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Study of trapping centers in undoped Al_2O_3 crystals using thermoluminescence methods

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The energy spectra of trapping centers (TC) in specially undoped α–Al_2O_3 crystals within temperature range of 80 to 500 K have been studied using thermoluminescence (TL). In this work, the oscillation regularity revealed before in the TC energy spectrum has been studied in more detail as well as the decay features of some anomalously broad TL peaks. The values of the TC thermal activation energy form the single oscillation series $E_n = \hbar\omega_{TL}(n + 1/2)$, $\hbar\omega_{TL} = 642$ cm^{-1} (0.079 eV). The corresponding Raman line 645 cm^{-1} is the highest frequency of the full-symmetric A_g modes. This regularity is concluded to be due to the polaron nature of the traps. A method has been proposed to establish the cause of TL peak broadening, i.e., to determine its structure. The TL peak at 280 K has been shown to have a complex structure being a superposition of at least two elementary peaks close to one another. The intensity of the complex peak low-temperature component increases faster than that of the high-temperature one as the light sum rises.

Методами термолюминесценции (ТЛ) исследован энергетический спектр ловушек в специально не легированных кристаллах α–Al_2O_3, в интервале температур 80–500 К. В данной работе подробнее исследована найденная ранее осцилляторная закономерность в энергетическом спектре ловушек, а также особенности высвечивания некоторых аномально широких пиков ТЛ. Обнаружено, что энергии активации ловушек формируют одну осцилляторную серию: $E_n = \hbar\omega_{TЛ}(n + 1/2)$, $\hbar\omega_{TЛ} = 642$ см$^{-1}$ (0.079 эВ). В спектре комбинационного рассеяния соответствующая линия 645 см$^{-1}$ отвечает наиболее высокочастотному из полносимметричных A_g колебаний. Сделан вывод, что эта закономерность обусловлена поляронной природой ловушек. Предложена методика, позволяющая установить причину расширения пика ТЛ, то есть определить его структуру. Показано, что пик ТСЛ при 280 К сложный и является суперпозицией, по крайней мере, двух близко расположенных элементарных пиков, причем интенсивность низкотемпературной компоненты сложного пика с увеличением светосуммы возрастает быстрее, чем высокотемпературной.

In [1–10], was reported the presence of oscillatory dependences in the trapping center (TC) energy spectra for $Ba_2NaNb_5O_{15}$, $CsCdCl_3$, $Y_3Al_5O_{12}$, $ZnWO_4$, $CdWO_4$, NaCl, and Al_2O_3 crystals:

$$E_n = \hbar\omega_{TL}(n + 1/2), \qquad (1)$$

the quantum energy $\hbar\omega_{TL}$ having values typical of the crystal lattice vibrations (100 to 1500 cm^{-1}). Depending on the crystal nature, from one ($Ba_2NaNb_5O_{15}$, NaCl) to five ($Y_3Al_5O_{12}$) series of the TC thermal activation energy were observed. To each series, there is a specific value of the oscillation quantum $\hbar\omega_{TL}$. In turn, a corresponding line has been found to each quantum in the Raman spectrum (except for NaCl). The difference between the corresponding value of $\hbar\omega_{TL}$ and $\hbar\omega_R$ is as small as 0.1 to 3 %.

Corundum Al_2O_3 belongs to structures being under intense and constant studies. There are dozens of publications devoted only to its thermoluminescence (TL). In spite of that attention of researchers, the mechanisms of processes accompanying the

TL are still unclear. The experimental data on the energy and kinetic parameters of TC are often contradictory. In particular, several dozens of methods have been proposed to determine the trap parameters from TL curves, but those are applicable only to isolated or weakly overlapped peaks. In practice, the TL peaks are often overlapped so that a single total maximum is observed. The increased width of such a peak results often from the quadratic decay kinetics, that causes the peak broadening as compared to the case of linear process kinetics.

The purpose of this work is to study in more detail the oscillation regularity revealed before in the TC energy spectrum for intentionally undoped α–Al_2O_3 crystals as well as the decay features of some TL peaks. A method has been proposed to establish the cause of TL peak broadening, i.e., to determine either the peak is an elementary one realized according to the linear kinetics or it has a complex structure due to superposition of several elementary TL peaks being close to each other.

The TL was studied within 80 to 600 K temperature range. The heating rate was 0.15 K/s. The linear heating was provided using a computer software. The experimental data were recorded and processed using the computer, too. The TL intensity was recorded every 0.05 mV of a Chromel-Copel thermocouple e.m.f., the step height answering to about 1.4 K at 80 K and about 0.6 K at 500 K. When studying the low-temperature TL peaks ($T < 150$ K), the thermocouple signal step of 0.02 mV was also used. The crystals of about $0.3 \times 10 \times 10$ mm^3 size were placed into a vacuum cryostat and excited by X-rays (U = 50 kV, I = 20 mA) through a 0.25 mm thick beryllium window at 80 K. The excitation duration was 10 min when survey curves were recorded. At fractional decay, the excitation lasted 20 to 30 min.

The study of regularities in the TC energy spectra requires a high accuracy in the activation energy determination, therefore, in [9, 10] we have described in detail some problems of experimental procedures and data processing. The activation energy was determined using the fractional TL curve method that has been tested for numerous materials. The method essence consists in that a series of initial sections of TL curves are recorded at an enhanced sensitivity of the recording scheme. After every heating and recording of the initial curve section, the crystal was cooled rapidly to the initial temperature. To provide an approximately equal intensity of the last experimental points, the crystal was heated at each next cycle to a temperature exceeding that of the precedent one. The heating/cooling cycles were performed till one or several closely positioned TL maxima were obtained. For some high-intensity TL maxima, this procedure provided a hundred or even more initial sections, thus, the accuracy of the TC energy determination is enhanced considerably. Moreover, the experimental data recording and the processing thereof are separated in time, thus, those are processed in a more thorough manner. These measures provide the TC energy determinations at a r.m.s. deviation (SD) of 1 to 3 meV, that is, at a substantially higher accuracy as compared to anyone other single-measuring method.

The activation energy was determined under assumption that at the initial section of the TL curve the concentration change of filled traps (the light sum) can be neglected. That is, the TL intensity is described by exponential dependence

$$I = I_0 \exp(-E/kT). \tag{2}$$

Basing on that dependence, the parameters of the straight line

$$\ln I = A - E/kT, \tag{3}$$

(where $A = \ln I_0$) were calculated. The energy E was determined by averaging it over all pairs of neighboring experimental points, i.e. as

$$E = -\frac{k}{n-1}\sum_{i=1}^{n-1}\frac{\ln I_{i+1} - \ln I_i}{1/T_{i+1} - 1/T_i}. \tag{4}$$

In all the data processing procedures, it is just the minimum SD (ε) value that was selected to be the completion criterion. It was calculated by averaging the differences between the experimental intensities and the corresponding value of the straight line (3) ordinate:

$$\varepsilon = \frac{1}{n}\left[\sum_{i=1}^{n}\left(\ln I_i - (A - E/kT_i)\right)^2\right]^{\frac{1}{2}}. \tag{5}$$

The parameter A was determined by averaging over all points of the experimental curve:

$$A = \frac{1}{n}\left(\sum_{i=1}^{n}(\ln I_i + E/kT_i)^2\right)^{\frac{1}{2}}. \qquad (6)$$

The data processing routine provides for a series of procedures described in [9, 10].

An individual sample of undoped Al_2O_3 does not show all the peaks characteristic for the corundum TL, but considering a group of spectra related to different crystals, it is possible to reveal some typical features of that TL (see, e.g., Fig. 1). In the low-temperature region, a peak at 100 K is observed in all the samples. Its intensity is very low and it is recorded only at a considerable amplification. Two peaks are also observed for all the samples (the total number being 9) with maxima within 223–240 K and 261–281 K ranges, depending on the individual sample. Those peaks are overlapped in part, that is why the maximum temperature shifts. The intensity ratio between those peaks depends on the excitation duration. Several partially overlapped peaks are observed in the high-temperature region (350 to 600 K). In some samples, the TL peak at 384–398 K is split into two ones. The next peak has the maximum temperature at 502–517 K. In two samples, only single peaks at 344 K and 419 K were observed. As a whole, the TL curves obtained do not differ in principle from those reported in other works for undoped Al_2O_3 [11].

A series of the corundum TL peaks has been studied using the fractional curve method. Two novel activation energy values have been found in comparison to [9], namely, for $n = 15$ and $n = 23$. The experimental values of the activation energy are presented in 3rd column of the Table below and the corresponding temperatures of TL peak maxima, in 4th column. The second column contains the activation energy values calculated using (3) and the first one, the corresponding quantum numbers n.

Most of activation energy values for undoped corundum crystal can be described by the single oscillatory series of (1) type, the oscillatory quantum energy being 0.079 eV (642 cm^{-1}). This value is within the lattice vibration range. A rather close line at 645 cm^{-1} is found in the Raman spectrum. It answers to the highest frequency of the full-symmetric A_g vibration. This suggests the formation of a polaron stabilized by local field of various defects forming no natural frequencies.

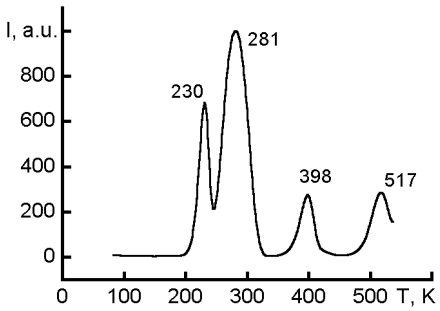

Fig. 1. TL curve for a corundum sample.

The oscillatory dependence evidences the same nature of the trapping centers. All the peaks revealed in this work are associated with hole traps [12].

As an example, Fig. 2 presents the results of fractional decay of the TL peak with a maximum at 398 K. The energy dependence on the slop number shows a plateau. According to the method, the obtained value 1.312 eV is the energy of the trapping center decay in this temperature range.

When studying the 280 K peak, two energy values have been found, 0.696 and 0.782 eV. The difference amounting 0.086 eV fits into the lattice vibration region (694 cm^{-1}), but no close frequency has been found in the Raman spectrum. These data are insufficient to state the presence another series caused, e.g., by local vibration at 694 cm^{-1}.

The 280 K peak is anomalously broad (Fig. 1). The broadening may be due to non-elementary nature of the peak, that is, overlapping of two or more elementary peaks. Another reason is a high re-trapping probability resulting in a prolonged process of the light sum decay. To elucidate the peak broadening mechanism, we have studied the regularities of the peak maximum position, T_m, and its halfwidth, δ, as functions of light sum that was varied by two methods: (1) by varying the excitation time and (2) by a partial decay, that is, by heating of the sample excited in standard conditions (T_{exc} = 80 K, τ_{exc} = 10 min) up to different intermediate temperatures followed by quenching to the excitation temperature with subsequent recording of the residual light sum ("trimming").

If the TL peak is elementary, both methods must give identical results while in the case of a complex peak, the corresponding dependences must differ from one another. In fact, if the peak is non-elementary and the light sum is changed by the intermedi-

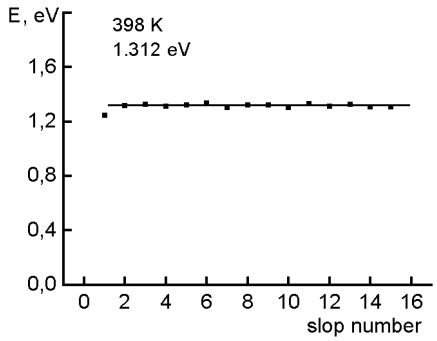

Fig. 2. Energy activation as a function of the fractional curve number for the 398 K peak.

ate heating, then it is just the traps associated with the low-temperature peak that will be emptied predominantly. Therefore, as the light sum decreases, the common peak must be shifted towards higher temperatures and its width must decrease. When the excitation time is varied, those parameters can change in both directions, depending on the relation between the filling rates of different trap kinds in the course of excitation.

Fig. 3 shows the fractional decay results of that peak. There is no clear plateau in the shown energy dependence on the slop number. This fact confirms the preliminary supposed complex nature of the 280 K peak.

The study of the maximum peak intensity on the excitation time has shown that

Table. Activation energy of corundum TC

n	E_{clc}, eV	E_{exp}, eV	T_{max}, K
8	0.677		
9	0.756	0.755	238
10	0.836	0.837	262
11	0.916		
12	0.995	0.994	344
13	1.075		
14	1.155		
15	1.234	1.23	390
16	1.314	1.312	398
17	1.393		
18	1.473		
19	1.553		
20	1.632		
21	1.712	1.71	502
22	1.791		
23	1.871	1.89	517

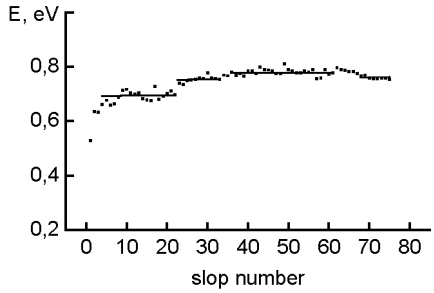

Fig. 3. Energy activation as a function of the fractional curve number for the 280 K peak.

the 230 K peak intensity increases initially with the irradiation time but, starting from τ_{exc} about 0.5 h, it is essentially independent of the excitation time. The 280 K peak intensity is independent of the excitation time already starting from τ_{exc} about 4 min. This evidences that the TC are defects that existed in the sample prior to excitation, that is, in the course of excitation, the centers are not formed at all or are formed in a small amount.

In the studies of 280 K peak by the excitation time variation as described lower, the data for the 230 K peak were recorded in parallel. The maximum position of the latter peak remains unchanged when the excitation time increases, thus evidencing the linear decay kinetics. Fig. 4 presents the dependence of the 280 K peak maximum position on the intensity in the maximum (actually light sum). When the light sum is varied by changing the excitation time (a), the maximum temperature drops dramatically as the light sum increases. Another curve (b) shows the results obtained when the light sum is varied by heating to an intermediate temperature ("trimming"). In this case, the maximum temperature is also shifted, but in opposite direction. In Fig. 5, presented is the dependence of the peak half-width on the light sum being varied by changing the excitation time (a) and by "trimming" (b). In both cases, the half-width increases with the light sum. The following conclusions can be drawn from those facts:

The simultaneous lowering of the maximum temperature and increase of the half-width evidences the presence of an additional maximum at the peak low-temperature branch. As the light sum increases, the intensity of that peak rises faster than that of the main one, that is, the main peak intensity goes to saturation while the additional one continues to rise. The smaller half-width of the peak in experiments with

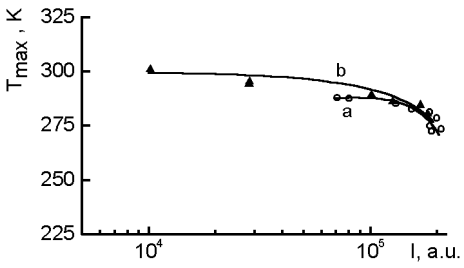

Fig. 4. Dependence of the 280 K peak maximum position on the intensity in the curve maximum at light sum varied by the excitation time variation (a) and by heating up to intermediate temperature ("trimming") (b).

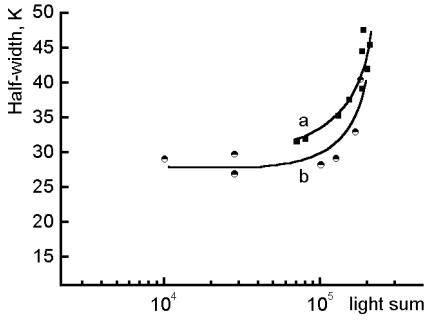

Fig. 5. Dependence of the 280 K peak half-width on light sum varied by the excitation time variation (a) and by "trimming" (b).

"trimming" as compared to that with the excitation time variation is explained by the complex nature of the peak, since at "trimming" emptied are predominantly the TC contributing to the low-temperature component. Thus, the TL peak at 280 K is a superposition of at least two neighboring elementary peaks. For the high-temperature peak component, a faster occupancy saturation of the corresponding traps is observed. The saturation evidences a limited concentration of the corresponding traps, and the extrinsic nature can be ascribed thereto.

To conclude, studies of the 280 K TL peak decay kinetics have shown that it has a complex structure and is a superposition of at least two neighboring elementary peaks. As the light sum increases, the low-temperature component intensity rises faster than that of the main one. The studied trapping centers have been shown to be defects that existed in the sample prior to excitation. It has been confirmed that in undoped Al_2O_3, the TC thermal activation energy values form the single oscillatory series, the oscillatory quantum energy $\hbar\omega_{TL}$ being 0.079 eV (642 cm^{-1}). New values for $n = 15$ and $n = 23$ have been found. The corresponding Raman line (645 cm^{-1}) is the highest frequency of the full-symmetric (A_g) vibration. Taking into account our previous results for numerous compounds, it can be concluded that the oscillatory dependence is of an universal character, it is satisfied at a high accuracy and is due to a strong charge-phonon interaction in crystals with predominant ionic binding type.

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Дослідження центрів прилипання у нелегованих кристалах Al_2O_3 методами термолюмінесценції

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Методами термолюмінесценції (ТЛ) досліджено енергетичний спектр центрів прилипання у спеціально не легованих кристалах α–Al_2O_3, в інтервалі температур 80–500 К. В даній роботі детальніше досліджено знайдену раніше осциляторну закономірність в енергетичному спектрі пасток, а також особливості висвічування деяких аномально широких піків ТЛ. Виявлено, що енергії термічної активації ЦП утворюють одну осциляторну серію: $E_n = \hbar\omega_{TL}(n + 1/2)$, $\hbar\omega_{TЛ} = 0.079$ еВ (642 см$^{-1}$). У спектрі комбінаційного розсіяння відповідна лінія 645 см$^{-1}$ є найбільш високочастотним з повносиметричних (A_g) коливань. Зроблено висновок, що закономірність зумовлена поляронною природою пасток. Запропоновано методику, яка дозволяє встановити причину розширення піка ТЛ, тобто визначити його структуру. Показано, що пік ТСЛ при 280 К має складну структуру і є суперпозиціє, принаймні двох близько розміщених елементарних піків, причому інтенсивність низькотемпературної компоненти складного піка із збільшенням світлосуми зростає швидше, ніж високотемпературної.