

Luminescence modification of CsI crystal activated by CsCl impurity

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Luminescence parameters of CsI–CsCl (0.5–1.0 mol.%) and CsI–PbCl₂ (0.5 mol.%) crystals have been studied under synchrotron and X-ray excitation. New bands have been revealed in the luminescence spectra of crystals which are ascribed to emission of microphase CsCl dispersed in CsI and radiative decay of electronic excitation on iodine vacancies of the matrix. The duration and intensity of slow component in a scintillation pulse of CsI–PbCl₂ (0.5 mol.%) crystals decreases essentially at the X-ray excitation.

Проведено исследование люминесцентных параметров кристаллов CsI–CsCl (0,5–1,0 mol.%) и CsI–PbCl₂ (0,5 mol.%) при синхротронном и рентгеновском возбуждении. В спектрах люминесценции кристаллов обнаружено новые полосы, которым приписывают излучение микрофазы CsCl, вкрапленной в CsI, а также излучательному распаду электронных возбуждений возле вакансий йода матрицы. В кристаллах CsI–PbCl₂ (0,5 mol.%) при рентгеновском возбуждении длительность и интенсивность медленной компоненты в сцинтилляционном импульсе существенно уменьшается.

Most spectral and luminescence studies of quantum-confined systems were carried out mainly on binary semiconducting nanocrystals of CdS, ZnS, CuI, PbI₂, etc. The formation of ternary CsPbX₃ compound phase has been revealed [1, 2] for PbX₂ doped CsX crystals (X= Cl, Br, I). The possibility of the dielectric nanophase formation in CsI host has been pointed out in [3]. It has been concluded that the scintillation of CsI–NaI is caused by the energy transfer from CsI matrix to NaI nanoparticles [3]. NaI nanoparticles embedded in CsI matrix were obtained by temperature annealing of CsI–NaI (0.1 mol.%) thin films. In this work, the possibility of dielectric nanoparticle synthesis is shown and its peculiarities are proposed to be used for the modification of scintillator luminescence characteristics. We propose a method for CsCl nanoparticle implantation into CsI host to modify the luminescence characteristics of CsI-based

scintillation materials. The impossibility of solid solution existence in CsI–CsCl system [4] is the favorable circumstance for the formation of CsCl nanoparticles in CsI host. CsCl nanoparticle formation has been studied in CsI–CsCl (0.5–1.0 mol.%) and CsI–PbCl₂ (0.5 mol.%) crystals being annealed at $T = 250^\circ\text{C}$ during 24 hours.

The luminescence kinetics of CsI–CsCl (1 mol.%) and CsI–PbCl₂ (0.5 mol.%) crystals has been studied using the synchrotron radiation from the DORIS storage ring at the Deutsches Elektronen Synchrotron (DESY, Hamburg) and the SUPERLUMI station equipment at HASYLAB [5]. Time-resolved spectroscopy technique has been used. Spectra of the fast emission component were registered just after the excitation pulse within 0–5 ns time gate. Emission spectra were measured using ARC Spectra Pro 308 monochromator in Czerny-Turner mounting equipped with HAMAMATSU R6358P photomultiplier.

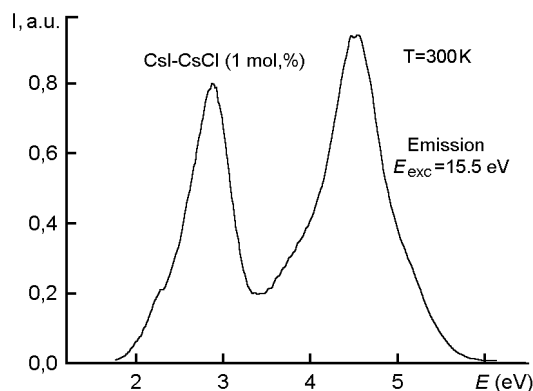


Fig. 1. Emission spectra for CsI-CsCl (1 mol.%) crystals at room temperature.

The luminescence excitation spectra were scanned at 3.2 \AA resolution within 4–27 eV range using the primary 2 m monochromator in 15° McPherson mounting. The X-ray emission spectra and X-ray luminescence decay kinetics were measured at a laboratory setup using X-ray source with parameters: $U_a = 40 \text{ kV}$, pulse duration 2 ns, repetition frequency 100 kHz.

Two series of emission bands in the ranges of 6.2–4.1 eV (200–300 nm) and 4.1–2.1 eV (300–600 nm) were revealed in CsI-CsCl (0.5–1.0 mol.%) crystals under excitation by quanta with $E = 15.5 \text{ eV}$ (Fig. 1). The characteristic σ -(285 nm) and π -(360 nm) emission bands of self-trapped exciton were not observed in CsI crystals at the room temperature. The so-called "exciton-like" luminescence peaked at 4.1 eV (305 nm) should not be also excited under excitation by quanta $E = 15 \text{ eV}$ [6]. Therefore, the observed emission bands of the CsI crystals could be caused by doping with CsCl impurity.

The emission band with maximum at 2.7 eV (450 nm) may be caused by radiative decay of electronic excitation on iodine vacancies in the matrix [7, 8]. It should be noted that annealing at $T = 250^\circ\text{C}$ promotes halogen vacancy formation in the matrix [8]. The luminescence excitation spectrum with maximum placed in the range of CsI matrix transparency at 5.2 eV (240 nm) (Fig. 2, curve 2) and low luminescence intensity at excitation in the range of band-to-band transition can evidence the defect nature of the 2.7 eV band. The slow luminescence component with $\tau > 1 \mu\text{s}$ dominates in decay kinetics of this band under high-energy excitation. The emission band in the 200–300 nm range (Fig. 1) can be

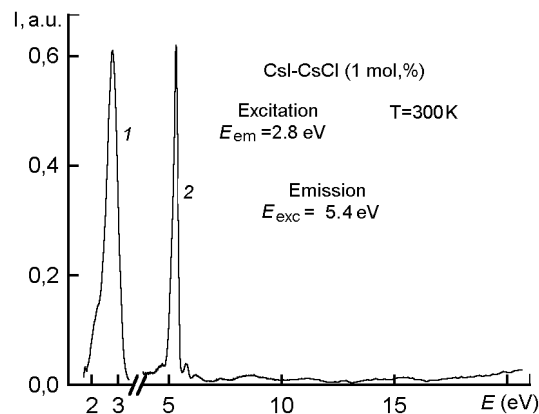


Fig. 2. Emission and luminescence excitation spectra for CsI-CsCl (1 mol.%) crystals at room temperature.

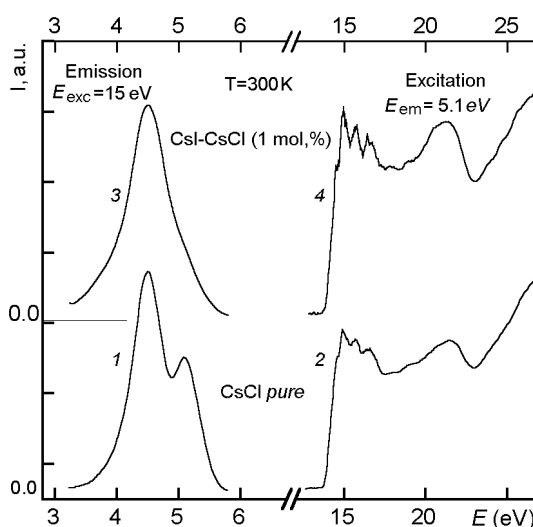


Fig. 3. Fast components of emission (curves 1, 3) and luminescence excitation (curves 2, 4) spectra for pure CsCl and CsI-CsCl (1 mol.%)

interpreted as the luminescence of CsCl microphase dispersed in CsI matrix. This is confirmed by the similarity between the spectral characteristics for observed luminescence and that of pure CsCl. The emission spectrum of pure CsCl (Fig. 3, curve 1) under excitation at 15 eV reveals two maxima at 4.5 and 5.1 eV which are ascribed to intrinsic core-valence luminescence (CVL) [9]. In studied pure CsCl crystals, these emission bands has the decay time constant of 1.2 ns being caused by the radiative recombination of $5p\text{Cs}^+$ core holes with $3p\text{Cl}^-$ valence electrons. The excitation spectrum measured for CsCl emission at 5.1 eV (Fig. 3, curve 2) has the characteristic threshold at 13.8 eV corresponding to the photoionisation of $5p\text{Cs}^+$ core states.

The fast emission component $\tau = 1.2$ ns has been also registered in the 3.2–5.8 eV range for CsI–CsCl (1 mol.%) crystal under excitation at 15 eV (Fig. 3, curve 3). The structure of the excitation spectrum measured for the fast emission of CsI–CsCl (1 mol.%) crystal at 5.1 eV (Fig. 3, curve 4) is rather close to that of intrinsic CVL in pure CsCl (curve 3). Therefore, the coincidence between the parameters of fast luminescence for CsI–CsCl (1 mol.%) crystal with the CVL for pure CsCl allow to attribute the fast luminescence of CsI–CsCl (1 mol.%) crystal to luminescence of CsCl microphase dispersed into the CsI matrix.

The reabsorption of high-energy CVL quanta by CsI host may take place in CsI–CsCl system. Consequently, a shape difference is observed between the high-energy side of CVL emission spectra for CsCl bulk crystal (Fig. 3, curve 1) and its microphase analog imbedded into CsI host (curve 3). The high-energy CVL band at 5.1 eV is suppressed in the case of CsI–CsCl (1 mol.%). The equal values of CVL decay time constant (1.2 ns) for CsCl and CsI–CsCl point out the absence of nonradiative decay of $5pCs^+$ -core holes in CsCl microphase due to their interaction with CsI host. We do not have any exact data on the size of CsCl microphase imbedded into CsI host. However, some estimation can be made using the data on NaI particle size in CsI host. The NaI nanoparticles of about 70 nm size were revealed in CsI–NaI (0.1 mol.%) after prolonged annealing at 250°C [3]. Thus, the size of CsCl particles can be expected in the range above 100 nm for the case of CsI–CsCl (0.5 mol.%). Therefore, the CsCl phase observed can be rather interpreted as microphase.

Of course, there is no chance to observe any quantum confinement effect on the luminescent characteristic for the particles of such a size. Moreover, it is probably difficult to observe the quantum confinement effect on CVL characteristics even in the case of nano-sized CVL-active particles, since the excitation and radiative relaxation processes appear within the CVL-active cation (Cs^+) and its nearest anion environment. The size of such so-called CVL-active cluster is comparable with the lattice constant. Therefore, it is necessary to examine the nanoparticles of few nanometers size in

order to reveal the quantum confinement effect on CVL parameters. The formation of CsCl microphase takes place not only in the case of CsI–CsCl (1 mol.%) but in the CsI– $PbCl_2$ (0.5 mol.%) system, too. This assertion is confirmed by the presence of CVL bands in 3.2–5.8 eV range with 1.2 ns decay time constant typical of CsCl crystals beside the intrinsic "exciton-like" emission of CsI crystal peaked at 4 eV (305 nm) for CsI– $PbCl_2$ (0.5 mol.%) crystals at $T = 300$ K under pulse X-ray excited luminescence measurements.

The doping of CsI crystal with $PbCl_2$ (0.5 mol.%) causes a strong decrease of intensity and decay time constant for the excitonic emission of CsI host. Under X-ray excitation ($T = 300$ K), the decay kinetic of intrinsic exciton emission contains two components with the characteristic decay time constants of 6 and 25 ns in the case of pure CsI crystal, whereas the slow component disappears in CsI– $PbCl_2$ (0.5 mol.%). Besides of CsCl phase, the formation of Cs_4PbI_6 and $CsPbI_3$ phases has been revealed earlier in CsI– $PbCl_2$ (1 mol.%) [10].

Thus, a possibility of the emission spectrum modification due to the microphase formation in CsI doped with CsCl and $PbCl_2$ impurities has been revealed as well as a high sensitivity of the luminescence methods has been demonstrated for the CVL-active microphase detection.

References

1. S.Myagkota, *Opt. and Spectr.*, **88**, 598 (2000).
2. A.Voloshinovskii, S.Myagkota, A.Gloskovsky et al., *Phys. Stat. Sol. B*, **225**, 257 (2001).
3. M.Nakayama, N.Ando, J.Hirai, H.Nishimura, *J. Luminescence*, **108**, 359 (2004).
4. J.Sougster, A.D.Pelton, *J. Phys. Chem. Ref. Data*, **16**, 509 (1987).
5. G.Zimmerer, *Nucl. Instr. and Meth. Phys. Res. A*, **308**, 178 (1991).
6. V.V.Gavrilov, A.V.Gektin, N.V.Shiran, T.A.Charkina, *Opt. and Spectr.*, **66**, 961 (1989).
7. A.V.Gektin, N.V.Shiran, V.Serebryanny et al., *Opt. i Spekr.*, **72**, 1061 (1992).
8. M.M.Hamada, Y.Nunoya, S.Kubota, S.Sakuragi, *Nucl. Inst. and Meth. Phys. Res. A*, **268**, 98 (1995).
9. P.A.Rodnyi, *Fiz. Tverd. Tela*, **34**, 1975 (1992).
10. S.Myagkota, A.Gloskovsky, I.Stefanskii, O.Mel'nik, *Functional Materials*, **7**, 774 (2000).

Модифікація люмінесценції кристала CsI при активуванні домішкою CsCl

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Проведено дослідження люмінесцентних параметрів кристалів CsI–CsCl (0,5–1,0 mol.%) і CsI–PbCl₂ (0,5 mol.%) при синхротронному та рентгенівському збудженні. У спектрах люмінесценції кристалів виявлено нові смуги, які приписуються випромінюванню мікрофази CsCl, що вкраплена в CsI, а також випромінювальному розпаду електронних збуджень біля вакансій галоїду матриці. У кристалах CsI–PbCl₂ (0,5 mol.%) при рентгенівському збудженні тривалість та інтенсивність повільної компоненти у сцинтиляційному імпульсі суттєво зменшується.