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# Growth of $\beta$-$Ga_2O_3$ single crystals by the solution-melt method

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The modes of growth of $Ga_2O_3$ crystals from a solution of gallium oxide in a $MoO_3$ melt in the process of $MoO_3$ evaporation at a temperature of 1050°C have been studied. It is shown that at this temperature the Ga2O3 crystalline phase is in equilibrium with the $MoO_3$ melt. As a result of the experiments, single crystals of $\beta$-$Ga_2O_3$ were obtained up to 1.5 mm in cross section. The composition and structure of the crystals were studied by X-ray diffraction and electron microscopy.

**Keywords:** gallium oxide, crystal growth, wide gap semiconductor.

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Gallium oxide (ultra-wide-gap semiconductor) is being studied extensively at present with an eye on its potential applications in high-voltage and power electronics, chemical sensors, catalysts, and solar-blind photodetectors [1,2]. Large bulk $\beta$-$Ga_2O_3$ crystals are grown efficiently from the melt [3–5]. At the same time, they still remain costly on account of a number of technological issues with crystal growth at a temperature of 1800°C and the use of expensive accessories that lose weight in the process of growth due to marked dissociation of gallium oxide during heating and oxygen release, which is especially intense at temperatures in excess of 1200°C [6]. Efforts are ongoing to find a more cost-effective way to produce gallium oxide crystals, since even small fragments of a crystal obtained by exfoliation along cleavage planes are suitable for the construction of instruments [7]. In the present study, the process of crystallization of gallium oxide by the solution-melt method at a temperature of 1000–1150°C is examined. Researchers have attempted earlier to reduce the crystallization temperature of gallium oxide in this way. The growth of gallium oxide crystals from solutions in $PbF_2$ [8,9] and $PbO$–$PbF_2$ [10] melts was reported in literature. Single crystals of gallium oxide were grown successfully in [11] from a $Ga_2O_3$–$Li_2O$–$PbO$–$B_2O_3$ melt by slow cooling from 1250 to 500°C within 150 h.

In our experiments, $\beta$-$Ga_2O_3$ was crystallized not in the process of cooling of a melt, but in the course of evaporation of a solvent ($MoO_3$). The entire procedure lasted for approximately 14 h. A mixture of $Ga_2O_3$ and $MoO_3$ powders was prepared by grinding them together in a porcelain mortar and introduced into a crucible. The platinum crucible was transferred into a protective corundum crucible and covered with another corundum crucible. Special precautions were made to avoid contact between corundum and the reaction powder. The charge was then placed into a quartz protective tube and introduced into a silicon carbide furnace. This tube protected the interior of the furnace from $MoO_3$ vapor. It was sealed at the top with thermally resistant corundum wool. The corundum cover and wool controlled the rate of extraction of $MoO_3$ vapor from the platinum crucible. Evaporated $MoO_3$ crystalized in the form of yellow needles on the surface of the quartz tube. Apparently, $MoO_3$ vapor interacted with corundum and corundum wool. The temperature was increased to 1050°C within 2 h. The samples were held at this temperature for 12 h, and then the furnace was turned off. The ingot formed in the platinum crucible had needle-shaped crystals of residual unevaporated $MoO_3$ in the upper part. Crystals of $Ga_2O_3$ were positioned in its lower part. In order to extract $MoO_3$ crystals, the ingot was dissolved in a 25% aqueous solution of ammonia. The dissolution of $MoO_3$ proceeded for several days and could be accelerated by heating. A coarse powder obtained as a result of this processing consisted of two easily distinguishable fractions. The first of them is small crystals. The second fraction was flake-like and could be separated easily from crystals by stirring in water and decanting. The obtained crystals were examined with a Carl Zeiss Jena Amplival optical microscope. The maximum size of grown crystals was 1.2–1.5 mm. These crystals were divided into two groups with different faceting. Crystals from the first group were often elongated and had faces with square angles (Fig. 1, *a*, *b*). The second group consisted of twin crystals with twinning plane (101) dividing them into two mirror-equal parts (Figs. 1, *c*, *d*). Line *AB* in Fig. 1, *d* is the line of intersection between plane (010) and the twinning plane. The angles between observed faces were measured by examining the photographic images of a group of crystals with twins. It was found that a set of angles of 104, 54, and 22°, which match the angles between the corresponding planes in a unit cell of $\beta$-$Ga_2O_3$ ($C2/m$), is repeated in all twinned crystals. In addition, twins with twinning plane (001) and a vertex angle of 90 degrees were often observed. The indicated geometry of twins is typical of monoclinic crystals (e.g., single crystals of gypsum and $MoO_2$ [12,13]) — a group to which $\beta$-$Ga_2O_3$ does also belong.

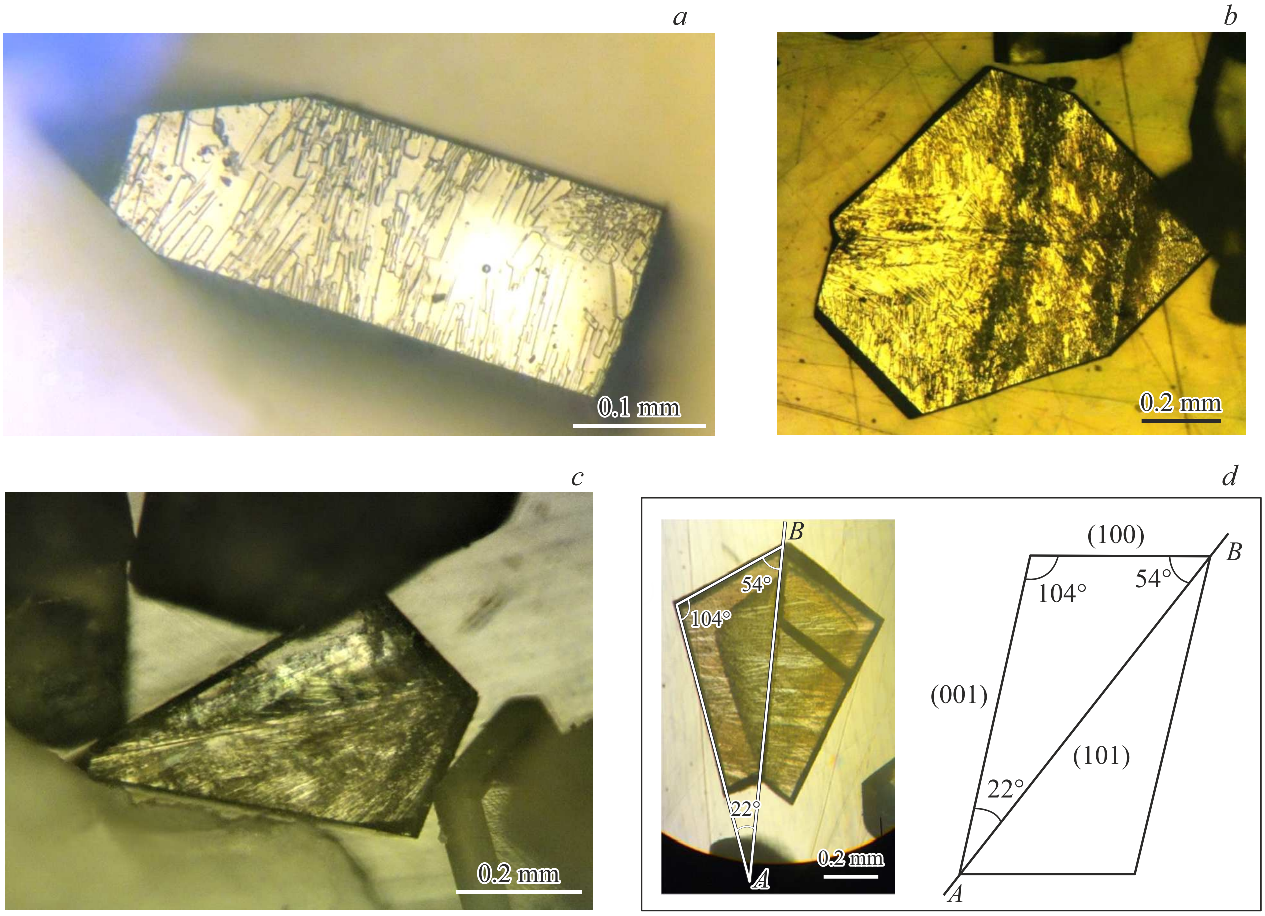

**Figure 1.** Crystals imaged with an optical microscope. *a*, *b* — Elongated crystals and faces with square angles; *c*, *d* — twin crystals and a unit cell of $\beta$-$Ga_2O_3$.

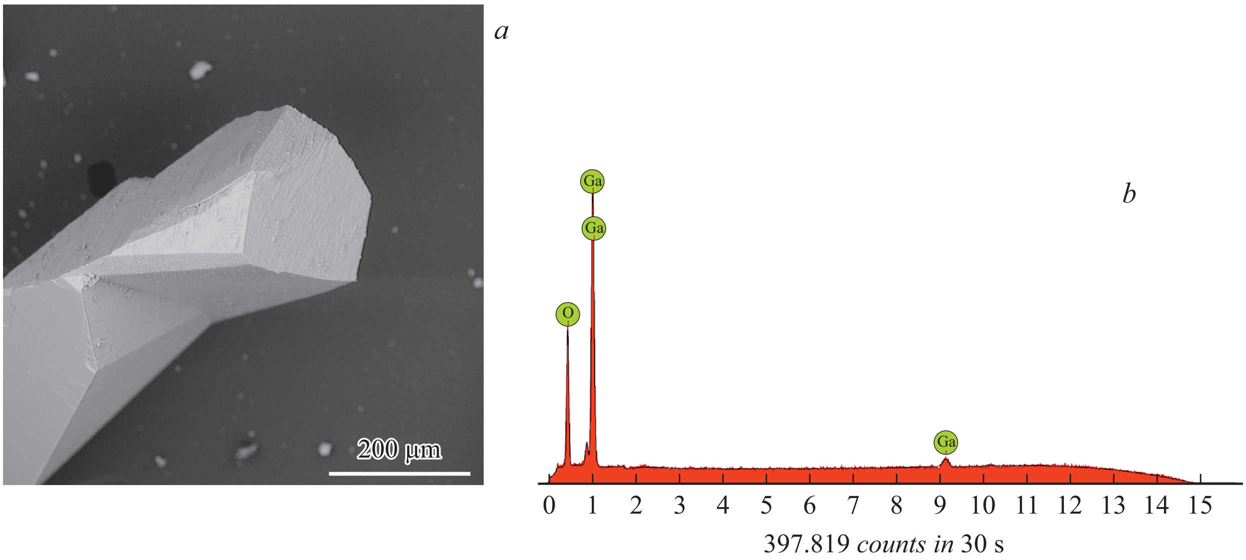

**Figure 2.** *a* — Crystals imaged with an electron scanning microscope; *b* — elemental analysis.

The results of elemental analysis with a Phenom Pro X electron scanning microscope (with an energy-dispersive attachment) revealed that both crystals and the flake-like fraction contain only two elements: gallium and oxygen. Their approximate atomic ratio was 40:60 (Fig. 2). It was found in X-ray diffraction analysis, which was performed using a DRON-8 diffractometer in the $\theta-2\theta$ scan mode within the $10-130^\circ$ angle range, that the diffraction patterns of both fractions agree completely with the pattern corresponding to $\beta$-$Ga_2O_3$ powders (index No. 01-074-1776).

We believe that these crystals nucleated and grew slowly in the process of $MoO_3$ evaporation, whereas the flake-like fraction formed as a result of rapid crystallization of gallium oxide, which was dissolved in residual (unevaporated) molybdenum oxide, after the furnace was turned off.

Using an original technique described above, we managed to grow single crystals of $\beta$-$Ga_2O_3$ for the first time from a solution-melt at a rate higher than those reported earlier for this method. Two groups of crystals (without twins and twinned) formed in the process of growth.

### Conflict of interest

The authors declare that they have no conflict of interest.

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