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Defect formation in CsI–CsBr mixed crystals

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The defect structure of CsI–CsBr mixed crystals has been studied by electroconductivity and thermostimulated depolarization current (TSDC) methods. The formation of $CsI_{0.93}Br_{0.07}$ solid solution is found to be accompanied by increase of conductivity as compared to that of pure CsI. The physical processes causing the appearance of TSDC maxima at 300 K and 385 K have been considered. The results obtained evidence the increase of anion vacancy concentration and unchanged concentration of cation vacancies in $CsI_{0.93}Br_{0.07}$ mixed crystals.

Дефектная структура смешанных кристаллов CsI–CsBr исследована методами электропроводности и токов термостимулированной деполяризации (ТСД). Установлено, что возникновение твёрдого раствора $CsI_{0,93}Br_{0,07}$ сопровождается увеличением проводимости по сравнению с проводимостью чистого CsI. Проанализированы физические процессы, обусловливающие возникновение максимумов ТСД при температурах 300 К и 385 К. Полученные результаты свидетельствуют о повышении концентрации анионных и неизменной концентрации катионных вакансий в смешанных кристаллах $CsI_{0,93}Br_{0,07}$.

Alkali halide mixed crystals are applied in information storage devices, as laser window materials, and in scintillating detecting systems. That is why the study of defect structure of these crystals is of importance in solid state physics. But the available information is mainly confined to alkali halide mixed crystal systems with NaCl structure. On the other hand, it is just the CsI-based scintillation crystals that are considered as promising materials for ionizing radiation detectors under hard operation conditions. The related investigations [1] indicate that the transition from pure CsI crystals to mixed ones causes an accelerated decay kinetics of the scintillation pulse and can be used as a method to vary the radiation stability of dielectrics. The dependence of luminescence and scintillation characteristics of CsI–CsBr mixed crystals on bromide concentration studied in [2] testifies to direct influence of the mixed crystal defect structure on performance parameters of the materials. This work aims at study of CsI–CsBr mixed crystal defect structure using electroconductivity (σ) and thermostimulated depolarization current (TSDC) methods. Temperature dependence of σ and TSDC measurements were performed using the experimental setup described in detail in [3].

The experimental crystals were obtained in our laboratory from raw material purified by methods proposed in [4]. The mixture of pre-specified molar composition was prepared using previously dried commercial (special purity grade) CsI, CsBr powders. The crystals were grown in evacuated quartz ampoules using the Stockbarger method at a rate of 4 mm/h. The mutual solubility range of the $CsBr_xI_{1-x}$ substitution solid solution was defined before [5], the solubility limits being 6 mol % CsI in CsBr and 9 mol % CsBr in CsI. The $CsBr_xI_{1-x}$ solid solution ($0.05 \le x \le 0.09$) was proposed before as a new dielectric material for storage targets of electron-beam memory devices. In this work, the main attention is given to a close study of $CsBr_{0.07}I_{0.93}$ crystal.

It follows from Fig. 1 that CsBr entering into CsI matrix, i.e. the formation of $CsBr_{0.07}I_{0.93}$, causes a conductivity increase

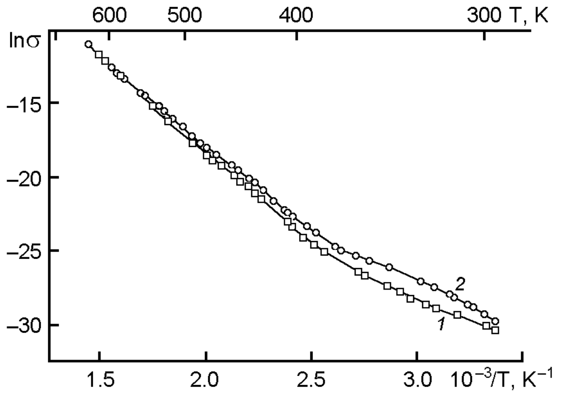

Fig. 1. Conductivity vs reciprocal absolute temperature for CsI (*1*) and $CsI_{0.93}Br_{0.07}$ (*2*).

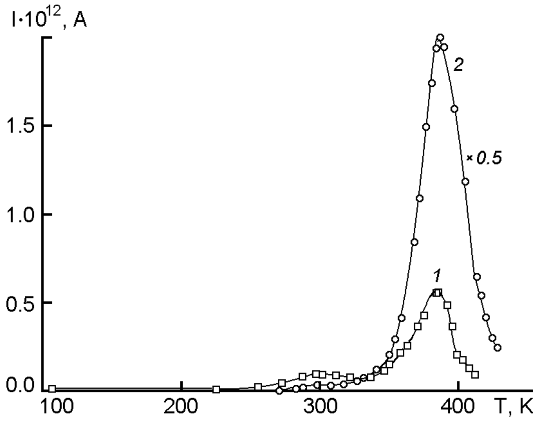

Fig. 2. TSDC spectra of CsI crystals at T_{pol} = 295 K (*1*) and T_{pol} = 375 K (*2*).

(curve *2*) as compared to that of pure CsI (curve *1*). This increase is within limits of one decimal order up to 400 K. At higher temperatures, the conductivity curves of both crystals coincide essentially. The curve *2* can be conventionally divided into three regions: I, above 670 K; II, 380 to 670 K; III, 330 to 380 K. The I section corresponds to the intrinsic conductivity region. The extrinsic conductivity region consists of two sections (II, III), either characterized by its own activation energy: E_a(II) = 1.04 eV; E_a(III) = 0.54 eV.

The conductivity increase of $CsBr_{0.07}I_{0.93}$ crystal as compared to that of pure CsI is somewhat unexpected because before [5], the CsBr entering into CsI matrix was found to reduce the conductivity. It was supposed and confirmed later by experimental results that due to substitution of iodide ions by bromine ones the lattice parameters become diminished, thus making worse the conditions for anionic vacancy motion. In other words, the activation energy for migration of anionic vacancies was increased and, consequently, the crystal conductivity was decreased. But the crystals studied in this work are grown from raw materials purified from oxygen-containing impurities. Removal of the latter (i.e. purification) results in a decreased conductivity [4]. To reveal the peculiarities of defect formation in CsI–CsBr mixed crystals, we have studied the TSDC, too. It is just this method that makes it possible to identify the type of defects (dipoles or their complexes) responsible for charge relaxation in a certain temperature interval.

It is known [4] that anion vacancies are the major carriers in CsI crystals. But their concentration in our samples was negligible. As follows from Fig. 2, there are two maxima at 300 K and 385 K in the TSDC spectrum of the CsI crystals grown from raw materials free of oxygen-containing impurities. These maxima are connected with volume charge polarization of the sample. Maxima at 300 K and 385 K are caused by migration of anion V_a^+ (E_a = 0.27 eV) and cationic vacancies V_c^- (E_a = 0.57 eV), respectively. The intensity of 300 K maximum (caused by V_a^+ migration) in purified crystals is several orders lower than in non-purified CsI crystals, studied before [4], thus testifying to a lower concentration of anion vacancies V_a^+ in the purified CsI crystals. Consequently, we can state a higher structure perfection of purified CsI crystals. The dipole relaxation in these crystals was not observed.

As is seen in Fig. 3, the intensity of similar TSDC maximum at 300 K in $CsI_{0.93}Br_{0.07}$ mixed crystals is one and a half order higher than in CsI, thus pointing to an increased concentration of the anion vacancies in the mixed crystals. The activation energy of these relaxation processes was calculated using Garlik-Gibson method [6], E_a = 0.24 eV. In other words, the activation energy value is somewhat lower in the mixed crystal. Thus, the observed conductivity increase in the $CsBr_{0.07}I_{0.93}$ crystal (Fig. 1, curve *1*) is caused by both increased anion vacancies concentration in mixed crystals and decreased activation energy of this relaxation process. The 375 K maximum amplitude is not changed as compared to that for CsI crystal. Thus, the value of TSDC maximum caused by migration processes of cationic vacancies is the same for

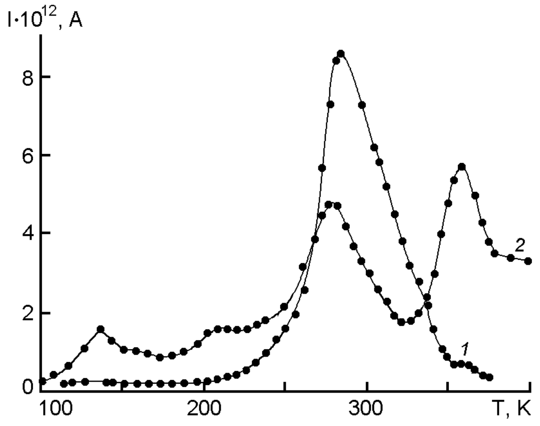

Fig. 3. TSDC spectra of $CsI_{0.93}Br_{0.07}$ crystals at T_{pol} = 295 K (*1*) and T_{pol} = 375 K (*2*).

the both crystals ($\approx 0.5 \cdot 10^{-12}$ Å). As polarization temperature is increased to 375 K (see Fig. 2, curve *2*), a negligible amplitude increase of high-temperature maxima at 300 K and a sharp intensity increase (by one order) of the 375 K maximum have been recorded. But the increase of polarization temperature for the $CsBr_{0.07}I_{0.93}$ samples (Fig. 3, curve *3*) resulted in other two low-temperature maxima at 140 K and 220 K. In that case, the intensity of 375 K maximum is increased by one order, too, but the 300 K maximum intensity becomes halved. Furthermore, this maximum shifts towards lower temperatures (T = 285 K). The analysis of TSDC spectra of $CsBr_{0.07}I_{0.93}$ crystals at changing polarization conditions evidences that during heating of the crystal, complex processes involving the defect structure modification take place. Therefore, it is difficult to make distinction between the relaxation processes occurring in the crystal. The formation of V_a^+–Br^- dipoles (T = 140 K, E_a = 0.13 eV) and V_a^+–V_c^- divacancies (T = 220 K, E_a = 0.07 eV) seems to be the most probable.

Summarizing, the results of electroconductivity and TSDC measurements in $CsBr_{0.07}I_{0.93}$ crystals are mutually correlated and give evidence to a change of defect structure in the anion sublattice during formation of the mixed crystals. The observed conductivity increase for $CsBr_{0.07}I_{0.93}$ is caused by an increased anion vacancy concentration. The cationic vacancy one remains unchanged during formation of mixed crystal. The appearance of dipole relaxation maxima at temperature increase may be caused by formation of divacancies and vacancy-impurity dipoles.

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Дефектоутворення у змішаних кристалах CsI–CsBr

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Досліджено дефектну структуру змішаних кристалів CsI–CsBr методами електропровідності та струмів термостимульованої деполяризації (ТСД). Встановлено, що утворення твердого розчину $CsI_{0,93}Br_{0,07}$ супроводжується збільшенням провідності порівняно з провідністю чистого CsI. Проаналізовано фізичні процеси, що спричиняють появу максимумів ТСД при температурах 300 К та 385 К. Одержані результати свідчать про підвищення концентрації аніонних та незмінну концентрацію катіонних вакансій в змішаних кристалах $CsI_{0,93}Br_{0,07}$.