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KINETIC PARAMETERS OF THERMOLUMINESCENCE IN NANO α-Al_2O_3: A HEATING RATE STUDY

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Abstract: This study investigates the thermoluminescence (TL) characteristics of nano α-Al_2O_3 (40 nm) subjected to different heating rates. The presented data demonstrates a notable shift in glow peaks towards higher temperatures with increasing heating rates, coupled with changes in TL peak height. If the glow curve plot expresses TL intensity in (counts* k^{-1}) versus temperature (K), the glow curve shifts to lower temperatures as the heating rate increases. The ln (T_M^2/β) versus $1/kT_M$ graph yields an activation energy of E = 1.15 ± 0.1 eV, which is in good agreement with the literature data.

Keywords: thermoluminescence, nano α-Al_2O_3, heating rate, activation energy.

1. Introduction

Most materials with insulating or semi-conducting properties display a thermoluminescence (TL) glow curve featuring one or more peaks upon the release of charge carriers [1]–[3]. Following exposure to ionizing radiation, a substance's glow curve is derived by subjecting the material to a constant temperature increase and measuring TL emission over time. The outcome is a graphical depiction of TL emission in relation to temperature. The configuration of the glow curve is connected to trap levels positioned at varying depths within the band gap between the conduction and valence bands of solids. These traps exhibit distinct parameters. The controlled assessment of the emitted light (glow curve) from a material is typically employed to ascertain the absorbed radiation dose. Thermoluminescence nano dosimeters are commonly utilized in diverse applications such as personal and environmental monitoring, as well as clinical dosimetry. Analyzing the glow curve and assessing trap parameters becomes essential for comprehending the behavior of TL materials. The determination of trap depth and frequency factor is often accomplished through the widespread use of various heating rates analysis[4]–[6]. It must be emphasized that during application of the variable heating rate methods of analysis, it is essential to have good thermal contact between the heating element in the TL apparatus and the sample.

The dependence of the temperature at peak maximum, $Tmax$, of a TL glow peak on the heating rate (for both first and second order kinetics) stands as a feature among the most known in the literature of TL and corresponding applications [7][8]. The effect of the $Tmax$ shifting as a function of the heating rate, makes the latter experimental parameter a very dynamic experimental tool. When the linear heating rate β changes, the temperature TM of the maximum TL intensity of the peak also changes: faster heating rates produce a shift in temperature toward higher values of T_{max}.

2. Materials and Methods

In this study, nano-sized α-Al_2O_3 particles with sizes of 40 and 50 nm α-AI_2O_3 commercially available from Skyspring Nanomaterials, Inc. were used as samples. The samples were irradiated at ambient temperature with a ^{60}Co gamma source with a dose rate of 1.76 Gy/s. The dose rate was determined using a Magnette Miniscope MS400 EPR spectrometer with individually packed BioMax alanine dosimetry films with barcode markings developed by Eastman Kodak Company. The Harshaw TLD 3500 Manual Reader was utilized to assess the TL sample characteristics using a different linear heating rate of from 323K to 673K in an N_2 atmosphere with a Pilkington HA-3 heat-absorbing filter. Three aliquots of 5 mg each were used for each measurement, and the TL data points represented the average of the three aliquots. A thin layer of the sample powder was uniformly distributed on the planchet surface to ensure a uniform TL signal.

3. Results and Discussion

A straightforward and almost empirical approach to grasp the shift of $Tmax$ in relation to β is as follows. The probability of thermal stimulation is determined during a thermoluminescence (TL) readout aimed at recording the TL peak. The duration for which the probability (t) operates within a temperature interval ΔT = 1K is contingent on the heating rate. For instance, at a heating rate of β = 1K⁄s, this duration is 1 second; at β = 2K⁄s, it is 0.5 seconds; at β = 5K⁄s, it reduces to 0.2 seconds. Generally, the time acting on ΔT = 1K is given by $1/\beta$. Consequently, as the heating rate increases, the time allocated to each ΔT = 1K diminishes. This implies that the number of trapped electrons thermally released within time intervals of $1/\beta$ per ΔT = 1K is β times fewer than those released in the 1 second of β = 1. The discrepancy in thermally released electrons at ΔT = 1K between the operating time of 1 second and ($1/\beta$) seconds necessitates waiting for the temperature to rise before thermal release occurs. This mechanism elucidates the shift of $Tmax$ as a function of the heating rate. Several methods have been proposed for determining the activation energy through different heating rates [8], [9]. The findings from numerous TL phosphors indicate that calculating the integral of TL emission, the glow curve, using a temperature scale results in a shift of the peak maximum temperature towards higher values. Additionally, there is a notable decrease in TL response in certain materials as the heating rate increases, a phenomenon attributed to thermal quenching.

When the glow curve plot expresses TL intensity in (counts* s-1) versus time (s), at the same values of n_o, the glow curve shifts to lower times as the heating rate increases. If the glow curve plot expresses TL intensity in (counts* k-1) versus temperature (K), the glow curve shifts to higher temperatures as the heating rate increases. In both cases, the total area, which is proportional to n_o, remains conserved.

When the linear heating rate β changes, the temperature T_M of the maximum TL intensity of the peak also changes: faster heating rates produce a shift in temperature toward higher values of T_M. This effect is shown in Figure 1.

It has been proposed [10], [11] a method of calculating E based on two different heating rates for a first-order peak. Considering the maximum condition equation and using two different heating rates, one obtains:

$$E = k\frac{T_{M1}T_{M2}}{T_{M1}-T_{M2}}ln\left[\frac{\beta_1}{\beta_2}\left(\frac{T_{M2}}{T_{M1}}\right)^2\right] \quad (1)$$

If T_M can be measured within an accuracy of 1◦C, this method yields E within an accuracy of 5%. In a slightly different method, Hoogenstraaten [10], [11], starting from the first-order equation, suggested the use of several heating rates to obtain the following linear relation:

$$ln\left(\frac{T_M^2}{\beta}\right) = \frac{E}{kT_M} + ln\left(\frac{E}{sk}\right) \tag{2}$$

The resultant plot of $\ln(T^2_M/\beta)$ versus $1/kT_M$ should yield a straight line with slope E and an intercept ln(E/sk).

For the case of second-order kinetics the above equation becomes:

$$ln\left[I_M\left(\frac{T_M^2}{\beta}\right)^2\right] = \frac{E}{kT_M} + C \tag{3}$$

This method is useful only when b is appreciably different from unity, since for b = 1 the temperature TM of maximum TL intensity is independent of the initial concentration n_0 of trapped electrons.

Chen and Winer [12] showed that in the case of a temperature-dependent preexponential factor s (s proportional to T α), the graph of $\ln(T^2_M/\beta)$ versus $1/kT_M$ should yield a straight line of slope $E + \alpha kT_M$ instead of the actual activation energy E.

The data presented in Figure 1 indicates that with an increase in heating rate, the glow peaks shift towards higher temperatures, accompanied by changes in the height of the thermoluminescence (TL) peak. Since TL experiments typically involve collecting the TL signal over time, the y-axis in Figure 1 is expressed in counts per second. However, these counts/s units are not suitable for graphing the actual TL glow curve, which is a function of temperature. To address this, each graph in Figure 1 is divided by the corresponding heating rate β to convert the y-axis into counts per Kelvin, as depicted in Figure 2.

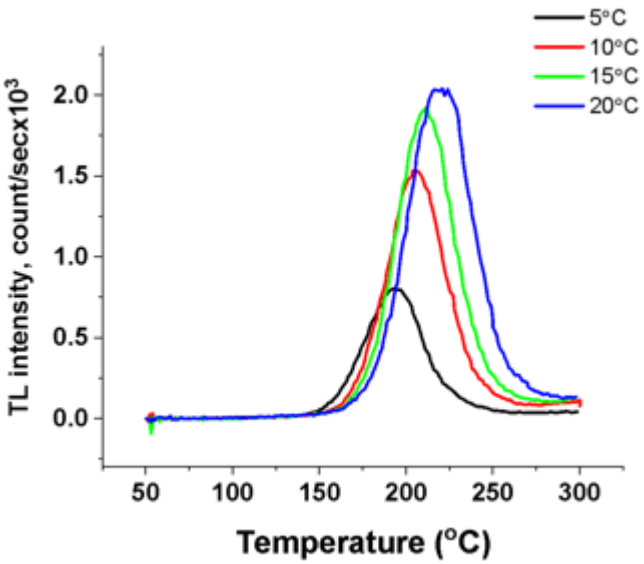

Fig. 1. The experimental TL glow curves for different heating rates. The y-axis is represented as counts/s

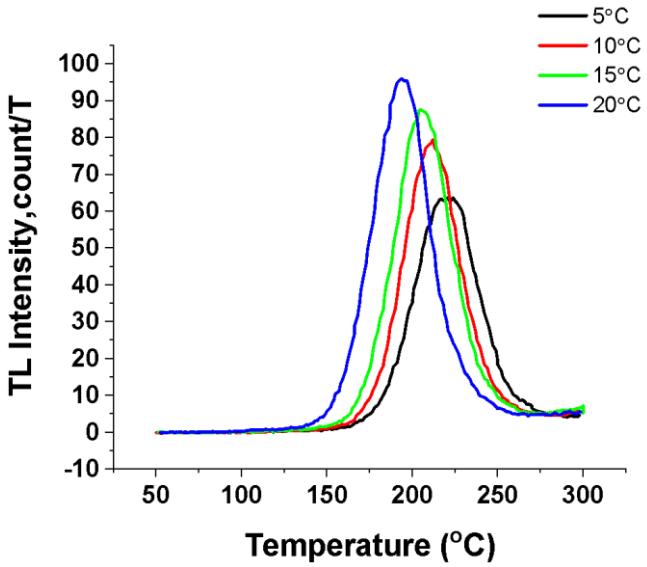

Fig. 2. The experimental TL glow curves for different heating rates. The y-axis is represented as counts/K

The area under the peaks in Figure 1 is directly proportional to the heating rate β, while the area under the glow curves in Figure 2 remains constant. Temperatures T_M, representing the maximum TL intensity, and heating rates at 2, 4, 6, 8, and 12°C determined from the curves of nano α-Al_2O_3 (40 nm) are listed in Table 1. The energy E can be calculated using the two-heating rate equation (equation (2)). The computations involve determining the values of $1/kT_M$ (where k represents the Boltzmann constant) and ln ($T_M{}^2/\beta$), as presented in Table 1 with β denoting the specified heating rates. As explained above, equation (2) establishes that the gradient of the ln ($T_M{}^2/\beta$) versus 1/kTM graph is equivalent to the activation energy E, while the y-intercept corresponds to ln(E/sk) (Fig. 3). Utilizing the slope and intercept obtained from the ln ($T_M{}^2/\beta$) versus $1/kT_M$ graph, we can subsequently derive the kinetic parameters E and s as outlined below.

Table 1

Calculation of ln(TM^2/β) and 1/kTM for flow curve of nano α-Al_2O_3 irradiated at 8 kGy

Heat rate, β (K/s)	Peak maximum, (°C)	Peak maximum, T_M (K)	Ln ($T_M{}^2/\beta$)	1/kT (eV)
2	185	458	11.56	25.34
4	199	472	11.93	24.59
6	203	476	10.54	24.38
8	207	480	10.27	24.18
12	213	486	9.89	23.88

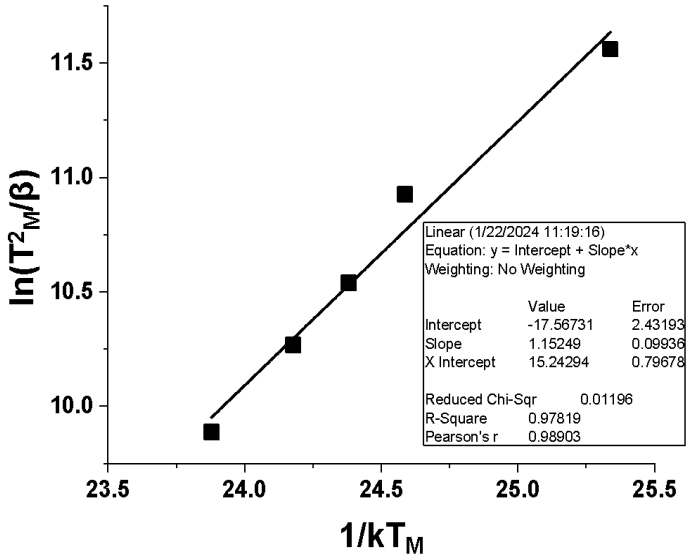

Fig. 3. Graph of ln (T2M /β) versus 1/kTM to determine E and s

From the slope of the graph, $E = 1.15 \pm 0.1$ eV.
From the value of the *y*-intercept = ln(*E/sk*), we obtain
$s = E*\exp(\text{intersept}/k) = 1.15*\exp(17.57)/(8.617 \times 10^{-5}) = 5.70 \times 10^{11} s^{-1}$

4. Conclusions

The analysis of the thermoluminescence (TL) behavior in nano α-Al_2O_3 (40 nm) under various heating rates reveals significant trends. As the heating rate increases, the glow peaks in Figure 1 shift towards higher temperatures, accompanied by alterations in the height of the TL peak. To appropriately represent the TL glow curve, Figure 1 is adjusted by dividing each graph by the corresponding heating rate β, converting the y-axis into counts per Kelvin, as illustrated in Figure 2.

The data in Table 1 further highlights the proportional relationship between the area under the peaks in Figure 1 and the heating rate β, while the area under the glow curves in Figure 2 remains constant. Temperatures T_M, denoting the maximum TL intensity, and corresponding heating rates are documented for nano α-Al_2O_3 irradiated at 8 kGy.

The calculation of ln (T_M^2/β) and $1/kT_M$ for various heating rates (2, 4, 6, 8, and 12 K/s) is presented in Table 1. Subsequently, utilizing the two-heating rate equation, the activation energy E is determined. The analysis of the ln (T_M^2/β) versus $1/kT_M$ graph yields an activation energy of $E = 1.15 \pm 0.1$ eV.

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КИНЕТИЧЕСКИЕ ПАРАМЕТРЫ ТЕРМОЛЮМИНЕСЦЕНЦИИ В НАНО α-Al_2O_3: ИЗУЧЕНИЕ СКОРОСТИ НАГРЕВА

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Резюме: В данной работе исследуются характеристики термолюминесценции (ТЛ) нано α-Al_2O_3 (40 нм), при разной скорости нагрева. Представленные данные демонстрируют заметный сдвиг пиков свечения в сторону более высоких температур с увеличением скорости нагрева в сочетании с изменением высоты пика ТЛ. Если график кривой свечения выражает интенсивность ТЛ в (интенсивность * k^{-1}) в зависимости от температуры (K), то кривая свечения смещается в сторону более низких температур по мере увеличения скорости нагрева. График зависимости ln (T_M^2/β) от $1/kT_M$ дает энергию активации E = 1,15 ± 0,1 эВ, что хорошо согласуется с литературными данными.

Ключевые слова: термолюминесценция, нано α-Al_2O_3, скорость нагрева, энергия активации.

NANO α-Al_2O_3-ün TERMOLÜMİNESSENSİYASININ KİNETİK PARAMETRLƏRİ: QIZDIRILMA SÜRƏTİNİN TƏDQİQİ

S.Q. Məmmədov, A.B. Əhədov

Xülasə: Bu məqalədə nano α-Al_2O_3-ün (40 nm) termolüminesans (TL) xüsusiyyətləri müxtəlif qızdırma sürətlərində tədqiq edilmişdir. Təqdim olunan məlumatlar göstərir ki, qızdırılma sürəti artdıqca lüminesans əyrilərindəki piklər də daha yüksək temperaturlara doğru sürüşür. Bu sürüşmə eyni zamanda pikin intensivliyinin azalması ilə də müşahidə olunur. Əgər parıltı əyrisinin qrafiki TL intensivliyini temperaturdan (K) asılı olaraq (intensivlik* k^{-1}) ifadə edirsə, qızdırma sürəti artdıqca parıltı əyrisi daha aşağı temperaturlara doğru sürüşür. Aktivləşdirmə enerjisininin qrafiki hesablanmış qiyməti E = 1,15 ± 0,1 eV verir ki, bu da ədəbiyyat məlumatları ilə yaxşı uyğunlaşır.

Açar sözlər: termolüminessensiya, nano α-Al_2O_3, qızdırma sürəti, aktivləşmə enerjisi.