

Effect of iodine impurity on the absorption spectrum and phase transitions in CsPbCl_3 thin films.

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The absorption spectra of thin films of solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 \leq x \leq 1$ were studied. It has been found that at low concentrations $x \leq 0.2$, excitonic spectra of an amalgamation type (according to the classification of Onodera-Tojazawa) are formed. The concentration shift of the exciton bands with increasing x at $x = 0.3$ indicates the formation of the exciton spectrum of a persistence type in the interval $0.3 \leq x < 1$. The iodine impurity leads to an insignificant increase of the phase transition temperatures in the orthorhombic (T_{c3}) and cubic (T_{c1}) phases of CsPbCl_3 .

Keywords: thin films, solid solutions, excitons, phase transition.

Исследованы спектры поглощения тонких пленок твердых растворов $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 \leq x \leq 1$. Установлено, что при малых концентрациях $x \leq 0.2$ формируются экситонные спектры смешанного типа по классификации Онодери-Тоязавы. Концентрационное смещение экситонных полос с ростом x при $x \geq 0.3$ указывает на образование экситонного спектра устойчивого типа в интервале $0.3 \leq x < 1$. Примесь I приводит к незначительному росту температур фазовых переходов в орторомбическую (T_{c3}) и кубическую (T_{c1}) фазы в CsPbCl_3 ($x \leq 0,2$).

Вплив домішки йоду на спектр поглинання і фазові переходи у тонких плівках CsPbCl_3 . *Е.Н.Коваленко, О.Н.Юнакова, Н.Н.Юнаков*

Досліджені спектри поглинання тонких плівок твердих розчинів $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 \leq x \leq 1$. Установлено, що при малих концентраціях $x \leq 0.2$ формуються екситонні спектри змішаного типу за класифікацією Онодери-Тоязави. Концентраційний зсув екситонних смуг з ростом x при $x \geq 0.3$ вказує на утворення екситонного спектра стійкого типу в інтервалі $0.3 \leq x < 1$. Домішка I призводить до незначного росту температур фазових переходів в орторомбічну (T_{c3}) і кубічну (T_{c1}) фази у CsPbCl_3 .

1. Introduction

CsPbCl_3 compound crystallizes into a perovskite-type structure. At low temperatures it has a rhombic lattice (D_{2h}^{16}) with the following parameters: $a = 11.2 \text{ \AA}$, $b = 11.2 \text{ \AA}$ and $c = 11.4 \text{ \AA}$ [1, 2]; with increasing temperature it has a number of phase

structural transitions with the lattice symmetry modification: from rhombic (D_{2h}^{16}) to orthorhombic (D_{2h}^{17}) at $T_{c3} = 310 \text{ K}$, to tetragonal (D_{4h}^5) at $T_{c2} = 315 \text{ K}$, to cubic (O_h^1) with the parameter $a = 5,605 \text{ \AA}$ at $T_{c1} = 320 \text{ K}$ [3, 4]. The structural element of the CsPbCl_3 crystal lattice is octahedra (PbCl_6)⁴⁻.

It is established that the first-order phase transitions take place at T_{c1} and T_{c3} , the second-order phase transition takes place at T_{c2} [3–6]. The temperatures of the phase transitions in CsPbCl_3 can be controlled by introducing an impurity [7]. In the solid solutions $\text{A}_x\text{Cs}_{1-x}\text{PbCl}_3$ ($\text{A} = \text{K}, \text{NH}_4, \text{Tl}, \text{Rb}$), $x \leq 0.2$ the phase transition temperatures increase insignificantly, and they decrease on the contrary when the Pb ions are substituted ($\text{CsB}_x\text{Pb}_{1-x}\text{Cl}_3$, $\text{B} = \text{Sn}, \text{Ca}, \text{Cd}$ $x \leq 0.2$) (insignificantly when the Pb ions are substituted by Sn, Ca ions and significantly at $\text{B} = \text{Cd}$) [7]. Effect of impurities in the anion sublattice of CsPbCl_3 on phase transitions has not been studied yet. At the same time, according to the crystallochemical studies [8], the compounds CsPbCl_3 and CsPbI_3 make a continuous series of solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$.

Absorption spectra of the CsPbCl_3 and CsPbI_3 compounds have been studied previously [6, 9–13]. CsPbI_3 crystallizes into the perovskite-type structure, like CsPbCl_3 . At low temperatures it has an orthorhombic lattice (D_{2h}^{17}) with the parameters $a = 10.46 \text{ \AA}$, $b = 4.8 \text{ \AA}$, $c = 17.78 \text{ \AA}$, which persists up to temperatures of 563–602 K. At the higher temperatures the crystal lattice becomes cubic with $a = 6.29 \text{ \AA}$ [14, 15]. The structural elements of the CsPbI_3 lattice are double chains consisting of octahedra $(\text{PbI}_6)^{4-}$ oriented along the short axis **b**.

It is interesting to study the absorption spectra of solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ and the influence of iodine impurity on the phase transitions in CsPbCl_3 . The absorption spectra of thin films of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ are being studied in the spectral range of 2–6 eV at $T = 90 \text{ K}$ and 290 K and in the region of the long-wavelength exciton band (2.4–3.7 eV) in the temperature range of 90–500 K, including the temperatures of the phase transitions.

2. Experimental

$\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ thin films were prepared by evaporation in a vacuum of a melt of a mixture of pure CsCl, CsI, PbCl_2 and PbI_2 powders of a given molar composition to quartz substrates heated to 373 K, followed by annealing the samples at $T = 413 \text{ K}$ in an hour. Such a technique was used earlier for preparation of the thin films of CsPbCl_3 and CsPbI_3 [6, 11].

The risk of synthesis of other binary and ternary compounds exists when the mixture evaporates. In the studied system CsHal-PbHal_2 $\text{Hal} = \text{Cl}, \text{I}$, except of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ films, $\text{Cs}_4\text{PbHal}_6$ complex compounds and their solid solutions can be formed. All these compounds have narrow and intense low-frequency bands, whose spectral positions (Cs_4PbI_6 (3.4 eV), Cs_4PbCl_6 (4.345 eV), CsCl (5.8 eV), CsI (5.8 eV), PbCl_2 (4.6 eV), PbI_2 2.5 eV) differs significantly from the positions of the exciton bands in CsPbCl_3 (3.04 eV [6]) and CsPbI_3 (3.013 eV [11]), which makes it possible to control the phase composition of the films under study from the absorption spectra. The phase composition of the films was monitored from the absorption spectra measured at $T = 90 \text{ K}$.

The absorption spectra were measured in the spectral range of 2–6 eV at $T = 90 \text{ K}$ and 290 K using spectrophotometer SF-46. In a narrower spectral range of 2.4–3.7 eV, in the region of the long-wave exciton band, the absorption spectrum was measured in a wide temperature range of 90–500 K, including the phase transitions temperatures. To measure the spectrum in the temperature range of 90–300 K, the sample was placed in a vacuum cryostat which is equipped by a carbon absorption pump. At the high-temperature measurements the sample was placed in an oven with a tungsten winding. The films of thickness 100–130 nm were used for measurements.

To determine the parameters of the long-wave exciton bands, they were approximated by the method [16] of a single and a two-oscillator symmetric mixed contour, which has an intermediate form between the Lorentz and Gaussian contours and representing their linear combination. The mixed contour differs little from the contour of the Focht. The parameters of the exciton bands (position E_m , half-width Γ and value of the imaginary part of the permittivity at the maximum of the exciton band $\varepsilon_{2m} \equiv \varepsilon(E_m)$) were chosen that the calculated contour well coordinated with the measured spectra on the long-wavelength slope of the bands.

3. Results and discussion

The absorption spectra of some films $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ $T = 90 \text{ K}$ are shown in Fig. 1. Similarity of the spectra of CsPbCl_3 ($x = 0$) and CsPbI_3 ($x = 1$) is well visible. The long-wave exciton band *A* and

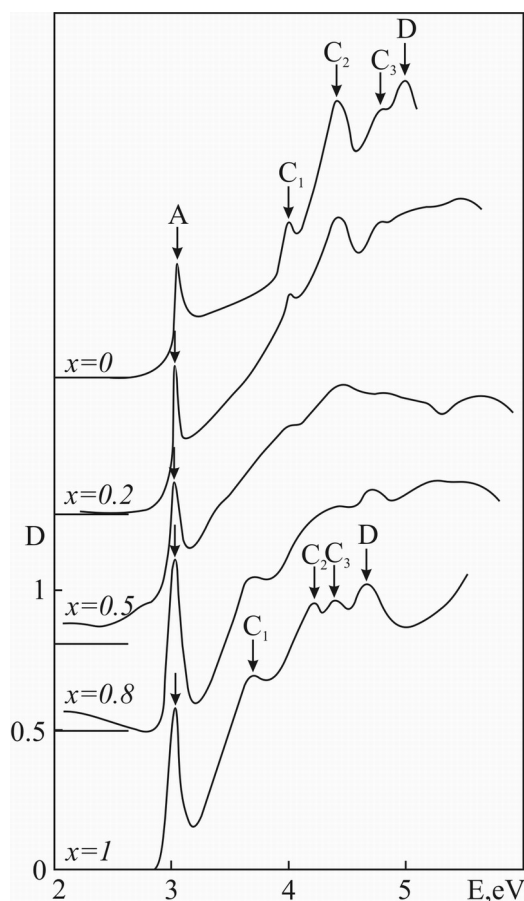


Fig. 1. Absorption spectra of thin films of solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ ($T = 90$ K).

shorter-wave bands *C* and *D* are observed in each of the compounds, their spectral position is given in Table 1. Localization of the exciton excitations in the structural elements of the crystal lattices $(\text{PbHal}_6)^{4-}$ $\text{Hal} = \text{Cl}, \text{I}$ was established for the both CsPbCl_3 and CsPbI_3 compounds. At that localization, the conduction band in CsPbCl_3 (CsPbI_3) is formed by $6p$ states of Pb , and the valence band by $6s$ states of Pb with an impurity of $3p$ state of Cl ($5p$ states of I). Their spectra are interpreted on the basis of electronic transitions in the octahedra $(\text{PbHal}_6)^{4-}$, similarly to the spectra of Pb^{2+} impurity ions in alkali-halide crystals [6, 9–13].

Table. The spectral position of the absorption bands in CsPbCl_3 and CsPbI_3 ($T = 90$ K)

| Compound | E_{A1} , eV | E_{C1} , eV | E_{C2} , eV | E_{C3} , eV | E_D , eV |
|-----------------------|---------------|---------------|---------------|---------------|------------|
| CsPbCl_3 [6] | 3.04 | 3.97 | 4.4 | 4.76 | 5.0 |
| CsPbI_3 [11] | 3.013 | 3.69 | 4.22 | 4.4 | 4.461 |

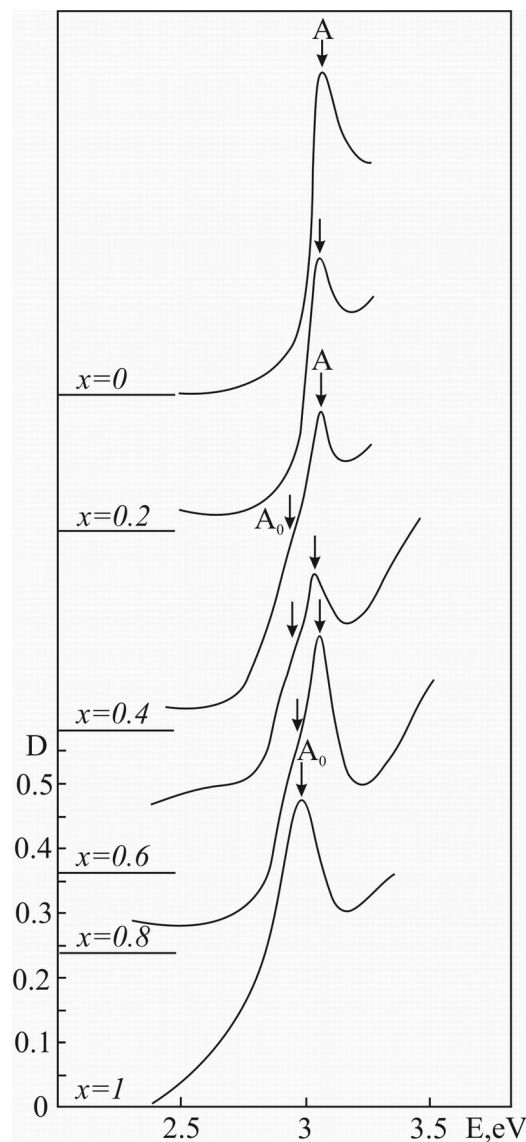


Fig. 2. Absorption spectra of thin films of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ solid solutions in the region of long-wavelength exciton bands ($T = 298$ K).

The spectra of the solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ ($T = 90$ K, Fig. 1) are similar to the spectra of CsPbCl_3 and CsPbI_3 . The long-wave exciton band *A* in $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ ($T = 90$ K) occupies an intermediate position between band *A* in CsPbCl_3 (3.04 eV) and in CsPbI_3 (3.013 eV), its spectral position varies insignificantly with increasing x . It is known that with increase of temperature the long-wavelength exciton band *A* in CsPbCl_3 shifts to the short-wave region of the spectrum due to the exciton-phonon interaction [6], and in CsPbI_3 , on the contrary, to the long-wavelength region [11]. Even at the room temperature, the spectral positions of the bands *A* in CsPbCl_3

and CsPbI_3 differ significantly (Fig. 2), and singularities appear at the edge of the intrinsic absorption band in the $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0.3 \leq x \leq 1$ spectra, which are not noticeable at $T = 90$ K. Therefore, the concentration dependencies of the parameters of long-wavelength exciton bands were determined at the room temperature $T = 298$ K.

The absorption spectra of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 1$ thin films in the region of the edge of intrinsic absorption band at $T = 298$ K are shown in Fig. 2. In the concentration range of $0 \leq x \leq 0.2$, the band A shifts to the long-wave region of the spectrum with increasing x (Fig. 2, Fig. 3a). The dependence $E_m(x)$ in this concentration range converges to the value of $E_m(1)$ at $x \rightarrow 1$ (Fig. 3a).

At $x = 0.3$ a weak band A_0 appears on the long-wavelength slope of the band A. The spectral position of this band is close to the long-wavelength band A_0 in CsPbI_3 . With increasing x , the band A_0 shifts to the long-wavelength region of the spectrum (Fig. 2, Fig. 3a), its oscillator strength increases. The band A, on the contrary, shifts to the short-wavelength region of the spectrum at $x \geq 0.3$, and its oscillator strength decreases with the increasing x . The maximum distance between the bands A_0 and A $\Delta E = 0.11$ eV is reached at $x = 0.5$ (Fig. 3a). Such concentration behavior of the bands A_0 and A in the interval $0.3 \leq x \leq 0.9$ is typical for the spectra of solid solutions of the persistence type according to the classification [17].

According to [17], the spectra of solid solutions are divided into the spectra of persistence and amalgamation types. In the spectra of solid solutions of the first type, two bands are observed which are inherent for compounds, forming the solid solution (in our case CsPbCl_3 and CsPbI_3), which persist throughout the interval x . With increasing x , the main exciton band shifts to the short-wave region of the spectrum, the exciton band of the impurity shifts to the long-wave region. In the spectra of the second type, one band is observed, whose position with the increasing x varies from the position in the first compound to the position in the second one. The criterion for separation of the spectra into the two types is the ratio of energy difference between the positions of the exciton peaks of the two components δ and width of the exciton band Δ . The persistence type zones are formed at $\delta/\Delta \geq 0.5$, the amalgamation type zones are

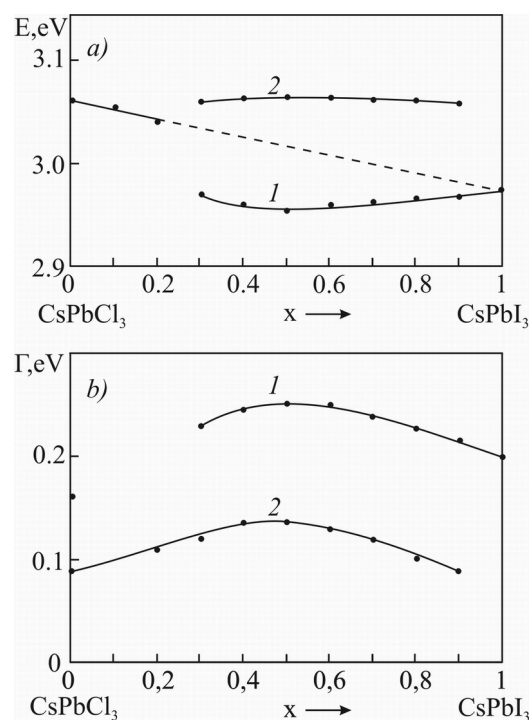


Fig. 3. Concentration dependence of the spectral position $E_m(x)$ (a) and half-width $\Gamma(x)$ (b) of exciton bands A (1) and A_0 (2) in solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$: experimental data (dots) and data calculated by Eq. (1) (solid lines) (b).

formed at $\delta/\Delta \leq 0.25$, and in the interval $0.25 < \delta/\Delta < 0.5$, the type of the solid solution depends on the concentration x [17].

Consequently, according to the classification [17], in the interval $0 \leq x \leq 0.2$, the spectra of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ solid solutions of amalgamation type are observed in the interval $0.3 \leq x < 1$ — of persistence type.

Majority of the binary and complex compounds form solid solutions of a the amalgamation type. Less often, solid solutions of inorganic compounds with a spectrum of the persistence type are formed. The persistence type spectra were observed in the solid solutions of quasi-one-dimensional complex compounds $\text{M}_2\text{Ag}_{1-x}\text{Cu}_x\text{I}_3$ ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) [18, 19], $\text{M}_2(\text{Cd}_{1-x}\text{Zn}_x)\text{I}_4$ ($\text{M} = \text{Rb}, \text{Cs}$) [20, 21], in which one of the parameters of the crystal lattice is much smaller than the others, and the exciton transfer occurs along the short axis of the crystal. In the solid solutions $\text{Cs}_2\text{Ag}_{1-x}\text{Cu}_x\text{I}_3$, as in our case, spectra of the persistence and amalgamation type were observed in different intervals of x [18].

The amalgamation and persistence type formation in one system is possible if the ratio of δ/Δ in the solid solutions is close to

the transition boundary from the solid solutions of amalgamation type to the solid solutions of persistence type. As already noted above the boundary value δ/Δ depends on x [17]. The transition of the amalgamation type solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ to the persistence type solid solutions at $x \geq 0.3$ indicates a narrowing of the exciton bands with increasing x . For $x \leq 0.2$ the main exciton and impurity bands overlap and merge into one, and one exciton band A is observed in the solid solutions spectra. At $x \geq 0.3$, due to decrease of width of the exciton bands, the main and impurity bands do not overlap, two exciton bands A and A_0 are observed in the solid solutions spectra. The main band A is genetically related to the excitation of excitons in octahedra $(\text{PbCl}_6)^{4-}$, the impurity band A_0 — to $(\text{PbI}_6)^{4-}$.

The difference in the structure of the crystal lattices CsPbCl_3 and CsPbI_3A can be a possible reason of the width decrease of the exciton bands in the solid solutions with increasing x . Despite the fact that the crystal lattices CsPbCl_3 and CsPbI_3 belong to the same spatial group, there is no complete similarity of their elementary cells. In aCsPbI_3 , the lattice parameter $b = 4.8 \text{ \AA}$ is significantly smaller than the parameters $a = 10.46 \text{ \AA}$ and $c = 17.78 \text{ \AA}$. The structural elements of the CsPbI_3 lattice are double chains consisting of the octahedra $(\text{PbI}_6)^{4-}$ oriented along the short axis \mathbf{b} . The interval between neighboring non-equivalent Pb atoms in the axis \mathbf{b} direction $b/2 = 2.4 \text{ \AA}$ is substantially less than in the direction of the axes \mathbf{a} and \mathbf{c} . Therefore, the exciton transfer occurs along the axis \mathbf{b} , which determines the 1D character of the exciton bands in CsPbI_3 . In CsPbCl_3 at the room temperature, the lattice parameters are close in value ($a = 1.2 \text{ \AA}$, $b = 11.2 \text{ \AA}$ and $c = 11.4 \text{ \AA}$ [1.2]). The excitons in CsPbCl_3 are three-dimensional [6]. In spite of the high ionicity of CsPbCl_3 , apparently, in CsPbI_3 the width of the exciton band is smaller because of the quasi-one-dimensional of the compound.

The concentration dependences of half-width of the exciton bands $\Gamma_{A_0}(x)$ and $\Gamma_A(x)$ are typical for solid solutions (Fig. 3b), they have a maximum at $x = 0.5$ and are well described by the dependence

$$\Gamma(x) = \Gamma(0)(1 - x) + \Gamma(1)x + \beta x(1 - x), \quad (1)$$

where $\beta = adE_{ex}/dx$, $\Gamma(0) = 0.18 \text{ eV}$, $\Gamma(1) = 0.2 \text{ eV}$, $\beta = 0.23 \text{ eV}$ for A_0 and $\Gamma(0) = 0.09 \text{ eV}$,

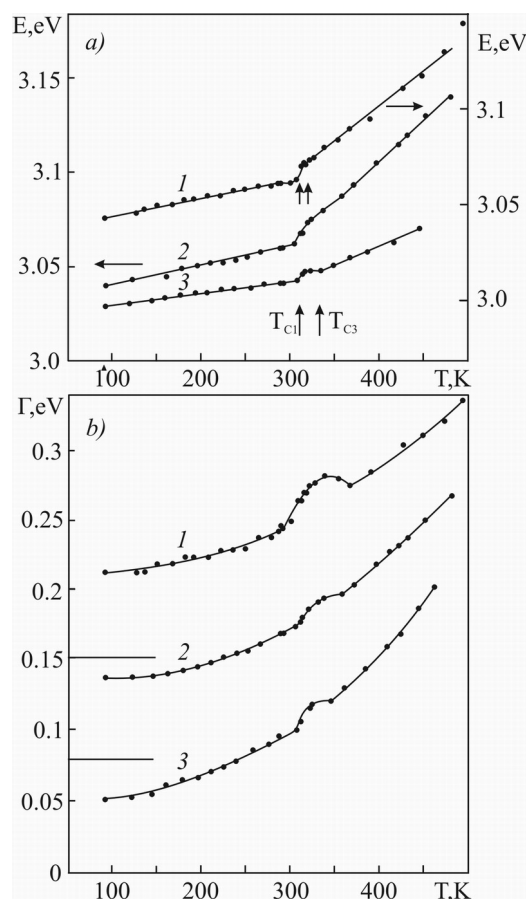


Fig. 4. Temperature dependence of spectral position $E_m(T)$ (a) and half-width $\Gamma(T)$ (b) of the long-wavelength exciton band in thin films $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $x = 0$ (1); 0.1 (2) and $x = 0.2$ (3).

$\Gamma(1) = 0.08 \text{ eV}$, $\beta = 0.19 \text{ eV}$ for band A . From this concentration dependence $\Gamma_{A_0}(x)$ and $\Gamma_A(x)$ it follows that the main cause of broadening of the exciton bands in $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ solid solutions is large-scale fluctuations in the composition of the films.

The effect of impurity on the phase transitions in CsPbCl_3 was studied in the interval $0 \leq x \leq 0.2$, in which the solid solutions of mixed type $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ are formed. For this absorption spectra were measured in the region of the long-wave exciton band A in the temperature range of 90–500 K. The temperature dependences of the spectral position $E_m(T)$ and the half-width $\Gamma(T)$ of the band A for $x=0; 0.1; 0.2$ are shown in Fig. 4a, b. In the dependences $E_m(T)$ and $\Gamma(T)$ the structural phase transitions appear as jumps at T_{c3} and T_{cI} (Fig. 4), which indicates the phase transitions of the first kind at these temperatures. For the concentrations

$x = 0$ and 0.1 $T_{c3} = 310$ K and $T_{c1} = 320$ K, for $x = 0.2$ the temperatures of the structural phase transitions $T_{c3} = 315$ K and $T_{c1} = 334$ K are slightly higher. The phase transition of the second kind at $T_{c2} = 315$ K weakly manifests itself in the dependencies $E_m(T)$.

Far from the phase-transition temperatures, the dependence $E_m(T)$ is linear and is determined by the exciton-phonon interaction (EPI). The coefficients of the temperature shift of the band A for $x = 0; 0.1$ and 0.2 in the temperature range of $90-290$ K are equal to $dE_m/dT = 8.76 \cdot 10^{-5}, 1.02 \cdot 10^{-4}, 6.26 \cdot 10^{-5}$ eV/K, in the interval $340-500$ K are equal $dE_m/dT = 3.67 \cdot 10^{-4}, 4.25 \cdot 10^{-4}, 1.92 \cdot 10^{-4}$ eV/K. The exciton band A in the solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 < x \leq 0.2$, as in CsPbCl_3 , shifts to the short-wave region of the spectrum due to EPI. However, with the impurity I increasing, the coefficients of the temperature shift dE_m/dT decrease (Fig. 4a). In CsPbI_3 , the long-wavelength exciton band shifts with increasing T to the opposite, the long-wave region of the spectrum, which apparently causes the decrease of dE_m/dT in $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ with the increasing x . Both the short-wave and long-wave shifts of the exciton bands with the increasing T , as well as the change in the sign of the shift with the increasing T , are explained by the extended model of the exciton-phonon system, if along with the linear one we take into account the quadratic interaction in phonon operators of the Hamiltonian of the exciton-phonon system [22].

In the half-width temperature dependence $\Gamma(T)$, the phase transitions appear as leaps at the same values of T_{c3} and T_{c1} for $x = 0; 0.1$ and 0.2 , as in $E_m(T)$. Far from the phase transition temperatures, the dependence $\Gamma(T)$ is nonlinear and is due to EPI. According to the theory [23], in this case, $\Gamma(T)$ for excitons of various dimensions d ($d = 1, 2, 3$) is defined as

$$\Gamma(T) \approx \left[\frac{\pi D^2}{\gamma(d/2)(2\pi B)^{d/2}} \right]^{2/(4-d)}, \quad (2)$$

where $\gamma(d/2)$ is the gamma function depending on d , B is the width of the exciton band and $D^2 = 0.5C^2 \hbar\omega_{\text{LO}} \text{cth}(\hbar\omega_{\text{LO}}/2kT)$, $C^2/2$ is the lattice relaxation energy at the excitation exciton, $\hbar\omega_{\text{LO}} = 27.77$ meV is the energy of the LO phonon in CsPbCl_3 [24]. Taking into account the residual broadening $\Gamma(0)$ due to the lattice defects and the

Gaussian shape of the band A , the total half-width

$$\Gamma = [\Gamma^2(0) + \Gamma^2(T)]^{1/2}, \quad (3)$$

where $\Gamma(T)$ obeys to (2) with an unknown factor Q that does not depend on T . Processing of the experimental dependences $\Gamma(T)$ for $x = 0; 0.1$ and 0.2 in the temperature ranges of $90-300$ K and $360-450$ K with the help of Eq. (2) for different d show that the best agreement between the calculation of Eq. (1) and experiment is obtained at $d = 3$. For $d = 3$

$$\Gamma(T) = Q \text{cth}^2(\hbar\omega_{\text{LO}}/2kT) \quad (4)$$

and the dependence of $\Gamma(T)$ in the coordinates Γ^2 on $\text{cth}^4(\hbar\omega_{\text{LO}}/2kT)$ is linear. The processing of this dependence by the method of the least squares gives the values $\Gamma(0) = 0.06; 0.051; 0.046$ eV and $Q = 0.017; 0.019; 0.021$ eV for $x = 0; 0.1$ and 0.2 accordingly. In Fig. 4b $\Gamma(T)$, calculated by Eq. (3, 4) with the found values of $\Gamma(0)$ and Q (solid curves) are in a good agreement with the experimental dependence. Consequently, in the solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 < x \leq 0.2$, as in CsPbCl_3 , excitons are of three-dimensional nature.

In the region of the phase transition temperatures, the half-width $\Gamma(T)$ appreciably increases. The structural phase transitions in CsPbCl_3 are due to rotations of the PbCl_6 octahedra around $[001]$ axis [3-5, 7], which during the transition leads to a different orientations of grains of crystallites in the film and increase in the excitons scattering at the grain boundaries and, respectively, to growth of $\Gamma(T)$ in the region of the phase transition temperature.

4. Conclusions

The absorption spectra of solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, $0 \leq x \leq 1$ at $T = 90$ K and 298 K in the spectral range of $2-6$ eV were studied. From analysis of the absorption spectra, the formation of the solid solutions in the all concentration range with the amalgamation type spectra in the range of $0 \leq x \leq 0.2$ and the persistence type at $x \geq 0.3$ was established. The formation of the amalgamation type spectra is indicated by the concentration dependence of the spectral position of A_0 and A bands in the interval $0.3 \leq x < 1$. Apparently, increase of

the impurity I contributes to the formation of quasi-one-dimensional exciton bands in the range of $0.3 < x < 1$ in the solid solutions, as in CsPbI_3 , which leads to their narrowing and transition from the amalgamation type spectra to the persistence type spectra of a at $x \geq 0.3$.

The absorption spectra of the solid solutions $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$, like the spectra of the initial components CsPbCl_3 and CsPbI_3 , are interpreted on the basis of electronic transitions in octahedra $(\text{PbHal}_6)^{4-}$.

The concentration dependences of the exciton bands half-width $\Gamma(x)$ are typical for the solid solutions and confirm the formation of $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ solid solutions in the entire concentration range of $0 \leq x \leq 1$. The concentration broadening of the exciton bands is due to the large-scale and small-scale fluctuations in the film composition.

The phase transition temperatures were determined from the temperature dependencies of the spectral position $E_m(T)$ and the half-width $\Gamma(T)$ of the long-wavelength exciton band in $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 0.2$. The phase transitions temperatures for $x = 0$ and 0.1 are $T_{c3} = 310$ K and $T_{c1} = 320$ K, for $x = 0.2$ are $T_{c3} = 315$ K and $T_{c1} = 334$ K. The iodine impurity leads to insignificant increase in the temperatures of the structural phase transitions in CsPbCl_3 .

3D character of the exciton excitations in $\text{CsPb}(\text{Cl}_{1-x}\text{I}_x)_3$ $0 \leq x \leq 0.2$ was established from the analysis of the $\Gamma(T)$ dependence far from the phase transitions temperature.

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