On the real structure of profiled anion-deficient corundum

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Abstract. Profiled Al₂O₃ single crystals grown by Stepanov’s method to obtain anion-deficient composition were characterized by neutron diffraction at T=300 K for the first time. Whereas the main structure motif of investigated crystals is checked to be of corundum-type, the scattering pictures of as-grown crystal demonstrate pronounced anomalies being probably indications on substructure forming. However, neutron scanning of synthesised crystal taken after annealing under restoring conditions reveals additional effects associated with displacement type superstructure.

1. Introduction

There is considerable interest in the refractory compounds (mainly oxides) to be adapted for a range of high-temperature and nuclear applications, variations of sintered corundum, or Al₂O₃, belong to large group of these numerous materials [see 1-3 and refs therein]. As an example based on experimentally investigated Al₂O₃ properties, the defect structure of these compounds is of great importance for atomic transport and for response to high-energy radiation [3].

In idealized model, represented by space group R-3c (trigonal syngony) the α-Al₂O₃ structure may be described as a slightly distorted hexagonal close-packed arrangement of oxygen ions (O²⁻), with interlayer coordinations related to displacements of aluminium atoms. Neglecting the known deviations from the "ideal" close-packing, the aluminium ions (Al³⁺) are placed in the octahedral sites [4, 5]. Hence the Al³⁺-ions occupy two-thirds of the interstices in the structure. In actual fact, the angle between in-plane <100> and <010> directions is not truly equal 120°, the angle difference from ideal packing is about 4.3° [see 6 and appropriate refs. therein]. The question about possibilities to form superstructures based on structure vacancies subsystem of real structure of Al₂O₃ is still open.

Profiled anion-deficient single crystals of corundum (α-Al₂O₃,δ) grown by Stepanov’s method under reducing conditions are widely used for the manufacture of radiation detectors of the type TLD-500 and Al₂O₃:C [7]. There are several models to describe recombination processes underlying radiation-detection base represented by thermo- or optical-stimulated luminescence read-out [8-12], but interpretation of the available experimental information obtained on anion-deficient Al₂O₃ is by no means clear cut to define mechanisms of radiation detection strictly.

The presented work is devoted to neutronographic characterization of structure states of anion-deficient corundum single crystals grown by Stepanov’s method; another purpose in view - to check
whether structure vacancies of anion-deficient corundum are possible to form any superstructures after restoring anneal of α-Al₂O₃ crystals.

2. Experimental

2.1. The samples
Two types of corundum single crystals were investigated by scattering of thermal neutrons at $T=300$ K. The first type (or $\alpha$-Al₂O₃) as grown crystal was with a concentration of anion vacancies $\sim 10^{17}$ cm$^{-3}$. The second type crystal obtained by the same synthesis was annealed at $T=1970$ K for 70 hours in oxygen atmosphere to restore the “natural” structure state of corundum or $\alpha$-Al₂O₃. In the second case concentration of anion vacancies was less than $10^{12}$ cm$^{-3}$. The single crystals were in cylindrical shape. (Their heights and diameters was about 0.4 cm.)

2.2. Experiment
The neutron diffraction experiment have been performed on D7b single crystal diffractometer ($\lambda=1.57$ Å) at IVV-2M research reactor (Sverdlovsk region, Zarechny, Russia).

3. Results and discussion
Major features of the idealized structure model identified by visible main Bragg peaks of thermal neutron diffraction allow the adequate adjustment of appropriate volume $\alpha$-Al₂O₃ single crystals for neutron diffraction experiments. As it was checked by neutronographic characterization, corundum structure is the main structure motif of both crystals. Appearance of very weak (003) and (009) reflections, forbidden for this structure, is in character for both investigated crystals and indicates on light deviations of the main structure motif from corundum type by, presumably, faults associated with, firstly, close-packing sequence and, secondly, non-pronounced disarrangements in related cation surrounding.

![Figure 1](image_url)

**Figure 1.** The $\omega$-scans of 006 (a, b) and 110 (c, d) reflections in (100) section: a, c — $\alpha$-Al₂O₃ crystal as grown (○); b, d — the second crystal after annealing (••). $T=300$ K.

From the scans of reflection curves (or $\omega$-scans) of the most intensive Bragg reflections, real structure of as grown $\alpha$-Al₂O₃ crystal is characterized by existence of single massive crystallite of
corundum structure in presence of large numbers of small fragments, with full volume of them being in commensurability with the volume of the main crystal block. As it is illustrated by fig.1, various scattering pictures in the vicinities of different reflections laying in one section plane point out strong disorientation in subsystem of micro crystallites. In $\alpha$-$\mathrm{Al}_2\mathrm{O}_3$-$\delta$ crystal these microfragments, almost of all, are deformed and irregular strains are seemed to be concentrated in their volumes. Data obtained on annealing crystal show suppression of fragmentation indications.

Information obtained by full scanning of (100) section is noteworthy. As it seen from fig 2a, turned “sublattice” can be identified in reciprocal lattice of anion-deficient crystal. The “turn angle” value is estimated to be of 4.5$^\circ$. Simple analysis put through the ”main” and ”additional” knots represented by fig. 2a shows that intensities of revealed sublattice reflections are few percent in comparison with identical structure reflections. Because of the “turn angle” is close to angle value given by imperfection from distorted atomic arrangement in (001) hexagonal plane, twinning effect seems to be involved in forming of the subsystem of reflections. Therefore additional striking fragmentation may be produced by twinning in $\alpha$-$\mathrm{Al}_2\mathrm{O}_3$-$\delta$ crystal. Instead sublattice knots, point system is revealed on scattering picture obtained from annealed sample (fig. 2b).

To compare intensity relations of the ”main” lattices of both crystals and sublattice of anion-deficient case, detailed scanning of each structure knot has been performed on both crystals, and sublattice knots presented by fig.2a have been also scanned. It is found, the intensities characterized both main lattices are identical ones, the sublattice intensity relations of anion-deficient crystals do not absolutely repeat analogous characterizations of the main lattice. (The experimental situation is
illustrated by fig.3, where the relative intensity of (0 0 12) “remote” sublattice reflection is of several times lower in comparison with the some relations for the “main” lattice.) The last fact indicates on existence of substructure characterized by lower symmetry built on the lack of anions.

The knot row placed along 3, 4, 5 lines represented on fig 2b (scattering data from annealed sample) is identified as superstructure knots. Observed very weak reflections is corresponded to wave vectors

\[ q = \left( \frac{1}{3} \frac{1}{9} 0 \right) \frac{2\pi}{a} + \left( 0 0 \frac{1}{3} \right) \frac{2\pi}{c} \]  

and their second and third harmonics. Bright points of this superstructure are situated along straight lines connecting “main structure” knots, containing places of the “twinning” knots in reciprocal lattice of the anion-deficient crystal. The most demonstrative effect is observed along line 5 on fig. 2b, the detailed scan of which is represented on fig.4.

Figure 4. Detailed scan along line connected (0 0 12) and (226) structure knots in (100) section of reciprocal lattice of \( \alpha - Al_2O_3 \) crystal (a), and \( \alpha - Al_2O_3 \) crystal after annealing (b).

Hence these pronounced additional coherent effects are associated with short-wave deformations. As it is pointed out by fig.2b, pronounced components of atomic displacements lay in (11l) planes, transverse to <11l> directions. Considering appearance of superstructure emerged on atomic displacements, we propose an answer, whether any superstructure can be formed throughout structure vacancies subsystem of \( \alpha - Al_2O_3 \) crystal obtained from \( \alpha - Al_2O_3 \) by annealing. As it is clear from idealized structure model of \( Al_2O_3 \), the anion position is surrounded by 4 cations and two structure vacancies gathering triangle-prismatic coordination or irregular tetrahedron built on cations. On this point of view, in simple manner, the data represented by figs 2b and 4 reflect possibilities arisen throughout numerous boundaries of micro crystallites to complete building of close-packed anion sublattice related to deficient case, in which structure restoring tends to form hexagonal axes along four "cubic" space directions simultaneously. Such unstable structure state can be supported by intrinsic defects and localized micro strains. As it is drawn from common formulae (1) giving the precision positions of superstructure knots, real structure displacements tend to form distorted rombohedral structure locally emerged to establish enlarged cell. The “new” hexagonal cell should be built on 18 close-packing anion layers, in which a parameter tends to be equal c. In this case, the rombohedral angle \( \alpha \) seems to be close to 90°. It reinforces our supposition about disordering of local c-axes appearing from turns of Al\(_4\)O-complexes, where these turns are accompanied by compensation deformations. Therefore, indications on double and triple superstructure phases seem to involve long-periodicities in real structure of the annealed crystal. Thus, Al- ions should be displaced along local <1-10> hexagonal directions (from filling anion vacancy) to form resulting “pseudocubic” continuum.
4. Conclusion
In this study, the fine features of the structural state of bulk $\alpha$-$\text{Al}_2\text{O}_3-\delta$ crystals, belonging to perspective detector materials, are considered for the first time by thermal neutron diffraction at $T=300$ K. In full, neutron scattering picture complicated by fragmented part allows to suppose that anion vacancies, being concentrated mostly in fragments, result in the highest vacancies content on the boundaries of these fragments. The other finding implying twinning effect is presented by additional knots in reciprocal space. Because of intensity relations of quasi-twin indications do not repeat main structure intensity relations, existence of substructure characterized by lower symmetry built on the lack of anions may be assumed. Annealing of $\alpha$-$\text{Al}_2\text{O}_3-\delta$ crystals in $\text{O}_2$ atmosphere leads to form modulated superstructure of displacement type. To obtain more precision information about atomic displacements in the anion-deficient corundum structure including its restoring sequences, experiments on heightened quality crystals, followed by specific modeling, are needed.

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