Exciton absorption spectrum of thin $(KI)_{1-x}(PbI_2)_x$ films

O.N.Yunakova, V.K.Miloslavskii, E.N.Kovalenko[*]

V.Karazin Kharkiv National University, 4 Svobody Sq.,
61022 Kharkiv, Ukraine
[*]Kharkiv National University of Radioelectronics, 14 Lenin Ave.,
61166 Kharkiv, Ukraine

The absorption spectra of thin films of $(KI)_{1-x}(PbI_2)_x$ $0.1{\leq}x{\leq}0.5$ were investigated in the spectral interval 2–6 eV. The formation of two compounds $KPbI_3$ and K_4PbI_6 in system $KI–PbI_2$ was determined on the basis of the spectra analysis. It was shown, that exciton excitations in the investigated compounds are localized in sublattice containing lead ions and related to excitons of the intermediate bond.

Исследованы спектры поглощения тонких пленок $(KI)_{1-x}(PbI_2)_x$ $0,1{\leq}x{\leq}0,5$ в спектральном интервале 2–6 эВ. Из анализа спектров установлено образование в системе $KI–PbI_2$ двух соединений — $KPbI_3$ и K_4PbI_6. Показано, что экситонные возбуждения в исследуемых соединениях локализованы в подрешетке, содержащей ионы свинца, и относятся к экситонам промежуточной связи.

1. Introduction

A diagram of $KI–PbI_2$ system condition was investigated by various methods [1–4] — visually-polythermal [1], X-ray phase analysis [2, 3] and the differential-thermal analysis [3, 4]. According to [1, 2] in $KI–PbI_2$ system the compound $KPbI_3F255$ is formed [1], but according to [3, 4] — the compound K_2PbI_4. The authors of the works [1–4] report about the formation of the one compound in the system $KI–PbI_2$ though there are disagreements as for it molecular structures. However researches of spectra of a luminescence of monocrystals $KI{:}Pb^{2+}$ [5] testify to formation of two ternary compounds with various spectra in $KI–PbI_2$ system, the authors attribute these spectra to $KPbI_3$ and K_2PbI_4 compounds.

In similar systems $MI–PbI_2$ (M=Cs, Rb) according to thermographic researches [4] two compounds $MPbI_3$ and M_4PbI_6 are formed, that proves to be true by the analysis of absorption spectra of thin films of the

compounds [6–8]. The spectrum of reflexion of monocrystals $KPbI_3$ [9] in the field of the long-wavelength exciton band is similar to the spectra of monocrystals $CsPbI_3$ and $RbPbI_3$ [9]. However in the work [9] measurements were accomplished in a narrow spectral interval 2.9–3.2 eV, which has not included the absorption edge of initial components KI and PbI_2, that is why it cannot be made the conclusion about the phase structure of the monocrystals on the basis of the spectra analysis.

Use of thin films allows to measure an absorption spectrum in a wide spectral interval. In the present work $(KI)_{1-x}(PbI_2)_x$ films of various molar structure were synthesized for the purpose of identification of the ternary compounds formed in this system and research of their spectra of absorption.

2. Experimental

Thin films $(KI)_{1-x}(PbI_2)_x$ $0.1{\leq}x{\leq}0.5$ were prepared by evaporation of mixture melt of pure powders KI and PbI_2 with a specified

molar composition on heated quartz substrates. The substrate temperature varied from 60 to 130°C. Such method was applied earlier for formation of thin films of $MPbI_3$ and M_4PbI_6, (M=Cs, Rb) compounds [7, 8].

In the range of concentrations $0.1 \leq x \leq 0.5$ absorption spectra of the obtained thin films $(KI)_{1-x}(PbI_2)_x$ are similar and coincide in the spectral position of exciton bands. At $T = 90$ K in the spectra 10 bands of absorption are observed, the most long-wave band A^1 is located at 3.027 eV. Presence of a great number of the bands testifies to the biphasic state of the films. The impurity of initial component in films is absent, that is easily supervised on absorption spectra: long wavelength exciton bands in PbI_2 are located at 2.5 eV, in KI — at 5.8 eV. Biphasic films turned out as well in systems CsI–PbI_2 [7] and RbI–PbI_2 [8] at evaporation of melt mixes of initial component on the quartz substrate, which temperature is $T_s < 100°$C. However the subsequent high-temperature annealing of films ($T_{an} > 100°$C in $(CsI)_{1-x}(PbI_2)_x$ [7] and $T_{an} > 300°$C in $(RbI)_{1-x}(PbI_2)_x$ [8]) transformed them in monophase with a spectrum corresponding M_4PbI_6. High-temperature annealing of the films $(KI)_{1-x}(PbI_2)_x$ does not result in their spectrum changing, but it should be mentioned that the temperature of annealing did not exceed 195°C, because at more heating the light scattering appears in the films.

The absorption spectra were measured with in the spectral range of 2–6 eV. Spectra of absorption of thin films were measured by the spectrophotometer CF-46 in the spectral range 2–6 eV. For the measurements the films with thickness in the framework of 100–140 were used.

Parameters of the long wavelength bands (position E_m, the half width Γ and and the imaginary part of permittivity in the maximum $\varepsilon_{2m} = \varepsilon_2(E_m)$) were determined accord-

ing to the technique described in [10], using an approximation of the exciton band 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.

3. Results and discussion

As already it was marked above, in the spectra of thin films $(KI)_{1-x}(PbI_2)_x$ ($0.1 \leq x \leq 0.5$) 10 absorption bands had been observed. The spectral positions of the bands are presented in Table. With an increase of temperature, the bands moved in long-wave area of the spectrum, broadened and decayed because of the exciton-phonon interaction (EPI) that points to their exciton origin.

Though X-ray researches of salts alloys KI and PbI_2 were fulfilled by several authors [2, 3], but they do not made conclusions as for the structure of crystal lattice of $KPbI_3$. From comparison of X-ray patterns of $KPbI_3$ and $CsPbI_3$ [2] it is possible to make a conclusion that they are isostructural: the most reflections are overlapped. However in the X-ray patterns of KI–PbI_2 [2] there are the additional reflexes which are absent in CsI–PbI_2, and, probably, connected with formation of other compounds at alloy KI–PbI_2. In a case isostructural compounds $KPbI_3$ and $CsPbI_3$, a structural element of crystal lattice $KPbI_3$, as well as $CsPbI_3$ [11], are octahedrons $(PbI_6)^4$ and in the analysis of spectra of absorption of both compounds it is necessary consider the electronic transitions in $(PbI_6)^4$ [6, 7].

Let's compare the investigated spectra $(KI)_{0.5}(PbI_2)_{0.5}$ (Fig. 1) with the spectra studied before for compounds $CsPbI_3$, $RbPbI_3$

Table. Spectral position of absorption bands, exciton binding energy R_{ex} and width of the band gap E_g in investigated compounds

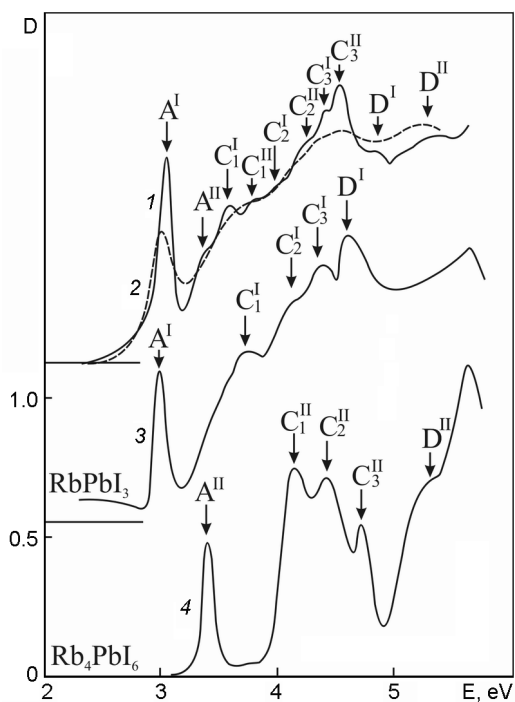| Compound	E_{A1}, eV	E_{A2}, eV	E_{C1}, eV	E_{C2}, eV	E_{C3}, eV	E_D, eV	R_{ex}, eV	E_g, eV
$CsPbI_3$ [9]	3.013	3.131	3.69	4.22	4.4	4.461	0.157	3.17
$RbPbI_3$	2.975	3.1	3.73	4.105	4.4	4.63	0.167	3.142
$KPbI_3$	3.027		3.58	3.97	4.4	4.84	0.143	3.17
Cs_4PbI_6 [9]	3.41	3.522	4.19	4.36	4.73	5.2	0.149	3.56
Rb_4PbI_6	3.41	3.512	4.1	4.43	4.73	5.28	0.133	3.543
K_4PbI_6	3.388		3.8	4.24	4.56	5.39		
$RbI:PbI_2$ [11]	3.543			4.5		4.87		

Fig. 1. Spectra of absorption of thin films $(KI)_{0.5}(PbI_2)_{0.5}$ (1 — $T = 90$ K, 2 — 290 K), $RbPbI_3$ (3 — $T = 90$ K) and Rb_4PbI_6 (4 — $T = 90$ K).

and Cs_4PbI_6, Rb_4PbI_6 [6–8]. Spectral positions of exciton bands for these compounds are resulted in Table. In the spectra of absorption $MPbI_3$ (M=Cs, Rb) it was observed 5 intensive $1s$ exciton bands A, C_1, C_2, C_3 and D corresponding to transitions in an octahedron $(PbI_6)^4$ (see the Table). The similar group of bands was observed in the spectra of M_4PbI_6, but shifted on 0.4 eV in short-wave area of the spectrum [7, 8]. The spectra of $MPbI_3$ and M_4PbI_6 are similar in structure to the impurity spectra of $CsI{:}Pb^{2+}$ ($RbI{:}Pb^{2+}$) [12, 13] and the spectra can be explained as well as the spectra of $MI{:}Pb^{2+}$ on the basis of electronic transitions in the complex $(PbI_6)^4$ [7, 8].

In the spectrum of $(KI)_{0.5}(PbI_2)_{0.5}$ the most intensive exciton A^I band at 3.027 eV is similar to A-bands in $CsPbI_3$ (3.013 eV) and $RbPbI_3$ (2.975 eV) as for the spectral position and it belongs, apparently, to compound $KPbI_3$. The affinity of spectral positions of long-wave exciton bands in compounds $MPbI_3$ (M=K, Rb, Cs) specifies the localization of exciton excitations in PbI_2 compounds sublattice. Next A^{II} band at 3.388 eV is shifted in short-wave area of the spectrum on 0.36 eV. As already it was marked above, similar short-wavelength shift of edge of absorption was observed in
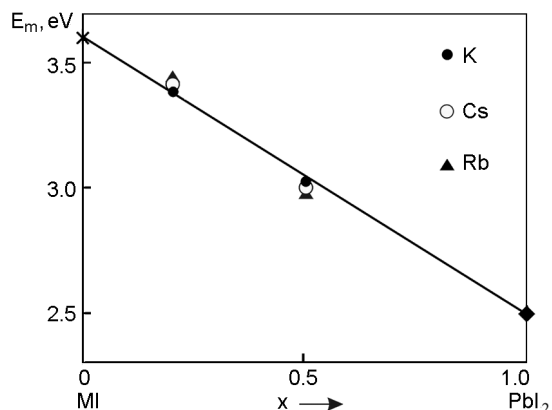
compounds M_4PbI_6 (M=Cs, Rb) in relation to $MPbI_3$ [7, 8]. Apparently, A^{II} band corresponds to compound K_4PbI_6. Hence in the spectrum of $(KI)_{0.5}(PbI_2)_{0.5}$ we observed two groups of bands: 5 exciton bands corresponding to $KPbI_3$ (I) and 5 bands, corresponding to K_4PbI_6 (II). Linear concentration dependence of spectral position of long-wave exciton bands in a sequence of compounds PbI_2, $KPbI_3$ and K_4PbI_6 (Fig. 2) testifies to a formation of compounds $KPbI_3$ and K_4PbI_6 in the system $(KI)_{1-x}(PbI_2)_x$. Long wave exciton bands in the sequence of compounds are shifted to high-energy according to the law

$$E_A(x) = E_1 x + E_2(1 - x), \qquad (1)$$

where x is molar concentration of PbI_2 in the compounds, E_1 is the position of the long wavelength exciton band in PbI_2. Extrapolation of the dependence (1) to $x \to 0$ gives value $E_2 = 3.599$ eV, a value much smaller than the spectral position of the exciton band in KI (5.8 eV) but similar to the position of Pb^{2+} impurity bands in KI at 3.56 eV [14]. The linear dependence (1) and its convergence with the spectral position of Pb^{2+} impurity bands in KI according to [15], indicate to excitation and localization of excitons in the cationic sublattice of ternary compounds containing lead ions.

In $KPbI_3$ we have estimated width of the band gap in inflection point of edge after splitting of the band A^I by a symmetric profile, $E_g = 3.17$ eV and accordingly the exciton binding energy $R_{ex} = E_g - E_{AI} = 0.143$ eV. It is difficult to perform the similar estimations for compound K_4PbI_6

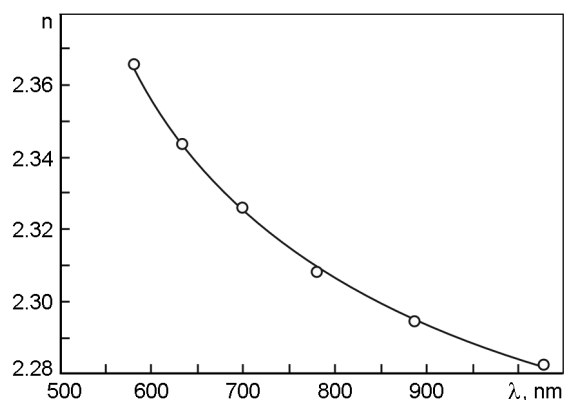Fig. 2. Concentration dependence of spectral position E_m for the compounds PbI_2, $MPbI_3$, M_4PbI_6 (M = K, Cs, Rb).

Fig. 3. Spectral dependence of the refraction index $n(\lambda)$ for KPbI$_3$ thin films: points — experiment, solid curve — calculation by Eq.(2).

using a spectrum of the mixed film because of overlapping of A^{II} band with band-to-band absorption and with an edge of band C_1^{I} in KPbI$_3$.

A dispersion of the refraction index $n(\lambda)$ has been defined for films (KI)$_{0.5}$(PbI$_2$)$_{0.5}$ by the interference method [16]. As we can see from an absorption spectrum (Fig. 1), KPbI$_3$ phase dominates in films (KI)$_{0.5}$(PbI$_2$)$_{0.5}$ because A^{I} bands oscillator strength f_{AI}, which inherent to KPbI$_3$, is essential bigger than f_{AII} of K$_4$PbI$_6$ A^{II} bands : $f_{AII}/f_{AI} \approx 0.16$. So we attribute the received dependence $n(\lambda)$ (Fig. 3) to compound KPbI$_3$. The index $n(\lambda)$ is well described by a Wemple single-oscillator model [17]:

$$\varepsilon_1 = n^2 = 1 + \frac{E_d E_0}{E_0^2 - E^2}, \qquad (2)$$

where $E = \hbar\omega$, E_0 and E_d are parametres of single-oscillator models. E_0 defines spectral position of the effective oscillator, connected with band-to-band optical transitions, value $E_0 > E_g$ [17], E_d is the dispersive energy, characterizing the force of band-to-band transitions.

Processing of the experimental data of $n(\lambda)$ in coordinates $(n^2 - 1)^{-1}$ from E_2 by the least-squares method gives values $(E_0 E_d)^{-1} = 0.0064 \pm 0.0002$ and $E_0/E_d = 0.247 \pm 0.0015$ and accordingly $E_0 = 6.226$ eV and $E_d = 25.208$ eV. A calculation of the dependence $n(\lambda)$ with received values E_0 and E_d (Fig. 3, a solid curve) yields good agreement with experimental dependence $n(\lambda)$ (Fig. 3, points).

Dependence approximation of $n(\lambda)$ on (2) to a low-energy limit gives a value of the an optical dielectric constant $\varepsilon_\infty = 1 + E_d/E_0 = 5.05$

which we used for an exciton radius estimation in KPbI$_3$:

$$a_{ex} = a_B \frac{R}{R_{ex}\varepsilon_{eff}}, \qquad (3)$$

where $a_B = 0.529 \cdot 10^{-8}$ cm is Bohr radius, $R = 13.6$ eV is Rydberg constant, ε_{eff} is effective permittivity, $R_{ex} = 0.143$ eV is the value of exciton binding energy, defined above, $\varepsilon_\infty < \varepsilon_{eff} < \varepsilon_0$ is static permittivity. For the exciton radius estimation we took the lowest limit of ε_{eff} because in the field of low-frequency exciton bands the basic contribution in ε_{eff} value is defined by the value ε_∞. The resulting value of the exciton radius $a_{ex} = 9.96$ Å indicates KPbI$_3$ intermediate coupling exciton excitation.

4. Conclusions

From the analysis of the spectra of absorption of thin films (KI)$_{1-x}$(PbI$_2$)$_x$ $0.1 \leq x \leq 0.5$ and their comparisons with the spectra of studied before compounds MPbI$_3$ and M$_4$PbI$_6$ (M = Cs, Rb) we have revealed a formation of two compounds KPbI$_3$ and K$_4$PbI$_6$ in the system KI–PbI$_2$. Formation of the compounds with such molar composition is confirmed by the linear concentration dependence of spectral position of long-wave exciton bands on concentration PbI$_2$ in the line of compounds PbI$_2$, KPbI$_3$ and K$_4$PbI$_6$. The convergence of this dependence at $x \to 0$ to the position Pb^{2+} impurity bands in KI testifies to localization of exciton excitations in the cationic sublattice of compounds KPbI$_3$ and K$_4$PbI$_6$ containing lead ions. Similar position of long-wave exciton bands in compounds MPbI$_3$ and M$_4$PbI$_6$ (M = Cs, Rb, K) also pointed to such localization.

Width of the band gap, the exciton binding energy and its radius in KPbI$_3$ have been estimated. It was shown, that exciton excitation in this compound belonged to the intermediate bond exciton.

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Екситонний спектр поглинання тонких плівок $(KI)_{1-x}(PbI_2)_x$

О.М.Юнакова, В.К.Милославський, О.М.Коваленко

Досліджено спектри поглинання тонких плівок $(KI)_{1-x}(PbI_2)_x$ $0{,}1{\leq}x{\leq}0{,}5$ у спектральному інтервалі 2–6 еВ. З аналізу спектрів встановлено утворення у системі KI–PbI_2 двох сполук — $KPbI_3$ та K_4PbI_6. Показано, що екситонні збудження у досліджуваних сполуках локалізовані у підгратці, у якій містяться іони плюмбуму, і відносяться до екситонів проміжного зв'язку.