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Monitoring of thermal fields on surface of alkali halide single crystals grown from the melt

O.Ts.Sidletskiy, V.I.Goriletsky, B.V.Grinyov, V.I.Sumin, O.V.Sizov, M.N.Tymoshenko

Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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Experimental data on brightness temperature distribution on the upper butt surface of large alkali-halide single crystals grown from the melt using automated semi-continuous method were obtained for the first time using radiation thermometry. It has been shown that different thickness of condensate deposited on the crystal surface from the vapor phase of the melt becomes a cause of significant mistakes at non-contact measurements. Crystal surface emissivity value and minimal thickness of the condensate has been determined experimentally allowing one to obtain correct temperature values when monitoring the ingot surface using infrared thermometer.

Впервые бесконтактным способом на различных стадиях роста получены экспериментальные данные по распределению яркостной температуры на верхней торцевой поверхности выращиваемых из расплава крупногабаритных щелочногалоидных монокристаллов автоматизированным полунепрерывным методом. Показано, что различная толщина конденсата, осаждаемого на поверхность кристалла из газовой фазы расплава, является причиной значительных ошибок при измерении температуры бесконтактным методом. Экспериментально определены величины излучательной способности исследуемой поверхности кристалла и минимальная толщина конденсата, позволяющие при детектировании поверхности слитка ИК-термометром получать корректные результаты.

Alkali-halide crystals (AHC) relate to the group of artificial single crystals, which are successfully used in modern materials science. They are more plastic than silicon and germanium, possess a sufficiently smaller thermal conductivity and by an order of magnitude greater coefficient of thermal expansion. Thus, they have rather bad combination of physical properties determining an influence of thermal stresses on the growing crystal and, consequently, formation of structural defects.

This fact creates many obstacles when growing large AHC. Some of them have been solved by the authors who worked out a one of the first automated semi-continuous (ASC) method modifications in the world [1–4], applying melt feeding by the raw material. Currently, several generations of "ROST" type growth setups [5, 6] work in industry allowing one to obtain single crystals of diameter up to 600 mm and weight up to 500 kg (ASC method is a modification of Kouropoulos growth with elements of Czochralsky method.).

A low vapour pressure of AHC is one of the main difficulties of experimental and theoretical studies of their growth process. Evaporating melt components form a condensate cover on the butt and side crystal surfaces. Gaseous phase deposition rate and, consequently, condensate cover thickness are functions of time and temperature at certain pressure and free melt square (F_L) between the crystal and crucible. The bigger crystal diameter, the smaller F_L

(growing crystal gradually overlaps a part of the free melt surface). On the axial growth stage, a non-uniform condensate layer deposits on the side crystal surface.

Other obstacles in experimental studies are a high hygroscopicity of majority of AHC requiring hermetic sealing and solving a series of engineering tasks at rotation of both the crystal and crucible.

Due to the abovementioned, a very small amount of information concerning thermal fields inside the growth furnace for both Kouropoulos method and its modifications and Czochralsky growth is known. Herein, there are many works on theoretical calculations of thermal fields and stresses, and computer modeling of thermal transfer in melts and growing ingots of Si and Ge [7–9], which are, unlike AHC, not covered with condensate, so, evidently, possess another picture of thermal fields in furnace.

The aim of this paper is development of the non-contact temperature measurements method, as well as obtaining of brightness temperature distribution on the upper butt of the ingot at different stages of the growth using this method. The data obtained are an initial stage in determination of full picture of heat transfer processes between the crystal, melt and furnace walls. The results of the measurements are valuable data for numerical modeling of heat transfer in the system. They open possibilities for infrared thermometers utilization in automated growth control system in order to optimize the technology of production of large alkali-halide crystals with improved structure and scintillation properties.

A one of appropriate methods of temperature studies in such conditions is non-contact measurements based on monitoring of infrared radiation emitted by heated objects [10–12]. For this purpose a Raytek Marathon MA2SC infrared thermometer (pyrometer) were chosen (working wavelength 1.6 μm, range of measured temperatures — 350–2000°C) with accuracy not worse than 0.3 % from the registered value. Measured data being transferred to PC and utilized using a Raytek Multidrop software.

Infrared pyrometry is used in temperature measurements of bodies that are opaque in IR region or have a known absorption value at the pyrometer working wavelength. It is known that CsI(Na) single crystals possess a high transmittance in IR band [13], so, direct pyrometric measurements inside these crystals are impossible.

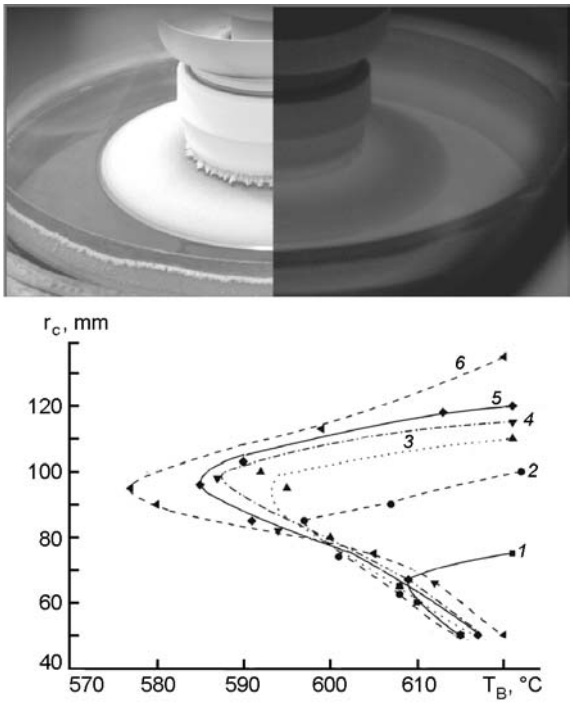

Fig. 1. Brightness temperature distribution on the upper butt of CsI(Na) crystal on the radial growth stage: *1* — crystal radius 75 mm, *2* — 100 mm, *3* — 110 mm, *4* — 115 mm, *5* — 120 mm, *6* — 135 mm. Above — photos of the upper butt of *t* growing crystal with illumination from outside (left part) and without it (right side).

To measure crystal surface temperature, it must be opaque to radiation at the pyrometer working wavelength (1.6 μm). Due to the fact that determination of a condensate layer transmission on the ingot surface is impossible at this stage, quartz glasses were placed in the growth furnace, and condensate layer of different thickness being deposited upon them. Measurements of transmission of theses layers (Hitachi 330 spectrophotometer) show that it transmits less than 1 % of radiation at the 1.6 μm wavelengths at layer thickness not less than 200 μm, i.e., in such conditions we measure real but not brightness temperature. In agreement with our observations, a majority of the crystal surface fulfill these requirements (see photo Fig. 1), except the region of 1–2 cm width (independently on crystal radius and length) near the crystallization front and, on some ingots (at higher growth rates this region exists, at smaller rates, presumably, this region "overgrows"), near the seed on the upper butt of crystal, below the hotwell (Fig. 2, position 10).

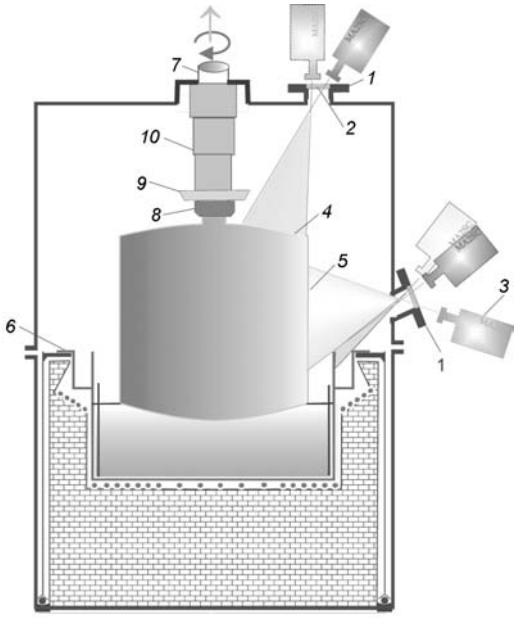

Fig. 2. Scheme of the experiment: *1* — illuminators, *2* — quartz window, *3* — pyrometer, butt (*4*) and side (*5*) studied surfaces, *6* — rotating crucible, *7* — rotating crystal holder rod, *8* — seed coupling nut, *9* — telescopic shield, *10* — hot well.

Condensate cover is an undesirable factor accompanying ingot growth. At the same time, this opaque cover is necessary at infrared thermometers utilization. On a crystal surface with less than 200 μm sublimate layer thickness, some kind of brightness temperature is measured which is affected by temperature of the melt and crucible (due to the high transparency of the crystal and radiative heat transfer). Determination of absolute temperature in this case is a troublesome problem and was not carried out in this paper.

Correct determination of emissivity ε accounting for radiation of external objects is the most important stage in pyrometric measurements. Emissivity values for different materials in handbooks [10–12, 14] (for CsI(Na), unfortunately, such data are absent) can serve only as checkpoint and strongly depend on the surface morphology, geometry of the experiment, current temperature value, working wavelength, etc.

Under the circumstances it was necessary to determine ε of the condensate cover on a CsI(Na) crystal. For this purpose we used methods of comparison of temperatures obtained with pyrometer and thermocouple, and calibration by the crystal melting temperature. But the main tool was a calibration using cavities as blackbody models [10, 14]. To create such cavities we drilled a series of holes with depth more than 6 times larger than their diameter. Walls of the every hole we covered with graphite dust to make them opaque. Then, the ingot being placed inside the growth furnace, heated up to the melting temperature, and ε value being measured.

Using these methods we determined the emissivity value for CsI(Na) condensate as 0.91. It is important to emphasize that this value is correct for the given geometry of experiment, inside the "ROST" type growth furnace that itself is a cavity, i.e., a rather good blackbody model. In other words, ε values for condensate cover situated outside the furnace, evidently, would be sufficiently lower.

Sighting on the object studied in "ROST" type units (Fig. *2*) was conducted through the side and upper removable quartz windows (*2*) (four illuminators in the growth furnace (*2* on the side and *2* above) are designed for control above the growth process and for growing crystal illumination from the outside) with transparency 89.5 % at the wavelength 1.6 μm. Minimal diameter of the measured spot on the ingot surface is 2.3 mm. The distance between the measured object and pyrometer lens can be varied from 650 mm till infinity. As one can see in Fig. 2, monitoring of the upper crystal edge (*4*) using a pyrometer (*3*) can be done both from the top and sideways.

Temperature measurements on the side surface of the ingot (*5*), platinum crucible (*6*), crystal holder rod (*7*), seed coupling nut (*8*), telescopic shield (*9*), hot well (*10*) should be carried out using the side illuminators.

Simultaneously, we made photos of the object in "own" light (radiation of the heated ingot, melt, and crucible elements) and with illumination from outside.

Monitoring of thermal fields on the surface of large CsI(Na) crystals were carried out (Fig. 1). One can see that on the radial growth stage the brightness temperature distribution on the upper butt of the crystals is nonlinear with sharp minimum. Herein, as the crystal diameter increases, the minimum on the dependence of temperature vs. crystal radius deposes closer to the crystal edge and stabilizes at $R = 0.7$–$0.75R_{cr}$. At crystal diameter 240 mm the brightness temperature in this region decreases at 35°C (Fig. 1, curve 5). On the photo (Fig. 3, at the upper left) one can see that in this region the condensate layer is

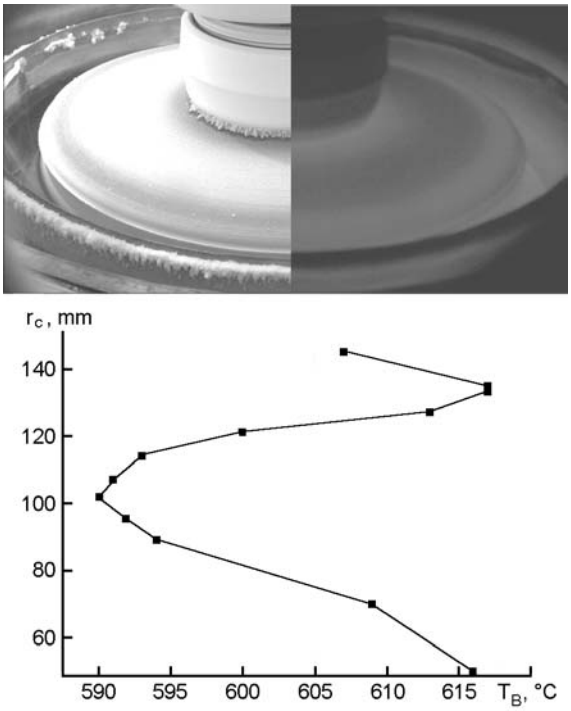

Fig. 3. Below — brightness temperature distribution on the upper butt of CsI(Na) crystal after the end of the radial growth stage. Above — photo of the upper butt with illumination from outside (left part) and without it (right side).

the most thick, providing the best isolation from the thermal radiation (Fig. 3, at the upper right) emitted from within the crystal.

At the same time, ingot surface brightness temperature near the seed remains almost constant and close to the melting one during the entire radial growth stage. This effect, in our opinion, is connected with the several factors. As we mentioned above, the basic role is played by a small thickness of the heat insulating condensate cover on the ingot surface. In this case, pyrometer monitors the radiation not only from the spot on the ingot surface, but from the melt and heated crucible elements behind the spot. Moreover, existence of this overheated region can be connected with reflection of the radiation from the hot well above the crystal (see Fig. 1, and Fig. 2, position *10*). Other factors are not excluded too.

It is worth to pay attention on the visual correspondence between the temperature data and the qualitative picture on the photos obtained from the opposite sides: from the illuminator side (left side of the photo, with outside illumination) and from the

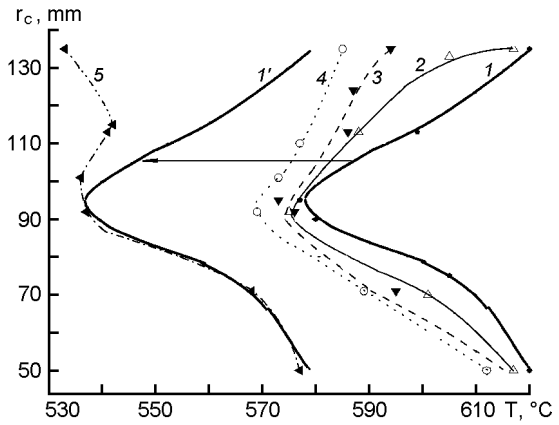

Fig. 4. Brightness temperature distribution on the upper butt of CsI(Na) crystal on the axial growth stage: *1* — end of radial growth stage, *2* — crystal height 5 mm; *2* — 10 mm, *3* — 20 mm, *4* — 125 mm; *1′* — curve *1* superposed with curve *2* at smaller radii.

melt side (right side of the photo, glow of the heated bodies in the furnace without outside illumination, it seems to us, the picture without illumination will be similar from the both sides of the crystal butt surface). It is seen that they qualitatively repeat the general picture of the heat transport through the upper butt of the crystal.

On the axial growth stage (Fig. 4) a general decrease of upper butt temperature reflecting a presence of axial temperature gradient inside the crystal is observed. Axial gradient value increases after emergence of the crystal upper edge from the crucible. It is connected with decrease in thermal radiation intensity from the side crucible walls, and with increase of heat transfer from the crystal surface to the cold walls of the growth furnace. This fact is confirmed by the qualitative changes in $T(R)$ curve shape in Fig. 4 and by formation of the "cold" region on the very edge of the crystal. This effect can be easily demonstrated if to compare the shape of the curve 1′ (shifted curve 1, corresponding to the end of the axial growth stage) and curve *2*. One can see that the difference in temperatures between these curves reaches 45°C on the very edge of the upper butt.

Accounting for our preliminary evaluations, at growth rate 4 mm/h, condensate layer of hundreds microns thickness deposits on the side crystal surface, e.g., layer with thickness several times greater than the minimal necessary one.

Thus, procedure has been developed allowing one to carry out a non-contact moni-

toring of heat transfer processes between the melt, growing crystal surface, and environment inside the growth furnace on the different growth stages. Experimental results on temperature distribution on upper butt of large CsI(Na) single crystals during their growth were obtained. Emissivity value of the studied surface and minimal required condensate layer thickness have been determined allowing one to obtain real thermodynamic temperature values at monitoring the ingot surface with infrared thermometer. Analyzing the obtained results, three stages of condensate formation can be noted: logically, temperature of the upper crystal butt must decrease with R. In reality, the situation sufficiently differs from crystal to crystal. If to watch on the upper butt after the end of radial growth stage (see Fig. 3, left photo), one can see that crystal surface near the seed remains semitransparent, though this part of surface was formed earlier. Then, condensate thickness increases with R, remains constant in the range $R = 0.3–0.85R_{cr}$, and smoothly increases closer to the crystal edge (condensate layer thickness, other conditions being equal, is determined by the radial growth rate). Data of temperature measurements qualitatively (see Fig. 3) confirm photo observations. Second stage of the condensate formation is observed at $R_{cr} > 0.85$ till the start of the axial growth stage. Then, free melt square becomes constant, melt retreats from the upper crystal edge, and condensate thickness not changes there. On the axial growth stage condensate thickness on the side surface distributes almost uniformly excluding a small region adjoining the crystallization front.

References

1. V.I.Goriletsky, A.V.Radkevich, I.V.Smushkov, L.G.Eidelman, Author Sertificate USSR 374902 (1969).
2. V.I.Goriletsky, V.A.Nemenov, V.G.Protsenko et al., *J. Cryst. Growth*, **52**, 509 (1981).
3. L.G.Eidelman, V.I.Goriletsky, V.A.Nemenov et al., *Crystal. Res. and Technol.*, **20**, 167 (1985).
4. L.G.Eidelman, V.I.Goriletsky, V.G.Protsenko et al., *J. Cryst. Growth*, **128**, 1059 (1993).
5. V.I.Goriletsky, S.K.Bondarenko, *J. Mat. Sci. &Ing. A*, **288**, 169 (2000).
6. V.I.Goriletsky, *Izvestiya VUZ*, Fizika, **38** (2000).
7. The Software of Bulk Crystal Growth Simulation, FEMAG Soft SA, Louvain-La-Neuve, Belgium (http://www.femagsoft.com).
8. CrysVun++, SHTAMAS3D, Crystal Growth Lab, University of Enlargen, Germany (www6.ww.uni-erlangen.de/cgi/downloads/ Manual).
9. CGSim, Flow Module, Module "Defects", STR Corp. (USA, Germany), Soft Impact (St.Petersburg, Russia (www.softimpact.ru)).
10. A.E.Sheyndlin, Radiative Properties of Solid Materials, Energiya, Moscow (1974) [in Russian].
11. O.A.Gerashchenko, Temperature Measurements, Naukova Dumka, Kiev (1989) [in Russian].
12. Transaction in Measurement and Control, v.1., Non-contact Temperature Measurements, Putman Publishing Company and OMEGA Press LLC, New-York (1998).
13. E.M.Voronova, B.N.Grechushnikov, G.I.Distler, I.P.Petrov, Optical Materials for Infrared Techniques, Nauka, Moscow (1965) [in Russian].
14. The Pyrometer Handbook, IMPAC Electronic GmbH (1999).

Моніторинг теплових полів на поверхні лужногалоїдних монокристалів, вирощуваних із розплаву

О.Ц.Сідлецький, В.І.Горилецький, Б.В.Гриньов, В.І.Сумін, О.В.Сизов, М.М.Тимошенко

Вперше безконтактним способом на різних стадіях вирощування отримано експериментальні дані щодо розподілу яскравистних температур на верхньому торці поверхні великогабаритних лужногалоїдних кристалів, вирощуваних із розплаву автоматизованим напівбезперервним методом. Показано, що різна кількість конденсату, що осаджується на поверхню кристала із газової фази розплаву, є причиною значних похибок при безконтактних вимірюваннях. Величини випромінювальної здатності та мінімальна товщина конденсату визначено експериментально, що дозволяє отримувати коректні значення температури при моніторингу поверхні зливку за допомогою інфрачервоного пірометра.