

On the state of activator in CsI(Na) crystals grown under forced mixing of the melt

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Effect of NaI concentration (C) on variations of some CsI(Na) crystal characteristics has been studied. The characteristics considered include: the optical absorption coefficient in the activator band; emission intensities of excitons localized at Na^+ ions (420 nm) and in the regular lattice (340 nm) in the radioluminescence (RL) at 80 K; yields of stationary RL (^{241}Am , 60 keV) (L_{RL}), γ -scintillation (^{137}Cs , 662 keV) (L_γ) and α -scintillation (^{241}Am , 5.9 MeV) (L_α) for CsI(Na) crystals grown under the forced melt mixing. The number of activator emission centers in those crystals has been shown to increase linearly as C rises up to about $2.2 \cdot 10^{-2}$ mol.%. The L_α value attains a maximum at $C \approx 2.3 \cdot 10^{-2}$ mol.% NaI while those of L_{RL} and L_γ at $C \approx 9 \cdot 10^{-3}$ mol.%. The NaI solubility in CsI has been concluded to be at least $2.2 \cdot 10^{-2}$ mol.% and thus to exceed substantially the literature data (from $8 \cdot 10^{-3}$ mol.% to $1 \cdot 10^{-2}$ mol.%). Therefore, the maximum L_γ value is due to a sufficient number of emission centers at the specified excitation density. The fact that the C value corresponding to the maximum L_γ of CsI(Na) is lower than for CsI(Tl) crystals (about $2.5 \cdot 10^{-2}$ mol.% of Tl) is assumed to be caused by a larger size of the distorted lattice volume in the neighborhood of the light Na^+ cation where the probability of the hole localization is increased.

Исследовано влияние концентрации (C) NaI на изменение: коэффициента оптического поглощения в активаторной полосе; интенсивностей в радиолуминесценции (РЛ) при 80 К свечения экситонов, локализованных у Na^+ -ионов (420 нм) и в регулярной решетке (340 нм); выхода стационарной РЛ (^{241}Am , 60 кэВ) (L_{RL}), γ -(^{137}Cs , 662 кэВ) (L_γ) и α -(^{241}Am , 5.9 МэВ) (L_α) сцинтилляций кристаллов CsI(Na), выращенных в условиях принудительного перемешивания расплава. Показано, что количество активаторных центров свечения в этих кристаллах линейно возрастает с увеличением C до $\approx 2.2 \cdot 10^{-2}$ мол.% NaI. Значение L_α достигает максимума при $C \approx 2.3 \cdot 10^{-2}$ мол.% NaI, тогда как L_{RL} и L_γ — при $C \approx 9 \cdot 10^{-3}$ мол.% NaI. Сделано заключение, что растворимость NaI в CsI составляет не менее $2.2 \cdot 10^{-2}$ мол.% и существенно выше известной в литературе ($8 \cdot 10^{-3}$ мол.%– $1 \cdot 10^{-2}$ мол.%). Поэтому максимальное значение L_γ обусловлено достаточностью количества центров свечения при данной плотности возбуждения. Предполагается, что меньшее значение C , при котором достигается максимальное значение L_γ кристаллов CsI(Na) по сравнению с CsI(Tl) ($\approx 2.5 \cdot 10^{-2}$ мол.% Tl), обусловлено большим размером искаженного объема решетки в окружении легкого катиона Na^+ , где вероятность локализации дырок увеличивается.

It follows from thermodynamical calculation of NaI solubility in cesium iodide made basing on the decomposition curve of the solid solution for CsI–NaI system [1] as well

as from electron microscopy of decorated cleavage pictures of CsI(Na) crystals grown by Stockbarger technique [2] that the solubility of NaI in CsI at room temperature (T_r)

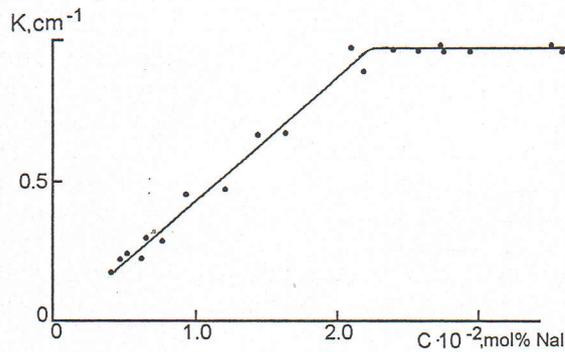


Fig. 1. Concentration dependence of the optical absorption coefficient for CsI(Na) crystals on 260 nm wavelength.

amounts from $8 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ moles per cent (from here on, this unit is referred to as %). The solid solution decomposition at T_c resulting in formation of isolated aggregates of about $2 \cdot 10^{-5}$ cm size occurs during several days [1]. The γ -scintillation yield (L_γ) for those crystals attains a maximum also at the activator concentration (C) $8 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$ % [3,4]. Therefore, the substantial difference in C values corresponding to the plateau origin of the $L_\gamma(C)$ dependence for CsI(Na) crystals and for CsI(Tl) ones (in the last case, $C \sim 2.5 \cdot 10^{-2}$ % of Tl [5]) can evidence that the maximum L_γ value for CsI(Na) is defined not by the sufficiency of the emission centers number at the specified excitation density but by the limited NaI solubility in CsI. At the same time, according to the concentration dependence of the optical absorption coefficient (K) at the activator band maximum wavelength (244 nm) for CsI(Na) crystals grown by Stockbarger method, the linear K increase up to C about $1 \cdot 10^{-2}$ % [6] is changed by its slight rise amounting about 20 to 25 % as C is increased up to $2 \cdot 10^{-2}$ % NaI [7]. This fact can point to a higher NaI solubility in CsI as compared to that specified in [1,2]. The reduction of the K elevation rate is accompanied by the increase of the number of non-scintillating activator aggregates. The last fact results in an impairment of the energy resolution (R) even in the initial section of the $L_\gamma(C)$ plateau. It has been concluded in [1,7] under account for [8] that the R deterioration is caused by increased fraction of regions enriched in the mentioned activator distribution nonuniformities in the crystal volume; the size of these nonuniformities ($2 \cdot 10^{-5}$ cm) is three times smaller than the electron free path. Those nonuniformities

arise due to the capturing of NaI admixture by the crystal in the course of growth at a low entry coefficient (0.02) resulting from an insufficient melt mixing as well as to the solid solution decomposition. The last process may be favoured by a great number of the growth defects (dislocations and grain boundaries) that are typical for crystals grown using Stockbarger technique [9].

The growing of CsI(Na) crystals under the forced melt mixing (pulling on a seed while the crucible with the melt and the crystal are rotated in opposite directions) [10] results in a substantial reduction of the activator aggregates number and in 1.5 times improved R [11]. The growth defect density in such crystals is 1.5–2 decimal orders lower than in those grown by Stockbarger method [9]. It is not known, however, how the emission centers number in those crystals changes as C increases. The information on this problem is of importance because it would allow to refine the NaI solubility in CsI and to improve the notions of the scintillation process mechanism in CsI(Na) crystals.

In this connection, the effect of NaI concentration (varied from $4.4 \cdot 10^{-3}$ to $(3 \pm 3.6) \cdot 10^{-2}$ %) on the emission centers number has been studied in this work for CsI(Na) crystals grown under the forced melt mixing [10]. Moreover, the concentration dependences of stationary radioluminescence (RL) yield (L_{RL}), of L_γ and of γ -scintillation (L_{RL}) ones have been considered.

The changes in the emission centers number were determined from the character of $K(C)$ dependence in the activator band as well as from the emission intensity ratio for excitons localized at Na^+ ions (420 nm) and in the regular lattice (340 nm) in the RL spectra taken at 80 K.

Samples of the same geometry, namely, 5 mm thick discs of 30 mm in diameter, were used in all experiments. The discs were cut out of large CsI(Na) crystals of 150 mm in dia. and 100–150 mm in height annealed at T_r for different time periods varying from several days to two years. The optical absorption was measured using a SF-26 spectrophotometer, the RL spectra (^{241}Am , 60 keV) were taken in a vacuum cryostat using a MDR-2 monochromator and FEU-100 photomultiplier; the excitation source being positioned on the outer cryostat side at an Al window. The standard techniques were used to determine the γ - and α -scintillation yield under excitation by

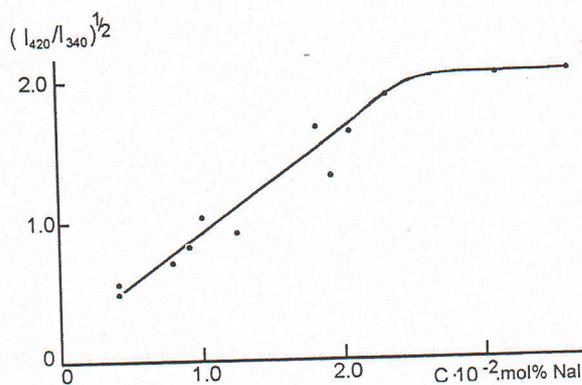


Fig. 2. Concentration dependence of the $(I_{420}/I_{340})^{1/2}$ ratio for RL of CsI(Na) crystals at 80 K.

^{137}Cs , 662 keV and ^{241}Am , 5.9 meV, respectively. The sodium concentration was determined by the flame photometry.

Since it is difficult to measure K in the activator band maximum (244 nm) at $C \geq 1 \cdot 10^{-2}$ % of NaI due to high optical density, we used K values measured on the long-wavelength band edge, namely, at 260 nm wavelength (K_{260}) where the transmission of the crystals under study was at least 40 % or more to get information on the $K(C)$ dependence character. The long-wavelength edge of the absorption band has been found to have the same shape for all samples, thus confirming that the K_{260} values were selected properly for the determination of changes in the emission centers number within the specified C range.

In RL spectra taken at 80 K, intensities of 420 and 340 nm bands (denoted as I_{420} and I_{340} , respectively) are redistributed in favour of the activator emission (420 nm) as C increases. Therefore, the value of $(I_{420}/I_{340})^{1/2}$ ratio should be proportional to the concentration of activator emitting centers. It is just this ratio that we have used to isolate from the total C value its fraction that enters the lattice and is responsible for the 420 nm emission.

The measurement results are presented in Figs. 1-3. Note that no effect of the annealing duration at T_r on character of dependences shown in these figures has been observed.

It is seen from Fig. 1 that the K_{260} value for examined crystals increases linearly ($K_{260} = bC$ where $b = 43.8 \text{ cm}^{-1}\%$) as C increases up to $2.2 \cdot 10^{-2}$ % of NaI. At higher C values, K_{260} does not change essentially. The dependence $(I_{420}/I_{340})^{1/2}(C)$

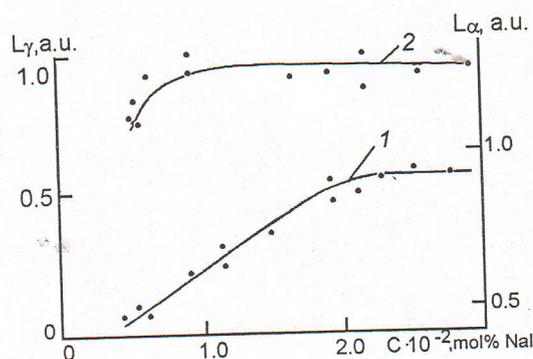


Fig. 3. Concentration dependence of α -scintillation yield (1) and γ -scintillation one (2) for CsI(Na) crystals.

shown in Fig. 2 points that the number of activator emitting centers increases also linearly as C grows up to $2.3 \cdot 10^{-2}$ % NaI.

The obtained $K_{260}(C)$ and $(I_{420}/I_{340})^{1/2}(C)$ dependences evidence that the activator centers responsible for the optical absorption and 420 nm RL of the crystals being studied arise from individual Na^+ ions up to C about $2.2 \cdot 10^{-2}$ % NaI. It follows therefrom that the NaI solubility in CsI at T_r is at least $2.2 \cdot 10^{-2}$ % and thus exceeds significantly that found in [1,2]. The above is confirmed by the concentration dependence of α -scintillation yield (Fig. 3, curve 1) showing that L_α value increases as C grows up to about $2.3 \cdot 10^{-2}$ % of NaI.

Unlike the $L_\alpha(C)$ dependence, the maximum L_γ value for studied crystals (Fig. 3, curve 2) is attained at $C \approx 9 \cdot 10^{-3}$ % NaI, as well as for crystals grown by Stockbarger method. The $L_{RL}(C)$ dependence is of the same character. This means that the saturation of $L_\gamma(C)$ and $L_{RL}(C)$ dependences is due to the sufficiency of the emission centers number at a specified excitation density. In this case, the distance between Na^+ ions amounts $22a$, a being the lattice constant, provided the ions are distributed uniformly. Unlike CsI(Na), the maximum L_γ value for CsI(Tl) crystals is attained at C about $2.5 \cdot 10^{-2}$ % of TlI, when the distance between Tl^+ ions is $16a$.

The difference between activator concentrations corresponding to maximum L_γ values for CsI(Na) and CsI(Tl) may be associated with that the number of centers responsible for scintillations is greater in CsI(Na) than in CsI(Tl) (according to the assumption stated in [12]), the activator concentrations are the same in both cases. In

the same time, it can be supposed that the probability of hole localization in the activator ion environment at the crystal interaction with γ -radiation is higher for CsI(Na) than for CsI(Tl). The last fact may be due to that the volume of the crystal lattice distorted by the light Na⁺ cation is greater than in the case of Tl⁺ one, since the Na⁺ radius is considerably smaller as compared to Tl⁺ and Cs⁺ ions. This assumption is evidenced by the inverse proportional dependence between distance ratio corresponding to L_γ maxima for CsI(Na) and CsI(Tl) crystals ($22a/16a = 1.37$) and effective ionic radii of Tl⁺ (1.59 Å) and Na⁺ (1.18 Å) in the CsCl type lattice ($1.59/1.18 = 1.35$). Spectral and kinetic characteristics of the crystals grown by the technique proposed in [10] will be studied to prove that assumption.

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Про стан активатора в кристалах CsI(Na), що вирошені в умовах примусового перемішування розплаву

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Досліджено вплив вмісту (С) NaI на зміни коефіцієнту оптичного поглинання в активаторній смугі, інтенсивностей в радіюлюмінесценції (РЛ) при 80 К світіння екситонів, локалізованих біля Na⁺-іонів (420 нм) та в регулярній ґратці (340 нм), виходу стаціонарної РЛ (²⁴¹Am, 60 кеV) (L_{RL}), γ -(¹³⁷Cs, 662 кеV) (L_γ) и α -(²⁴¹Am, 5.9 меV) (L_α) сцинтиляцій для кристалів CsI(Na), вирошених в умовах примусового перемішування розплаву. Показано, що кількість активаторних центрів світіння в цих кристалах лінійно зростає при збільшенні С до $\approx 2.2 \cdot 10^{-2}$ мол.% NaI. Значення L_α досягає максимуму при $C \approx 2.3 \cdot 10^{-2}$ мол.% NaI, тоді як L_{RL} та L_γ - при $C \approx 9 \cdot 10^{-2}$ мол.% NaI. Зроблено висновок, що розчинність NaI в CsI не менше ніж $2.2 \cdot 10^{-2}$ м % і значно вища відомої з літератури ($8 \cdot 10^{-3}$ - $1 \cdot 10^{-2}$ мол.%). Тому максимальна величина L_γ обумовлена достатньою кількістю світіння при даній щільності збудження. Припускається, що менше значення С, при якому досягається максимальна величина L_γ кристалів CsI(Na) в порівнянні з CsI(Tl) ($\approx 2.5 \cdot 10^{-2}$ мол.% Tl), зумовлена більшим розміром викривленого об'єму ґратки навколо легкого катіону Na⁺, де ймовірність локалізації дірок збільшується.