CONDENSED-MATTER SPECTROSCOPY

Exciton Absorption Spectrum of Thin CsPbI₃ and Cs₄PbI₆ Films

O. N. Yunakova[a], V. K. Miloslavskii[a], and E. N. Kovalenko[b]

[a] Kharkiv National University, Kharkiv, 61077 Ukraine
[b] Kharkiv National University of Radioelectronics, Kharkiv, 61166 Ukraine
e-mail: Vladimir.K.Miloslavsky@univer.kharkov.ua, Olga.N.Yunakova@univer.kharkov.ua, kovalenko.elena@bk.ru
Received May 19, 2011

Abstract—A method for preparing thin films of $CsPbI_3$ and Cs_4PbI_6 complex compounds has been developed. Their absorption spectrum is investigated in the energy range of 2−6 eV at temperatures from 90 to 500 K. It is found that the $CsPbI_3$ compound is unstable and passes to the Cs_4PbI_6 phase upon heating at $T \geq$ 400 K.

DOI: 10.1134/S0030400X12010249

In contrast to the $CsI_{1-x}CdI_{2x}$ system [1], which yields only the Cs_2CdI_4 complex compound with a change in the molar concentration, solid solutions formed in the $CsI-PbI_2$ system include two ternary compounds: $CsPbI_3$ and Cs_4PbI_6. According to the thermographic measurements [2], these compounds have similar melting temperatures (476 and 468°C, respectively). Studies of the crystal structure of $CsPbI_3$ [3, 4] showed that it is crystallized into the orthorhombic lattice with four molecules per unit cell; the unit-cell parameters are $a = 10.46$ Å, $b = 4.8$ Å, and $c = 17.78$ Å (sp. gr. *Pnma*) at 20°C. The structural elements of the $CsPbI_3$ lattice are double chains composed of $(PbI_6)^{4-}$ octahedra and oriented along the short **b** axis. The orthorhombic lattice is retained up to temperatures of 563−602 K; at higher temperatures, it passes to the monoclinic phase (according to earlier data [3]) or to the cubic phase with $a = 6.29$ Å (according to later detailed studies [4]).

The Cs_4PbI_6 crystal structure has been less investigated [5, 6]. It was indicated that Cs_4PbI_6 has a hexagonal lattice with the unit-cell parameters $a = 14.52$ Å and $c = 18.31$ Å and the number of molecules $z = 6$ per unit cell.

The existence of two complex compounds in the $CsI_{1-x}PbI_{2x}$ system called for studying their electron absorption and reflection spectra. The reflection spectra of $CsPbI_3$ single crystals were measured for the first time in [7]; their analysis revealed the $1s$ exciton band at 3.02 eV (4.2 K) and a weak shift of this band for polarized light (the light field **E** oriented perpendicularly or parallel to the **c** axis): $\Delta E \approx 0.002$ eV. However, the later study [8] revealed a Cs_4PbI_6 impurity in $CsPbI_3$ single crystals. Somma et al. [9], who investigated the absorption spectra of films obtained by evaporation of $CsPbI_3$ powder and its deposition on a quartz substrate, revealed not only an exciton band at

410 nm (3.02 eV), but also a narrow strong band at 365 nm (3.4 eV). This band was attributed to the Cs_4PbI_6 compound in [9], and it was concluded that $CsPbI_3$ is unstable in the gas phase and decomposes to form Cs_4PbI_6. The results of [7, 9] encouraged Japanese physicists [10, 11] to develop methods for preparing pure $CsPbI_3$ and Cs_4PbI_6 phases to measure their absorption spectra. Kondo et al. [10, 11] proposed to deposit successively thin CsI and PbI_2 layers of a certain thickness on a transparent substrate cooled to 77 K. The ratio of the thicknesses of the two layers was chosen according to the molar composition of the desired compound. Fast deposition of layers on a cold substrate conserved the specified thickness ratio in the two-layer compound. Then the latter was annealed at different temperatures, after which the absorption spectra were measured at 77 K. This procedure made it possible to obtain for the first time a pure $CsPbI_3$ spectrum at an annealing temperature of 400 K and the absorption spectrum of a Cs_4PbI_6 film annealed at 500 K.

The method that was developed in [10, 11] to obtain pure $CsPbI_3$ and Cs_4PbI_6 phases is rather labor-intensive and does not always lead to the desired result. We proposed an alternative and simpler method for preparing thin films of impurity-free compounds, which is based on the difference between the melting temperatures of $CsPbI_3$ and Cs_4PbI_6. The thus-prepared samples were used to measure the exciton absorption spectra in the range of photon energies of 2−6 eV and in the temperature range of 90−500 K. The data obtained were used to determine the main parameters of the exciton bands (spectral position, half-width, etc.) and their temperature dependences.
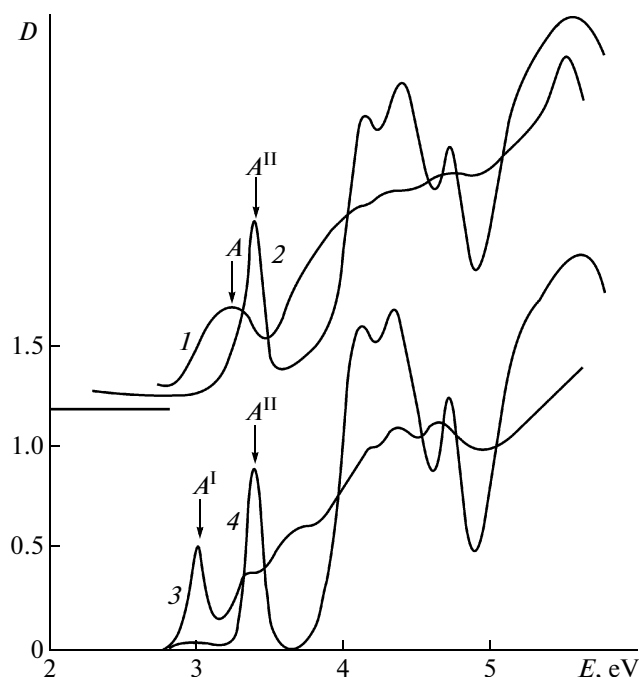
Fig. 1. Absorption spectra of thin $(CsI)_{1-x}(PbI_2)_x$ films ($x = 0.4$, $T = 90$ K) formed under different conditions: (*1*, *2*) the films deposited on a substrate at a temperature $T_s = 60°C$, with subsequent annealing at $T_{ann} = $ (*1*) 60 and (*2*) 130°C, (*3*) the film deposited on a substrate at $T_s = 100°C$, and (*4*) the same film annealed at $T_{ann} = 130°C$.

EXPERIMENTAL

Thin $CsPbI_3$ and Cs_4PbI_6 films were prepared by evaporating a mixture of pure CsI and c powders with a specified molar composition and depositing it on heated quartz substrates. The substrate temperature was varied from 60 to 130°C. The powder mixture was previously melted under a screen located between the evaporator and substrate. This method was previously applied to obtain thin films of M_2CdI_4 and M_2ZnI_4 ferroelastics ($M = $ Cs, Rb, or K) [1] and is based on the fact that the melting temperature of ternary compounds is generally much lower than those of the initial binary compounds. Note that, upon heating in vacuum, the mixture of powders $(CsI)_{1-x}(PbI_2)_x$ forms a melt in the concentration range of $0.2 \leq x \leq 0.4$; at other x values, the compound is sublimated from the powder, and, in this case, the initial components are present in the films as impurities. When the mixture is explosively evaporated, the films contain also the initial components as impurities. Therefore, we used a $(CsI)_{1-x}(PbI_2)_x$ mixture with $x = 0.4$ to prepare $CsPbI_3$ films and a stoichiometric mixture to form Cs_4PbI_6 films.

The phase composition of the films was controlled by measuring the absorption spectra at $T = 90$ K. This control is based on the significant difference in the

spectral positions of the long-wavelength exciton bands in $CsPbI_3$ (3.013 eV), Cs_4PbI_6 (3.4 eV), PbI_2 (2.5 eV), and CsI (5.8 eV).

It was found that the mixture evaporation from the melt with subsequent deposition on quartz substrates heated to $T_s \leq 80°C$ form films, the absorption spectra of which contain a wide absorption band; it takes an intermediate position between the long-wavelength exciton bands A^I and A^{II} in the $CsPbI_3$ and Cs_4PbI_6 spectra (Fig. 1, curve *1*); apparently, this intermediate band corresponds to the solid solutions of two compounds. At the substrate temperature $T_s > 100°C$, two-phase films are formed, the absorption spectra of which contain bands typical of both $CsPbI_3$ and Cs_4PbI_6 (Fig. 1, curve *3*). These phases are transformed into the Cs_4PbI_6 phase, with a typical spectrum [11], several days later or after their annealing at $T = 400$ K for 4 h (Fig. 1, curve *2*). The aforementioned films pass also to the Cs_4PbI_6 phase after annealing at temperatures above 400 K (Fig. 1, curve *4*). Therefore, Cs_4PbI_6 is the more stable of the two compounds formed in the $CsI-PbI_2$ system. We will consider the temperature transformations in the films in more detail below. Thin Cs_4PbI_6 films can also be obtained by evaporating a molten mixture of stoichiometric powders in vacuum and deposing it on quartz substrates heated to 130°C, with their subsequent annealing for 2 h at the same temperature.

It is more difficult to form a $CsPbI_3$ film without Cs_4PbI_6 impurity by evaporation from a melt, because these compounds have similar melting temperatures [1]. Since the $CsPbI_3$ melting temperature ($T_m = 476°C$) is somewhat higher than that of Cs_4PbI_6 ($T_m = 468°C$) [1], one can obtain a $CsPbI_3$ film without Cs_4PbI_6 impurity by partial evaporation of the melt on a screen, with subsequent evaporation of the rest on the substrate at a higher temperature (Fig. 2a).

The absorption spectra were measured with an SF-46 spectrophotometer on films 100−150 nm thick in the spectral range of 2−6 eV at $T = 90$ and 290 K. In the narrower spectral range of 2.4−3.7 eV (within the long-wavelength exciton band), the absorption spectrum was measured in a wide temperature range of 90−590 K, including the temperature of possible phase transition.

The parameters of the long-wavelength band A (position E_m, half-width Γ, and the imaginary part of permittivity in the maximum $\varepsilon_{2m} = \varepsilon_2(E_m)$) were determined according to the technique of [12], using an approximation of the band A by a single-oscillator symmetric profile (which is a linear combination of Lorentzian and Gaussian profiles). The parameters of the exciton band (E_m, Γ, and ε_{2m}) were chosen so as to provide the best agreement between the calculated and experimental profiles on the long-wavelength side of the band.

EXCITON SPECTRA OF CsPbI₃ AND Cs₄PbI₆

The absorption spectrum of thin $CsPbI_3$ films (Fig. 2a) contains a narrow strong band A_1^I at 3.013 eV (90 K) at the long-wavelength edge of the intrinsic absorption band and four shorter wavelength bands: C_1^I (3.69 eV), C_2^I (4.22 eV), C_3^I (4.4 eV), and D^I (4.661 eV); these bands are located against the interband absorption background. The absorption edge of Cs_4PbI_6 is blue-shifted by 0.4 eV in comparison with $CsPbI_3$ (Fig. 2b). The spectral positions of the Cs_4PbI_6 bands are 3.41 (A_1^{II}), 4.19 (C_1^{II}), 4.36 (C_2^{II}), 4.73 (C_3^{II}), and 5.2 eV (D^{II}).

With an increase in temperature, the A and C bands in the spectra of $CsPbI_3$ and Cs_4PbI_6 become red-shifted, broaden, and weaken due to the exciton–phonon interaction (EPI), which indicates their relationship with exciton excitations.

Splitting off the A_1^I band by a symmetric profile on the long-wavelength side of the C_1^I band in $CsPbI_3$ reveals a shoulder A_2^I at 3.131 eV (Fig. 2a); we associate this feature with the exciton excitation to the state characterized by the principal quantum number $n = 2$ (2s exciton). On the assumption that the A_1^I and A_2^I bands belong to the exciton series with the main band A_1^I, we used the spectral position of these bands to estimate the exciton binding energy $R_{ex} = 4/3\,(E_{A2} - E_{A1}) = 0.157$ eV and the band gap $E_g = E_{A1} + R_{ex} = 3.17$ eV. The thus-obtained R_{ex} and E_g values are close to those for single crystals (within the determination errors): $R_{ex} = 0.115$ eV and $E_g = 3.14$ eV [7].

A weak A_1^{II} band at 3.522 eV (Fig. 2b) arises in the Cs_4PbI_6 spectrum after splitting off the A_2^{II} band by a symmetric profile; this band is likely to correspond to the 2s-exciton excitation. We determined the exciton binding energy $R_{ex} = 0.149$ eV and the band gap $E_g = 3.56$ eV in Cs_4PbI_6 from the spectral positions of the A_1^{II} and A_2^{II} bands.

In the sequence of PbI_2, $CsPbI_3$, and Cs_4PbI_6 compounds the long-wavelength exciton bands are blue-shifted (Fig. 2, inset) according to the law

$$E_A(x) = E_1x + E_2(1 - x), \quad (1)$$

where x is the molar concentration of PbI_2 in the compounds and E_1 is the position of the long-wavelength exciton band in PbI_2. Extrapolation of dependence (1) for $x \to 0$ yields $E_2 = 3.6$ eV, a value much smaller than the spectral position of the exciton band in CsI (5.8 eV) but close to the position of the Pb^{2+} impurity bands in CsI, RbI, and KI [13, 14]. Linear dependence (1) and its convergence to the spectral position of the Pb^{2+} impurity bands in CsI indicate, according
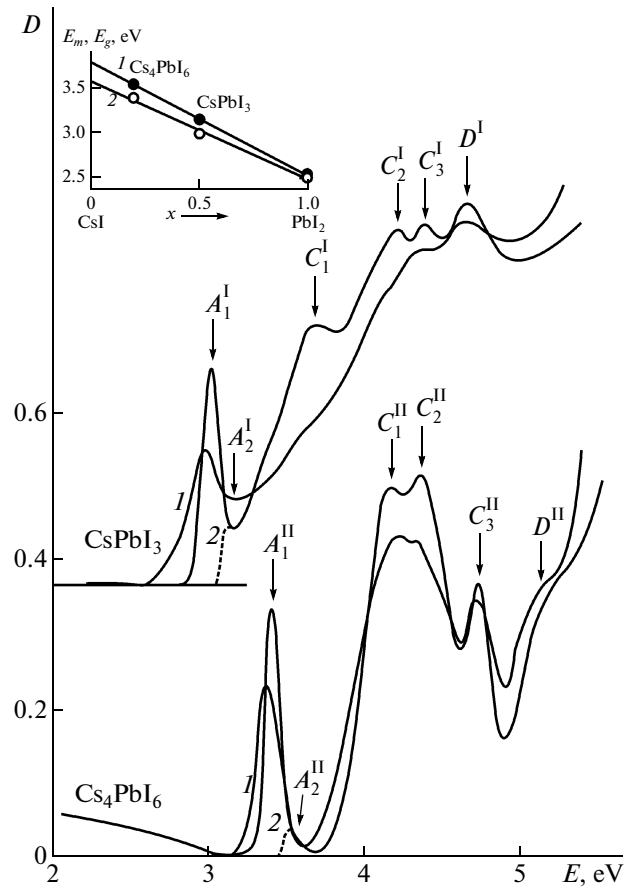

Fig. 2. Absorption spectra of thin $CsPbI_3$ and Cs_4PbI_6 films recorded at $T = (1)$ 290 and (2) 90 K; the dotted line indicates the absorption edge after splitting off the A_1 band by a symmetric profile. The concentration dependences of (2) the spectral position E_m and (1) the band gap E_g in the series of PbI_2, $CsPbI_3$, and Cs_4PbI_6 compounds are shown in the inset.

to [15], the excitation and localization of excitons in the cationic sublattice of ternary compounds containing lead ions.

In the case of this localization, the conduction band in the compounds under study is formed (as well as in PbI_2) by the Pb 6p states, while the valence band is formed by the Pb 6s states with an admixture of I 5p states. With allowance for the fact that the exciton excitations in PbI_2 [16] and other Pb-containing multicomponent compounds (for example, $CsPbCl_3$ and $CsPbBr_3$ [17]) are of cationic type, the exciton bands in the $CsPbI_3$ and Cs_4PbI_6 spectra are assigned to the electronic transitions in Pb^{2+} ions, which are octahedrally coordinated by I ions (PbI_6 complexes). Pb^{2+} impurity ions in a lattice of symmetry D_{3d} exhibit the following transitions: $A - {}^1A_{1g} \to {}^3T_{1u}$ (${}^1S_0 \to {}^3P_1$ in a free Pb^{2+} ion) (A band), ${}^1A_{1g} \to {}^3T_{2u}$ or ${}^3E_u$ (${}^1S_0 \to {}^3P_2$)
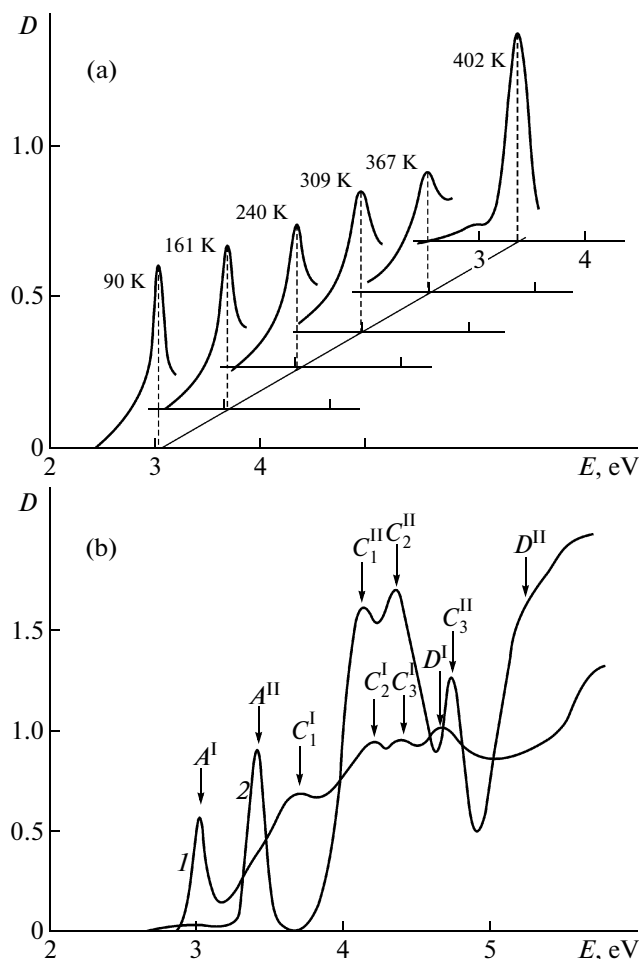
Fig. 3. (a) Long-wavelength exciton band in the spectra of a 150-nm-thick $CsPbI_3$ film, recorded at different temperatures upon heating. (b) The absorption spectrum of the $CsPbI_3$ film ($T = 90$ K) (*1*) before and (*2*) after heating above 400 K.

TEMPERATURE DEPENDENCE OF THE PARAMETERS OF THE LONG-WAVELENGTH EXCITON ABSORPTION BANDS IN $CsPbI_3$ AND Cs_4PbI_6

The absorption spectrum of a thin $CsPbI_3$ film in the range of 2.4–3.7 eV was measured at temperatures from 90 to 460 K upon heating and cooling; the spectrum of a thin Cs_4PbI_6 film was measured only upon heating in the temperature range of 90–533 K.

At temperatures from 90 to 367 K, the A_1^I band of $CsPbI_3$ is linearly red-shifted ($dE_m/dT = -2.4 \times 10^{-4}$ eV/K) upon heating (Figs. 3, 4); the half-width of the A_1^I band increases nonlinearly in this temperature range. In the relatively narrow range of 367–422 K, the absorption spectrum of the thin film changes as follows: the absorption edge is blue-shifted, and the long-wavelength exciton band becomes narrower and sharper (Figs. 3a, 4). Upon cooling the film to $T = 90$ K, its absorption spectrum is not recovered. The spectrum of the cooled film (Fig. 3b, curve *2*), measured in a wide energy range (2–6 eV) at $T = 90$ K, is typical (in both the structure and the position of the fundamental absorption bands) of Cs_4PbI_6. Therefore, we can suggest that heating a $CsPbI_3$ film above 420 K leads to the formation of Cs_4PbI_6 compound; this suggestion is in agreement with the results of [10, 11]. However, the question of excess PbI_2 must be solved in this case. The excess PbI_2 phase does not manifest itself in the spectrum of the cooled film (Fig. 3b, curve *2*), as is evidenced by the absence of additional absorption at 2.5 eV (which corresponds to exciton absorption in PbI_2) in the transparency region. Apparently, the excess lead manifests itself in the film spectrum as Pb^{2+} impurity bands in CsI, which are imposed on the Cs_4PbI_6 absorption spectrum. According to [13], the longest wavelength band A_1 in the spectrum of $CsI:Pb^{2+}$ is located at 3.38 eV (i.e., it is imposed on the A_1^{II} band in the spectrum of Cs_4PbI_6 (3.41 eV)); the shorter wavelength B and C bands are in the range of 4.3–5.04 eV [13]; correspondingly, they are also imposed on the C bands in the Cs_4PbI_6 spectrum. Apparently, this is the reason for the much higher intensity of the Cs_4PbI_6 exciton bands in the film with a higher PbI_2 content ($x_{PbI_2} = 0.4$) (Fig. 3b, curve *2*) in comparison with the stoichiometric composition ($x_{PbI_2} = 0.2$) (Fig. 2b). This suggestion is substantiated by the much higher oscillator strength of the A_1^{II} band in the cooled film ($x_{PbI_2} = 0.4$) $-f = 19.4 \times 10^{-2}$ (a value calculated for the volume occupied by the Pb^{2+} ion), in comparison with the oscillator strength of the corresponding band in Cs_4PbI_6 stoichiometric films: $f = 9.4 \times 10^{-2}$.

Thus, the temperature dependence of the parameters of the long-wavelength exciton band recorded upon heating the $CsPbI_3$ sample is typical of this com-

band), and $^1A_{1g} \rightarrow {}^1T_{1u}(^1S_0 \rightarrow {}^1P_1)$ (C band) [13]. The structure of the $CsPbI_3$ and Cs_4PbI_6 spectra is similar to that of the impurity spectra of Pb^{2+} in CsI [13]; the A and C exciton bands are likely to correspond to the same direct allowed transitions in the PbI_6 octahedron. The weak B band of $CsI:Pb^{2+}$, which is due to the forbidden $^1S_0 \rightarrow {}^3P_2$ transition in free Pb^{2+} ions, was not observed in our spectra.

The blue shift of the absorption bands with a decrease in the Pb content in the compounds under study indicates a decrease in the widths of allowed bands and an increase in the band gap E_g. The latter linearly increases in the series of PbI_2, $CsPbI_3$, and Cs_4PbI_6 compounds (Fig. 2, inset), which is additional proof of the localization of exciton excitations in $(PbI_6)^{4-}$ octahedra.

pound, whereas the same dependence recorded upon cooling corresponds apparently to a mixture of Cs_4PbI_6 and $CsI:Pb^{2+}$.

Let us consider in more detail the temperature dependences of the spectral position and half-width of the long-wavelength A_1^I exciton band obtained upon heating and cooling the $CsPbI_3$ sample and the temperature dependence of the parameters of the A_1^{II} band in the Cs_4PbI_6 spectrum (Fig. 4).

As was noted above, the long-wavelength exciton band A_1^I in the spectrum of $CsPbI_3$ is linearly red-shifted with $dE_m/dT = -2.45 \times 10^{-4}$ and -2.53×10^{-4} eV/K upon heating and cooling, respectively. The A_1^{II} band in the Cs_4PbI_6 spectrum is also linearly red-shifted ($dE_m/dT = -2.12 \times 10^{-4}$ eV/K) with an increase in T (Fig. 4a). This shift is typical (in order of magnitude) of most ionic crystals, including the compounds under study. The interaction of excitons and longitudinal optical (LO) phonons dominates in ionic crystals, and the largest temperature changes in the parameters of exciton bands occur at $\hbar\omega_{LO} \leq kT$. We do not know the $\hbar\omega_{LO}$ values for $CsPbI_3$ and Cs_4PbI_6. They can be estimated based on the known parameters $\hbar\omega_{LO} = 13.7$ meV for PbI_2 [18] and $\hbar\omega_{LO} = 11$ meV in CsI [19]. With allowance for the molar contents of the compositions, $\hbar\omega_{LO} \sim 12.35$ meV for $CsPbI_3$ and 11.54 meV for Cs_4PbI_6.

The dE_m/dT values for $CsPbI_3$ and Cs_4PbI_6 are slightly larger than $dE_m/dT = -1.6 \times 10^{-4}$ eV/K for thin PbI_2 films [20], but are much smaller than those for other ionic crystals [1]. The weak temperature shift of the exciton bands in PbI_2 is related to the compensation of the EPI-induced red shift by the blue shift caused by the thermal lattice expansion [20]. Apparently, the small dE_m/dT values for the compounds under study are also caused (as for PbI_2) by the compensation of the EPI-induced negative shift by the positive shift related to the lattice expansion.

The temperature behavior of the half-width Γ of the long-wavelength exciton bands of both compounds is nonlinear (Fig. 4). According to the theory [21], the temperature dependence $\Gamma(T)$ for excitons of different dimensions d ($d = 1, 2,$ or 3) is determined as

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

where $\gamma(d/2)$ is the gamma function (which depends on d), B is the exciton-band width, and $D^2 = 0.5C^2\hbar\omega_{LO}\coth(\hbar\omega_{LO}/kT)$ ($C^2/2$ is the lattice relaxation energy upon exciton excitation). While processing the experimental dependence $\Gamma(T)$, we took into account the shape of the exciton band and the contribution of the residual broadening of $\Gamma(0)$ to Γ due to
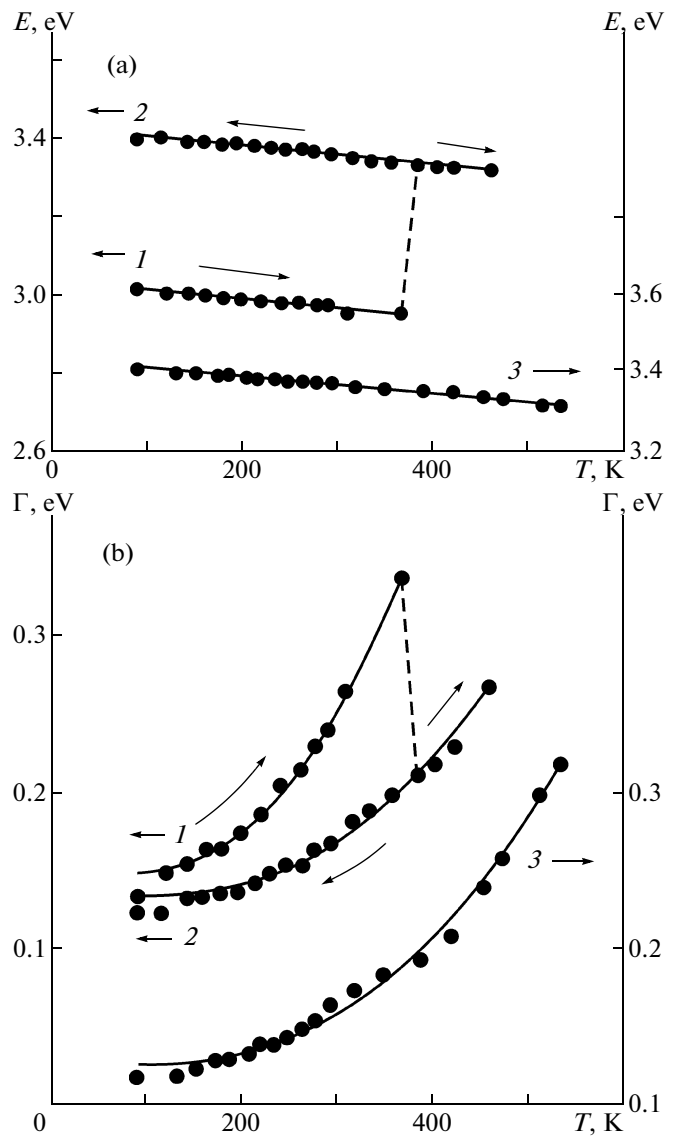

Fig. 4. Temperature dependences of (a) the spectral position $E_m(T)$ and (b) the half-width $\Gamma(T)$ of the long-wavelength exciton band A_1^I in the spectrum of $CsPbI_3$, obtained upon (*1*) heating and (*2*) cooling the sample, and (*3*) the A_1^{II} band in the spectrum of a 100-nm-thick Cs_4PbI_6 film.

the lattice defects. In the spectrum of $CsPbI_3$ recorded at liquid-nitrogen temperature, the shape of the band found according to the technique [12] is a linear combination of Lorentzian and Gaussian profiles; the Gaussian component increases upon heating. At the same time, the band in the spectrum of Cs_4PbI_6 is a Gaussian in the entire temperature range under study. In the case of Gaussian profile the total half-width is determined by the relation

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

where $\Gamma(T)$ is described by (2) with an unknown factor A, which is independent of T. Processing the experimental dependence $\Gamma(T)$ using (2) for different d showed that the best agreement of the calculation based on (2) with the experimental data can be obtained at $d = 3$. In this case,

$$\Gamma(T) = A\coth^2(\hbar\omega_{LO}/kT), \qquad (4)$$

and the dependence $\Gamma(T)$ in the $\Gamma^2 - \coth^4(\hbar\omega_{LO}/kT$ coordinates is linear. Processing this dependence by the least-squares method yields $\Gamma_1(0) = 0.145 \pm 0.002$ eV and $A_1 = (1.3 \pm 0.05) \times 10^{-4}$ eV upon heating and $\Gamma_2(0) = 0.134 \pm 0.002$ eV and $A_2 = (2.4 \pm 0.07) \times 10^{-5}$ eV upon cooling the CsPbI$_3$ sample and $\Gamma_3(0) = 0.126 \pm 0.002$ eV and $A_3 = (2.1 \pm 0.07) \times 10^{-5}$ eV for Cs$_4$PbI$_6$. A calculation (based on (3) and (4)) of the temperature dependence of the half-width with the obtained $\Gamma(0)$ and A values yields good agreement with the experimental dependence $\Gamma(T)$ (Fig. 4b).

Thus, as follows from the analysis of the temperature dependence $\Gamma(T)$, the excitons in CsPbI$_3$ and Cs$_4$PbI$_6$ are of 3D type.

CONCLUSIONS

The technique developed for preparing thin CsPbI$_3$ and Cs$_4$PbI$_6$ films made it possible to study the exciton absorption spectra in the energy range of 2.0–6.0 eV and the temperature range of 90–500 K. Based on these data, we drew certain conclusions about the temperature dependence of the main exciton-band parameters (spectral position and half-width). It was shown that the long-wavelength exciton excitations in the crystals under study are localized in the sublattices containing Pb^{2+} ions coordinated by I$^-$ ions. However, the significant difference between the oscillator strengths of the exciton bands in the spectra of Cs$_4$PbI$_6$ films prepared by two different methods (direct deposition and annealing of CsPbI$_3$ films) should be explained in more detail. To this end, it is necessary to investigate thoroughly the lattice of Cs$_4$PbI$_6$ films prepared in different ways.

REFERENCES

1. O. N. Yunakova, V. K. Miloslavskii, and E. N. Kovalenko, Fiz. Nizk. Temp. (Kiev) **29**, 922 (2003).
2. I. N. Belyaev, E. A. Shurginov, and N. S. Kudryashov, Zh. Neorg. Khim. **17**, 2812 (1972).
3. C. K. Müller, Nature **182**, 1436 (1958).
4. D. M. Trots and S. V. Myagkota, J. Phys. Chem. Solids **69**, 2520 (2008).
5. C. K. Müller, Mat.-Fus. Medd. K. Dan. Vidensk. Selsk. **32** (3), 1 (1960).
6. B. D. Stepin, G. M. Serebrennikova, G. P. Chicherina, V. K. Trunov, and Yu. V. Oboznenko, Zh. Neorg. Khim. **22**, 3148 (1976).
7. N. S. Pidzyrailo, A. S. Voloshinovskii, and S. V. Myagkota, Opt. Spectrosc. **64** (6), 708 (1988).
8. S. V. Myagkota, Opt. Spectrosc. **87** (2), 290 (1999).
9. F. Somma, M. Nikl, K. Nitsch, C. Giampaolo, and A. R. Santucci. S. Phani, Superfic. Vac. **9**, 62 (1999).
10. S. Kondo, A. Masaki, T. Saito, and H. Asada, Solid State Commun. **124**, 211 (2002).
11. S. Kondo, K. Amaya, and T. Saito, J. Phys.: Condens. Matter **15**, 971 (2003).
12. O. N. Yunakova, V. K. Miloslavskii, and E. N. Kovalenko, Opt. Spectrosc. **104** (4), 552 (2008).
13. S. Radhakrishna and K. P. Pande, Phys. Rev. B **7**, 424 (1973).
14. S. B. S. Sastry and K. Balasubramanyam, J. Phys. C: Solid State Phys. **11**, 4213 (1978).
15. Y. Onodera and Y. Toyasawa, J. Phys. Soc. Jpn. **22**, 833 (1967).
16. I. Ch. Schlüter and M. Schlüter, Phys. Rev. B **9**, 1652 (1974).
17. K. Heidrich, H. Künzel, and J. Treusch, Solid State Commun. **25**, 887 (1978).
18. G. Lukovsky, R. M. White, J. A. Benda, W. Y. Liang, R. Zallem, and P. H. Schmidt, Solid State Commun. **18**, 811 (1976).
19. F. Beerwerth, D. Frohlich, and V. Leinweber, Phys. Status Solidi (b) **145**, 195 (1988).
20. V. V. Mussil, V. K. Miloslavskii, and V. V. Karmazin, Sov. Phys. Solid State **17**, 545 (1975).
21. M. Schreiber and Y. Toyasawa, J. Phys. Soc. Jpn. **51**, 1528 (1982).

Translated by Yu. Sin'kov

SPELL: OK