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On some factors having an effect on heat exchange and stability of the process of automated pulling from melt of alkali halide crystals

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Abstract

Isotherms in CsI(Tl) crystals were calculated for the case of automated pulling of the latter from melt in cylindrical and conical crucibles. For the conical crucible the crystallization isotherm has a more convex form towards the melt. This is explained by higher temperature gradients and intensive heat removal from the lower part of the growing crystal, this part being very close to the crystallization front. The conical crucible promotes increase of thermal stability of the pulling process. The calculation results were confirmed experimentally. Application of the conical crucible allowed to automate the stage of radial growth and to increase the pulling rate for large crystals to 5.5 mm/h even at a replenishment with fine crystalline raw material.

1 Introduction

One of the disadvantages of the methods of pulling alkali halide crystals from melt is connected with an intense evaporation of the melt and formation of a sublimated layer on the inner surfaces of the growth chamber; this layer significantly deteriorating heat removal from the growing crystal. The duration of pulling NaI(Tl) or CsI(Tl) crystals 400-500 mm in diameter and more than 400 mm in height is from 100 to 200 hours. For this time a layer of the sublimated salt 2-3 mm thick is precipitated on the chamber walls as a result of evaporation. This layer is an efficient reflector not only for the radiation component of heat removal but it is also a heat insulator for molecular heat removal. A loose layer of the sublimated salt is also formed on the surface of the growing crystal. It impedes the heat removal from the crystal.

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As the sublimated layers on the surfaces of the chamber and crystal become thicker the mass crystallization rate decreases. To maintain the diameter of the growing crystal constant at the automated control its puling rate should be slowed. Further, as the crystal mass increases the heat removal conditions stabilize and there appears a possibility to increase the pulling rate. However, the value 2.5-3 mm/h cannot be elevated. One of the conventional methods to increase heat removal from the growing crystal and thermal stability of the process consists of making higher the pressure of the inert and heat-conducting gas or gas mixture in the growth chamber (e.g. nitrogen, helium or argon). This, however, leads very often to other difficulties and undesirable consequences, for instance, to the formation of bubbles or harmful oxygen-containing impurities in the crystal if the gas is not pure enough. Usually, the working pressure in the chamber at pulling large scintillation alkali halide crystals does not exceed 100 torr.

A pulling method with a varying geometry of the melt in the conical crucible [1] and replenishment by the melted raw material was suggested earlier. In this method the free surface of the melt remains minimal during the whole pulling process. This retards formation of sublimated layers on the surfaces of the chamber and crystal. The experience of growing large scintillation alkali halide crystals according to this method allowed to reveal a number of specific features related to both its advantages and disadvantages.

Replenishment by melt has at least three essential advantages as compared with replenishment by crystalline raw material [2]. Since the already melted material enters the crystal growth zone, i.e. crucible, and no thermal power is needed for melting raw material near the growing crystal there appears an additional possibility to make the pulling rate higher thus increasing the efficiency of growth equipment. More versatile possibilities in the choice of optimal ratio of the power of the side and bottom heaters providing thermal stability of the growth process also contribute to this advantage [3].

One more important advantage of feeding with melt consists of the fact that no requirements to dispersion and free-flow of the raw material are made. Thus, reused can be wastes (pieces, fragments and chips) as raw material. Besides, there appears a possibility of additional purification of the melted raw material from different impurities right in the feeder. At the same time, disadvantages of such replenishment by melt are connected with the design peculiarities and particular technical solutions included in the growth equipment. A limited volume of the feeder should be noted. Due to it the size of the grown crystals is also limited provided preliminarily dried raw material is not charged to the feeder. The form of the crucible turned out to have a significant effect on heat exchange between the crystal and different radiating and absorbing surfaces inside the furnace and thermal field in the growing crystal. The use of the conical crucible made it possible to increase essentially the growth process stability and to achieve pulling rates as high as 6-6.5 mm/h when growing large CsI(Tl) crystals - more than 200 kg in mass [1]. An attempt to estimate quantitatively the effect of the crucible form on the stability of the process was made in this paper. This can be done by the value of the temperature gradient along the length of the growing crystal and by the form of isotherms by the shape of the crystallization

front, in particular. The calculations were made on the example of pulling CsI(Tl) crystals from the melt charged in the conical and cylindrical crucibles.

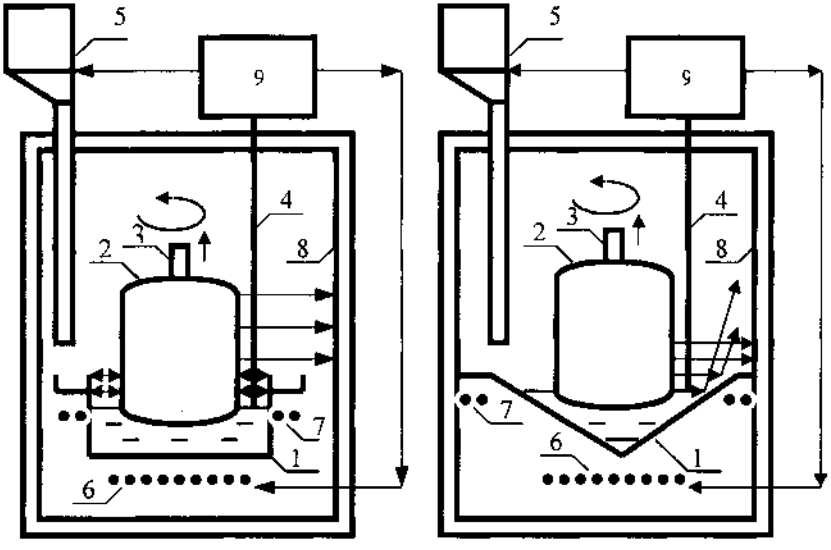

Figure1: Block–scheme of automated unit for pulling crystals from cylindrical (a) and conical (b) crucibles.

These data may turn out to be useful for designing automated growth installations of the next generation.

2 A model and initial data for calculation

As a model for calculation the authors used an experimental automated installation on which CsI(Tl) crystals can be grown using both cylindrical and conical crucibles without any significant change of the heating unit design. The scheme of the installation is shown in Fig.1. In case of a cylindrical crucible 1 (Fig.1a) the radial growth proceeds without replenishment and at a small drop of the melt level in the crucible caused by the difference in the density of the crystal and melt. The operator corrects the melt temperature by hand according to a visual evaluation of the radial growth rate. In the second case (conical crucible 1, Fig.1b), the same way as in [1] the radial growth is automated. The melt level at this stage is continuously rising owing to replenishment by the signal of the going upward sensor 4. The control device 9 was created on the base of personal IBM computer. In both cases the replenishment at growth in height is provided by fine crystalline raw material. The system of replenishment and the design of the feeder 5 do not practically differ from those described in [2].

It is difficult to derive analytical expressions in the general form. Therefore, for the calculation the authors used real specific values of the parameters and sizes of the heaters, crucibles, growth chamber, heat insulation and other elements of

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the furnace participating in the formation of the thermal field in the growing crystal. Also taken were the reference values of thermal physical constants of CsI(Tl) crystals and used constructional materials.

The calculations were made for crystals 200 mm and 340 mm in diameter, the diameter of the melt mirror being 400 mm in case of a cylindrical crucible, 260 and 400 mm - in case of a conical crucible. In both cases the design of the heating unit, interlocation of the heaters, their geometrical dimensions and working temperature intervals were assumed the same. The side and bottom heaters form the thermal field, which is necessary for keeping the raw material in the crucible melted and provision of the growth process stability. The bottom heater 6 has the form of a planar Archimed spiral 300 mm in diameter. The working temperature range of the bottom heater is 700-950 °C. The side heater 7 is also made in the form of a planar ring spiral with the inner diameter 450 mm and the outer one 550 mm. The working temperature range of the side heater is 700-900 °C. The cylindrical growth chamber 8 with the inner diameter 950 mm has a water-cooled jacket. Consumption of the cooling water is 1.5-2 m^3/h and is regulated so that the temperature of water at the exit did not exceed 40 °C. The diameter of the water-cooled shaft of the crystal holder is 60 mm, diameter of the seed crystal 3 is 60 mm. Thus, the models for comparison differ only in the form of the crucible. In one case it is a cylindrical crucible 400 mm in diameter and 150 mm high; in the other case it is conical with a diameter 400 mm near the base and angle 120° at the top.

3 Calculation of thermal fields in a crystal

The authors believe that it is correct to evaluate the effect of any parameter on the stability of the process by its effect on the thermal field in the growing crystal, i.e. on the form of isotherms and, in particular, on the form of the crystallization isotherm.

Alkali halide crystals are semitransparent media in which heat transfer proceeds by both molecular and radiation way. Owing to the radiant component of the heat transfer each elementary volume of the crystal exchanges thermal energy not only with the adjacent regions but also with all its elementary volumes. Besides, the exchange of the radiant energy occurs with all unshaded with respect to each other surfaces of the furnace, walls of the crucible etc.. As a consequence, heat exchange obeys the integral-differential heat transfer equations. The authors use a simplified approach, assuming the radiation exchange in the crystal to prevail over the molecular one. In the approximation of optically thick layer the coefficient of thermal conduction according to [3] is described as

$$\lambda = 4\varepsilon\sigma_B T^3 / \beta \qquad (1)$$

where ε is the coefficient of crystal radiation, σ_B is the Stefan-Boltzmann constant, $T=T(\vec{r})$ is the crystal temperature at the point $\vec{r}$, β is the coefficient of light absorption at the wavelength of the maximum of the radiation spectrum. The equation of the heat balance for the crystal can be written in the cylindrical coordinates as follows:

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$$\frac{1}{r}\frac{\partial}{\partial r}(r\lambda(T)\frac{\partial T}{\partial r})+\frac{\partial}{\partial z}(\lambda(T)\frac{\partial T}{\partial z})-I(r,z)=0 \qquad (2)$$

where $I(r,z)$ is the radiation flow from the elementary volume with the coordinates (r,z) outside the crystal.

We assume that $I(r,z)=\varepsilon\sigma_B f(r,z)T^4$, where $f(r,z)$ is the function that allows for the share of radiation, quitted the crystal. The boundary conditions on the crystal surface have the form:

$$-\lambda(T)\frac{\partial T}{\partial n}\Big|_S=\varepsilon\sigma_B T^4\Big|_S-\sum_{i=1}^{N}F_i\varepsilon T_i^4 \qquad (3)$$

where F_i is the coefficient of irradiance of the given element of the crystal surface by elements with the number i and temperature T_i. The coefficient of the irradiance of dA surface element by the surface B means the share of the spatial angle at which the surface B is seen from the considered area on the surface A. Crystal surfaces exchange radiation energy with the walls of the crucible, melt mirror and inner surfaces of the growth chamber. The coefficient of the element dA_1 irradiance by the surface A_2 according to [3] is determined by the formula:

$$F_{dA1\longrightarrow A2}=\int_{(A_2)}\frac{\cos\theta_1\cos\theta_2 dA_2}{\pi r^2} \qquad (4)$$

Thus, for example, the coefficient of the irradiance of the element of the crystal side surface by the part of the crucible surface, from which this element is seen, is:

$$F_{d1\to 4}=\frac{2}{\pi}\int_{R_Z}^{R_{\max}}\rho d\rho \times \int_0^{\arccos(R_S/l)}d\varphi\frac{(\rho\cos\varphi-R_S)\left[\tan\alpha(\cos\varphi-R_Z)-z_1\right]}{\left[\rho^2+{R_S}^2-2\rho R_S\cos\varphi+(\tan\alpha(\rho-R_Z)-z_1)^2\right]^2} \qquad (5)$$

Here, 2α is the angle of opening of the conical crucible; φ and ρ are the angular and radial variables of integration, R_Z is the radius of the melt mirror, R_S is the crystal radius, $R_{\max}$ is the maximum radius of the conical crucible.

Solution of the system (2)-(3) depends on the geometry, interlocation, relative size and physical properties of the surfaces, participating in the heat exchange. Boundary conditions for the upper end of the crystal are the same as for the side surface. Calculation according to [3] was made by division of the side surface of the crystal into 10 zones and of the inner side surface of the furnace, absorbing

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radiation – into 16 zones of equal height. It is obvious that the increase of the number of zones will make the calculation more accurate, however, will complicate it significantly. At the same time this will be hardly necessary for the qualitative evaluation. Within the limits of each zone the temperature was assumed to be constant. Distribution of temperature over the side inner heat removing surfaces of the furnace, that of the melt and walls of the crucible was calculated preliminarily. The balance of the thermal power applied to the heaters of the furnace and removed through the water-cooled surfaces controlled correctness of the calculation.

4 Results and discussion

Isotherms in crystals 200 mm and 340 mm in diameter, calculated by the equation (2) with conditions (3) for the cylindrical and conical crucibles are shown in Fig.2. If to compare the forms of the isotherms for crystals with different diameters, pulled from one and the same crucible one can see that with the increase of the diameter the isotherm becomes less convex towards the melt. This result can be explained by the fact that removal of the crystallization heat from the elementary volumes, situated in the depth of the crystal is impeded as compared with the volumes that are on the surface. It should be expected that with the enlargement of the crystal diameter the form of the isotherm would become flat and then concave. Comparison of the isotherms for crystals of the same diameter grown under the same thermal conditions shows evident dependence of the isotherm form on that of the crucible. In case of the conical crucible the crystallization isotherm of CsI(Tl) crystallization (621°C) is convex while as at pulling from the cylindrical crucible the isotherm is concave. This is explained by the fact that the vertical walls of the crucible and cylindrical surface of the lower part of the crystal exchange radiation. Removal of the crystallization heat in this zone to the water-cooled walls of the furnace is impeded due to a mutual reflection of the radiant energy by these surfaces, i.e. mutual shielding. In case of the conical crucible a significant part of the radiant energy from the lower part of the crystal (located close to the crystallization front) is reflected directly to the water-cooled walls and lid of the furnace. Shown in Fig.2 isotherms were calculated for a fixed temperature on the bottom heater (800°C). The results of the calculation do not claim at all that crystallization isotherms at pulling from the conical crucible will always have the form convex towards melt and at pulling from the cylindrical one – concave. Both type isotherms can be obtained for the conical and cylindrical crucibles. However, in case of the conical crucible a convex crystallization front can be formed at higher temperatures on the bottom heater. As it follows from the equation (5), heat removal from the lower part of the crystal will increase with the enlargement of the conical crucible opening angle; this will allow to raise the crystallization (pulling) rate. However, in practice there exist limitations connected with the real size of the melt submerged part of the crystals and crystallization front from which do not allow to enlarge the opening angle of the conical crucible.

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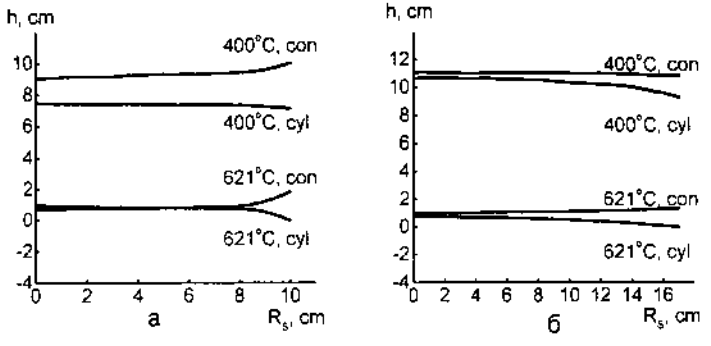

Figure2: Isotherms for CsI(Tl) crystals calculated for the cases of pulling from melt in conical (con) and cylindrical (cyl) crucibles. a)–crystal diameter 200 mm, b)–diameter 340 mm.

The experiments showed that the angle 120-130° is optimal. The required velocity of the increment of the melt mirror diameter is provided; it being matched with the preset one of the radial growth of the crystal. Qualitatively the results of the calculation of thermal fields in the crystals were confirmed experimentally at growing 30 CsI(Tl) ingots 320-420 mm in diameter and to 400 mm in height using both cylindrical and conical crucibles. The experience shows that stability of the process of radial growth in the cylindrical crucible strongly depends on the position of the melt level in the crucible. Very often radial growth is accompanied by a local crystallization on the melt surface (the so-called sludge ice is formed). This restricts the growth rate and impedes control of the process. At getting to the growth in height the pulling rate usually does not exceed 2 mm/h. At an attempt to raise it while preserving the crystal diameter one should lower the melt temperature. This may lead to a noncontrolled change of the front form and dendrite crystallization. Further, when the crystal height is increased, the conditions of heat removal from the crystal become better because the effect of the crystal shielding by the walls of the crucible becomes lower; thus the pulling rate can be made higher, but the authors did not manage to achieve pulling rate higher than 4 mm/h. It should be noted that thermal conditions at which flat or concave crystallization front is formed are created as a rule at high temperatures on the bottom heater. On the other hand, it is just at high temperatures on the bottom heater and rather low temperatures on the side heater formed are necessary thermal conditions and sufficiently high temperature gradients that provide stable growth of the crystal. It is also worthy to note that the side heater temperature must not be lower than a certain value, ensuring melting of the replenishing raw material at a necessary mass velocity equal to that of crystal growth. Nevertheless, in reality there always exists the ratio of temperatures of the side and bottom heaters at which stable growth of crystals is

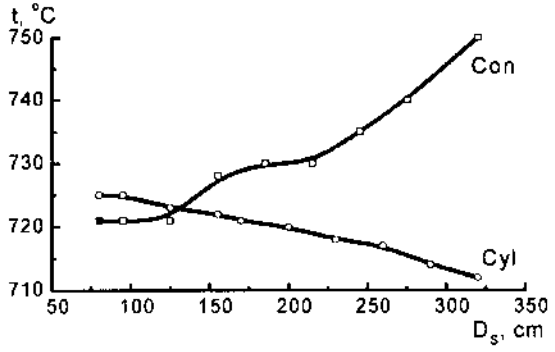

Figure3: Temperature change of the bottom heater for radial growth of crystals in cases of pulling from the melt in conical and cylindrical crucibles.

provided. With this, pulling rates are relatively low, about 2-3 mm/h.
Replacement of the cylindrical crucible for the conical one broadens the possibilities of the automated pulling even if replenishment is realized by fine crystalline raw material with which the choice of optimal ratio of the power of side and bottom heaters is essentially restricted. Automation of the process, including the stage of radial growth, the same way as in [1] has been implemented using time intervals between replenishments as a controling parameter. Improvement of heat removal from the lower part of the crystal adjacent to the crystallization front owing to the change of the crucible form and reflection of radiation right to the water-cooled walls of the crucible allowed to increase the pulling rate of CsI(Tl) crystals up to 5.5 mm/h. At growing large crystals 420 mm in diameter and over 400 mm in height no noncontrolled change of the crystallization front form, spontaneous crystallization in the melt volume, its surface or bottom of the crucible were observed. This gives evidence to the stability of the process. Application of the automated control system using time intervals between replenishments as a controlling parameter allowed to automate the stage of radial growth. The accuracy of the diameter control at growing in height is ±1%, which practically compares favorably with that achieved in [1] at replenishment by melt. Thermal stability of the process can be evaluated by the character of the melt temperature variation during the growth process. Note that if some stage of the process is accompanied by temperature lowering this is an evidence of the stability decrease. If heat removal from the growing crystal is insufficient the operator (at manual control) or autotune system (at automated control) are to decrease the melt temperature. Fig.3 shows the dependences of the variation of the bottom heater temperature upon variation of the crystal diameter at growing in the cylindrical (cyl) and conical (con) crucibles. At radial growth in the cylindrical crucible the temperature of the bottom heater was corrected manually. This being so, the temperature had to be lowered during the whole growth process in order to ensure radial growth. From the moment of radial growth beginning and till the final value of the diameter (320 mm) the temperature was lowered by 13°C. Radial growth of the crystal till the same size in the conical crucible in the automated mode was accompanied by temperature

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increase which by the end of growth made 27 °C. The rise of the heater temperature at the stage of radial growth in case of the conical crucible also testifies to the increase of heat removal and improvement of the process stability. Let us note as well that in none of the experiments on pulling large CsI(Tl) crystals the authors observed noticeable deformation of the seed crystal though its cross-section did not exceed 20 cm^2.

5 Conclusions

The analysis of the thermal fields in crystals shows that in case of their automated pulling from melt charged in the crucible of the conical form created are more favorable conditions for the removal of crystallization heat than at pulling from the cylindrical crucible. This occurs due to the fact that a part of the heat flow from the side surface of the lower part of the crystal which is situated in a direct vicinity to the crystallization front is reflected from the tilted wall of the crucible right to the heat absorbing water-cooled surfaces of the growth chamber. Owing to the improvement of the conditions of heat removal from the growing crystal by changing the form of the crucible the authors managed to increase the rate of pulling large CsI(Tl) crystals to 5.5 mm/h.

References

[1] Zaslavsky, B.G., Automated pulling of large diameter alkaly halide scintillation single crystals from the melt. *Journal of Crystal Growth*, **200**, pp. 476–482, 1999.

[2] Goriletsky, V.I., Nemenov, V.A., Protsenko, V.G., Radkevich, A.V., & Eidelman, L.G. Automated pulling of large alkaly halide single crystals. *Journal of Crystal Growth*, **52**, pp. 509 – 513, 1981.

[3] Kreit, F., & Black, W.Z., *Basic heat transfer*, Harper and Row Publ., New York, pp. 316–320, 1980