Spectral and kinetic characteristics of luminescence in CsI–Ca crystals

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The spectral and kinetic luminescence properties of CsI–Ca crystal (C_{Ca} = 1 mol.% in the initial melt) have been studied at 10 K and 295 K in the energy range 4–16 eV. The luminescence efficiency has been examined upon the excitation of CsI-Ca within the range of transparency and fundamental absorption of CsI host. The nature of CsI-Ca luminescence is discussed.

Исследованы спектрально-люминесцентные и люминесцентно-кинетические свойства кристалла CsI–Ca (C_{Ca} = 1 мол.% в расплаве) при 10 и 295 K в энергетическом интервале 4–16 эВ. Проанализирована природа люминесцентных центров, которые возникают в кристалле CsI–Ca, и эффективность их возбуждения в области прозрачности и фундаментального поглощения матрицы CsI.

Luminescence properties of CsI crystals favor the use of CsI crystalline matrix in the development of scintillation materials for various functional applications. Incorporation of either a cation or anion impurity provides the possibility to modify the luminescence characteristics of CsI based scintillators. Doping of CsI crystals with divalent Ca^{2+}, Sr^{2+}, Mn^{2+}, Mg^{2+} ($C<10^{-2}$ mol.%) ions results in the appearance of so-called "blue" emission band peaked at 415 nm [1]. The emission of CsI–Me^{2+} (Me^{2+} = Ca^{2+}, Sr^{2+}, Mn^{2+}, Mg^{2+}) with a maximum around 415 nm had been shown to be caused by the emissive decay of exciton at the cation vacancy arising due to compensation of a divalent cation residual charge in CsI matrix and independent of the impurity chemical nature. A luminescence with a similar spectrum was observed for CsI–Na^+ [2] and intentionally undoped CsI crystal after its plastic straining [3]. The luminescence of those crystals is believed to be caused by the decay of exciton near a V_a^+ anion vacancy. The similarity of the luminescence spectral characteristics of CsI–Me^{2+}, CsI–Na^+ and intentionally undoped CsI crystal after its plastic straining indicate a rather complex origin of the emission centers in CsI–Me^{2+} crystals (Me^{2+} = Ca^{2+}, Sr^{2+}, Mn^{2+}, Mg^{2+}). An explanation of the nature of the emission centres of CsI–Me^{2+} crystals is of a great practical interest since it indicates a way to purposeful modification of the luminescence spectral characteristics of CsI-based scintillation materials.

Moreover, worth of attention is a possibility of impurity ions aggregation with formation of impurity phase in CsI matrix. It is known that Cs_4PbI_6 and $CsPbI_3$ microphases appear in $CsI–Pb$ crystal and NaI one in $CsI–Na$ crystal. To verify the formation of CaI_2 or $CsCaI_3$ microphases embedded in CsI matrix, we have investigated $CsI–Ca$ crystals with a considerably higher concentration of Ca ions (C_{Ca} = 1 mol.%) than in [1].

We have investigated the spectral luminescence properties of $CsI–Ca$ doped with $CsCaCl_3$ (C = 1 mol.%) at 10 and 295 K under excitation by light quanta in 4–16 eV energy range. The simultaneous doping of CsI matrix with Ca^{2+} and Cl^- ions causes an increase of local distortions in CsI matrix because the ion radii differ considerably, being equal to 1.65 and 1.04 Å for Cs^+ and Ca^{2+} ions and 2.2 and 1.81 Å for I^- and Cl^- ones, respectively. Such distortions of crystal lattice may result in stabilization (at room temperature) of vacancy luminescence in CsI based crystals [4, 5].

$CsI–Ca$ single crystals (C_{Ca} = 1 mol.% in the initial mixture) were grown in evacuated quartz ampoules using the modified Stockbarger technique. The grown crystals were annealed (about 100 h at 150–200°C).

The luminescence excitation and emission spectra as well as decay kinetics were measured at Deutsches Elektronen Synchotron (DESY, Hamburg) using the equipment of SUPERLUMI station at HASYLAB [6]. Helium flow type cryostat was used to carry out the measurements within 10–300 K temperature range. The luminescence spectra were measured at a resolution of about 10 nm in 300–800 nm range using a secondary ARC "Spectra Pro 308" 30 cm monochromator-spectrograph, CCD detector or a HAMAMATSU R6358P photomultiplier. The time-resolved spectroscopy technique was used. The integrated spectra correspond to the total signal formed by the photomultiplier. The luminescence decay kinetics was recorded up to 200 ns range, defined by the excitation pulse frequency of a DORIS III storage ring. The excitation energy for the kinetics decay accumulation was selected to minimize the overlapping of neighbor luminescence bands. The luminescence excitation spectra were scanned at the resolution of 3.2 Å in 4–16 eV range using the primary 2 m monochromator. The luminescence excitation spectra were corrected for the incident photon flux.

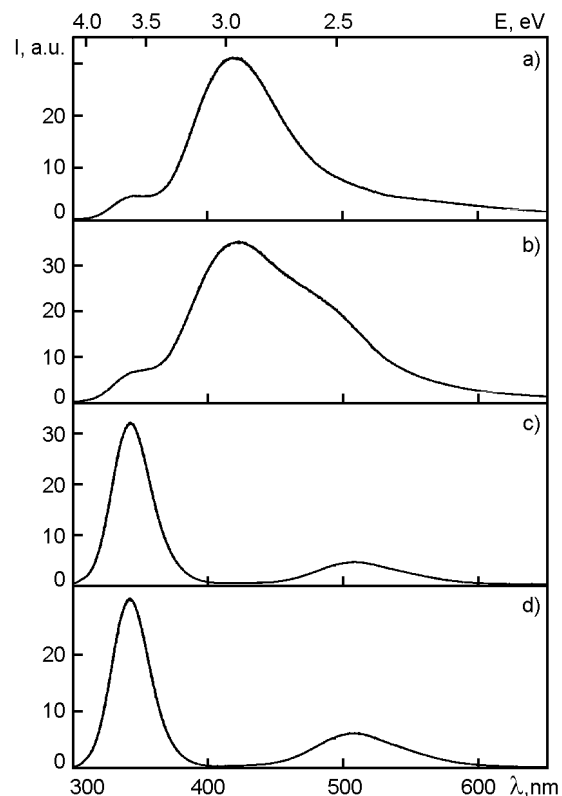Fig. 1 shows luminescence spectra of a $CsI–Ca$ crystal (T = 10 K) at the excitation

Fig. 1. Emission spectra of $CsI–Ca$ crystal at T = 10 K: a – E_{exc}=5.23 eV, λ_{exc} = 237 nm; b – E_{exc}=5.56 eV, λ_{exc} = 223 nm; c – E_{exc}= 6.11 eV, λ_{exc} = 203 nm; d – E_{exc}=12.92 eV, λ_{exc} = 96 nm.

in transparency energy range (a, b), excitonic absorption (c) and band-to-band transitions of CsI matrix (d). The main luminescence bands of $CsI–Ca$ crystal are around 340, 420, 510 nm. Fig. 2 shows excitation spectra for those bands.

The emission around 340 nm is excited both in the exciton generation and in the band-to-band transition regions of CsI matrix (Fig. 2, a). Its decay kinetics includes one component with the time constant 0.9 μs under excitation by quantum with E_{exc} = 6.11 eV, λ_{exc} = 203 nm. The spectral luminescence characteristics of the 340 nm emission correspond to those for π-component of self-trapped exciton luminescence in CsI matrix [7, 8]. The decay time constant for the self-trapped exciton emission of CsI is known to be of 1.8 μs [7]. This value is reduced down to 0.9 μs for the case of Ca^{2+} presence in $CsI–Ca$ crystal. Such a reduction was also observed in CsI crystals doped with Na^+, Pb^{2+}, Cl^- ions [4, 5, 9].

The emission around 420 nm is excited mainly within transparency range
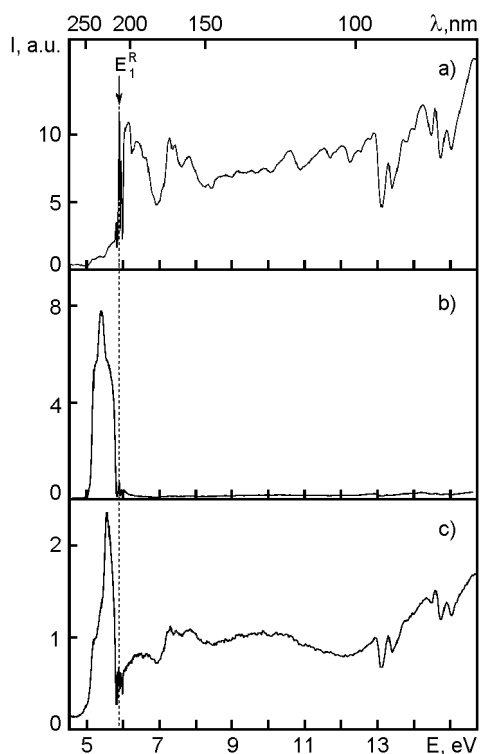
Fig. 2. Luminescence excitation spectra of CsI–Ca crystal at $T = 10$ K: λ_{lm}, nm: a – 340, b – 420, c – 510. The energy position of CsI anion exciton absorption is indicated with the arrow and dashed line.

(5.0 eV$<E_{exc}<$5.8 eV) of CsI matrix (Fig. 2,b). That luminescence band arises after CsI activation with Ca^{2+} ions, but it can hardly be attributed to the direct transitions between the electron states of a single Ca^{2+} ion, since those are located beyond the transparency range of CsI matrix. However, the presence of single Ca^{2+} ions results in generation of a charge-compensation cation vacancy V_c^- and formation of an appropriate cation-vacancy dipole $Ca^{2+}-V_c^-$ on which the emissive decay of self-trapped exciton occurs. The formation dynamics of $Ca^{2+}-V_c^-$ dipoles in CsI–Ca ($C_{Ca} \sim 10^{-2}$ mol.%) crystal was investigated in [1]. The quenching from 500°C or annealing at the same temperature was shown to result in an increased amount of $Ca^{2+}-V_c^-$ dipoles but new centers, e.g. $(Ca^{2+}-V_c^-)_n$ aggregates, were not formed. This fact was concluded from the consideration of absorption spectrum of annealed CsI–Ca crystals. In such crystals, no new absorption bands appear, thus suggesting the absence of $(Ca^{2+}-V_c^-)_n$ aggregate complexes. To increase the number of $Ca^{2+}-V_c^-$ centers, the concentration of impurity Ca^{2+}

ions was augmented significantly (up to $C_{Ca} = 1$ mol.% in the initial mixture). Taking into account the low incorporation coefficient of Ca^{2+} ions into CsI matrix, the resultant concentration of Ca^{2+} would be lower than in initial mixture. In addition, prolonged annealing was used as an effective way to form the impurity-vacancy dipoles. In annealed samples, an increased intensity of the luminescence band peaked at 420 nm was observed, which confirms definitely its vacancy nature, namely the exciton localization around $Ca^{2+}-V_c^-$ dipole.

The formation of $Ca^{2+}-V_c^-$ complex is confirmed by the characteristic excitation spectrum hereof: in the near-exciton absorption region of CsI matrix, a non-elementary absorption band was observed ($\lambda_1 = 217.5$, $\lambda_2 = 227.5$ nm) with the spectral position in agreement with results from [1]. The CsI–Ca crystal luminescence band around 420 nm is essentially not excited in the range of CsI matrix intrinsic absorption. Such characteristic structure of excitation spectrum confirms the vacancy entering into the emissive complex. The exciting quanta at band-to-band excitation penetrate the crystal to very small depth, about several tens of nanometers, due to the considerable absorption of matrix, while the concentration of the vacancies in the near-surface layer is considerably less than in the crystal bulk due to draining of vacancies from the near-surface layer directly to the crystal surface itself [10]. The effective excitation of the 420 nm luminescence band in the CsI matrix transparency range and ineffective excitation in the range of band-to-band transition indicates the exciton localization just near a cation vacancy but not near Ca^{2+} cation. A similar model of emissive complex with V_k center localized near a vacancy has been proposed in [1]. This conclusion has been made basing on independence of luminescence spectra of CsI–Me^{2+} ($Me^{2+} = Ca^{2+}$, Sr^{2+}, Mn^{2+}, Mg^{2+}) crystals of the impurity chemical nature. Our conclusion on the localization of self-trapped exciton near the cation vacancy is based on characteristic excitation spectrum of this luminescence band in the transparency range and fundamental absorption of the matrix. The model of this radiative complex is shown in Fig. 3.

Under excitation of 420 nm luminescence band in CsI–Ca with 5.39 eV and $T = 10$ K (Fig. 4, curve *2*), two components of the decay kinetic were obtained: a fast one with decay time constant 8 ns and a slow one with the decay time constant in microsecond
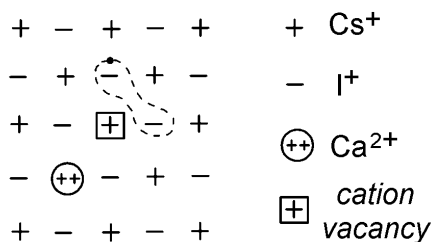
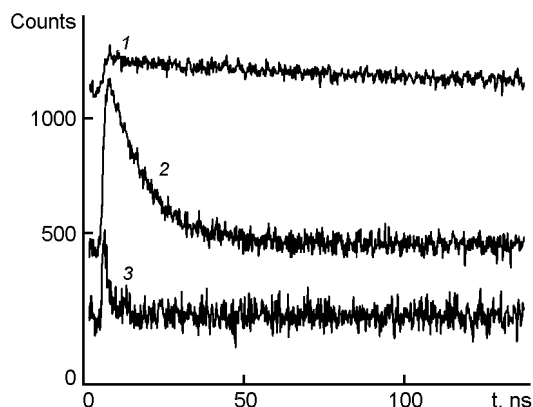Fig. 3. Model of emissive complex in CsI–Ca crystals.

Fig. 4. Decay kinetics of CsI–Ca luminescence at T = 10 K: $1 - E_{exc}$ = 6.11 eV, λ_{exc} = 340 nm; $2 - E_{exc}$ = 5.39 eV, λ_{exc} = 420 nm; $3 - E_{exc}$ = 6.11 eV, λ_{exc} = 510 nm.

Fig. 5. Emission spectra of CsI–Ca crystal at T = 300 K: $a - E_{exc}$=5.12 eV, λ_{exc} = 242 nm; $b - E_{exc}$ = 5.28 eV, λ_{exc} = 235 nm.

range. Such constants are peculiar for the self-trapped exciton luminescence in iodide matrix [7, 11].

Effective excitation of the λ_{max} 510 nm band in the transparency range (4.9 eV– 5.8 eV), exciton and band-to-band absorption of CsI matrix (E_{exc}>5.8 eV, Fig. 2, c) suggests a resemblance of the excitation mechanisms for that band and for π-component of the self-trapped exciton luminescence of CsI matrix (Fig. 2, a, c). In addition, the characteristic time constants of the 510 nm band decay kinetics both are in microsecond range. Such characteristics are typical of the π-component of self-trapped exciton luminescence, too. The similarity in the time features of 510 nm band and π-component as well as a resemblance of their excitation spectra allow to attribute the luminescence with maximum at 510 nm to emission of an exciton localized near the matrix defect, although not of vacancy nature. Ca^{2+} ion with interstitial Cl^- ion would be such a defect. By the way, in [1] this band was not observed under activation

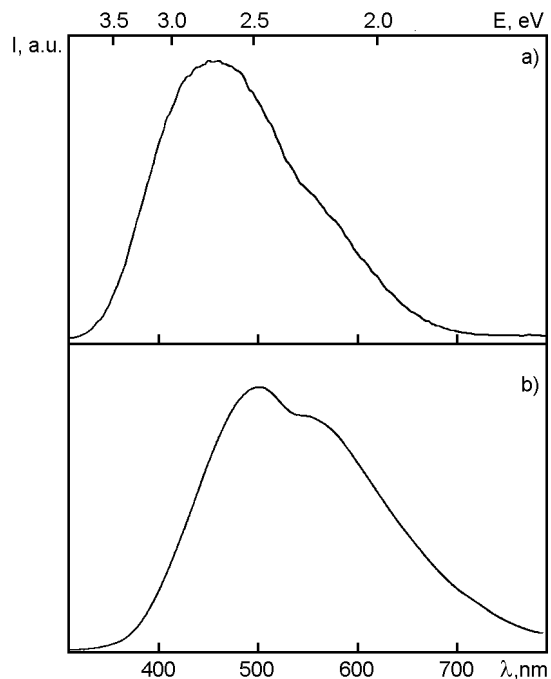of CsI matrix by Ca^{2+} ions. The fast component (1.3 ns) in decay kinetics of that luminescence band (Fig. 4, curve 3) appears most probably due to recording of scattered exciting light.

The luminescence of emissive $Ca^{2+}-V_c^-$ dipoles with maximum at 420 nm at room temperature is quenched [1], in other words, the wide bands with maxima at 460 and 570 nm (Fig. 5, a and b) in CsI–Ca crystal luminescence spectrum at room temperature are not associated with emission of ($Ca^{2+}-V_c^-$s) dipoles. The short-wave side of 420 nm band is excited mainly in the transparency range of CsI matrix (4.8 eV– 5.5 eV) (Fig. 6, curve 1). Such a structure of excitation spectrum is typical of luminescence bands of vacancy nature and can be ascribed to the luminescence of excitons localized near the anion vacancies, appeared due to the presence of Cl^- ions in CsI matrix [5, 12, 13].

The 570 nm band (Fig. 5, curve 2) is effectively excited both in the CsI matrix transparency range and in fundamental adsorption one (Fig. 6,b). As stated above, such excitation spectrum is typical of the defect luminescence band of CsI–Ca crystal, but not of the vacancy nature.

At room temperature, slow components of decay kinetics constants in microsecond
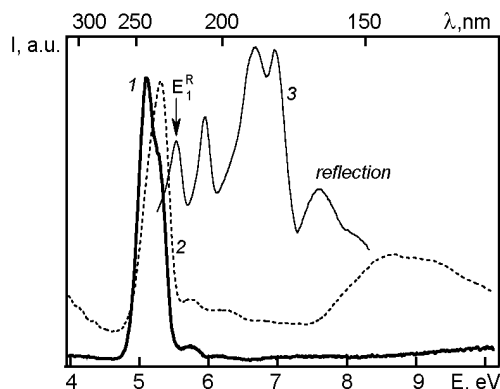
Fig. 6. Excitation spectra of CsI–Ca crystal for 460 nm (curve *1*) and 570 nm (curve *2*) emission. Curve *3* presents the reflection spectrum of CsI–Ca. $T = 300$ K.

range are prevailed. This fact confirms a conclusion on the possible attribution of both luminescence bands with 460 and 570 nm maxima to the self-trapped exciton localized near the defect. This is typical of a self-trapped exciton in CsI matrix.

Thus, in spite of a considerable concentration of Ca^{2+} ions ($C_{Ca} = 1$ mol. % in the initial mixture), any luminescent phenomena were not observed which could show the formation of Ca-contained impurity phases in CsI matrix. The results of our work confirm the model of emissive complex that had been offered in [1], the complex containing $Ca^{2+}-V_c^-$ dipole and localized exci-

ton near cation vacancy. The localization of exciton near cation vacancy of $Ca^{2+}-V_c^-$ dipole is confirmed by characteristic features of excitation spectrum structure of luminescence band peaked at 420 nm. The 510 nm band ($T = 10$ K) is connected with the matrix defect of non-vacancy nature.

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Спектрально-люмінесцентні властивості кристалів CsI–Ca

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Досліджено спектрально-люмінесцентні і люмінесцентно-кінетичні властивості кристала CsI–Ca при температурах 10 і 295 K в енергетичному інтервалі 4–16 еВ. Проаналізовано природу люмінесцентних центрів, які виникають у легованому кристалі CsI–Ca, та ефективність їх збудження в області прозорості та фундаментального поглинання матриці CsI.