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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 α-Al_2O_3 had a main dosimetry peak at Tm = 435 K, while nano-α-Al_2O_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 α-alumina; Thermoluminescence.

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Introduction

Luminescent materials have widespread applications in ionizing radiation dosimetry. Among these materials, aluminum oxide (Al_2O_3) sensitized with various dopants has been identified as potential thermoluminescence (TL) dosimeter [1]–[3]. Al_2O_3 has good mechanical stability, making it a commonly used material for radiation detection and dosimetry. In addition, Al_2O_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_2O_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_2O_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 α-Al_2O_3 particles with sizes of 40 and 50 nm and micro-sized α-AI_2O_3 (5–8 μm, α 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

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-Al_2O_3 and two particle sizes of nano-sized α-Al_2O_3 irradiated by ^{60}Co 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-Al_2O_3 samples with particle sizes of 40 and 50 nm and the micro-sized α-Al_2O_3 samples display TL signals with different intensities (Fig. 1, curves 1–3). The experimental glow curve of micro-sized α-Al_2O_3 shows a dominant dosimetry peak at the maximum temperature Tm = 435 K (Fig. 1, curve 1).

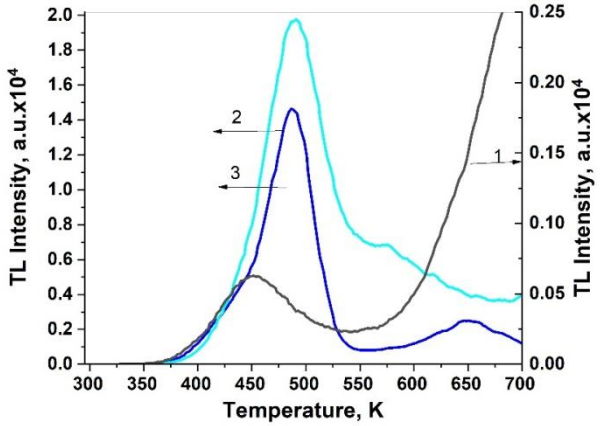

Fig.1. TL glow curve of (1) micro-sized α-AI_2O_3 and nano-sized α-AI_2O_3 (2) 50 nm and (3) 40 nm irradiated at a dose of 2,645 Gy with a heating rate of 5K/s.

The TL sensitivity of nano-sized alumina is approximately ten times higher than that of micro-sized alumina. The luminescence curves of nano-Al_2O_3 samples are similar to those. of α-Al_2O_3, 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-Al_2O_3 is approximately two times higher than that of the 40 nm nano-α-Al_2O_3. Figures 2 and 3 exhibit TL glow curves obtained from nano-α-Al_2O_3 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.

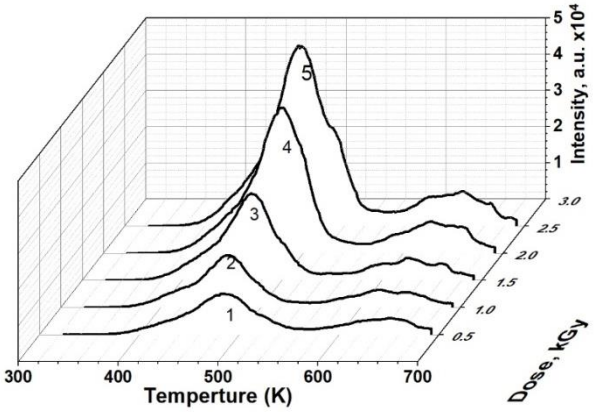

Fig. 2. TL glow curves of nano-AI_2O_3 (40 nm) irradiated at doses of 529.1 Gy (1), 1058.1 Gy (2), 1587.2 Gy (3), 2116.0 Gy (4), and 2645.4 Gy (5).

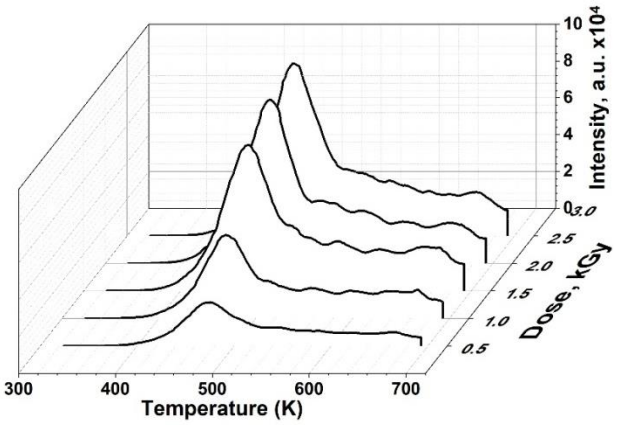

Fig. 3. TL glow curves of nano-AI_2O_3 (50 nm) irradiated at doses of 529.1 Gy (1), 1058.1 Gy (2), 1587.2 Gy (3), 2116.0 Gy (4), and 2645.4 Gy (5).

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-Al_2O_3, where T_m= 465 K [14], but significantly higher than that determined for alumina crystal (T_m=450 K) [5], bauxite (T_m= 412 K)[15], and Al_2O_3 doped with Sr, Li, and Ge (T_m= 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]. Diapores 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]. Al_2O_3 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-Al_2O_3) [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 Al_2O_3:C, which are used for a lower dose range of 1 μGy to 4.5 Gy [19] or $CaSO_4$: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].

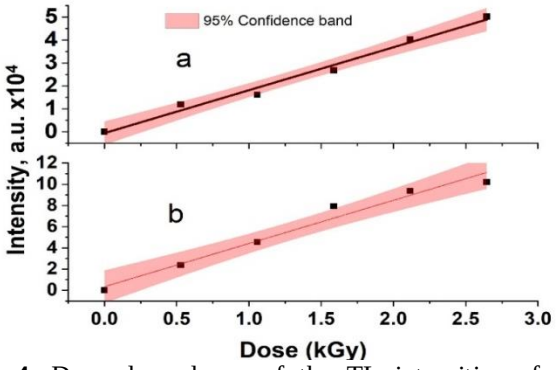

Fig.4. Dose dependence of the TL intensities of the irradiated nanoα-Al_2O_3 with particle sizes of 40 (a) and 50 nm(b).

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 thermo-luminescence 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.

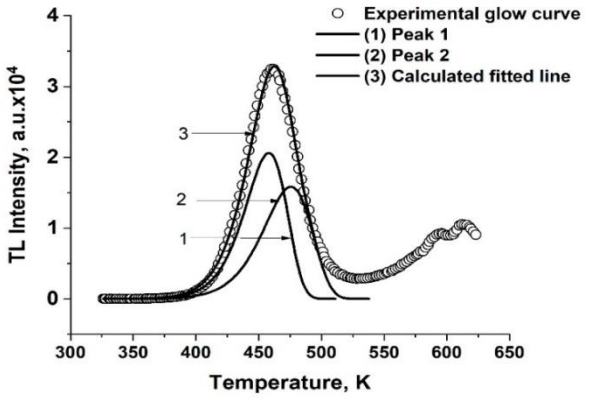

Fig. 5. Deconvolution of the 460 K TL glow peak of the irradiated nano-α-Al_2O_3 with the particle size of 40 nm using a first-order kinetic expression.

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 $s \approx 1.01 \times 10^{10}$ and 1.3×10^{10} s^{-1} for the peak with $T_m = 458 \pm 3$ K and, accordingly, 2.06×10^{11} for the peak with Tm = 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 (Al_2O_3: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 Al^{3+} vacancies,

Table 1.

Kinetic parameters resulting from analyzing the TL glow curves of nano-α-alumina with particle sizes of 40 and 50 nm. Deconvolution is performed using GlowFit, assuming first-order kinetics

Peak Index	Intensity, %	Max Temperature, Tm, K	E, eV	s, 1/sec	lifetime, day
Al2O3 40nm Peak 1	41.9	458	0.97	1.01E+10	56
Al2O3 40nm Peak2	58.1	476	1.05	2.06E+11	65
Al2O3 50nm Peak1	77.3	458	0.97	1.3E+10	43
Al2O3 50nm Peak2	22.7	471	1.05	2.06E+11	65

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 Al_2O_3: C, which is usually employed to estimate environmental doses [3] and in natural diaspore [12]. The lifetime for the traps in nano-α-Al_2O_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-α-alumina particles with varying particle sizes. The TL glow curve of nano-α-Al_2O_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 α-Al_2O_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-Al_2O_3 as dosimeters. For instance, the traps in nano-α-Al_2O_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 lower-temperature region of the glow curve.

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[1] M. A. Jowhari, S. A. Farha Al-Said, A. Abuhoza, and H. Donya, *Dosimetric studies of pure and Ag-doped alumina as nanodosimeter for high gamma radiation doses*, Mater. Today Proc., 65, 2615 (2022); https://doi.org/10.1016/J.MATPR.2022.04.879.
[2] N. S. B. Saharin, N. E. Ahmad, H. A. Tajuddin, and A. R. Tamuri, T*hermoluminescence properties of aluminium oxide doped strontium, lithium and germanium prepared by combustion synthesis method*, EPJ Web Conf., 156, (2017); https://doi.org/10.1051/epjconf/201715600001.
[3] E. G. Yukihara et al., *The effects of deep trap population on the thermoluminescence of Al_2O_3:C*, Radiat. Meas., 37(6), 627 (2003); https://doi.org/10.1016/S1350-4487(03)00077-5.
[4] M. Osvay and T. Biró, *Aluminium oxide in TL dosimetry*, Nucl. Instruments Methods, 175(1), 60 (1980); https://doi.org/10.1016/0029-554X(80)90253-0.
[5] V. S. Kortov, A. Orozbek Uulu, and I. A. Vainshtein, *Characteristic features of thermoluminescence kinetics in dosimetric aluminum oxide crystals*, J. Appl. Spectrosc., 73(2), 206 (2006), https://doi.org/10.1007/s10812-006-0059-3.
[6] N. S. Saharin, H. Wagiran, and A. R. Tamuri, *Thermoluminescence Characteristics of Aluminium Oxide Doped Carbon Exposed to Cobalt-60 Gamma Radiation*, Adv. Mater. Res., 1107, 553 (2015); https://doi.org/10.4028/www.scientific.net/AMR.1107.553.
[7] A. J. J. Bos, *High sensitivity thermoluminescence dosimetry*, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 184(1–2), 3 (2001); https://doi.org/10.1016/S0168-583X(01)00717-0.
[8] M. Puchalska and P. Bilski, *GlowFit-a new tool for thermoluminescence glow-curve deconvolution*, Radiat. Meas., 41(6), 659 (2006); https://doi.org/ 10.1016/j.radmeas.2006.03.008.
[9] A. Delgado and J. M. Gómez Ros, *Computerised glow curve analysis: A tool for routine thermoluminescence dosimetry*, Radiat. Prot. Dosimetry, 96(1–3), 127 (2001), https://doi.org/10.1093/oxfordjournals.rpd.a006568.
[10] V. Correcher, J. Garcia-Guinea, R. Gonzalez-Martin, E. Crespo-Feo, and D. Jimenez-Cordero, *Study of aluminium oxide from high-alumina refractory ceramics by thermoluminescence*, Bull. Mater. Sci., 31(6), 891 (2008); https://doi.org/10.1007/s12034-008-0142-x.
[11] J. Garcia-Guinea, V. Correcher, J. Rubio, and F. J. Valle-Fuentes, E*ffects of preheating on diaspore: Modifications in colour centres, structure and light emission*, J. Phys. Chem. Solids, 66(7), 1220 (2005), https://doi.org/10.1016/j.jpcs.2005.04.001.
[12] V. Correcher, J. Garcia-Guinea, and F. J. Valle-Fuentes, *Recent results on the thermoluminescence properties of diaspore*, Geophys. Res. Lett., 30(18), 5 (2003); https://doi.org/10.1029/2003GL018028.
[13] M. G. Rodriguez, G. Denis, M. S. Akselrod, T. H. Underwood, and E. G. Yukihara, T*hermoluminescence, optically stimulated luminescence and radioluminescence properties of Al_2O_3:C,Mg*, Radiat. Meas., 46(12), 1469 (2011); https://doi.org/10.1016/j.radmeas.2011.04.026.
[14] D. R. Mishra *et al.*, *Luminescence properties of α - Al_2O_3:C crystal with intense low temperature TL peak*, Radiat. Meas., 42(2), 170 (2007); https://doi.org/10.1016/j.radmeas.2006.06.007.

[15] A. El-Taher, H. T. Mahdy, and J. H. AlZahrani, *Determination of Thermoluminescence Kinetic Parameters of Bauxite by Computer Glow Curve Deconvolution Method (CGCD)*, Life Sci. Journal, 10(2), 1475 (2013).
[16] J. Garcia-Guinea, J. Rubio, V. Correcher, and F. J. Valle-Fuentes, *Luminescence of α-Al_2O_3 and α-AlOOH natural mixtures, Radiat. Meas.*, 33 (5), 653 (200); https://doi.org/10.1016/S1350-4487(01)00078-6.
[17] N. Salah, Z. H. Khan, and S. S. Habib, *Nanoparticles of Al2O3:Cr as a sensitive thermoluminescent material for high exposures of gamma rays irradiations*, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 269(4), 401 (2011); https://doi.org/10.1016/j.nimb.2010.12.054.
[18] G. Molnár et al., Thermally Stimulated Luminescence and Exoelectron Emission Mechanism of the 430 K (D') Dosimetric Peak of a-Al_2O_3, Radiat. Prot. Dosimetry, 84(1–4), 253 (1999); https://doi.org/10.1093/oxfordjournals.rpd.a032731.
[19] M. Zahedifar, L. Eshraghi, and E. Sadeghi, *Thermoluminescence kinetics analysis of α-Al_2O_3:C at different dose levels and populations of trapping states and a model for its dose response*, Radiat. Meas., 47(10), 957 (2012); https://doi.org/10.1016/j.radmeas.2012.07.018.
[20] N. Salah, P. D. Sahare, S. P. Lochab, and P. Kumar, *TL and PL studies on : Dy nanoparticle*s, Radiat. Meas., 41(1), 40 (2006); https://doi.org/10.1016/j.radmeas.2005.07.026.
[21] A. I. Surdo, R. M. Abashev, I. I. Milman, and E. V. Moiseykin, *Accumulation features and TL of TLD-500 detectors in a wide temperature range at pulsed and continuous high-dose irradiation*, Radiat. Meas., 90, 192 (2016); https://doi.org/10.1016/j.radmeas.2015.12.027.
[22] R. Chen, V. Pagonis, and J. L. Lawless, *Evaluated thermoluminescence trapping parameters–What do they really mean?*, Radiat. Meas., 91, 21 (2016); https://doi.org/10.1016/j.radmeas.2016.04.006.
[23] G. Molnár et al., *Thermally Stimulated Luminescence and Exoelectron Emission Mechanism of the 430 K (D') Dosimetric Peak of a-Al_2O_3*, Radiat. Prot. Dosimetry, 84(1–4), 253 (1999); https://doi.org/10.1093/oxfordjournals.rpd.a032731.
[24] E. G. Yukihara, V. H. Whitley, S. W. S. McKeever, A. E. Akselrod, and M. S. Akselrod, *Effect of high-dose irradiation on the optically stimulated luminescence of Al_2O_3:C*, Radiat. Meas., 38(3), 317 (2004); vhttps://doi.org/10.1016/j.radmeas.2004.01.033.

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Термолюмінесцентні властивості нанооксиду алюмінію з двома різними розмірами частинок

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Дане дослідження спрямоване на вивчення властивостей термолюмінесценції (ТЛ) нанорозмірного оксиду алюмінію та включає взаємозв'язок між інтенсивністю ТЛ та поглиненою дозою, ідентифікацію окремих піків люмінесценції та визначенням параметрів пастки для використання у якості можливого дозиметра. Зразки опромінювали 60Co дозами від 530 до 2646 Гр. Результати показують, що мікророзмірний α-Al_2O_3 мав головний дозиметричний пік при Tm = 435 K, тоді як зразки нано-α-Al_2O_3 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 K). На первинний дозиметричний пік впливав розмір наночастинок, з максимумом 460 K для зразка 40 нм і 467 K для зразка 50 нм. Суперпозиція двох піків описує спостережуваний дозиметричний пік.

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