

## IMPURITY MICROSEGREGATION DUE TO PERIODIC CHANGES IN THE TEMPERATURE AND PULLING RATE OF CRYSTAL GROWN BY THE STEPANOV METHOD

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*A mathematical model is proposed to describe the behavior of a doping impurity concentration in a crystal grown by the Stepanov method from a melt and subjected to periodic changes in its pulling rate and temperature of the thermal node. Various modes of these effects are discussed. The results obtained are given by graphs that characterize their influence on concentration distribution.*

**Introduction.** Crystals of lithium niobate with a periodic domain structure are capable of direct frequency doubling of laser light. Such crystals are suitable for designing compact light sources. By microinhomogeneities is meant the situation when crystal properties change within the limits of less than a millimeter.

Several methods exist for obtaining periodic ferroelectric domain structures of the crystals of lithium niobate during their growth [1-4]. All of them are based on periodic changes in the growth parameters that lead to periodic changes in the doping impurity. In its turn, the domain structure obtained is determined by the concentration gradient of the impurity. It seems that the most attractive method for obtaining periodic structures in  $\text{LiNbO}_3$  is the Stepanov method. First, it is rather simple to obtain a desired shape of volumetric ferroelectric domains since they are a replica of the working surface of the shaper. Second, a domain structure is obtained by modulation of such parameters of crystal growth as the growth rate of the crystal, the pressure in the melt meniscus, the temperature of the thermal node, etc. These parameters allow computer-aided control with a high accuracy.

The present work is aimed at the development of a mathematical model of the behavior of an impurity stipulated by periodic changes in the conditions of crystal growth by the Stepanov method. As a rule, it represents concentration fluctuations of the doping impurity which are caused, in turn, by fluctuations of a pulling rate  $V$  and the temperature of the thermal node  $T$ . The latter total fluctuations determine the change in the growth rate  $V_c$  of a crystal. Actually, an expression for  $V_c$  may be written as  $V_c = V - \dot{h}(t)$ , where  $h(t)$  is the position of the crystallization front at time  $t$ . The behavior of the phase boundary  $h(t)$  reflects the behavior of both  $V$  and  $T$ . Considering the temperature effect on  $h(t)$ , we must distinguish two kinds of influence, namely, a direct influence by changing the oscillator power (the temperature of the thermal node) and an influence due to unsteady-state gravitational convection. We shall consider only the former influence, bearing in mind that the crystals are grown by the Stepanov method, in which gravitational convection may be made insignificant most successfully or suppressed entirely by a proper choice of the growth parameters and thermal zone. Two approaches to solution of this problem exist: 1) use of the notion of the effective coefficient of impurity segregation and the boundary-layer model [5] and 2) direct numerical solution of the basic equations [6] (disregarding the change in the length of a growing crystal). The first method results, by reducing to dimensionless form, in a singularly perturbed equation, i.e., one with a perturbation parameter at a higher derivative, which may be solved by the known method. Strictly speaking, knowing the concentration distribution at a sufficiently large distance from the crystallization front, one may determine the concentration in the crystal near the crystallization front by performing multiplication by this coefficient. However, this way fails to find an analytical solution in the general case when changes in the length of the growing crystal and in the phase boundary position are taken into account.

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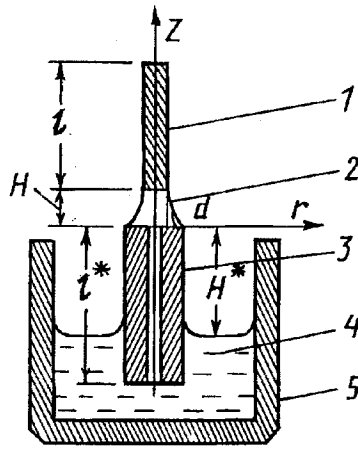


Fig. 1. Schematic of crystal growth: 1, crystal; 2, meniscus; 3, shaper; 4, melt; 5, crucible.

To describe mathematically this problem, we have solved numerically the one-dimensional nonstationary Stefan problem, the diffusional equation for concentration, and the capillary Laplace equation. So far, the mathematical model suggested allows the most complete and exact description of the behavior of an impurity concentration in a growing crystal. The equations of this model given below have been solved numerically by the semidiscrete Galerkin method.

**Statement of the Problem.** We shall consider the process of crystal growth from a melt by the Stepanov method. The crystal represents a thin cylinder with radius  $R_0$ , and the radius of the capillary channel is  $b$  (see Fig. 1).  $U_p$  to some moment the crystal growth corresponded to stationary growth of the crystal, having, by this time, length  $l_0$ , and the position of the crystallization front  $h_0$ . Then the melt-crystal system was subjected to perturbations that represented periodic fluctuations of the pulling rate and temperature. These fluctuations lead to deviation of the current radius  $R(t)$  of the crystal from  $R_0$  and of the position of the phase boundary  $h(t)$  relative to  $h_0$ . We shall assume that the  $R(t)$  fluctuations do not cause substantial changes in the temperature field in the crystal and, moreover, the melt lying directly under the profile curve of the meniscus also exerted a slight influence on this temperature field. These assumptions allow us to reduce the formulated problem to solving the following system of differential equations for the temperatures in liquid and solid phases  $T_l$  and  $T_s$  and the phase boundary  $h(t)$ :

$$\begin{aligned} \frac{\partial T_l}{\partial t} &= a_l \frac{\partial^2 T_l}{\partial z^2} - \gamma_{1l} \frac{\partial T_l}{\partial z} - \gamma_{2l} T_l + \gamma_{3l} z \frac{\partial T_l}{\partial z} + \gamma_{2l} \Theta_1, & 0 < z < H(t), \\ \frac{\partial T_s}{\partial t} &= a_s \frac{\partial^2 T_s}{\partial z^2} - \gamma_{1s} \frac{\partial T_s}{\partial z} - \gamma_{2s} T_s + \gamma_{3s} z \frac{\partial T_s}{\partial z} + \gamma_{2s} \Theta_2, & H(t) < z < l, \\ h(t) &= H(t) \cdot l(t). \end{aligned} \quad (1)$$

In these equations temperatures  $T_i$  and all temperatures discussed below pertain to the melt temperature  $T_0$  at the shaper outlet at the initial moment of time. Furthermore, we have passed to the dimensionless coordinate  $z' = z/l(t)$ , where  $l(t)$  is the current length of the calculated zone:

$$l(t) = h_0 + l_0 + \int_0^t V(\tau) d\tau.$$

For convenience, instead of  $z'$  the variable  $z$  is again used. The temperatures of outer media are expressed in terms of  $\Theta_i(z)$  ( $i = l, s$ ); they may be prescribed by a single formula. The coefficients  $a_i, \gamma_{1i}, \gamma_{2i}, \gamma_{3i}$  ( $i = l, s$ ) in Eqs. (1) are of the form

$$a_j = \frac{k_i}{l^2 c_{pj} \rho_j}, \quad \gamma_{1s} = \frac{V}{l}, \quad \gamma_{1l} = \frac{V \rho_l R_0^2}{l \rho_s b^2}, \quad \gamma_{2j} = \frac{2h_j}{c_{pj} \rho_j R_0}.$$

Over the crystallization front  $z = H(t)$  the condition of interphase energy balance

$$k_l \frac{\partial T_l}{\partial z} - k_s \frac{\partial T_s}{\partial z} = (V - \dot{h}) \left. \frac{\rho_s \Delta H_f l}{T_0} \right|_{z=H(t)}, \quad \dot{h} = \dot{H}l + VH, \quad (2)$$

where  $\Delta H_f$  is the latent heat of melting, and the continuity condition of the temperature with its equality to the melting temperature  $T_m$

$$T_s(H(t)) = T_l(H(t)) = T_m. \quad (3)$$

must be fulfilled. Moreover, the initial temperature distribution and the initial  $H(t)$  are prescribed:

$$T_l(0, z) = T_l^0(z), \quad 0 \leq z \leq H(t), \quad T_s(0, z) = T_s^0(z), \quad H(t) \leq z \leq 1, \quad H(0) = H_0. \quad (4)$$

Finally, the boundary conditions

$$T_l(t, 0) = T_l(t), \quad T_s(t, 1) = T_c(t), \quad (5)$$

are set which determine the regime of temperature fluctuation.

Solution of problem (1)-(5) allows us to determine the behavior of the phase boundary  $H(t)$  and, consequently, the behavior of the crystal radius  $R(t)$ . Actually,  $R(t)$  may be described by a system of differential equations

$$\dot{R}(t) = (V - \dot{h}) \tan(\varepsilon - \varepsilon_0), \quad (6)$$

where  $\varepsilon$  is the angle between the tangent to the profile curve of the meniscus  $\xi(r)$  and to the straight line  $r = R(t)$  at the triple junction point while  $\varepsilon_0$  is the angle of growth, which is a known value typical for a chosen material. The angle  $\varepsilon$  is determined from the equality

$$-\cotan \varepsilon = \left. \frac{d\xi}{dr} \right|_{r=R(t)}, \quad (7)$$

where  $\xi(r)$  is a function that describes the equilibrium shape of the liquid meniscus subjected to the forces of gravity and surface tension. It satisfies the capillary Laplace equation

$$\rho_l g (\xi + H^*) = \sigma \left( \frac{\xi''}{(1 + \xi'^2)^{3/2}} - \frac{\xi'}{r(1 + \xi'^2)^{1/2}} \right) \quad (8)$$

and the boundary conditions

$$\xi(R(t)) = h(t), \quad \xi(d) = 0. \quad (9)$$

In the last formula, we have introduced the following designations:  $\sigma$  is the coefficient of surface tension;  $g$  is the gravitational acceleration;  $H^*$  is the difference of melt heights in the crucible and on the upper edge of the shaper;  $d$  is the distance from the  $z$ -axis to the point of meniscus engagement with the shaper edge. Note that at  $H^* = 0$  one may use a formula that is easily obtained from the expression relating the crystal radius  $R$ , the meniscus height  $H$ , and the angle  $\varepsilon$  [7], which is well known for the Czochralski method, by its conversion provided that  $d$  is sufficiently large ( $d \approx 3R_0$ ):

$$\varepsilon = -\frac{\pi}{2} + \arcsin \frac{2\sigma - h^2 \rho_l g}{\sigma \sqrt{\left(\frac{h^2}{R^2} + 4\right)}} + \arcsin \frac{2}{\sqrt{\left(\frac{h^2}{R^2} + 4\right)}}.$$

The distribution of the impurity concentration  $C_s$  in a growing crystal may be found by solving the differential equation describing the behavior of the impurity concentration in the melt  $C_l$  and introducing the segregation coefficient  $k_0 = C_s/C_l$ :

$$\frac{\partial C_l}{\partial t} = \frac{D}{l_c^2} \frac{\partial^2 C_l}{\partial z^2} - \frac{V}{l_c} \frac{\partial C_l}{\partial z} + \frac{\dot{h}}{l_c} z \frac{\partial C_l}{\partial z}, \quad (10)$$

where  $l_c = l^* + h(t)$ .

The initial concentration distribution  $C_0$  in the melt is considered to be uniform, but due to fluctuations of the crystal pulling velocity and temperature it will change with time thus influencing, naturally, the impurity distribution in the crystal. It is also assumed that at a sufficiently large distance  $l^*$  from the upper edge of the shaper down the capillary channel, the concentration  $C_l$  is constant and equal to  $C_0$ . Thus, the initial and boundary conditions may be formulated as

$$C_l|_{t=0} = C_0, \quad (11)$$

$$-\frac{D}{l_c} \frac{\partial C_l}{\partial z} = (V - \dot{h})(k_0 - 1) C_l|_{z=1}, \quad C_l|_{z=0} = C_0. \quad (12)$$

On writing Eq. (10) and conditions (11) and (12), we also passed to the dimensionless variable  $z' = z/l_c$  and then again used its former notation.

The set of the equations, boundary and initial conditions (1)-(12) describes completely the formulated problem in its one-dimensional approximation.

**2. Method of Finite Elements and Numerical Results.** The semidiscrete Galerkin method is based on passing to a differential equation in its weak form. At inhomogeneous boundary conditions the Galerkin approximation  $\tilde{T}_l, \tilde{T}_s$  of the temperatures  $T_l, T_s$ , on solving the Stefan problem (1)-(5), may be represented as

$$\tilde{T}_l = W_l(z, t) + \sum_1^N \alpha_i(t) \varphi_i(z), \quad \tilde{T}_s = W_s(z, t) + \sum_{N+1}^M \alpha_i(t) \varphi_i(z), \quad (13)$$

where the functions  $W_l, W_s$  satisfy boundary conditions (3) and (5). They may be prescribed, for instance, in the form

$$W_l = T_0(t) + \frac{T_m - T_0(t)}{H} z, \quad W_s = \frac{T_c(t) - T_m}{1 - H} z + \frac{T_m - HT_c(t)}{1 - H},$$

while the functions  $\varphi_i$  form a basis of the the subspaces of energetic spaces (Sobolev spaces, functions that vanish at the boundary):  $\varphi_i \in \tilde{W}_2^{(1)}[0, H(t)], \tilde{W}_2^{(1)}[H(t), 1]$ .

Then the Galerkin approximation is determined from a system of ordinary differential equations for the functions  $\alpha_i(t)$  that are the finite-element analog of the equations (1) ( $i = 1, \dots, M$ ) and  $H(t)$ :

$$A_j \tilde{\alpha}_j(t) = - (B_j + \gamma_{1j} C_j + \gamma_{2j} A_j) \alpha_j(t) + Q_j \quad (j = l, s),$$

$$\dot{H}(t) = V_0(t) + \left[ q_s \frac{d\tilde{T}_s}{dz} - q_l \frac{d\tilde{T}_l}{dz} \right]_{z=H(t)}. \quad (14)$$

$$q_s = \frac{k_s}{\Delta H_f \rho_s l}, \quad q_l = \frac{k_l}{\Delta H_f \rho_l l}. \quad (15)$$

In system of Eq. (14) and (15) we have introduced the following designations: matrices  $A_j, B_j, C_j, D_j$  ( $j = l, s$ ) of the form

$$A_j = (\varphi_i, \varphi_k), \quad B_j = (\partial\varphi_i, \partial\varphi_k), \quad C_j = (\varphi_i, \partial\varphi_k), \quad D_j = (z\varphi_i, \partial\varphi_k),$$

$i, k = 1, \dots, N$  for the subscript  $j = l$ ;  $i, k = N + 1, \dots, M$  for the subscript  $j = s$ . The vectors  $\mathbf{Q}_j$  correspond to the temperatures  $\Theta_j$  from Eq. (1) as well as to condition (3) and boundary conditions (5). They are represented by the formulas

$$\mathbf{Q}_j = A_j \cdot \mathbf{F}_j,$$

in which the  $\mathbf{F}_j$  components are the values of the  $F_j$  functions and their derivatives at the nodes of the partition network:

$$F_j = -\frac{\partial W_j}{\partial t} + L_j W_j + \gamma_{2j} \Theta_j,$$

while the  $L_j$  operators have the form

$$L_j = a_j \frac{\partial^2}{\partial z^2} - \gamma_{1j} \frac{\partial}{\partial z} - \gamma_{2j} + \gamma_{3j} z \frac{\partial}{\partial z}, \quad j = l, s.$$

The basis elements  $\varphi_i$  represent the Hermite cubic functions obtained by displacing the functions

$$\psi(z) = (|z| - 1)^2 (2|z| + 1), \quad \omega(z) = z(|z| - 1)^2.$$

to the corresponding node of the partition network.

Thus, each node of partition of the regions  $[0, H(t)]$ ,  $[H(t), 1]$ , corresponding to liquid and solid-state zones, contains two basic functions  $\psi, \omega$ , with the exception of the boundary nodes at which only the function  $\omega$  is contained.

Initial conditions for the system (14) and (15) may be preset as

$$\alpha_i(0) = 0, \quad H(0) = H_0, \quad i = 1, \dots, M, \quad (16)$$

if the initial temperature distributions  $T_j^0(z)$  from (4) are considered to be linear. Actually, they are insignificant for times at a sufficient distance from the initial one.

For numerical solution of the capillary Laplace Eq. (8) we may use the results of [8, 9], in which an equilibrium shape of the liquid menisci engaged with an arbitrary contour has been found and their stability has been investigated, therefore we do not give here the equations that describe this situation.

If we designate  $C = C' + C_0$  and represent  $C'$  as a sum

$$C'(z) = \sum_{i=1}^K \beta_i(t) \varphi_i(z),$$

then the finite-element analog of Eq. (10) for the concentration  $C'$  may be written as

$$A_c \beta = \left( -\frac{D}{l_c^2} B_c - \frac{V}{l_c} C_c + \frac{l'_c}{l_c} D_c \right) \beta + \nu \beta_c + \nu C_0, \quad (17)$$

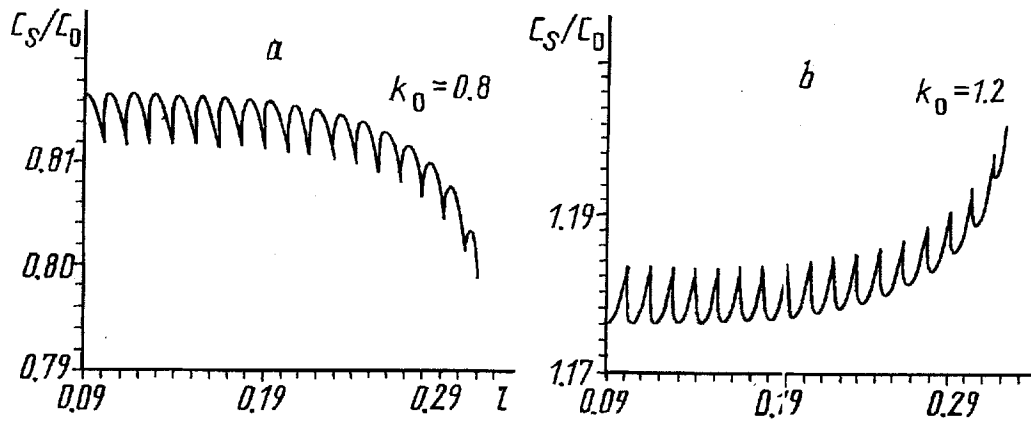


Fig. 2. Impurity concentration distribution with respect to the crystal length at harmonic fluctuations of the pulling rate and the temperature of the thermal node: a, distribution coefficient  $k_0 < 1$ ; b, distribution coefficient  $k_0 > 1$ .  $l$ , cm.

where

$$\nu = -\frac{1}{l_c} (V - h) (k_0 - 1);$$

$$\beta_c = (\beta_1, 0, \dots, 0); \quad C_0 = (C_0, 0, \dots, 0).$$

The matrices entering Eq. (17) have the same designations as in (15). And, finally, the initial conditions corresponding to them are as follows

$$\beta_i(0) = 0, \quad i = 1, \dots, K. \quad (18)$$

The systems of Eq. (14), (15), and (17) with their boundary conditions have been solved by the Runge-Kutta method combined with the Gauss method, since these equations have not been solved for derivatives.

We now pass to the numerical results obtained. We have considered two types of periodic changes in the pulling rate, namely, harmonic fluctuations and fluctuations representing a stepwise function. Simultaneously, the temperatures  $T_l(t)$ ,  $T_c(t)$  and the ambient temperature have also periodically changed. For this, harmonic oscillations of the the pulling rate  $V$  of the crystal are represented analytically as

$$V = V_0 (1 + A \sin(\omega t + \psi)), \quad A < 1, \quad T_c(t) = T_{c0} + T_{c1} \sin \omega_1 t + \Delta T (l(t) - l_0),$$

$$T_l(t) = T_0 + T_{01} \sin \omega_1 t.$$

In these formulas, the parameters have the following values:

$$V_0 = 10^{-3} \text{ cm/sec}, \quad A = 0.5, \quad \psi = 0, \quad \omega = \frac{\pi}{8} \text{ sec}^{-1}, \quad \omega_1 = \frac{\pi}{8} \text{ sec}^{-1},$$

$$T_0 = 2075^\circ\text{C}, \quad \Delta T = -500^\circ\text{C}, \quad T_{c0} = 2000^\circ\text{C}, \quad T_{c1} = 10^\circ\text{C},$$

$$T_{01} = 30^\circ\text{C}, \quad T_m = 2050^\circ\text{C}, \quad l_0 = 1. \quad (19)$$

The values of the physical parameters of the problem are given for lithium niobate.

Figure 2 shows the relative concentration distribution of the impurity  $C_s/C_0$  with respect to crystal length which is a result of numerical solution of problem (1)-(13) for growth conditions (19). In accordance with it, we

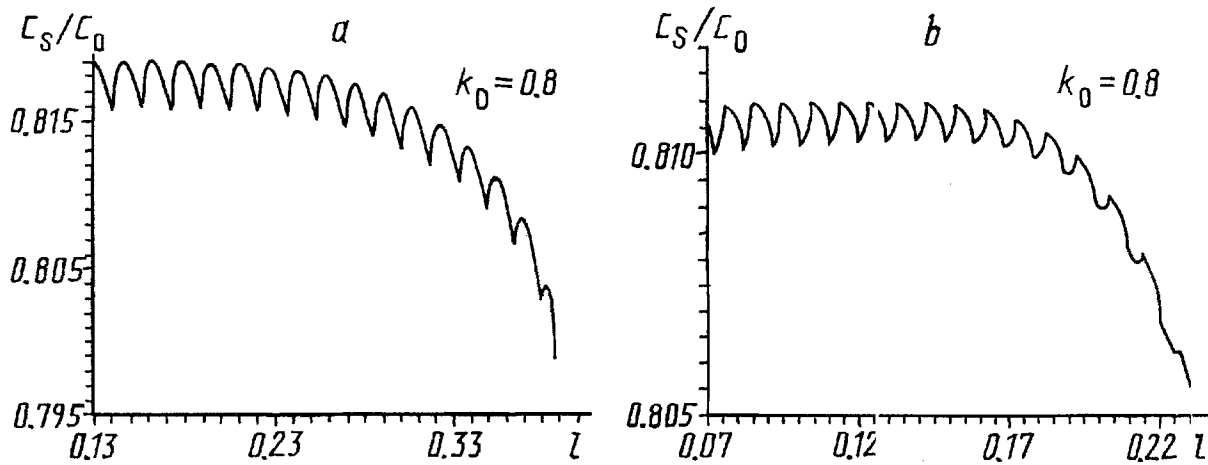


Fig. 3. Impurity concentration distribution with respect to the crystal length with sinusoidal (a) and stepwise (b) changes in the pulling rate and at a constant temperature of the thermal node.

have determined the impurity concentration in the melt  $C_l(t, z)$  and then the impurity concentration in the crystal  $C_s$  from the relation

$$C_s(t) = k_0 C_l(t, z) \Big|_{z=H(t)}$$

for distribution coefficients of  $k_0 = 1.2$  and  $0.8$ . It is seen that the concentration  $C_s$  either decreases in an oscillating manner (Fig. 2a) or increases (Fig. 2b) and next reaches a stationary oscillating regime that corresponds to its distribution coefficient. The time needed to attain this regime and the oscillation amplitude depend on the diffusion coefficient  $D$ . For instance, with decreasing  $D$  from  $10^{-2}$  to  $10^{-3}$  cm<sup>2</sup>/sec the impurity concentration  $C_s$  increases against its mean value from 0.5 to 5%. Note that the depicted curves are their mirror representation. Furthermore, we have considered two cases of the most important periodic disturbances that occur at a constant temperature of the thermal zone: at harmonic fluctuations of the pulling rate of the crystal and at its stepwise disturbances (Fig. 3):

$$V = \begin{cases} V_0, & 0 \leq t \leq t_0, \\ V_{01}, & t_0 \leq t \leq S, \end{cases}$$

$V_0 = 5 \cdot 10^{-3}$  cm/sec,  $V_{01} = 5 \cdot 10^{-4}$  cm/sec,  $t_0 = 8$  sec,  $S = 16$  sec, with the other parameters of the growth regime (19) being equal.

The behavior of  $C_s/C_0$  as a function of the other parameters does not change qualitatively and must be determined in each particular case. The results obtained serve as a basis for optimization of the efficiency of a waveguide manufactured from crystals with their domain structure obtained as described above.

## CONCLUSIONS

1. The mathematical model proposed qualitatively reflects the impurity distribution in a growing crystal (all our results obtained are well consistent with those of the authors of [5, 6] in all the cases when their parameters are close to ours) and so far it represents the most complete description of a crystallization process under periodic disturbances.

2. It should be noted that the relative concentration  $C_s/C_0$  does not reach, on the average, the stationary level corresponding to an oscillation-free regime when it acquires a value equal to unity, i.e., its mean value is either higher ( $k_0 < 1$ ) or lower ( $k_0 > 1$ ) than the concentration in the case of stationary crystal growth dependent on the distribution coefficient.

## NOTATION

$V$ , pulling rate of the crystal;  $V_c$ , crystallization rate;  $V_l$ , velocity of melt motion;  $h(t)$ , position of the crystallization front at the time  $t$ ;  $H(t)$ , dimensionless height of the crystallization front;  $l_0$ , initial length of the crystal;  $R(t)$ , crystal radius;  $k_j$  ( $j = l, s$ ), thermal conductivities of the melt and the crystal;  $c_{pj}$  ( $j = l, s$ ), specific heats of the melt and the crystal;  $\rho_j$  ( $j = l, s$ ), densities of the melt and the crystal;  $\Delta H_f$ , latent heat of melting;  $\varepsilon_0$ , angle of growth;  $\sigma$ , coefficient of surface tension;  $T_m$ , melting point;  $T_j$  ( $j = l, s$ ), temperatures of the melt and the crystal;  $T_0$ , temperature of the melt at the shaper outlet at the initial moment of time;  $l^*$ , length of the capillary channel;  $C_l$ , impurity concentration in the melt,  $k_0$ , coefficient of impurity distribution;  $b$ , radius of the capillary channel.

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