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Changes in crystallization conditions when growing large single crystals at melt feeding

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It has been shown that the dopant concentration fluctuates by volume of different single crystals with the same diameter due to the changes in crystallization front volume. It has been established that the cause of this effect is radiative heat transport from the crystal to the crucible upper part and, then, local changes in thermal conditions near crystallization front. It has been shown that minimal side heater temperature needed for melting of the raw material depends on the ingot length at the moment. An algorithm of the process control is developed providing temperature stabilization in the peripherical circular vessel at the axial growth stage and allowing one to obtain single crystals with uniform dopant distribution with good reproducibility.

Показано, что основной причиной колебания концентрации активатора в объеме разных монокристаллов одинакового диаметра является изменение объема фронта кристаллизации. Установлено, что причиной, приводящей к данному эффекту, является лучистый транспорт тепла от кристалла к элементам верхней части тигля и последующее локальное изменение тепловых условий вблизи фронта кристаллизации. Выявлено, что минимально необходимая температура бокового нагревателя, обеспечивающая плавление сырья, различна при разной длине слитка. Разработан алгоритм управления процессом выращивания, предусматривающий стабилизацию температуры в периферической кольцевой емкости на этапе роста слитка в длину, позволяющий воспроизводимо получать монокристаллы с равномерным распределением активатора.

Studies of the grown large-size CsI(Tl) and NaI(Tl) scintillation single crystals with the same diameter show the different dopant content (10–15 %) in the ingots from experiment to experiment. In order to find out the causes of the effect observed, the crystallization front (CF) transformations were studied in dependence on the crystal diameter at different growth stages. Under the CF we mean the crystal part immersed into the melt.

The experiments were carried out at the first and second generation of "ROST" type vacuum-compression units [1]. CsI(Tl) and CsI(Na) single crystals of 270–320 mm diameter in the crucible of 375 mm diameter, and CsI(Tl) and NaI(Tl) crystals of 480–540 mm diameter in the crucible of 600 mm diameter were obtained under automated control of the growth process. Melt feeding was carried out by the raw material alternately from the accessory hopes, thus, sustaining the constant melt level in the crucible. The growth process control was executed using a feedback circuit of the bottom heater temperature T_{bot} based on the current information about the melt level in the crucible [2].

Bottom heater (1) in "ROST" type units (Fig. 1) is the main one providing controlled crystallization of melt on a seed. Its contribution into melt temperature is decisive, hence, measured changes in T_{bot} mainly mirrors the changes in heat removal from the crystal. The main task of the bottom

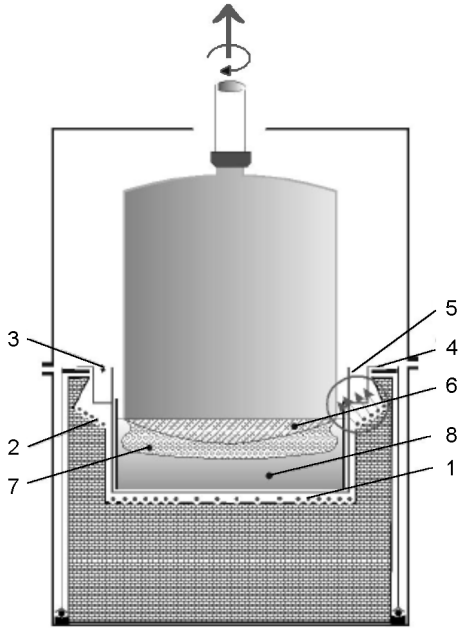

Fig. 1. Scheme of the large alkali halide single crystals growth using "ROST" type unit, with and without bottom heater temperature correction: *1* — side heater, *2* — bottom heater, *3* — crucible peripherical circular vessel, *4*, *5* — crucible vertical wall, *6* — crystallization front when the side heater temperature correction is applied, *7* — crystallization front without the side heater temperature correction, *8* — melt. The region of the side heater influence is shown by arrows and circles.

heater 2 is melting of the raw material on the bottom of the peripherical circular vessel 3 of the rotated crucible 4, which is separated from the crystal by the vertical wall 5. Herewith, crucible construction itself decreases the T_{bot} influence to minimum. More precisely, the crucible construction itself reduces to minimum the influence of temperature field near the side heater on total temperature field of the crucible, and even of the furnace (the confined overheated region of the crucible, crystal and melt are denoted by the arrows, Fig. 1).

Conscious limitation of T_{bot} influence (only for raw material melting in the peripherical circular vessel) was found to be successful as well for salvation of the main task of crystallization process — formation of the sufficient temperature gradient in melt and, consequently, formation of the convex CF.

The temperature field character in melt determines convective fluxes in it, which, in turn, take part in CF formation, is determined by the ratio of the crystal diameter d to the crucible diameter D. The formed convex front at $d/D = 0.8$ becomes almost plane at $d/D = 0.5$, and occupies significant volume at $d/D = 0.9$ as were noted in [3]. Accounting for these conditions and considerations of the best promising reliability of the growth process, the optimal d/D value not exceeds 0.8 for these setups. In this case the observed non-significant increase in the CF volume (the left crystal in Fig. 2) is compensated by the programmed decrease of the dopant concentration in the feeding salt at the crystal elongation. For second generation units this correlation can be increased up to $d/D = 0.85$.

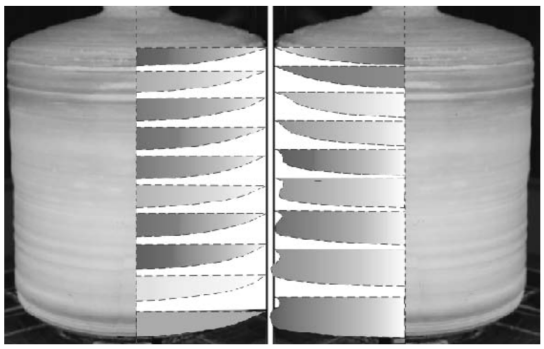

Fig. 2. Scheme of transformations in CF volumes (shown by dashed lines and shaded) when growing single crystals with the side heater temperature correction (on the left in the right figure) and without the correction (on the right in the left figure).

When trying to grow single crystals of bigger diameter at $d/D > 0.83$ the sufficient changes in CF volume at crystal elongation are observed. The gap between the crystal and crucible walls influences the evaporation rate of the volatile dopant (such as thallium iodine). Such process is accompanied by the changes in CF shape (Fig. 1, position 6: Fig. 2, the right crystal; Fig. 3, curve 1). In the issue, this can result in bigger CF diameter in compare to the crystal diameter above the melt surface. Due to the melt volume decrease during the process this should affect the corresponding dopant concentration increase in the crystal in the end of the growth process (Fig. 3).

Manifestation of such effect in the same time promotes the emergence of the sequential chain of negative factors, such as a disturbance of laminarity of convective fluxes in melt due to decrease of the real melt column height in the crucible with the corresponding loss of CF smoothness (Fig. 4). Bigger CF decreases the ratio of real melt column height to diameter.

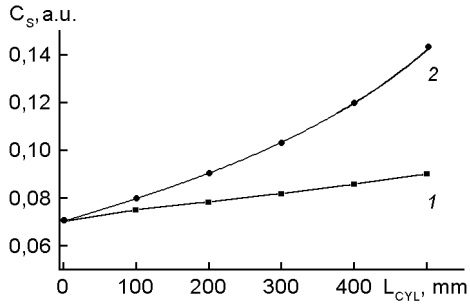

Fig. 3. Dopant content in crystal vs. crystal length when the melt volume decreases in the end of growth by 20 % (curve *1*) and by 50 % (curve *2*).

On the other hand, such process is accompanied (as the ingot length rises) by the decrease of axial temperature gradient in a crystal part near the CF and by an increase of evaporation rate of the volatile dopant in the circular vessel. The both effects are connected with increase in circular vessel temperature.

Probably, the fact is that the ingot itself is an isotropic semitransparent medium performing a radiative heat transport from the heaters and melt in the radial direction to the water cooling internal walls of the growth furnace. The external body of the furnace consists of double shell with water between. When the crystal cylindrical surface becomes closer to the crucible walls at d/D = 0.83, this effect is more noticeable. The internal vertical wall (Fig. 1, position 5) of the peripherical circular vessel is subjected to thermal radiation of the crystal. Receiving a thermal flux increasing with the height of the cylindrical part of the crystal (L_{cyl}) the vertical wall, in turn, increases temperature of the entire circular vessel and of a melt surface layer. Evidently, these changes in conditions influence the CF shape of the growing crystal (Fig. 2, the right crystal, and Fig. 3, curve 2). When growing doped crystals, this, in turn, leads to changes in dopant concentration in the crystal and, correspondingly, in the melt.

Scheme of such changes in CF shape is well observed in the end of growing (Fig. 1) in compare to another crystal that was growing at T_{bot} being held permanently at minimal value. It should be noted that temperature deviation on the bottom of the peripherical circular vessel can be identified visually (within the accuracy ±2°C) comparing the bottom colour with that of the melt near the meniscus between the crystal and

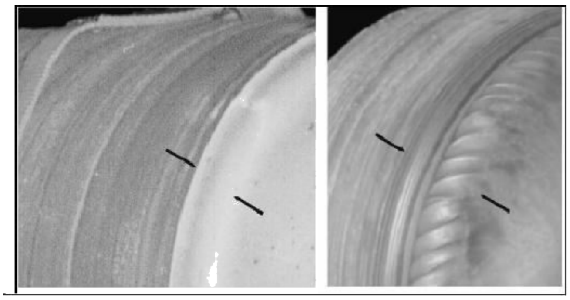

Fig. 4. Real shapes of crystallization fronts (shown by arrows) in NaI(Tl) ingots of 520 mm dia. observed when growing single crystals of limiting diameter with the temperature correction (on the left) and without one (on the right).

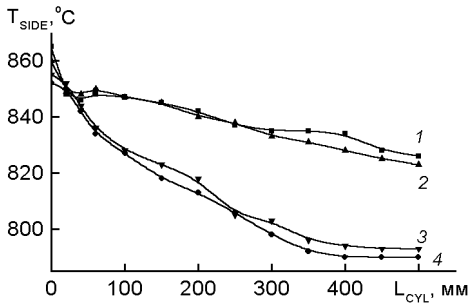

Fig. 5. Side heater temperature vs. length of CsI(Na) ingots of 270 mm dia. (curves *1*, *2*), and CsI(Na) and CsI(Tl) ones of 320 mm dia. (curves *3*, *4*).

melt. Temperature near the crystal and, consequently, a melt colour remain almost invariable during the growth.

The ideology of growth of limiting diameter crystals is the following. The initial T_{bot} value is being set at 20–30°C higher than the temperature required for salt melting in the circular vessel at feeding. At the radial growth stage T_{bot} is being decreased smoothly as the crystal radius increases in order to T_{bot} would be approximately as minimal as necessary at the initial moment of the growth. The optimal T_{bot} value and the rate of its decrease were determined experimentally. Further, when the crystal elongates and the thermal flux from the melt to the circular vessel increases, T_{bot} is being continued to decrease (see Fig. 5) proportionally to the crystal length. In other words, as can be seen from the experiment (Fig. 5), the minimal necessary temperature T_{bot} providing the raw material melting in the circular vessel on the axial growth stage were found to be different at the different lengths of the ingot, as well as for the crystals with the different diameters (the

curves *1*, *2* correspond to the diameter 270 mm, the curves *3*, *4* were obtained for the crystals of 320 mm diameter). As one can see, in the first case the value of the circular vessel overheat compensation is 39°C, the one in the second case is 71°C. This fact itself is very notable and contains additional information about kinetics of the heat removal. Similar dependences were obtained for the crystals of 520 mm diameter.

Thus, the following conclusions can be made:

— according to expectations, the main cause of the dopant fluctuations by volume of the crystals of different diameter is the changes in CF volume at the different current T_{side} values;

— the educed effect exhibits under local changes in thermal conditions near the CF as a result of heat exchange between the cylindrical part of the crystal (rising during the growing) and the upper crucible part, in particular, the peripherical circular vessel;

— the improved algorithm of the growth process control has been developed allowing one to account in total thermal balance for increasing additional overheat of the peripherical circular vessel by the growing crystal. This overheat, in turn, leads to non-significant changes of the CF shape of limiting diameter ingots and, correspondingly, to the reproducible dopant distribution along their lengths.

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Зміна умов кристалізації при вирощуванні великогабаритних монокристалів з підживленням розплаву

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Показано, що основною причиною коливання концентрації активатора в об′ємі різних монокристалів однакового діаметра, є зміна об′єму фронту кристалізації. Встановлено, що причиною, яка призводить до даного ефекту, є променистий транспорт тепла від кристала до елементів верхньої частини тигля і наступна локальна зміна теплових умов поблизу фронту кристалізації. Виявлено, що мінімально необхідна температура бічного нагрівача, що забезпечує плавлення сировини при різній довжині злитка, виявляється різною. Розроблено алгоритм керування процесом вирощування, що передбачає стабілізацію температури у периферичній кільцевій ємності на етапі зростання злитка в довжину, що дозволяє відтворювано одержувати монокристали з рівномірним розподілом активатора.