Exciton absorption spectra of KPb$_2$Br$_5$ thin films

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Absorption spectra of KPb$_2$Br$_5$ thin films of tetragonal (I) and monoclinic (II) structures were investigated in the spectral region of 2–6 eV and the temperature range of 90–440 K. It was found that KPb$_2$Br$_5$(I) of the tetragonal structure irreversibly transferred in KPb$_2$Br$_5$(II) of the monoclinic structure when T = 293 K. It was found that low-frequency exciton excitations of KPb$_2$Br$_5$(I,II) were localized in the sublattice, which contained Pb^{2+} ions and were two-dimensional nature.

Keywords: thin films, absorption spectra, exitons, phase transition.

Исследован спектр поглощения тонких пленок KPb$_2$Br$_5$ тетрагональной (I) и моноклинной (II) структур в области спектра 2–6 эВ и температурном интервале 90–440 К. Установлено, что при T = 293 К KPb$_2$Br$_5$(I) тетрагональной структуры необратимо переходит в KPb$_2$Br$_5$(II) моноклинной структуры. Установлено, что низкочастотные экситонные возбуждения в KPb$_2$Br$_5$(I,II) локализованы в подрешетке, содержащей ионы Pb^{2+}, и носят двухмерный характер.

Екситонний спектр поглинання тонких плівок KPb$_2$Br$_5$. *В.В.Коваленко, Е.М.Коваленко, О.М.Юнакова, М.М.Юнаков.*

Досліджено спектр поглинання тонких плівок KPb$_2$Br$_5$ тетрагональної (I) та моноклинної (II) структур в області спектра 2–6 еВ і інтервалі температур 90–440 К. Установлено, що при T = 293 К KPb$_2$Br$_5$(I) тетрагональної структури незворотньо переходить в KPb$_2$Br$_5$(II) моноклинної структури. Установлено, що низькочастотні екситонні збудження у KPb$_2$Br$_5$(I,II) локалізовані у підгратці, яка містить іони Pb^{2+}, і мають двомірний характер.

1. Introduction

KPb$_2$Br$_5$ compound exists in two modifications: in tetragonal (I), NH$_4$Pb$_2$Br$_5$ type structure (space group $I4/mcm$, lattice parameters are a = 8.14 Å, c = 14.10 Å, z = 4 [1, 2]) and in monoclinic (II), NH$_4$Pb$_2$Cl$_5$ type structure (sp. gr. $P2_1/c$, lattice parameters are a = 9.264 Å, b = 8.380 Å, c = 13.063 Å, γ = 90.06°, z = 4 [1–3]). KPb$_2$Br$_5$ crystals with monoclinic structure are formed at high-temperature crystallization from melt, the crystals with tetragonal crystal structure are formed under crystallization from the aqueous solution.

MPb$_2$Hal$_5$ crystals (M = K, Rb, Hal = Cl, Br) have a broad band of transparency in infrared region of the spectrum and narrow phonon spectrum, which allows their use as a matrix for alloyage by rare-earth ions in creation of the laser gain mediums [4–7]. In recent years, the research of excitation spectra, luminescence, photoluminescence of MPb$_2$Hal$_5$ crystals doped with rare-earth

ions is actively conducted [4–7]. At the same time, the spectra of the compounds are not studied enough.

Reflection spectrum of $KPb_2Br_5(II)$ single crystals of the monoclinic structure was studied in [6]. Long-wavelength exciton band at 3.87 eV (8 K) and a range of short-wave bands were detected in the reflection spectrum. The investigations of $KPb_2Br_5(II)$ absorption spectrum are unknown to us. The spectrum of $KPb_2Br_5(I)$ crystals with the tetragonal structure has not been studied too.

Ferroelectric first-order phase transition is found at 519.5 K from the temperature studies of birefringence of $KPb_2Br_5(II)$ crystal [8]. The presence of the phase transition at 519.5 K in $KPb_2Br_5(II)$ is confirmed by polarization-optical and calorimetric studies [8, 9].

In this paper we investigate the absorption spectra of KPb_2Br_5 thin films both modifications in the range of 2–6 eV and at the temperature range of 90–440 K.

2. Experimental

KPb_2Br_5 thin films were prepared by vacuum evaporation of melt mixture of pure KBr and $PbBr_2$ powders with a stoichiometric molar composition on a cold quartz substrate at $T_s = 278$ K. This method has been used previously to produce thin films of multicomponent compounds [10–12]. Typically, ternary compounds melting temperature is significantly lower than the melting temperatures of the initial binary compounds, which allows producing monophasic films of complexes compounds without impurity of initial binary components under evaporation of the melt. The KPb_2Br_5 melting temperature $T_m = 335°C$ [13] is lower than the melting temperature of the starting components ($T_m = 373°C$ for $PbBr_2$ and $T_m = 735°C$ for KBr [14]). The film, that was produced by this method, corresponded, apparently, to $KPb_2Br_5(I)$. Phase of the prepared films and formation of $KPb_2Br_5(II)$ will be discussed in more detail later, in the discussion of the absorption spectra.

The phase composition of the films was monitored by absorption spectra measured at $T = 90$ K. This control was possible because of different spectral position of the long-wavelength exciton bands in KPb_2Br_5 (3.66–3.84 eV), $PbBr_2$ (3.98 eV) and KBr (6.76 eV).

The film with thickness of 80–100 nm was used to measure the absorption spectra. The absorption spectra were measured in the spectral range of 2–6 eV at $T = 90$ and 290 K by a spectrophotometer SF-46. The
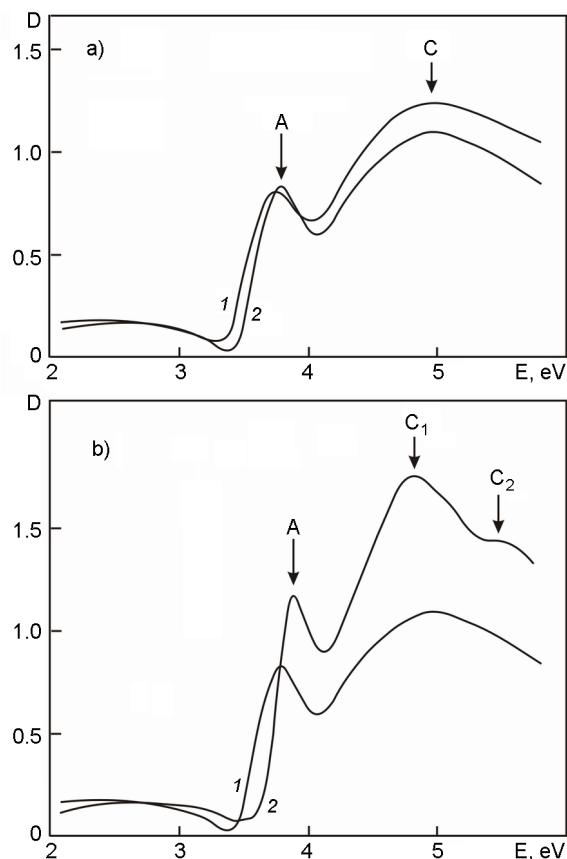

Fig. 1. Absorption spectra of KPb_2Br_5 thin films: a)tetragonal structure (I) at $T = 282$ K (*1*) and 90 K (*2*) and b)monoclinic (II) (*2*) and tetragonal (I) (*1*) structures at $T = 90$ K.

absorption spectrum in the range of the long-wavelength excitonic band (3.0–4.2 eV) was measured over a wide temperature range of 90–440 K.

Parameters of the long-wavelength exciton band A (position E_m, and half-width Γ and value of the imaginary part of permittivity at the maximum of the band $\varepsilon_{2m} = \varepsilon_2(E_m)$) were determined by the method of [15], by approximating the band with a symmetric one oscillator profile (a linear combination of the Lorentzian and Gaussian profiles). The band parameters $(E_m, \Gamma$ and $\varepsilon_{2m})$ were chosen to obtain the best agreement of the calculated profile to the measured spectrum at the long-wavelength slope of the band.

3. Results and discussion

3.1. Absorption spectra of thin KPb_2Br_5 films of triclinic and monoclinic structures

The absorption spectrum of a thin KPb_2Br_5 film $T = 90$ K (Fig. 1a) have long-

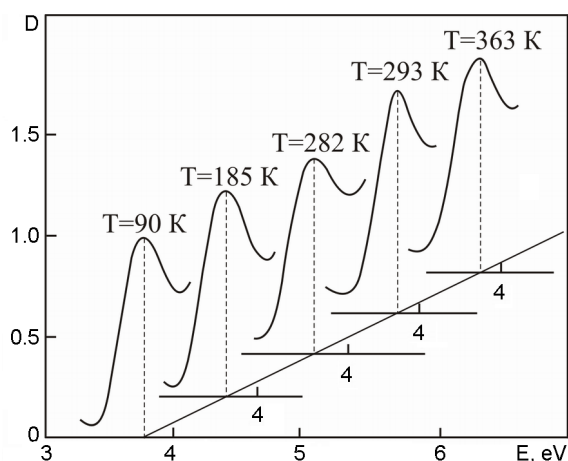Fig. 2. Spectra of long-wavelength exciton band A in KPb_2Br_5 thin film at different temperatures.
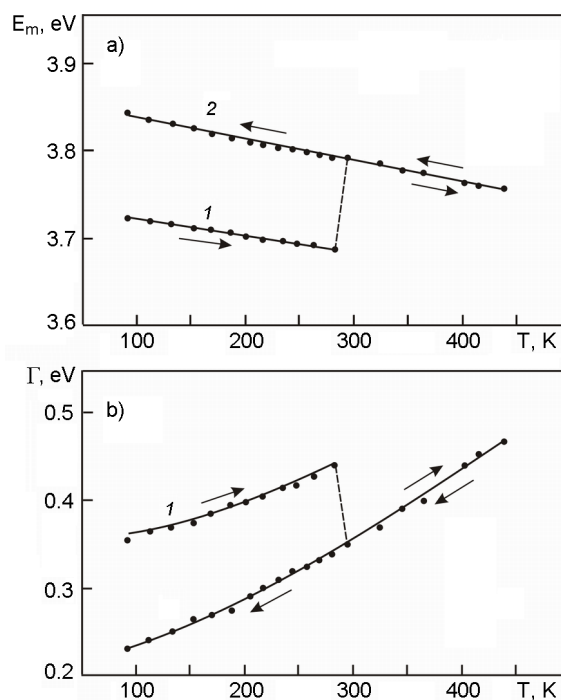

Fig. 3. Temperature dependences of the spectral position $E_m(T)$ (a) and half-width $\Gamma(T)$ (b) of the long-wavelength exciton band A in KPb_2Br_5 thin film: experimental (points) and calculation from Eqs. (2) and (3) (solid curve).

wavelength A^I band at 3.72 eV and broad C^I band at 4.95 eV. With increase in temperature A^I and C^I bands are shifting to the longer wavelengths, are broadening and weakening due to the exciton-phonon interaction (EPI), which indicates their exciton origin. After separating of a A^I band by symmetric profile the band gap $E_g =$ 3.95 eV and exciton binding energy $R_{ex} =$ 0.23 eV were determined on inflection point of the absorption edge.

A^I band, as the temperature increases, shifts linearly to the longer wavelengths with $dE_m/dT = -(1.87\pm0.04)\cdot10^{-4}$ eV/K (Fig. 2, 3) in the temperature range of 90–282 K. At $T_c = 293$ K there are short-wave shift, constriction and sharpening of the long-wavelength exciton band (Fig. 2, 3). The jump of the spectral position in the temperature dependence and half-width of the long-wavelength exciton band at $T_c =$ 293 K indicates first-order phase transition. This transition is irreversible. Cooling of the film down to 90 K temperature does not restore the spectrum (Fig. 1b).

Apparently, evaporation of the melt mixture of $KPb_2Br_5(I)$ with tetragonal structure

is crystallized onto cold substrate. The phase transition occurs in $KPb_2Br_5(II)$ monoclinic structure when the film is heated to $T \geq T_c$. This assumption evidenced by the following. The long-wavelength exciton band A^{II} observed in the $KPb_2Br_5(II)$ thin film spectrum (90 K) at 3.84 eV, a short-wave band C_1^{II} observed at 4.8 eV and C_2^{II} observed at 5.5 eV (Fig. 1b). The structure of the spectrum and the position of the absorption bands of the $KPb_2Br_5(II)$ spectrum is consistent with the reflection spectrum of $KPb_2Br_5(II)$ single crystals of the monoclinic structure (see Table) [6]. The obtained values of the band gap $E_g = 4.08$ eV and the exciton binding energy $R_{ex} = 0.24$ eV in the

Table. Spectral position of exciton bands, width of the gap E_g and exciton binding energy R_{ex} in $KPb_2Br_5(I,II)$ compounds

Compound	E_{mA}, eV	E_{mC1}, eV	E_{mC2}, eV	E_g, eV	R_{ex}, eV
$KPb_2Br_5(I)$ (thin film)	3.72	4.95		3.95	0.23
$KPb_2Br_5(II)$ (thin film)	3.84	4.8	5.5	4.08	0.24
$KPb_2Br_5(II)$ (single crystal) [6]	3.87			4.12	0.25
$PbBr_2$ [16]	3.98	4.86	5.69	4.23	0.25
$KBr:Pb^{2+}$ [19]	4.16	5.54	5.75		

thin $KPb_2Br_5(II)$ film are also close to the corresponding values in the single crystal ($E_g = 4.12$ eV and $R_{ex} = 0.25$ eV) [6].

The structure of the spectrum and the position of the exciton bands in the thin $KPb_2Br_5(II)$ films spectrum (Fig. 1b) is close to $PbBr_2$ spectrum in the investigated spectral range (see Table 1). In the range of 2–6 eV in the $PbBr_2$ spectrum there were observed exciton band at 3.98 eV, 4.85 eV and 5.7 eV ($T = 78$ K) [16], the same exciton bands in the $KPb_2Br_5(II)$ spectrum were slightly shifted to the longer wavelengths (see Table). It is known that the excitons in $PbBr_2$ have cationic character. The top of the valence band is formed by $6s$ Pb^{2+} and $4p$ Br^- orbitals, the bottom of the conduction band is formed by $6p$ Pb^{2+} orbitals [16–18]. The $PbBr_2$ long-wavelength exciton band in the model of cationic exciton is genetically associated with the transition $6s \rightarrow 6p$ in lead ion [16–18]. The cationic character of the exciton excitations is typical not only for binary lead compounds [16–18], but also for the triple [10–12] ones. Apparently, in $KPb_2Br_5(II)$, as well as in $PbBr_2$, the excitons have cationic character, as indicated by the closeness of their spectra, as well as near the position of the long-wavelength exciton bands in the Pb^{2+} impurity band in KBr [19]. The exciton excitation in this case is located in the compound sublattice containing lead ions. The similarity of the spectra of $KPb_2Br_5(II)$ and $PbBr_2$ is due to the proximity of their crystal lattices [1–3]. In $KPb_2Br_5(II)$, as in $PbBr_2$, each Pb^{2+} ion is surrounded by nine Br^- ions [1–3]. But unlike $PbBr_2$, in $KPb_2Br_5(II)$ ninth ion Br^- is shared by the two neighboring Pb^{2+} ions [1–3], i.e. coordination number is 8.5, in $PbBr_2$ the coordination number is 9. This causes the smaller ionicity of $KPb_2Br_5(II)$ and, respectively, a little bigger long-wavelength absorption edge compared to $PbBr_2$.

The $KPb_2Br_5(I)$(absorption spectrum (Fig. 1) is also similar to the spectra of $PbBr_2$ and $KPb_2Br_5(II)$ (C_1 and C_2 bands in $KPb_2Br_5(I)$, evidently, are not separated and merge into a single wide band C). Accordingly, in the model of cationic exciton the spectrum of $KPb_2Br_5(I)$, as well as $PbBr_2$ and $KPb_2Br_5(II)$ spectra, is treated on the basis of the electronic transitions in Pb^{2+} ion. The absorption edge in $KPb_2Br_5(I)$ is significantly shifted to the longer wavelengths relatively to $KPb_2Br_5(II)$ and $PbBr_2$ (Fig. 1b, Table), indicating the lower ionicity of $KPb_2Br_5(I)$. The $KPb_2Br_5(I)$ tetragonal structure in the

layered image is shown in [2]. The coordination number of Br^- ions in $KPb_2Br_5(I)$ is 7 [1, 2], which causes the lowest ionicity of the compound and thus the biggest long-wavelength absorption edge in a line of compounds $PbBr_2$, $KPb_2Br_5(II)$, $KPb_2Br_5(I)$.

3.2. Temperature dependence of parameters of the long-wavelength exciton bands in KPb_2Br_5

As noted above, with the temperature increase the long-wavelength exciton A^I band in $KPb_2Br_5(I)$ shifts linearly to the longer wavelengths with $dE_m/dT = -(1.87\pm0.04)\cdot10^{-4}$ eV/K (Fig. 3a) in the temperature range of 90–282 K. Then, in a narrow temperature range of 282–293 K, the short-wavelength shift of the band spectral position occurs, indicating the first-order phase transition. Above it was shown that this is the irreversible phase transition to the monoclinic $KPb_2Br_5(II)$ structure. And then in the entire temperature range of 90–440 K A^{II} band, as the temperature increases, shifts linearly to the longer wavelengths with $dE_m/dT = -(2.44\pm0.03)\cdot10^{-4}$ eV/K. At the higher temperatures, the light scattering occurs in the film, which made not possible to verify the presence of the high-temperature phase transition at 519.5 K in $KPb_2Br_5(II)$, as was reported in [8, 9]. The temperature coefficients of the shift of the exciton bands in $KPb_2Br_5(I)$ and $KPb_2Br_5(II)$ are typical for the ionic crystals, which include test compounds.

Interaction of the excitons with longitudinal optical (LO) phonons dominates in the ionic crystals and the greatest temperature changes of parameters of the exciton bands occur at $\hbar\omega_{LO} \leq kT$. With the temperature increase, the half-width of A^I band grows nonlinearly in the range 90–282 K (Fig. 3b). In the narrow temperature range of 282–293 K a half-width of the exciton band abruptly decreases, which confirms the first-order phase transition in $KPb_2Br_5(II)$ of the monoclinic structure at 293 K. And further down to 440 K the half-width of the exciton A^{II} band increases nonlinearly. The dependence of $\Gamma(T)$, measured while cooling the film in the range of 293–440 K coincides with $\Gamma(T)$, measured during heating. According to [20] the broadening of the exciton band is due to the exciton-phonon interaction $\Gamma(T)$ for various dimensions of excitons d ($d = 1, 2, 3$) is defined as

$$\Gamma(T) \approx \left[\frac{\pi D^2}{\gamma(d/2)(2\pi B)^{d/2}} \right]^{\frac{2}{4-d}}, \qquad (1)$$

where $\gamma(d/2)$ — gamma function depending on d, B — width of the exciton band and $D^2 = 0.5 \cdot C^2 \hbar \omega_{LO} \cdot \mathrm{cth}(\hbar \omega_{LO}/2kT)$, $\hbar \omega_{LO} = 17.35$ meV — energy of LO phonons in KPb_2Br_5 [6], $C^2/2$ — relaxation energy of the lattice at the exciton excitation. It is also necessary to take into account a contribution of the residual broadening of $\Gamma(0)$ due to lattice defects in the general half-width Γ of the exciton band. Form of the exciton A^I band is Gaussian, A^{II} band close to the Gaussian at the low temperatures and is fully Gaussian at the high temperatures. The exciton band general half-width Γ in the case of the Gaussian profile can be represented as

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

where $\Gamma(T)$ obeys Eq. (1) with unknown factor Q, does not depend on T. Processing of the experimental dependences $\Gamma_I(T)$ in the temperature range of 90–282 K and $\Gamma_{II}(T)$ in the range of 90–440 K using Eq. (1) for different d gives the best agreement with the experiment at $d = 2$. In this case

$$\Gamma(T) = Q\,\mathrm{cth}(\hbar \omega_{LO}/2kT) \qquad (3)$$

and dependences $\Gamma_I(T)$ and $\Gamma_{II}(T)$ in the coordinates of Γ^2 from $\mathrm{cth}^2(\hbar \omega_{LO}/2kT)$ are linear. Processing of these dependences by the least-squares method gives the values $\Gamma_I(0) = 0.34\pm0.002$ eV, $\Gamma_{II}(0) = 0.2\pm0.002$ eV and $Q_I = 0.096\pm0.001$ eV, $Q_{II} = 0.0959\pm0.0005$ eV. The calculated temperature dependence of $\Gamma_I(T)$ and $\Gamma_{II}(T)$ from Eqs. (2) and (3) with the found values $\Gamma_{I,II}(0)$ and $Q_{I,II}$ well agrees with the experiment (Fig. 3b). Analysis of the temperature dependences $\Gamma_I(T)$ and $\Gamma_{II}(T)$ indicates two-dimensional nature of the excitons in the both modifications of KPb_2Br_5, with consistent the layered structure of tetragonal (I) and monoclinic (II) crystal lattices of the compound [1–3].

4. Conclusions

We investigated the absorption spectra of KPb_2Br_5 thin films of tetragonal (I) and monoclinic (II) modifications in spectral re-

gion of 2–6 eV. The irreversible first-order phase transition of the KPb_2Br_5(I) tetragonal structure in the monoclinic structure KPb_2Br_5(II) was found from the analysis of temperature dependence of spectral position $E_m(T)$ and half-width $\Gamma(T)$ of the long-wavelength exciton band at $T = 293$ K.

The absorption spectrum of KPb_2Br_5(I,II) thin film is close to $PbBr_2$ spectrum in the structure of the spectrum and the position of the exciton bands, which is due to similarity of the crystal structures of the compounds. Excitons in KPb_2Br_5(I,II) are located in sublattice containing Pb^{2+} ions and have cationic character. In the model of cationic exciton the spectrum KPb_2Br_5(I,II), as well as the spectrum $PbBr_2$, are defined by the transitions in ion Pb^{2+}. The long-wavelength shift of the absorption edge in the line of compounds $PbBr_2$, KPb_2Br_5(II), KPb_2Br_5(I) is due to decrease of the compounds ionicity.

The temperature dependence of the spectral position $E_{mI,II}(T)$ and half-width $\Gamma_{I,II}(T)$ in KPb_2Br_5(I,II) is determined by the exciton-phonon interaction. The analysis of the temperature dependences $\Gamma_{I,II}(T)$ indicates the two-dimensional 2D nature of the exciton excitations in KPb_2Br_5(I,II).

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