			
Grasswiener	(τ)	1.19±0.03	2	2×10^{11}			
Lushchik	(δ)	1.07±0.08	2	3×10^{10}			
Halperin & Braner	(τ)	1.19±0.03	2	10^{11}			
Chen	(ω)	1.11±0.05	2	5×10^{11}			
	(τ)	1.24±0.05		1.5×10^{11}			
Chen (general)	(δ)	1.19±0.03		2×10^{11}			
	(ω)	1.21±0.03		4×10^{11}			
Area		1.14±0.02	2	–			
Deconvolution		1.26±0.02	2	2×10^{11}	0.88±0.03	2	2×10^{7}

– Deconvolution

Owing to the little shoulder on the fall-off part of main peak, the equation of the glow-curve can be written as

$$Y(T) = \sum_{1}^{2} I_i(T) + A + B\exp(cT)$$

where A is a constant including the reader and the intrinsic TL background and the exponential term takes into account the TL contribution in the infrared region. The sum $\sum_{1}^{2} I_i(T)$ is extended over the two components and each $I_i(T)$ is expressed by the general order peak equation.

The mathematical approach to the deconvolution has been already discussed elsewhere [11]. It has to be remembered here that the method of least squares is applied for deconvolution procedure by using the library program Minuit [12], able to minimize the χ^2 parameter for a multidimensional function as the following

$$\chi^2 = \sum_{T} \frac{[Y_{exp}(T) - Y(T)]^2}{\sigma^2(T)}$$

where

$Y_{exp}(T)$ is the experimental value for TL light at the temperature T,

$Y(T)$ is the expected value for $Y_{exp}(T)$,

$\sigma^2(T)$ is the expected value for variance.

Figure 1 shows the experimental glow-curve of $Mg_2SiO_4(Tb)$ as well as the fitted curve; the deconvolution in two peaks is also given.

The frequency factor s can be calculated, after determination of the activation energy and the kinetic order, using the following expression useful for a second order kinetics

$$s = \frac{\exp(E/kT_m) \cdot \frac{\beta E}{kT_m^2}}{[1 + \frac{2kT_m}{E}]}$$

All the results obtained by the previous methods are reported in Table 1.

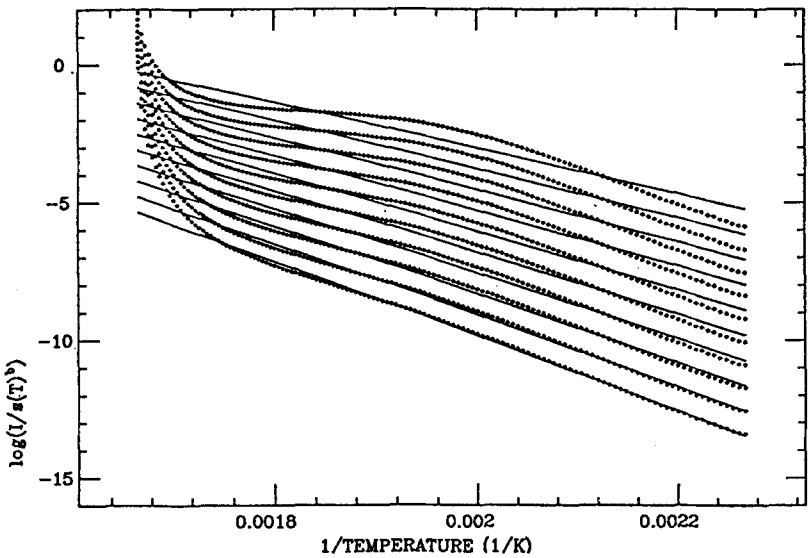

Fig. 3 Area method

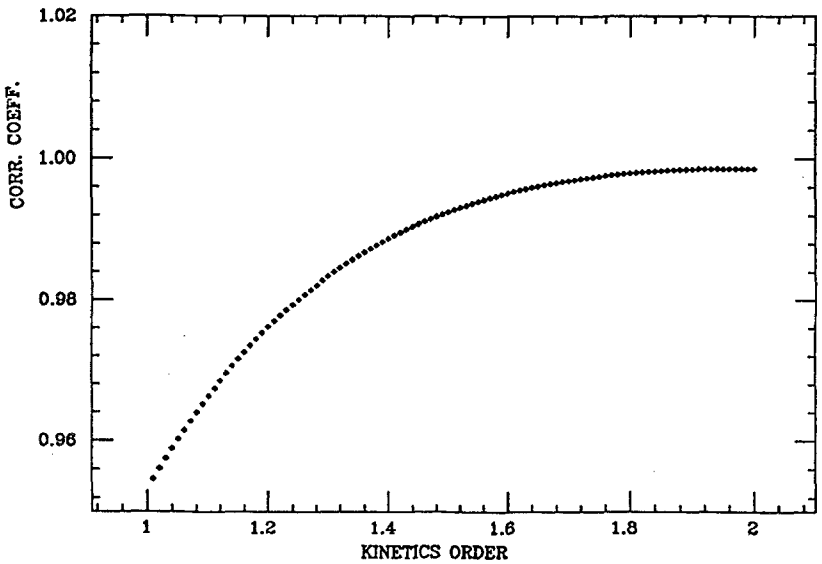

Fig. 4 Area method: correlation coefficient kinetic order

Discussion

It has to be mentioned that the present work is the first in reporting experimental values on trapping parameters for Mg_2SiO_4:Tb. The values of E given here

show good agreement among them. The spread among the values is about 11% excluding the deconvolution method. The high value obtained by deconvolution may arise from the method itself having taken into account a second peak in the glow curve: any way, the values spread about 15% including the deconvolution.

Looking at the glow-curve, it can be observed that the shoulder on the right part of the peak influences its half-amplitude; in this way the μ_g value is more larger than that one of the appropriate second order value:0.55 in our case instead of 0.52 as suggested by Chen [4]. In the same way the δ value becomes larger than the usual one compared to τ.

All of that influences the E values calculated using the shape methods: E_τ is always more larger than E_δ.

To get more informations about the glow curve structure, different analytical methods have to be used, i.e. TSC, or ESR. A study of the ESR properties of this material are in progress and the aim of the future work will be to give more informations about the trapping parameters as well as the structure of the glow curve.

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Zusammenfassung — Mittels verschiedener Methoden werden in erster Näherung die kinetischen Parameter von terbiumaktiviertem Magnesiumorthosilikat ermittelt. Zur Berücksichtigung einer komplexeren Thermolumineszenzkurve wurde auch eine Dekonvolution angewendet.