NEW METHODS OF THE GROWING COMPLICATED SHAPED SAPPHIRE PRODUCTS: VARIABLE SHAPING TECHNIQUE AND LOCAL DYNAMIC SHAPING TECHNIQUE

V.A. Borodin, **V.V. Sidorov**, **T.A. Steriopolo**

Experimental Factory of Scientific Engineering, Russian Academy of Sciences,

Institute of Solid State Physics, Russian Academy of Sciences and ROSTOX-N Ltd.

Borodin V.A., Experimental Factory of Scientific Engineering,

Chernogolovka, Moscow Region, 142432, RUSSIA,

Phone: +7 (095) 913-2108; Fax: +7 (096) 524-9588; E-mail: bor@ezan.ac.ru

Classification code:

Keywords: EFG method, die, complicated sapphire crystals

Abstract

Detailed description of the crystal growth methods permitting one to obtain complicated shape crystals from the melt is given. The variable shaping technique provides the growth of crystals with a discrete altering cross-section configuration during crystallization. The dynamic local shaping technique enables one to grow items with a continuous alteration of the side surface profile by a preset program.

Introduction

The conventional Stepanov (EFG) method can provide shaped crystals with constant cross-section configuration along the pulling direction. But development of various technical applications requires that crystalline units of more complicated configurations be produced, namely, shaped crystals with variable configuration along the crystal growth direction. For example, molecular beam epitaxy and liquid phase epitaxy need sapphire crucibles and boats, sapphire envelopes can be applied for the development of new types lamps using the discharge in vapour of the alkaline metals, high temperature optical applications require sapphire hemispheres.

Since 1981 we have concentrated on the solution of this problem. Our objective was to create the technology that could permit one to enlarge greatly the range of shapes of crystalline bodies that can be grown directly from a melt. The way to solve this problem is to change the size and configuration of the crystal cross-section in the course of the growth process. As a result, two main technologies have been developed. The first of these, providing only discrete variation of the dimension and geometry of the crystal cross-section during the growth, was called «variable shaping technique» [1,2]. The second technique was developed to provide a continuous alteration of the lateral profile of crystal. It was called «local dynamic shaping technique» [3]. In our earlier works [4-6] we mentioned that sapphire bodies of complicated configuration such as hemispheres, hole cones and other sophisticated forms were obtained from a melt. The details and know-how of these new techniques are discussed in this paper.

1. Variable shaping technique

As mentioned above, the variable shaping technique makes it possible to grow crystals with discrete altering cross-section configuration. It is known that the meniscus catching at the edge of the die top surface is one of the conditions to provide stability of the growth process by EFG [7]. Therefore in order to change the given crystal shape in the process of the crystallization and to preserve the altered cross-section configuration during the further growth, it is necessary to alter the geometry of the meniscus from which pulling is being made. This is accomplished by breaking the meniscus away from the die edge that defines the initial crystal shape, and catching it at the other die edge defining a new desired shape. So, the crystal growth procedure by the variable shaping technique may be treated as a sequence of the steady-state growth steps with different transition crystallization modes. During the transition the base of the meniscus moves across the top surface of the die assembly from one edge to another, and the meniscus mass is altered. The melt mass alteration on the die top is obtained either by adjusting the melt flow through capillary channels of the die or by adjusting the melt temperature and pulling rate. The process parameters that control the transition stages are the melt flow, pulling rate and melt temperature.

We investigated a number of technological ways, integrated under the term «variable shaping technique», to obtain gradual transition from one given configuration of the crystal cross-section to another in the course of growth. The most reliable scheme of variable shaping technique [8] is illustrated in Fig.1. The sequence of operations to alter the crystal cross-section configuration is shown from the left to the right. The set of dies is not connected with the crucible. So the crucible can be translated along the vertical axis relative to a fixed position of the die assembly. The dies should be of different lengths so as to provide the separate dipping of their lower parts into the melt located inside of the crucible. To realize the shape transition mode the lateral surfaces of the neighboring dies are separated by narrow gaps which can serve as capillary feeding channels for the melt. When the crucible is raised so that next die is dipped into the melt, the capillary gap supplies an additional mass of the melt to the top of the die assembly. This portion of the melt contacts with the already existing meniscus and with the edge of the die just dipped into the melt. As a result a new type of the meniscus forms, and the growing crystal alters its shape that is controlled by the dies dipped into the liquid. If the crucible is lowered, so that one of the dies is withdrawn out of the melt, the pulled crystal will suck the rest of the melt out of the die capillary channel and out of the capillary gap between the neighboring dies. In this case the base of the meniscus will move to the top surface edges of the die which is still dipped in the melt. This causes the alteration and reduction of the crystal cross-section.

Some sapphire products grown by this method were already shown in the work [2].

2. Local shaping technique

The local shaping technique enables one to grow crystals having the configurations of tube or cylindrical rod. This method is shown schematically in Fig. 2. In contrast to the conventional EFG method, in this process the die forms only a single element of the cross-section being pulled, while the whole of the cross-section is obtained by means of the crystal rotation. This technique was first applied to grow lithium fluoride tubes [9]. We employed this method to obtain sapphire tubes [4-6] and Al_2O_3-$ZrO_2(Y_2O_3)$ eutectic composite tubes and rods [10]. In the works [4-6] we studied the growth process of sapphire tubes by this method, and discussed the presenting the growth model and the process stability investigations results. To describe that technique we used the term "local shaping technique".

3. Fundamentals of the local dynamic shaping technique

We also mentioned the further development of local shaping technique for growing complicated sapphire products with a continuous alteration of the lateral surface profile achieved by us back in 1985 [11] and presented some of these products for the first time in [4,6]. This development was already carried out in 1985 [11]. But the detailed description of the new technology has not been yet published.

To alter the profile of the lateral surface according to a preset program we introduced an additional growth process parameter: the horizontal die position relative to the crystal rotation axis [11]. Under the variation of the horizontal die coordinate the inner and the outer radii of the sapphire tube being pulled alter, and the profile of the lateral surface changes, accordingly. This new method was called «local dynamic shaping technique».

The inner r_1 and outer r_2 radii of the tube grown by the local shaping technique are determined by the expressions:

$r_1 = R - p/2\, r_1 = R - \frac{p}{2}$ and $r_2 = R + p/2, r2 = R + \frac{p}{2}$ where R is the distance between the crystal rotation axis and the die top center, and p is the wall thickness of the tube. The process is characterized by the three parameters: melt temperature of meniscus (T_m), rotation rate (n) and pulling rate (V). The variables of the process will be the inner r_1 and outer r_2 radii of a tube being grown and the height of the meniscus h. If distance R is considered as a variable parameter then to each $R(t)$ value should correspond the defined values of $r_1(t)$ and $r_2(t)$, that can physically be obtained under the conditions

$dR/dt \leq dr_1/dt$ and $dR/dt \leq dr_2/dt$. $\frac{dR}{dt} \geq \frac{dr_1}{dt}$ and $\frac{dR}{dt} \leq \frac{dr_2}{dt}$

These conditions mean that the crystallization process is possible in the case where the velocity of $R(t)$ variation does not exceed the range of values that limits the velocity variation of the outer r_2 and inner r_1 radii of the growing crystal.

The variation of the parameter $R(t)$ provides a change in the lateral surface profile of the crystal in the process of growth. In order to modify the distance between the die and the crystal rotation axis, the die or the seed-holder can be moved relatively to each other on a straight line, in a circle, or along an arbitrary trajectory [3]. The preset shape of the crystal lateral surface profile in the pulling direction z is governed by the whole set of the process parameters. In general the inner $r_1(t)$ and the outer $r_2(t)$ radii of the crystal growing in the complicated rotating body configuration can be described by the function

$r_{1,2}=f(T_m, n, v, R, t)$. $r_{1,2} = f(T_m, n, V, R, t)$

Using the results of our earlier experiments on the displacement of the seed holder and the die relative to each other along different trajectories, we have developed a very reliable device, which involves a die moving in a circular line. In this device the die transfer is accomplished by the crucible rotation. The local dynamic shaping technique for this case is shown schematically in Fig. 3. The die (5) is rigidly connected to the crucible (4) being displaced relative to the crucible rotation axis (7) by a distance b. The crystal rotation axis (8) is not coaxial with the crucible rotation axis (7) and is displaced from it by a distance a. In this device the rotation of the crucible by an angle φ results in a horizontal transition of the die relative to the crystal rotation axis. The variables $R(t)$ and $\varphi(t)$ are interconnected by:

$$R(t) = \sqrt{a2 + b2 - 2ab \cdot \cos(\varphi(t))} \qquad (1)$$

Let us assume that the die top surface diameter is q. In the case that $R(t) > \frac{q}{2}$ $R(t) > q/2$, the crystal demonstrates an internal concavity of radius $r_1 = R - \frac{p}{2}$ $r_1 = R - p/2$. In the case that $R(t) < \frac{q}{2}$ $R(t) < q/2$, we shall obtain the solid crystal with a controllable lateral surface configuration. Transition from the growth mode providing the solid crystal to that providing the hollow one and backward can be realized with the use of a crucible-die unit characterized by $|a - b| < \frac{q}{2}$ $|a - b| < q/2$. Therefore, the device in which $a=b$ allows one to obtain both hollow and solid crystalline bodies.

In the scheme given in Fig. 3 (where $a=b$) the die is translated from the position (A) to the position (C) through the position (B) by means of the crucible rotation. When the die is in the position (A) the rotation axis of the seed-holder is coaxial with the die. The growth of the crystal is initiated by the rotating of rod seed. In this position $\varphi(t)=0$ and accordingly to the equation (1) $R(t)=0$. Then under the translation of the die from (A) to (B) the crystal inner r_1 and outer r_2 radii continuously enlarge in accord with increasing the R. In the position (B) the translation of the die is stopped for some time period. During this period φ and R are constant. As a result the crystal keeps the configuration of a tube. Further moving of the die to the position (C) changes the shape of the lateral surface of the growing body.

3. Determination of the main process parameters in the local dynamic shaping technique

Experimentally it is found [6] that when growing a sapphire tube with preset inside r_1 and outside r_2 radii and the set of the parameters (φ, V, n) of this process are not strictly predetermined, but they can be selected in some ranges. However, the above parameters are interconnected, and the variation of one of them requires an adjustment of the two others in order to maintain assigned values of r_1 and r_2. Therefore, the first step to the system engineering, process automation and software development is to determine the ranges of the process parameters while growing crystals with the local dynamic shaping technique.

As first step, computer calculates initial, sufficiently rough, initial values for the V and n by certain expressions. Second step includes correction of the initial values V and n due to the set of the inequalities. And finally, the adjustment of the derivatives $\frac{dV}{dt}$ dv/dt and $\frac{dn}{dt}$ dn/dt should be executed.

For the first step we assume the rate of the crystal mass change $\frac{dm}{dt}$ dm/dt during the growth process should be constant for providing sufficient productivity of the process and obtain the next expression for the rate of crystal pulling:

$$V = \frac{1}{2\pi R \cdot q \cdot \rho_S} \frac{dm}{dt} \text{ v= } (2\pi Rq\rho_s)^{-1} \times dm/dt \tag{2}$$

The initial value for the rotation rate should be found from the condition of the necessary accuracy of maintaining the crystal geometry, i.e. increase or decrease of the crystal size in the radial direction per one revolution should be equal to the displacement of a die in horizontal direction for the same period of time. Thus we obtain the expression:

$$n = V \frac{|tg\alpha|}{\delta R_{\tau,max}} \text{ n= v } |\text{ tg } \alpha| / \delta R_{\tau \max}, \tag{3}$$

here $\alpha = arctg\ R(z)$ is an angle between the vertical direction and tangent to the lateral surface of crystal $R(z)$, $\delta R_{\tau,max}$ is the upper limit of die displacement per one revolution of the crystal.

The next step is to correct the rotation rate by its minimal and maximal limits. It is obvious that $n_{min} > 0$, as far as the method cannot be realized without rotation of the crystal, and n_{min} should provide a certain productivity of the pulling process. . The upper limit n_{max} must be determined experimentally considering the technological possibilities of the growth equipment and the appropriate quality of crystals. However, tentative evaluation can be made. We assume that in this method as well as in other methods of crystal pulling from the melt, the meniscus formation takes place under action of capillary forces, while forces of inertia, stipulated by movement of the melt, can be neglected. In cases where the crystallization velocity is less than 1-10 cm/sec, influence of the inertia forces can be neglected [7]. Assuming that the melt flow rate does not exceed the crystal linear rotation rate $\upsilon=2\pi rn$, and accepting $\upsilon=10$ cm/sec, we obtain $n_{max} = \frac{10}{2\pi r}$ $n_{max} = 10/2\pi r$. When r is increased from 1 up to 6 cm, n_{max} changes from 1,6 sec^{-1} up to 0,32 sec^{-1} (or 96 prm up to 19.2 prm). Concerning control program it is possible to put $0 < n_{max} \le 15$ prm as a maximal value of rotation rate. For automatic analysis of this condition we also install in the optimization algorithm additional inequality $n \le \frac{\upsilon}{2\pi R}$ $n \le \upsilon / 2\pi R$.

From the point of view of the process productivity it is desirable that $\frac{V}{n} \to h$ $v/n \Rightarrow h$, but this results in increase of the depth of periodic microrelief on the crystal lateral surface [6]. Condition $\delta z_\tau << h$ of a more smooth lateral surface is obtained. The compromise range $K_1 h \le \frac{V}{n} \le K_2 h$, $K_1, K_2 \in (0,1)$ $K_1h \le v/n \le K_2h$; $K_1, K_2 \subseteq (0,1)$, here K_i are the constants are being recommended to the growth of crystals of good quality. After above possible corrections of the rotation rate it is necessary to analyze again the value δR_τ of die displacement and, if it is necessary, make correction of pulling rate V. So we use analysis of inequality

$$v\,|\,tg\,\alpha\,|\,/n \le \delta R_{\tau\,max} \quad \frac{V|tg\alpha|}{n} \le \delta R_{\tau,max}$$ for this purpose.

To grow a crystal of preset complicated shape, the variation of the parameters V and n must be accomplished by the respective change of the melt temperature in meniscus (T_m). The heater of growth equipment is characterized by a specific relaxation time. Therefore, some time is required to make a change of the melt temperature T_m at a die top as a result of the heating power change, which was made for compensation of the V and n change. This condition results in some restrictions of the derivatives of V and n changes:

$$|dv/dt| \leq (dv/dt)_{max} \text{ and } |dn/dt| \leq (dn/dt)_{max}$$

$$\left|\frac{dV}{dt}\right| \leq \left(\frac{dV}{dt}\right)_{max} \cup \left|\frac{dn}{dt}\right| \leq \left(\frac{dn}{dt}\right)_{max}$$

An arbitrary preset profile of the lateral surface of the crystal can be presented as a set of several parts, which can be described by linear function

$(R=c_0+c_1z)\, R = c_0 + c_1 z$

or by section of a circle function

$(R^2 = R_0^2 + z^2 + c_2z + c_3), R2 = R_0^2 + z^2 + c_2 z + c_3$

where c_0, c_1, c_2 and c_3 are the functions constants. Let denote the length of crystal to be grown as L. This approach enables us to evaluate the parameters $V(L)$ and $n(L)$ before the growth process and to develop controlling software for realizing regimes providing the growth of the crystal of the necessary shape. After the trial growth these parameters may be slightly corrected to obtain required shape of the lateral surface of the crystal.

The optimised curves of V and n depending on the current crystal length are represented in Fig.4. There have been considered two main cases of the pulling of conic and spherical crystals expanding during the process.

Relating to the growth of the conic crystal hyperbolic change of pulling rate V during the process should be explained by the use of equation (2) and defined by the required rate of the mass change. With increase of the crystal radius in the course of pulling process the square of ring-shaped cross-section increases and pulling rate decreases in accordance with requirement of the constant mass change rate. A high value of the pulling rate calculated from (2) at the initial stage of crystal growth process is restricted by the condition of the maximal meniscus height Rotation rate calculated for the beginning of the process by (3) should be constant and decreases later at sufficiently large radii according to the condition of maximal linear rotation rate (see Fig. 4).

In the case of the crystal sphere shaping the pulling rate decreases at sufficiently large radii, too, but not so fast in comparison with cone, because the rate of crystal expanding decreases (Fig. 4). At the initial stage of sphere shaping pulling rate is restricted not only by condition of maximal meniscus height but mainly by the condition of maximal die displacement per one crystal revolution. At the beginning the angle of the crystal expanding is very large (near π) and the pulling rate must be very small in order to provide sufficiently small die displacement. Then pulling rate increases from minimal value with gradual increase of this angle. Rotation rate decreases also, as in the previous case, not by restrictions, but according to (3). The character of the rotation rate change is defined by the change of angle of spherical surface during the process. At the beginning the large value calculated in equation (3) is restricted by maximal value. At large radii (3) produces very small values, which are restricted by the minimal value.

4. Growth of the complicated shape sapphire products

Earlier we reported [6] about a new type of the apparatus named «crystallization center». It has the following operation modes:

- growth of crystals with constant cross-section configuration (ordinary EFG method);
- discrete variation of the crystal cross-section configuration during the growth process (variable shaping technique);
- continuous alteration of the lateral surface profile according to the preset program (local dynamic shaping technique);
- growth of crystal items with thread on the lateral surface.

The complicated sapphire items grown by the local dynamic shaping technique under the special program with «crystallization center» are shown in Fig.5.

Summary

1. The variable shaping technique provides the discrete alteration of the cross-section of growing crystal. The reliable procedure of obtaining crystalline bodies of complicated shape by this method is the vertical translation of crucible relative to a fixed die assembly position comprising dies of different length.

2. The local dynamic shaping techniques provides the continuous alteration of the lateral surface profile of growing crystalline bodies. With this method, to obtain the predetermined crystal profile, the rotated seed holder and the die must be moved relative to each other in the horizontal direction. In general the trajectories of these transfers can be arbitrary. The reliable technology is to displace the die by means of the crucible rotation. This technology is described in detail.

3. The modified growing apparatus "crystallization center" has been developed. It combines the local dynamic shaping technique, the variable shaping techniques and the traditional EFG method. The combination of these techniques greatly enlarges the variety of growing crystalline products of complicated shape.

References

[1] V.A. Borodin, T.A. Steriopolo, V.A. Tatarchenko, T.N. Yalovets, Izv. AN SSSR, Ser. Fiz. 47 (1983) 368.

[2] V.A. Borodin V.V. Sidorov, T.A. Steriopolo, V.A. Tatarchenko, J. Crystal Growth 82 (1987) 89.

[3] V.V. Sidorov, in: Candidate thesis, (Chernogolovka, 1991) p. 53-69.

[4] V.A Borodin, V.V. Sidorov, T.A. Steriopolo, V.A. Tatarchenko, T.N. Yalovets, Izv. AN SSSR, Ser. Fiz. 52 (1988) 2009.

[5] V.A. Borodin, V.V. Sidorov, T.N. Yalovets, Kristallografiya 35 (1990) 185.

[6] V.A Borodin, V.V Sidorov, S.N Rossolenko, T.A. Steriopolo, V.A. Tatarchenko, J. Crystal Growth 104 (1990) 69.

[7] V.A. Tatarchenko, in: Stable Growth of Crystals (Nauka, Moccow, 1988) (in Russian).

[8] V.A. Borodin, T.A. Steriopolo, V.A. Tatarchenko, Patent SU 1064660 AC 30 B 15/34, (1981) 18.12.81.

[9] P.I. Antonov, Yu.G. Nosov and S.P. Nikanorov, Bull. Acad. Sci. USSR, Phys. Ser.49 (1985) 2296.

[10] V.A. Borodin, V.V. Sidorov, M.Yu. Starostin, T.N. Yalovets, Izv. RAN, Ser. Fiz. 28 (1994) 118.

[11] V.A. Borodin, V.V. Sidorov, T.A. Steriopolo, V.A. Tatarchenko, Patent SU 1415820 C 30 B 15/34, (1985) 05.12.85.

FIGURES CAPTIONS

Fig 1. The scheme of the variable shaping technique.

Fig. 2. The scheme of the local shaping technique.

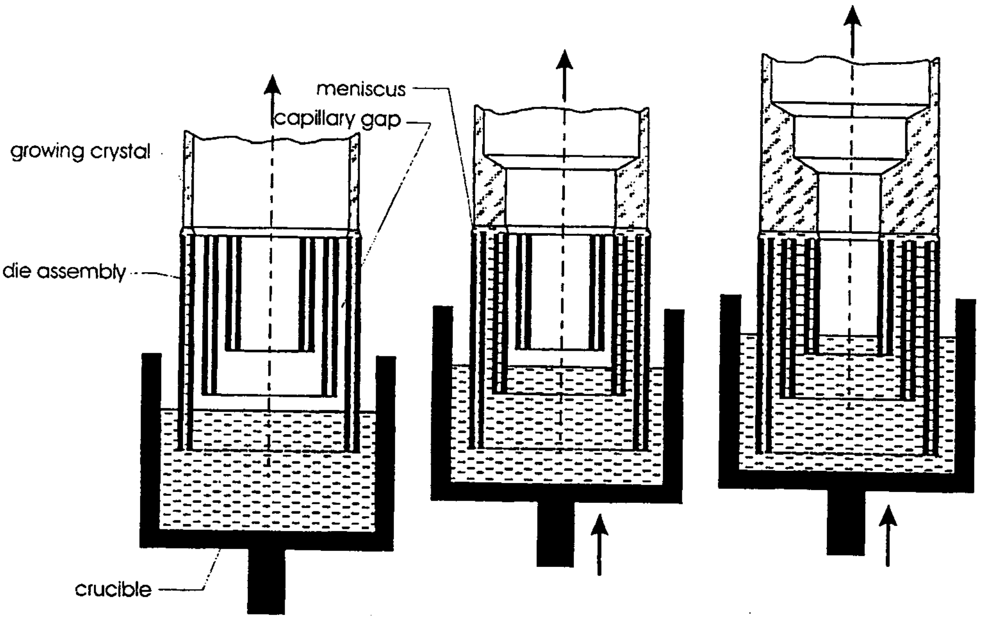
Fig. 3. The scheme of the local dynamic shaping technique. The case of the die displacement by means of the crucible rotation:

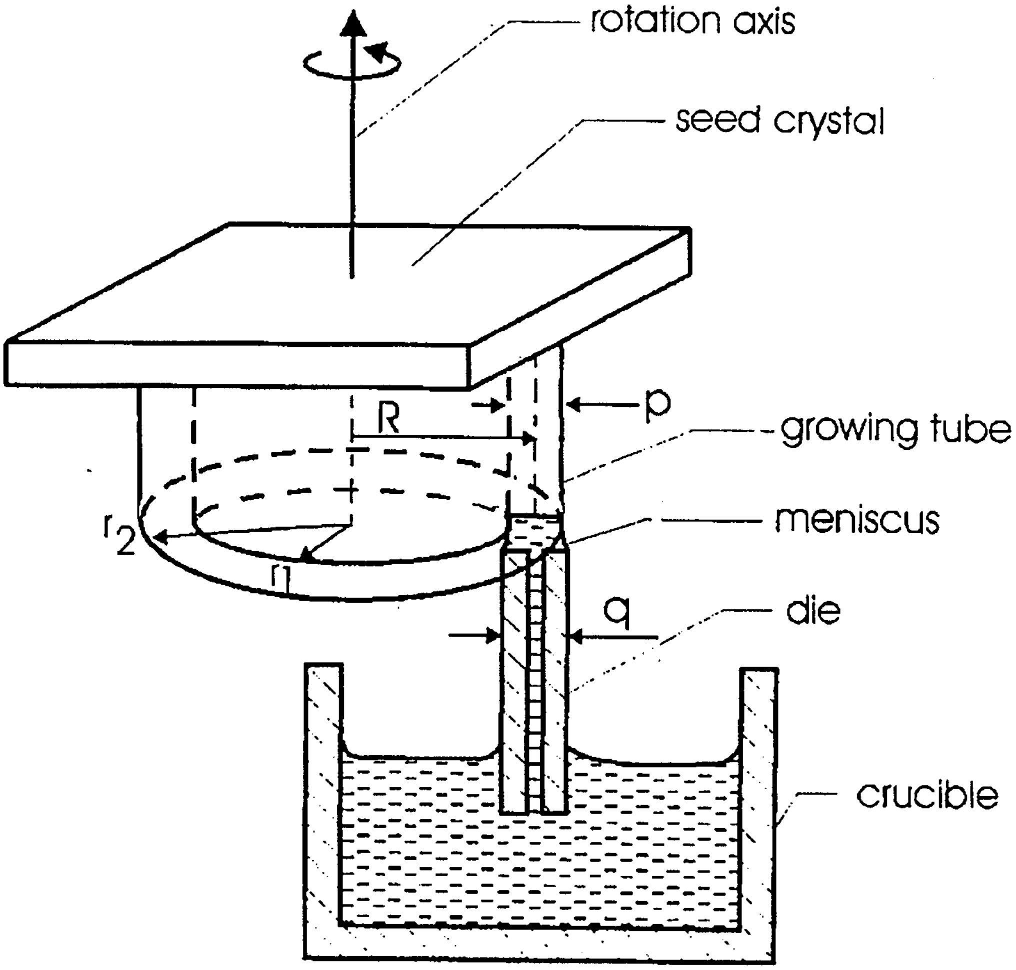
1 - seed holder; 2 - seed; 3 - growing crystal; 4 - crucible; 5 - capillary die; 6 - meniscus; 7 - crucible rotation axis; 8 - rotation axis of the crystal.

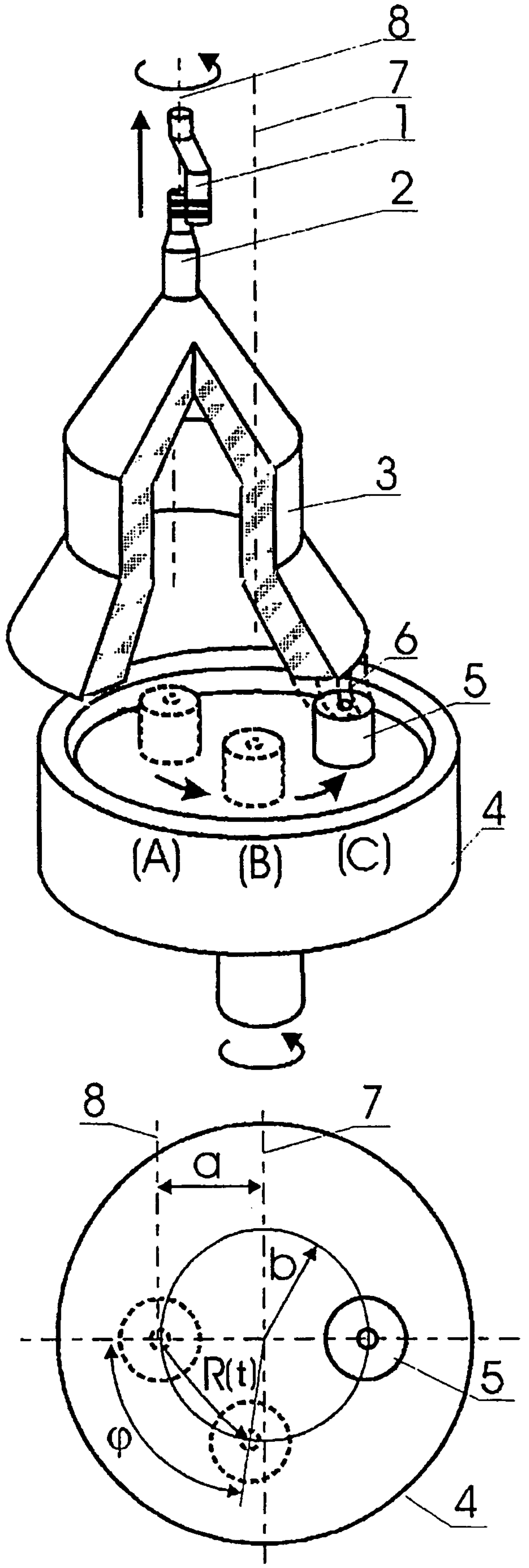
Fig. 4. The optimised curves of v and n depending on the current crystal length for conical and spherical crystals expanding during the process.

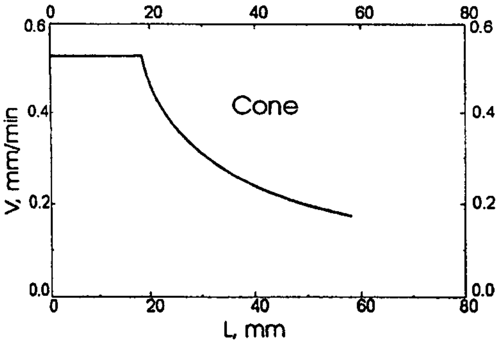
Fig. 5. Complicated sapphire products grown by the local dynamic shaping technique.

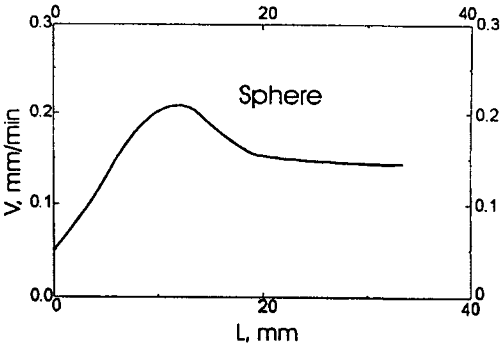
1- items with the shape of wine-glass; 2-tube with periodical bottlenecks: 3-hollow item consists of conic and hemispherical parts; 4-hollow cone; 5-hollow item consists of tubular and hemispherical parts; 6-rod with thread; 7-tube with the periodical spherical elements; 8- hollow item consists of two conic parts; 9-hollow item includes spherical elements and tube; 10-hollow item; 12 hollow item consists of two conic parts.

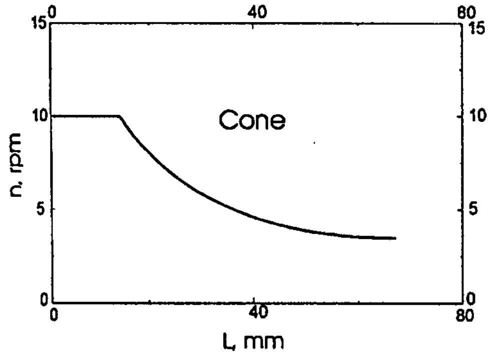

meniscus
capillary gap
growing crystal
die assembly
crucible

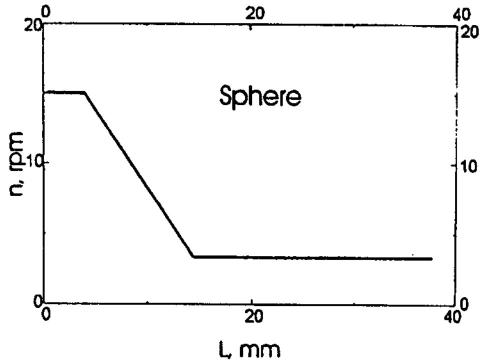

rotation axis
seed crystal
R
p
growing tube
meniscus
r_2
r_1
q
die
crucible


8
7
1
2
3
6
5
4
(A)
(B)
(C)
8
7
a
b
R(t)
φ
5
4


Cone
V, mm/min
L, mm
0.0
0.2
0.4
0.6
0
20
40
60
80


Sphere
V, mm/min
L, mm
0.0
0.1
0.2
0.3
0
20
40


Cone
n, rpm
L, mm
0
5
10
15
0
40
80


Sphere
n, rpm
L, mm
0
10
20
0
20
40