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Growing of large-sized high-quality sapphire by the Kyropoulos method

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A transparent large-scale sapphire approximately 250 mm in diameter and about 30 kg in weight were grown by the Kyropoulos technique along the crystallographic direction $<10\bar{1}0>$. An analysis of the crystallization front shape at various stages of crystal growth was carried out. The dislocation structure was studied by selective chemical etching and X-ray diffraction, the thermoplastic stresses were assessed in large boule using the polarized light methods. The crack resistance was determined using the Vickers method, the optical absorption in sapphire was also investigated.

Keywords: sapphire, Kyropoulos tecnique, optical absorption, dislocation density, chemical etching, X-ray diffraction, fracture toughness.

Вирощування високоякісного сапфіра великого розміру методом Кіропулоса.
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Прозорий сапфір діаметром приблизно 250 мм і вагою близько 30 кг вирощено методом Кіропулоса в кристалографічному напрямку $<10\bar{1}0>$. Проведено аналіз форми фронту кристалізації на різних стадіях вирощування. Методами вибіркового травлення та рентгенодифрактометричного аналізу вивчено дислокаційну структуру, поляризаційно-оптичним методом проведено оцінку термопластичних напружень у вирощеній булі. Методом Віккерса визначено тріщиностійкість, досліджено оптичне поглинання у сапфірі.

1. Introduction

Sapphire is a very important material with excellent properties that make it desirable of many high technology applications: in micro- and optoelectronics, instrument making (optical and laser technology), mechanical engineering [1,2]. Sapphire has emerged as the preferred substrate for epitaxial layers of semiconductors for high brightness, light emitting diodes (LEDs). LEDs are considered as the most promising lighting sources in 21st Century for the advantages in high brightness, long lifetime (more than 50,000 hours), low energy consumption, short corresponding time, good shock resistance, safety. The global LED lighting market is expected to witness a compound annual growth rate of 11.0% from 2023 to 2030 to reach USD 168.87 billion by 2030 [3]. The requirement of substrate wafer size is getting larger and larger, from 2″ to 4″, 6″ and 8″ [4]. Therefore, the growth and development of large size sapphire crystal have attracted increasing attention all over the world. Dislocations in the sapphire substrate can affect the epilayer quality, if dislocations in the substrate propagate into the epilayer. The dislocation density in high-quality sapphire should not exceed 10^3 cm^{-2}, and for some applications - 10^2 cm^{-2} [4,5].

Nowadays sapphire crystals are obtained by various techniques, such as horizontal directional crystallization (HDC), heat exchanger method (HEM), Kyropoulos (KY) techniques,

Stepanov and Czochralski methods [5]. Each method has its own advantages and drawbacks, but none of them makes it possible to obtain sapphire crystals which dislocation density is not higher than 10^3 cm^{-2}.

A promising way to solve this problem is optimization of the crystallization conditions in the KY and HEM methods. These are the methods that have the greatest potentials for creation of large low-dislocation crystals due to record low temperature gradient at the crystallization front. Technically the KY method is simpler than the HEM technique [5-9]. During the whole growth process by the KY method, the crystal is in the crucible but no contact with the crucible wall, thus the thermal stress in the crystal is small. Nowadays, KY technique is one of the effective methods to grow large diameter sapphire substrate crystals.

In 2009, 200 kg weight sapphire boule are successfully grown by Rubicon Technology Inc. using the improved KY method [4]. In 2015, pilot ingots of extra-large size, 500-mm diameter, 350 kg were grown using fully automated furnaces. The advanced KY technique is successfully used for the mass production of sapphire boules weighing about 30, 60, 80 kg.

Increase of the size of the crystals and high requirements to the structural perfection of sapphire to be used as a material meant for LED substrates set new technological tasks bound up with reconstruction of thermal units of the growth setups and optimization of their technological regimes [6-10].

The goal of the present work was to improve the technology for the obtaining of large-size sapphire crystals with high optical and structural homogeneity.

2. Experimental

In order to create an energy-saving technology for crystallization of sapphire on the growth setup Omega-200, there was used ceramics based on zirconium oxide stabilized with yttrium oxide, as a material for heat-insulating layers of the crystallizer working zone (Fig.1). To reduce thermal load on the heat-insulating shell and diminish the axial temperature gradient in the working zone of the thermal unit, 2.5 – 3.0 mm thick cylindrical tungsten shield was installed. This shield takes over maximum thermal load, and can be replaced in case of failure in the process of operation.

The vertical temperature gradient inside the growth zone of the crystallizer is formed by

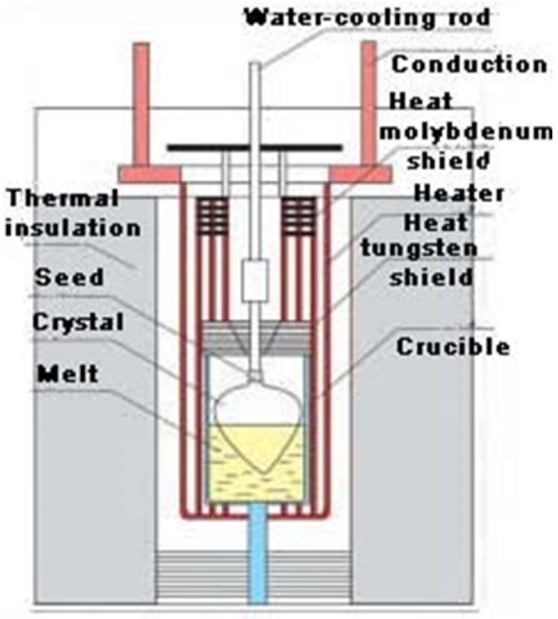

Fig.1. Schematic diagram of upgraded crystal growth setup Omega–200 [4].

the upper and lower blocks of the molybdenum shields. To optimize the radial and axial gradients, a block of shields consisting of three separate packets is mounted on the crucible.

The most promising materials to be used in the crucibles are tungsten and molybdenum. The crucibles are manufactured by the method of powder metallurgy. After pressing and annealing the inner crucible cavity is bored into a cone to avoid «freezing» of the crystal to the crucible walls.

Heat generated outside of the heat shields is removed by water that cools the walls of the crystallization chamber and the current conductors.

The sapphire substrates for LED have to be c-plane because of the lattice match between the deposition gallium nitride (GaN) and sapphire. Therefore, the most efficient growth process that yields the largest material utilization will be *c*-plane parallel to [0001]. The *c*-plane (0001) is one of low energy surfaces and growth rate on a plane (0001) is inherently the slowest. Under identical conditions, sapphire grows at the highest rate along $<10\bar{1}0>$. The crystal is grown along the $<10\bar{1}0>$ and then the rods are drilled along the *c*-axis perpendicular to the growth direction.

As seed crystals, there were used sapphire rods with a length up to 160 mm and a diameter of 12-18 mm grown by the Stepanov method. The content of impurities in the raw material did not exceed 10 ppm for each

chemical element. Formation of a constriction («thin neck», as proposed by Dash) in the initial part of the crystal essentially improves the structural quality of the rod. The sapphire rods grown along the crystallographic direction $<10\bar{1}0>$ are preferred.

From the initial part, central and bottom parts of the boule there were cut the plates perpendicular to the growth direction $<10\bar{1}0>$ that had been used for fabricating 40x15x2 mm^3 samples of the orientation (0001).

The samples were machined on a ASM 80/63 diamond scaife and using 40 boron carbide grinding powders with a grit size of 28–40 μm (as per State Standard GOST 5744) on a Mod. ZShP350M grinder with a spindle speed of 100 rpm and contact pressures of 0.22 kPa (for a loose abrasive) and 0.3 to 0.7 kPa (for a fixed abrasive). The ground samples were polished on a polycaprolactam polishing pad using loose ASM 28/20 diamond micron powders. This operation was realized on a Mod. 4PD200 machine tool, at 100 rpm and a contact pressure of 0.22 kPa. Then the samples were annealed in vacuum at 1850 ^{0}C during 2 hours to remove surface stresses.

The dislocation structure was examined by means of a Zeiss Axioskop 40 A POL microscope. Dislocations were revealed by selective chemical etching. The surface of the basal plane was etched in orthophosphoric acid at 325°C for 15 min. The etching patterns thus revealed were counted over the surface areas of the cross section of the crystal located at different distances from the seed. From such data, we evaluated the dislocation density distribution (ρ, cm^{-2}) in the crystal bulk.

The structural imperfections in the grown crystals were also studied using high-resolution three crystal X-ray diffractometry (TXD). We used Cu$K\alpha_1$ radiation and T (n, n, $-m$) geometry of the monochromators and the sample. In this scheme, high-perfection (111) germanium crystals were applied as monochromators. The samples were moved during diffraction reflection curve measurements at 1–1.5 mm scanning pitch with respect to the incident beam. This makes it possible to estimate the uniformity of the distribution of a finer microblock structure over the crystal cross-section. The dislocation density ρ was also measured based on the change of the integral reflection power R_{exp} on different crystallographic planes [11,12].

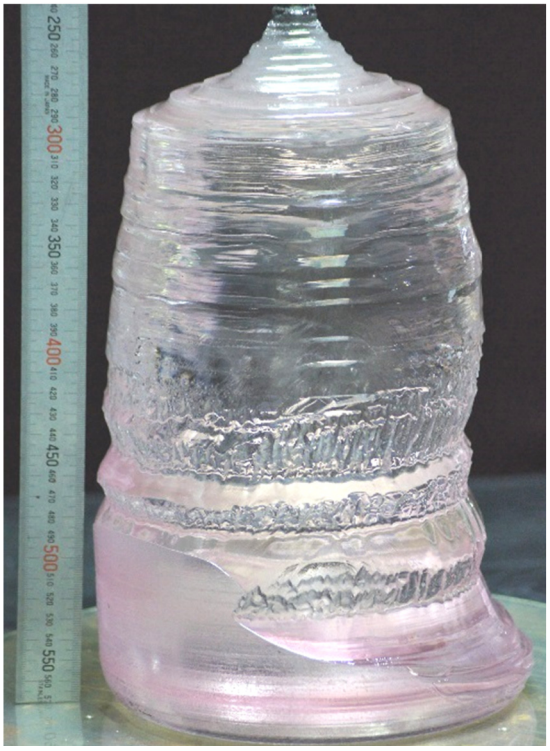

Fig.2. Sapphire crystal grown by the KY method along the direction $<10\bar{1}0>$.

The value of thermoplastic stress in the crystals was investigated in polarized light using a PKS125 general-purpose konometer and in convergent polarized light (conoscopy) by means of a Zeiss Axioskop 40 A POL. Anomalous biaxiality (2V angle) measurement results were used to calculate the maximum shear stress $2\tau_{max} = \sigma_1 - \sigma_2$ (the difference between quasi-major stresses), following Indenbom and Tomillovskii.

The value of cracking resistance was determined according to the method described in [13] by means of a PMT–3 device at the indenter load P = 3.5H from the results of not less than 30 measurements.

The absorption spectra of the grown boule were measured in the range of 200-1100 nm using a Perkin-Ember Lambda–35 spectro photometer.

3. Results and discussion

For crystallization there were used the waste products of sapphire crystals grown by the KY method that remained after manufacture of finished products from them. The volume of the initial crucible loading of the crucible with a diameter of 250 mm and a height of 370 mm was 30 kg. The seed crystal was

Fig. 3. Experimeal sapphire crystal with a weight of 30 kg grown in «Omega–200» setup equipped with ceramic thermal insulation.

16.6 mm in diameter and 160 mm high and had the orientation $<10\bar{1}0>$. Crystallization was realized at a reduction of the heater power of 40 Wt/h without lifting the crystal.

Shown in Fig. 2 is the crystal with a weight of 30 kg grown using the setup Omega–200 with ceramic thermal insulation.

The crystals grown by the KY method were investigated by the method of selective etching. After the performed etching, on the crystal surface there were observed contrasting figures shaped as pointed triangles that corresponded to the crystallography of the basal plane. These etch pits were formed at the intersection of the dislocation line with the basal surface. The dislocation density in the samples cut from the initial part of the boule was $1.7 \cdot 10^3$ cm^{-2}. For the samples obtained from the central parts of the boule it was $2.1 \cdot 10^2$ cm^{-2}. The character of dislocation distribution in the crystal bulk is bound up with the change of the temperature gradient in the vicinity of the crystallization front. The increase of the dislocation density in the initial part of the crystal is caused by the fact that during the growth of the crystal the thermal conditions are not stationary, that results in increase of stresses in the crystal. At

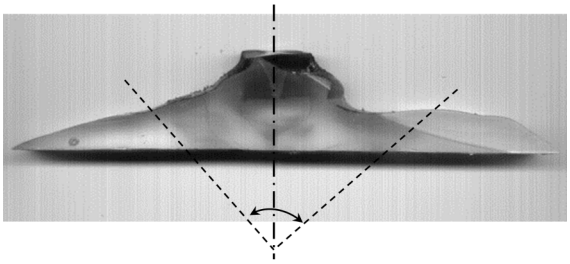

Fig. 4. Seed-adjusting part of sapphire crystal grown in «Omega –200» setup.

the stage of linear growth residual stresses in the central part of the boule were the lowest. Therefore, the dislocation density in the central part of the boule were minimal in comparison with that of the crystals grown by other methods of the obtaining of corundum crystals (the Verneuil method: 10^5-10^6 cm^{-2}, the Czochralski method: 10^3-10^4 cm^{-2}, the HEM method: 10^3-10^5 cm^{-2}, HDC: 10^3-10^4cm^{-2}).

To determine the shape of the crystallization front, 80 hours after the beginning of crystallization the technological regimes were perturbed In particular, power supply of the heater was switched off during 60 s, then the regime of crystallization was restored and the growth of the crystal continued. The grown crystal (Fig. 3) was divided into three parts by transverse cuts the seed-adjusting part, the part of stable stage of growth process prior to the technological perturbation and the part of the crystal grown after restoration of the technological regime.

In the seed-adjusting region the shape of the crystallization front can be approximated by a cone with the angle at its apex $\boldsymbol{\alpha} \approx 90^o$. This fact can be established according to the shape of the crystal area where gas bubbles have been frozen (Fig. 4).

Unlike the Czochralski and HDC methods, for which the shape of the crystallization front is relatively constant during the growth process, in case of the KY method the crystallization front can essentially change its shape due to uneven local changes of the crystallization rate on its separate sections. This can give rise to formation of crystal structure defects and promote capture of gas micro-bubbles from the melt by the crystallization front. For conical shape of the crystallization front change of the front shape parameter is bound up with the fact that the normal crystallization rate decreases on the periphery of the crystallization front and increases at its top.

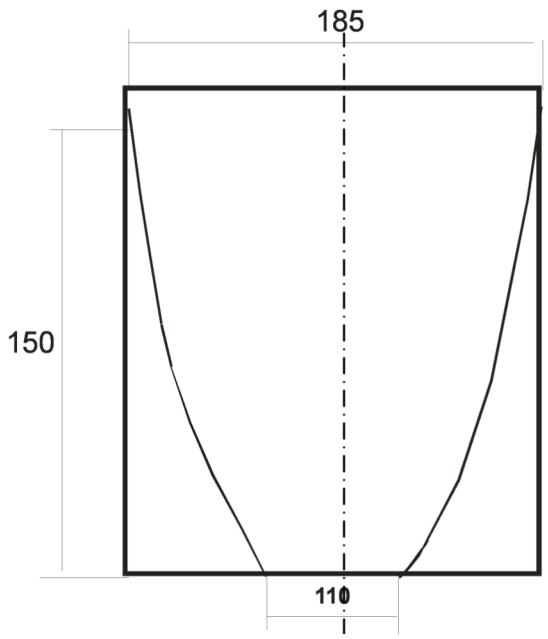

Fig. 5. Scheme of crystallization front of sapphire in «Omega–200» setup (after 60 s heating switch-off during crystallization).

By the end of the stable stage of growth process, when the crystal has reached the crucible bottom, the crystallization front takes the shape presented in Fig 5, which can be approximated by the shape of the cone with the angle at the apex $\alpha \approx 30^{o}$.

Shown in (Fig. 6) is the plate of the orientation (0001) from the lower part of the crystal cut along its axis. On the plate there are clearly observed two characteristic regions: the central region of the crystal grown before the technological perturbation (Fig. 7,a) and the peripheral region formed after this perturbation (Fig. 7,b).

In transmitted polarized light in the direction [0001] in the central region there is observed practically undistorted conoscopic figure. In the peripheral region optical inhomogeneities arise. The observed picture allows to make the following assumption. Before the technological perturbations the crystal has not contained blocks. After the technological perturbations and active capture of a large number of bubbles by the crystallization front, in the peripheral part of the crystal there have appeared block boundaries. Stresses along the latter give rise to distortions in the optical image of the crystal in polarized light.

These results confirm the data obtained by the method of three crystal X-ray diffractometry of the corresponding crystal regions. The crystal structure perfection was estimated for the samples of the crystallographic orientation (0001) cut from the central and peripheral crystal regions. According to the performed studies, in the central region of the grown crystal the value of dislocation density does not exceed $\rho < 10^3$ cm^{-2} in the absence of micro-blocks. In the peripheral region of the crystal $\rho = 3 \cdot 10^4$ cm^{-2}, in the presence of micro-blocks with the disorientation angle $\Delta\theta = 2$”-10”.

Quantitative investigations of the dislocation structure by the method of chemical etching give the results that coincide with those of X-ray diffractometric analysis. In the central part of the grown crystal the dislocation density does not exceed $\rho < 10^3$ cm^{-2}, in the peripheral part $\rho = 3 \cdot 10^4$ cm^{-2} (Fig. 7).

The defect structure of the opaque region of the boule that separates the central and peripheral regions is characterized by the presence of bubbles. As seen from the etching figures obtained on the opaque region, the etching figures merge with each other (Fig. 8).

The results of the studies performed in convergent polarized light confirm high structure perfection of the grown boule. The internal stress level in the crystal is extremely low and equals 1.2 MPa for the central part of the

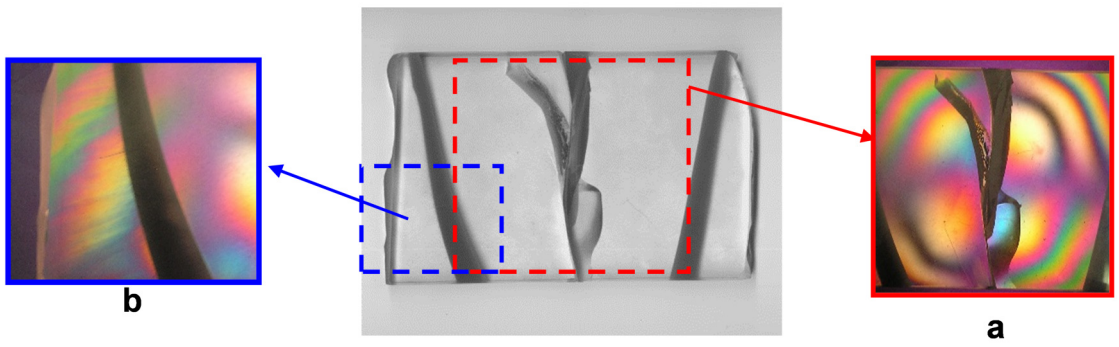

Fig. 6. Central (**a**) and peripheral regions (**b**) of the lower part of the grown crystal in convergent polarized light.

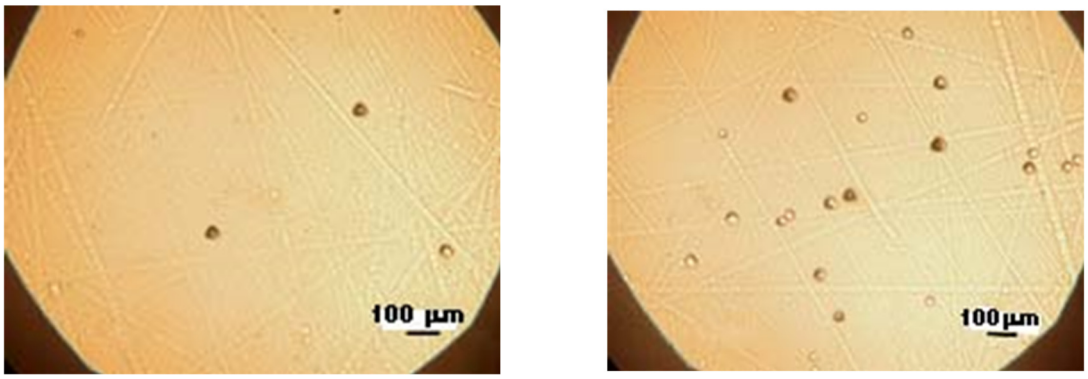

Fig. 7. Dislocation structure of the crystal before (a) and after (b) technological perturbations.

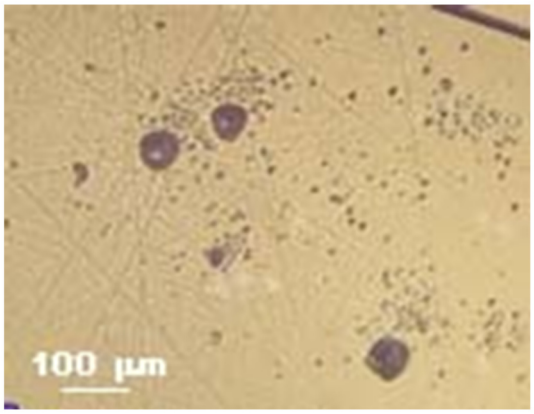

Fig. 8. Dislocation structure of opaque region.

crystal. Observed in this region is practically undistorted conoscopic figure (Fig. 9,a). The presence of blocks in the peripheral part of the crystal slightly increases the value of residual stresses in it – up to 1.6 MPa (Fig. 9,b). As shown while studying the actual distribution of the stress fields in the crystal, in the process of its growth and cooling there have been created technological conditions for their relaxation. In comparison, the values of shear stresses in a block-free ribbon obtained by the Stepanov method in a modified furnace, in the transition region of a growing crystal and in the full crystal cross section part is 1.8 and 5 MPa, respectively [14].

The crystal demonstrates high crack propagation resistance. The value of fracture toughness equals 4.6 MN·m$^{-3/2}$. In the defect regions the crack resistance decreases slightly and makes 3.8 MN·m$^{-3/2}$. The study of cracking resistance of sapphire crystals grown by different methods shows that effective energy of damage is a structure-sensitive characteristic dependent on the dislocation density. The coefficient of cracking resistance of sapphire with the lowest dislocation density (KY method) exceeds similar values obtained for crystals grown by Czochralski (3.5 MH·м$^{-3/2}$),

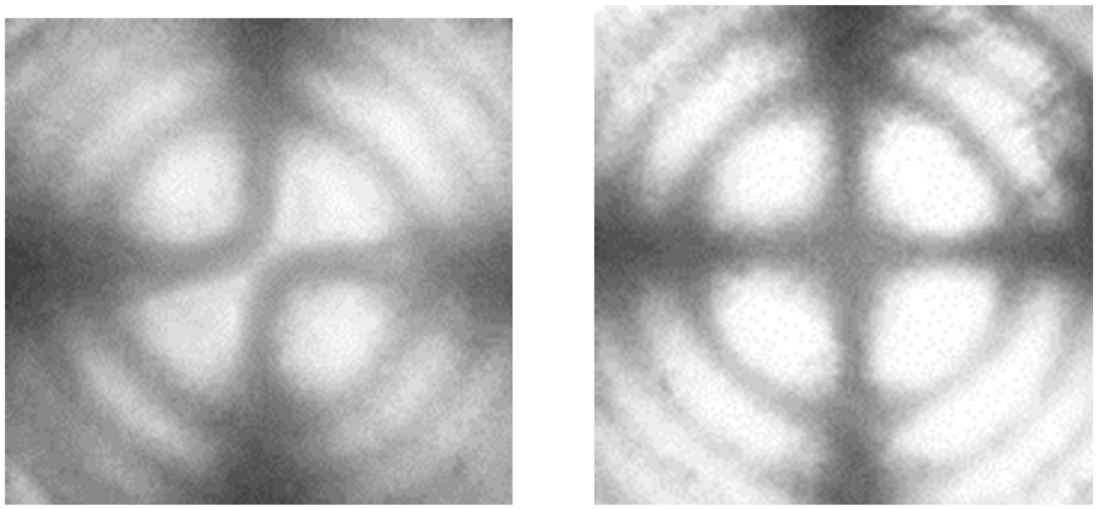

Fig. 9. Interference pattern of sapphire in the basal plane perpendicular to the growth direction: a – central part, b – peripheral crystal part.

Fig.10. Indentation pattern of sapphire on the basal plane (a), low-dislocation sample, (b), sample with high dislocation density.

Stepanov (3,0 МН $м^{-3/2}$) and Verneuil methods (2,8 МН $м^{-3/2}$) [5].

The optical absorption spectrum of the crystal has no color centers in the visible and UV spectral regions (Fig. 11). This testifies that both stoihiometry violations of the crystal lattice and uncontrolled accompanying impurity are absent. This is explained by the fact that the chemical potential of the crystallization medium is close to neutral. Moreover, this testifies that the content of foreign chemical impurities in the raw material produced by EMT ("Emergence Material Technology", USA) is low.

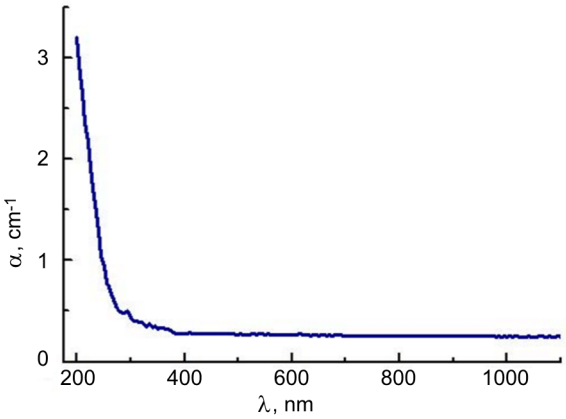

Fig. 11. Optical absorption spectrum of sapphire grown by the KY method from EMT raw materials.

4. Conclusions

Using a modified furnace with ceramic thermal insulation, sapphire approximately 250 mm in diameter and approximately 30 kg in weight were obtained by the KY method parallel to $<10\bar{1}0>$ direction. It was found that in the seed-adjusting region the shape of the crystallization front looks like a cone with an apex angle of 90^0, at the stage of stable growth – is a cone with an angle at the apex 30^0. The grown crystals are transparent in the wavelength range of 200-1100 nm. The dislocation density in the central parts of the boule was - $2.1 \cdot 10^2$ cm^{-2}, in the initial part of the boule the number of dislocations was slightly higher - $1.7 \cdot 10^3$ cm^{-2}. X-ray diffraction confirmed that in the regions of the boule before the technological perturbation, the dislocation density was less than 10^3 cm^{-2} in the absence of micro-blocks. In the peripheral region formed after perturbation there are micro-blocks with disorientation within the limits 2"-10". The study in polarized light confirmed the high structural perfection of the grown crystals - internal stress in the central part of the crystal not higher than 1.2 MPa.

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