

Effect of CO_3^{2-} and OH^- impurities on thermal growing conditions of large-size NaI:Tl crystals and their quality

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The effect of OH^- and CO_3^{2-} ions on thermal growth conditions of large size NaI:Tl crystals and their quality has been studied. The raw material sodium iodide salt, when subjected to long-term dehydration at room temperature in vacuum, provides the crystals free of CO_3^{2-} and OH^- . In IR absorption spectra of grown crystals the CO_3^{2-} bands are not observed. In TSL curves there are no peaks associated with storage on F -centers. The detectors produced are characterized by the absence afterglow in minute range and do not change the background count rate when being irradiated by 50 Rad dose. The improvement of thermal stability of crystal growth process at replenishment by melted raw material containing CO_3^{2-} and OH^- is explained by a significant change in thermophysical properties of the melt and crystal in the presence of those impurities.

Изучено влияние OH^- и CO_3^{2-} ионов на тепловые условия роста крупногабаритных кристаллов NaI:Tl и их качество. Показано, что исходная соль иодида натрия, подвергнутая длительной дегидратации при комнатной температуре в вакууме, позволяет получать кристаллы без примесей CO_3^{2-} и OH^- . В спектрах инфракрасного поглощения выращенных кристаллов не наблюдаются полосы CO_3^{2-} , а на кривых ТСЛ отсутствуют пики, связанные с запасанием на F -центрах. Изготовленные детекторы характеризуются отсутствием минутного послесвечения и не изменяют фоновую скорость счета после облучения дозой 50 рад. Улучшение тепловой устойчивости процесса выращивания кристаллов с подпиткой расплавленным сырьем, содержащим ионы CO_3^{2-} и OH^- , объяснено заметным изменением теплофизических свойств расплава и кристалла в присутствии этих примесей.

1. Introduction

NaI:Tl crystals are currently the most popular scintillation materials [1]. A distinctive feature of this material is the high hygroscopicity. Therefore, the initial salt is subjected to thorough drying before crystal growing. There are many ways to prepare salt for crystal growth, some of which are described in [2, 3]. It is believed that at final stage of the drying process must occur

at $T \geq 69^\circ\text{C}$ [4]. It is known that NaOH is a highly undesirable impurity, because its presence reduces the scintillation yield [5] and stimulates the formation of F -centers in irradiated NaI and NaI:Tl crystals [6, 7]. It is also known that the appearance of F -centers leads to the photochemical coloration of crystals in day light [8]. Recently we have shown that drying of salt at $T \geq 40^\circ\text{C}$ results in contamination of the product with OH^- ions, while long-term dehydration of raw

Table. Characteristics of NaI:Tl crystals of types I and II.

№	Type	C_{Tl} , ppm	C_{K} , ppm	ΔN , c^{-1}	$(T_H - T_0)$, K
1	I	610	2.1	57000	0...+48
2	II	400	–	0	0...+44
3	II	620	–	0	-1...+3
4	I	440	1.5	240000	-2...+4

materials at room temperature in vacuum provides a dry product that contains no OH^- and CO_3^{2-} [9].

In this study, we investigated the effect of CO_3^{2-} and OH^- impurities on the thermal conditions of growth and scintillation characteristics of NaI:Tl single crystals pulled from the melt in a platinum crucible without using additional purification methods of the melt from oxygen-containing impurities, as described in [10]. This eliminates the possible influence of uncontrollable factors, typical, for example, of the crystals grown by the Bridgman-Stockbarger method in quartz ampoules [2] due to the interaction of impurities with the ampoule material.

2. Experimental

We used the modified pulling method of crystals growing with the replenishment of melted raw material [11]. One of the features of the method is the use the platinum feeder shaped as a ring-container of rectangular cross-section located under the conical crucible. Two types of crystals were grown.

Type I. The crystals of NaI:Tl were grown in accordance with [2, 11]. Dehydration of salt was carried out with a gradual increase of feeder temperature from 25 to 400°C at a rate of 50°C/h. The dimensions of crystals were: 250 mm in diameter (D) and ≈ 330 mm height (H) of the cylindrical part of the ingot. Curves 1 and 2 (Fig. 1) show the change of the temperature-controlling (bottom) heater during the growth process at a constant D for the two crystals of this type. The temperature change is presented as T_H/T_0 , where T_H is the current temperature (K) of the heater and T_0 , the heater initial temperature when D of the crystal is constant. It is seen that the crystal growth at a constant diameter occur at gradual increase of the bottom heater temperature. It is known that this situation is most favorable for the stable growth of large crystals [12, 13]. The optimum pulling rate is 4 mm/h. The ingots grown in argon atmosphere are visually transparent, had a

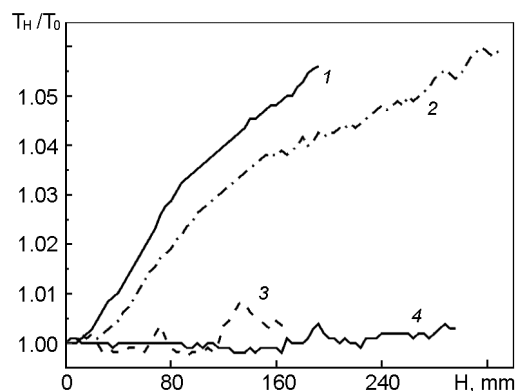


Fig. 1. Change of temperature at bottom heater during the growth in height for NaI:Tl crystals of first (1, 2) and second (3, 4) types.

smooth side surface and convex crystallization front shape, which indicates the stability of the crystallization conditions in automatic mode.

Type II. The growth was carried out in accordance with the guidelines [9]. The raw material (NaI) was subjected to prolonged dehydration (10 days) in vacuum at 30°C. All other operations are consistent with growing crystals of Type I. Curves 3 and 4 (Fig. 1) correspond to T_H during growth with $D = \text{const}$ for crystals of Type II. When growing these crystals, the same problems took place as described in [12] for the pure CsI crystals. First, the temperature of the bottom heater was at 30–40°C lower than at the growing of Type I crystals. This temperature difference persisted at seeding and all subsequent stages of growth, including the radial growth and growth in height. Secondly, the growth with $D = \text{const}$ a trend to reduce the temperature of the bottom heater was sometimes observed, as is evident from Table and Fig. 1. Ingots were visually transparent, do not contain bands of capture, although they have less smooth side surface than the crystals of Type I, which is associated with non-monotonic change of temperature. Unlike the first type crystals, the crystallization front was almost flat. This indicates the

absence of impurities absorbing thermal radiation in the melt [12, 13].

Table and Fig. 1 show that the growth conditions for crystals of different types differs markedly. The crystals of Type I are characterized by tendency to a steady rise in temperature of bottom heater. This indicates a stable and efficient heat removal from the crystallization front. To provide the constancy of the crystal diameter temperature of control heater continuously increases, which slows the crystallization rate. For second type crystals, on the one hand, typical is the constant temperature and even some poorly marked trend towards a decrease (curves 3 and 4 in Fig. 1). On the other hand, the convection currents in the melt due to the low-temperature bottom heater may be weakened and ineffective for temperature equalization throughout the crucible volume. In both cases, there comes a point when the average melt temperature was lowered to a critical value, and the center of the parasitic crystallization at the wall of the crucible was arisen. The growth process was stopped at that moment when there was a danger of contact between the rotating ingot and gradually growing parasitic crystal. For this reason, both crystals of Type II had the same diameter but less height.

Control of the impurity composition of crystals was studied by spectrophotometry and thermally stimulated luminescence (TSL). The witness samples of different sizes were cut out of the top and bottom of each ingot. IR spectra were obtained on samples $20 \times 20 \times 60 \text{ mm}^3$ of size using a UR-20 spectrophotometer. The TSL was measured on samples $\varnothing 30 \times 5 \text{ mm}^3$ after irradiation at 77 K for 10 minutes with γ line source of ^{241}Am (60 keV, 1.8 Ci). The sample heating rate was 0.04 K/s. Carbonate content in the crystals was evaluated from the intensity of the absorption band of the bending vibration ν_2 at 880 cm^{-1} with account for the coefficient of proportionality, whose value was $9.76 \cdot 10^{-3} \text{ mol.}\% / \text{cm}^{-1}$ [14]. The concentration of activator (C_T) determined by the polarographic method [15] was within $(4-6) \cdot 10^{-2} \text{ mol.}\%$. Spectrometric characteristics and afterglow in the minute range were measured for the standard sample size of $\varnothing 25 \times 25 \text{ mm}^3$, packed in sealed containers with a MgO reflector, using standard equipment. Changing the background count rate (ΔN , pulse/s) were meas-

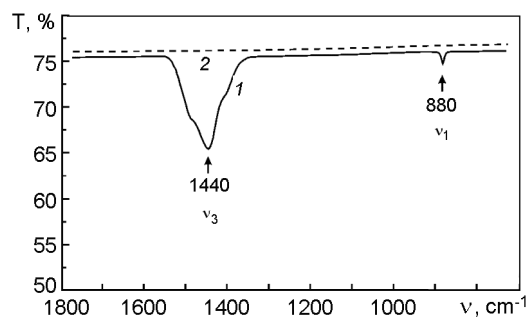


Fig. 2. Spectra of IR absorption for NaI:Tl crystals of first (1) and second (2) types.

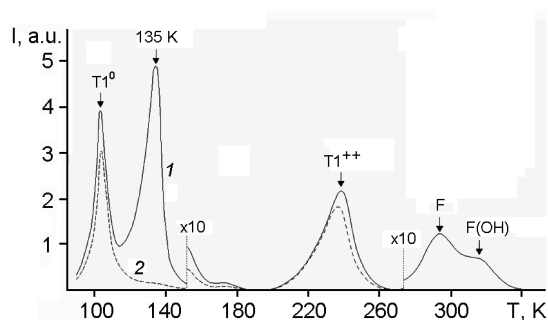


Fig. 3. TSL curves for NaI:Tl crystals of first (1) and second (2) types.

ured after γ -irradiation with 50 Rad (662 keV, ^{137}Cs) 10 min after exposure.

3. Results

As can be seen from Fig. 2, absorption bands in the curve 1 with maxima at 880 and 1440 cm^{-1} are related to the absorption of bending (ν_2) and valence (ν_3) vibrations of the molecular ion CO_3^{2-} in the lattice of NaI, respectively [16]. It is seen that the crystals of Type I differ significantly in the impurity composition from crystals of Type II. Curve 2 has no absorption bands corresponding to vibrations of CO_3^{2-} . Since the CO_3^{2-} ion is stable only in basic medium, we can conclude that the melt was free of OH^- impurity. This result agrees well with the data of Fig. 1 — melt and growing crystal does not absorb infrared radiation (curves 3 and 4).

The most sensitive test for the presence of CO_3^{2-} and OH^- impurities in the crystals are the TSL curves (Fig. 3). It is known that in the TSL crystals NaI:Tl after irradiation at 77 K there are several peaks associated with traps of activator and non-activator nature. Thus, the peaks of 103 and 236 K are associated with the centers Tl^0 and Tl^{++} and due to capture of electrons and holes by activator ions, respectively [17].

Electron peak at 135 K appears only in crystals with oxygen-containing impurities, presumably associated with Na_2O [18]. In the 295 and 313 K the F -centers are broken down [7]. At 295 K destroyed the ordinary F -centers are broken down, while at 313 K, the same centers located near OH^- ions.

Fig. 3 shows that in contrast to crystals I, samples of Type II do not show peaks near to 135, 295 and 313 K in the TSL. The fact that the curve 2 is free of 313 K peak is direct evidence of a sharp decrease in OH^- ion concentration in the samples of this type. Curve 2 shows that the grown crystals are free of CO_3^{2-} ion (peak 295 K) and sodium oxide (peak at 135 K). TSL dates are in a good agreement with the results on the thermal conditions of crystal growth (see Fig. 1) and infrared spectra (Fig. 2).

Since the TSL peaks in the 295 and 313 K region are responsible for the afterglow of the crystals in the minute range [6, 7], we can expect that the background count rate of pulses will not increase after irradiation of the Type II crystals. To test this hypothesis, four packed scintillators with the crystal size $\varnothing 30 \times 63 \text{ mm}^3$ were constructed and background count rate of pulses (ΔN) at the threshold of discrimination of 20 keV were measured (see Table). It is seen that $\Delta N = 0$ after irradiation for crystals of type II contrary to $\Delta N > 50\,000$ for type I.

4. Discussion of results

Two aspects should be pointed when considering the results. First, the indirect (Fig. 1) as well as direct (Fig. 2 and Fig. 3) experimental data suggest strongly that the crystals of the Type II are free of OH^- and CO_3^{2-} ions. This means that prolonged evacuation of the raw material at room temperatures does not result in the salt contamination with these impurities. The disadvantage of this method is its duration. To speed up the drying process, in [9, 19] vacuum-microwave heating is recommended.

Another thing worth to discussion is the change of the control heater temperature character. As seen from Fig. 1, the parameter for the both types of crystals differs significantly. This fact can be explained by the dates reported in [13] concerning the effect of CO_3^{2-} ions (C_K) on the change the bottom-heater temperature at automated pulling of CsI:Tl crystals. In this case, there was a clear relationship between the velocity of temperature increase and the content

of CO_3^{2-} ions in the crystal. Influence of the CO_3^{2-} impurity is reduced to the change of radiation-conductive heat transfer conditions in the crystal and the melt. The results of numerical simulations carried out using the CGSim (LLC SoftImpact) software show that an increase in the absorption coefficient of the crystal and the melt results in an increase in the temperature gradient in the melt and near the crystallization front and in contrast, to its decrease in the bulk of crystal [20]. One of the features of heat transfer at pulling of transparent (in IR region) crystals is the low melt temperature in the crucible. The average melt temperature is as a rule not much higher than the melting point of crystallizing material. The latter circumstance is very undesirable in terms of technology. The fact that the real growing furnace is characterized by a number of unavoidable and uncontrollable factors, such as a degree of blackening of the crucible surface, some asymmetric location of the crucible with respect to the heaters, and so on. These factors make a small perturbation on the heat transfer at pulling crystals of Type I and do not totally counted by the automated control system.

But at growing crystals of Type II (low melt temperature), these perturbations result in the emergence of local regions where temperature may reach the melting temperature. A consequence of that is a high probability of occurrence of parasitic crystallization centers mainly at the surface of the crucible. It is this circumstance that very complicates the pulling of the crystals transparent in IR-region.

5. Conclusions

Effect of OH^- and CO_3^{2-} ions on the thermal growth conditions of large-size NaI:Tl crystals and their quality has been studied. It has been shown that the raw material (sodium iodide), subjected to long-term dehydration at room temperature in vacuum, permits to obtain the crystals free of CO_3^{2-} and OH^- impurities. In IR-spectra of the grown crystals, the absorption bands of CO_3^{2-} ion are not observed, and the TSL curves show the absence of the peaks associated with the F -centers. The scintillators produced are characterized by absence of afterglow in minute range and do not change the background count rate after irradiation with dose of 0.5 Gy. An explanation of improved thermal stability has been proposed for the process of crystal growth with replenishment by melt containing CO_3^{2-} and

OH⁻ ions. The explanation is based on significant change of thermo-physical properties of the melt and the crystal in the presence of these impurities, which absorb thermal radiation.

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Вплив домішок CO₃²⁻ та OH⁻ на теплові умови вирощування великорозмірних кристалів NaI:Tl та їх якість

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Досліджено вплив OH⁻ і CO₃²⁻ іонів на теплові умови росту великорозмірних кристалів NaI:Tl та їх якість. Показано, що вихідна сіль йодиду натрію, що піддана тривалій дегідратації при кімнатній температурі у вакуумі, дозволяє одержувати кристали без домішок CO₃²⁻ і OH⁻. У спектрах інфрачервоного поглинання вирощених кристалів не спостерігаються смуги CO₃²⁻, а на кривих ТСЛ відсутні піки, пов'язані з запасанням на F-центрах. Виготовлені детектори характеризуються відсутністю хвилинного післясвітіння і не змінюють фонову швидкість рахування після опромінення дозою 50 рад. Покращення теплової стабільності процесу вирощування кристалів з підживленням розплавленою сировиною, що містить іони CO₃²⁻ та OH⁻, пояснено помітною зміною теплофізичних властивостей розплаву й кристала у присутності цих домішок.