

Absorption spectra peculiarities of thin films of $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ system

O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko *

V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine

*Kharkiv National University for Radioelectronics,
14 Lenin Ave., 61166 Kharkiv, Ukraine

Received January 27, 2004

Absorption spectrum of $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ thin films has been investigated in the fundamental band region. The $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions have been found to be formed within the concentration ranges $0 \leq x \leq 0.08$ and $0.34 \leq x \leq 1$. In the $0.1 \leq x \leq 0.6$ range, there is a mixture of two phases in the thin films, namely, of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions and $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$. The latter phase appears as a result of a strong disordering of the CsCu_2Cl_3 anionic sublattice as Cl^- ions are substituted by I^- ones having a larger radius. A new absorption band corresponds to that phase in the absorption spectrum peaked at 4.8 eV; it is associated with the excitation of quasi-impurity Cu^+ ions in the cationic sublattice of the compound in the vicinity of I^- ions. The concentration dependences of the exciton band position $E_{ex}(x)$ and half-width $GAAM(x)$ are typical of solid solutions and confirm the formation thereof in the mentioned concentration ranges.

Исследован спектр поглощения тонких пленок $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ в районе фундаментальной полосы. Установлено, что твердые растворы $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ образуются в интервале концентраций $0 \leq x \leq 0,08$ и $0,34 \leq x \leq 1$. В интервале $0,1 \leq x \leq 0,6$ в тонких пленках имеет место смесь двух фаз: твердых растворов $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ и $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$. Фаза $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$ возникает в результате сильного разупорядочения анионной подрешетки CsCu_2Cl_3 при замещении ионов Cl^- ионами большего радиуса I^- , ей соответствует в спектре новая полоса поглощения при 4,8 эВ, связанная с возбуждением квазипримесных ионов Cu^+ в катионной подрешетке соединения в окрестности ионов I^- . Концентрационные зависимости положения $E_{ex}(x)$ и полуширины $\Gamma(x)$ экситонных полос типичны для твердых растворов и подтверждают их образование в указанных интервалах концентраций.

In the $\text{CsHal}-\text{CuHal}$ system ($\text{Hal} = \text{Cl}, \text{I}$), complex compounds $\text{CsCu}_2\text{Hal}_3$ and $\text{Cs}_3\text{Cu}_2\text{Hal}_5$ are formed [1]. CsCu_2I_3 and CsCu_2Cl_3 form orthorhombic lattice with 4 molecules per unit cell (the C_{mcm} space group) and lattice parameters $a = 10.3\text{\AA}$, $b = 12.89\text{\AA}$, $c = 6.07\text{\AA}$ (CsCu_2I_3) and $a = 9.5\text{\AA}$, $b = 11.9\text{\AA}$, $c = 5.6\text{\AA}$ (CsCu_2Cl_3) [2]. Absorption spectra of both compounds have been considered in detail in [3, 4]. The low-frequency electron and exciton excitations have been established to belong to the CuHal

sublattices. In CsCu_2I_3 , the exciton spectrum is interpreted basing on the Vanier-Mott exciton model [3], while in CsCu_2Cl_3 , on the Frenkel one [4].

The close values of lattice parameters for CsCu_2I_3 and CsCu_2Cl_3 must favor the formation of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions. According to [5], complex compounds $\text{CsCu}_2\text{ClI}_2$ (I) and $\text{CsCu}_2\text{Cl}_2\text{I}$ (II) are formed in the $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ system. The I has orthorhombic structure with lattice parameters $a = 10.04\text{\AA}$, $b = 13.05\text{\AA}$, $c = 5.92\text{\AA}$ while II, a monoclinic one presented by [5]

as a distorted orthorhombic lattice. It is of interest to study the effect of composition fluctuations in the anionic sublattice on the absorption spectrum of $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_{3x}$ complex compounds. In this work, the absorption spectra of $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ thin films were investigated within the concentration range $0 \leq x \leq 1$.

The thin films $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ were prepared by vacuum evaporation of pure CsCl, CsI, CuI, CuCl powder mixtures of the pre-specified molar composition onto quartz substrates heated up to 100°C . The mixture was melted previously in a boat under a screen. The evaporation rate was low ($v \approx 6 \text{ \AA/s}$). When prepared in that manner, the film answers in the composition to the pre-specified stoichiometry of the mixture, since the complex compound has the melting point considerably lower than those of the initial binary compounds [6]. The film phase composition was controlled by absorption spectra and using electron diffraction patterns. The optical examination of the phase composition is possible due to significant differences in the long-wave exciton band positions that are at 7.8 eV (CsCl), 5.8 eV (CsI), 3.06 eV (CuI) and 3.23 eV (CuCl) while being within the range of 3.9 to 4.3 eV for $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_{3x}$ complex compounds. The absorption spectra were measured using an SF-46 spectrophotometer in the 3 to 6 eV range at $T = 90 \text{ K}$. The film thickness was measured by Tolansky method. The exciton band parameters (the position E_m , half-width Γ and ϵ_{2m}) were determined as in [7]. The long-wave exciton bands were approximated by a symmetrical two-oscillator contour being a combination of Lorentzian and Gaussian ones. E_m , Γ , and ϵ_{2m} values were selected so that the calculated and experimental contours were fit together in the best manner at the long-wave band slope.

A small CsCu_2I_3 impurity in CsCu_2Cl_3 does not result in any appreciable change in the absorption spectrum of the latter (Fig. 1). In the $0 \leq x \leq 0.08$ range, the absorption spectrum of $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_{3x}$ thin films is identical to that of CsCu_2Cl_3 [4]: intense A_0 , A_1 , and B bands are observed at the absorption edge at 4.67; 4.46; and 4.65 eV, respectively, as well as a weak C band at 5.0 eV. A further increase of the impurity content results in a substantial change in the spectrum. As early as at $x = 0.1$, a high-intensity Q band appears at 4.8 eV while the exciton A band retained at the absorption

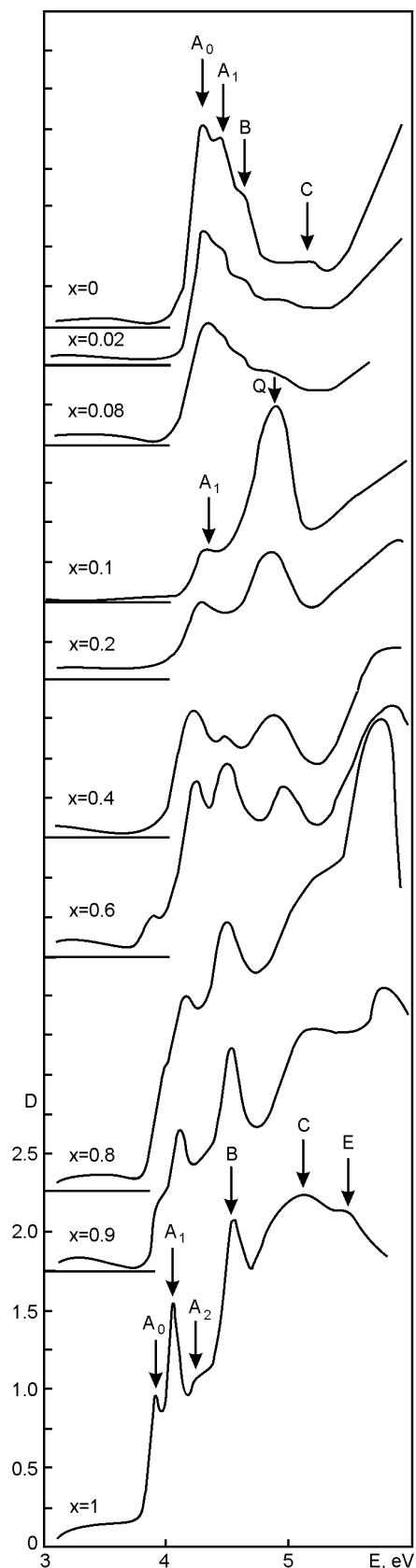


Fig. 1. Absorption spectra of $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_{3x}$ thin films.

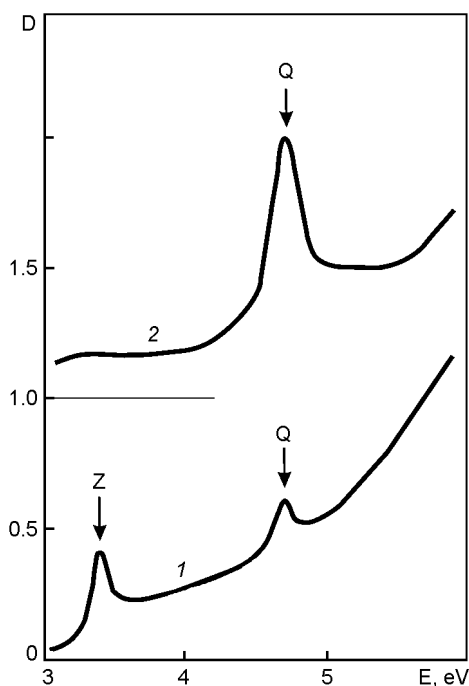


Fig. 2. Absorption spectra of $\text{CuCl}_{1-x}\text{I}_x$ thin films. $x = 0.2$ (1), $x = 0.3$ (2).

edge becomes strongly weakened. The further increase in CsCu_2I_3 content results in weakening of the Q band and increased intensity of long-wave exciton bands. The Q band is observed up to $x = 0.6$.

In the $0.6 \leq x \leq 1$ range, the absorption spectrum of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ thin films is identical to that of CsCu_2I_3 [3]: intense A_0 and A_1 exciton bands are observed at the absorption edge, while B and C bands, in contrast to CsCu_2Cl_3 , are superposed on the interband absorption background.

It has been shown [3, 4] that the low-frequency exciton and electron excitations in $\text{CsCu}_2\text{Hal}_3$ ($\text{Hal} = \text{Cl}, \text{I}$) are localized in the CuHal sublattice of the compounds. In this connection, it is reasonable to compare the absorption spectra of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ thin films with those of solid solutions of CuCl and CuI binary compounds. It has been found that no solid solutions are formed in the CuCl-CuI system: a small CuI admixture to CuCl results in an appreciable weakening of the long-wave exciton absorption bands (Z band) (Fig. 2) and appearance of an additional absorption band at 4.8 eV (Q band). As the CuI concentration rises, the exciton band become disappeared and only the interband absorption background remains in the exciton absorption region; at the same time, the Q band intensity increases sharply. Such absorption spectrum is observed up to

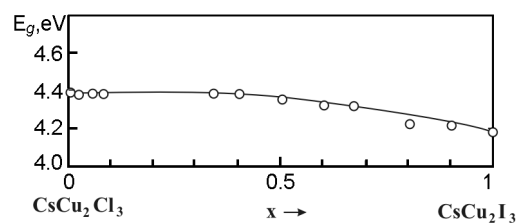


Fig. 3. Concentration dependence of band gap width $E_g(x)$.

$x = 0.5$. The Q band is close to the extrinsic Cu^+ ones in alkali halide crystals (NaCl:Cu^+ , 4.81 eV; KCl:Cu^+ , 4.75 eV; RbCl:Cu^+ , 4.69 eV [8]). The Cl^- ionic radius, $r_i = 26$ pm, is almost a half of the I^- $r_i = 50$ pm [9]. Substitution I^- for Cl^- seems to cause a such strong disordering of the CuCl near to the I^- ion that only the band associated with Cu^+ ion excitation remains in the absorption spectrum. A similar case seems to be also in the $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ thin films at $x \geq 0.1$: substitution I^- for Cl^- in the structure elements of CuCl_4 lattice causes a strong distortion of the tetrahedrons resulting in a considerable weakening of the exciton bands and appearance of an intense Q band at 4.8 eV associated with excitation of Cu^+ ions. The absence of the Q band at low x values in CuCl and $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ is likely associated with its superposition on the continuous interband absorption spectrum, thus causing its broadening and weakening. The Q band attains its highest intensity at $x = 0.1$ and becomes weakened at a further increase of x . This can be explained as follows. At $x = 0.1$, we observe likely the absorption spectrum of $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$. As x increases in the $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ system, partial formation of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions occurs while the $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$ phase is retained, what is evidenced by the Q band in the spectrum. Due to the solid solution formation, the intensity of extrinsic Q band decreases while that of long-wave exciton bands increases.

In the concentration range $0.6 < x \leq 1$, the absorption spectrum of the films under study is similar to that of CsCu_2I_3 ones [3] and answers to the $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions. The solid solution formation in that concentration range is favored by a considerably smaller Cl^- ionic radius as compared to I^- and larger Cu-I distances in CsCu_2I_3 ($d_{\text{Cu-I}} \approx 260; 269$ pm) as compared to those in CsCu_2Cl_3 ($d_{\text{Cu-Cl}} \approx 229; 249$ pm [2]). The substitution Cl^- for I^- does not cause such a strong disordering of the CuHal sublattice.

Thus, it follows from the consideration of absorption spectra that $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_3x$ solid solutions are formed within the concentration ranges $0 \leq x \leq 0.08$ and $0.6 < x \leq 1$. In the $0.1 \leq x \leq 0.6$ range, there is a mixture of two phases in the thin films, namely, of $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_3x$ solid solutions and $\text{CsCu}_2\text{Cl}_3\text{:Cu}^+$ (CsCu_2Cl_3 with strongly disordered anionic sublattice due to substitution of Cl^- ions by I^- ones having a larger radius). This conclusion is confirmed also by concentration dependences of the exciton band parameters.

The concentration shift of the long-wave exciton bands A_0 and A_1 towards low energy observed at increasing x evidences a narrowing band gap E_g as I^- substitutes for Cl^- in the anionic sublattice of the compounds. In the $0.8 \leq x \leq 1$ range, a shoulder A_2 is observed on the long-wave edge of the B band after discrimination of A_0 and A_1 bands. This shoulder is ascribed to the excitation of $2s$ exciton. In that concentration range, the E_g^1 value was determined from the positions of A_1 and A_2 bands [3]. In the $0.34 \leq x < 0.8$ range, the E_g^1 value was determined from the position of the edge inflexion point after discrimination of A_0 and A_1 bands, while in the $0 \leq x \leq 0.08$ range, from the position of the edge inflexion point after discrimination of A_0 , A_1 , and B bands. When determining the band gap E_g , the distance between the lower and upper subbands, $\Delta E = E_{A1} - E_{A0}$, was taken into account in the $0.34 \leq x \leq 1$ range and $\Delta E = E_B - E_{A0}$, in the $0 \leq x \leq 0.08$ one. Thus, $E_g = E_g^1 - \Delta E$.

In $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_3x$, E_g decreases from 4.39 eV ($x = 0$) to 4.18 eV ($x = 1$) (Fig. 3). Within $0 \leq x \leq 0.4$, E_g remains constant to within the experimental error. It follows from the absorption spectra, the CsCu_2Cl_3 spectrum is observed up to $x = 0.08$ while mainly the $\text{CsCu}_2\text{Cl}_3\text{:Cu}^+$ one with a small admixture of $\text{CsCu}_2\text{Cl}_3\text{-}3x\text{I}_3x$ solid solutions, at $0.1 \leq x \leq 0.4$. This seems to cause E_g values close to 4.39 in CsCu_2Cl_3 . In the $0.4 \leq x \leq 1$ range, E_g decreases linearly as

$$E_g(x) = E_g(0) - a(x - 0.4), \quad (1)$$

where $E_g(0) = 4.39$ eV, $a = 0.35$ eV.

As is mentioned above, the solid solutions are formed in the concentration ranges $0 \leq x \leq 0.08$ and $0.34 \leq x \leq 1$. In those ranges, as x increases, the A_0 and A_1 exciton bands are shifted linearly towards longer wavelengths (Fig. 4a) according to the law

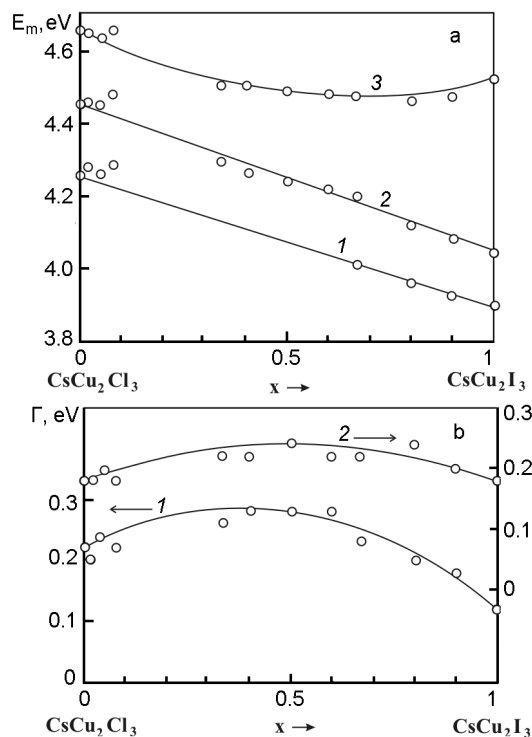


Fig. 4. Concentration dependence of exciton band positions $E_m(x)$ [(a): A_0 (1), A_1 (2), B (3)] and half-width $\Gamma(x)$ [(b): A_1 (1), B (2)].

$$E_{ex}(x) = E_{ex}(0) - ax, \quad (2)$$

where $E_{ex}(0) = 4.265$ and 4.455 eV, $a = 0.36$ and 0.4 eV for the A_0 and A_1 bands, respectively. The concentration dependence of the B band position is bent towards lower energy values, this phenomenon being well known for solid solutions of binary compounds and discussed theoretically more than once. The bend in the $E_{ex}^B(x)$ dependence is due mainly to the small-scale fluctuations of the solid solutions. $E_{ex}^B(x)$ is described well as

$$E_{ex}^B(x) = E_{ex}^B(1)x + E_{ex}^B(0)(1 - x) + bx(1 - x) \quad (3)$$

where $E_{ex}^B(0) = 4.66$ eV, $E_{ex}^B(1) = 4.525$ eV, $b = -0.425$ eV.

The concentration dependences of half-width of the A_1 and B exciton bands (Fig. 4) are typical of solid solutions and are presented well as

$$\Gamma(x) = \Gamma(0)(1 - x) + \Gamma(1)x + \alpha x(1 - x), \quad (4)$$

where $\alpha = \beta(dE_{ex}/dx)$; β is a dimensionless constant ($\alpha = 0.44$ and 0.24 eV for A_1 and B bands, respectively). Thus, the concentration dependence $\Gamma(x)$ is defined mainly by

the concentration shift of the exciton bands, dE_{ex}/dx , thus indicating the large-scale composition fluctuation in the $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions as the main cause of the exciton band broadening.

Thus, the concentration dependences of the position and width of the long-wave exciton bands in $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ are typical of solid solutions and do not confirm the formation of complex compounds $\text{CsCu}_2\text{ClI}_2$ (I) and $\text{CsCu}_2\text{Cl}_2\text{I}$ (II) in the system, as has been predicted in [5].

To conclude, the examination of absorption spectra has shown that the solid solutions $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ are formed in the concentration ranges $0 \leq x \leq 0.08$ and $0.34 \leq x \leq 1$. In the $0.1 \leq x \leq 0.6$ range, there is a mixture of two phases in the thin films, namely, of $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ solid solutions and $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$. The $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$ phase results from a strong disordering of the anionic sublattice due to substitution of Cl^- ions by I^- ones having a larger radius. It is just the new Q band associated with the excitation of Cu^+ ions that answers to that phase. The formation of complex compounds in $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ predicted in [5] is confirmed neither by absorption spectra nor concentration dependences of the exciton band parameters. It is like that the compound (I) in [5] corresponds to the solid solution with $x = 0.66$ while (II), to that

with $x = 0.34$ and a high concentration of $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$ that causes a strong distortion of orthorhombic lattice with its symmetry reduction down to monoclinic one [5]. The concentration dependences of the position of exciton bands $E_{ex}(x)$ are typical of solid solutions and are defined by small-scale composition fluctuations. The concentration dependence of half-width $\Gamma(x)$ is due mainly to the large-scale composition fluctuations.

References

1. E.M.Holt, D.Hamilton, L.Mansker et al., in: Abstr. of 197 th ACS Nat. Meet. (Dallas, Tex., 1989), Washington (1989), p.565.
2. G.Mejer, *Z.Anorg.Allg.Chem.*, **515**, 127 (1984).
3. V.K.Miloslavsky, O.N.Yunakova, E.N.Kovalenko, *Functional Materials*, **4**, 12 (1997).
4. V.K.Miloslavsky, E.N.Kovalenko, O.N.Yunakova, *Optika i Spekr.*, **84**, 940 (1998).
5. S.Geller, J.M.Gaines, *J. Solid State Chem.*, **59**, 116 (1985).
6. J.V.Bradley, P.D.Greene, *Trans.Farad.Soc.*, **63**, 424 (1967).
7. V.K.Miloslavsky, O.N.Yunakova, Sung Tsia-Ling, *Optika i Spekr.*, **78**, 436 (1995).
8. M.Bertolaccini, P.Gagliardelli, G.Padovini, *J. Luminescence*, **14**, 281 (1976).
9. I.T.Goronovsky, Yu.P.Nazarenko, E.F.Nekryach, Brief Chemical Handbook, Naukova Dumka, Kiev (1987) [in Russian].

Особливості спектрів поглинання тонких плівок системи $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$

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

Досліджено спектр поглинання тонких плівок $(\text{CsCu}_2\text{Cl}_3)_{1-x}(\text{CsCu}_2\text{I}_3)_x$ у районі фундаментальної смуги. Встановлено, що тверді розчини $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ утворюються в інтервалі концентрацій $0 \leq x \leq 0,08$ та $0,34 \leq x \leq 1$. В інтервалі $0,1 \leq x \leq 0,6$ у тонких плівках має місце суміш двох фаз: твердих розчинів $\text{CsCu}_2\text{Cl}_{3-3x}\text{I}_{3x}$ і $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$. Фаза $\text{CsCu}_2\text{Cl}_3:\text{Cu}^+$ виникає в результаті сильного розупорядкування аніонної підґратки CsCu_2Cl_3 при заміщенні іонів Cl^- іонами більшого радіуса I^- , їй відповідає в спектрі нова смуга поглинання при 4,8 еВ, пов'язана із збудженням квазідомішкових іонів Cu^+ у катіонній підґратці з'єднання поблизу іонів I^- . Концентраційні залежності положення $E_{ex}(x)$ і напівширини $\Gamma(x)$ екситонних смуг типові для твердих розчинів і підтверджують їхнє утворення у зазначених інтервалах концентрацій.