EXCITON ABSORPTION SPECTRUM OF KPb_2Br_5THIN FILMS

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The KPb_2Br_5 compound exists in two modifications – tetragonal (I) (space group *I4/mcm*, a = 8.14 Å, c = 14.10 Å, z = 4) and monoclinic (II), (space group $P2_1/c$, lattice parameters are a = 9.264 Å, b = 8.380 Å, c = 13.063 Å, γ = 90.06°, z = 4). [1, 2]

KPb_2Br_5 thin films were prepared by evaporation in vacuum of a melt mixture of pure KBr and $PbBr_2$ powders of stoichiometric molar composition on cold quartz substrates T_s = 278K. The films, prodused by this method, correspond to KPb_2Br_5 (I). The phase composition of the films was monitored from the absorption spectra measured at T = 90K. Such control is possible due to the difference in the 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 absorption spectrum of the KPb_2Br_5 (I) thin film (Fig.1a) contains a long-wavelength A^I band and a wide C^I band (the spectral positions of the bands are given in Table 1).

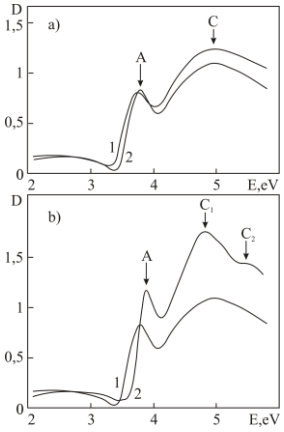

Fig. 1. Absorption spectra of a thin film of KPb_2Br_5 a) tetragonal structure (I) at T = 282K (1) and 90K (2) and b) monoclinic (II) (2) and tetragonal (I) (1) structures at T = 90K.

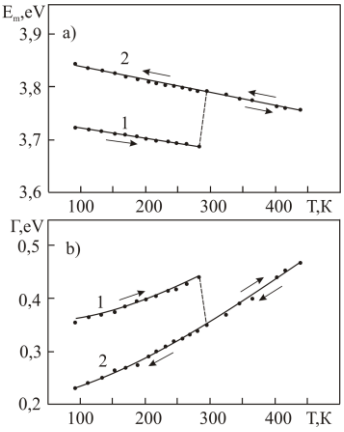

Fig. 2. Temperature dependence of the spectral position E_m(T) (a) and half-width Γ(T) (b) of the long-wavelength exciton band A in the KPb_2Br_5 thin film.

The A^I band with increasing temperature shifts linearly to the long-wavelength region of the spectrum with $dE_m/dT = - = -(1{,}87\pm0{,}04)\cdot10^{-4}$ eV/K (Fig. 2) in the temperature range 90-282 K. At T_c = 293K there are short-wavelength shift of the long-wavelength exciton A^I band, which indicates an increase of the unit cell volume, narrowing and sharpening of the band. A jump in the temperature dependences of the spectral position and half-width of the long-wavelength exciton band A at Tc = 293K indicates a first-order phase transition. This transition is irreversible. Cooling of the film down to a temperature 90 K does not restore the spectrum (Fig. 1b). Apparently, upon evaporation of the melt mixture on a cold substrate, the tetragonal compound KPb_2Br_5 (I) crystallizes. When the film is heated to $T \geq T_c$, a phase transition occurs to the monoclinic structure of KPb_2Br_5 (II).

The structure of the absorption spectra of KPb_2Br_5 thin films (I, II) is similar to the $PbBr_2$ spectrum and close in the position of the exciton bands, which is due to the similarity of the crystal structures of the compounds. Apparently, in thin films of KPb_2Br_5 (I, II), as in $PbBr_2$, excitons have a cationic character, which is indicated by the similarity of their spectra in structure and the close spectral position of the absorption bands. And also the close position of the long-wavelength exciton bands to the Pb_2^+ impurity band in KBr. In this case, exciton excitations are localized in the compound sublattice containing lead ions

Table 1: Spectral position of exciton bands E_m, band gap Eg, and exciton binding energy R_{ex} in KPb_2Br_5 (I, II) and $PbBr_2$.

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
$PbBr_2$	3.98	4.86	5.69	4.23	0.25

In the cationic exciton model, the KPb_2Br_5 (I, II) spectrum, like the $PbBr_2$ spectrum, is determined by transitions in the Pb_2^+ ion. The long-wavelength shift of the absorption edge in the series of compounds $PbBr_2$, KPb_2Br_5(II), KPb_2Br_5(I) is due to a decrease in the ionicity of the compounds due to a decrease in the number of Br^- ions surrounded by the Pb^+ ion. In $PbBr_2$, the coordination number of Br^- ions is 9, in KPb_2Br_5 (II) is 8.5, in KPb_2Br_5 (I) is 7.

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

REFERENCES

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