

The crystallization of β -Ga₂O₃ from a solution-melt and the study of the obtained crystals by cathodoluminescence

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The results of studies of crystallographic, crystalloptical and luminescent properties of β -Ga₂O₃ crystals obtained for the first time from a solution in molten MoO₃ are presented.

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The gallium oxide — ultra-wide bandgap semiconductor (4.6–5.3 eV), prospective for creation of new generation of power and optoelectronic engineering devices [1]. Substrates for epitaxy of structures based on β -Ga₂O₃ are obtained from large single crystals grown from melt at temperature of $\sim 1850^\circ\text{C}$ (melting point of gallium oxide). Growth is performed mainly using expensive iridium tooling and heat-resistant zirconium ceramics. Unfortunately, vapors and products of dissociation of gallium oxide have high chemical activity leading to that during long-time processes there is gradual dissolving of the crucible and iridium tooling, i.e. it practically becomes a consumable [2]. This feature and some unsolved technological problems make crystals expensive. So, alternative, more low-temperature methods of producing single crystals of gallium oxide are of a great interest.

One of such approaches is growth from solution-melt (flux), frequently used to grow single crystals of hard-melting materials for studying their physical properties [3,4]. This process is based on the fact that in some temperature range the dissolvent and the crystallized substance (in our case gallium oxide) do not form any intermediate compounds. For the target component crystallization two options are possible: cooling of the solution or dissolvent evaporation. The most important part of this experiment is the selection of dissolvent, which determines not only growth temperature range, but also method of its removal from the setup. In case of β -Ga₂O₃ as dissolvent previously toxic fluoride (PbF₂) and lead oxide (PbO) [5,6] were used with process temperature range 500–1200°C. Note that the selection of dissolvent and crystallization conditions produce not only stable polymorph β -Ga₂O₃, but also metastable α -Ga₂O₃ [7].

In this paper we studied Ga₂O₃ crystals, obtained by dissolvent evaporation using molybdenum oxide MoO₃ as dissolvent. It has melting temperature 801°C and boiling point 1155°C, comfortable for the experiment execution.

In platinum crucible 4.5 g of gallium oxide 4N (99.99) and 45 g of molybdenum oxide AG (GOST 3760-79) were loaded. Temperature increasing to 1000–1150°C was performed for 2 h, holding at constant selected temperature was 12–14 h, then furnace was switched out. Crystals of gallium oxide then were washed of residual molybdenum oxide with aqueous solution 25% of ammonia P.A. (GOST 3760-79). Process is described in details in paper [8]. As a result lamellar crystals were obtained with thickness of several microns with maximum linear dimensions of major face up to 2.5 mm. By method of X-ray diffraction it was confirmed that crystals correspond to β -Ga₂O₃ with monoclinic structure [8].

Habit of crystals was studied in optical microscope Carl Zeiss Jena Amplitval. Examples of obtained gallium oxide crystals are shown in Figure 1. As per form of faceting they can be divided into two groups: single crystals and twinned crystals. The single crystals generally have view of elongated rectangular plates, and correspond to those obtained in paper [5]. Such crystal is shown in Figure 1, *a*, and, based on the ratio of the lengths of its side faces, we believe that it lies on the plane (100), which is the cleavage plane in β -Ga₂O₃. Besides, we for the first time detected growth from solution-melt of twinned β -Ga₂O₃ crystals, and twins of two types were detected. First — with twinning plane (101) (see Figure 1, *b*), previously not observed in crystals β -Ga₂O₃, obtained by other methods. Second — with twinning plane (100) (see Figure 1, *c*), well known for β -Ga₂O₃ (for example, see paper [9]). In this paper we for the first time have faceted twin-crystal, i.e. we see faces participating in growth. The angles between side faces were measured by examining the photos of a large number of crystals with twins. For them sets of angles 104, 54 and 22° are repeated, which coincides with angles between planes in the unit cell of β -Ga₂O₃ (*C2/m*) [6].

To confirm twin structure, the crystals were studied in the polarization microscope PLM-2 in crossed nicols.

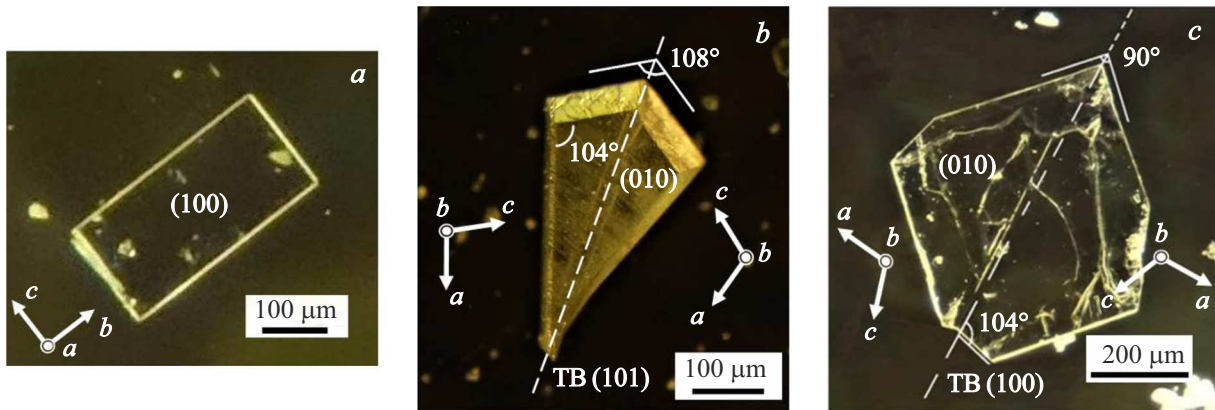


Figure 1. Gallium oxide crystals grown from MoO_3 solution-melt; *a* — single crystal with face (100); *b* — crystal twinned by (101); *c* — crystal twinned by (100), white arrows indicate direction of crystallographic axes, TB — twin boundary.

Change in passage of plane-polarized light through the crystal during rotation on table between the polarizer and analyzer was considered [10]. Study of crystal twinned by plane (101) (see Figure 1, *b*) showed that extinction of single crystals in twin occurs asynchronously. Such crystal rotation by 360° gives 8 cases of extinction, where extinctions of both parts of twin alternate. In this case, the angles of rotation of the crystal from the extinction position of one single crystal to the extinction position of the other one were 18 or 72° depending on the direction of measurement. Large angle in 72° correlates with angle between directions of axes *a* [100] in twin single crystals, which confirms presence of twinning plane. In crystal, twinned by (100) plane (Figure 1, *c*) extinction of both parts of twin occurred simultaneously, i.e. during rotation by 360° it gives 4 extinctions through 90° (like in single crystal). This is associated with the fact that axis *a* is perpendicular to twinning plane and at mirror reflection the crystallographic axes *a* and *c* of single crystals are collinear, but directed opposite [10].

Composition and luminescent properties of the largest crystal (1×2 mm) with twinning plane (101) were studied by methods of energy-dispersive spectroscopy (EDS) in scanning electron microscope (SEM) Zeiss Auriga with detector Aztec Oxford Instruments and by cathodoluminescence (CL) in SEM chamber Zeiss Supra 40VP with Gatan MonoCL3+ attachment. The crystal surface was charging under electron beam irradiation, which indicates its low electrical conductivity, hence, for its surface grounding a thin layer of carbon was deposited.

Figure 2, *a* shows SEM-image in secondary electrons (SE), recorded near twin boundary of crystal with marked region of EDS signal acquisition. The contrast in the form of uneven white spots and dots is probably due to solvent residues on the surface. Element analysis showed that this crystal corresponds by composition to Ga_2O_3 , in which impurities were identified: copper (0.52%), nickel (0.12%), iron (0.08%) and molybdenum (0.2%), they enter the crystal composition from the initial load of powders Ga_2O_3

and MoO_3 . Presence of molybdenum in EDS spectrum can be explained by presence of residues of dissolvent MoO_3 on the crystal surface. When studying at high magnification separate micron-size particles were identified, which correspond to increased content of Mo and O (mass fraction of oxygen in MoO_3 is higher than in Ga_2O_3) on element maps, and decreased of Ga (not shown for brevity).

On CL panchromatic map (CL Pan) of crystal shown in Figure 2, *b* a linear contrast from twin boundary is well pronounced. In crystals themselves, see inserts to Figure 2, *b*, the stripped contrasts with width of several microns with gaps $\sim 10\text{--}20\ \mu\text{m}$ between them with direction of strips being symmetrical relative to twinning plane and parallel to one of side faces of domain. This is similar to structure of antiphase boundaries near the twinning plane in separate $\varepsilon(\kappa)\text{-Ga}_2\text{O}_3$ microcrystal hexagonal prisms [12] and can indicate incoherent and curvilinear actual structure of twin boundary at atomic level. The left (in Figure 2, *b*) single crystal, composing the twin, showed rather lower intensity of CL, this is expressed in its dark-gray contrast relative to right single crystal. Nevertheless CL spectra taken from both single crystals composing the twin, and in juncture region are similar and have plot shown in Figure 2, *c*. CL spectrum is wide band in blue-UV range with noticeable main peak in ~ 3.3 eV and with second order of this band in IR-red range 1.5–2.0 eV (not shown for brevity). Such CL spectrum is typical for epitaxial $\beta\text{-Ga}_2\text{O}_3$ [1,13], and also corresponds to spectrum registered from massive crystal $\beta\text{-Ga}_2\text{O}_3$, obtained by Czochralski method from same initial powder of gallium oxide [11]. Detected linear contrasts in CL, presumably, correspond to planar defects. Their increased recombination activity is either a property of these defects, or they are preferred for segregation of impurities. The latter is supported by the variability in the magnitude of the CL contrast between different stripes. On other hand, dark stripes can also demonstrate decorated growth layers, and differences in CL intensity of single crystals can be associated with nonuniform crystal cooling, which manifests itself in anisotropic distribution of

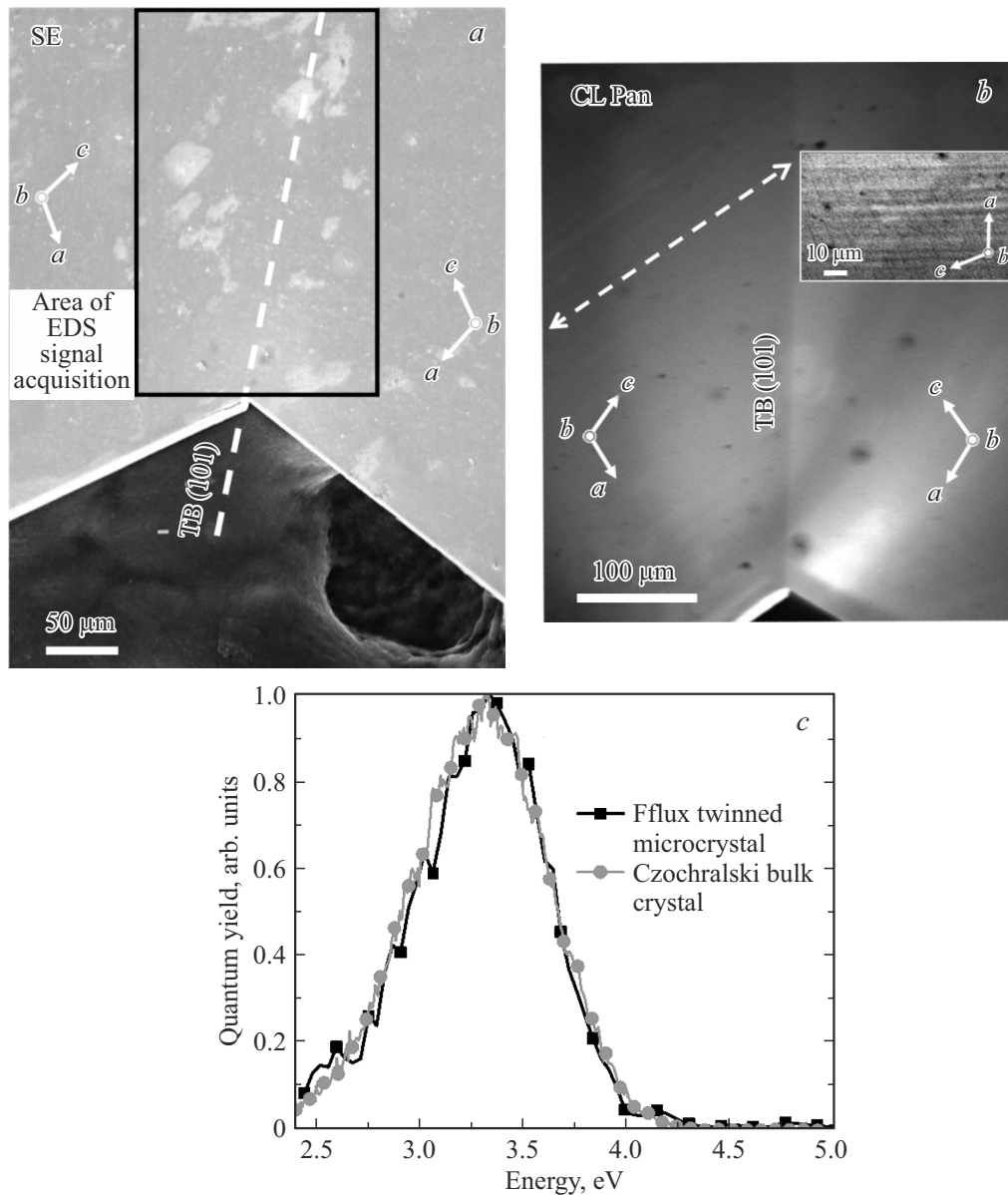


Figure 2. Results of SEM study of crystal twinned in (101): *a* — SEM SE microgram near the twin boundary (TB — white dashed line), the black rectangle shows the region of EDS signal collection; *b* — panchromatic map of cathodoluminescence (CL Pan) near the twin boundary (TB); the dashed white line with arrows shows the directions of linear CL contrasts in the left single crystal, visible at higher magnification in the insert; white solid arrows (*a*, *b*) show the direction of crystallographic axes; *c* — normalized CL spectrum in blue-UV range of the twin crystal (solid black line with squares); for comparison, the grey graph with circles shows the spectrum recorded from a massive crystal obtained by the Czochralski method from the same Ga_2O_3 powder, which was used for growth from solution-melt [11].

point defects participating in formation of CL signal [14]. Besides, it is necessary to consider also presence of iron in form of impurity (detected by EDS method), which increases the luminescence intensity in IR-red range [15] at significantly lower concentrations. Unfortunately, by EDS method it is impossible to evaluate the spatial variations of iron concentration at such level of its content in the crystal.

In paper from solution-melt MoO_3 thin single crystals $\beta\text{-Ga}_2\text{O}_3$ were obtained, and also crystals twinned with each other (two orientations). Data on their structural, optical and luminescent properties show closeness of samples from

the solution-melt experiments to the crystals obtained from own melt of gallium oxide. Thin crystals $\beta\text{-Ga}_2\text{O}_3$, grown from solution-melt, are, among others, of practical interest, as for device applications poorly heat-conductive gallium oxide requires thinning or splitting of large crystals of [16].

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Conflict of interest

The authors declare that they have no conflict of interest.

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