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## The Exciton Absorption Spectrum of $\text{KPbI}_3$ Thin Films

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Received May 20, 2013

**Abstract**—The absorption spectrum of  $\text{KPbI}_3$  thin films is studied in the spectral range 2–6 eV within the temperature interval 90–470 K. Localization of excitons in the sublattice of the compound containing lead ions is established. Excitons are shown to be of two-dimensional nature.

DOI: 10.1134/S0030400X1401024X

### INTRODUCTION

The halogenides with the general formula  $\text{APbX}_3$  ( $A = \text{K}, \text{Cs}, \text{Rb}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ) iodides—specifically,  $\text{KPbI}_3$ —are the least studied. There is not even a general view regarding the molar composition of the compound formed in the system  $\text{KI}–\text{PbI}_2$ . According to [1, 2], the compound  $\text{KPbI}_3$  is formed in the system  $\text{KI}–\text{PbI}_2$ , while, according to [3, 4], it is the compound  $\text{K}_2\text{PbI}_4$ . At the same time, from studies of luminescence spectra of single crystals  $\text{KI}:\text{Pb}^{2+}$  [5], it has been deduced that, in the  $\text{KI}–\text{PbI}_2$  system, two ternary compounds are formed with different spectra ascribed by the authors to the compounds  $\text{KPbI}_3$  and  $\text{K}_2\text{PbI}_4$ . From analysis of the absorption spectra of thin films  $(\text{KI})_{1-x}(\text{PbI}_2)_x$  ( $0.1 \leq x \leq 0.5$ ) [6], the authors drew the conclusion that there is formation of compounds  $\text{KPbI}_3$  and  $\text{K}_4\text{PbI}_6$ . This conclusion is supported by the linear dependence of the spectral position of the long-wavelength excitonic bands in the series of compounds  $\text{PbI}_2$ ,  $\text{KPbI}_3$ , and  $\text{K}_4\text{PbI}_6$  on the concentration of  $\text{PbI}_2$ ,  $x$ , converging, at  $x \rightarrow 0$ , to the spectral position of the impurity bands of  $\text{Pb}^{2+}$  in  $\text{KI}$  [6].

In spite of numerous X-ray structural studies of the alloy salts of  $\text{KI}$  and  $\text{PbI}_2$  [2, 3], no data are available concerning the crystal structure of the compounds formed in the  $\text{KI}–\text{PbI}_2$  system. From comparison of the X-ray diffraction pattern of  $\text{KPbI}_3$  and  $\text{CsPbI}_3$  [2], one can draw a conclusion regarding their isostructural lattices. In contrast to  $\text{KPbI}_3$ , the crystal structure of  $\text{CsPbI}_3$  has been studied rather well [7, 8]. The compound  $\text{KPbI}_3$ , like  $\text{CsPbI}_3$ , presumably crystallizes into an orthorhombic perovskite-type structure, with its structural elements in the form of double chains consisting of octahedra  $(\text{PbI}_6)^{4-}$  aligned along the minor axis of the crystal.

The reflection spectrum of the  $\text{KPbI}_3$  single crystals in the region of the long-wavelength excitonic band at  $T = 4.2$  K was studied in [9].

In this paper, we study the absorption spectra of the  $\text{KPbI}_3$  thin films in a wide temperature range including temperatures of possible phase transitions.

### EXPERIMENTAL

$\text{KPbI}_3$  thin films were prepared by evaporating a mixture of pure powders of  $\text{KI}$  and  $\text{PbI}_2$  with a proper molar composition onto a silica substrate heated up to  $100^\circ\text{C}$  with subsequent annealing of the samples at  $130^\circ\text{C}$  for 2 h. The mixture of the powders was preliminarily melted under a shield mounted between the vaporizer and substrate. Under these conditions, there was no admixture of the phase  $\text{K}_4\text{PbI}_6$  in the films. We failed to obtain single-phase films of  $\text{K}_4\text{PbI}_6$ . This compound is quite likely to be unstable and is preserved only partially upon fast cooling of the film down to room temperature.

The phase composition of the films was monitored by the absorption spectra measured at  $T = 90$  K. Such monitoring was possible due to significant difference between the spectral positions of the long-wavelength excitonic bands in  $\text{KPbI}_3$  (3.027 eV),  $\text{K}_4\text{PbI}_6$  (3.388 eV [6]), and  $\text{PbI}_2$  (2.5 eV), and  $\text{KI}$  (5.8 eV).

The absorption spectra were measured in the spectral range 2–6 eV at  $T = 90$  and 290 K using an SF-46 spectrophotometer. In the narrower spectral range of 2.4–3.7 eV (in the region of the long-wavelength excitonic band), the absorption spectrum was measured in the wide temperature range of 90–470 K including temperatures of possible phase transitions. For spectral measurement in the temperature range of 90–350 K, the sample was placed into a vacuum cryostat supplied with a carbon-adsorption pump. For high-temperature measurements, the sample was placed into a furnace with a tungsten heater.

Parameters of the long-wavelength excitonic bands were approximated, in accordance with [10], by a symmetric single-oscillator mixed profile having a shape intermediate between Lorentzian and Gaussian and representing their linear combination. This mixed profile does not differ much from that of Voigt. The parameters of the excitonic bands (position  $E_m$ ; half-width  $\Gamma$ ; and  $\varepsilon_{2m} \equiv \varepsilon(E_m)$ , the imaginary part of the permittivity at the peak of the excitonic band) were chosen to obtain the best fit of the calculated profile to the measured spectrum at the long-wavelength slope of the band.

### TEMPERATURE DEPENDENCE OF PARAMETERS OF THE LONG-WAVELENGTH EXCITONIC BAND IN $\text{KPbI}_3$

The absorption spectrum of the  $\text{KPbI}_3$  thin film at  $T = 90$  K reveals, at the edge of the intrinsic absorption band, a narrow excitonic  $A_1$ -band at 3.027 eV (Fig. 1). Positions of shorter-wavelength  $C$ - and  $D$ -bands are given in the table. The  $A_1$ -band, in its spectral position, is close to the long-wavelength excitonic bands in  $\text{CsPbI}_3$  (3.013 eV [11, 12]) and  $\text{RbPbI}_3$  (2.975 eV [13]). Close spectral positions of the long-wavelength excitonic bands in the compounds  $\text{MPbI}_3$  ( $M = \text{K, Rb, Cs}$ ) indicated localization of excitons in the sublattice containing Pb ions. As was mentioned above, we assume the compound  $\text{KPbI}_3$  to be isostructural with the compounds  $\text{CsPbI}_3$  and  $\text{RbPbI}_3$ , with the structural elements of their crystal lattice being octahedra  $(\text{PbI}_6)^{4-}$  [7, 8]. This assumption is supported by the similarity of the spectra of  $\text{MPbI}_3$  ( $M = \text{K, Rb, Cs}$ ) in terms of structure and position of the main absorption bands (Fig. 1 and table). Thus, excitons in  $\text{KPbI}_3$ , as well as in  $\text{CsPbI}_3$  [11, 12] and  $\text{RbPbI}_3$  [13], are localized in the complexes  $(\text{PbI}_6)^{4-}$  and the excitonic spectrum is interpreted in terms of electron transitions in the  $(\text{PbI}_6)^{4-}$  octahedron like spectra of impurity ions  $\text{Pb}^{2+}$  in the alkali-halide crystals [14]. In other words, the  $A$ -bands in the  $\text{MPbI}_3$  spectra correspond to the transitions  $^1A_{1g} \rightarrow ^3T_{1u}$ , while the  $C$ -bands correspond to the transitions  $^1A_{1g} \rightarrow ^1T_{1u}$ .

The absorption spectrum of the  $\text{KPbI}_3$  thin films in the range of the long-wavelength excitonic band (2.4–3.7 eV) was measured in the temperature range of 90–470 K upon heating and cooling of the sample.

With increasing temperature, the  $A_1$ -band in  $\text{KPbI}_3$  shifts to longer wavelengths, broadens, and becomes weaker due to exciton-phonon interaction (EPI) (Fig. 2). However, the temperature behavior of spectral position  $E_m(T)$  of the  $A_1$ -band (Fig. 2a) obtained by heating of the sample shows some specific features. In the narrow temperature interval from 205 to 247 K, we observed a short-wavelength shift of the  $A_1$ -band by 0.03 eV; in the range of 247–276 K, the  $A_1$ -band shifts

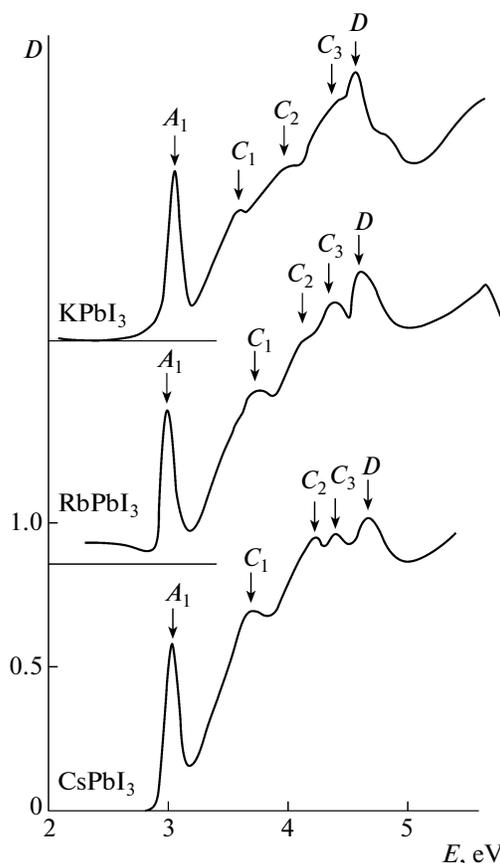


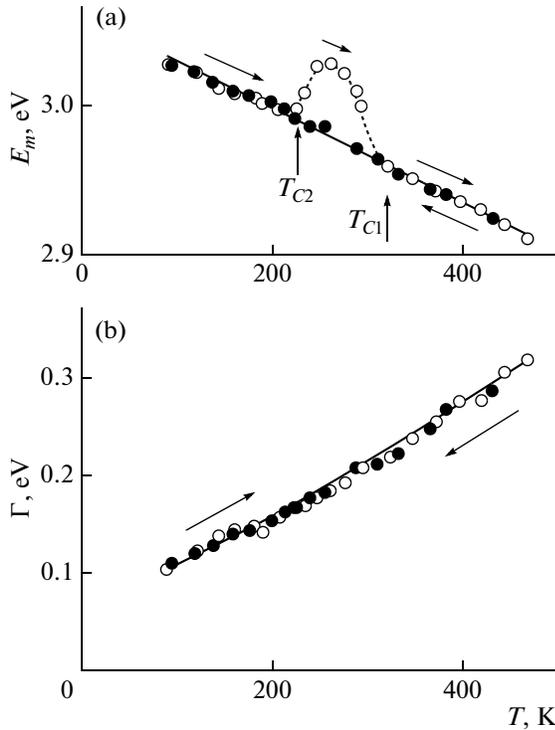
Fig. 1. Absorption spectra of the  $\text{KPbI}_3$ ,  $\text{RbPbI}_3$ , and  $\text{CsPbI}_3$  thin films ( $T = 90$  K).

linearly to shorter wavelengths with  $dE_m/dT = -1.7 \times 10^{-4}$  eV/K; and, in the range of 276–321 K, it sharply shifts toward longer wavelengths by 0.07 eV.

The short-wavelength shift of the  $A_1$ -band with increasing  $T$  in the range of 205–247 K indicates an increasing volume of a unit cell. This increase may be related either to a phase transition or to intercalation of the film by  $\text{CO}_2$  molecules effused from the carbon-adsorption pump of the cryostat upon heating. The latter is supported by the fact that starting temperature of the short-wavelength shift  $T_{c2} = 205$  K is close to that of sublimation of  $\text{CO}_2$ ,  $T = 194.5$  K, and by the absence of specific features in the temperature behavior of  $E_m(T)$  measured under cooling of the sample.

Spectral position of the  $\text{MPbI}_3$  absorption bands ( $M = \text{K, Rb, Cs}$ )

Compound	$E_{A1}$ , eV	$E_{C1}$ , eV	$E_{C2}$ , eV	$E_{C3}$ , eV	$E_D$ , eV
$\text{KPbI}_3$	3.027	3.58	3.97	3.36	4.56
$\text{RbPbI}_3$ [13]	2.975	3.73	4.105	4.4	4.63
$\text{CsPbI}_3$ [12]	3.013	3.69	4.22	4.4	4.461



**Fig. 2.** Temperature dependence of (a) spectral position  $E_m(T)$  and (b) halfwidth  $\Gamma(T)$  of the long-wavelength excitonic band  $A_1$  in  $\text{KPbI}_3$  ( $t = 135$  nm): (dots) experiment (open circles correspond to heating and filled circles to cooling of the sample), (solid lines) calculation by (a) Eq. (1) and (b) Eqs. (2) and (3).

Temperature dependence  $E_m(T)$  under cooling of the sample, as well as under heating of the sample in the temperature regions from 90 to 205 K and from 321 to 468 K, is described by the linear dependence

$$E_m(T) = E_m(0) + \alpha T, \quad (1)$$

where  $E_m(0) = 3.06$  eV and  $\alpha = dE_m/dT = -3.11 \times 10^{-4}$  eV/K.

Intercalation of the films with  $\text{CO}_2$  upon heating in the cryostat was observed earlier in  $\text{ZnI}_2$  and  $\text{K}_2\text{ZnI}_4$  thin films [15, 16] and was accompanied by a noticeable short-wavelength shift of the absorption edge. It should be noted that the short-wavelength shift of  $E_m(T)$  within the interval of 205–321 K was observed in all  $\text{KPbI}_3$  samples upon heating. However, the value of the greatest shift was not the same, which is likely to be related to different degrees of intercalation of the  $\text{KPbI}_3$  films by  $\text{CO}_2$  molecules. It is possible that, after heating up to  $T \sim 195$  K,  $\text{CO}_2$  molecules start to effuse from the carbon pump and partially intercalate into the  $\text{KPbI}_3$  film, which causes the short-wavelength shift of the  $A_1$ -band. This process is saturated at 247 K, and later, in the interval 247–276 K, a long-wavelength shift of the excitonic band in the intercalated film occurs due to the EPI. Further heating of the

$\text{KPbI}_3$  film leads to gradual removal of the intercalant accompanied by a sharp long-wavelength shift of the  $A_1$ -band in the interval 276–321 K. Starting from  $T_{c1} = 321$  K, the short-wavelength shift of the excitonic band is related exclusively to the EPI and is described by Eq. (1), which indicates total removal of the intercalant from the film. Upon cooling of the cryostat, the  $\text{CO}_2$  molecules are frozen out and intercalation of the  $\text{KPbI}_3$  film occurs only upon heating.

Intercalation of the  $\text{KPbI}_3$  film by  $\text{CO}_2$  molecules indicates a layered structure of crystal lattice of the compound under study. Unfortunately, we are not aware of the  $\text{KPbI}_3$  crystal structure, but, since the spectra of the  $\text{MPbI}_3$  ( $M = \text{K}, \text{Rb}, \text{Cs}$ ) are isostructural, we suggest that these compounds are isostructural as well. The compounds  $\text{RbPbI}_3$  and  $\text{CsPbI}_3$  crystallize, at room temperature, into a perovskite-like orthorhombic lattice with four molecules in a unit cell and close parameters  $a = 10.27; 10.46$  Å,  $b = 17.38; 17.78$  Å, and  $c = 4.77; 4.8$  Å (space group  $Pnma$ ) for  $\text{RbPbI}_3$  and  $\text{CsPbI}_3$ , respectively [7, 8]. In spite of the layered structure, intercalation of the  $\text{RbPbI}_3$  and  $\text{CsPbI}_3$  films by  $\text{CO}_2$  molecules was not observed [12, 13]. The layered crystals are characterized by van der Waals bonding between the layers. Intercalation of the  $\text{KPbI}_3$  films indicates, most likely, a weaker van der Waals bonding as compared to the  $\text{RbPbI}_3$  and  $\text{CsPbI}_3$ . However, to draw an unambiguous conclusion regarding manifestation of intercalation in  $\text{KPbI}_3$ , one has to know the lattice parameters of the compound under study. It is also interesting to examine the effect of other, more efficient, intercalants on spectra of the compounds.

In order of magnitude, the values of  $dE_m/dT$  in  $\text{KPbI}_3$  are typical for most ionic crystals, including this compound. As is known, in ionic crystals, excitons predominantly interact with longitudinal optical (LO) phonons and the most essential temperature changes in parameters of the excitonic bands may occur at  $\hbar\omega_{\text{LO}} \leq kT$ . We estimated the unknown values of  $\hbar\omega_{\text{LO}}$  in  $\text{KPbI}_3$  using known values of  $\hbar\omega_{\text{LO}} = 13.7$  meV in  $\text{PbI}_2$  [17] and  $\hbar\omega_{\text{LO}} = 17.5$  meV in  $\text{KI}$  [18]. Taking into account the molar composition of the  $\text{KPbI}_3$  compound,  $\hbar\omega_{\text{LO}} \sim 15.6$  meV.

In spite of the jumps in temperature dependence of the spectral position  $E_m(T)$  of the  $A_1$ -band (Fig. 2a), the temperature dependence of halfwidth  $\Gamma(T)$  is smooth, with no characteristic features (Fig. 2b).

In conformity with theory [19], broadening of excitonic bands associated with excitonic interaction for excitons of different dimensionality  $d$  ( $d = 1, 2, 3$ ) is defined as follows as

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

where  $\gamma(d/2)$  is the  $\Gamma$ -function dependent on  $d$ ,  $B$  is the width of the excitonic band,  $D^2 = 0.5C^2\hbar\omega_{LO} \coth(\hbar\omega_{LO}/2kT)$ ,  $C^2/2$  is the lattice relaxation energy related to formation of excitons. With allowance for the residual broadening  $\Gamma(0)$  of the excitonic band due to the lattice defects and Gaussian shape of the excitonic bands  $A_1$  in the studied temperature range, the whole width  $\Gamma$  is given by the relationship

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

where  $\Gamma(T)$  obeys Eq. (2) with an unknown temperature-independent factor  $A$ . Processing of experimental dependence  $\Gamma(T)$  using Eq. (2) for different  $d$  gives the best fit with the experimental data at  $d = 2$ . In this case,

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

and the dependence  $\Gamma(T)$  in the coordinates  $\Gamma^2$  on  $\coth^2(\hbar\omega_{LO}/2kT)$  appears to be linear. Processing of this dependence by the least-squares method yields the values  $\Gamma(0) = 0.075 \pm 0.004$  eV and  $A = 0.059 \pm 0.0005$  eV. The computed temperature dependence  $\Gamma(T)$  from Eqs. (2) and (3) with the found values of  $\Gamma(0)$  and  $A$  well agrees with the experiment (Fig. 2b).

Thus, analysis of temperature dependence  $\Gamma(T)$  of the  $A_1$  band indicates a two-dimensional nature of excitons in  $\text{KPbI}_3$ , which confirms the layered structure of the compound. It should be noted that, in spite of the layered structure of the compounds  $\text{RbPbI}_3$  and  $\text{CsPbI}_3$ , the excitons in these compounds are three-dimensional [12, 13]. It is most likely that, in the series of compounds  $\text{KPbI}_3$ ,  $\text{RbPbI}_3$ , and  $\text{CsPbI}_3$ , the first one is the most layered, which is supported not only by the two-dimensional nature of excitons in this compound, but also by intercalation of the film by  $\text{CO}_2$  molecules.

## CONCLUSIONS

As follows from the structure of the spectrum and positions of the main absorption bands, the spectrum of the  $\text{KPbI}_3$  thin films is isostructural with those of  $\text{MPbI}_3$  ( $M = \text{Rb, Cs}$ ) and, like the spectra of  $\text{MPbI}_3$ , is interpreted based on electronic transitions in the octahedron  $(\text{PbI}_6)^{4-}$ .

In the studies of the temperature dependence of spectral position  $E_m(T)$  of the long-wavelength  $A_1$ -

band obtained under heating of the sample, the short-wavelength shift of the band is found at  $T_{c2} = 205$  K, which is likely to be associated with intercalation of the film by  $\text{CO}_2$  molecules, giving rise to an increase of the unit cell volume. The temperature behavior of  $\Gamma(T)$  indicates creation of 2D excitons in  $\text{KPbI}_3$ .

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*Translated by V. Zapasskii*