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MELT GROWTH

New Advances and Developments in the Stepanov Method for the Growth of Shaped Crystals

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Abstract—The main recently developed versions of the Stepanov method are analyzed, and a brief review of the main achievements in the growth of shaped crystals is given. © *2002 MAIK "Nauka/Interperiodica"*.

INTRODUCTION

The ideas and publications of A.V. Stepanov on crystal growth gave rise to a new line of research in this field and laid a foundation for the industry of shaped crystals. The new principle of crystal shaping is formulated in the following way: "A shape or an element of a shape that we need to form is created in the liquid state owing to different effects allowing the liquid to retain its shape; then, this shape or its element can be transformed to the solid state by choosing the appropriate crystallization conditions" [1].

The technique of Stepanov differs from the other methods of crystal growth from the melt in the presence of a new element, namely, a shaper, which provides an opportunity to form a liquid column of the melt in a free state without any contact with the crucible walls. Different types of single-crystal products with complicated cross-section shapes, geometry, and various sizes are obtained due to the crystallization of the liquid melt column formed by the shaper. Stepanov paid special attention to the latter. In his manuscripts, we found the following note: "A shaper should be distinguished from a die. A die is the embodiment of a brute force; its action can be described by the proverb 'It cries but crawls through.' A shaper is a more spiritual system. Its aim, first of all, is to provide a delicate effect on the curvature and shape of the mobile column of the liquid melt stretching itself behind the crystal by creating new boundary conditions along its contour."

The technique of Stepanov should be considered a natural extension of the Czochralski method. Conscious implementation of the shaping concept for liquids and the usage of shapers give rise to qualitatively new results. Hence, the technique of Stepanov gains importance and a life of its own. In this case, one could say that the crystallization is performed under the most controlled conditions, in comparison to all other methods.

Stepanov was the first person to realize the significant advantages of manufacturing shaped products: economizing on materials, automation of the process, and the creation of novel engineering materials. It is not an accidental fact that his book, published in the USSR in 1963, was entitled *The Future of Metal Processing* [1]. On the basis of the classical works of Stepanov, new versions of his technique are being developed; both the range of materials and the scope of applications for shaped crystals and products have become more and more broad. Stepanov paid considerable attention to the development of his technique in 1998. He initiated in 1967 the First All-Union Meeting on Manufacturing Shaped Products and Their Applications in Industry. The last, 11th, meeting was held, as always, at the Ioffe Institute of Physics and Technology, Saint Petersburg, Russia, and was dedicated to the 90th Anniversary of Stepanov. The proceedings of all the meetings were published in the journal *Bulletin of the Russian Academy of Sciences, Ser. Physics*, and in separate collections of papers of the Ioffe Institute.

Papers on the growth of shaped single crystals were also published in a separate issue of the *Journal of Crystal Growth* (1980, vol. 50). The Stepanov technique has been the subject of review articles and books [2–9]. The International Conferences on the Growth of Shaped Single Crystals were held in Budapest in 1986 and 1989.

As early as in his first papers, Stepanov clearly formulated the shaping concept: the design and operation of shapers wetted and not wetted by the melt. Many versions of the Stepanov technique have been tested and applied in industry.

However, some researchers revised the Stepanov technique and introduced new terms. Therefore, we would like once more to draw attention to certain aspects concerning the sense of the different versions of

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the Stepanov technique and to the disputes on the problems of priority.

In the present paper, we analyze the main recently developed versions of the Stepanov technique and give a brief review of the main results achieved in shaped crystal growth.

THE GROWTH OF SHAPED CRYSTALS WITH A CONSTANT CROSS-SECTION USING A CAPILLARY FEED

The worldwide boom in the research concerning the growth and analysis of shaped single crystals was initiated by the papers of LaBelle and Mlavsky [10–12] at the end of the 1960s and the beginning of the 1970s. They proposed edge-defined, film-fed growth (EFG), which turned out to be very convenient for the growth of shaped sapphire when molybdenum was used as a material for the shaper. The main original idea of this method is that the melt wets the shaper and is fed to the edges through capillaries manufactured in the shaper bulk. As a result, in the course of the melt consumption, the melt is continuously supplied from the crucible. However, the authors of these papers completely avoided any reference to the Stepanov technique. N.N. Sheftal', acting on behalf of the Institute of Crystallography, USSR Academy of Sciences, Moscow, sent a letter [13] wherein he pointed out the role and the priority of Stepanov in connection with the EFG method, which had just appeared at that time. In his reply to this letter, Mlavsky noted that "the Stepanov method deals with shapers that are *not wetted* by the melt, whereas the EFG technique employs *wetted* shapers" (underlined by Mlavsky). This is schematically represented in Figs. 1a and 1b. Such a classification demonstrates a misunderstanding or a reluctance to understand the essence of the Stepanov method.

The EFG technique is one version of the Stepanov method that implements shapers wetted by the melt, where the catching by the outer edges is engaged and the melt column is fed through the capillary channel in the course of pulling the crystal (see Fig. 1b). This version became especially popular in the crystal growth of oxides (of sapphire, above all), silicon, germanium, alkali halides, metal fluorides, etc.

The efforts of different laboratories contributed to solving the problem of manufacturing different forms of shaped crystals directly in the process of their growth. The EFG technique was used to grow thin filaments, bars of various cross section, tapes of different thickness and width, tubes, bars and tapes with capillary channels, etc. As an example, we can mention the growth of silicon tubes up to 50 cm in diameter (14) and sapphire tapes up to 30 cm in width [15].

One of the most topical problems is improvement of the quality of the grown crystals. This would help to broaden significantly the range of application for shaped crystals.

An automated control system implementing a weight sensor was developed to monitor the state of the crystallization front and to avoid the formation of defects caused by supercooling. The design features of the control system for monitoring the state of the crystallization front in the course of the growth process are discussed in detail in paper [16].

The main parameter used to control the state of the crystallization front was the amplitude of the oscillations in the deviations of the actual mass variation rate from that specified. It was the analysis of the oscillation amplitude and its adjustment by the corresponding changes in the heating power and/or the crystal pulling

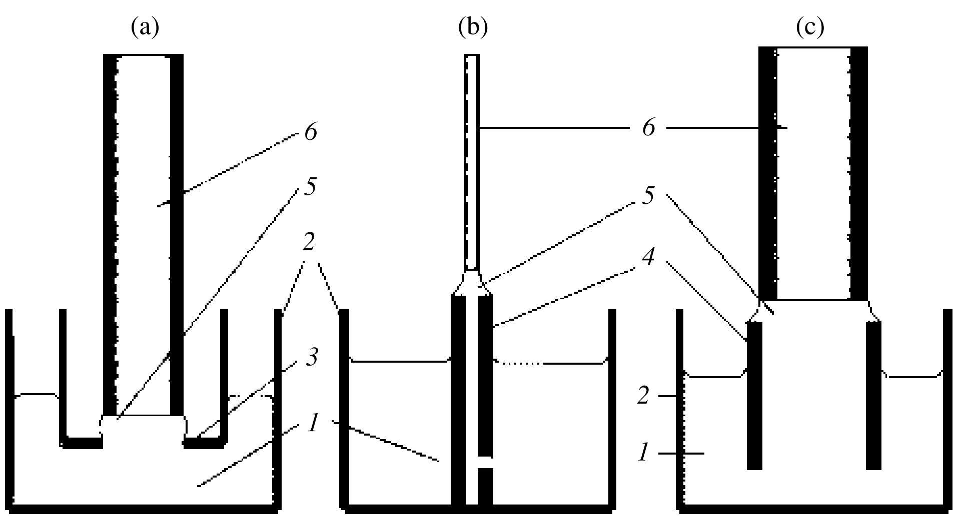

Fig. 1. The layout of different versions of the Stepanov method: (a) the classical version with the use of the shaper not wetted by the melt; (b) the EFG method; (c) the method with the use of the noncapillary feeding; (*1*) melt; (*2*) crucible; (*3*) shaper not wetted by the melt; (*4*) shaper wetted by the melt; (*5*) meniscus; (*6*) crystal.

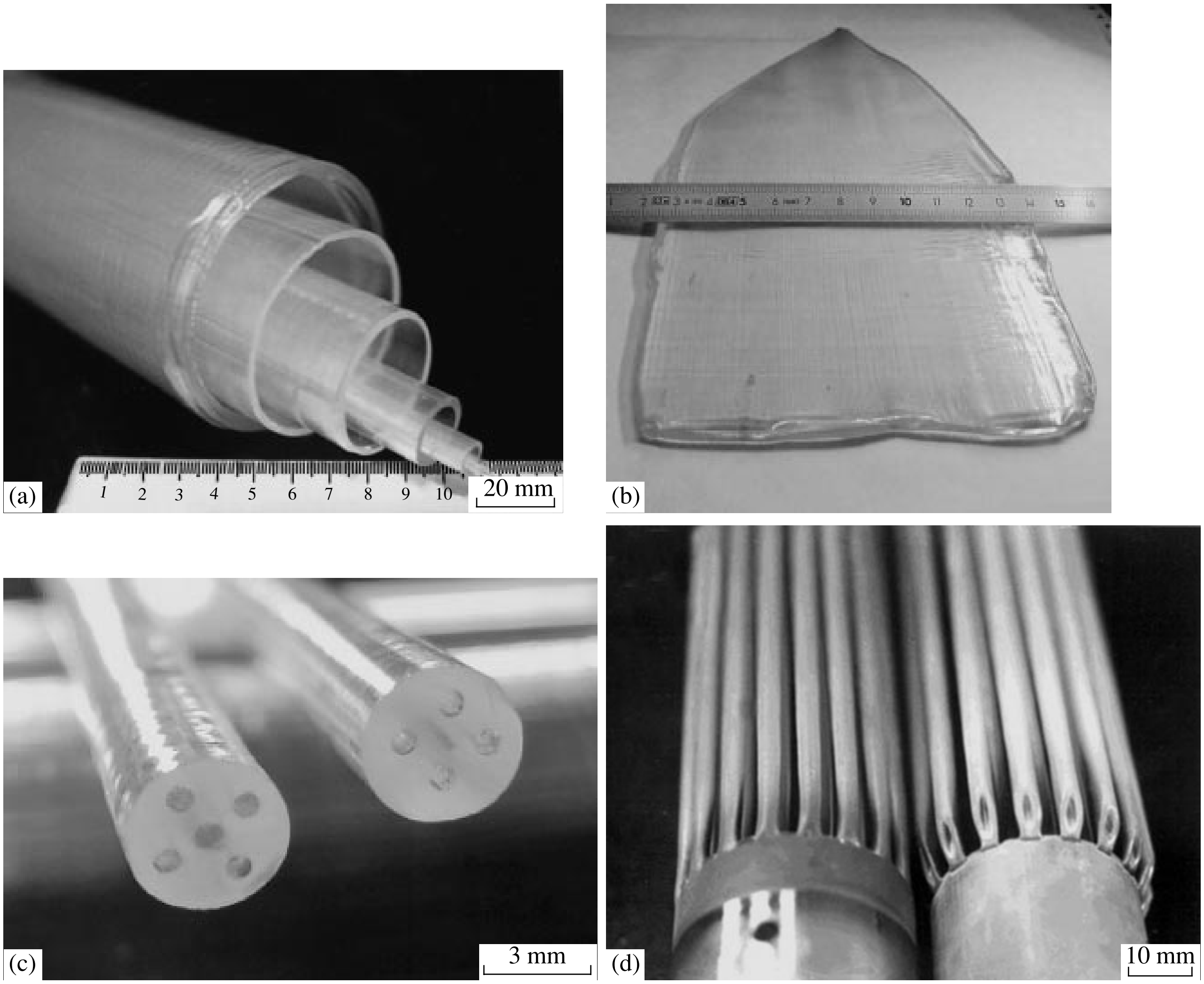

Fig. 2. The shaped crystals grown by the Stepanov method (EFG with the weight control): (a) tube up to 85 mm in diameter; (b) tape 120 mm wide; (c) bar with channels 0.7 mm in diameter; (d) bars and tubes grown in the group mode.

rate that provided the opportunity to control the shape and quality of growing crystals. The developed system was successfully implemented for the growth of large size sapphire tubes [17] and tapes [18], bars with capillary channels, filaments, bulk shaped crystals, and bars and tubes in the group growth mode (up to 50 crystals simultaneously) [16].

The shaped sapphire crystals with different shapes of their cross-section grown through the use of the automated control system are shown in Fig. 2.

THE METHOD OF VARIED SHAPING

A very important problem is the development of technologies allowing one to change the shape and size of crystals in the course of their growth. First of all, it is related to the use of shaped sapphire crystals in the form of complete products such as crucibles, boats, etc.

Different versions of changing the profile of the growing crystal which could be considered under such common name as “varied shaping” were developed based on the Stepanov method. In this technique, the base of the melt meniscus is torn off the edges of one shaper specifying the initial shape and then it catches on the edges of another shaper specifying the subsequent shape of the cross-section. The mass flow rate of the melt supplied to the crystallization front is controlled by different technological means: the change in the relative position of different parts of the shaper, the change in the shaper position with respect to the melt level, the subsequent use of different shapers, the temperature variation in the crystallization zone, the changes of pressure, crystal pulling rate, etc. [19–22].

In Fig. 3, we show the sapphire crucibles, boats, and other shaped crystals with varying cross-section grown by the method of varied shaping.

Fig. 3. Shaped crystals with varying cross section grown by the method of varied shaping.

THE CRYSTAL GROWTH WITH THE USE OF NONCAPILLARY SHAPING (NCS) METHOD

The noncapillary shaping (NCS) method was developed for the growth of high-quality shaped crystals with a large cross-sectional area. The essence of the NCS method is the feeding of the crystallization front by the melt from the crucible via a noncapillary channel (the channel cross-sectional size exceeds the value of the capillary constant for the melt). This promotes melt motion in the meniscus from the center to the periphery. Such an approach allows one to eliminate the formation of counterflows in the melt under the crystallization front, which are characteristic of the growth of a bar with a large cross-sectional area through the use of the EFG technique with capillary feeding. In the regions where the melt flows in the meniscus meet each other, the components of the flow rate have a minimum value. The regions adjacent to these are those with an enhanced content of gas impurities pushed off by the interface between the phases. Such regions are the most probable locations of the nucleation and capture of gas inclusions.

The NCS method implements a version of the Stepanov technique with the shaper wetted by the melt where the melt is fed under a negative pressure, whereas in the classical version of the Stepanov technique with the shaper not wetted by the melt, the melt is fed under a positive pressure (Fig. 1c).

For the growth of bulk crystals, different kinds of the initial growth stage and the subsequent feeding via a noncapillary channel can be used: with a pointlike seed (Fig. 4a), bulk seed (Fig. 4b), and ring-shaped capillary channel (Fig. 4c) [8, 9, 23]. The seed rotation can be used simultaneously with its advance at the stages of seeding, transient growth, and steady-state growth. In all these cases, the shape of the bulk crystal is determined by the catching at the outer edge of the shaper.

In the case of the pointlike seeding (Fig. 4a), after the transient growth stage, when the crystal dimensions coincide with those of the shaper, the melt becomes caught in the shaper edges. This actually corresponds to a transition from the Czochralski method to the NCS method. The version with the bulk seed (Fig. 4b) allows one to avoid the transient growth stage. Both cases are implemented when the level of the working edges in the shaper coincides with the melt level in the crucible.

The version with the ring-shaped capillary channel (Fig. 4c) is described in detail in [23]. The melt lifting in the shaper to the crystallization zone was performed via the noncapillary channel owing to the pressure difference between the growth chamber and the closed volume under the seeding plate. An analogous technique for the lifting of the melt to the crystallization front was used for the growth of sapphire crucibles.

In the NCS method, the optimum relationship of the diameter of the noncapillary channel to the cross-sectional size of the growing crystal, the pulling rate, and the end face geometry of the shaper makes it possible to feed the crystallization front through the melt strictly from the center to the periphery of the crystal cross section. In this case, the free surface of the meniscus is a sink for gas impurities. Thus, we can produce shaped crystals of a large diameter without gas inclusions in their bulk (Fig. 5).

The NCS method has been successfully applied also to the growth of monolithic sapphire crystals with different cross-sectional shapes, thick-wall tubes, plates, and threaded joints [23]. Noncapillary feeding was used to grow sapphire crucibles up to 65 mm in diameter without any inclusions in the bottom part of the crystals. The NCS method also provides an opportunity to control the shape of the crosspiece at the crossover between the hollow and monolithic parts of the crystal and vice versa by using a certain end face geometry of the working edge in the shaper. This is important for the growth of sapphire hemispherical blanks for high-temperature optical devices [24].

The development of the above version of the Stepanov method confirms once more the diversity of the techniques used to produce shaped crystals.

CRYSTALLIZATION FROM AN ELEMENT OF SHAPE

When the growth from an element of shape (GES) was first implemented [25], it seemed to be a technique rather different from the Stepanov method. However, it soon became clear that the sagacity of Stepanov manifested itself in this case also. His formulation of the capillary shaping principle also contained this version: “a shape or an element of the shape is created in the liquid state… .”

In the GES technique, the shaper does not entirely determine the form of the crystal cross section; it specifies only its thickness. The crystal growth is performed

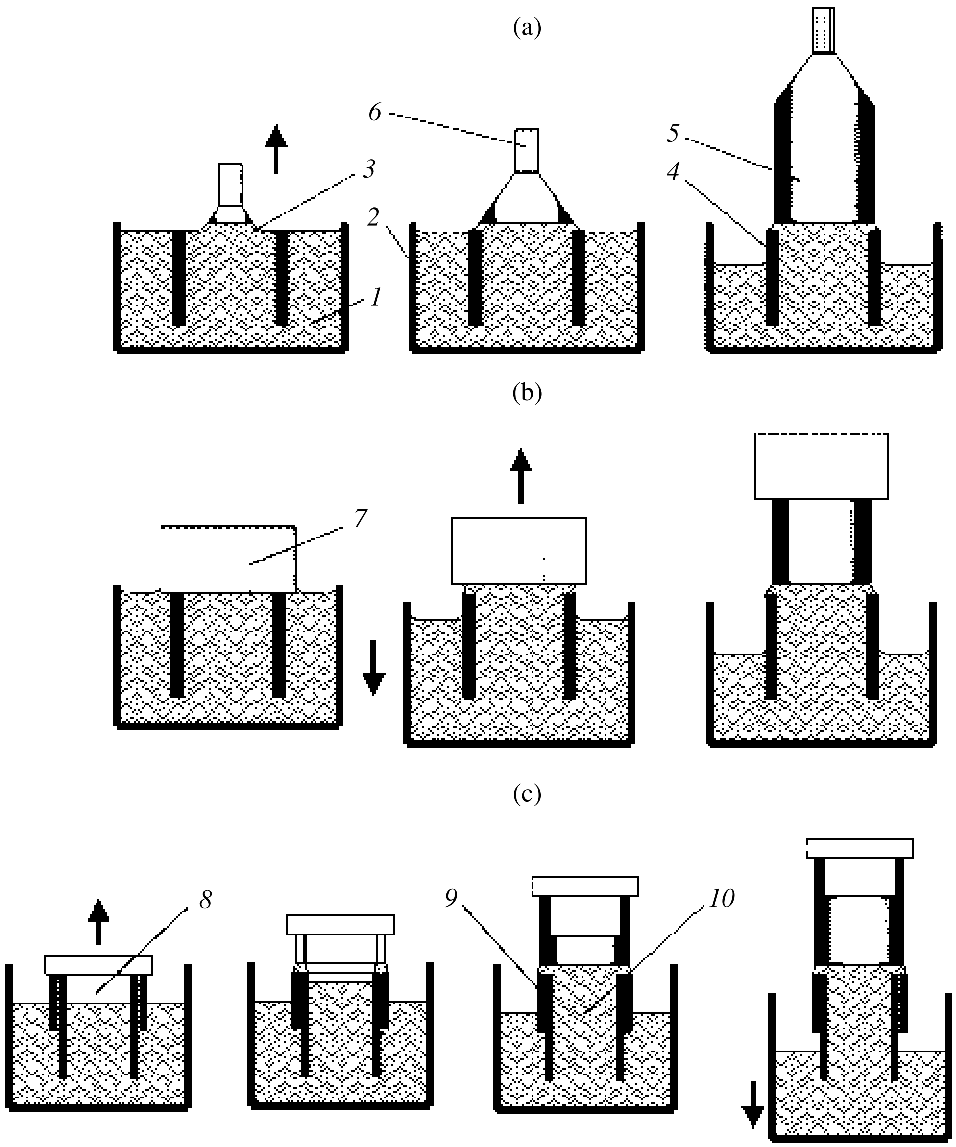

Fig. 4. Schematic picture illustrating the growth of shaped bulk crystals by the NCS technique: (a) with the use of pointlike seed; (b) with the use of bulk seed; (c) with the use of a capillary channel; (*1*) melt; (*2*) crucible; (*3*) meniscus; (*4*) shaper; (*5*) crystal; (*6*) pointlike seed; (*7*) bulk seed; (*8*) closed volume under the seeding plate; (*9*) capillary channel; (*10*) noncapillary channel.

layer by layer, and in the simplest case of simultaneous rotation and pulling of the crystal, its length increases during one turn by the value $l = V/\omega$, where V is the pulling rate and ω is the rotation frequency of the crystal (Fig. 6). By creating a relatively small melt volume and promoting various displacements of it with respect to the seed, it is possible to produce crystals of the most complicated shape. In the course of crystallization, a displacement can be given either to the seed crystal or to the shaper, or even to both of them simultaneously. The term "local shaping" introduced later [26] is not quite adequate. The authors of this technique [25] do not see any reason to change its name and argue that it is more correct to use the terminology suggested by Stepanov himself, namely, growth from an element of shape (GES).

The growth of sapphire hemispheres by the GES technique turned out to be the most advantageous application of this technique. The sapphire hemispheres were grown by the GES technique due to the integrated solution of a number of different problems: the formation of the initial stage of the hemisphere growth and maintaining a constant wall thickness of the blank during the whole growth process, optimization of the growth conditions for producing crystals free from gas and solid inclusions in their bulk, obtaining block-free crystals, reduction of thermoelastic stresses, and prevention of cracking in the hemispheres in the course of the growth process [27, 28].

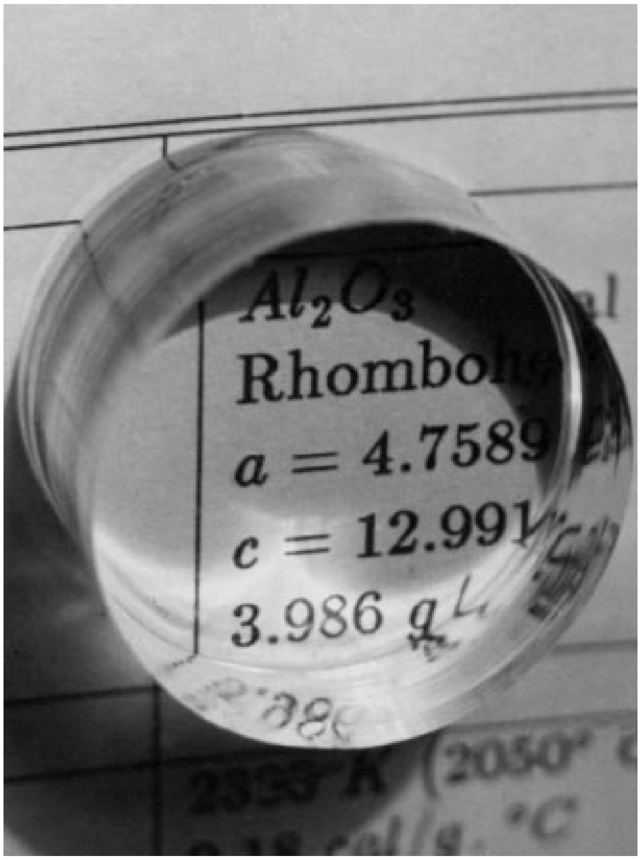

Fig. 5. Sapphire bar 40 mm in diameter grown by the NCS technique.

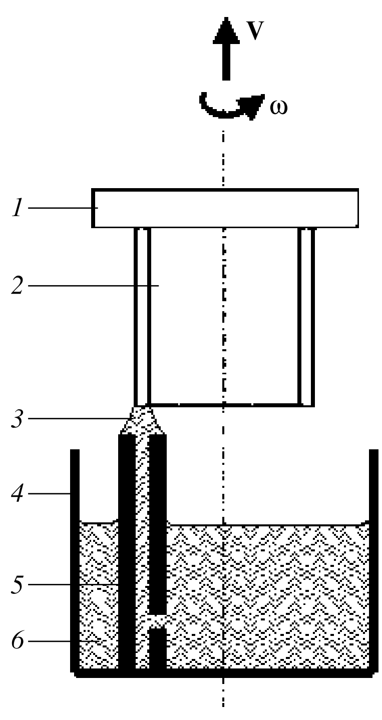

Fig. 6. Schematic picture illustrating the growth of crystals by the GES technique: (*1*) seeding plate; (*2*) crystal; (*3*) meniscus; (*4*) crucible; (*5*) shaper; (*6*) melt.

At the initial stage of the hemisphere formation, when after seeding, the pulling is performed nearly along the horizontal direction, the size of the crystal cross section tends to zero if the shaper with the plane horizontal end face is used. In this case, crystal growth is impossible because the melt meniscus is not caught by the edges of the shaper. The way to solve this problem is based on the use of a shaper with an inclined end face [27], which provides an opportunity to grow hemispherical blanks with a slightly variable wall thickness upon simultaneous displacement and rotation of the seed crystal both in the vertical and horizontal directions. The molybdenum shaper with a working end face placed at an angle of 45° with respect to the vertical axis is optimum for pulling crystals in a wide range of inclination angles characterizing the direction of the pulling.

An important parameter characterizing the growth of hemispherical sapphire blanks by the GES technique is the height of the layer grown during one 180-degree turn of the crystal. Its value is determined by the relationship between the rates of vertical and horizontal displacements and the crystal rotation rate. For a large thickness of the grown layer (20–120 μm), there appear periodically arranged clusters of gas and solid inclusions in the crystal bulk. These inclusions cause a significant lowering of the optical quality of the grown crystals. Experiments involving the growth of crystals with complicated shapes by the GES technique have demonstrated that a layer thickness of the order of 3–5 μm is the optimum thickness for manufacturing crystals free of gas and solid inclusions in its bulk [28]. The angular rotation rate was varied in such a way as to meet two conditions: maintaining a constant layer thickness and constant linear velocity of the rotation in order to prevent the nucleation of cracks in the course of the growth and cooling of the crystals.

The manufacture of sapphire hemispheres by using GES technique posed the problem of crack formation in the course of the crystal growth [27]. The crack arose directly above the shaper where a local distortion of the temperature field and the related enhancement of stresses took place. To estimate the thermoelastic stresses in crystals and to find the optimum modes for the growth of the crack-free sapphire hemispheres, the temperature measurements were performed using thermocouples grown into the crystals [29].

The temperature distribution for the GES technique demonstrated that the melted layer thickness above the shaper was 0.2–0.6 mm. This value far exceeds the value of $L = V/\omega$. For the crystals grown following the GES technique, the temperature distribution in the vicinity of the crystallization front demonstrated that the temperature peak corresponding to the melt meniscus passing under the thermocouple can be as high as 18°C.

Thus, we see that the shaper significantly affects the temperature distribution in the crystal. This, in turn,

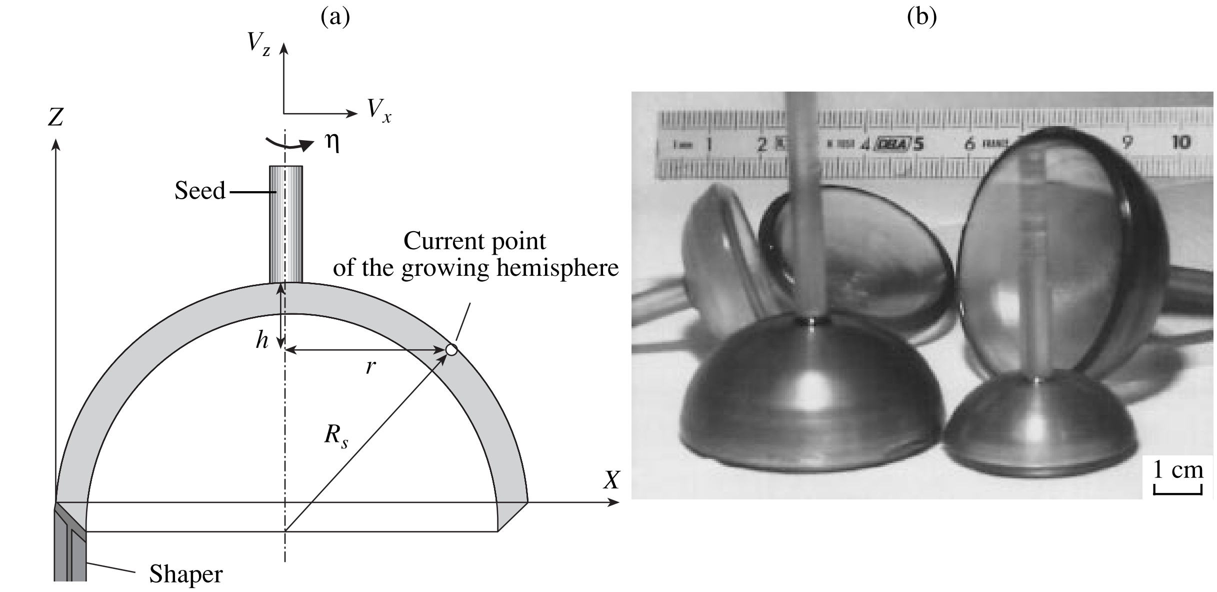

Fig. 7. The growth of hemispheres by the GES technique: (a) the growth scheme using the shaper with an inclined end face; (b) photos of sapphire hemispheres up to 50 mm in diameter with walls up to 4 mm thick.

should produce a certain effect on the level of thermally induced stresses. The EFG technique gives rise only to a nonlinear temperature distribution along the crystal growth axis, whereas in the GES technique, it is additionally supplemented by distortion of the temperature field above the shaper, which moves in the course of the crystal rotation.

Despite all this, the performed estimates of thermoelastic stresses calculated using the method of finite elements in the isotropic approximation for the case of planar stresses demonstrate that the stress level for the GES technique is not higher than that characteristic of the EFG technique [29]. To analyze the possible mechanisms of the stress formation in the crystals grown by the GES technique, the results of the numerical simulation for the time-dependent stressed and strained state of the growing crystal were used [27]. The model involved calculations of the temperature field, as well as elastic and viscoplastic stresses. The nucleation of the initial crack parallel to the crystal growth direction can stem from a high positive value (tensile force) of the hoopential component $\sigma_{\theta\theta}$ of the stress tensor. Further evolution of the crack takes place occurs gradually with the crystal growth and is related to the relaxation of the thermoplastic stresses continuously increasing with the crystal size. Based on this model, the optimum modes for the growth of sapphire hemispheres were chosen to eliminate the cracking in the course of their growth. To attain this optimum in the temperature range under study, it is necessary to have a plastic deformation rate that is not lower than the rate characterizing the growth of elastic stresses with the crystal size. The approximate estimates of these rates for the hemispheres allowed us to find the relationships between the growth parameters corresponding to the case when the condition of the plastic relaxation is met for thermoelastic stresses. In Fig. 7, we present a schematic illustration for the growth of hemispheres by the GES technique using a shaper with an inclined end face, as well as photos of sapphire hemispheres up to 50 mm in diameter with walls up to 4 mm thick [27].

SHAPED CRYSTALS WITH DOPED SPATIAL STRUCTURES

A topical task in the field of optoelectronics is the development of novel materials combining several functions. One way to fulfill this task to grow shaped crystals with modulated spatial structures. Different versions of the Stepanov technique have paved the way not only to the manufacture of crystals of any complicated shape but also to the creation of a new class of materials, namely, crystals with doped spatial structures.

Manufacturing of periodic structures. To produce shaped crystals with periodic spatial structures, a version of the GES technique was implemented wherein two or more kinds of melt with different impurity content were used (Fig. 8a).

The first layered crystals were produced based on the LiF–LiF:Mg^{2+} system (Fig. 8b) [25]; these crystals were used as a model material for the study of mechanical characteristics. These studies demonstrated that the nucleation of plastic shears occurs near the interface between layers. This leads to a more uniform distribution of strains in the samples and hence to enhancement of their plasticity. The plastic shears always nucleate in the impurity-free layers near the interfaces both at the

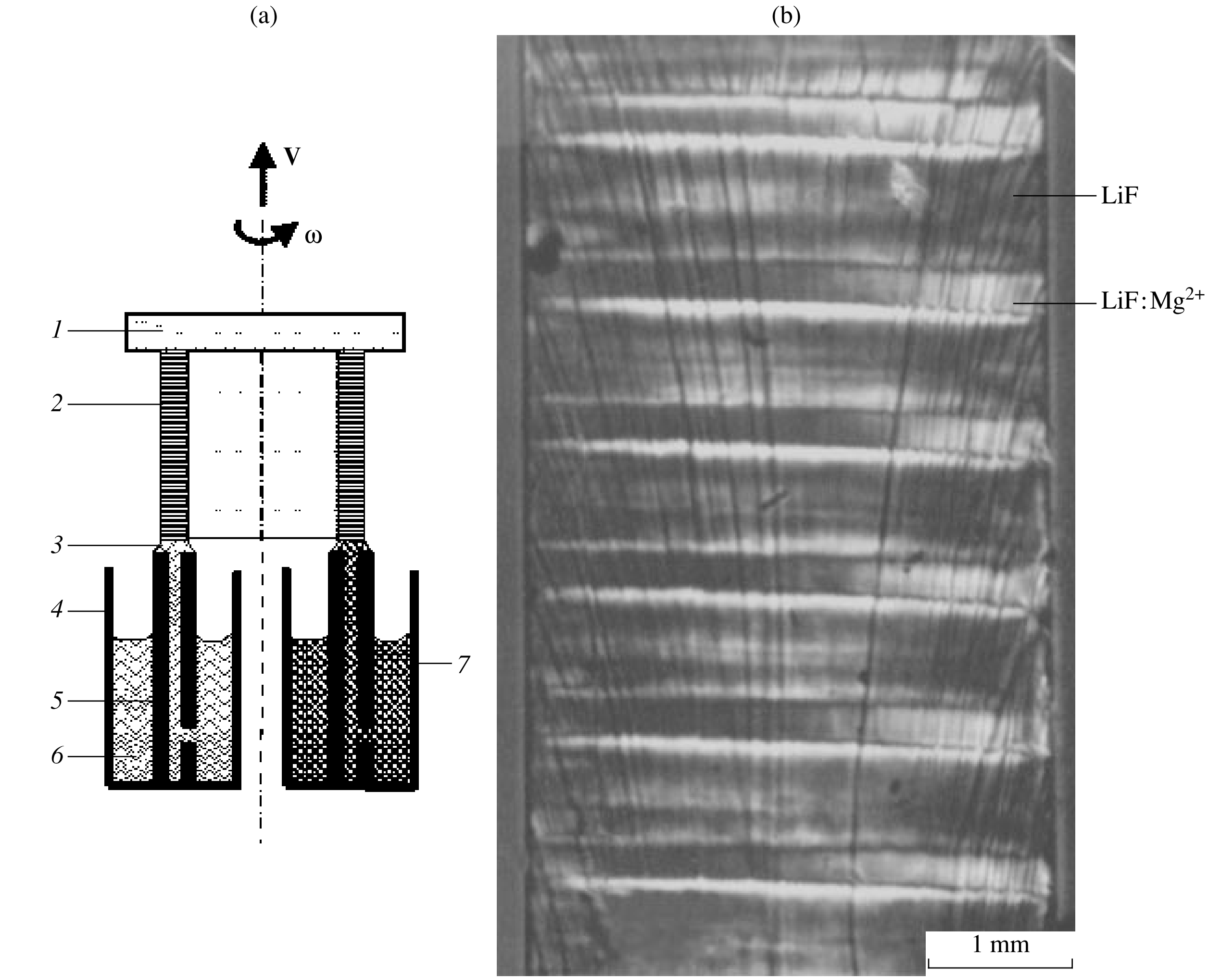

Fig. 8. Manufacturing of periodic structures by the GES technique: (a) layout of the growth setup ((*1*) seed; (*2*) crystal with the periodic structure; (*3*) melt meniscus; (*4*) crucible; (*5*) shaper; (*6*) undoped melt; (*7*) doped melt); (b) LiF–LiF:Mg^{2+} crystal with the periodic structure (the photo is taken in polarized light).

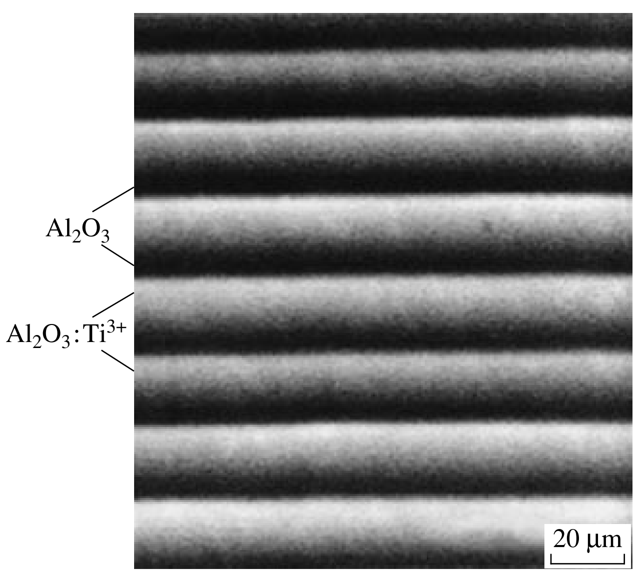

Fig. 9. Periodic Al_2O_3–Al_2O_3:Ti^{3+} structure produced by the GES technique.

sample surface and in the bulk. The layered transparent crystals are highly anisotropic in two mutually perpendicular directions; therefore, one should expect they be applied in the generation of modulated signals for beam transmission.

Further studies in the field of producing shaped crystals with periodic spatial structures were performed using the Al_2O_3:Ti^{3+} system [30, 31]. These crystals contain spatial resonant structures, i.e., periodic structures of variable chemical composition. This causes a drastic lowering of the generation thresholds and makes them nearly independent of the parameters of the external resonator. Al_2O_3–Al_2O_3:Ti^{3+} structures with a period of 5–100 μm were produced (Fig. 9). The Ti^{3+} content in the structures produced in such a way differed by 2–3 orders of magnitude, ranging from 10^{-4} wt % in the undoped part of the crystal to 0.2 wt % in its doped part. The width of the transient region has a value of the order of several tenth parts of l, where l is the increase in the crystal length during its 360° rotation.

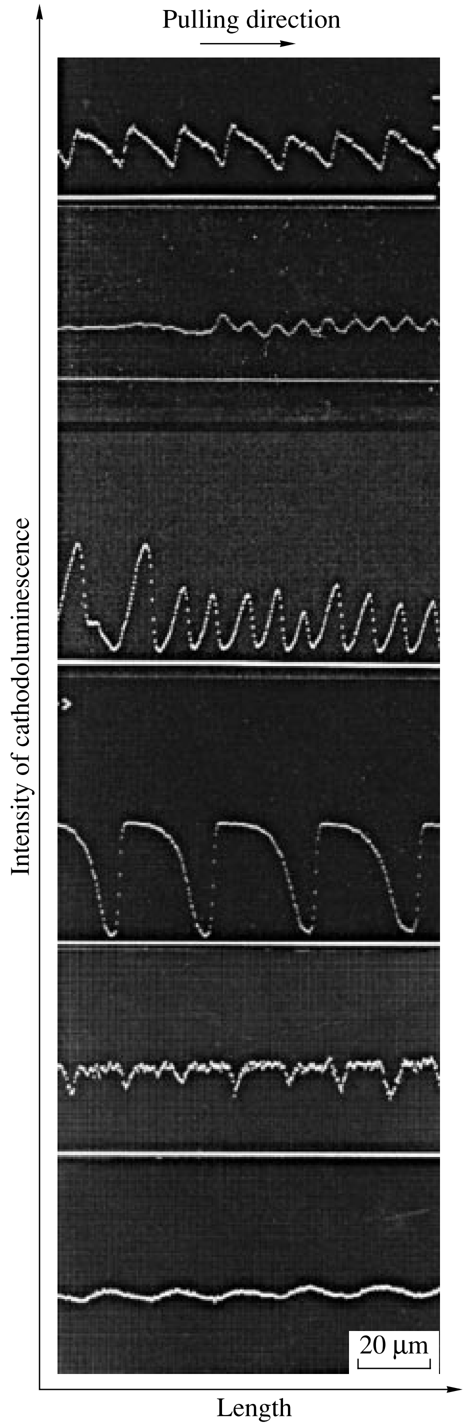

Fig. 10. The intensity distribution for the cathodoluminescence corresponding to the content of the luminescent impurity for different kinds of Al_2O_3–Al_2O_3:Ti^{3+} structures produced by the GES technique.

The implementation of the GES technique provides an opportunity to substantially broaden the range of the various periodic spatial structures produced *in situ*. The following structures were produced: with a crossover from one period to another owing to the variation in the relationship between the pulling rate and the frequency of rotation; with a crossover from periodic structures to homogeneously doped or undoped regions owing to the "switching off" of the melt feed to one of the shapers during the growth process; with a specified ratio of layer heights within one period; etc. In Fig. 10, we show the intensity distribution for the cathodoluminescence corresponding to the content of the luminescent impurity for different kinds of structures produced by the GES technique. The developed techniques allow us also to control the characteristic features of the frequency distribution in the crossover region.

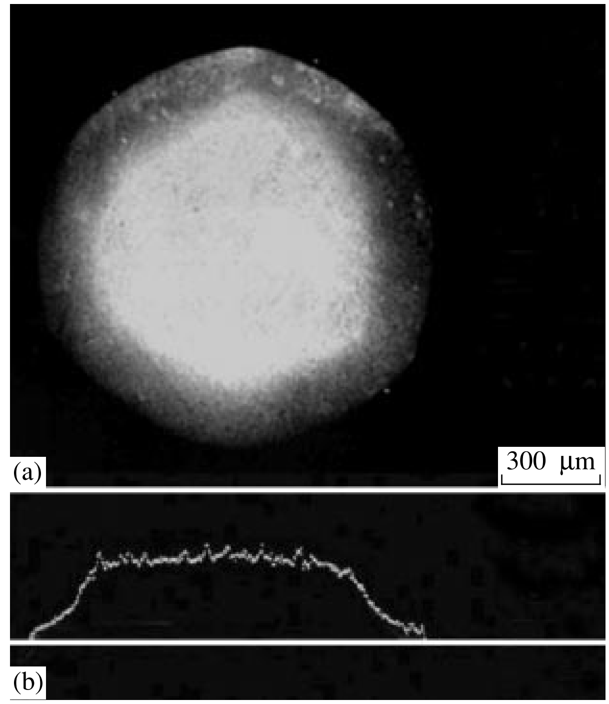

Fig. 11. (a) The cross section of an Al_2O_3–Al_2O_3:Ti^{3+} filament grown with the use of the weight control system and (b) the corresponding intensity distribution for the cathodoluminescence.

Filaments with a central doped region. The high-quality single-crystalline filaments with the central part doped by activating ions are of special interest. In such crystals, the energy of optical pumping is absorbed only within the central region. This results in enhancement of the transformation efficiency and in a decrease in thermal losses.

For the growth of sapphire filaments of variable composition, a crucible with two vessels (for the doped and undoped melt) was used. In addition, a special shaper was developed, which provided an opportunity to feed the meniscus using these two melts simultaneously [32]. The main task in this growth scheme is to feed the meniscus by melts with varying composition at fixed flow rates and to maintain the spatial distribution of concentration dictated by this method. The main problems involved, which were solved in producing these filaments, were optimization of the growth parameters and maintaining the temperature within a narrow range, first, to prevent the mixing of melts in the meniscus and, second, to eliminate the formation of defects related to the supercooling of the crystallization front. In Fig. 11, we show the cross section of the Al_2O_3–Al_2O_3:Ti^{3+} filament and the corresponding intensity distribution for the cathodoluminescence.

CONCLUSIONS

The ideas of Stepanov are being intensively developed. New versions of his method are being suggested, and the range of materials used is growing. Intensive research is being carried out in the following directions: improvement of the structure and quality of grown crystals, cost saving, growth of large shaped crystals and crystals with a complicated shape, and production of crystals with a specified doping structure. Shaped crystals are widely used as constructional, optical, and functional materials in science, technology, medicine, microelectronics, and laser technology.

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