Thermoluminescence of Irradiated Nanocomposite Material Based on Aluminum Oxide

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Abstract. We numerically investigated thermo-stimulated luminescence (TSL) of irradiated pure $\alpha$-Al$_2$O$_3$ and nanocomposite material Al$_2$O$_3$+SrO. We showed that the thermoluminescence intensity peak depends on the absorbed dose of ionizing radiation in case of low and high power irradiation.

1. Introduction
Electrophysical properties of materials, including thermo-stimulated luminescence (TSL), depend on the spectrum of localized states stipulated by different structural defects and impurities (including nanoparticles). Alumina oxide has deep traps for electrons, which could accumulate and store the information about the absorbed dose, that makes Al$_2$O$_3$ and nanocomposites, based on it, the promising material for dosimeters [1-3].

TSL of materials stems from the irradiative recombination of electrons, released from traps due to the thermal activation, and holes, trapped on the recombination center. Rouse-Fowler model allows researchers to describe the kinetics of charge carriers, taking into account their generation and recombination, as well as capturing of charge carriers by traps and release from them. Previously, the authors [4-6] investigated the thermally stimulated luminescence of anion-defected $\alpha$-Al$_2$O$_3$. In paper [4] the simple model for TSL curves was used to assess the parameters of localized states. And in [5, 6] the authors used the specific case of Rouse-Fowler model, which was implemented for two localized states with the traps parameters from [4]. The thermoluminescence intensity was defined by the recombination term $I=\alpha np$, where $\alpha$ is a recombination coefficient, $n$ is the concentration of free electrons, and $p$ is the concentration of holes on the recombination center.

Obtained results have a good quantitative agreement with the experiments, though models from [4-6] are not applicable for the description of such complex materials, as nanocomposites. In this paper we present a model, suitable (in perspective) for the description of TLS curves both pure and nanocomposite materials.

2. TSL model of nanocomposite material
Thermoluminescence properties of material are determined by the charge carrier kinetics and, therefore, depend on the energy spectrum of localized states. The spectrum of pure Al$_2$O$_3$ localized states could be described as two deep traps [4-6]. To calculate the energy spectrum of localized states, originated from the nanoparticles introduction, we should solve the task of spherical potential well,
which depth is determined by the difference in work functions of materials of the matrix and the nanoparticle [7, 9].

Rouse-Fowler equation system (1)-(4) describes the kinetics of charge carriers, taking into account the generation and recombination of charge carriers, their capture by localized states and their release because of the thermal activation:

\[ \dot{n} = S + S_{pat} - \alpha n \left[ p + \sum_{l=1}^{l_{max}} p_{l} \right] - n \sum_{m=1}^{m_{max}} K_{m} + \sum_{m=1}^{m_{max}} n_{m} \tau_{m} \]  
(1)

\[ \dot{p} = S + \left( S_{pat} - S'_{pat} \right) - \alpha p \left[ n + \sum_{m=1}^{m_{max}} n_{m} \right] - p \sum_{l=1}^{l_{max}} K_{l} + \sum_{l=1}^{l_{max}} p_{l} \tau_{l} \]  
(2)

\[ \dot{n}_{m} = K_{m} n - \frac{n_{m}}{\tau_{m}} - \alpha n p_{m} - S'_{pat} \delta_{m,m_{0}}, \quad 1 \leq m \leq m_{0} \]  
(3)

\[ \dot{p}_{l} = K_{l} p - \frac{p_{l}}{\tau_{l}} - \alpha n p_{l} + \left( S_{pat} - S'_{pat} \right) \delta_{l,0}, \quad 1 \leq l \leq l_{0} \]  
(4)

where \( S = \left( 1 - f_{pat} \right) \rho D / w_{j} \) is the charge carrier generation rate in the matrix; \( S'_{pat} = f_{pat} \cdot \left( \rho D / w_{j} \right)_{pat} \) and \( S'_{pat} = 0 \) are the carrier generation rate for donor inclusion and acceptor inclusion, respectively; \( \rho \) is the mass density; \( D \) is the radiation energy absorbed by unit mass per unit time; \( w_{j} \) is the average energy of free carrier pair formation; \( f_{pat} \) is the inclusion volume fraction. Values in brackets with \( pat \) are determined for the inclusions; \( n, p \) are the concentrations of free electrons and holes; \( n_{m}, p_{l} \) are the concentrations of trapped electrons and holes, where \( 1 \leq m \leq m_{0}, 1 \leq l \leq l_{0} \) are the numbers of energy levels for electrons and holes. Other notations: \( \alpha \) is the recombination coefficient; \( K_{m} = k_{m} (M_{m} - n_{m}), K_{l} = k_{l} (P_{l} - p_{l}), \) where \( k_{m}, k_{l} \) are capture coefficients on electron and hole traps, \( M_{m}, L_{l} \) are the concentrations of electron and hole traps, respectively; \( \tau_{m,l} = \exp \left( E_{m,l} / kT \right) / v_{0} \) are the life times of charge carrier on electron and hole traps with energies \( E_{m,l} \) [5, 7].

We presented the solution method of the equation system (1)-(4) for an arbitrary spectrum of localized states in [7], and we used this equation system to investigate electrical conductive properties of both pure and nanocomposite materials after irradiation [7-9]. We will consider the homogeneous ionization, ignoring loading effects and drift of charge carriers [7].

The equation system (1)-(4) determines the concentrations of free and trapped charge carriers, which allows us to assess the emissive and absorption abilities of nanocomposite material.

The emissive ability of a material is defined by the irradiative recombination of charge carriers. In pure material the emission is possible only because of the recombination of free charge carriers, like in ideal semiconductor. Real materials have their own spectrum of localized states, which stem from different structural defects and nanoparticles introduction (nanocomposite material). Therefore, the recombination of free charge carriers with the trapped ones will also contribute to the radiation spectrum.

Assuming the concentration of free charge carriers obey the Boltzmann distribution law, we obtained the following expressions for the spectral emission ability of a material \( Q(h\omega) \), which depends on the frequency of recombination of free charge carriers (5), free electrons with trapped holes (6), and free holes with trapped electrons (7):

\[ Q_{l}(h\omega) = a_{l} h\omega \frac{NP}{(kT)^{2}} \frac{(h\omega - \Delta E)^{2}}{2} \exp \left( -\frac{h\omega - \Delta E}{kT} \right), \quad \text{for } h\omega \geq \Delta E, \]  
(5)
\[ Q_s(h\omega) = a h\omega \frac{2}{\sqrt{\pi} (kT)^{3/2}} \sum_j p_j(e_j) \sqrt{e_j + h\omega - \Delta E} \exp \left( \frac{-e_j + h\omega - \Delta E}{kT} \right), \text{ for } h\omega \geq \Delta E - e_j, \] (6)

\[ Q_s(h\omega) = a h\omega \frac{2}{\sqrt{\pi} (kT)^{3/2}} \sum_m n_m(e_m) \sqrt{e_m + h\omega - \Delta E} \exp \left( \frac{-e_m + h\omega - \Delta E}{kT} \right), \text{ for } h\omega \geq \Delta E - e_m. \] (7)

Here \( k \) is the Boltzmann constant; \( T \) is the temperature; \( e_j = E_j \) and \( e_m = \Delta E - E_m \) are depths of localized states, counted from the top of valence band; \( \Delta E \) is the band gap; \( E_l, E_m \) are the energies of electron and hole localized states, respectively.

The resulting emission ability can be calculated as a sum over the all processes:

\[ Q(h\omega) = \sum Q_s(h\omega) \]

The charge carriers trapping is a nonradiative process, as the energy, emitted at such transitions, is absorbed by the lattice [10].

The adsorption of a material depends on the interband transitions of charge carriers \( \Sigma_s(h\omega) \) and the polarization interaction of charge carriers with the electromagnetic field \( \Sigma_p(h\omega) \) [10]. The resulting spectral absorption coefficient \( \Sigma(h\omega) \) is defined as a sum over the all processes: \( \Sigma(h\omega) = \Sigma_s(h\omega) + \Sigma_p(h\omega) \). Here \( \Sigma_p(h\omega) = 2n''\omega/c \) (\( \omega \) is the emission frequency, \( c \) is the light speed, \( n''(\omega) \) is the imaginary part of refraction index, which is defined by the imaginary \( e''(\omega) \) and real \( e'(\omega) \) parts of the permittivity).

If we know the emissive ability of a nanocomposite material, as well as its spectral absorption coefficient, we can solve the kinetic equation of radiation transport through the matter and determine the spectral emittance of this material. In case of no external photoexcitation, no scattering (the impurity concentration is small), and isotropic emission we will have the following kinetic equation of radiation transport for 1D systems:

\[ I(z,\cos \vartheta,\omega) = \int_0^\infty \frac{1}{4\pi} Q(z - \xi \cos \vartheta,\omega) e^{-iz(z - \xi \cos \vartheta,\omega)} d\xi \]

Here \( z' = z - \xi \cos \vartheta, \xi \in [0, a] \) is a coordinate on the \( Z \)-axis; \( a \) is the sample thickness; \( d\xi = dz/\cos \vartheta \), \( \vartheta \) is the angle between the \( Z \)-axis and the motion direction of a quantum of radiation; \( \tau(z, z', \omega) = \int_0^\infty \Sigma(z', \omega) d\xi' \) is the optical path length of a radiation with the frequency \( \omega \) from point \( z' \) to \( z \).

For 1D systems the spectral emittance \( Y(a, \omega) \) and the radiation yield \( I(a) \) are defined by the formulas \( Y(a, \omega) = 2\pi \int_0^\infty I(a, \cos \vartheta, \omega) \cos \vartheta d\cos \vartheta \) and \( I(a) = \int_{\omega_{\min}}^{\omega_{\max}} Y(z, \omega) \cdot d\omega \), where \( \omega_{\min} \), \( \omega_{\max} \) are the minimal and maximal frequency of a quantum of radiation.

To calculate the TSL we heated the samples uniformly and with the constant heating rate.

3. Results

In the experiment [4] the irradiated alumina oxide was preheated to the temperature of 436 K, then it was rapidly cooled to the room temperature. Only after that the TSL curve was recorded under the heating from 300 to 620 K at the heating rate of 2 K/s. This preheating procedure reduces the population of the first trap, which allows us to observe two comparable peaks on the resulting picture (figure 1, curve 1). Without the preheating, the second peak is too small. Also, the sample was preheated to 500 K, and, as a result of this treatment, the first trap was completely emptied. Therefore,
after the TSL curve recording, only the second peak was observable on the resulting picture, which indicates that alumina oxide spectrum includes two electron traps [4].

![Figure 1](image)

**Figure 1.** Thermoluminescence intensity of the pure Al₂O₃ at the heating rate of 2 K/s after preheating. 1 is the experiment [4], 2 is our result.

In our model we used the following parameters for electron localized states in the pure Al₂O₃:

- Em₁ = 1.3 eV, Em₂ = 1.6 eV,
- kᵣ₁ = 10⁻²⁰ m²/s, kᵣ₂ = 10⁻²⁵ m²/s,
- Mᵣ₁ = 10²¹ m⁻³, Mᵣ₂ = 10²⁰ m⁻³,
- νᵣ₁ = 9.7 · 10¹³ s⁻¹, νᵣ₂ = 2 · 10¹³ s⁻¹.

The recombination center (hole trap) parameters:

- El₁ = 1.1 eV,
- kl₁ = 10⁻¹¹ m²/s, Lᵣ₁ = 10²⁵ m⁻³, νᵣ₁ = 10⁴ s⁻¹.

At first, the pure alumina oxide with all empty traps was exposed to the radiation with the power of 0.002 W/kg and duration of 100 s. At the second step the sample was pretreated (heating to 456 K and cooling to 300 K). Finally, we recorded the TSL intensity under the heating to 620 K with the heating rate of 2 K/s.

Unfortunately, the initial population of localized states after the irradiation, as well as the heating and cooling rates during the sample processing were unknown to us. Thus, we heated the sample at the rate of 2 K/s, and the cooling rate was varied from 0.1 to 2 K/s. We obtained the curve 2 in figure 1 at the cooling rate of 0.2 K/s. The concentration ratio of trapped charge carriers on the first trap to the second trap after the treatment was 1.73. The hole concentration was 1.34 · 10¹⁹ m⁻³, which is an order of magnitude higher than the concentration of trapped electrons. This result is in good agreement with the experiment [4].

Table 1 demonstrates the TSL first peak position dependency on the heating rate. The difference between our and experimental results lies within the measurement accuracy of the experiment [4] in most cases.

Figure 2a presents the dependency of the TSL peak intensity of the pure Al₂O₃ (curves 1-3) on the absorbed energy of ionizing irradiation of low power and duration from 3 to 10⁴ s. Curve 2 corresponds to the sample with pretreatment, curve 1 to the sample without pretreatment. Curve 3 corresponds to the intensity of the second peak, which does not depend on the treatment because the release of electrons from the second trap starts from 500 K.

The increase of the TSL peak intensity with the rise of absorbed energy of ionizing radiation is related to the increase of concentrations of electrons and holes, generated during irradiation and trapped by the corresponding localized states.
Table 1. The dependency of the position of the first peak of Al₂O₃ thermoluminescence intensity on the heating rate.

| Heating rate β (K/s) | Temperature position of the first peak of TSL |
|----------------------|---------------------------------------------|
|                      | $T_{\text{max}}^a$ (K) | $T_{\text{max}}^b$ (K) | $T_{\text{max}}^c$ (K) |
| 0.19                 | 432±2                      | 432±1                     | 436                     |
| 0.50                 | 452±2                      | 444±1                     | 447                     |
| 2.00                 | 461±3                      | 462±1                     | 465                     |
| 6.00                 | 474±7                      | 476±1                     | 477                     |
| 11.00                | 494±7                      | 486±1                     | 485                     |

$^a$ Experiment [4].
$^b$ Simulation [4].
$^c$ Our results.

In [7–9] we showed that the most promising nanocomposite materials for investigations in the field of dosimetry are the nanocomposites with the inclusion of small-radius nanoparticles, which concentration does not exceed the concentration of intrinsic localized states due to matrix defects. So, in this work we investigated the nanocomposite materials based on alumina oxide with spherical nanoparticles of SrO with radius of 2 nm and concentration of $5\times10^{-5}$ vol.%. The energy spectrum, which stems from such inclusions, lies in the range from 0.06 to 0.85 eV [9]. The capture coefficient of “impurity” localized states $k_E \sim 10^{-19}$-10$^{-20}$ m$^3$/s, the frequency factor $\nu_E \sim 10^{12}$ s$^{-1}$.

Before irradiation, we calculated the equilibrium concentrations of charge carriers of the nanocomposite material without any external influence. Initial conditions were as follows: all intrinsic traps are empty, all “impurity” traps are completely filled. We used the obtained values of concentrations as the initial condition for the study of TSL.

**Figure 2.** Thermoluminescence intensity peak dependency on radiation energy absorbed by unit mass material: 1-3 – the pure Al₂O₃, 4-5 – Al₂O₃+SrO nanocomposite. 1, 4 – the first peak without preheating, 2, 5 – the first peak after preheating, 3 – second peak. (a) the pulse duration range is 3–1000 s, the absorbed dose rate is 0.002 W/kg; (b) the pulse duration is 100 ns, the absorbed dose rate range is 10$^5$-10$^{10}$ W/kg.
Figure 2 indicates that the thermoluminescence intensity of the nanocomposite without preheating lies higher than the curves for pure Al$_2$O$_3$. In [9] we showed that in the nanocomposite material the intrinsic localized state $E_{trp}=1.3$ eV makes the major contribution to the accumulation of information about the absorbed dose of ionizing radiation. When the nanocomposite is in the equilibrium conditions, this localized state is partially filled by charge carriers released from the small “impurity” traps. And this initial population density makes the additional contribution to the first TSL peak.

The thermoluminescence intensity of the nanocomposite without preheating (plot line 5) lies far lower than other curves, though its growth rate is much larger. During the preheating of the nanocomposite, part of the charge carriers, released from the “impurity” traps and the intrinsic localized state of 1.3 eV depths, are recaptured by the “impurity” traps, because their trapping coefficient is bigger in comparison with the intrinsic traps. Bigger trapping coefficient decreases the possibility of the charge carrier recombination, which leads to the bigger differences in values of the “impurity” traps population density on the irradiation dose change.

We also investigated the impact of high-power irradiation (the pulse duration 100 ns) on the pure Al$_2$O$_3$ and Al$_2$O$_3$+SrO nanocomposite (figure 2b). Again, in the case of the pretreated nanocomposite we registered a significant response of the thermoluminescence intensity peak to the absorbed dose rate. Comparing figures 2a and 2b, we noticed that when we use high-power irradiation the TSL curves are saturated faster than in case of low-power irradiation. The possible explanation is as follows: in case of high power the equilibrium is reached mainly by the charge carrier recombination, and in case of low power – by capturing on traps.

4. Conclusion
We developed the model to describe TSL of irradiated pure Al$_2$O$_3$ and Al$_2$O$_3$+SrO nanocomposite. The results of the TSL calculation for irradiated pure Al$_2$O$_3$ are completely consistent with experiment, which indicates the adequacy of the proposed model.

The introduction of nanoparticles SrO into Al$_2$O$_3$ leads to increase the TLS intensity of resulting materials without preheating after irradiation, because nanoparticles are sources of additional charge carrier.

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Since in case of high power the equilibrium is reached mainly by the charge carrier recombination, and in case of low power – by capturing on traps, in case of high-power irradiation the TSL curves are saturated faster than in case of low-power irradiation.

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