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Luminescent properties of Ga_2O_3 ceramics synthesized by the electron beam method

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For the first time, β-Ga_2O_3 ceramics were synthesized by the electron beam method. The presence of a pulsed cathodoluminescence band at 2.75 eV was found. It has been shown that the thermoluminescence curve of the obtained ceramics is described by the sum of two elementary peaks of second order kinetics. The calculated values of the energy depths of traps and frequency factors indicate differences in the mechanisms of formation of the luminescent response of ceramics synthesized by the electron beam method, compared with single crystals and ceramics obtained by other methods.

Keywords: oxide ceramics, thermoluminescence, cathodoluminescence, kinetic parameters.

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Gallium oxide (β-Ga_2O_3) ($E_g = 4.8$ eV) single crystals and ceramics are promising materials for power electronics, optoelectronics, and thermoluminescent radiation detectors [1]. One promising method for production of oxide ceramics is their synthesis in the field of an intense high-energy radiation flux. The radiation synthesis method was used successfully to obtain ceramics based on YAG:Ce and MgO [2,3]. This technique has an advantage in that it does not require any additional substances or processing steps to facilitate the process of formation of a new phase and offers high production rates (approximately 2 g/s in laboratory conditions). The aim of the present study is to investigate the feasibility of synthesis of Ga_2O_3 ceramics by the radiation method and to examine the luminescent properties of obtained samples.

During the process of synthesis of ceramics, the initial Ga_2O_3 powder (Ochv, Moscow) was irradiated by an electron flux generated at the ELV-6 accelerator (Institute of Nuclear Physics, Novosibirsk) with an energy of 1.4 MeV and a power density of 19 kW/cm^2. The powder was introduced into copper crucibles $120 \times 60 \times 40$ mm in size. A crucible moved at a rate of 1 cm/s relative to the plane of the electron beam with a cross section of 1 cm^2 scanning at a frequency of 50 Hz. Thus, each region of the charge material surface was irradiated for approximately 1 s. The overall scan time of the charge material surface was 10 s.

The ceramics synthesized in this manner had the form of glassy opaque plates. To measure their luminescent properties, these plates were cut into irregularly shaped samples weighing 0.03 g.

Thermoluminescence of ceramics (TL) was excited by room-temperature irradiation with a pulsed electron beam (60 A/cm^2, 2 ns) with an electron energy of 130 keV produced by the „RADAN-EXPERT“ accelerator. The irradiation dose was 1.5 kGy per pulse. The same accelerator was also used to excite pulsed cathodoluminescence (PCL). TL was measured under linear heating with the use of a FEU-130 photomultiplier tube with a spectral sensitivity region of 200–650 nm. A Rigaku MiniFlex 600 diffractometer was used to perform X-ray phase analysis of the studied samples. The impurity composition of samples was determined by X-ray fluorescence analysis with an ARL QUANT'X energy dispersive spectrometer.

The X-ray diffraction patterns of the examined ceramic samples revealed that they are comprised of a monoclinic

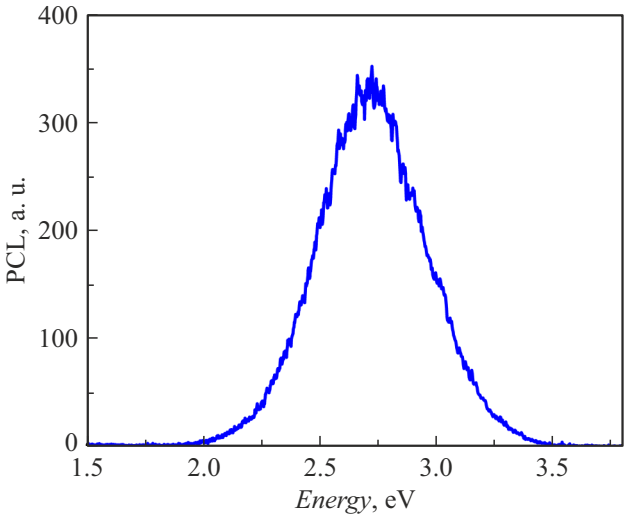

Figure 1. Pulsed cathodoluminescence spectrum.

Kinetic parameters of TL

Speed of heating, K/s	Peak *A*				Peak *B*				FOM, %
	T_m, K	E, eV	S, $10^9\,s^{-1}$	b	T_m, K	E, eV	S, $10^9\,s^{-1}$	b	
1.0	385	0.84	6.1	1.9	427	0.95	9.2	2.0	4.4
2.0	395	0.84	6.1	1.9	437	0.95	9.7	2.0	3.4
4.0	411	0.84	4.4	1.9	452	0.95	7.8	2.0	3.5
6.0	431	0.84	1.8	1.9	471	0.95	4.0	2.0	4.4
8.0	432	0.84	2.5	1.9	472	0.95	5.0	2.0	4.1

β-phase of Ga_2O_3. According to X-ray fluorescence data, gallium oxide constituted 98.5 % of the studied ceramics. A certain amount (no more than 1.5 %) of Al_2O_3 and SiO_2 impurities was also present.

PCL spectra (Fig. 1) were measured in order to identify luminescence centers. It can be seen that the spectrum contains a luminescence band with a maximum at 2.75 eV. It is known that gallium oxide single crystals and ceramics luminesce in the blue region of the spectrum due to the recombination of donors and acceptors [4]. In this case, donors are oxygen vacancies, which set *n*-type electrical conductivity. Pairs of gallium and oxygen vacancies act as acceptors [4].

The indicated defects may form in the studied samples as a result of high-power high-energy irradiation during synthesis. According to the data from [5], the processed material is ionized in the course of electron-beam synthesis of metal-oxide and yttrium-aluminum garnet ceramics, and when the ionization density threshold is exceeded, the conditions for electron-ion plasma formation are established. The relaxation of thermalized electron–hole pairs produced during material ionization induces the formation of defects in the crystal structure. The position of the luminescence maximum in the ceramics we studied differs slightly from the one determined in [4] (2.95 eV), possibly due to variation of the energy structures of donors and acceptors corresponding to different methods of sample synthesis [6]. Further studies are needed to determine conclusively the nature of luminescence centers in the ceramics examined here.

The TL method was used to investigate the properties of trapping centers in the synthesized samples. When TL was measured immediately after irradiation, intense luminescence of shallow traps was observed at $T = 300-350$ K. Since this emission makes it difficult to calculate the parameters of trapping centers, the samples were kept at $T = 323$ K for 5 min after irradiation. Shallow traps were emptied almost completely in the process. TL was observed at 330–525 K in this case (Fig. 2).

The method of decomposing TL curves into elementary peaks detailed in [7] was used to calculate the kinetic TL parameters (activation energy E, frequency factor S, and order of kinetics b). TL curves measured at different heating rates (from 1 to 8 K/s) were examined to obtain more reliable kinetic parameter values.

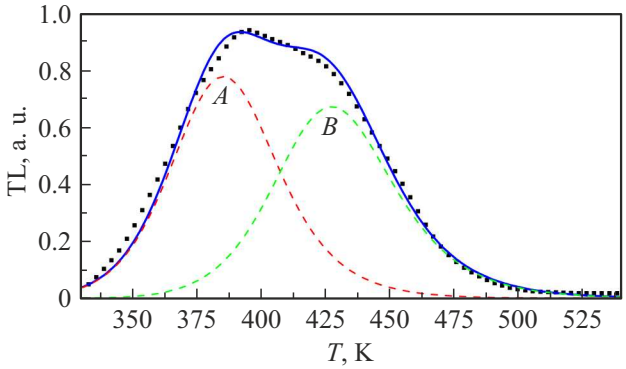

Figure 2. TL curve of the studied ceramics at a heating rate of 1 K/s. Symbols and the solid curve represent the experimental data and the result of decomposition into elementary peaks *A* and *B* (dashed curves), respectively.

It is known that the thermal quenching of luminescence, which, according to literature data, is observed within the range of $T = 350-500$ K for luminescence at 2.64 eV in β-Ga_2O_3 [4], coinciding with the temperature range of TL emission in the samples we studied (Fig. 2), needs to be taken into account in TL kinetics calculations. It has been established earlier that in the case of thermal quenching, the area under the TL peak decreases with an increase in heating rate [8]. According to the results of our measurements with the heating rate increasing from 1 to 8 K/s, the area under the peak varied randomly by no more than 20 %, which is comparable to the irradiation dose error and suggests that no thermal TL quenching is observed in the examined samples.

The obtained kinetic parameter values are listed in the table. The error of approximation of the experimental TL curves was estimated using the FOM (figure of merit) criterion. The procedure for its calculation is detailed in [9]. An approximation is considered accurate if the FOM value does not exceed 5 % [9]. An example decomposition of the TL curve into elementary peaks at a heating rate of 1 K/s is shown in Fig. 2.

The obtained results demonstrate that the experimental TL curves are characterized well (FOM < 5 %) by a superposition of two elementary peaks with near-second-order kinetics. The latter fact is indicative of active carrier retrapping during thermal stimulation [9]. The determined values of trap activation energies in the studied ceramics (0.84 and 0.95 eV) are slightly higher than those calculated in [6] (0.18–0.73 eV), suggesting that the energy structures of trapping centers differ. The obtained frequency factor values (on the order of $10^9\,s^{-1}$) are typical of traps emptied within the studied temperature range. Notably, they are several orders of magnitude higher than the values reported in [6] ($1-10^5\,s^{-1}$). The lack of anomalous kinetic parameters of traps in the examined ceramics may be indicative of a negligible contribution of electron tunneling, which was assumed to be a contributing factor in [4,6], to the TL process.

Thus, β-Ga_2O_3 ceramics were synthesized in a fast electron flux. They were found to be characterized by a PCL band at 2.75 eV, which is presumably associated with vacancy defects. The TL curve of the obtained ceramics is characterized by a superposition of two elementary peaks with near-second-order kinetics. The difference in TL activation energy and frequency factor between the ceramics synthesized here and those examined in earlier studies may stem from a difference in TL response mechanism (specifically, the lack of a noticeable contribution of thermal quenching of luminescence and electron tunneling processes in ceramics synthesized by the electron beam method).

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Conflict of interest

The authors declare that they have no conflict of interest.

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