Specific features of the thermoluminescence kinetics of shallow traps in anion-defective single crystals of aluminum oxide

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The kinetics of thermoluminescence (TL) arising from shallow traps in single crystals of anion-defective aluminum oxide has been considered. It has been shown that the TL peak at 320–350 K is characterized by identical kinetic parameters in samples containing various concentrations of shallow traps. Kinetic TL parameters for this peak have been calculated by analyzing of the luminescence isothermal decay curves, varying the heating rate, and the peak shape. An interactive relationship of shallow and dosimetric traps in the crystals under study has been supposed.

Проведен анализ кинетики термолюминесценции (ТЛ), обусловленной мелкими ловушками в монокристаллах анион-дефектного оксида алюминия. Показано, что ТЛ пика при 320–350 К характеризуется идентичными кинетическими параметрами у образцов с различной концентрацией мелких ловушек. Рассчитаны кинетические параметры ТЛ этого пика методом анализа кривых изотермического затухания люминесценции, вариации скоростей нагрева и анализа формы пика. Высказано предположение о наличии интерактивной взаимосвязи мелких и дозиметрических ловушек в исследуемых кристаллах.

The interest in thermoluminescence (TL) properties of anion-defective aluminum oxide single crystals is explained by wide use thereof as ionizing radiation detectors [1, 2]. The thermoluminescence curve for α-Al_2O_3 includes several peaks. The dominating peak is that at 450–500 K, which is used in dosimetric measurements [1]. Moreover, peaks of high-temperature TL connected with deep traps [3], and a TL peak at 320–350 K associated with shallow traps [4] are revealed in these crystals. The study of TL properties of this peak presents an important task since shallow traps may compete with dosimetric centers under irradiation and distort information on the accumulated dose. However, the TL kinetics in this peak has not been studied in detail to date. This study deals with specific features of the TL kinetics arising from shallow trapping centers in anion-defective corundum single crystals.

The objects of study were samples of nominally pure anion-defective α-Al_2O_3 single crystals grown by Stepanov method under reducing conditions. Thermoluminescence was excited using a $^{90}Sr/^{90}Y$ beta-radiation source. The source dose rate was 32 mGy/min. Measurements of TL in shallow traps are complicated because those start to empty immediately after excitation at room temperature. To provide reproducible measurement results for TL in shallow traps, the irradiated samples were kept in dark for the same time period (20 s). TL was recorded during linear heating or in the isothermal regime in the luminescence band of *F*-centers (420 nm). The photostimulated transfer of charge carriers from deep traps to a shallow one was realized using an optical radiation source providing a high spectral intensity at the 470 nm wavelength.

Fig. 1 presents TL curves for three samples of anion-defective aluminum oxide after exposure to a standard dose of beta-

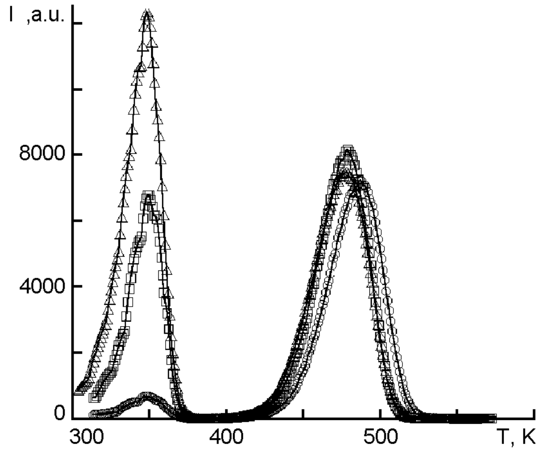

Fig. 1. Thermoluminescence curves for anion-defective single crystals of aluminum oxide exposed to the same irradiation dose. Heating rate 5 K/s.

radiation for 1 min at a heating rate of 5 K/s. It is seen that the dosimetric peak at 480 K is accompanied by a peak at 350 K, which is connected with shallow trapping levels. The study has shown also that samples having a nearly the same dosimetric sensitivity as estimated from the light sum in the dosimetric peak, could be characterized by considerably different intensities of TL determined by the concentration of shallow traps. An examination of Fig. 1 shows that the intensity of the TL peak at 350 K can differ by more than one order of magnitude. However, the temperature position and the shape of this peak remain unchanged in various samples. This observation points to the identity of kinetic parameters of TL in various samples. It has been found also that parameters of the low-temperature TL peak do not depend on the crystal dosimetric sensitivity.

When the irradiated samples were kept at room temperature, the shallow traps are emptied, and the trap depletion is seen as the intensity decrease of their associated TL peak during subsequent measurements. Fig. 2 presents dependences of the 350 K TL peak intensity on the holding time at room temperature for five irradiated samples having different concentrations of shallow traps. It is seen that the curves exhibit a nearly coincident trend in all the samples studied, the depletion kinetics of shallow traps being characterized by close parameters.

Kinetic TL parameters in the peak under study were determined using several different methods. The kinetics order was calculated by analyzing of the luminescence iso-

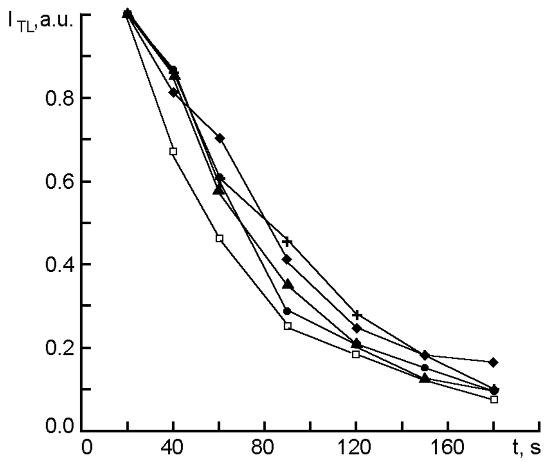

Fig. 2. Intensity of the 350 K TL peak vs. holding time at room temperature for five irradiated samples of anion-defective aluminum oxide.

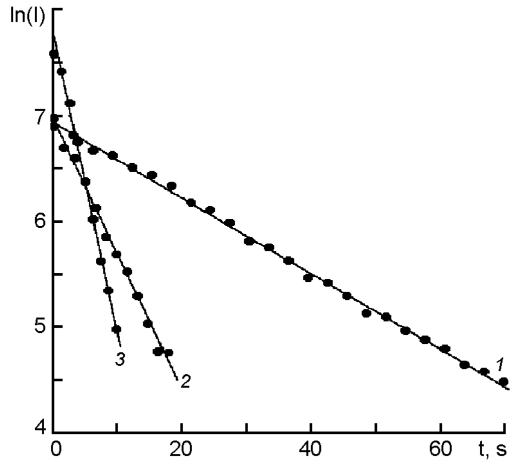

Fig. 3. Curves of isothermal luminescence decay at 40°C (*1*), 50°C (*2*) and 60°C (*3*).

thermal decay curves [5]. The isothermal decay curves were measured at different temperatures. The curves obtained at 40, 50, and 60°C are shown in Fig. 3 where the ordinate is the natural logarithm of the TL intensity. It is seen that these dependences are described well by a linear function. Therefore, the TL decay is exponential. From this experiment, it may be inferred that the peak at 350 K is due to a single mono-energy trap and the TL kinetics is of the first order. It has been found that the temperature of the peak associated with a shallow trap does not change as the irradiation dose increases. This is one more evidence confirming the supposed first order of the TL kinetics. Plotting of the dependence $\ln(m) = \ln(S\exp(-E/kT))$, where m is the slope of the straight lines in Fig. 3

Table. Kinetic parameters of the 350 K TL peak

Method	Activation energy, eV	Frequency factor, s^{-1}
Isothermal decay	0.79	$7.8 \cdot 10^{13}$
Heating rate variation method	0.82	$2.2 \cdot 10^{11}$
Analysis of the peak shape	0.82	$0.76 \cdot 10^{11}$

against the inverse temperature ($1/T$) also gives a straight line, its slope could be used to determine the TL activation energy. In this case, the frequency factor is found from parameters of the intersection point of the straight line and the ordinate axis. The obtained values and results of calculations made by other methods are given in the Table.

The kinetic parameters were also determined from the peak shape [6]. This method is the simplest one for determination of the TL activation energy and the frequency factor, since only several points in the TL curve are used. The maximum temperature T_m and the temperatures T_1 and T_2 which are determined left-side and right-side of T_m at FWHM, are employed most frequently in calculations. In [8], equations are presented relating the activation energy to the peak full width ω, the width of its low-temperature part $\tau = T_m - T_1$, and the high-temperature part δ. The general formula for calculating the E value is

$$E = C_\gamma(kT_m^2/\gamma - B_\gamma(2kT_m), \tag{1}$$

where k is the Boltzmann constant and γ is ω, τ, or δ. The constants C_γ and B_γ are expressed through the shape factor and have different values depending on the quantity used as the parameter γ. Analytical expressions for these constants are also given in [8]. The E value was calculated using each of the three possible methods and then was averaged. The frequency factor was calculated from the formula [7]

$$S = \frac{\beta E}{kT_m^2}\exp\left(\frac{E}{kT_m}\right), \tag{2}$$

where β is the heating rate. The obtained results are summarized in the Table.

The kinetic parameters were also calculated by the heating rate variation method [8]. The activation energy was determined from the formula

$$E = \frac{kT_{m1}T_{m2}}{T_{m1} - T_{m2}}\ln\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2, \tag{3}$$

where T_{m1} and T_{m2} denote temperatures of the peaks corresponding to heating rates β_1 and β_2 [8]. The activation energy was calculated for different pairs of heating rate values. Then its average was used to determine the frequency factor from Eq.(2). The relevant results are given in the Table.

An examination of the Table shows that values of the kinetic TL parameters in the peak under study determined by different methods are in a good mutual agreement. The only exception is the frequency factor determined from the analysis of the isothermal decay curves. This discrepancy can be explained by inaccuracies incurred in the temperature measurements and the calculations. According to our estimates, this error may be as large as one order of magnitude of the frequency factor.

The validity of the obtained results was verified by comparing experimental TL curves and those calculated in the frame of a simplest TL model with one trapping level [5]. The approximation error was estimated by the formula [9]

$$\varepsilon = \frac{\sum_i |I_{\exp}(T_i) - I_{fit}(T_i)|}{\sum_i I_{\exp}(T_i)} \cdot 100\%. \tag{4}$$

The approximation error of an experimental TL curve was found to be less than 10 %, thus corresponding to the criteria adopted in the literature for the analytical description of TL curves [9].

It was found also that TL properties of shallow traps depend on TL parameters of dosimetric trapping centers. A correlation between the 350 K TL peak intensity and FWHM of the dosimetric peak at 470 K has been revealed. The obtained results are shown in Fig. 4. It is seen that in samples with a small FWHM of the dosimetric peak (35–45 K), the value of the 350 K peak may change within broad limits depending on the concentration of shallow traps. However, in samples with a wide main peak (FWHM over 45 K), the intensity of the at 350 K peak is very low in all the samples. This regularity was observed more than once in samples having different dosimetric sensitivities. The interpretation of the obtained results calls for further research.

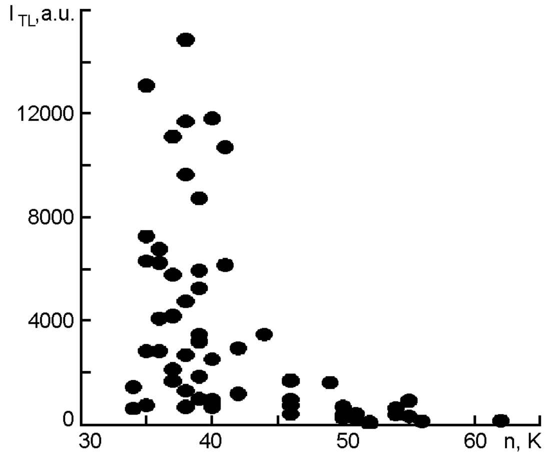

Fig. 4. Intensity of the 350 K TL peak vs. FWHM of the dosimetric peak.

Nevertheless, the following comments may be made even now. It is known that FWHM of the main peak may change due to the presence of traces of various impurities, specifically tetravalent titanium, in the lattice of nominally pure aluminum oxide [10]. Impurity ions act as traps for charge carriers and give rise to their characteristic thermoluminescence, distorting the shape of the dosimetric peak. In this case, the charge may be carried between shallow traps and impurity titanium ions, which are responsible for widening of the main peak. This charge transfer competes with the recombination of carriers at luminescence centers, resulting in the decrease in the TL intensity of the 350 K peak. In this case, the charge exchange processes of between shallow and dosimetric traps can be described in terms of the interactive trap system model similarly to the explanation of specific features of main peak TL [3]. At least it may be stated even now that pre-filling of main traps can influence TL parameters of shallow centers.

Measurements of the phototransferred thermoluminescence (PTTL) (Fig. 5) due to the optical migration of carriers from deep electron traps [11], demonstrates that shallow traps are of electron origin. Their physical nature will be revealed in further research.

Thus it has been found that the concentration of shallow traps can change considerably in samples of anion-defective single crystals of aluminum oxide having an equal dosimetric sensitivity. Kinetic parameters of the TL peak at 350 K, which is associated with shallow traps, have been calculated. The obtained results describe well the TL curve in terms of a simplest TL model.

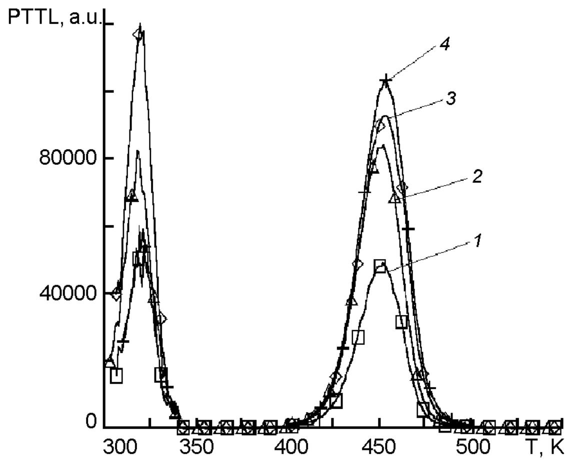

Fig. 5. Phototransferred thermoluminescence of α-Al_2O_3 single crystals with pre-filled deep traps depending on the duration of stimulation with a light flux at 470 nm wavelength (min): *1* — 2, *2* — 3, *3* — 4, *4* — 5 min. The heating rate was 2 K/s.

An interrelationship between the intensity of the TL peak at 350 K and FWHM of the main peak has been established. This observation points to possible charge exchange processes in the system of shallow and dosimetric traps.

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Особливості кінетики термолюмінесценції мілких пасток в аніон-дефектних монокристалах оксиду алюмінію

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Виконано аналіз кінетики термолюмінесценції (ТЛ), обумовленої мілкими пастками в аніон-дефектних монокристалах оксиду алюмінію. Показано, що ТЛ піка при 320–350 К характеризується ідентичними кінетичними параметрами для зразків з різними концентраціями мілких пасток. Обчислено кінетичні параметри цього піка методами аналізу кривих ізотермічного згасання люмінесценції, варіювання швидкості нагрівання та аналізу форми піка. Висловлено припущення про наявність інтерактивного взаємозв'язку мілких та дозиметричних пасток у кристалах, що досліджувалися.