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Growth and optical properties of the solution-melt $K_2O \times 8Ga_2O_3$ crystals

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The results of studying the crystallographic, electrical and optical properties of $K_2O \times 8Ga_2O_3$ crystals obtained by interaction of a Ga_2O_3 solution with a KF melt are presented. The crystal structure of the samples corresponded to hexagonal $P6_3/mmc$ β-gallate with the lattice parameters $a = 5.80$ Å and $c = 23.5$ Å. The crystals were insulators with a resistance of about 2−3 GΩ per 450 μm of length. For the first time, the optical band gap of 3.77 eV and the intrinsic luminescence band in the range of 2.0−2.5 eV were determined for $K_2O \times 8Ga_2O_3$.

Keywords: Crystal growth, crystal structure, gallate, cathodoluminescence.

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One of the most promising wide-bandgap semiconductors for the new generation of power and optoelectronics is currently considered gallium (III) oxide, Ga_2O_3 all polymorphic modifications of which exhibit only electron *n*-type conductivity. Therefore, in the search for ways to create *p−n* transitions in electronic devices based on Ga_2O_3 research worldwide is being conducted on related wide-bandgap semiconductor oxides with *p*-type conductivity suitable for obtaining heterostructures. Thus, in recent works [1,2], it was demonstrated that thin layers of certain anhydrous gallates of various metals ($ZnGa_2O_4$, $LiGa_5O_8$ and others), obtained by epitaxy, exhibit *p*-type conductivity. Other representatives of this group of compounds are highly symmetric β- and β''-gallates of alkali and alkaline earth elements, which can be obtained as bulk crystals by various solution and solution-melt methods and which were previously intensively studied as efficient ionic conductors [3], but were not considered as materials with semiconductor properties. In this work, relatively large crystals of one of the representatives of the indicated group — β-gallate of potassium with the composition $K_2O \times 8Ga_2O_3$ were grown for the first time, and studies of their structure, optical, and electrical properties were conducted.

Samples of potassium β-gallate (general formula $K_2O \times nGa_2O_3$) were obtained from a solution of β-Ga_2O_3 (4N) in a KF melt of analytical grade by slow evaporation of the solvent over 12 h. Melting was carried out in a platinum crucible in air at a temperature of 1200 °C, which is significantly higher than the melting temperature of KF at 858 °C. The initial load was a thoroughly ground mixture of KF and Ga_2O_3 powders in a mass ratio of 9:1. The charge weight was 30 g. The remaining KF after the experiment was removed by boiling in water. As a result, plate-like crystals of hexagonal shape with linear dimensions on the order of 1−3 mm and thickness ∼ 0.2 mm were formed (Fig. 1, *a*). The obtained samples were investigated using X-ray diffraction (XRD), transmission optical spectroscopy (TS), analytical scanning electron microscopy (SEM), including energy-dispersive X-ray spectroscopy (EDS) and cathodoluminescence (CL).

The X-ray diffraction pattern recorded in $\theta-2\theta$ mode is shown in Fig. 1, *b*. Peak indexing and refinement by the Rietveld method were performed using the Profex program [4]. There are no cards for $K_2O \times nGa_2O_3$ in public crystallographic databases, so the known structural motif of hexagonal $P6_3/mmc$ β-gallate of barium $BaO \times 6Ga_2O_3$ was taken as the basis [5]. Using it, the series of reflections from the basal (000n) and inclined (10-1n) planes was indexed for the obtained diffractogram. The determined parameters $a = 5.80$ Å and $c = 23.5$ Å correspond to the values previously obtained for β-gallate of the composition $K_2O \times 8Ga_2O_3$ [3]. The average composition calculated from EDS data is close to the XRD result in the K_2O to Ga_2O_3 ratio: $K_2O \times 7.75\,Ga_2O_3$. The large value of the *c* parameter (> 2 nm) is due to the fact that (on average) K ions are randomly incorporated into one of 6 unit cells in an additional structural position in the Ga_2O_3 lattice. The alternation of cells with and without potassium atoms can occur in any direction of the structure, ensuring uniformity of the composition distribution.

For electrophysical measurements on an individual hexagonal $K_2O \times 8Ga_2O_3$ crystal of known thickness (450 μm) contacts from In_xGa_y eutectic were applied to the basal surface on the front and back sides, or two laterally (Fig. 2, *a*). Volt-ampere characteristics (VAC) were symmetric and quasilinear at small bias voltages (±1 V) with an ohmic resistance of 2−3 GΩ but became nonlinear at higher voltages, with the form shown in Fig. 2, *b*, and coinciding

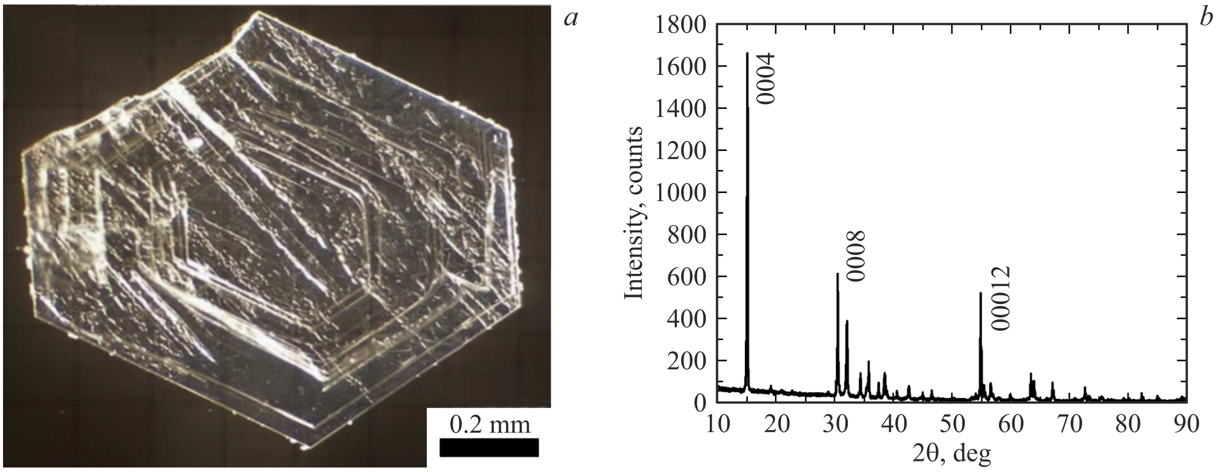

Figure 1. (*a*) Individual $K_2O \times 8Ga_2O_3$ crystal of hexagonal shape obtained from the KF solution-melt; (*b*) $\theta - 2\theta$ diffractogram (XRD) of $K_2O \times 8Ga_2O_3$ with indicated reflections of the basal series.

for measurements along and across the studied crystal. The asymmetry of the VACs is evidently due to lateral inhomogeneity of the surface layer, while the region of negative differential conductivity is most likely caused by the presence of a thin semi-insulating tunnel-transparent interlayer near one of the contacts.

Transmission spectra (TS, Fig. 3, *a*), measured in the wavelength range from 260 to 750 nm, revealed a small absorption step near 700 nm (apparently associated with iron impurity, consistent with CL results, Fig. 4, *b*). The main TS absorption edge was located at ~ 310 nm, and its shape was well approximated by a Tauc plot (Fig. 3, *b*) for indirect transitions [6], which allowed the optical band gap (E_g) of $K_2O \times 8Ga_2O_3$ to be determined for the first time as ~ 3.77 eV.

SEM images of the hexagonal crystals obtained in secondary electron detection mode demonstrated a plate-like surface relief formed by protruding parts of growing hexagonal micropisms. Simultaneously recorded CL maps (Fig. 4, *a*) more clearly revealed surface growth steps corresponding to crystallization fronts during layer-by-layer lateral expansion of the hexagonal crystal structure, as well as linear defects, which, for example, may be antiphase boundaries.

CL spectra recorded at different points on the surface of $K_2O \times 8Ga_2O_3$ crystals showed variability in intensity and spectral composition (Fig. 4, *b*). They contained three characteristic bands in the 1.5–4 eV range with varying relative intensities. The first was close in position (2–4 eV) and spectral shape to CL spectra obtained in epitaxial Ga_2O_3 films [7]. The second spectral feature of CL was an intense narrow peak at ~ 1.74 eV (~ 715 nm) corresponding in spectral position to a small step in TS, which is associated with intracenter transitions in impurity Fe^{3+} ions [8]. Auto-doping with iron, whose source is likely the initial analytical-grade KF powder, is the cause of the measured low electrical conductivity of the crystals [9]. The third, most intense broad band of 2.0–2.5 eV with a maximum position around 2.25 eV cannot be attributed to gallium oxide and is apparently the characteristic luminescence of $K_2O \times 8Ga_2O_3$.

The inhomogeneity of luminescence properties (and possibly the plate-like relief) may be related to the fact that the obtained potassium β-gallate crystals have a superstructure on the scale of the SEM CL method. It manifests as the predominant grouping of K polyhedra into connected layers, leading to phase separation of gallium oxide and potassium β-gallate on the nanoscale. Then, spectra with emission up to 4.0 eV correspond to superstructure regions with predominant Ga_2O_3 layers (blue curve in Fig. 4, *b*), while those with the predominant intrinsic band correspond to potassium β-gallate (red curve in Fig. 4, *b*).

Thus, high-resistance crystals of millimeter size, close in composition to Ga_2O_3 were obtained as a result of the reaction of $K_2O \times 8Ga_2O_3$ with the KF melt. The determined optical band gap was 3.77 eV, which allows $K_2O \times 8Ga_2O_3$ to be classified as a wide-bandgap compound. They exhibit inhomogeneous luminescent properties and a plate-like structure, which may be related to their layered superstructure.

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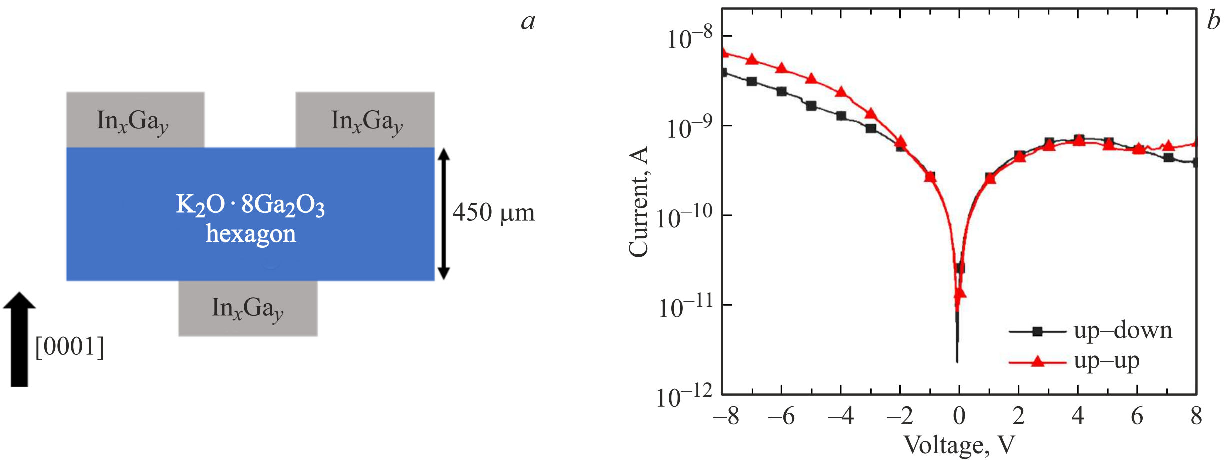

Figure 2. (*a*) Schematic of electrophysical measurements; (*b*) current-voltage characteristics measured in the vertical (black line with squares) and lateral (red line with triangles) directions of the hexagonal $K_2O \times 8Ga_2O_3$ crystal.

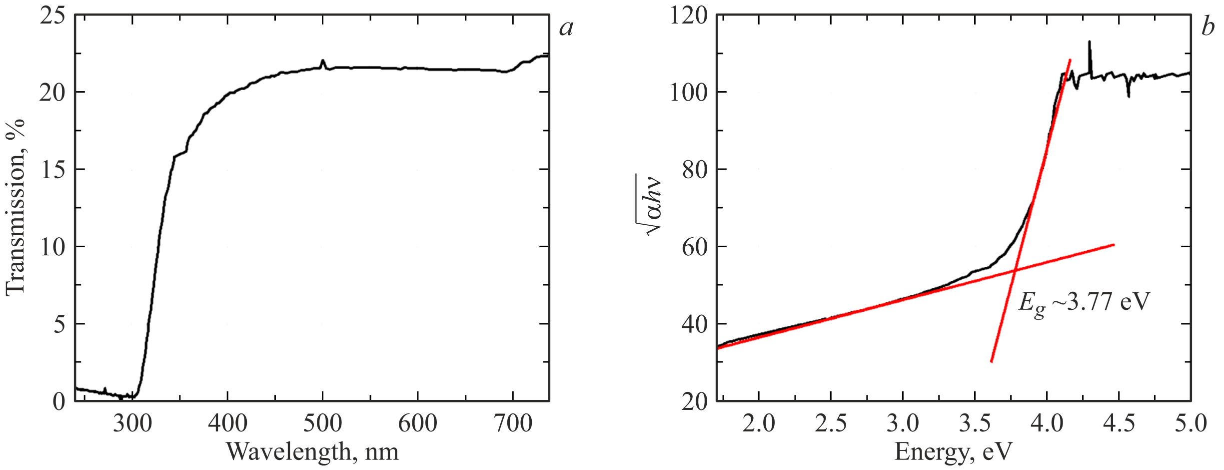

Figure 3. (*a*) Transmission spectrum of $K_2O \times 8Ga_2O_3$, (*b*) Tauc plot for Fig. 3, *a*, with the determined optical band gap.

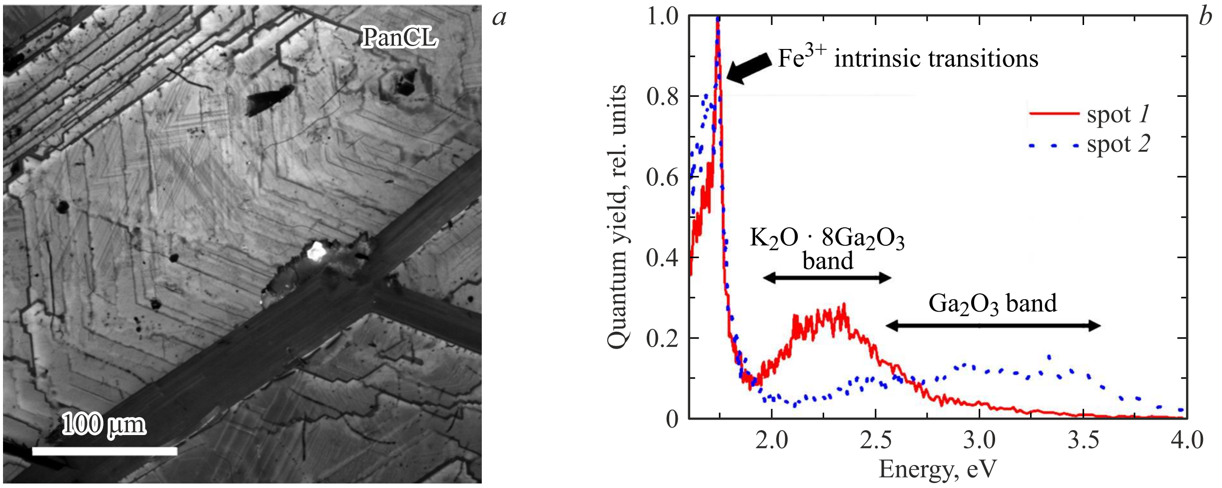

Figure 4. (*a*) Panchromatic CL map (PanCL) of the surface of a hexagonal $K_2O \times 8Ga_2O_3$; (*b*) crystal; (*b*) CL spectra recorded at different points on the $K_2O \times 8Ga_2O_3$ crystal.

Conflict of interest

The authors declare that they have no conflict of interest.

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