

The influence of gaseous atmosphere composition on heat transfer at pulling of CsI crystals

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Influence of some polyatomic gases (H_2O , CO_2 , C_2H_5OH) having high heat conductivity and heat capacity as well as some inert gases (He, Ar) being used traditionally in crystal growing on the heat transfer has been studied. It was shown that the gaseous atmosphere composition in the furnace and the state of growing crystal surface are the key factors in the heat transfer and growth process stability. Water and ethanol vapors introduced intentionally into the furnace atmosphere in small amounts do not deteriorate crystal properties while influencing heavily the heat transfer. Introduction of helium into the growing furnace atmosphere makes the largest impact on convective heat transfer during the crystal growing process forcing the control system to raise intensively the of controlling heater temperature in order to keep back the increasing mass growth rate (or diameter) of the crystal. Helium introduction into the furnace atmosphere seems to be an effective way to improve the heat stability of the growing process.

Изучено влияние на теплоперенос некоторых полиатомных газов (H_2O , CO_2 , C_2H_5OH), обладающих высокой теплопроводностью и теплоемкостью, а также инертных газов (He, Ar), традиционно используемых при выращивании кристаллов. Показано, что определяющее влияние на теплоперенос и на устойчивость процесса роста оказывает состав газовой атмосферы в печи и состояние поверхности растущего кристалла. Пары воды, этанола, преднамеренно введенные в атмосферу печи в небольших количествах, не ухудшают характеристик кристалла и оказывают сильное влияние на теплоперенос. Введение гелия в атмосферу ростовой камеры оказывает наибольшее влияние на конвективный теплоперенос в процессе роста кристалла, вынуждая систему управления интенсивно повышать температуру управляющего нагревателя для сдерживания увеличивающейся массовой скорости роста (или диаметра) кристалла. Введение гелия в атмосферу печи представляется эффективным приемом для повышения тепловой устойчивости процесса роста.

At automated pulling of large-sized scintillation single crystals CsI(Tl) and NaI(Tl), the radiative heat removal from the growing crystal is often impeded. The cause lies in the fact that a sublimate layer is formed on the surface of the crystal upper part (Fig. 1,b). Being an effective reflector, this layer returns radiation from the crucible through the transparent crystal back to the

crucible. The crystal pulling speed in this case is 1.5 to 2 mm/h and it is impossible to increase it. Besides, the solidifying interface acquires a complex shape due to local superheated areas of the crucible and may contain twists, thus resulting in origination of gas-filled cavities. The sublimate layer often is so thick that heat transfer becomes deteriorated sharply already on the radial

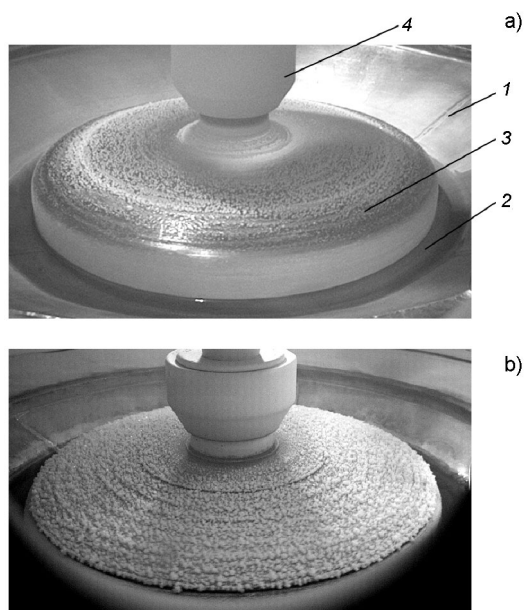


Fig. 1. Examples of surface state at radial growth of CsI(Tl) crystals: without sublimates (a); thick layer of sublimates on the surface (b). 1, crucible; 2, melt; 3, crystal; 4, crystal holder.

growth stage and it is impossible to continue the growth in height. In this situation, an augmentation of convective component of heat transfer from the crystal is the only way to provide the preset growth rate and to increase the growing furnace productivity. The intensity of convective heat transfer from the crystal should depend on the atmosphere composition and especially on partial pressure of components having high heat transmission and heat capacity. To date, the influence of various gases on the heat transmission at crystal growing remains almost unstudied. In the experiments on influence of gases on crystal growth thermal regimes, we used an automated unit for crystal pulling from the melt in the variable cross-section crucible with replenishment by melted raw material [1]. In this method, a system using the melt flow sensor with electric contact probe (Fig. 2) controls the crystal diameter. The probe 1 controls continuously the melt consumption for crystallization at a dosed discrete replenishment and provides the feedback with base heater 2 temperature. The corrective actions of the control system (blocks 3 and 4) on the heater temperature occur after each replenishment and these actions are directed to provide the time-constant melt consumption. The crystal diameter or mass growth rate at such mode of control is kept

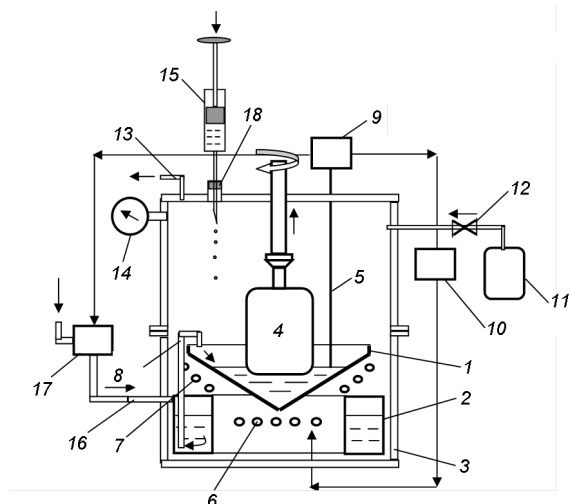


Fig. 2. Scheme of unit for crystal growing [1] and investigation of gaseous atmosphere influence on heat transfer: 1, crucible; 2, feeder; 3, furnace body; 4, crystal; 5, probe; 6, base heater; 7, side heater; 8, transportation tube; 9, feeder control block; 10, temperature correction block; 11, gas vessel; 12, valve; 13, evacuation line; 14, pressure/vacuum gauge; 15, syringe for liquid introduction; 16, gas introduction line to the feeder; 17, gas charging valve; 18, rubber membrane.

with high accuracy up to 0.5 % at crystal diameters of 200 to 400 mm. Total value of control heater temperature change Δt and its behavior in time τ or depending on the growing crystal length may provide a very accurate and unequivocal information concerning alterations of the process thermal stability of heat transfer conditions.

It has been shown before [2] that the presence of oxygen-containing admixtures (OA) absorbing in IR-area, such as CO_3^{2-} , SO_4^{2-} , OH^- , in amounts of $1 \cdot 10^{-4}$ to $3 \cdot 10^{-4}$ mass %, does not deteriorate the crystal scintillation characteristics while improving considerably the pulling process heat resistance. In contrast, the presence of sublimates causes reflection of thermal radiation from the sublimates and its return through the transparent phase boundary to the crucible base, so that the effect of heat transfer augmentation due to OA in crystal is totally or partially compensated. How can we augment the heat removal from the growing crystal? The first way is to prevent the sublimates formation on crystal surface or to reduce it considerably by blasting the crystal top with a gentle stream of inert gas, as it is recommended in [3]. The second way is to increase the inert gas pressure in the fur-

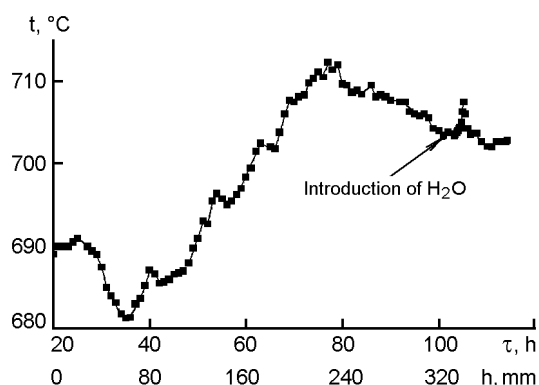


Fig. 3. Water vapor influence on the base heater temperature. Arrow shows the moment of water introduction.

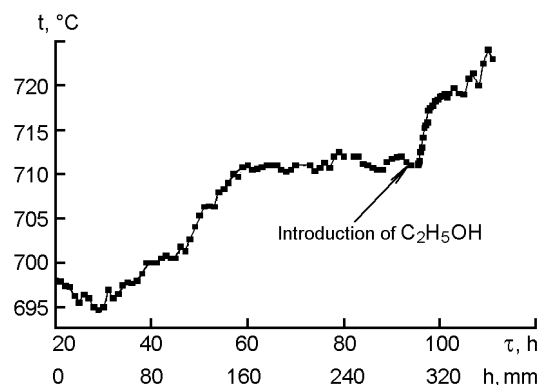


Fig. 4. Ethanol vapor influence on the base heater temperature. Arrow shows the moment of ethanol introduction.

nance; however, there is a danger of bubbles formation in crystal. Finally, there is the third way, that seems to be very effective, it consists in the introduction of a gas with high heat conductivity and heat capacity into the furnace. From this standpoint, it is of interest to investigate the influence of some polyatomic gases on heat transfer. In particular, it is interesting to study the water vapor influence, heat capacity of these vapors is two times as high as that of inert gases. Taking into consideration the fact that water and carbon dioxide are the most common admixtures, it is of interest to evaluate their influence not only on the growth thermal regimes but also on scintillation characteristics of crystals.

The experiments consisted essentially in what follows. During the pulling process of a 260 mm diameter CsI(Tl) crystal at Ar working pressure in the furnace 30–40 Torr, when crystal height reached approximately 300 mm, a preset volume of the gas under study was introduced into the furnace in small portions. The gas (H_2O , $\text{C}_2\text{H}_5\text{OH}$, He, H_2 , CO_2) was introduced directly from the gas vessel 11 (Fig. 2) or from other intermediate tank, which had been preliminary evacuated and purged with the gas under study. The amount of introduced gas was monitored additionally using a manovacuummeter 7 indicating the pressure increase. The gas introduction rate was controlled so that the diameter controlling system had the time to respond to thermal disturbances by the base heater temperature auto correction in order to keep crystal diameter within the set limits.

Distilled water and ethanol were introduced as liquids in small portions of 0.2 to 0.5 cm^3 using a medical syringe 15 through

a rubber membrane 16. The total volume of water introduced during 30 min was 2 ml and ethanol, 5 ml. Getting into the furnace, the liquid evaporated quickly and vapors mixed with the furnace atmosphere (argon). The total gas pressure increased only insignificantly due to liquid injection, however, we restored it to the initial value by means of pumping out, thus, isobaric conditions were kept in all the experiments. Taking into consideration the fact that the free volume of the growing vessel was approximately 0.6 m^3 , water vapors partial pressure was about 3 Torr. (or about 10 %). In the experiment with ethanol, its partial pressure was 2.5 Torr (or about 7 %). The results of the experiments are given in Figures 3 through 6.

Water introduction. While introducing each portion of water, we noticed a very familiar effect that occurs when water drops get on an incandescent surface. Small water drops moved randomly on the melt surface and evaporated. We did not observe any signs of stray melt crystallization in the drop evaporation spot. There was no color alteration of gas atmosphere and melt, and this indicates the absence of melt hydrolysis reaction with iodine evolving. The pressure increase in the furnace at introduction of each water portion was insignificant and did not exceed 1 Torr. Almost immediately after injection, the diameter controlling system raised temperature of the control heater. Fig. 3 shows the time dependence of the base heater temperature, $t(\tau)$. The arrow indicates the beginning of water introduction. The total temperature increase was 5 to 6°C, then, after injection termination, the control system restored initial temperature within 1.5 to 2 h. We did not observe any significant diameter change

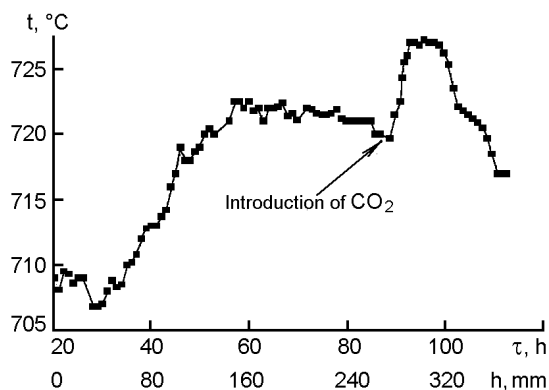


Fig. 5. Carbon dioxide influence on the base heater temperature. Arrow shows the moment of carbonic acid introduction.

at water introduction. The subsequent optical investigation showed that the OA content in the crystal was $< 2 \cdot 10^{-5}$ mass %. The specimens cut from different parts of ingot possessed high spectrometric characteristics. The energy resolution R_{662} measured using the γ -line of ^{137}Cs ($E = 662$ keV) was within limits of 6.2 to 6.5 %.

Ethanol introduction. We supposed that ethanol will influence the growth thermal regime stronger as compared to water, because, in accordance with the gas kinetic theory, ethanol should have a higher heat conductivity due to more complex molecular structure and a greater number of degrees of freedom. At ethanol introduction (total amount 5 ml), there was no effect of drops moving on the surface. Drops of more easily boiling liquid were evaporated before reaching the melt surface. As well as in the previous case, we did not observe any signs of the melt hydrolysis. The control system corrective action on the temperature of base heater in order to keep the diameter within the set limits amounted $+35^\circ\text{C}$ (Fig. 4). Unlike the experiment with water, the heater temperature increase remained till the end of the growing process (during 20 h after the injection). CO_3^{2-} content in the crystal was $< 2 \cdot 10^{-5}$ mass %. The ethanol presence (or its decomposition products) in the atmosphere made no impact on the crystal quality. R_{662} of samples was also within limits of 6.2 to 6.5 %.

CO_2 introduction. The gas was introduced in small portions of 0.5 l and that resulted in pressure increment by no more than 1 Torr. After the exposure during 1–2 min, the pressure restored by pumping. The total introduced amount of CO_2 was 3 l (at $t =$

20°C , $P = 760$ Torr) and that corresponded with the partial pressure in furnace about 4 Torr (10 % of the total pressure). The $t(\tau)$ dependence is shown in Fig. 5. At the outlined trend to the base heater temperature decrease, CO_2 introduction forced the control system increase sharply the temperature (by 7– 10°C) and after stabilization during 5 to 7 h, the temperature began to decrease. 20 hours after the beginning of CO_2 introduction, the temperature was 2– 3°C lower than prior to gas introduction. At carbon dioxide introduction, we also did not observe any external signs of reaction with iodine evolving. Subsequent IR absorption measurements on the crystal samples cut from different parts of ingot showed increase of CO_3^{2-} content in the end part of ingot from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mass % and that might indicate carbon dioxide absorption by the melt resulting in formation of carbonate ions. Mass spectrometric measurements also verify the decrease of CO_2 concentration in the furnace atmosphere. During the last 20 h of growth, the CO_2 content decreased from 2.82 vol % to 2.66 vol %. As to CO_2 influence on spectrometric properties of crystal, those are practically similar to those of crystals grown in pure inert gas atmosphere.

He introduction. The $t(\tau)$ dependence for this case is presented in Fig. 6. Helium influence on the heat transfer is so strong that even if the gas was introduced in small portions (0.2 l during 15 min), the control system did not have time to affect in full measure the base heater temperature in order to keep the preset growth mass rate (or crystal diameter). The introduced 3 l of helium (step 1) resulted in sharp temperature increase of base heater by 35°C . After the crystal diameter was restored, the temperature stabilized and we observed no trend to its decrease. After the additional introduction of 2 l of He (step 2), the temperature increased jump-like again by 20°C and this increase trend remained till the end of growing process. In the picture presented near the plot, the crystal diameter enlargements after He introduction are seen, however the crystal diameter is restored within some time.

H_2 introduction. According to reference data, H_2 possesses the highest thermal capacity (almost by one decimal order higher than water, carbon dioxide, and all inert gases) and high heat conductivity [4]. Due to this reason, we expected that H_2 influ-

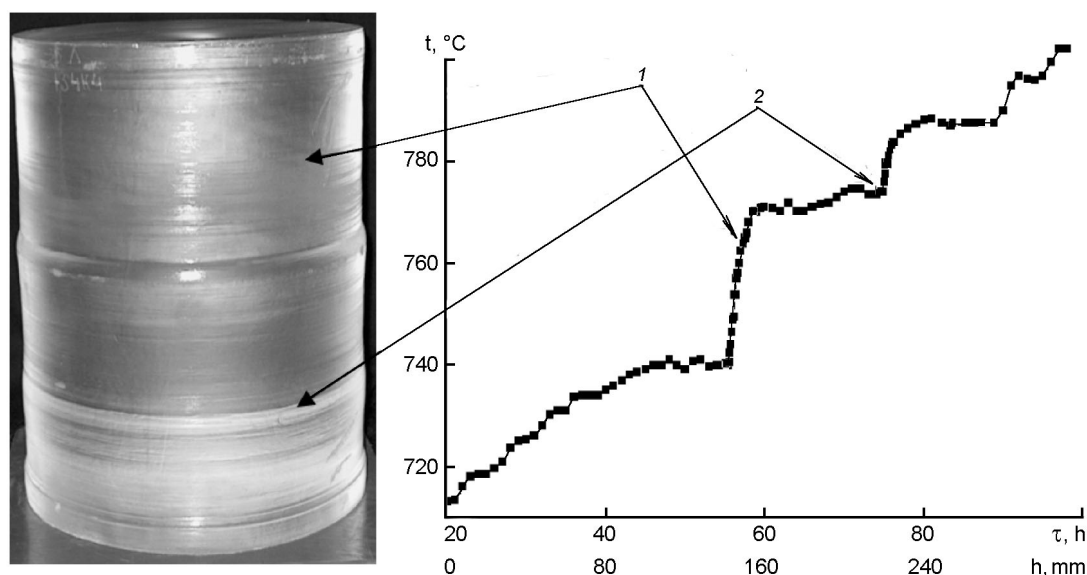


Fig. 6. Helium influence on the base heater temperature. Arrows show the moments of helium introduction.

ence on heat transfer would be the strongest and that is why we introduced gas very carefully, in small portions 0.1 to 0.2 l every 15 min. However, it turned out that H_2 introduction in the amount of 10 l (at $P = 760$ Torr) into the furnace atmosphere had practically no influence on the ordinary $t(\tau)$ relationship. The main reason therefor is apparently the fact that hydrogen possessing high solubility is quickly absorbed by melt, the furnace construction materials and especially by platinum crucible, causing no pressure increase of the furnace atmosphere.

We should mention that when the atmosphere composition in the furnace was changed, thermal disturbances arising in the crystal-melt system in all the experiments were timely compensated by automatic control system and did not cause formation of any visible macro defects in the form of captures and gas bubbles.

In conclusion, water vapors and carbon dioxide introduced intentionally into the furnace atmosphere in small amounts influence considerably the heat transfer and increase the stability of CsI(Tl) scintillation crystal growing process, however, this influence is of a short-term character. The control heater temperature return to the initial values is apparently connected with dissolution of carbon dioxide and water vapors in cesium iodide melt. The absence of oxygen in the furnace atmosphere is a very important condition that provides high scintillation quality of crystals, since otherwise, hydrolysis reactions will run with forma-

tion of hydroxides and carbonates. Hydrogen has to make a similar influence on heat transmission, however, due to its high solubility in melt and in platinum, it is impossible to provide the necessary partial pressure in the furnace atmosphere. Ethanol vapors exert even stronger influence on heat transfer, moreover, this influence remains till the end of growing and does not become weaker in time. Apparently, ethanol itself and its decomposition products (ethylene), in case such thing occurs, are not absorbed by melt and its partial pressure in the atmosphere of furnace remains essentially unchanged.

Helium exerts the strongest influence on convective heat transfer. Its introduction in small portions into furnace (5 to 10 % of the total pressure 30 to 40 Torr) increases significantly thermal stability of growing process. This technique works effectively at large CsI(Tl) and NaI(Tl) crystal growing, when the crystal upper part is coated with sublimate layer and radiation heat transfer becomes hindered. The presence of helium increases the intensity of convective heat transfer and thus allows to keep the preset pulling mass rate and even to increase it.

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Вплив складу газової атмосфери на теплоперенесення при витягуванні кристалів на основі CsI

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Вивчено вплив на теплоперенесення деяких поліатомних газів (H_2O , CO_2 , C_2H_5OH) що мають високу теплопровідність та теплоємність, а також інертних газів (He , Ar), що традиційно використовуються при вирощуванні кристалів. Показано, що визначальний вплив на теплоперенесення і на стійкість процесу росту чинить склад газової атмосфери в печі і стан поверхні кристала що росте. Пари води і етанолу, як навмисно було введено в атмосферу печі в невеликих кількостях, не погіршують характеристик кристала і в значній мірі впливають на теплоперенесення. Введення гелію в атмосферу ростової камери приводить до найбільшого впливу на конвективне теплоперенесення у процесі росту кристала, змушуючи систему управління інтенсивно підвищувати температуру керуючого нагрівача для стримування масової швидкості (або діаметра кристала), що збільшується. Введення гелію в атмосферу печі представляється ефективним прийомом для підвищення теплової стійкості процесу росту.