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Isothermal Decay Analysis of Thermoluminescence Peaks of Nano-α-Alumina

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This work examines the thermoluminescence (TL) characteristics of nano α-Al_2O_3 (40 nm) at temperatures ranging from 110 to 160°C in order to understand the kinetic mechanisms that control its TL behavior. An analysis was conducted on the isothermal decay curves in order to ascertain the kinetics order and activation energies of the TL peaks. The plot of the natural logarithm of I versus time showed a deviation from linearity beginning at a temperature of 140°C, suggesting that the TL peaks in this temperature range do not conform to first-order kinetics. Further research verified that the TL data are consistent with second-order kinetics, with a kinetic-order parameter of b = 2.0 yielding the most accurate linear fit. Upon further analysis of the relationship between the natural logarithm of the slope and the reciprocal of temperature (1/kT), it was discovered that the TL response had a composite structure consisting of three separate linear sections. The portions mentioned correspond to activation energies of 0.6±0.12 eV, 1.07±0.25 eV, and 1.61±0.47 eV, respectively. This suggests that there are three distinct centers that contribute to the dosimetric peak. The results emphasize the intricate characteristics of the thermoluminescence (TL) response in nano α-Al_2O_3, emphasizing the need to take into account various kinetic elements while analyzing its TL features.

Keywords: Activation energy; Nano α-alumina; Thermoluminescence; Isothermal decay method; GlowFit.

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Introduction

The development of new thermoluminescent (TL) materials for radiation dosimetry necessitates a deeper understanding of trapping parameters such as activation energy (or trap depth), kinetic order, and frequency factor [1]–[3]. This understanding can be achieved by analyzing the glow curve produced when the material, after being exposed to ionizing radiation: excited by radiation, electrons transition from the valence band to the conduction band and thereafter occupy a metastable state within the forbidden band. Trapped electrons will be emitted when heated and then recombine with trapped holes, resulting in the emission of light. Various methods exist to determine trapping parameters [2]. Most current methods for obtaining the frequency factor rely on prior determination of activation energy, based on certain assumptions about kinetic order. This approach leads to inconsistencies in reported trapping parameters due to significant variations in activation energy values obtained through different methods. Therefore, a method independent of trap depth determination is necessary.

Aluminum oxide is a promising alternative to the thermoluminescent materials [4], [5] currently used for in vivo dosimetry in quality control programs [6]–[8]. Interest in alumina has grown with the development of new materials based on its structure, such as α-Al_2O_3:C, which contain oxygen vacancies and offer high TL sensitivity [9].

Isothermal luminescence decay (ILD) method requires no prerequisite conditions and it can be applied to first-order, second-order, and general-order kinetics [10]. This paper presents studies on alumina in the context of kinetic parameters, which are crucial for describing the physical characteristics of thermoluminescent materials. In ILD method, TL glow curve is recorded as a function of time at a fixed, constant temperature. Various methods utilize the isothermal decay curve to

determine the order of kinetics [11]. One approach evaluates the variation in the gradient of the isothermal decay curve as time progresses, while another evaluates the scale of the area beneath the isothermal decay plot. The primary benefit of these methods is that they provide an approximation of the kinetics order and are the sole techniques unaffected by temperature-dependent variables such as frequency factor and quantum efficiency.

The objective of this study is to explore the isothermal decay of the TL data of alpha-alumina (α-Al_2O_3) and conducting kinetic analysis of the primary glow peak.

I. Materials and methods

Nano-sized α-Al_2O_3 particles with sizes of 40 nm produced by Skyspring Nanomaterials, Inc. were used as samples. Fig.1 illustrates the XRD pattern of the sample. The samples were scanned in the range $5 \leq 2\Theta \leq 80°$ at a scan rate of 1.2 °/min. Semi-quantitative estimates of the abundance of mineral phases were derived from the PXRD data using the intensity of specific reflections, density, and mass absorption coefficients of the elements for CuKα radiation. A comprehensive description of the irradiation sources and dosimetry was provided in [12]. The dose rate of 1.76 Gy/s was measured using a Magnette Miniscope MS400 EPR spectrometer with individually packaged BioMax alanine dosimetry produced by Eastman Kodak Company. The irradiation was performed at an ambient temperature. The Harshaw TLD 3500 Manual Reader was used to measure the glow curve of the TL sample. A constant heating rate of 2°C/s was used, with the temperature ranging from 323 K to 673 K. The experiment was conducted in a N_2 environment, using a Pilkington HA-3 heat-absorbing filter. Three aliquots of 4 mg each were used for each measurement. The sample powder was evenly spread throughout the surface of the planchet to provide a consistent thermoluminescence (TL) signal.

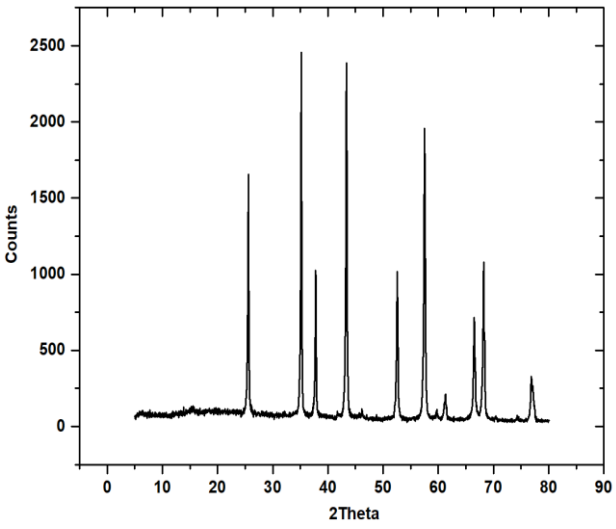


Fig. 1. XRD pattern of nano-α- alumina with the particle size of 40 nm.

II. Results and Discussions

This research explores the experimental data in Figure 1 for the isothermal decay curves of a TL peak, which were measured for seven different temperatures of T = 110, 120, 130, 140, 150, 155 and 160ºC.

Fig. 2 depicts the plot of ln (TL) against time (t), within temperature range from 110 to 160ºC representing the temperature while recording isothermal decay curves. The decay curves of the TL signal change exponentially over time at a constant temperature and are described by the equation of $I=I_0 \exp(-s \exp(-E/kT)t)$. According to this equation, the dependency of ln(I) on time will be linear and $|\text{slope}| = s \exp(-E/kT)$, which allows the calculation of the activation energy by the formula: $\ln(/\text{slope}/) = \ln s - E/kT$. The first-order kinetics can be excluded by analyzing the graph of ln (TL) versus time, as shown in Figure 3. The Fig. 3 shows that starting from 140°C, the relationship is nonlinear, indicating that the data in question do not correspond to first-order kinetics.

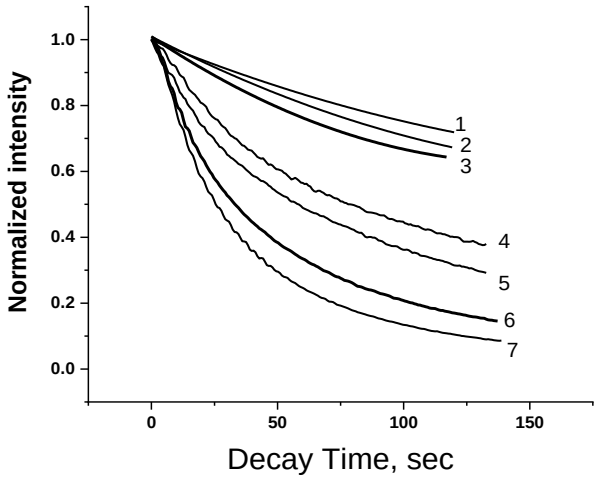
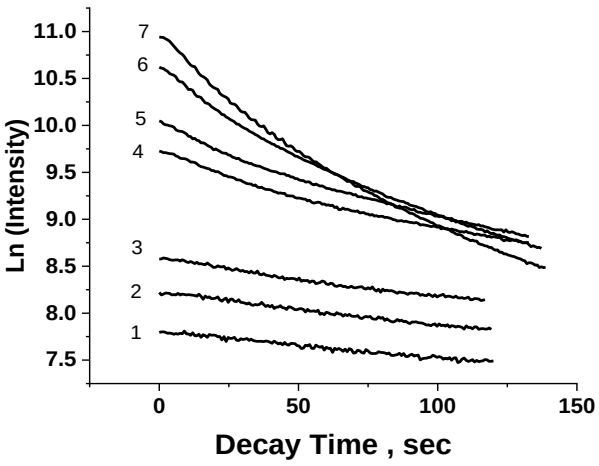


Fig. 2. Isothermal decay curves of TL nano-α-Al_2O_3 at temperatures of T= 110 (1), 120 (2), 130 (3), 140 (4), 150 (5), 155 (6) and 160ºC (7).



g. 3. The isothermal TL decay curves of nano-α-Al_2O_3 on the semi log scale of T= 110 (1), 120 (2), 130 (3), 140 (4), 150 (5), 155 (6) and 160ºC (7).

The isothermal decay curves of TL peaks corresponding to general order kinetics with the kinetic

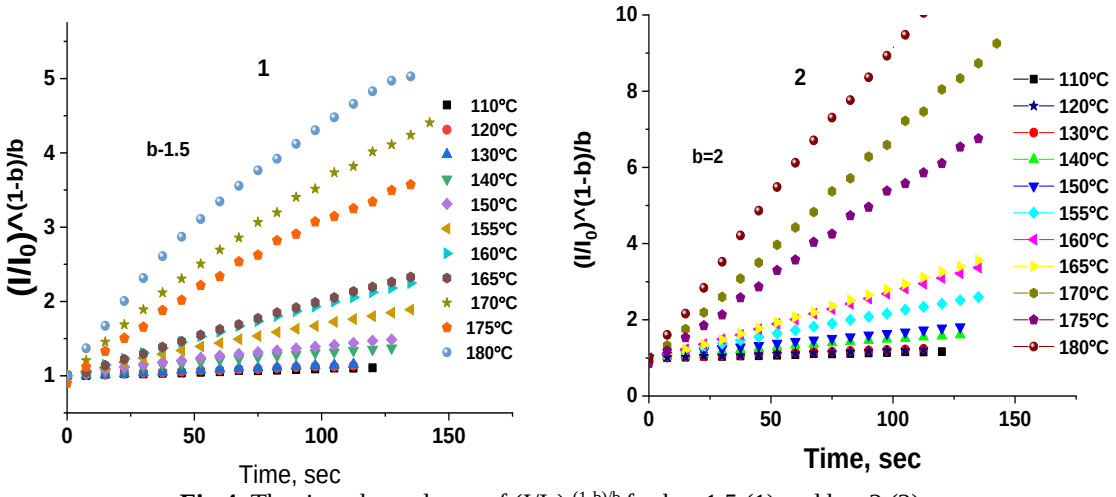


Fig.4. The time dependence of $(I/I_0)^{(1-b)/b}$ for b = 1.5 (1) and b = 2 (2).

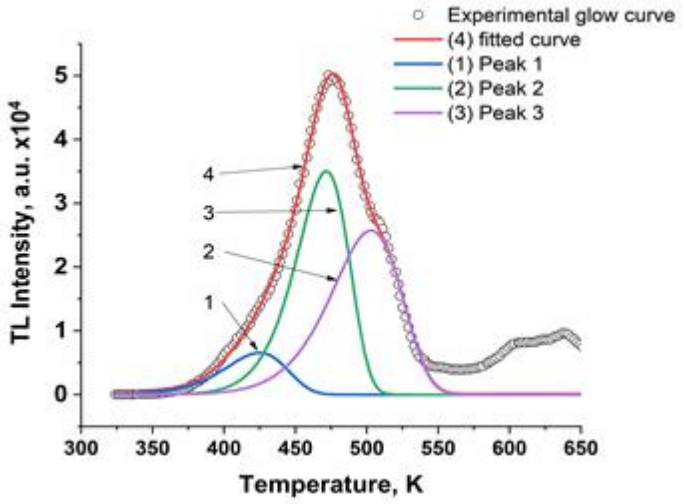


Fig. 5. Deconvolution of the 460 K TL glow peak nano-α-Al_2O_3 with into three peaks. Particle size = 40 nm.

order parameter denoted as "b" will be characterized as follows [11]:

$$\left(\frac{I_t}{I_0}\right)^{\frac{1-b}{b}} = 1 + s' n_0^{b-1} (b-1) t exp^{\left(-\frac{E}{kT}\right)} \qquad (1)$$

where T = temperature of isothermal decay; n_0 = initial trapped charged population; E = activation energy; s' = s/N = effective frequency factor; I_0 = initial TL intensity; It = the TL intensity at time t.

Equation (1) suggests that the dependency $(I_t / I_0)^{(1-b)/b}$ against time (t) should form a straight line with an appropriate value of b. After determining the value of b, we will plot $(I_t / I_0)^{(1-b)/b}$ against time t for the five different decay temperatures, resulting in a set of straight lines with a slope (m) given by the formula:

$$m = s' n_0^{b-1} (b-1) exp^{\left(-\frac{E}{kT}\right)} \qquad (2)$$

Thus, Equation (2) allows for the determination of the activation energy (E) and the effective frequency factor s" = $s'n_0^{b-1}$ from the slope and y-intercept of the graph of ln(m) vs 1/ kT.

The parameter of $(It/I_0)^{(1-b)/b}$ at different isothermal decay temperatures (from 110 to 180 °C) was calculated using values b = 1.5 and b = 2, and the results are presented in Fig. 4. Figure 4 shows that b = 2 is the best linear fit. This means that the main dosimetric peak's isothermal decay follows second-order kinetics.

However, the dependence of ln(slope) on the parameter 1/kT also shows a complex linearity, i.e., it consists of a superposition of three linear sections. Accordingly, each of these sections corresponds to a particular activation energy (E), namely 0.6 ± 0.12, 1.07 ± 0.25 and 1.61 ± 0.47 eV consequently. Thus, it can be assumed that the observed dosimetric peak has a complex character and consists of three centers.

To address the above behavior for nano-sized alumina, the main dosimetric peak was also deconvoluted into three peaks applying the Computerized Glow Curve Deconvolution (CGCD) procedure using GlowFit program [13] (Fig. 5). The maximum temperatures of the three component glow peaks were found to be 425, 472 and 503 K. Correspondingly, the activation energies for these peaks were found to be 0.68 eV, 1.01 eV and

0.85 eV, while the corresponding frequency factors were calculated to be $5.10 \cdot 10^6$, 3.45×10^{10} and $1.29 \cdot 10^8$ s^{-1}.

Zahedifar et al. deconvoluted the main glow peak of TLD-500 (α-Al_2O_3) into three peaks using the CGCD procedure, incorporating the results of Tm-Tstop tests [14]. The maximum temperatures of the three component glow peaks were 441 K, 460 K, and 478 K, with corresponding activation energies of 1.3 eV, 1.23 eV, and 1.12 eV, and kinetic orders of 1.69, 1.35, and 1.08, respectively. These values show significant differences when compared with the results for the TLD 500.

The appearance of the main dosimetric peak in the low-temperature region of the TL spectrum of nano-α-alumina and various modifications of α-alumina, along with similar values of activation energies (E) and frequency factors (s) reported in the literature [15]–[20], suggests that the nature of defects in these samples is approximately the same. A possible model to explain the experimental results includes a composite main dosimetry trap, a deep hole trap, a deep electron trap, and F and F+ centers [21], [22]. During irradiation, excited electrons are either trapped in the main dosimetry trap or recombine with the F+ centers to create an F center. The electrons released from the main dosimetry trap during the heating stage recombine with the F+ centers, creating an excited F center, which leads to light emission.

Conclusions

Analysis of thermo luminescence (TL) data between 110 to 160°C provides key insights into the material's kinetic behavior. The plot of ln(I) versus time (t) becomes nonlinear from 140°C, indicating that first-order kinetics do not apply to the TL peaks in this temperature range. Further examination using isothermal decay data identifies a best-fit linear relationship with a kinetic-order parameter of b = 2.0, confirming second-order kinetics for the TL response.

The plot of ln(slope) against 1/kT reveals a more complex scenario, showing three distinct linear segments, each representing a different activation energy: 0.6 ± 0.12 eV, 1.07 ± 0.25 eV, and 1.61 ± 0.47 eV. This suggests that the dosimetric peak observed is not singular but composed of three different centers, each contributing to the TL signal.

Overall, the material's TL behavior is characterized by second-order kinetics and a complex dosimetric peak structure involving multiple centers with various activation energies. These findings provide a more comprehensive understanding of the TL response and the processes underlying the material's dosimetric properties.

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Аналіз ізотермічного розпаду піків термолюмінесценції нано-α-оксиду алюмінію

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У роботі досліджено характеристики термолюмінесценції (TL) нано α-Al_2O_3 (40 нм) при температурах від 110 до 160°C з метою пояснення кінетичних механізмів, які контролюють поведінку його TL. Для встановлення порядок кінетики та енергії активації піків TL проведено аналіз ізотермічних кривих розпаду. Графік залежності натурального логарифма I від часу показав відхилення від лінійності, починаючи від температури 140°C, що свідчить про те, що піки TL у цьому діапазоні температур не відповідають кінетиці першого порядку. Подальші дослідження підтвердили, що дані TL узгоджуються з кінетикою другого порядку, причому параметр кінетичного порядку b = 2,0 дає найточнішу лінійну відповідність. Після подальшого аналізу зв'язку між натуральним логарифмом нахилу та величиною, зворотною температурі (1/kT), було виявлено, що відповідь TL має складну структуру, яка складається з трьох окремих лінійних ділянок. Зазначені частини відповідають енергіям активації 0,6 ± 0,12 еВ, 1,07 ± 0,25 еВ і 1,61 ± 0,47 еВ, відповідно. Це свідчить про те, що існують три чіткі центри, які сприяють дозиметричному піку. Результати підкреслюють складні характеристики реакції термолюмінесценції (TL) у нано α-Al_2O_3, наголошуючи на необхідності брати до уваги різні кінетичні елементи під час аналізу його TL характеристик.

Ключові слова: енергія активації; нано α-алюміній; термолюмінесценція; метод ізотермічного розпаду; GlowFit.