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Thermoluminescence properties of nano-alumina with two different particle sizes

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This research aims to examine the thermoluminescence (TL) properties of nano-sized alumina, including the relationship between TL intensity and absorbed dose, the identification of individual luminescence peaks, and determining trap parameters for use as a possible dosimeter. The samples were exposed to 530 to 2646 Gy doses from $^{60}$Co irradiation. The results show that micro-sized $\alpha$-Al$_2$O$_3$ had a main dosimetry peak at $T_m = 435$ K, while nano-$\alpha$-Al$_2$O$_3$ samples with particle sizes of 40 and 50 nm displayed a TL luminescence glow curve, with the primary dosimetry peak located in the low-temperature range and a complex structure at higher temperatures (above 500 K). The primary dosimetry peak was influenced by nanoparticle size, with a maximum of 460 K for the 40 nm sample and 467 K for the 50 nm sample. The superposition of two peaks described this dosimetry peak.

Keywords: Activation energy; Frequency factor; GlowFit; Nano $\alpha$-alumina; Thermoluminescence.

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Introduction

Luminescent materials have widespread applications in ionizing radiation dosimetry. Among these materials, aluminum oxide (Al$_2$O$_3$) sensitized with various dopants has been identified as potential thermoluminescence (TL) dosimeter [1]–[3]. Al$_2$O$_3$ has good mechanical stability, making it a commonly used material for radiation detection and dosimetry. In addition, Al$_2$O$_3$ possesses numerous advantages for ionizing radiation dosimetry, such as linearity of TL signal over a wide range of doses, ease of handling, affordability [4], high sensitivity, high TL signal per unit absorbed dose, and low fading during storage in the dark [5]. Moreover, Al$_2$O$_3$ has garnered scientific interest due to its high optical, chemical, and thermal stability when exposed to radiation. However, achieving sensitivity to radiation in Al$_2$O$_3$ is challenging, and much research has been conducted on the TL of alumina sensitized with different dopants [6],[7]. This study aims to investigate the essential TL characteristics of nano-alumina with different particle sizes as a potential matrix to develop doped dosimeters for ionizing radiation. A comprehensive analysis of electron and hole traps is also significant when using aluminum nano-oxides as catalysts or composite materials. The primary focus of this study is the parameters of the TL response of gamma-irradiated nano-alumina, particularly the linearity of the dose-dependent response and its dependence on particle size.

I. Materials and Methods

In this study, nano-sized $\alpha$-Al$_2$O$_3$ particles with sizes of 40 and 50 nm and micro-sized $\alpha$-Al$_2$O$_3$ (5–8 µm, $\alpha$ phase content 97.26%, water content 0.25%) 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 linear heating rate of 5K/s from 323 K to 673 K in an N$_2$ atmosphere with a Pilkington HA-3 heat-absorbing filter. Three aliquots of 5 mg each were used for each
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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. The peak fitting and analysis were conducted using computerized glow curve analysis [8], [9].

II. Results and Discussion

Figure 1 presents the TL glow curves of micro-sized α-Al2O3 and two particle sizes of nano-sized α-Al2O3 irradiated by 60Co gamma radiation at a dose of 2,645 Gy. The curves are measured at a heating rate of 5K/s and in the temperature range of 323–673K. The unirradiated samples do not exhibit any TL signal in this temperature range. Upon irradiation, the TL glow curves of the nano-sized α-Al2O3 samples with particle sizes of 40 and 50 nm and the micro-sized α-Al2O3 samples display TL signals with different intensities (Fig. 1, curves 1–3). The experimental glow curve of micro-sized α-Al2O3 shows a dominant dosimetry peak at the maximum temperature Tm = 435 K (Fig. 1, curve 1).

![Fig. 1. TL glow curve of (1) micro-sized α-Al2O3 and nano-sized α-Al2O3 (2) 50 nm and (3) 40 nm irradiated at a dose of 2,645 Gy with a heating rate of 5K/s.](image)

The TL sensitivity of nano-sized alumina is approximately ten times higher than that of micro-sized alumina. The luminescence curves of nano-Al2O3 samples are similar to those of α-Al2O3, which has been reported in the literature [10]–[12]. The main dosimetry peak is observed in the low-temperature region, and a complex structure is seen at higher temperatures (above 500K), associated with a continuous distribution of traps. The main dosimetry peak can also be described by the superposition of two peaks [8]. The maximum of the main dosimetry peak depends on the nanoparticle size in nano-alumina, with a value of 460K for the sample with a particle size of 40 nm and 467 K for the sample size of 50 nm at a heating rate of 5K/s. These variations are due to the interactions of different components of this TL peak with deep traps[3], which determine the shape and size of the TL peak. A change in the deep trap parameters affects the TL properties of the dosimetry peak. The sensitivity of the nano-sized alumina is significantly higher than that of the micro-sized alumina, and the sensitivity of the 50 nm nano-α-Al2O3 is approximately two times higher than that of the 40 nm nano-α-Al2O3. Figures 2 and 3 exhibit TL glow curves obtained from nano-α-Al2O3 samples irradiated with doses between 529 and 2,645 Gy, recorded at a linear heating rate. Regardless of the radiation dose, all samples exhibit this dosimetry peak with a consistent Tm position within experimental error (±3 K), which suggests that all peaks in the glow curve follow first-order kinetics, at least for the lower-temperature segment of the glow curve.

![Fig. 2. TL glow curves of nano-Al2O3 (40 nm) irradiated at doses of 529.1 Gy (1), 1058.1 Gy (2), 1587.2 Gy (3), 2116.0 Gy (4), and 2645.4 Gy (5).](image)

The maximum value of the main dosimetry peak temperature is close to that determined for alumina doped with carbon, with a predominant TL peak centered at 471 K [13] and α-Al2O3, where Tm=465 K [14], but significantly higher than that determined for alumina crystal (Tm=450 K) [5], bauxite (Tm=412 K)[15], and Al2O3 doped with Sr, Li, and Ge (Tm=448 K)[2]. Natural diaspores exhibit TL glow curves with a low-temperature maximum peaked at 453 K and a wide broad curve above 490 K [11]. Diaspores samples show a discrete distribution of electron traps at a lower temperature (~463 K) and a continuous structure of traps at a higher temperature (above 500 K), which is due to dehydroxylation and oxidation of the chromophore[16]. Al2O3 nanoparticles doped with Cr (particle size of 25 nm) show a prominent peak at approximately 474 K and a linear response from...
100 Gy to 20 kGy [17]. The low-temperature peak (at 470K) has also been detected in synthetic doped alumina (α-Al₂O₃) [18].

Figure 4 shows a linear relationship between the TL spectra and increasing dose, indicating that the TL response is directly proportional to the irradiation dose. The results show a linear dose-response with the delivered dose up to 3 kGy, with regression coefficients of linear fitting (R-square) for 40 and 50 nm nano-Al₂O₃ measuring 0.985 and 0.988, respectively. These results demonstrate a broader coverage of the dose area when compared to commercially available phosphors such as Al₂O₃:C, which are used for a lower dose range of 1 µGy to 4.5 Gy [19] or CaSO₄:Dy (TLD-900) in the microcrystalline form with a saturation level of 1 kGy [20]. TLD-500 also shows a linear dose dependence, ranging from 104 to 106 Gy [21].

The GlowFit tool was employed to estimate the TL trapping parameters for the low-temperature section of the curve. Fig. 5 illustrates the results of the CGCD fitting of the TL glow curves of nano-α-alumina particles with a size of 40 nm, assuming two peaks in the low-temperature region.

The GlowFit program is utilized to estimate the physical trapping parameters for the low-temperature portion of the curve. This program is founded on Randall and Wilkins’ first-order kinetics model with a constant heating profile. The glow curve fitting is accomplished through an iterative Levenberg–Marquardt algorithm [8]. Additionally, GlowFit assesses the fitting quality by calculating a figure of merit (FOM) that measures the agreement between experimental and deconvolution curves.

Deconvolution and determination of trapping parameters typically involve fitting the glow curves of a luminescent material to a first-order formula in thermoluminescence spectrum analysis. This fitting seeks to extract values for key parameters like the glow peak’s activation energy (E) and frequency factors (s). Comparing experimental and theoretical glow curves aids in refining these parameter values.

![Fig. 5. Deconvolution of the 460 K TL glow peak of the irradiated nano-α-Al₂O₃ with the particle size of 40 nm using a first-order kinetic expression.](image)

Table 1 shows the results of the best estimates of peak parameters for both nano-α-alumina with particle sizes of 40 and 50 nm. The table shows that the calculated activation energies for the nano-α-alumina with two particle sizes are comparable. The estimated value of the frequency factor, which indicates the probability per second of the release of a trapped charge carrier, is $s = 1.01 \times 10^{10}$ and $1.3 \times 10^{10}$ s⁻¹ for the peak with $T_m = 458$ ± 3 K and, accordingly, $2.06 \times 10^{11}$ for the peak with $T_m = 473$ ± 3 K. Isolated peaks' frequency factor (s) and activation energies (E) vary within physically significant numbers. They are in good agreement with the results reported in the literature [5] [11] [22].

Similar behavior can be observed in the widely used commercial TL dosimeter TLD 500 (Al₂O₃:C). Studies have indicated that both the position and width of the 450 K TL peak can vary with the dose of ionizing radiation [21] [23]. The sensitivity of the 450 K TL peak has also been found to vary depending on the irradiation type, whether it is beta or UV radiation [24]. Researchers have interpreted this phenomenon as either non-first-order recombination kinetics or a series of overlapping first-order peaks. The 458 ± 3 K corresponds to the peak at 430K in [10]. It may be attributed to radiative decay F-centers formed through material reduction, leading to the creation of oxygen vacancies (F-type centers) that serve as emission centers[10]. According to [23], the trap responsible for this peak could be linked to Al³⁺ vacancies.

<table>
<thead>
<tr>
<th>Peak Index</th>
<th>Intensity, %</th>
<th>Max Temperature, Tm, K</th>
<th>E, eV</th>
<th>s, 1/sec</th>
<th>lifetime, day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ 40nm Peak 1</td>
<td>41.9</td>
<td>458</td>
<td>0.97</td>
<td>1.01E+10</td>
<td>56</td>
</tr>
<tr>
<td>Al₂O₃ 40nm Peak 2</td>
<td>58.1</td>
<td>476</td>
<td>1.05</td>
<td>2.06E+11</td>
<td>65</td>
</tr>
<tr>
<td>Al₂O₃ 50nm Peak 1</td>
<td>77.3</td>
<td>458</td>
<td>0.97</td>
<td>1.3E+10</td>
<td>43</td>
</tr>
<tr>
<td>Al₂O₃ 50nm Peak 2</td>
<td>22.7</td>
<td>471</td>
<td>1.05</td>
<td>2.06E+11</td>
<td>65</td>
</tr>
</tbody>
</table>
often associated with charge compensators like oxygen vacancies, resulting in a complex defect (an electron trap).

As observed in natural diaspore, the TL spectrum peaking at 473 ± 3 K can be linked to a discrete trap structure [11]. This peak has also been detected in $\text{Al}_2\text{O}_3$:C, which is usually employed to estimate environmental doses [3] and in natural diaspore [12]. The lifetime for the traps in nano-$\text{Al}_2\text{O}_3$ was estimated as 43–56 days for the first trap and approximately 65 days for the second trap, responsible for TL emission at the low-temperature part of the glow curve.

CONCLUSIONS

This investigation explores the basic thermoluminescence characteristics of irradiated nano-$\text{Al}_2\text{O}_3$ particles with varying particle sizes. The TL glow curve of nano-$\text{Al}_2\text{O}_3$ with a particle size of 40 nm displays a peak at 460 K, with a broad feature spanning from 523 K to 623 K. The alumina nanoparticles' peak temperature relies on the particle size and measures 467 K for the 50 nm variant. The low-temperature region peak can be separated into two first-order kinetic peaks at 458 ± 1 K and 476 ± 2 K using the GlowFit software [8]. As such, two types of luminescence behaviors exist - discrete electron trap distribution at a lower temperature (~460 K) and a continuous trap configuration at a higher temperature (above 520 K), which is typical of $\alpha$-$\text{Al}_2\text{O}_3$, is characteristic of nano-alumina as well.

Furthermore, the TL intensity of the exposed nanoparticles proportionally increases with the radiation dose, indicating the prospect of using alumina nanoparticle powder as a dosimetry substrate material for ionizing radiation dosimetry. However, it's crucial to acknowledge certain limitations when utilizing nano-$\text{Al}_2\text{O}_3$ as dosimeters. For instance, the traps in nano-$\text{Al}_2\text{O}_3$ have relatively short lifetimes, estimated at approximately 43–56 days for the first trap and around 65 days for the second trap. These traps are responsible for the TL emission in the low-temperature region of the glow curve.

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Термолюминесцентные властивості нанооксиду алюмінію з двома різними розмірами частинок

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Дано дослідження спрямоване на вивчення властивостей термолюминесценции (ТЛ) нанорозмірного оксиду алюмінію та включает взаємозв’язок між інтенсивністю ТЛ та поглиненою дозою, ідентифікацію окремих піків люмінесценції та визначенням параметрів пастки для використання у якості можливого дозиметра. Зразки опромінювали 60Со дозами від 530 до 2646 Гр. Результати показують, що мікророзмірний а-Al2O3 мав головний дозиметричний пік при Тм = 435 К, тоді як зразки нано-α-Al2O3 із розміром частинок 40 і 50 нм демонстрували криву світіння ТЛ, причому основний дозиметричний пік знаходився в області низьких температур і характеризувався складною структурою при більш високих температурах (понад 500 К). На первинній дозиметричний пік впливаю розмір наночастинок, з максимумом 460 К для зразка 40 нм і 467 К для зразка 50 нм. Суперпозиція двох піків описує спектрореєструваній дозиметричний пік.

Ключові слова: енергія активації; частотний фактор; GlowFit; нано-оксид алюмінію; термолюминесценція.