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Growth of long-length sapphire rods of optical quality

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The technological possibilities of the growth of optical-quality sapphire rods with a diameter of 12...20 mm and a length of 500...1000 mm by the Stepanov method. The influence of crystallization rate and crystallographic growth direction on the optical quality of the crystals was investigated. The technological procedure of "cold" narrowing of the growing crystal at the beginning stage of seeding was proposed to improve crystals structure. It was shown that heat treatment of the grown crystal in a gas environment with neutral chemical potential leads to destruction of optical color centers and scattering foreign-phase inclusions in its volume. It was shown that the main reason of color and scattering centers foundation in sapphire is anionic stoichiometry violation and the presence of uncontrollable impurities in the melt. To obtain long sapphire rods of optical quality the crystallographic oriented growth [11$\bar{2}$0] is preferred. In the process of growing a rod with a diameter of 14 mm, the depth of the surface-adjacent defective layer does not exceed 0.4 mm and the small-angle optical scattering doesn't have to be greater than 0.01 cm^{-1}.

Рассмотрены технологические возможности выращивания стержней сапфира оптического качества диаметром 12...20 мм и длиной 500...1000 мм методом Степанова. Исследовано влияние кристаллографического направления роста и скорости кристаллизации на оптическое качество кристаллов. Предложен технологический метод "холодной перетяжки" растущего кристалла на этапе затравления для улучшения его структурного совершенства. Показано, что термообработка выращенного кристалла при нейтральном химическом потенциале среды отжига позволяет разрушить оптические центры окраски и рассеивающие инофазные включения в его объёме. Установлено, что основной причиной образования центров окраски и рассеивающих центров в сапфире является анионная расстехиометрия расплава и наличие в нём сопутствующих неконтролируемых примесей. Для получения длинномерных сапфировых стержней оптического качества предпочтительным кристаллографическим направлением роста является [11$\bar{2}$0]. При выращивании стержня диаметром 14 мм толщина приповерхностного дефектного слоя не превышает 0,4 мм, а малоугловое оптическое рассеяние не более 0,01 $см^{-1}$.

The Stepanov method (EFG) allows to grow the crystals of preset profiles, and this essentially decreases loss of the material caused by mechanical treatment in the process of manufacturing sapphire articles. However, due to high density of structure defects, these crystals are mainly used as a constructional material. The obtaining of optical-quality crystals with a length exceeding 500 mm will permit to widen the application field of sapphire. In the frame of this research technological potentialities of the Stepanov method for the growth of long (up to 1000 mm) optical-quality sapphire crystals with a diameter of 12...20 mm were investigated.

The crystals — 14 mm in diameter and 800 mm long — were grown in Mo crucible in argon medium at high-frequency (8 kHz) heating. The heater (a hollow graphite cyl-

inder) was insulated from the inductor by graphite cloth and quartz shell. Thermal field was formed in the crystallization zone by means of a system of screens made from molybdenum and porous "Olcarb"-type graphite-containing material. Fragments of sapphire crystals grown by the Verneuil method were used as a raw material. Content of impurities in the raw material, ppm: Fe — 50, Si — 30, Ti — 20, Mg — 15, Ca — 5, (Cu, Ni, Mo, V, Mn, Cr) — < 5.

To improve the structure quality of the growing crystals a special shaping unit with centered feed of the melt and conical shape-forming surface was used. This allowed to form a stable convex crystallization front and to organize rejection of gas bubbles in the melt film at the crystallization front towards the growing crystal periphery. To avoid the appearance of inherited structure defects in the crystal from the seed-adjacent region, the method of 'cold Desh neck' was used. The shaping unit design permits to realize such a technological procedure without overheating the melt. Thereat, the crystal cross-section diminishes due to the power drop in the inductor until the diameter of 2–3 mm is reached.

The influence of the crystallization rate on the optical quality of the crystals grown along the crystallographic directions [0001], $[11\bar{2}0]$, $[10\bar{1}0]$ was investigated. The crystals were annealed in saturated aluminium oxide vapors at 1900°C [1]. The method of optical microscopy was used to control the presence and distribution of foreign-phase inclusions. The presence of the blocks was investigated in polarized light, its perfection was examined by means of three-crystal X-ray diffractometer with an angular resolution of diffraction reflection curve of ~1 arcsec. KSVU-2 spectrophotometer was used to measure the spectra of optical absorption. The optical homogeneity of the crystals was determined by IKD-101 interferometer from the quantity of interference bands and their local distortion. The change of the crystal refractive index values in the radial direction (Δn) was calculated from the formula:

$$\Delta n = \frac{N \cdot \lambda}{2L} \cdot 10^{-6},$$

where N is the quantity of interference bands; λ is the wavelength of the interferometer's radiation source (nm); L is the length of the crystal (mm).

The presence of light scattering at large angles was visually controlled while passing He–Ne laser beam through the crystal [2]. The value of low-angle scattering (σ) was measured using US-94 nephelometer with an error not exceeding 15 % and calculated under the formula:

$$\sigma = \frac{1}{L} \cdot \ln \frac{(1 + I_{sc}/I_0)_{\text{crys}}}{1 + I_{sc}/I_0} \text{ [cm}^{-1}\text{]},$$

where $(I_{sc}/I_0)_{crys}$ and (I_{sc}/I_0) are the relative intensities of optical scattering of the nephelometer beam with the crystal and without it.

The use of graphite heater and graphite components allows to form a growth medium with reducing chemical potential [3]. Sapphire rods grown in such a medium were characterized by anionic-type violation of the crystal lattice stoichiometry. The optical absorption of the grown sapphire at 206, 225 and 255 nm corresponds to that at F^- and F^+-centers [4–7].

The concentration of anionic vacancies ($[V_O]$) in the grown rods increases from the crystal nose to its tail. It takes place because of the increase of the degree of anionic-type violation of the melt stoichiometry in the process of crystallization. Their quantity in the crystals was determined by the Smacula formula [8] and the intensity of optical absorption at 206, 225 and 255 nm as a total concentration of F- and F^+-centers:

$$[V_O] = [F] + [F^+] =$$
$$= (1.86 \cdot \alpha_{206} + 0.292 \cdot \alpha_{225} +$$
$$+ 0.167 \cdot \alpha_{255}) \cdot 10^{16} = 6.3 \cdot 10^{17} \text{cm}^{-3},$$

where α_{206}, α_{225}, α_{255} — are the coefficients of sapphire optical absorption at the wave length 206, 225 and 255 nm.

It is possible to estimate the value of effective chemical potential of the growth medium [9] knowing concentration of anionic vacancies in the grown rods one can estimate the value:

$$\varepsilon = -[2E_V + 2RT \cdot \ln(A^{-1} \cdot [V_O] \cdot P_O)] =$$
$$= -235 \text{ kJ/mole},$$

where R is the universal gas constant; T is the temperature of the technological process; P_O is the equilibrium partial pressure of oxygen vapors in the products of thermal dissociation of corundum with stoichiometric composition; $[V_O]$ is the equilibrium concentration of anionic vacancies in the crys-

tal; coefficients $E_V = 1.12 \cdot 10^3$ J/mole, $A = 5.5 \cdot 10^{33}$ at·cm^{-3} were determined by the anionic vacancies concentration in the sapphire annealed in the saturated vapor of aluminium (under closed system condition) [3].

Some of the crystals had yellowish-brown color. The presence and intensity of the color depended on the crystallization rate and crystallographic direction. Thereat, the absence of Tyndall light scattering testified to the absence of foreign-phase inclusions. In these crystals color centers had optical absorption in 330...450 nm wavelength region with an absorption maximum at 387 nm. The rods grown along the crystallographic direction [10$\bar{1}$0] at crystallization rates of 20...27 mm/hr acquired color centers only at the initial crystallization stage when their length was not larger than 80 mm. Whereas the rods grown along the crystallographic direction [11$\bar{2}$0] had color centers only at crystallization rates higher than 25...27 mm/hr. This shows a better ability of the crystal which grows along the direction [11$\bar{2}$0], to reject uncontrollable impurity contained in the melt. The absence of color centers in the rods grown along the crystallographic direction [10$\bar{1}$0] when their length was larger than 80 mm may be explained by the fact that the efficiency of impurity rejection to the crystal periphery grows due to the increase of the axial gradient at the crystallization front in the process of crystal growth [10].

The crystals grown along the direction [0001] even at a rate of 15 mm/h had grayish-black inclusions in their bulk over the whole of the rod length. Tyndall light scattering of the laser beam pointed to foreign-phase nature of the inclusions. X-ray structure analysis could not establish the nature of such foreign-phase inclusions due to their low concentration, and no absorption bands characteristic of such defects were revealed in the optical absorption spectra.

Annealing of the crystals in saturated vapors of the thermal dissociation products of aluminium oxide ($\varepsilon \approx 0$ kJ/mole) at 1800...2030 E°C allows to destroy the defects and to achieve transparency of the crystals in the visible region of the spectrum. The kinetics of the destruction of the foreign-phase inclusions and color centers at such an annealing has a diffusive character. The crystal becomes transparent starting from its surface and then transparency extends into its bulk in the process of annealing (Fig. 1). This allows to conclude

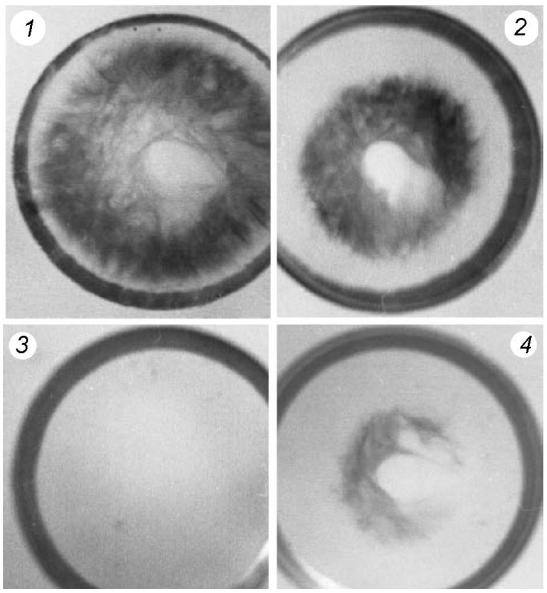

Fig. 1. Distribution of foreign-phase inclusions in sapphire rod with a diameter of 14 mm: *1* — before annealing; *2* — after 8-hour annealing; *3* — after 12-h annealing; *4* — after 15-h annealing.

that the foreign-phase inclusions and color centers with an absorption band at 330...450 nm are based on the complexes formed by impurity ions and anionic vacancies. The foreign-phase inclusions appear in the crystals with anionic-type stoichiometry violation when the impurity concentration is higher than a critical value. Annealing of the crystals in a medium with a low chemical potential (-50 kJ/mole $\le \varepsilon \le +50$ kJ/mole) reduces the degree of the stoichiometry violation and favors the destruction of the foreign-phase inclusions and color centers based on the impurity-vacancy complexes.

Localized in the surface-adjacent part of the crystal is a layer of gas inclusions with a depth of 0.2...2.4 mm which consists of a defect-free zone and zones with elevated and low defect densities (Fig. 2). Certain critical crystallization rate each crystallographic direction there exists for higher rate a sharp increase of the depth of the defective surface-adjacent layer is observed. For the crystals grown along the directions [11$\bar{2}$0] and [10$\bar{1}$0] the critical growth rate is 24–26 mm/h and 18–20 mm/h, respectively. In the crystals with [0001] orientation the surface-adjacent defective layer has a depth of 0.2...0.4 mm in the vicinity of the seed, however, their critical growth rate is limited by foreign-phase inclusions observed even at 15 mm/h crystallization rate.

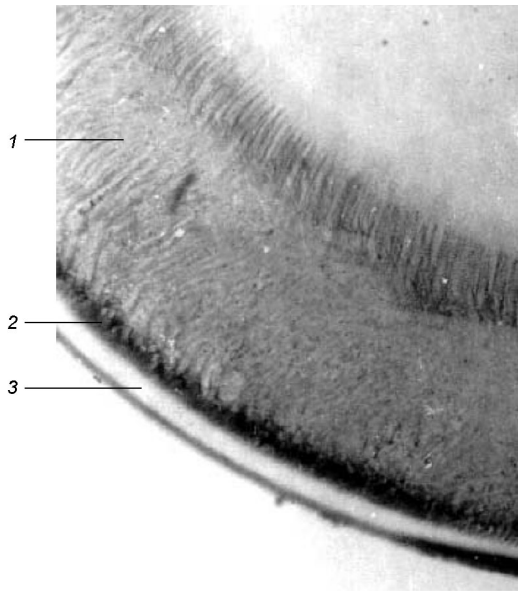

Fig. 2. Surface-adjacent defective layer of the sapphire rod with a diameter of 14 mm grown by the Stepanov method using conical shaper at growth rate of 40 mm/h. *1* — low defect density zone; *2* — high defect density; *3* — defect free zone.

As a rule, the depth of the surface-adjacent defective layer decreases when the temperature gradient between the shaper and the crystal increases. Such an effect appears with the increase of the length of the crystal (Fig. 3). As it follows from the dynamics of the change in the heater power in the process of growth, it may be assumed that the temperature gradient at the crystallization front will increase by 5...6 % after seeding at a crystal length of 100...130 mm. This increases the critical crystallization rate which at a crystal length of 100 mm makes 29–31 mm/h and 25–27 mm/h for the crystals grown along the directions [11$\bar{2}$0] and [10$\bar{1}$0], respectively.

No rough macro-block structure was revealed in the grown crystals. This is also confirmed by examination of the crystals in polarized light. Smearing of the diffraction reflection curves of the samples is mainly connected with micro-blocks with a cross-section of 100...200 μm and disorientation angles of low-angle dislocation boundaries running into 10 arcsec. The use of "Desh neck" essentially improves the structure perfection of the crystals which is evident from the fact that the half-width of the diffraction reflection curve decreases by 3.5...4 times.

Intense rejection of the impurity towards the crystal periphery and its localization on low-angle block boundaries leads to the ef-

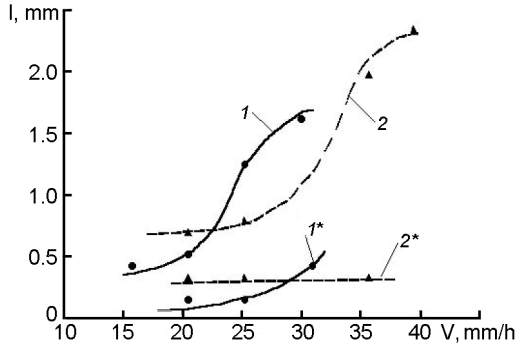

Fig. 3. The depth of the surface-adjacent layer of the sapphire rod grown by the Stepanov method depending on the crystallization rate: — [10$\bar{1}$0] growth direction, crystal nose (*1*), crystal tail (*1**); — [11$\bar{2}$0] growth direction, crystal nose (*2*), crystal tail (*2**).

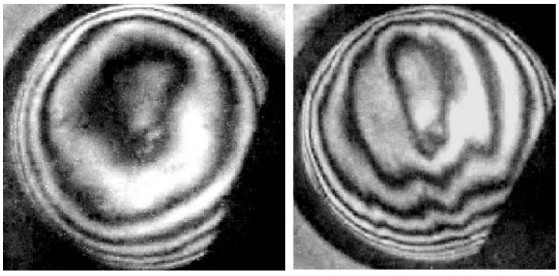

Fig. 4. Interferogram of ordinary (*1*) and extraordinary (*2*) beam of the sapphire rod with a diameter of 14 mm and a length of 100 mm grown by the Stepanov method.

fect of pseudo-lens and local non-uniformity of the refractive index (Fig. 4). Therefore, the crystals optical non-uniformity is noticeably influenced by an elevated (greater than 10 ppm) content of Fe, Si and Mg impurity in the raw material. The rods grown along the direction [11$\bar{2}$0] are characterized by higher local non-uniformity and monotonous change of the refractive index in comparison with the rods grown along the directions [10$\bar{1}$0] and [0001] (Table). This can be explained by the better ability of the crystal growing along the direction [11$\bar{2}$0] to reject the impurity contained in the melt. The lowest optical non-uniformity is characteristic of the crystals grown along the direction [0001] after thermal destruction of the foreign-phase inclusions in their bulk.

Low-angle disorientation of the inter-block boundaries and the effect of pseudo-lens essentially limit the value of optical scattering under low angles. In terms of the parameter, the crystals grown by the

Table. Optical non-uniformity and low-angle scattering (σ) of sapphire rods with a diameter of 14 mm grown by the Stepanov method

Crystallographic growth direction	Crystallization rate (mm/h)	Local distortion of the waving front (cm^{-1})	Change of refractive index Δn	σ (cm^{-1})
[10$\bar{1}$0] Stepanov method	20	λ/20	$1.63 \cdot 10^{-5}$	0.008
	25	λ/17	$1.63 \cdot 10^{-5}$	0.009
	30	λ/17	$1.96 \cdot 10^{-5}$	0.004
[11$\bar{2}$0] Stepanov method	20	λ/13	$1.94 \cdot 10^{-5}$	0.008
	25	λ/15	$2.14 \cdot 10^{-5}$	0.006
	35	λ/16	$1.81 \cdot 10^{-5}$	0.006
[0001] Stepanov method	15	λ/45	$2.22 \cdot 10^{-5}$	0.011
[11$\bar{2}$0] Verneuil method	10...15	λ/8...λ/25	$5 \cdot 10^{-6}$...$1 \cdot 10^{-4}$	0.025
[11$\bar{2}$0] Czochralski method	4...8	λ/9...λ/30	$5 \cdot 10^{-6}$...$5 \cdot 10^{-5}$	0.015

Stepanov method can compete with those obtained by other methods (see Table).

Thus, the Stepanov method allows to obtain optical-quality sapphire rods with a length up to 1000 mm and a diameter larger than 12 mm. The content of impurities in the raw material does not have to exceed 10 ppm for each of the chemical element. The preferential direction of crystallization is [11$\bar{2}$0]. Sapphire rods with a diameter of 14 mm grown along this direction at a rate of 30 mm/h will have optical quality if a depth of defective surface-adjacent layer is not larger than 0.4 mm. Color centers and foreign-phase inclusions caused by anionic-type violation of the crystals' stoichiometry and uncontrollable impurities contained in the raw material are eliminated by after-growth annealing in a medium with chemical potential $-50\ \text{kJ/mole} \le \varepsilon \le +50\ \text{kJ/mole}$.

References

1. Patent USSR №591210.
2. M.A.Chernyshev, S.V.Grum-Grzhimailo, N.M.Melankholin, Ruby and Sapphire, Nauka, Moscow (1974), p.85 [in Russian].
3. Ye.V.Kryvonosov, *Functional Mmaterials*, **1**, 105 (1994).
4. B.D.Lee, J.H.Ir, *Phys. Rev. B*, **15**, 4065 (1977).
5. B.D.Evans, B.Stapelbrock, *Phys. Rev. B*, **18**, 7089 (1978).
6. S.Y.La, R.H.Bartram, R.T.Cox, *J. Phys. Chem. Solids*, **34**, 1079 (1973).
7. D.Y.Smith, D.L.Dexter, *Prog. Optics*, **10**, 165 (1972).
8. D.L.Dexter, *Solid State Phys.*, **6**, 353 (1958).
9. S.D.Vyshnevskiy, Ye.V.Kryvonosov, L.A.Lytvynov, *Functional Materials*, **10**, 238 (2003).
10. A.A.Chernov, D.E.Temin, A.M.Mel'nikov, *Krystallographiya*, **21**, 652 (1976).

Вирощування довгомірних стержнів сапфіру оптичної якості

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Розглянуто технологічні можливості вирощування стержнів сапфіру оптичної якості діаметром 12...20 мм і довжиною 500...1000 мм методом Степанова. Досліджено вплив кристалографічного напрямку росту і швидкості кристалізації на оптичну якість кристалів. Запропоновано технологічний метод "холодного перетягнення" кристала, що росте, на етапі затравлення для поліпшення його структурної довершеності. Показано, що термообробка кристала при нейтральному хімічному потенціалі середовища відпалу дозволяє зруйнувати оптичні центри забарвлення і розсіюючі інофазні включення в його об'ємі. Встановлено, що основною причиною утворення центрів забарвлення і розсіюваючих центрів у сапфірі є аніонна розстехіометрія розсплаву та присутність в ньому неконтрольованих домішок. Для отримання довгомірних сапфірових стержнів оптичної якості необхідно віддавати перевагу кристалографічному напрямку росту [11$\bar{2}$0]. При вирощуванні

стержня діаметром 14 мм товщина приповерхневого шару не перебільшує 0,4 мм, а малокутове оптичне розсіювання не більш ніж 0,01 $см^{-1}$.