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OPTICAL PROPERTIES

Luminescent and Dosimetric Properties of Nanostructured Ceramics Based on Aluminum Oxide

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Abstract—The main features of thermoluminescence (TL) of nanostructured ceramics based on anion-defective aluminum oxide have been investigated. The kinetic parameters of the TL dosimetric peak at 475 K have been determined. The possibility of using nanostructured ceramics for beta-radiation dosimetry of high doses (up to 1 kGy) with thermoluminescence of deep traps has been justified. It has been found that the light sum of the dosimetric peak decreases with an increase in the heating rate due to the temperature quenching of the luminescence. The obtained results have confirmed that the mechanism of TL quenching in anion-defective aluminum oxide is associated with the temperature dependence of the probability of the capture in deep traps, which can be caused by thermal ionization of excited states of *F*-centers.

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1. INTRODUCTION

Nanostructured phosphors are promising materials for detecting large doses of ionizing radiations (above 100 Gy) due to their high radiation resistance [1, 2]. The luminescent and dosimetric properties of a number of powder nanophosphors have been described in the literature [3–8]. It has been found that, for nanopowders of different chemical compositions, the possibility exists of detecting high radiation doses. Among the materials promising for the use in high-dose dosimetry are anion-defective nanostructured ceramics based on aluminum oxide. Ceramic nanostructured detectors are more stable than powder detectors, have a high mechanical strength, and are suitable for mass production of detectors with specific sizes.

At present, the single-crystal modification of anion-defective Al_2O_3 has been widely used as thermoluminescent detectors (TLD-500) [9] and dosimeters based on optically stimulated luminescence [10]. Previous investigations performed on anion-defective single crystals of α-Al_2O_3 demonstrated that oxygen vacancies are necessary to ensure a high quantum yield of oxide phosphors [9]. Oxygen vacancies capture one or two electrons and thus create F^+- and F-centers involved in the luminescence processes. Earlier, it was established that the photoluminescence excitation and luminescence spectra of nanostructured ceramic α-Al_2O_3 are similar in shape and position to the corresponding spectra of the single crystal, but, unlike the latter spectra, they are noticeably broadened [11]. This indicates a significant contribution from the F- and F^+-centers created by oxygen vacancies to the luminescent properties of both the single-crystal and nano-sized samples of α-Al_2O_3.

This paper has been devoted to the investigation of the main luminescent and dosimetric characteristics of nanostructured ceramic aluminum oxide and to the evaluation of the possibilities of its use in high-dose dosimetry.

2. OBJECTS OF INVESTIGATION AND EXPERIMENTAL TECHNIQUE

For synthesizing the nanostructured ceramics, aluminum oxide nanopowders were preliminarily prepared using the method of an electric explosion of aluminum wire [12]. The subsequent sedimentation made it possible to obtain lots of weakly aggregated powders with relatively uniform particle sizes in the range of 20–70 nm. The X-ray diffraction analysis performed on a D8Discover X-ray diffractometer (CuK_α radiation, graphite monochromator) revealed that the powders contained metastable phases of aluminum oxide: γ (65%) and δ (35%). The powders were subjected to magnetic pulsed compaction [13] under a pressure of approximately 2 GPa at a temperature of 450°C. This made it possible to obtain workpieces for test samples in the form of tablets with a diameter of 10–15 mm and a thickness of 1 mm. For the preparation of ceramic samples, the obtained compacts were sintered at a temperature of 1200–1550°C for 1 h in a vacuum furnace (10^{-4} Torr). Heat treatment under vacuum was necessary to form the stable α-Al_2O_3 phase in the samples and also to create an oxygen deficiency in them.

As is known, the high-temperature treatment of nanopowders and compacts leads to an increase in the size of nanoparticles. In order to decrease this effect, the aluminum oxide powders before the compaction

were doped with approximately 1 wt% of magnesium oxide in the form of an ultrafine powder, which is a stabilizer and provides suppression of the grain growth [14]. The powders were subjected to thorough mechanical mixing. The sizes of particles on a ceramic cleavage were analyzed using a Zeiss Sigma VP scanning electron microscope with a Schottky cathode. It was found that the sizes of crystals in the synthesized anion-defective ceramics did not exceed 150–200 nm. Furthermore, it is known that magnesium ions encourage the formation of additional centers, including oxygen vacancies, in aluminum oxide [15].

The single-crystal samples of anion-defective α-Al_2O_3 were grown by the Stepanov method in the presence of carbon that provided the reducing conditions [9]. According to the optical absorption data, the concentration of *F*-centers was approximately equal to 10^{17} cm^{-3}. The studied samples of the single crystals were transparent and had the form of disks with a thickness of 1 mm and a diameter of 5 mm.

Thermoluminescence (TL) was excited by beta radiation from a $^{90}Sr/^{90}Y$ source or by unfiltered UV radiation from a DRT-240 mercury lamp. The TL curves were recorded using the experimental setup described in [16]. The measurements were performed in the luminescence band of *F*-centers (420 nm) with the use of a FEU-130 photomultiplier. The spectral band was separated using an interference filter.

3. RESULTS AND DISCUSSION

The TL curve of the nanoceramic aluminum oxide samples measured upon excitation with a test dose from the beta-radiation source (25 mGy) contains the dominant dosimetric peak at 475 K, which is shifted with respect to the TL peak of the α-Al_2O_3 single crystal at 25 K toward the high-temperature range (Fig. 1, curves *1* and *2*). A similar result was obtained for Al_2O_3 : Cr nanopowders [5]. In this case, the TL intensity at low doses for the nanostructured samples is lower than that for the single crystals. Moreover, if the TL is recorded immediately after irradiation at room temperature, there is a low-temperature TL peak at 350 K, which is associated with shallow traps. A similar peak is also characteristic of α-Al_2O_3 single crystals.

The form factor of the TL dosimetric peak at 475 K was calculated according to the technique described in [17]. Its value was found to be close to 0.50. The obtained result indicates that the TL peak at 475 K for the nano-sized samples is described by the order of kinetics of 1.7 [17].

The activation energy (*E*) and the frequency factor (*S*) of the TL process in the temperature range of the main peak were determined by the heating rate variation method [17]. This method is based on measuring the temperature of the maximum of the TL curve at different heating rates. In order to implement this method, we experimentally measured the TL curves of the nanostructured Al_2O_3 samples at several different heating rates in the range of 0.5–10.0 K/s and determined the temperatures $T_{(m,x)}$ of the main TL peak (see table, column 2). Since the samples had a sufficiently large thickness (1 mm), it was necessary to take into account the temperature gradient between the sample and the heater. The method used for calculating the true values of the temperature of the TL peak and the heating rate in the presence of a temperature gradient was described in [18]. First, from the results of measurements at low heating rates, where the temperature gradient is negligible, we calculated the constant *c* according to the expression

$$c = \frac{T_{m2} - T_{m1}}{\ln 2}, \quad (1)$$

Results of the calculation of the parameters characterizing the temperature gradient

β, K/s	$T_{(m,x)}$, K	$T_{(m,x)\mathrm{corr}}$, K	ΔT, K	$\beta_{\mathrm{eff},x}$, K/s
0.5	453	453	0	0.5
1	466	466	0	1
2	475	479	–4	2.04
4	500	492	8	3.85
6	516	500	16	5.57
8	529	505	24	7.19
10	548	509	39	8.47

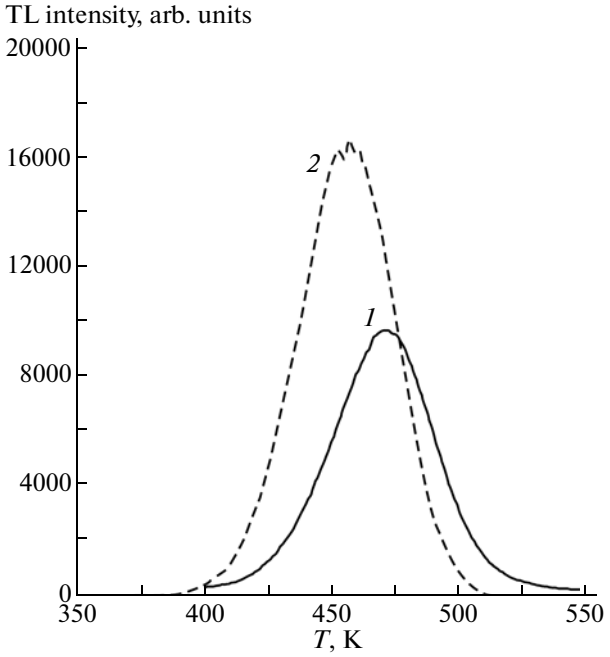

Fig. 1. Thermoluminescence curves of (*1*) nanoceramic aluminum oxide and (*2*) single-crystal aluminum oxide after irradiation from the beta-radiation source with a dose of 25 mGy at room temperature. The heating rate is 2 K/s.

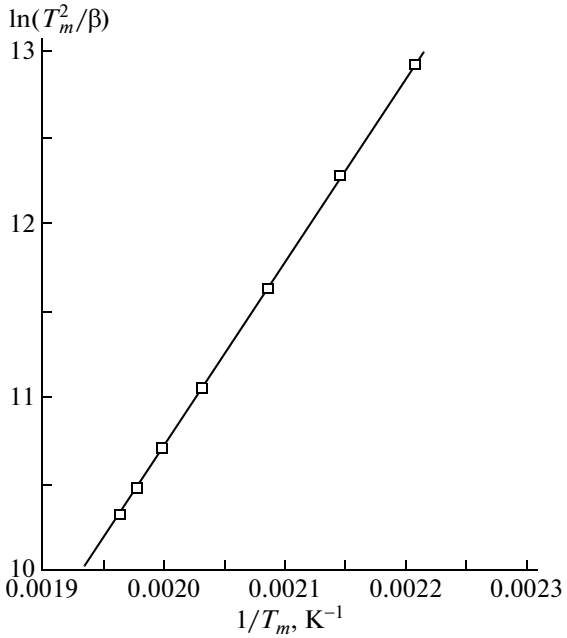

Fig. 2. Experimental dependence of $\ln(T_m^2/\beta)$ on $1/T_m$ (points) and its approximation by the straight line.

where T_{m1} and T_{m2} are the temperatures of the TL peak at heating rates of 0.5 and 1.0 K/s, respectively. The value of c was found to be 18.76. Next, using formula (2), we calculated the true temperature of the sample at a specified rate β:

$$T_{(m,x)\text{corr}} = T_{m1} - c\ln\left(\frac{\beta_1}{\beta_x}\right), \quad (2)$$

where $\beta_1 = 0.5$ K/s. The values of $T_{(m,x)\text{corr}}$ are listed in the third column of the table. The temperature gradient at the rate β_x was estimated using the formula

$$\Delta T = T_{(m,x)} - T_{(m,x)\text{corr}}. \quad (3)$$

The true value of the heating rate $\beta_{\text{eff},x}$, taking into account the temperature gradient, was calculated according to the formula

$$\beta_{\text{eff},x} = \frac{T_{(m,x)} - T_0 - \Delta T}{T_{(m,x)} - T_0}\beta_x, \quad (4)$$

where T_0 is room temperature (293 K). The results of the calculation are presented in the table.

The obtained true values of the temperature of the TL peak and the heating rate were used to calculate the activation energy and frequency factor [17]. For this purpose, we plotted the dependence of $\ln(T_m^2/\beta)$ on $1/T_m$. The obtained result is presented in Fig. 2. The experimental dependence is well approximated by the linear function $Y = 10727.5x - 10.754$. According to [17], the slope of this straight line gives the value of E/k, and the coordinate of the point of intersection with the ordinate axis corresponds to the value of $\ln(Sk/E)$, where k is the Boltzmann constant. From these relations, we found the activation energy $E = 0.92$ eV and the frequency factor $S = 5.0 \times 10^8$ s^{-1}. Taking into account the error in the experimental determination of the temperatures T_m, the error in the calculation of the activation energy E did not exceed ±0.1 eV, while the error in the determination of the frequency factor S did not exceed one order of magnitude.

It is also found that the nanoceramic samples are highly sensitive to UV radiation. In particular, the TL intensity of the main peak at 475 K after UV irradiation for 4 min is eight times higher than the TL intensity after irradiation from the beta source with a dose of 32 mGy. It is known [19, 20] that UV radiation effectively ionizes F-centers in aluminum oxide, and, as a result of photoconversion, they transform into F^+-centers. Free electrons generated in this case are captured by traps. Taking into account the opacity of the nanostructured samples, we can assume that they are characterized by a sufficiently high concentration of surface F_s-centers that are responsible for the high TL output under UV excitation.

Furthermore, it is known that, under UV irradiation at high temperatures, in Al_2O_3 single crystals the deep traps with the depletion temperature higher than the temperature of the main TL peak are efficiently filled [21]. Our investigations have demonstrated that, under UV excitation of the nanoceramic samples at a temperature of 550 K, the TL curve exhibits high-temperature peaks at 620, 730, and 790 K, associated with deep trapping centers (Fig. 3). The peak at 730 K is also observed for single-crystal aluminum oxide. The temperature positions of the other high-temperature TL peaks of the nanostructured samples differ from those of the single-crystal samples. This difference can be associated with the difference in the nature of the defects forming deep traps. It is quite probable that the studied samples contain defects and their aggregates that are characteristic only of nanocrystalline aluminum oxide ceramics.

In order to evaluate the possibility of using nanostructured aluminum oxide ceramics for the detection of high radiation doses, we investigated the dose dependence of the TL response in the main peak at 475 K under beta-radiation excitation of the sample. A fragment of the dose response of nanostructured aluminum oxide is shown in Fig. 4 in comparison with the corresponding fragment of single-crystal Al_2O_3. It can be seen that the dose response of single-crystal detectors is characterized by a clearly pronounced superlinear section at doses above 0.2 Gy, which limits the capabilities of dosimetric measurements. The TL response of nanoceramics varies almost linearly in the dose range of 0.01–10 Gy, which makes it possible to extend almost 50 times the range of detected doses.

The use of the TL peaks associated with deep traps as a source of dosimetric information opens up even greater possibilities for high-dose dosimetry. Figure 5

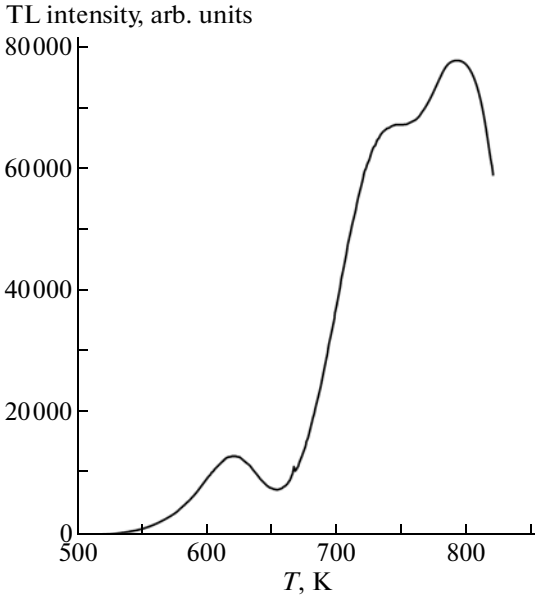

Fig. 3. Thermoluminescence curve for deep traps of nanoceramic aluminum oxide upon excitation by UV radiation at a temperature of 550 K.

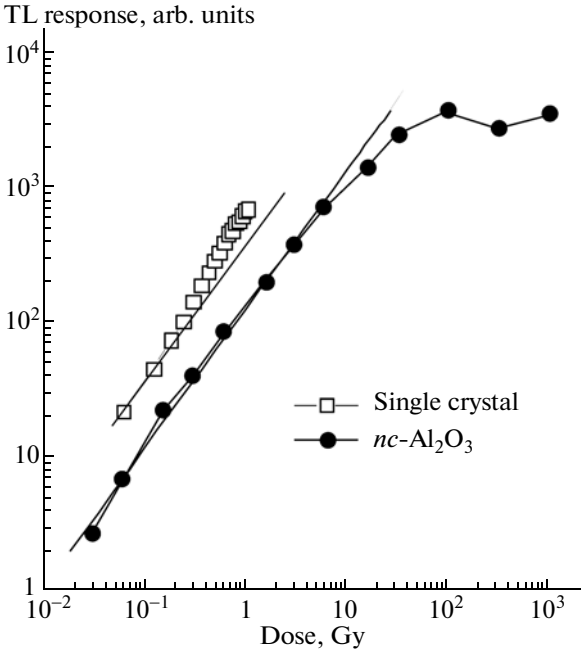

Fig. 4. Fragments of the dose dependences of the TL response in the dosimetric peak for nanostructured aluminum oxide (*nc*-Al_2O_3) and single-crystal aluminum oxide (TLD-500 detectors). A $^{90}Sr/^{90}Y$ beta-radiation source was used.

shows the TL curves of the nanostructured sample for three beta-radiation doses. The curve exhibits two TL peaks: the main peak at temperatures of 450–500 K and a broad high-temperature peak with the maximum at 670 K. It can be seen from this figure that, with an increase in the radiation dose, the intensity of the main TL peak first increases and then begins to decrease. At the same time, the intensity of the TL peak at 670 K, which is attributed to deep traps, increases with an increase in the dose. It can also be noted that, after the beta irradiation, the TL peak associated with one or several deep traps is observed at temperatures different from the case of the UV excitation (Fig. 3). This result can be explained by the fact that, under UV excitation, the ionization of *F*-centers leads to filling of predominantly electron traps, whereas under excitation by ionizing radiation, which creates free charge carriers due to the interband transitions, hole trapping centers can also be filled and participate in the luminescence processes.

The dose dependence of the TL intensity in the peak at 670 K for nanostructured ceramics is shown in Fig. 6. It can be seen that this dependence is almost linear in the dose range of up to 1 kGy. The obtained result suggests the possibility of using detectors based on nanostructured aluminum oxide ceramics for dosimetry of high beta-radiation doses.

A specific feature of single-crystal detectors based on anion-defective aluminum oxide is the dependence of the light sum of the dosimetric peak on the heating rate, which can lead to an increase in the error of the dose measurement [9]. The investigation of the TL properties of nano-sized Al_2O_3 samples after the beta irradiation has revealed that the light sum of the peak at 475 K decreases more than three times when the heating rate increases from 0.5 to 10.0 K/s (Fig. 7, curve *1*). Noteworthy is the almost complete coincidence of the dependences of the light sum of the dosimetric peak on the heating rate for the nanoceramic sample (curve *1*) and the aluminum oxide single crystal (curve *2*). The

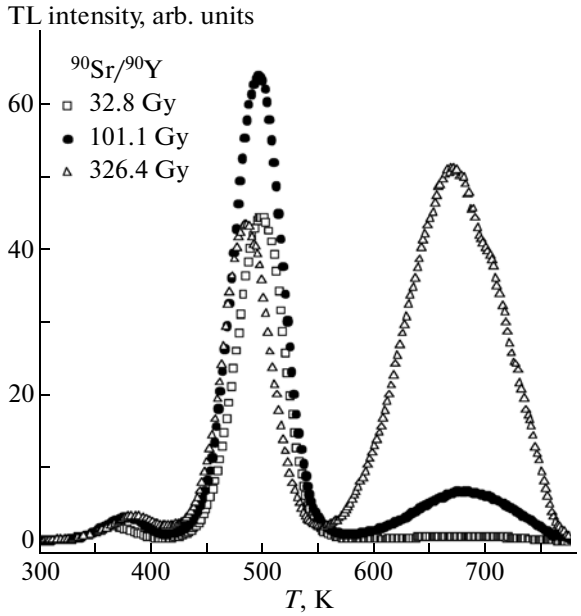

Fig. 5. Thermoluminescence curves of the nanostructured ceramic sample for different beta-radiation doses.

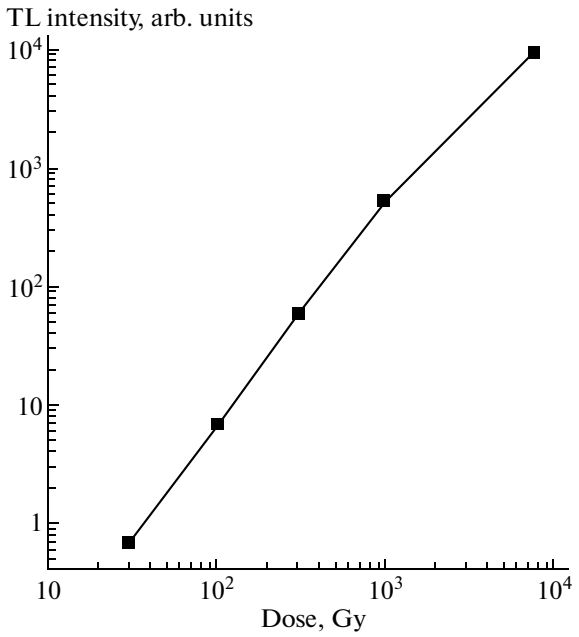

Fig. 6. Dose dependence of the intensity of the TL peak at 670 K in nanostructured ceramic Al_2O_3.

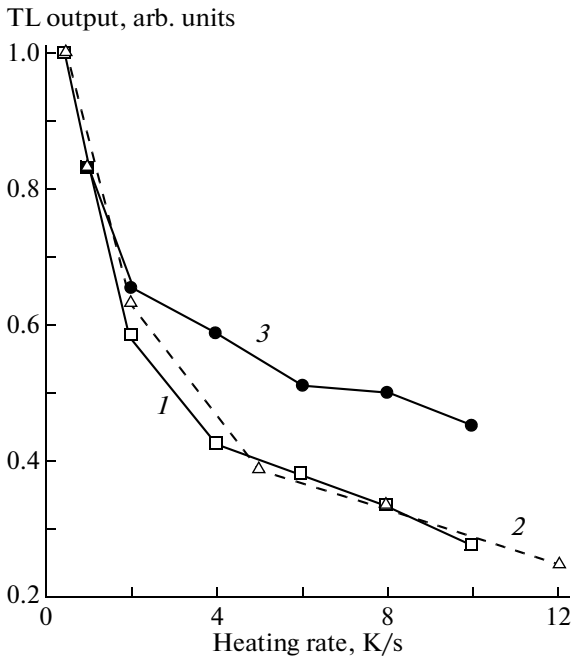

Fig. 7. Dependences of the light sum of the TL dosimetric peak on the heating rate for (*1*, *3*) nanostructured aluminum oxide and (*2*) single-crystal aluminum oxide (*1*, *2*) before and (*3*) after filling the deep traps.

decrease in the light sum of the TL peak with an increase in the heating rate indicates the existence of temperature quenching of the luminescence in the nano-sized α-Al_2O_3 samples in the range of the main TL dosimetric peak. As regards the mechanism of luminescence quenching in anion-defective aluminum oxide, there is no consensus of opinion among researchers. According to one point of view, it is the intracenter quenching of luminescence of *F*-centers [22]. Another interpretation of this effect is based on the relation between the luminescence quenching and the competing temperature-dependent carrier capture in deep traps [21]. In this respect, the investigation of the influence of the population of deep traps on the luminescence quenching in nanoceramic aluminum oxide samples can provide important information counting in favor of one or other quenching mechanism.

We measured the dependence of the light sum of the main dosimetric peak at 475 K on the heating rate in nanostructured samples with partially filled deep traps (Fig. 7, curve *3*). The deep traps were filled under UV irradiation at 600 K. It can be seen that, in the samples with filled deep centers, the decrease in the light sum of the peak at 475 K with an increase in the heating rate becomes less significant. The obtained results indicate that the temperature quenching of thermoluminescence in anion-defective aluminum oxide ceramics cannot be explained only in the framework of the classical Mott–Seitz intracenter mechanism. This quenching can also be associated with the charge transfer processes involving deep traps [21].

Another feature of the mechanism of TL quenching in ceramic samples of nanocrystalline aluminum oxide is the difference in the temperature dependences of the TL intensity of the main dosimetric peak upon excitation by UV radiation (Fig. 8, curve *1*) and beta radiation (Fig. 8, curve *2*). It can be seen that, in the case of UV excitation, the TL intensity of the peak at 475 K increases with an increase in the temperature (curve *1*), whereas in the case of the beta irradiation, such dependence is absent (curve *2*). The obtained results have demonstrated that the temperature dependence of the TL intensity of the peak at 475 K is not related to the specific features of the cross section of charge carrier capture in dosimetric traps. One possible reason for this fact can be the temperature dependence of the ionization efficiency of *F*-centers under UV excitation, which is also observed in single-crystal samples [23]. Therefore, it can be concluded that thermal ionization of excited states of *F*-centers is the general feature for anion-defective aluminum oxide sample, regardless of their structural state. The relation between the TL quenching and *F*-centers is also supported by the fact that, in the case of empty deep traps, the dependences of the light sum of the main TL peak on the heating rate are almost identical for the single-crystal and nano-sized aluminum oxide samples (Fig. 7), although these samples are characterized by different concentrations of deep traps, which, possibly, can be different in nature.

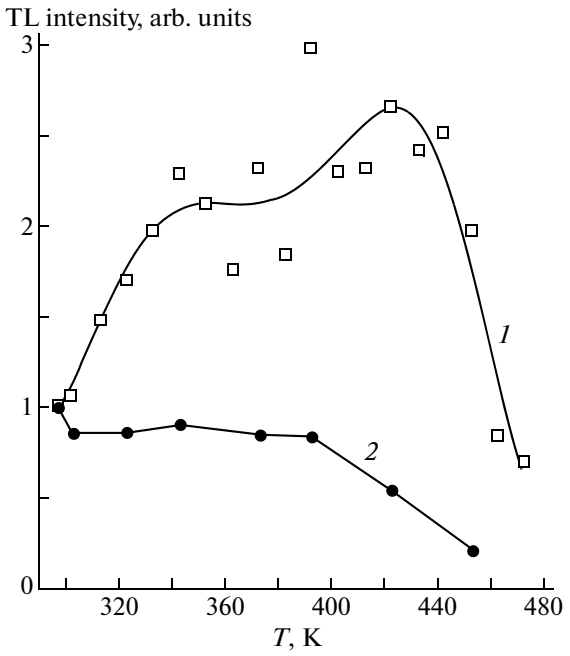

Fig. 8. Dependences of the TL intensity of the main peak at 475 K for nano-sized ceramic aluminum oxide sample on the temperature of excitation by (*1*) UV radiation and (*2*) beta radiation.

4. CONCLUSIONS

(1) Samples of nanostructured ceramics based on anion-defective aluminum oxide with crystal sizes of 150–200 nm have been synthesized and their main thermoluminescent properties have been investigated. For these sizes of nanoparticles, a number of TL properties are similar to those observed in single crystals: the presence of the isolated main peak, whose light sum decreases with an increase in the heating rate; the existence of deep traps effectively filled under UV radiation. It can be expected that a decrease in the size of nanoparticles in the ceramic material will be accompanied by an increase of the differences between their properties and the properties of the single crystal.

(2) The obtained results have confirmed the role of deep traps in the mechanism of luminescence quenching in nanoscale ceramics based anion-defective aluminum oxide. It has been concluded that this mechanism is common to single-crystal and nanostructured aluminum oxides and can be associated with the thermal ionization of excited states of *F*-centers.

(3) It has been shown that, in radiation detectors based on nanostructured ceramic Al_2O_3, the main TL peak at 475 K can be used in measuring higher doses of beta radiation (up to 10 Gy) as compared to single crystals. The presence of the linear section in the dose dependence of the TL intensity in the peak at 670 K up to 1 kGy and the high radiation resistance of nanosized samples allow us to recommend the nanostructured ceramics based on aluminum oxide for the use in high-dose TL dosimetry.

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