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Cathodoluminescent properties of ceramics β-Ga_2O_3 obtained by gasthermal plasma synthesis

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Ceramics β-Ga_2O_3 was synthesized for the first time by using the gasthermal plasma deposition method (with the synthesis rate of 2 μm/s). The results of studying its microscopic parameters, structural and phase composition, and cathodoluminescent properties are presented. The intrinsic cathodoluminescence spectrum contains only a broad blue band which, being deconvoluted, becomes divided into two bands with the maxima in the vicinity of 426 and 488 nm. The band in the vicinity of 426 nm has the highest intensity. An increase in the incident electron energy from 40 to 70 keV leads to only minor changes in the cathodoluminescence spectrum, which is caused by peculiar features of the emission centersńature.

Keywords: gallium oxide, ceramics, cathodoluminescence, plasma synthesis.

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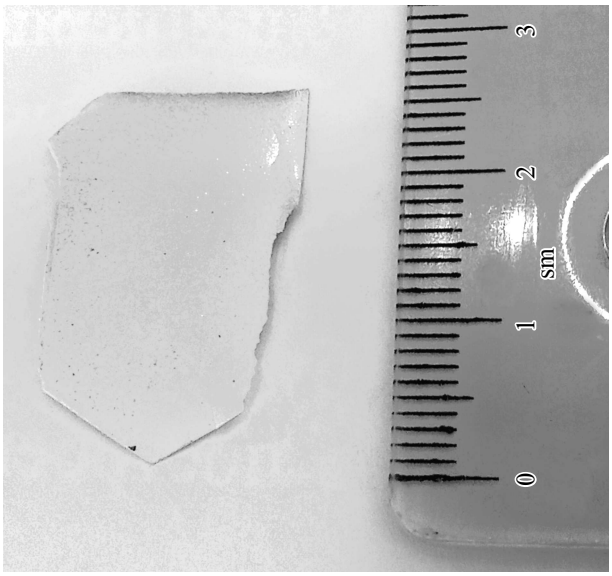
Gallium oxide (Ga_2O_3) is regarded as a promising material because of the possibility of its application in power electronics, solarblind optoelectronics, hightemperature sensors, and scintillation technology [1–4]. Gallium ions involved in the gallium oxide structure have tetrahedral and octahedral coordination. In the β-modification of Ga_2O_3, the coordination polyhedra share common edges; due to this, this modification is the most stable one.

Despite the wide demand for the β-Ga_2O_3based materials, their synthesis is, however, a problem. The matter is that the growth of bulk crystals faces technological challenges. Being heated above 1200 °C [5], gallium oxide dissociates with the formation of active gaseous gallium able to interact with the crucible material. Ceramic technologies are among the most fastevolving areas of modern electronics. There are known studies [6,7] devoted to the β-Ga_2O_3 ceramics synthesis and examination of its properties; however, the efficiency of methods proposed there still remains low. To our mind, a quite efficient method is gasthermal synthesis of ceramics involving lowtemperature thermal quasiequilibrium plasma with a temperature of up to 10^4 K [8,9]. The basic idea is that the initial powder is heated extremely quickly to the melting point, atomized in the plasma flux and deposited onto the base surface where it hardens and separates from the base. The main problem with this method for ceramics synthesis is possible overheating of the samples and initiation of intense gallium desorption. Temperature of the synthesized samples depends on the time of exposure to plasma; therefore, it has been proposed to use a shortterm synthesis (no longer than 1 min). Regardless of the short synthesis duration, changes in the stoichiometry, structuralphase composition, and crystalline quality of the synthesized β-Ga_2O_3 ceramics with respect to those of the initial powder are highly probable. One of important characteristics of the β-Ga_2O_3 ceramics is luminescence appearing in the case of excitation by ionizing radiation. It is known [10] that the luminescent properties are very sensitive to the β-Ga_2O_3 structuralphase composition and crystalline perfection.

In this work, samples of ceramics β-Ga_2O_3 were synthesized by the method of gasthermal plasma deposition, and peculiar features of their luminescence excited by a fast electron beam were examined.

In synthesizing the β-Ga_2O_3 ceramics, a gasthermal plasma deposition setup designed based on a plasma torch with an expanding gas discharge path [11] was used. A sample of the β-Ga_2O_3 powder consisting of particles up to 50 μm in size was fed together with the carrier gas (argonnitrogen mixture) into the anode of a lowtemperature DC plasma generator (carrier gas flowrate 0.2 g/s, arc current 250 A). Then the processed powder was deposited onto a singlecrystal sapphire substrate located at the distance of 7 cm from the plasma torch outlet. The ceramic sample sintering was associated with the synthesis process and was performed under the exposure to the plasma flux. The synthesis time was 25−30 s. After cooling, the gallium oxide ceramics was mechanically detached from the substrate. The synthesis time was 25−30 s.

The β-Ga_2O_3 ceramics structure was studied by Xray diffraction using diffractometer Empyrean produced by PANalytical (Netherlands) (CuK_α- radiation, $\lambda = 1.5406$ Å, BraggBrentano geometry). Scanning parameters were as



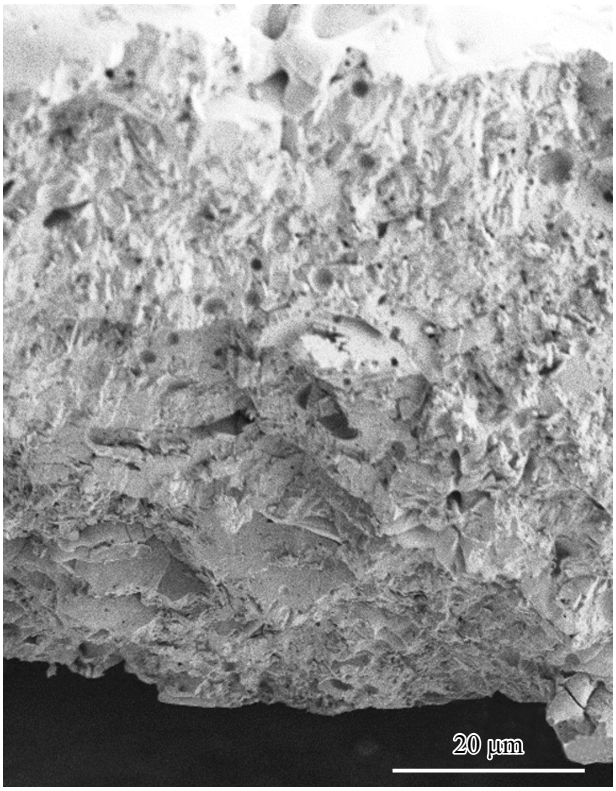


Figure 1. Optical image (a) and SEM image (b) of the β-Ga_2O_3 ceramics crosssection.

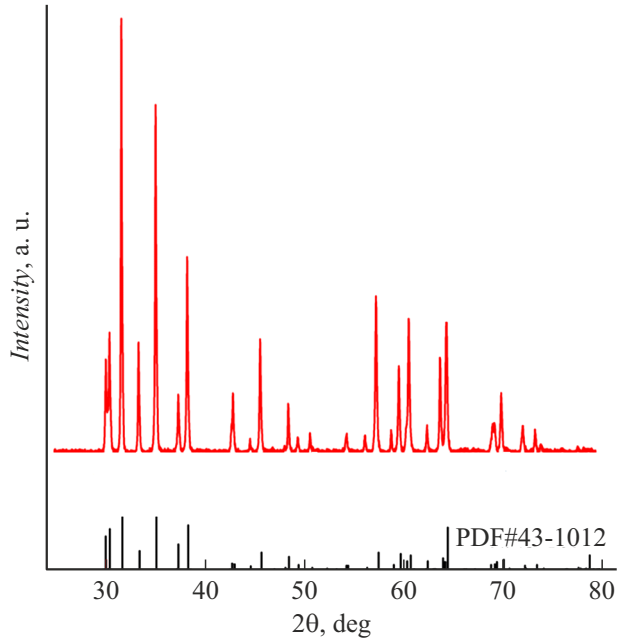


Figure 2. X-ray diffraction pattern of the β-Ga_2O_3 ceramics: upper curve (red) — experimental data, lower curve (black) — tabular values. The colored figure is given in the electronic version of the article.

follows: scanning angle range of 20 to 80°, scanning step of 0.008°, scanning time of 240 min.

The cathodoluminescence analysis was performed on electronograph EG-75 (Russia) equipped with an optical spectrometer. Cathodoluminescence (CL) spectra were recorded with the following electron beam parameters: electron energy of 40 and 70 keV, diameter of 2 m. Microscopic studies were performed on scanning electron ion microscope (SEM) Scios (FEI, USA) equipped with an attachment for energydispersive Xray (EDX) microanalysis.

In the process of gasthermal synthesis, a sample of ceramics (Fig. 1) 24 mm long and 16 mm wide was obtained. Average thickness of the sample was 60 μm, the synthesis rate was about 2 μm/s.

As per the electron microscopy data, there was formed a homogeneous ceramic material with an insignificant content of large pores. The ceramics internal microstructure was of the layered type. According to the EDX microanalysis data, the composition (atomic contents) of the initial powder was as follows: O — 60.52 %, Ga — 39.48 %; the ceramics composition was: O — 55.71 %, Ga — 44.29 %, i. e. the ceramics sample exhibited a gallium content exceeding that implied by stoichiometry.

The Xray diffractometry data on the Ga_2O_3 ceramics sample are presented in Fig. 2. The diffraction reflections demonstrate that gasthermal plasma synthesis gives rise to the monoclinic β-modification of Ga_2O_3 (JCPDS # 43-1012). The lattice parameters were: $a = 11.85$ nm, $b = 2.92$ nm, $c = 5.62$ nm, $\beta = 103.65°$. The unit cell volume was $V = 0.189\,\text{nm}^3$.

The CL spectra were measured at the accelerating voltages of 40 and 70 kV (Fig. 3). As shown, the CL spectra remain almost unchanged as the accelerating voltage increases, except for local features. At the voltage of 70 kV there is a slight increase in the baseband maximum intensity, as well as a slight spectrum broadening towards long waves. In addition, in the vicinity of the maximum at 426 nm, the CL spectrum smoothness becomes distorted (subtle effects

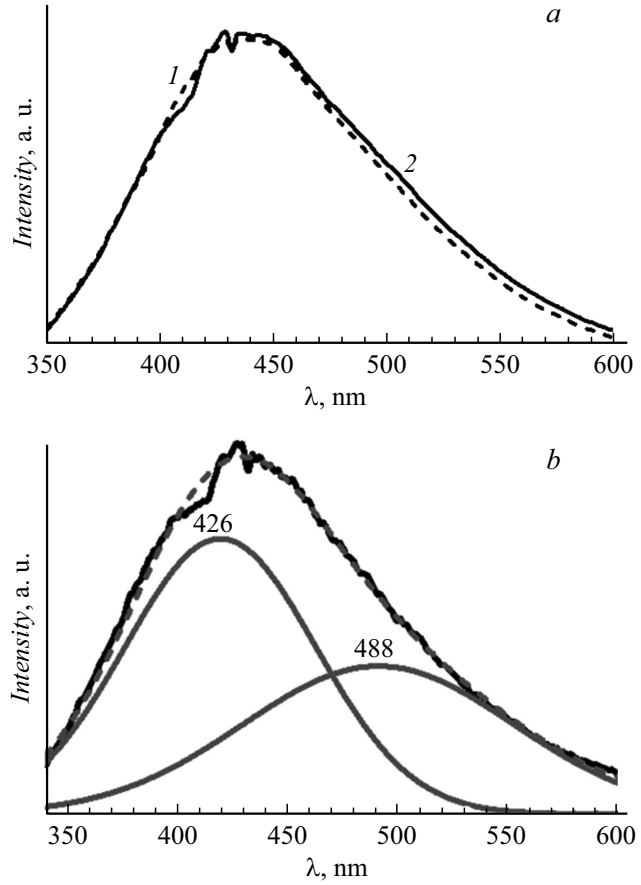


Figure 3. *a* — intrinsic CL spectra of the β-Ga_2O_3 ceramics at the accelerating voltages of 40 (*1*) and 70 kV (*2*). *b* — result of the CL spectrum deconvolution at the accelerating voltage of 70 kV. Black solid line represents the experimental data, gray dashed line is the result of fitting.

manifest themselves). As a result of deconvolution, the CL spectrum gets divided into two broad bands with the maxima in the vicinity of 426 and 488 nm. The band in the vicinity of 426 nm has the highest intensity.

The procedure of gasthermal plasma synthesis may be described as follows: the initial powder microparticles are heated in the arc discharge plasma and, being accelerated by the plasma flux, hit the surface of ceramics to be formed. Since in the process of synthesis the gallium oxide ceramics is permanently kept in the zone of thermal and ionization impacts from the arc discharge plasma, the probability of gallium atoms desorption is high. Just with this the compression of the β-Ga_2O_3 ceramics lattice volume $V = 0.189\,\text{nm}^3$ as compared to the crystalline sample lattice volume $V = 0.208\,\text{nm}^3$ is associated [7]. At the same time, the EDX data show an excess of gallium, and gallium atoms may be assumed to diffuse towards the grain boundaries.

In the spectra of the β-Ga_2O_3 intrinsic luminescence, three emission bands are typically observed: in the ultraviolet (UV) (380−390 nm), blue (420−490 nm), and green (520−540 nm) ranges. The UV band is characteristic of bulk crystals or perfect singlecrystal films of β-Ga_2O_3. Blue luminescence is associated with recombination of excitons captured by acceptor traps and is governed by electron tunneling from the donor cluster to the acceptor trap. Green luminescence is associated with isolated gallium vacancies [13].

In the synthesized β-Ga_2O_3 ceramics, no bands were observed in the UV range (Fig. 3); this evidences low crystalline quality of the ceramics. The green band, although visible in the spectrum, is not observed after deconvolution. As a result of deconvolution, the blue band gets split into two bands. Broadening of the bands is associated with interaction with phonons and with a difference in distances between interacting ionized donors and acceptors according to relation [12]:

$$E = E_g - (E_a + E_d) + e^2/4\pi\varepsilon R \pm nE_{ph}, \qquad (1)$$

where E is the photon energy, E_g is the bandgap width, E_a is the acceptor ionization energy, E_d is the donor ionization energy, R is the distance between the interacting ionized donors and acceptors (Coulomb interaction), E_{ph} is the energy of phonons participating in the radiative transition with $n = 0, 1, 2, \ldots$.

Noteworthy are the weak dependence of the CL intensity on accelerating voltage and the absence of spectral mixing (Fig. 3). A slight increase in the CL maximum intensity with increasing energy of incident electrons is associated with an increase in the probability of electron tunneling. The absence of spectral shifts of the CL bands follows from (1): energy of the emitted photons is determined only by the band structure features and distribution of donors and acceptors.

Thus, the paper presents the results of synthesizing the β-Ga_2O_3 ceramics by gasthermal plasma deposition and studying its morphology, composition and cathodoluminescence properties. An extremely high synthesis rate of 2 μm/s was achieved. A distinctive feature of the synthesized β-Ga_2O_3 ceramics cathodoluminescence is the absence of ultraviolet and green bands. The cathodoluminescence spectrum contains only a broad blue band which, being deconvoluted, gets divided into two bands with the maxima in the vicinity of 426 and 488 nm.

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Conflict of interests

The authors declare that they have no conflict of interests.

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