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About the distribution of structural defects in sapphire

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Using sapphire as an example, the distribution of structural defects in crystals grown by the most widely used methods today has been researched. Relationship between the length-to-diameter ratio and the distribution of defects in crystals is shown.

Про розподіл структурних дефектів у сапфірі. *Л.Литвинов*

На прикладі сапфіру досліджено розподіл структурних дефектів у кристалах, вирощених найбільш поширеними нині методами. Показано зв'язок відношення довжини до діаметра на розподіл дефектів у кристалах.

Keywords: growth method, dislocation, crystal, sapphire, grain boundaries, polygonization, crystallization front

1. Introduction

Among the structural defects, the density of dislocations and grain boundaries were singled out, which are formed during crystal growth and cannot then be significantly reduced by subsequent technological procedures (annealing, irradiation, etc.). Vacancies are not considered in this work, since methods of annealing in media with a controlled redox potential have been developed to control the density of anionic and cationic vacancies in already grown crystals over a wide range.

The relationship between the mechanical and optical properties of sapphire and structural defects was considered in many works [1, 3], but without taking into account the distribution of these defects over the crystal. The distribution of dislocations over crystals up to 150 mm long was described in [1]. Currently, crystals hundreds of mm long are grown now. An increase in the ratio of length to diameter of a crystal is associated with the appearance of new regularities.

The density of structural defects is mainly determined by the temperature gradients in the zone of crystal growth and cooling. Depending on the growth method, they differ by an order of magnitude (Table 1). They correspond to a change in the dislocation density (ρ) by several orders of magnitude. The table shows the average data. In a crystal, dislocations are unevenly distributed.

The purpose of this work is to study, using the example of sapphire, the regularities in the distribution of structural defects in crystals grown by the most widely used methods. A number of mechanical and optical properties are associated with the structural perfection of the crystal. Knowing the regularities of the distribution of structural defects in a crystal makes it possible to choose the most perfect regions, take into account the conditions under which it is possible to achieve a critical dislocation density when polygonization of dislocations occurs with the formation of a block structure [1,2], correct the thermal and kinetic conditions of the crystallization process in order to minimize the density of defects structures.

Let us consider in more detail the distribution of dislocations in crystals grown using the most common methods in the world: Verneuil, Stepanov and Kyropoulos. Up to 90% of sapphire is now grown using these methods. The table shows the relationship of dislocation density with temperature gradients in the growth zone and fracture toughness coefficient for crystals grown by six methods to show the range of changes in these parameters and the place in this range of the Verneuil, Stepanov and Kyropoulos methods.

Let us consider the distribution of dislocations in sapphire grown by Kyropoulos method. A crystal with a diameter of D_c = 200 and a height of L_c = 230 mm (Fig. 1) was grown in a vacuum in the direction $(11\bar{2}0)$ (the C axis is perpendicular to the generatrix), then cut into disks perpendicular to the growth axis. Samples oriented along two crystallographic axes were cut from disks. Dislocations ρ were measured on the planes of the prism and basis. The results were averaged. The range of dislocation density is basically 10^2-10^3 cm^{-2}. The maximum values at the upper butt of the crystal are explained by the necessary heat removal through the seed and by the butt radiation. The minimum values are in the middle part of the crystal and at the bottom butt. Moreover, in zones with $\rho \sim 10^2$ cm^{-2}, even numerous dislocation-free areas with an area of up to 5 mm^2 were found.

The distribution of dislocations reflects the complex relationship between the radial and axial temperature gradients in a growing crystal, which in the Kyropoulos method changes with increasing L_c, which is especially noticeable in the initial stage of growth. In zones where tensile stresses meet compressive stresses (zones **A**), the minimum dislocation density is observed. Figure 1 also shows an approximate diagram of compressive and tensile stresses in the middle part of the crystal - the most stable growth zone. The minimum values of ρ in zones **B** are explained by additional heating of the crucible from the bottom heater and a decrease in the rate of heat removal from the growing crystal.

A feature of the Ky-method is the conical crystallization front. The top of the cone **D** reaches the bottom of the crucible much earlier than finish of complete crystallization, which occurs when the cone expands in the direction of the arrow in Fig.1. Thus, the near-bottom part of the crystal (especially its central part) stays for a longer time in the areas of action of the minimum temperature gradients and the minimum rate of their changes, which explains its high structural perfection. No areas with $\rho \sim 10^4$ cm^{-2} were found in these zones.

The distribution ρ of the same type is typical for crystals grown by other nonstationary methods at a ratio $L_c : D_c < 2.5$.

In [4], the distribution of the stress tensor components in the cross section of a rectangular sapphire rod grown by the Stepanov method was considered. Similarly to Fig.1, it is shown that tensile stresses act along the perimeter of the section, and compressive stresses act in the center of the section. Based on the results

Table 1. Temperature gradient in the growth zone, dislocation density (ρ), critical dislocation density (ρ_{cr}) and fracture toughness coefficient (K_{1c}) of sapphire grown with different methods

Growth method	ΔT, degree/cm	Dislocation density, cm^{-2}		Fracture toughness coefficient, K_{1c}, $MN \cdot m^{-3/2}$
		ρ	ρ_{cr}	
Verneuil *Regular furnace *Furnace with additional heater	 200-250 ~80	 $(2…8) \cdot 10^5$ $\sim 1 \cdot 10^5$	$(2\text{-}4) \cdot 10^5$	 2.6…2.8 2.9…3.1
Stepanov (EFG)	50-55	$10^4…10^5$	$(1\text{-}2) \cdot 10^5$	3…3.5
Czochralski (Cz)	40	$10^3…10^5$	$(5\text{-}7) \cdot 10^4$	3.8…4
Kyropoulos (Ky)	25	$10^2… 10^3$	-	4…4.5
HEM	20	$10^2… 10^3$	-	4…4.5
HDS	40	10^3	$(2\text{-}3) \cdot 10^4$	3.8…4

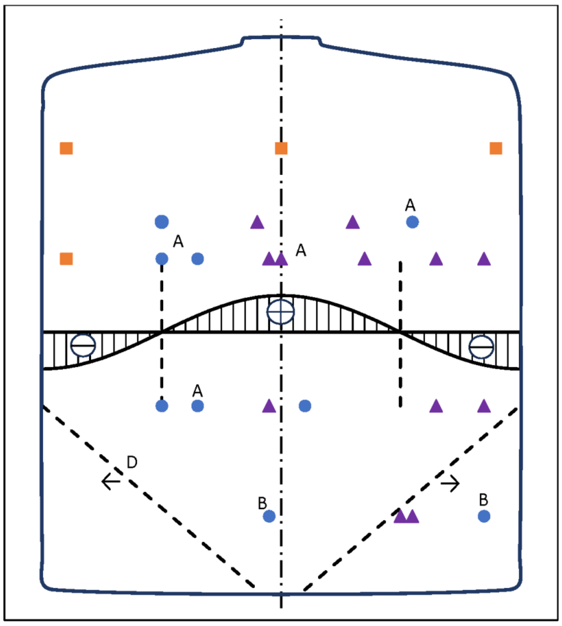

Fig.1 Density of dislocations distribution (circle-10^2 cm^{-2} , triangle-10^3 cm^{-2} , square-10^4 cm^{-2})

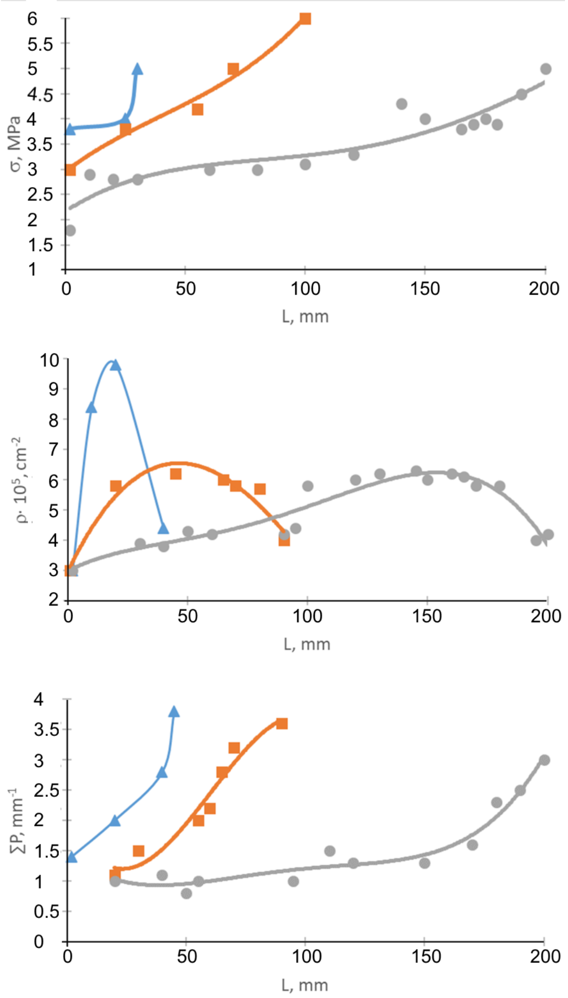

Fig.2 Stress distribution, dislocation density and length of block boundaries in crystals of different lengths

of measurements of anomalous biaxiality, the maximum shear stresses $2\tau_{max} = \sigma_1 - \sigma_2$ (difference of quasi-principal stresses) were calculated in accordance with [5].

Polygonization processes in basal-plane-faceted sapphire ribbons 50 mm wide, 15 mm thick, and 450 mm long grown by the Stepanov method [6] were studied using the polarization-optical method, selective etching, and X-ray diffraction analysis.

Dislocation distribution density on the surface of a basal-plane-faceted blockfree ribbon increases with length both in the middle part of the ribbon section and in the peripheral part of the ribbon. And in a block ribbon, with increasing length, the dislocation density increases to large values. In zones where the stress is greater than the critical shear stresses, plastic deformation occurs with the formation of dislocations. Plastic deformation in the peripheral part of the ribbon proceeds at a lower temperature than in the central part due to more intense heat removal.

In [6], it was determined that the values of microhardness and crack resistance along the length of a blockless sapphire ribbon with a cross section of 15x50 mm and L_c = 450 mm differ slightly. At $\rho<10^3$cm^{-2}, polygonization is observed in the areas of accumulation of pores. In block ribbons, residual stresses increase monotonically with increasing L_c due to the formation of new dislocations in the places where pores accumulate [7], polygonization of dislocations, and multiplication of blocks.

These considerations apply to relatively thick-walled (>10 mm) sapphire profiles grown according to Stepanov. Thin-walled profiles grow at a significant temperature difference between the central and peripheral parts of the wall. When growing a sapphire tube with a wall thickness of 3 mm at a distance of only one mm from the center of the wall, ρ can increase more than double (Fig.3), especially near the outer part of the wall. In this part of the wall in a thin near-surface layer, due to the mirror image forces, some of the dislocations can come to the surface. (This effect is described in more detail in [1]).

When the critical density of dislocations is reached (see Table 1), blocks are formed. The table clearly shows the relationship between ρ_{cr} and temperature gradients in the growth zone.

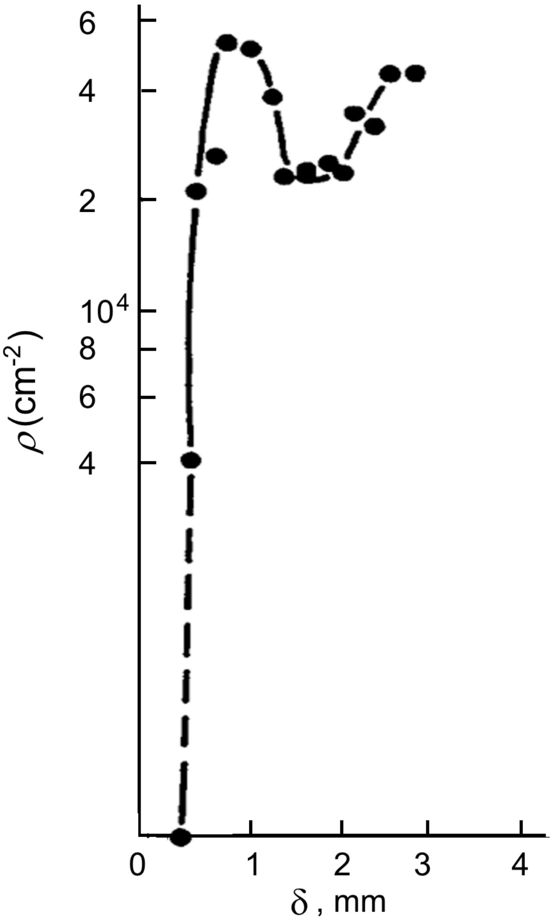

Fig.3 Distribution of dislocations over the wall thickness of a sapphire tube

In crystals grown by the Verneuil, Cz, and EFG methods, the L_c:D_c ratio can reach 50. At $L_c >> D_c$, the radiative-convective heat transfer in a growing crystal is close to stationary. The change in the density of structural defects depending on the crystal length was studied on crystals D_c = 20 mm grown by the Verneuil method with a cylindrical part length of 40, 90, and 200 mm (Fig. 2яф).

As the crystal length increases, the value of the maximum stresses decreases, and, consequently, the dislocation density also decreases. With a sufficiently large length of the rods (L_c > 8 D_c), the crystallized sections are cooled at lower rates of temperature decrease; therefore, the stresses, dislocation density, and length of block boundaries (∑p) increase in length more slowly than in shorter crystals. Accordingly, the change in length and strength properties is less. The decrease in ρ in the end part of the rod with a simultaneous increase in ∑p is explained by the polygonization of dislocations.

Conclusion

For sapphire-type crystals grown under nonstationary conditions, with a ratio $L_c : D_c < 2.5$, the dislocation density in different zones can vary by two orders of magnitude. The dislocation density is minimal in zones where compressive stresses are replaced by tensile stresses.

When the length of the rods is L_c > 8 D_c, the crystallized sections are cooled at lower rates of temperature decrease; therefore, the stresses, dislocation density, and length of block boundaries increase more slowly along the length and their maximum values are lower than in shorter crystals.

At the ratio $L_c >> D_c$, the dislocation density in blockless crystals almost does not change along the length, except for the initial and final parts of the crystal.

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