

INFLUENCE OF POLYATOMIC IMPURITY IONS ON THE GROWTH PROCESS OF ALKALI METAL IODIDE CRYSTALS

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ABSTRACT It has been shown that by introduction of polyatomic impurity ions the combined bands of the oscillation absorption of which partially overlap the region of the Plank radiation one can strongly affect the heat transfer and crystallization conditions. When growing large crystals by the automated method of pulling on a seed with feeding by the melt a positive effect of doping with impurity is achieved at relatively small concentrations of impurity ions which do not change yet the main scintillation characteristics of CsI(Tl) and CsI(Na). A qualitative explanation of the observed effect by the results of measurements of the absorption coefficient at room temperature is given in the present paper.

INTRODUCTION

A fundamental problem of crystal growth is that of heat removal from the crystallization front. It is customarily to differentiate the polar cases of heat transfer [1]: growth of opaque media when heat is removed only at the expense of molecular (phonon) heat conduction and media that are fully transparent to thermal radiation. In the last case a significant role plays radiant energy transfer that strongly depends on the form, size and state of the surfaces of the growing crystal on which reflection and refraction of radiation take place.

Known are the theoretical calculations [2] which demonstrate that even an insignificant increase of the absorption coefficient (k) of the crystal in the region of the maximum of Plank distribution of thermal radiation results in essential changes of heat transfer. One can vary the crystal transparency by introducing impurity that has absorption in the appropriate part of the spectrum. Such obvious solution, to our knowledge, has not been practically implemented so far. The growth of YAG crystals has been shown in [3,4] to have a typical faced character while for the dysprosium-aluminum garnet typical is normal growth and planar crystallization front, the second material being practically opaque in the thermal radiation region. Introduction of dysprosium as an impurity to YAG promotes improvement of crystallization conditions but leads to a loss of its functional properties as a laser material. For a long time just this circumstance (negative effect of impurities) restrained the search for new ways of controlling the growth process by varying transparency of the growing crystal.

EXPERIMENTAL DETAILS

Given in this paper are the data on growth of crystals by a modified Kyropoulos method in a conical crucible with replenishment by the melted raw material. The geometry of the crucible and growing crystal is schematically shown in Fig.1 and a detailed description of the method is given in [5]. Methods of additional purification of melt were used for growing transparent in the IR region crystals [6]. Experimental details are described in [7] for producing CsI(Tl) doped by carbonate and sodium. In this paper we analyze experiments on growing CsI-based scintillation crystals 160 mm

and 250 mm in diameter and to 75 kg in weight in inert gas atmosphere (Ar, pressure – 5-10 Torr). Additional experiments on growing crystal with variation of Ar pressure (5-20 Torr) during the process gave us an arguments to exclude this factor from our consideration.

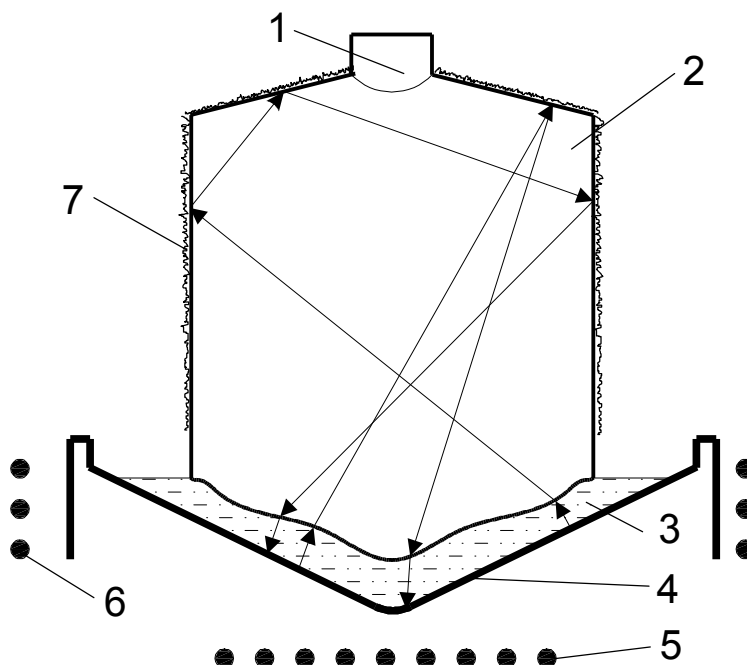


Figure 1. Schematic imagination of growing crystal and crucible. 1 – seed; 2 – crystal; 3 – melt; 4 – conical crucible; 5 – bottom heater; 6 – side heater; 7 - a layer of a diffuse reflector. Arrows show a possible way of photons.

The carbonate impurity is doped into the melt as Cs_2CO_3 or more thermally stable Na_2CO_3 compound. The content of this impurity is determined by the absorption coefficient in the maximum of the band of deformation oscillations at the frequency 880 cm^{-1} [8]. Crystals doped by NO_2^- and NO_3^- ions are grown in nitrogen atmosphere. The content of these impurities is proportional to the absorption coefficient in fundamental bands of its absorption at 1235 and 1360 cm^{-1} , respectively.

RESULTS

The experience in the automated growth of undoped CsI crystals and scintillation $\text{CsI}(\text{CO}_3)$ material showed the following. Temperature regime of processes for growing crystals of the same diameter differ essentially. These differences can be divided on 3 groups:

- Growth in height accompanied by temperature increasing of the bottom heater;
- Growth in height accompanied by temperature decreasing of the bottom heater;
- Temperature of the bottom heater don't change.

Fig.2 shows the data on temperature variation of the bottom heater (control of this heater temperature allows to maintain the diameter of the ingot constant) over the height of the crystal 160 mm in diameter during the growth process. One can see that in case of CsI the current temperature T_i varies relatively weakly as the height and mass of the crystal rise and has a tendency to decrease. Such tendency is dangerous since can lead to the overcooling of melt. The pulling rate in this case was 4 mm/h; to increase the rate the temperature should be decreased but this results in a parasite crystallization on the walls of the crucible. A different situation is observed for $\text{CsI}(\text{CO}_3)$: T_i is

smoothly increased, i.e. at a rate of 4 mm/h the automatics permanently restrains the crystal growth to maintain the diameter constant. This means that the pulling rate can be increased. The crystals grow stably even at a rate of 9 mm/h; with this the behavior of T_i variation is preserved.

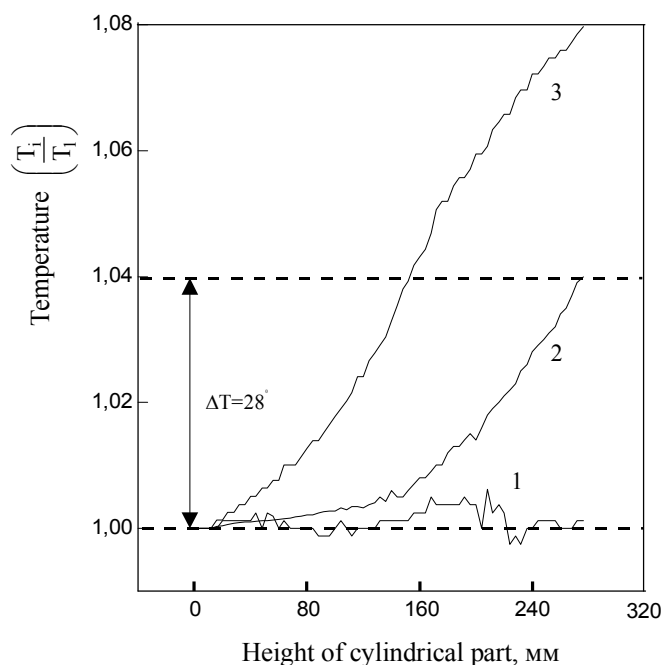


Figure 2. Variation of bottom heater temperature (T_i/T_1) on the stage of growth with constant diameter 160 mm. 1 – pure CsI; 2 – CsI with $\sim 9 \cdot 10^{-5}$ % of CO_3 ; 3 – with $\sim 2 \cdot 10^{-3}$ % of CO_3 .

From the data in Fig.2 one can see that it is convenient to characterize the stability of growth process and possibility of increasing the pulling rate by the parameter $\Delta T = (T_2 - T_1)$, where T_2 is the temperature of the bottom heater at the final stage of growth (we give T_2 for the crystal height 330 mm) and T_1 is a steady-state temperature which corresponds to the initial stage of crystal growth with a constant diameter. The data on growing CsI(Tl) ingots 250 mm in diameter are summarized in Table 1. One can see from these data that there is a clear correlation between ΔT and content of carbonate in the crystal. If $k_{880} > 5 \cdot 10^{-3} \text{ cm}^{-1}$ then $\Delta T > 10^\circ$ and in this case the crystallization front is always convex; growth proceeds stably in the automatic regime, the accuracy of maintaining the diameter is $\pm 1\%$.

The same results were obtained for CsI(Na) grown in N_2 atmosphere and containing NO_2^- and NO_3^- ions. In table 1 (line 5, 9, 11) we represent data for mixed doping of CsI(Tl). It's clear, that the ΔT value is higher than the expected one, which would correspond to the concrete carbonate content.

DISCUSSION

Let us consider the situation when T_i has a tendency to decrease. For CsI crystals that are transparent in the wavelength range beginning from 0.24 and till 55 μm the difference of ΔT makes the value from -12 to $+3^\circ\text{C}$. The particular value of ΔT strongly depends on the state of the growing crystal surfaces. Usually they are covered by a film of the main material which creates a layer of a varying thickness of rather efficient diffuse reflector. The absorption coefficient of the purest CsI crystals is comparatively small in the IR region. The measurements give the value $k \sim 5 \cdot 10^{-3} \text{ cm}^{-1}$ for the wavelength range 0.6-2 μm (spectrophotometry) and $\sim 1.0 \cdot 10^{-5} \text{ cm}^{-1}$ for the wavelengths 5.5 and

10.6 μm (laser calorimetry [9,10], record values). Let us assume for certainty $k=1 \cdot 10^{-3} \text{ cm}^{-1}$ which is real for the case of pure CsI, then the characteristic length of radiation extinction $\ell=10 \text{ m}$. From here it is clear that the reverse heat flow for the crystals of the mentioned size is mainly defined by the conditions of reflection on boundaries.

Table 1
Influence of the impurities on crystallization of CsI(Tl) for 250 mm in diameter

№	$T_1, ^\circ\text{C}$	$\Delta T, ^\circ\text{C}$	Content of $\text{CO}_3, \text{mol.}\%$	k_{880}, cm^{-1}	Other impurities
1	696	- 8	-		
2	702	0	-		
3	705	- 7	-		
4	710	- 12	-		
5	722	+ 40	$0,5 \times 10^{-4}$	0.5×10^{-2}	NO_2, NO_3
6	739	+ 31	2×10^{-4}	2×10^{-2}	SO_4
7	743	+ 29	$1,5 \times 10^{-4}$	1.5×10^{-2}	
8	743	+ 23	$4,5 \times 10^{-4}$	4.5×10^{-2}	
9	750	+ 28	3×10^{-4}	3×10^{-2}	NO_2
10	752	+ 38	$8,0 \times 10^{-4}$	8×10^{-2}	
11	755	+ 43	$9,0 \times 10^{-4}$	9×10^{-2}	NO_2
12	741	+ 48	$20,0 \times 10^{-4}$	20×10^{-2}	

For a rough estimation of the share of the radiant energy returned to the melt we shall use the concept of light collection coefficient τ which is widely used in scintillation engineering and is defined as the ratio of the number of photons that got out of the detector through the output window to the total number of scintillation photons. Such approach is justified by the following considerations. Firstly, the theory of light collection was elaborated in detail in [11]; secondly, it takes into account the cases of real reflectors with different degree of diffuseness; thirdly, a reflector in the form of incrustation of small crystals of the same material slightly differs from conventionally used powders MgO and Al_2O_3 [12]; and, finally, a clear analogy is traced: τ characterizes the number of photons that reached PMT (by analogy – walls of the crucible) through the layer of the immersion liquid (through the layer of the transparent melt) with account taken of multiple reflections and refraction of light.

The calculations made in [11] give the value $\tau \sim 0.4-0.65$ at $k=5 \cdot 10^{-3} \text{ cm}^{-1}$, diameter of the cylinder 25 cm, height 25-50 cm and value of the relative refraction coefficient $n^*=1.23$ at the interface crystal-immersion liquid depending on the degree of diffuseness of the reflector. Thus, the reverse heat flow under real conditions easily reaches half energy carried away by the radiant transfer. Since the only strongly absorbing material in the system turns to be platinum (see Fig.1) the temperature distribution on the bottom of the crucible and in the melt noticeably changes, this leading to a transformation of convection flows and crystallization front form. For a more accurate evaluation of the reverse heat flow necessary is the allowance for temperature dependence and dispersion of refraction indices of the crystal and melt and, what is more important – curvature of the crystallization front. These problems will be the subject of separate investigation.

It should be particularly emphasized that CsI(CO₃) crystals with $k_{880} \sim 2.10^{-1} \text{ cm}^{-1}$ grow stably and always with $\Delta T > 50^\circ$. The state of the surface affect the concrete value ΔT but never changes the character of T_i change. We can suppose that the reverse heat flow is strongly decreased in this case. Fundamental and combined oscillation frequencies of CO₃²⁻, NO₂⁻ and NO₃⁻ ions are shown in Table 2 according to the data [13,14]. The calculation of maximum position of black body emission $b(T, \ln \lambda)$ for the temperatures $\sim 893\text{-}913 \text{ K}$ (the melting temperature of CsI is 894 K) by a formula: $T \cdot \lambda_{MAX} = 0.3668 \text{ cm} \cdot \text{K}$ [15] shows $\lambda_{MAX} \sim 4 \text{ }\mu\text{m}$. The data presented in Table 2 shows that combined oscillations $2\nu_3$ и $\nu_1+\nu_3$ are in the maximum of thermal radiation. One can see that as the temperature increases above room one the absorption bands broaden and merge. There can also appear new bands, for example, $\nu_3+\omega_0$, where ω_0 is the frequency of intrinsic oscillations of the lattice [14]. Let us consider CsI(CO₃) crystal with $k_{880} = 0.1 \text{ cm}^{-1}$. As we can see from Table 2 the absorption coefficient at a wavelength $4 \text{ }\mu\text{m}$ has the value $\sim 6.4 \cdot 10^{-2} \text{ cm}^{-1}$. At such absorption the value ℓ is 15.6 cm which is comparable with the crystal diameter. With the rise of the crystal height and extension of its diameter, taking into account multiple reflections, even lower values of k are to have an effect on the heat flow extinction.

Table 2

Positions of absorption band maxima of CO₃²⁻, NO₃⁻ and NO₂⁻ ions in CsI crystals

Material	Position of band maximum		Relative absorption coefficient, k/k_{880}	Assignment
	ν, cm^{-1}	$\lambda, \mu\text{m}$		
CO ₃ ²⁻ in CsI	1033	9.68	0.065	ν_1
	878	11.4	1	ν_2
	1362	7.34	13.6	ν_3
	1385	7.22	13.2	
	667.5	15.0	0.264	ν_4
	678.5	14.7	0.229	
	1693	5.9	0.091	$\nu_1+\nu_4$
	1705	5.87	0.1	
	2390	4.18	0.090	$\nu_1+\nu_3$
	2410	4.15	0.133	
2690	3.7	0.018	$2\nu_3$	
2770	3.61	0.068		
CO ₃ ²⁻ in CsI(Na)	1775	5.6	0.078	$\nu_1+\nu_4$
	2495	4.00	0.64	$\nu_1+\nu_3$
	2590	3.86	0.01	
	2850	3.5	0.026	$2\nu_3$
	2940	3.4	0.012	
NO ₃ ⁻ in CsI	2418	4.14		$\nu_1+\nu_3$
	1768	5.66		$\nu_1+\nu_4$
	2090	4.78		$\nu_3+\nu_4$
	2752	3.63		$2\nu_3$
NO ₂ ⁻ in CsI	2060	4.85		$\nu_1+\nu_3$
	2548	3.92		$2\nu_3$

It should be noted, that the effect of impurity absorption was partially masked when growing crystals of a small size. It is obvious, this was the reason we couldn't reveal it earlier. It should be emphasized that the discussion data only qualitatively explains the results. Real absorption coefficients in the actual range are too low to decrease the reflected heat flow strongly, particularly by relatively small impurity content. Therefore we use a possible evolution of absorption bands with the increase of temperature. The experiments concerning the definition of k at high temperatures have to be carried out.

Additional introduction of impurities to the crystal certainly presents a certain danger since characteristics of the ready products often strongly depend on impurity composition. In our case this is just true when growing CsI pure (fast scintillators for high energy physics). The impurity dipoles of the $\text{CO}_3^{2-} \text{V}_a^+$ - type significantly decrease the output of the fast component of luminescence and stimulate emergence of ultimately undesirable afterglow. A contrary situation is realized in case of growing CsI(CO_3) in which the mentioned dipoles create active luminescence centers and, therefore, the carbonate admixture is necessary [15]. For a long time the oxygen containing impurities including CO_3^{2-} ions were considered to deteriorate essentially the scintillation characteristics of CsI(Na) and CsI(Tl) crystals, especially their radiation resistance. However, it turned out that the course of radiation-chemical reactions with the participation of carbonate ions [8] responsible for the deterioration of crystals' properties after irradiation becomes blocked by the sodium ions in CsI(Na) and does not occur in CsI(Tl) provided the latter is additionally doped with sodium. A more detailed information can be found in [7, 16]. It turned out that at a content of carbonate ions at the level of $(1-2) \cdot 10^{-4} \%$ the characteristics of dopantcomposite scintillators have nothing different from usual CsI(Tl) crystals [16]. As one can see from Table 1 and Fig.1 these impurity concentrations are already sufficient for a stable growth of crystals.

CONSLUSION

The main conclusion of this paper can be formulated as follows. It has been shown that by introduction of an impurity the absorption of which overlaps the region of thermal radiation one can significantly affect the heat transfer and crystallization conditions. A peculiar feature of the described approach consists of the fact that used were not the main (usually observed) but weak combined bands of the oscillatory absorption. When growing rather big crystals a positive effect of doping is achieved at relatively low concentrations of polyatomic ions which do not yet change the basic functional characteristics of the material. By the additional contribution of the impurity absorption by the results of the measurements at room temperature one can only qualitatively explain the observed effect. For the quantitative evaluations necessary are special investigations of the absorption coefficient variations at temperatures close the premelting one.

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