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Functional properties of CsI(Tl) scintillation crystals obtained from deeply purified technological residues.

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The multifold low-temperature mixed crystallization method (LTMC) was used for deep purification of the technological cesium iodide solutions (residues of the large-scale crystal growth). This treatment provided the raw of high-quality suitable for obtaining the low-background CsI crystals due to low content of K and Rb. Even after 30 LTMC cycles the yield of CsI raw is higher compared to a traditional routine of 3 mass crystallizations. The shape of excitation and emission photoluminescence spectra for CsI(Tl) crystals grown from the obtained raw agrees with those from existing literature. The shapes of photoluminescence and X-ray spectra are also close. The functional parameters (light yield, energy resolution) of crystals grown from the raw obtained after 16 LTMC cycles are not worse than those of the commercially available CsI(Tl) crystals.

Keywords: crystallization, cesium iodide, thallium, luminescence, scintillation.

Функціональні властивості сцинтиляційних кристалів CsI(Tl), вирощених із глибокоочищених техногенних залишків. *В.Л. Чергинець, Т.В. Пономаренко, Т.П. Реброва, А.Г. Варич, О.Л. Ребров, К.Ю. Брильова, Т.В. Шеїна, Я.А. Бояринцева, О.В. Зеленська, О.І. Юрченко*

Для глибокого очищення технологічних розчинів CsI (залишки після вирощування великогабаритних сцинтиляційних монокристалів) було використано метод багаторазової низькотемпературної мішаної кристалізації (LTMC). Це дозволило отримати сировину високої якості, придатну для отримання кристалів CsI з низьким фоном завдяки низькому вмісту K та Rb. Вихід сировини CsI навіть після 30 циклів LTMC перевищує вихід CsI, одержаного після 3 масових кристалізацій. Форма спектрів збудження та емісії фотолюмінесценції кристалів CsI(Tl), отриманих з підготовленої сировини, узгоджується з даними з існуючої літератури. Форми спектрів фотолюмінесценції та рентгенівських спектрів також близькі. Функціональні параметри кристалів, вирощених з отриманої шихти після 16 циклів LTMC (світловий вихід, енергетична роздільна здатність), не гірші, ніж відповідні параметри комерційно доступних кристалів CsI(Tl).

1. Introduction

The production of large-sized scintillation single crystals based on cesium iodide followed by the production of elements for smaller detection devices is necessarily accompanied by the accumulation of residues, the proportion of which reaches 30–50 % of the mass of the

initial raw for the crystal growth. This makes a simple disposal of the residues economically unfavorable and unforces the development of technological routines for reprocessing residues back into the raw suitable for the crystal growth.

The traditional way of the reprocessing is threefold crystallization of the technogenic solutions, which were preliminary purified from mechanical admixtures by filtering. More detailed description of the reprocessing of CsI wastes is as follows. The wastes are dissolved in water and insoluble thallium iodide is deposited and the solution is filtered through active coal to remove of organic admixtures and reduce Tl content. After TlI separation the wastes solution is treated by $Ba(OH)_2$ to precipitate sulfates (in the form of insoluble $BaSO_4$) and heavy metals, aluminum and magnesium (insoluble hydroxides). Then the solution is treated by Cs_2CO_3 to precipitate the excess of barium and alkaline earth metals (as insoluble carbonates). However, such a way does not provide the essential separation of alkali metal cations (residual content of sodium is varied from 0.1 to 1 mas. %). The removal of alkali metal cations is the hardest problem, which is solved by multiple crystallization from aqueous solutions that possesses essential disadvantage caused by relatively small changes of CsI solubility with the temperature: from 86 g/100 g of water at 25 °C to 170 g/100 g of water at 75 °C [1]. It is obvious that one cycle of recrystallization leads to the loss of approximately 40 % of CsI in the mother waters and the direct yield of CsI after 3rd recrystallization is ca. 25 %. The treatment of the mother waters is more difficult since the concentration of admixtures in them is considerably higher. This forces material scientists to develop alternative ways of crystallization or chemical treatment of the waste solutions, which can result in higher yield of extra pure CsI free from Na, K and Rb.

Recently we developed a routine of multifold low-temperature mixed crystallization (LTMC) [2] with each stage consisting in sequential freezing of technogenic CsI solution to crystallization degree of 0.97, removing of liquid residue and defrosting (end of cycle). Performing enough LTMC cycles permits to remove isomorphic admixtures of potassium and rubidium to concentrations lower than the norms established in Ukraine by TU U 24.13.31331736-002-2004. The mentioned admixtures cause natural radioactive background of the scintillators due to ^{40}K ($T_{1/2}=1.248\cdot10^9$ years) and ^{87}Rb (ß, $T_{1/2}=4.923\cdot10^{10}$ years) isotopes presence. This created relatively simple method of obtaining low-background raw for obtaining single crystals in nuclear physics.

Unfortunately, LTMC does not allow to remove thallium and copper similarly to other crystallization purification methods. Luckily, the preliminary treatment of the technogenic solution with Mg powder allows to decrease the contents of the said impurities to the levels lower than requirements of TU U 24.13.31331736-002-2004 [3].

The purpose of this work is to report functional properties of CsI(Tl) single crystals grown from the raw obtained by multifold LTMC and compare them with those of the single crystals grown from the standard purum CsI 17-2 (17 standardized admixtures with the total content of 10^{-2} mas.%).

2. Experimental

LTMC was performed using technogenic solutions of cesium iodide concentrated to a salt content of 38 mas.% (density at room temperature, RT, is 1.4 g·cm $^{-3}$). 42 liters of the solution were poured into 1.5 l PET containers (2 batches of 14 containers each). Each LTMC cycle consisted of loading the batch into a freezer cooled to –14 °C and crystallization of salt and water-salt eutectic $CsI\text{-}H_2O$ to a degree of crystallization of 0.96-0.97. The liquid residues were drained while the crystallized masses were defrosted and averaged [2]. A sample of the purified solution (120 ml) was submitted for analysis. After 12, 16, 20 and 30 cycles of LTMC the solutions were sampled in amounts sufficient to obtain 2 kg of dry cesium iodide.

Analytical determinations. Determination of Tl in CsI was performed by differential pulse anodic stripping voltammetry after processing of samples with concentrated nitric acid. Voltammetric measurements were carried out at a hanging mercury drop electrode as a working electrode using 797 VA Computrace (Metrohm, Switzerland). The acetic buffer solution with EDTA (pH=5.5) was the supporting electrolyte. Peaks of thallium were observed at -0.45 V and -0.23 V (vs. Ag/AgCl (3 M KCl)).

The flame spectrometry was used for Na, K, and Rb determination. Measurements were carried out using iCE 3500 atomic absorption spectrophotometer (Thermo Fisher) in an emission mode. Flame of acetylene-air gaseous mixture was used as an excitation source. The low

determination limit for Na and K is $2 \cdot 10^{-5}$ and for Rb – $5 \cdot 10^{-6}$ mas. %. Relative standard deviation values for concentration interval of $2 \cdot 10^{-5}$ to $2 \cdot 10^{-1}$ mas. % are within the range of 0.01 – 0.15.

To compare the quality of the raw material obtained after purification of technogenic cesium iodide solutions for 12, 16, 20 and 30 LTMC cycles experimental samples of CsI(Tl) single crystals were grown by Bridgman method. CsI 17-2 (purum) was used for the comparison of scintillation properties. Thallium iodide of reagent quality was used for doping of all CsI-based scintillation crystals.

For growing single crystals of 20 mm diameter and a length of 80–90 mm quartz ampoules with a diameter of 25 mm, a wall thickness of 1.5 mm and a height of 500 mm were used. Before the crystal growing process a layer of carbon was sprayed onto the inside of the ampoules to prevent the direct contact of cesium iodide-based melt with quartz. 125 g of the cesium iodide raw was weighed and poured into the prepared quartz ampoule through a glass funnel. The growth ampoule was connected to a smaller one with thallium iodide and vacuum pump so that an activator could be added to a melt without exposing it to air. When the vacuum was achieved the growth ampoule was heated to the temperature of 650 °C and was kept for 15 hours.

Next, 0.6 g of thallium iodide was added to the melt and the growth ampoule was immediately sealed. Sealed ampoule was placed into the upper section of two-zoned furnace with its lower end being 3–5 mm above the diaphragm. The temperature at the diaphragm corresponded to the melting point of cesium iodide – 632 °C. After a settling time of 1 hour the process of crystal growth started. The growth ampule was descending into the lower zone of a furnace with a speed of 3.2 mm $\cdot h^{-1}$ for 48 h. Then descending mechanism was turned off and the furnace started to cool down to RT with the rate of 10 °C $\cdot h^{-1}$. After cooling down the obtained single crystal was extracted and a sample of 15 mm diameter and the length of 30 mm was prepared for the determination of functional properties.

Infra-red spectra of the obtained crystalline samples were recorded using IRAffinity-1 Fourier transform infrared spectrometer (Shimadzu, Japan).

Photoluminescence. The investigation of luminescent properties (recording photoluminescence excitation and emission spectra) of the obtained samples was performed using a combined fluorescent lifetime and steady-state spectrometer FLS 920 (Edinburgh Instruments) equipped with a xenon Xe 450 W and hydrogen filled nF 900 nanosecond flashlamp for time correlated single photon counting measurements. Photoluminescence excitation spectra were corrected on the incident photon flux. Photoluminescence emission spectra were corrected for the spectral sensitivity of the detection system.

X-ray luminescence. The X-ray luminescence spectra were obtained under X-ray (Cu, 40 kV, 4 nm) excitation in transmission mode.

Light yield, energy resolution. These parameters were estimated by the comparison method [4]. The measurement results were recorded using a pulse processing chain consisting of an R1307 SU 0192 PMT (Hamamatsu, Japan), a charge-sensitive preamplifier BUS 2-95, a custom shaping amplifier and a multichannel analyzer AMA-03F. Relative light yield was determined by comparing the peak position (abscissa) of the grown crystals and the standard CsI(Tl) sample with technical light yield of 22,500 photon $\cdot MeV^{-1}$ and the energy resolution of 9 %. All measurements were done under the same conditions using the shaping time of 8 μs. The error of the light yield and energy resolution measurements was less than 5 %.

3. Results and discussion

The level of isomorphic admixtures. A total of 30 cycles of LTMC were performed. The result of the isomorphic admixture content determination in the samples of LTMC-purified CsI are presented in Table 1.

It can be seen that as the LTMC passes, the concentration of alkali metal impurities in cesium iodide monotonically decreases, while for the thallium impurity the opposite trend is observed – it somewhat accumulates in the product. Similar dependencies for the indicated impurities were described in [2]. In the indicated work, a general conclusion was made that any crystallization methods are unsuitable for deep purification of cesium iodide from thallium impurities.

As for the behavior of other isomorphic impurities, the impurity of the closest analogue of cesium – rubidium – is the easiest to remove: after 15 cycles of LTMC the concentration of rubidium becomes less than the limit of determination by analytical methods. The concentrations of sodium and potassium impurities decrease

Table 1. Concentrations of isomorphic admixtures: sodium (c_{Na}), potassium (c_K), rubidium (c_{Rb}) and thallium (c_{Tl}), mas. % in CsI samples obtained after different number of LTMC cycles.

Number of LTMC cycles	c_{Na}	c_K	c_{Rb}	c_{Tl}
0	$7.0\cdot10^{-1}$	$6.5\cdot10^{-3}$	$6.5\cdot10^{-4}$	$1.4\cdot10^{-4}$
8	$7.5\cdot10^{-2}$	$8.0\cdot10^{-4}$	$5\cdot10^{-5}$	$1.2\cdot10^{-4}$
10	$4.5\cdot10^{-2}$	$5.0\cdot10^{-4}$	$4\cdot10^{-5}$	$1.2\cdot10^{-4}$
12	$2.0\cdot10^{-2}$	$2.8\cdot10^{-4}$	$2\cdot10^{-5}$	$1.3\cdot10^{-4}$
16	$3.6\cdot10^{-3}$	$4.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$1.4\cdot10^{-4}$
18	$1.7\cdot10^{-4}$	$4.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$1.6\cdot10^{-4}$
20	$6.5\cdot10^{-4}$	$4.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$2.0\cdot10^{-4}$
24	$1.6\cdot10^{-4}$	$3.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$1.8\cdot10^{-4}$
25	$9.0\cdot10^{-5}$	$3.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$1.8\cdot10^{-4}$
27	$5.1\cdot10^{-5}$	$3.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$1.9\cdot10^{-4}$
30	$3.0\cdot10^{-5}$	$2.0\cdot10^{-5}$	$<1\cdot10^{-5}$	$2.0\cdot10^{-4}$
35	$1.5\cdot10^{-5}$	$1.5\cdot10^{-5}$	$<1\cdot10^{-5}$	$2.1\cdot10^{-4}$
TU U requirements	–	$2.0\cdot10^{-4}$	$1\cdot10^{-5}$	$6\cdot10^{-5}$

monotonically with increasing the number of LTMC cycles, but upon reaching concentration values of the order of $(4\div5)\cdot10^{-5}$ mas. %, the purification rate decreases significantly. This observation can be explained by the fact that crystallization is a non-equilibrium process, during which numerous defects are formed in the solid phase and both the main substance (cesium iodide) and impurities (sodium iodide, potassium iodide, etc.) are captured equally on these defects. The approaching of the impurity concentration to that of the defects should cause the distribution coefficient approaching to 1 that reduces the purification efficiency.

As for the behavior of the thallium impurity, it should be noted that in this case there is no directional shift of the distribution coefficient (which is close to 1) together with the increase of LTMC cycle number. Due to the high concentration of thallium the purified solutions can be immediately used to obtain a cesium iodide salt suitable exclusively for growing single crystals of CsI(Tl).

It should be noted that after 30 LTMC cycles the direct yield of CsI is 40 % against 20–25 % after 3 mass crystallizations used in the existing purification technology. As for the quality of the obtained raw, it is not inferior regarding potassium and rubidium admixtures, which content is significantly lower than the requirements of TU U 24.13.31331736–002–2004. From the above results and dependencies it is possible to estimate the limit of the final content of isomorphic impurities in the the purified CsI raw as approximately $1\cdot10^{-5}$ mas. % which makes it undoubtedly suitable for the manufacturing of low-background CsI(Tl) single crystals for high-energy physics.

Infra-red spectra of the CsI *raw obtained by multifold LTMC method*. IR-spectra of CsI(Tl) samples grown from the standard (17-2, purum) raw and the one obtained by LTMC are presented in Fig. 1 The main detectable admixtures are of organic origin – cyanate ion, CNO^- (characteristic frequencies, CF, are within 600–800 cm^{-1} for N–C oscillation, 1200–1400 for C–O oscillation and 2100–2250 cm^{-1} for C≡N one) and C–H valence oscillation with CF of 2860–3090 cm^{-1} [5].

The presence of the above said admixtures is caused by the decomposition of organic substances containing carbon, nitrogen and oxygen at the heating of the raw during the crystal growth. The somewhat increased CNO^- concentration in the LTMC-originated crystals is caused by the contact with organic (PET) containers.

Photoluminescence spectra. The presence of two bands in the excitation spectrum was attributed to two different luminescence centers existing in CsI(Tl) single crystals [6, 7]: Tl(I) and Tl(II). The former is Tl^+ ion surrounded by the Cs^+ cations and the latter can be considered as Tl(I) center perturbed by the neighboring Tl^+ ion. The emission band consists of two bands with the maxima near 410 nm and 540 nm that is also common for CsI(Tl) materials. The shape

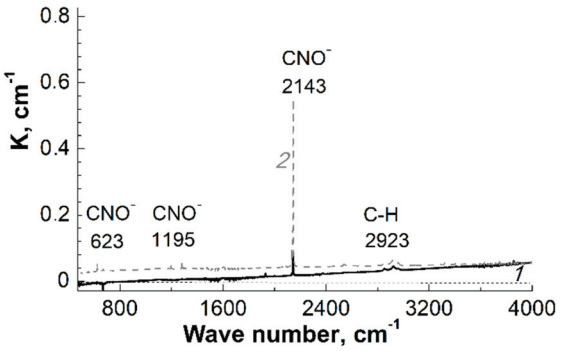

Fig.1. Infra-red absorption spectra of CsI(Tl) single crystals grown from the CsI 17-2, purum (1) and the raw obtained from technogenic cesium iodide solution after 16-fold LTMC (2).

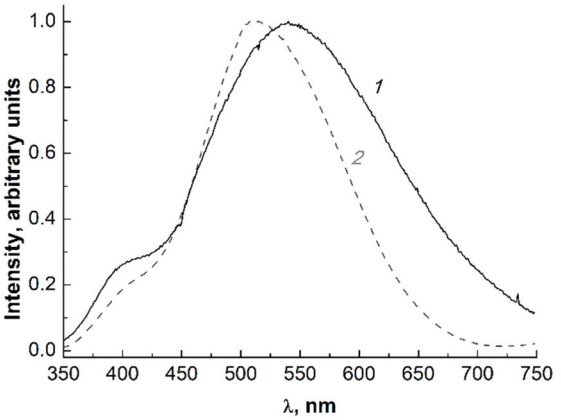

Fig.3. Emission photoluminescence (1) λ_{ex}= 300 nm) and X-ray luminescence (2) of CsI(Tl) single crystal grown from the raw obtained from technogenic CsI solution by 16-fold LTMC.

of the excitation and emission spectra are close to the corresponding data of [8].

Emission spectrum of photoluminescence of CsI(Tl) material together with the corresponding X-ray spectrum are presented in Fig.3. Both spectra are similar and the data of Fig. 3 confirm that the luminescence spectra are practically the same and caused by the luminescence of Tl centers.

Light yield, energy resolution.

The pulse-height spectra of CsI(Tl) single crystals recorded for the standard sample and the samples obtained from the raw purified by LTMC of cesium iodide technogenic solutions are presented in Fig. 4.

It can be seen that the relative light yield (the ratio of the abscissas corresponding to the maxima of the photopeaks of the tested samples and the standard) for the sample obtained from technogenic solutions purified by the 16-fold LTMC method is at least not worse than that for the standard sample with practically the

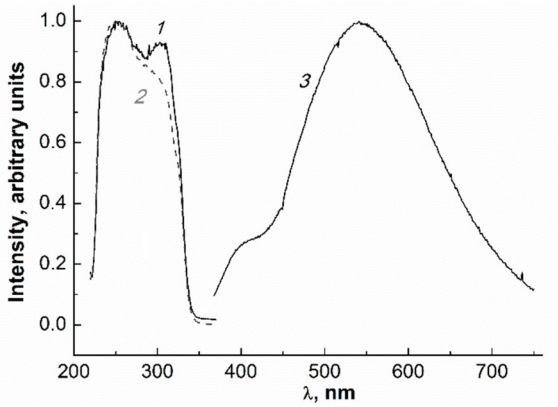

Fig.2. Excitation (1 – λ_{em}=410 nm, 2 – λ_{em}=560 nm) and emission (3 – λ_{ex}=300 nm) of CsI(Tl) single crystal grown from the raw obtained from technogenic CsI solution by 16-fold LTMC.

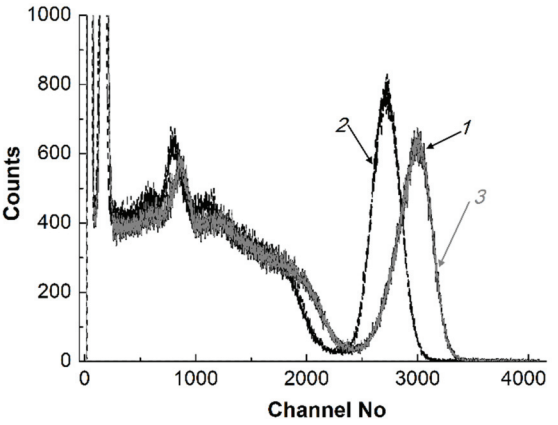

Fig. 4. The pulse-height spectra of CsI(Tl) crystals (Tl content is 0.09 mas. %): 1 – the standard 17-2 CsI raw (black), 2 – raw obtained by 12-fold LTMC (black), 3 – raw obtained by 16-fold LTMC (grey).

same energy resolution (the ratio of FWHM of the photopeak to the abscissa of its maximum) – 9.2 % and 8.9 %, respectively. It was determined [9] that the optimal concentration of the activator within 0.05–0.13 mas. % range is 0.06 mas. %. In our investigations the content of TlI in the samples was 0.09 mas. %. The light yield for the sample grown from raw after 12 LTMC cycles is 89% with respect to the standard sample (see Experimental part) and 100% for the sample grown after 16 LTMC cycles.

So, summarizing the results of the performed investigations it should be emphasized that multifold LTMC method permits to purify technogenic CsI aqueous solution to purity level corresponding to that of the raw suitable for obtaining optical (scintillation) materials and the functional properties of the final crystals are practically the same. Additionally, the final contents of K and Rb in the raw are less than

the requirement of the corresponding normative documentation. This means that multifold LTMC method can be used for the obtaining of low-background CsI raw for growing single crystals for high-energy physics.

Conclusions

The multifold low-temperature mixed crystallization method (LTMC) can be used for deep purification of the technogenic CsI solutions. It permits to obtain the raw of high-quality suitable for growing the low-background CsI crystals. Even after 30 LTMC cycles the yield of CsI raw is higher compared to the standard 3-fold mass crystallization.

The luminescence properties of CsI(Tl) crystals grown from the obtained raw are close to those from the literature data. The scintillation parameters of crystals grown from the raw obtained after 16 LTMC cycles are not worse than those of the crystals grown from standard CsI raw.

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