

Optical and scintillation properties of CsI:In crystals

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The work is dedicated to study of optical and scintillation properties of CsI:In crystals. Using the Bridgeman method a concentration row of CsI:In single crystals was grown with the dopant content from 10^{-4} to 10^{-1} mol. %. The segregation coefficient of In in CsI was estimated to be ~ 0.15 . In CsI:In luminescence spectra one symmetric band is observed, peaking around 545 nm, with FWHM of 0.46 eV. Under intracenter excitation 1.9 μ s exponential decay was observed. The light yield under gamma excitation of ^{137}Cs isotope (662 keV), measured with a shaping time of 10 μ s, was 27 000 photons/MeV. The radio-luminescence yield of CsI:In, measured by the current mode method, approached to that of CsI:Tl. Probably, this difference is connected with the presence of a stronger afterglow in CsI:In crystals.

Работа посвящена исследованию оптических и сцинтилляционных свойств кристаллов CsI:In. Методом Бриджмена выращен концентрационный ряд монокристаллических образцов CsI:In с содержанием активатора от 10^{-4} до 10^{-1} мол. %. Коэффициент сегрегации In в CsI составляет ~ 0.15 . В спектре люминесценции наблюдается одна симметричная полоса с максимумом 545 нм, полушириной 0.46 эВ. При внутрицентровом возбуждении наблюдается экспоненциальное затухание с характерным временем 1.9 мкс. Световой выход при возбуждении гамма-квантами изотопа ^{137}Cs с энергией 662 кэВ при измерении с временными воротами 10 мкс составил 27 000 фотонов/МэВ. Тем не менее, при измерении токовым методом выход радиолюминесценции CsI:In приближается к выходу CsI:Tl. Вероятно, такое различие связано с наличием более сильного послесвечения в кристаллах CsI:In.

Оптичні та сцинтиляційні властивості кристалів CsI:In. С.Гридін, Н.Шіран, М.Мосжинський, А.Бельський, А.Синтфельд-Казух, В.Тарасов, О.Гектін.

Роботу присвячено дослідженню оптичних і сцинтиляційних властивостей кристалів CsI:In. Методом Бриджмена вирощено концентраційну серію монокристалічних зразків CsI:In з вмістом активатора від 10^{-4} до 10^{-1} мол. %. Коефіцієнт сегрегації In в CsI становить ~ 0.15 . У спектрі люмінесценції наявна одна симетрична полоса з максимумом 545 нм та півшириною 0.46 еВ. При активаторному збудженні спостерігається експоненційне загасання з характерним часом 1.9 мкс. Світловий вихід при збудженні гамма-квантами ізотопу ^{137}Cs з енергією 662 кєВ при вимірюванні з часом генерації імпульсу 10 мкс склав 27 000 фотонів/МеВ. Тим не менше, при вимірюванні токовим методом вихід радіолюмінісценції CsI:In наближається до виходу CsI:Tl. Вірогідно, така відмінність пов'язана з наявністю більш сильного післясвітіння у кристалах CsI:In.

1. Introduction

CsI crystals are the basis for efficient scintillators. Undoped CsI scintillators have a short decay time and are successfully used in high energy physics [1, 2]. CsI:Tl, CsI:Na and CsI:CO₃ — are widely known as spectroscopic scintillators for various industrial and medical applications [3, 4]. Thus, there are certain general regularities allowing to obtain an efficient scintillation response in differently doped cesium iodide crystals. It is reasonable to assume that with some other dopants an efficient scintillation material based on CsI could be made. To check this assumption it seems appropriate to study scintillation characteristics of CsI:In crystals.

First of all it should be mentioned that In⁺ ions are homologues of Tl⁺ ions and have a similar *s*² electronic configuration in CsI lattice. Therefore we can expect the optical properties of CsI:In crystal and traditional CsI:Tl scintillator to be similar. There are only several descriptions of CsI:In spectroscopic properties [5, 6]. It is known that the luminescence band has a maximum around 545 nm which coincides well with spectral sensitivity of silicon photodiodes. At the same time, the scintillation properties are practically not studied. The only known thing is the temperature dependence of light output under α - and γ -excitation [7].

The aim of the present work is to study luminescent and scintillation properties of CsI:In crystals to determine the potential of their use as scintillation detectors.

2. Experimental

Pure and In doped CsI crystals (indium concentrations from 10⁻⁴ to 10⁻¹ mass. %) have been grown from pure dry salt CsI (5N) and InI (4N) dope. Bridgman technique in evacuated sealed quartz ampoules was used for the single crystal growth. The polished plates of 2 mm thickness were used for absorption and luminescence measurements. Content of In⁺ ions in the samples was determined by chemical and absorption methods. The segregation coefficient was found to be around 0.15. A photo of CsI:In crystal is presented in Fig. 1.

The absorption spectra in UV-VIS range were measured at room temperature by means of SPECORD 40 spectrophotometer. Using IR spectroscopy methods, trace amounts of some oxyanion radicals, in particular OH⁻ and CO₃²⁻ were observed in the investigated crystals. Spectral and kinetic

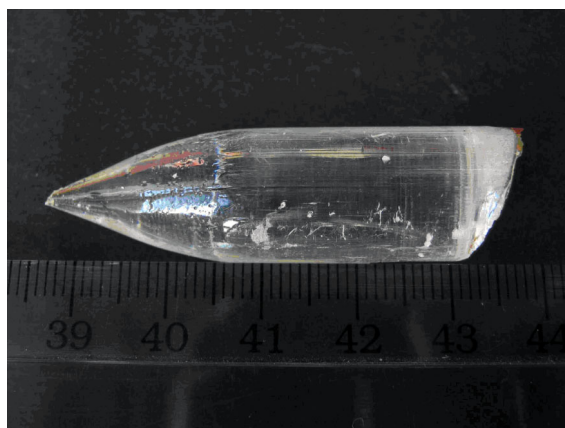


Fig. 1. CsI:In single crystal.

characteristics of photoemission were obtained using FLS 920 combined steady state fluorescence lifetime spectrometer. Xenon lamp Xe900, 450V was used as a source of UV excitation. X-ray luminescence was excited by a Cu-anode X-ray tube (40 kV, 40 μ A). Irradiation of the samples for radiation stability investigation was performed by an X-ray tube with W-anode, 9 mA, 160 kV, 10 Gy/min.

Cylinders $\varnothing 14 \times 20$ mm² were used for scintillation parameters measurements. For the sake of comparison, standard CsI:Tl crystalline samples of the industrial manufacture [8] were used. Relative light yield was measured using the current mode method with respect to a standard CsI:Tl, and also by the position of the photo-peak of pulse height spectra under gamma-excitation of ¹³⁷Cs (662 keV). Absolute values of the light yield were obtained by the technique [9] using a calibrated XP2020Q PMT.

3. Results and discussion

3.1. Absorption and luminescence properties

Absorption spectra of CsI, CsI:Tl and CsI:In crystals are presented in Fig. 2. In CsI:In and CsI:Tl within the region of 240–310 nm absorption bands are observed, corresponding to intracenter transitions in the activator ions. A-bands of absorption with maxima of 310 nm and 299 nm (for CsI:In and CsI:Tl, respectively) correspond to partially allowed $^1S_0 \rightarrow ^3P_1$ transitions. In weakly doped CsI:In crystals at 300 K B absorption bands –290 nm ($^1S_0 \rightarrow ^3P_2$ transitions) and C — of 260–270 nm ($^1S_0 \rightarrow ^1P_1$) [10] are also observed. In general, the spectra are similar but in the crystals contain-

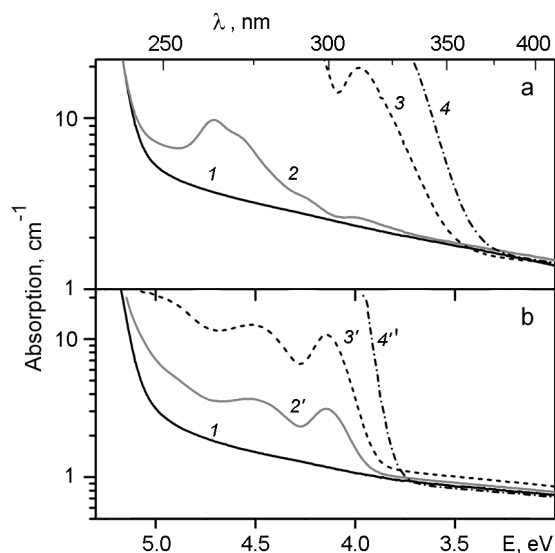


Fig. 2. Absorption spectra of pure CsI (curve 1); CsI:In (a): 2 — 10^{-4} % In, 3 — 0.005 % In, 4 — 0.045 % In; and CsI:Tl (b): 2' — 10^{-4} % Tl, 3' — $5 \cdot 10^{-4}$ % Tl, 4' — 0.021 % Tl.

ing In the activator bands are slightly shifted to the low-energy region.

The band with the maximum of 545 nm can be observed in CsI:In luminescence spectrum at room temperature, under both intracenter and X-ray excitation (Fig. 3). Luminescence and excitation spectra do not overlap which confirms the absence of re-absorption. The luminescence spectrum under photo-excitation almost does not depend on indium content. Unlike CsI:Tl crystal (maximum — 550 nm, FWHM — 0.71 eV), in CsI:In the luminescence band has a much smaller FWHM (0.46 eV), the additional luminescence band around 400 nm is also absent.

CsI:In crystals show exponential decay of luminescence with the decay time constant of 1900 ns under intracenter excitation (Fig. 4). The decay constant does not depend on the indium concentration. At the same time, excitation at the edge of the fundamental absorption (230 nm) reveals a longer decay component.

Under X-ray excitation 545 nm band predominates in the luminescence spectra (like under photo-excitation). In addition, the band of intrinsic luminescence in the region of 300 nm is also observed (Fig. 5). With an increase of the activator content, UV emission intensity falls down, and at In concentrations higher than 10^{-2} mol. % it is completely suppressed.

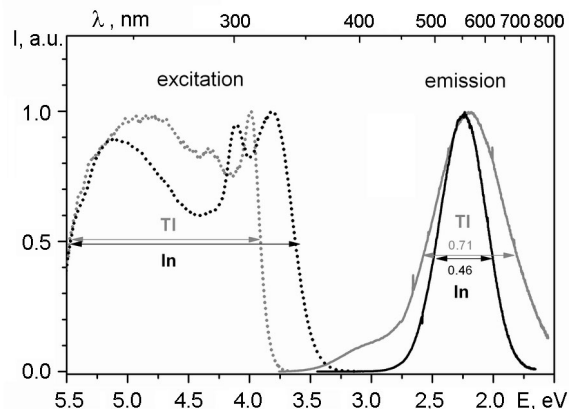


Fig. 3. Emission (solid) and excitation (dotted) spectra of CsI:In and CsI:Tl.

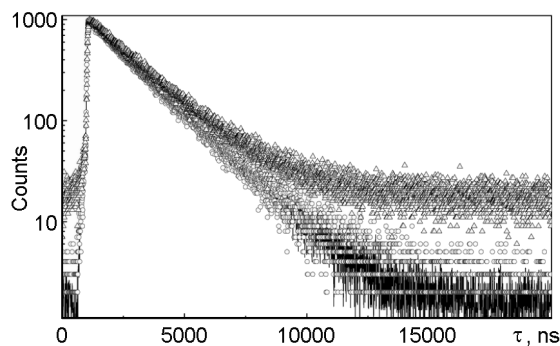


Fig. 4. Decay kinetics of 550 nm luminescence for CsI:In at different excitation wavelengths: 330 nm — solid, 250 nm — circles, 230 nm — triangles.

3.2. Scintillation properties

Pulse height spectra of CsI:In and CsI:Tl crystals, measured with the shaping time of 12 μ s under ^{137}Cs source (662 keV) are shown in Fig. 6. It can be seen that the light yield of the In-doped crystal is about 50 % of CsI:Tl. Absolute light yield of CsI:In measured using the method [9] gives 27 000 photons/MeV (with triangle shaping time 10 μ s). Light output of CsI:In crystal, measured using the current mode method under ^{90}Sr - ^{90}Y β -excitation (546 keV), attains CsI:Tl yield. This means that almost a half of the emitted light has slow components, not registered within the used time gates. Actually, measurement of the afterglow after 150 ms has shown that the signal in CsI:In is 4–5 times higher than the equivalent signal level of CsI:Tl crystals.

Under a pulsed X-ray excitation, CsI:In luminescence has in general an exponential

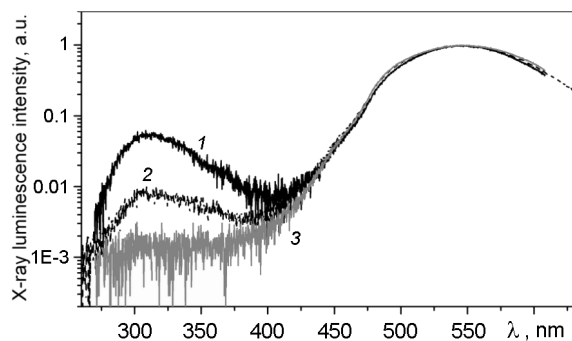


Fig. 5. X-ray luminescence of CsI:In crystals at 300 K, depending on the dopant concentration: 1 — 0.002 % In, 2 — 0.005 % In, 3 — 0.029 % In.

decay component about 2.1 μs , which is close to the decay time obtained by us under intracenter activator excitation (1.9 μs). Whereas a decay with the exponential part of about 1.0 μs is usually observed for CsI:Tl.

The inset of Fig. 6 demonstrates the concentration dependence of CsI:In light yield relative to a standard CsI:Tl scintillator, measured by the current mode method — circles, and by the position of the photopeak — squares. With the concentration increasing up to ~0.02 mol. % In, the light yield of CsI:In crystal measured by both methods reaches a saturation.

3.3. Radiation damage

First of all it should be noted that the exposure of the samples to day light (>360 nm, 12 h) and to UV photons (254 nm, Hg-lamp, ~1 h) does not reveal any coloration of CsI:In crystals. At the same time, X-irradiation leads to the formation of coloring of the samples with the high indium content (0.05 and 0.1 %). Absorption spectra of the colored CsI:In samples manifest a set of overlapping bands in the visible and near IR regions (Fig. 7). The most intensive bands, peaking around 518, 582–610, 800–900 nm, progressively decay during the crystals storage at room temperature. Similar band structure in the absorption spectrum of the irradiated crystals was also observed in CsI:Tl crystals and was attributed to transitions in Tl^+ or Tl^0 , localized in the vicinity of some defects [11]. Bands in the region of 800 nm can be connected with *F*-type centers, distorted by the presence of the dopant ions [12].

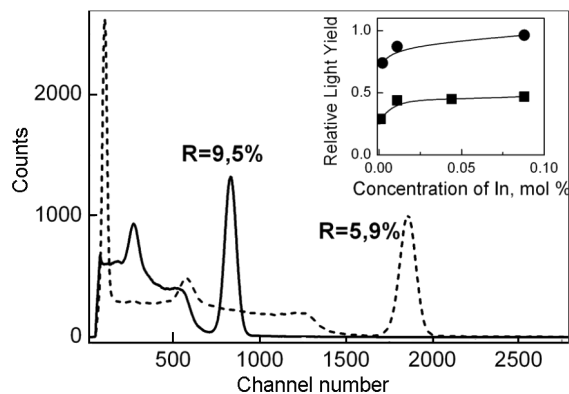


Fig. 6. Pulse height spectra of CsI:In (solid) and CsI:Tl (dashed) crystals with the shaping time of 12 μs . Inset — concentration dependence of the pulse light yield at γ -excitation of 662 keV ^{137}Cs (squares) and radioluminescence at β -excitation of 546 keV ^{90}Sr - ^{90}Y (circles) in relation to CsI:Tl.

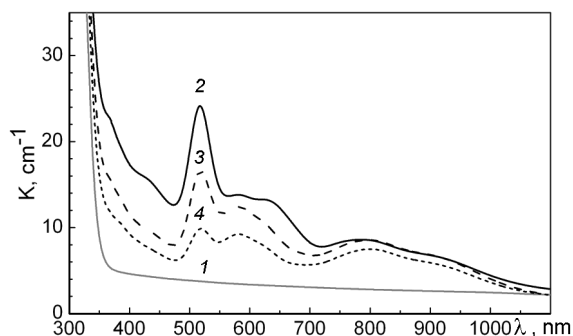


Fig. 7. Absorption spectra of CsI:0.05 % In crystal: initial — 1, X-ray irradiated ($3 \cdot 10^4$ rad) — 2, after 1 day (3) and 3 days (4) storage at room temperature.

3.4. Discussion

It should be mentioned that the obtained data for scintillation efficiency of CsI:In crystals are comparable with that for CsI:Tl scintillators. Relative simplicity of synthesis, emission band position (545 nm) convenient for registration and the light output, comparable with CsI:Tl, indicate the potential feasibility of such crystals use in scintillation applications. Relatively slow decay (1.9 μs) still allows the possibility to use such crystals for spectrometric measurements.

The data obtained deals with the study of laboratory samples. This is the first step in the full-scale study of this kind of scintillation material. This is why the data about functional and structural perfection of CsI:In should be considered as a lower esti-

mate of potential of the new material. From this point of view the potential steps for implementation of industrial technologies of CsI:In scintillators growth should be analyzed.

Secondly, relatively fast saturation in the concentration dependence of the light output should be noted (Fig. 6). Within the framework of the laboratory samples growth using the Bridgeman method, we managed to obtain transparent and uniform CsI:In samples. However, the concentration of indium ions (regardless of the sufficiently high loads of InI) in the crystals remains low (up to 0.1 mol. %). Segregation coefficient of In in CsI was estimated to be about or less than ~ 0.15 . Concentration of the activator in the upper and lower parts differs by the factor of 2–3. When exceeding the limiting solubility, a decomposition of the solid solution occurs, manifesting in micron size inclusions appearance in the crystal. We suppose that alternative growth methods and use of co-doping can allow attaining a higher dopant concentration.

Another possible way to improve the scintillation properties of CsI:In crystals is to reduce the amount of unwanted anionic impurities. Their presence in the crystals determines the detrimental contributions of slow scintillation component and afterglow (similarly to CsI:Tl [13, 14]). Delayed luminescence kinetics under excitation at the fundamental absorption edge, as well as millisecond afterglow indicate the presence of deep carriers trapping levels in CsI:In crystals. In this assumption the difference between light yield of the crystals, measured by the current mode method, and the yield (determined by the position of the photo-peak of pulse height spectra) can be explained. In the latter case not all the light emitted by the crystal is integrated.

The factor of the crystal purity plays a significant role in the generation and accumulation of radiation defects. We shall note that the radiation resistance of CsI:In crystals decreases with the increase of the dopant concentration which is similar to CsI:Tl. The tendency to the radiation coloration of CsI:In can be explained by a number of reasons. One of them is more significant difference in In^+ and Cs^+ ionic radii, providing a higher probability of creation and stabilization of structural defects (color centers) in the vicinity of the dopant ions. The

second one is connected with the tendency of In^+ ions to charge carriers capture with formation of In^0 and In^{2+} centers. Moreover, the increased radiation damage can be related to the presence of oxygen-containing admixture traces which is testified by the corresponding peaks in IR absorption spectra of the investigated crystals.

4. Conclusions

CsI:In single crystals with the dopant concentrations from 10^{-4} — to 10^{-1} mol. % were grown using the Bridgman method. Indium segregation coefficient in CsI lattice was estimated to be about 0.15.

In CsI:In luminescence spectra under photo and X-ray excitation there is an intense band around 545 nm characterized by FWHM of 0.46 eV. Excitation and luminescence spectra do not overlap, which preconditions the absence of re-absorption. Thus the spectral composition and decay kinetics of luminescence are sufficiently close to the parameters of conventional CsI:Tl scintillator.

The data on scintillation properties of the material are of the most importance and interest. It was shown that the absolute light output of CsI:In crystals, obtained from the pulse height spectra measurements with the shaping time of 12 μs is 27 000 photons/MeV. A significant part of the emitted light is concentrated in the longer decay components of the scintillation pulse and afterglow of the scintillator. Measurements of the integral light output in the current mode have shown that the total light yield of CsI:In attains that of CsI:Tl (60 000 photons/MeV).

Overall, Indium can be an efficient activator for alkali halides, and considered as an alternative dopant for CsI, because of its sufficiently high light yield and absence of toxicity. Main disadvantages of CsI:In are high afterglow and low radiation stability.

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