

Exciton absorption spectrum of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions

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The exciton absorption spectra of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions were studied in the spectral range of 2 to 6 eV. The formation of solid solutions that are isostructural with CsCu_2Cl_3 was found in the concentration range $0 \leq x \leq 0.6$, the formation of solid solutions that are isostructural with RbCu_2Cl_3 was detected in the range $0.6 < x \leq 1$. A linear concentration dependences of the parameters of the exciton bands and the bandgap width were found in the ranges $0 \leq x \leq 0.6$ and $0.6 \leq x \leq 1$. Exciton spectra of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ $0 \leq x \leq 1$ solid solutions were interpreted on the basis of the transitions in the Cu^+ ions.

Keywords: solid solutions, thin films, absorption spectra, excitons.

Спектр поглинання екситонів в тонких плівках твердих розчинів $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$.
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Досліджено екситонні спектри поглинання тонких плівок твердих розчинів $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ області спектра 2 – 6 еВ. Установлено утворення твердих розчинів ізоструктурних CsCu_2Cl_3 в інтервалі концентрацій $0 \leq x \leq 0,6$ та ізоструктурних RbCu_2Cl_3 в інтервалі $0,6 \leq x \leq 1$. Виявлено лінійний концентраційний хід параметрів екситонних смуг та напівширини забороненої зони в інтервалах $0 \leq x \leq 0,6$ та $0,6 \leq x \leq 1$. Екситонні спектри твердих розчинів $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ $0 \leq x \leq 1$ трактуються, виходячи з переходів в іоні Cu^+ .

Исследованы экситонные спектры поглощения тонких пленок твердых растворов $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ в области спектра 2 – 6 эВ. Установлено образование твердых растворов изоструктурных CsCu_2Cl_3 в интервале концентраций $0 \leq x \leq 0,6$ и изоструктурных RbCu_2Cl_3 в интервале $0,6 \leq x \leq 1$. Обнаружена линейная концентрационная зависимость параметров экситонных полос и ширины запрещенной зоны в интервалах $0 \leq x \leq 0,6$ и $0,6 \leq x \leq 1$. Экситонные спектры твердых растворов $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ $0 \leq x \leq 1$ трактуются на основе переходов в ионе Cu^+ .

1. Introduction

Complex compounds with a unique crystal structure [1–3] and a complex optical spectrum in the UV region are formed in the MeHal–CuHal system (Me = K, Rb, Cs; Hal = Cl, Br, I). Many complex compounds with a high copper content have a high

ionic conductivity and belong to the solid electrolytes [1, 2, 4]. Some compounds crystallize into lattices with significantly varying parameters [1, 3]. Low-dimensional excitons are excited in them [5, 6]. Such compounds can be decent luminophores [7] and can be used in light-emitting devices. To date, the crystal structure of many com-

pounds of this system and their conductivity has been well studied. However, their electronic optical spectra and excitons have been less studied.

In this work, we studied the absorption spectra of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions. The absorption spectrum of CsCu_2Cl_3 thin films was studied earlier [8]. The cationic character of excitons in CsCu_2Cl_3 was determined. The absorption spectrum of RbCu_2Cl_3 was analyzed in detail in [9].

Two compounds, CsCu_2Cl_3 and $\text{Cs}_3\text{Cu}_2\text{Cl}_5$, crystallize in the CsCl-CuCl system. The CsCu_2Cl_3 compound is more stable than the other one; its ionic conductivity for Cu is equal to $10^{-4} \Omega^{-1}\cdot\text{cm}^{-1}$ at 500 K [1, 10]. According to the phase diagram, RbCu_2Cl_3 , $\text{Rb}_2\text{Cu}_3\text{Cl}_5$ and Rb_2CuCl_3 compounds are formed in the RbCl-CuCl system [11]. RbCu_2Cl_3 has the highest ionic conductivity of $5\cdot 10^{-3} \Omega^{-1}\cdot\text{cm}^{-1}$ at room temperature [12]. But other authors use other compounds for the highly conductive phase, $\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$ [13] and $\text{Rb}_4\text{Cu}_9\text{Cl}_{13}$ [14], which are close by molar composition to RbCu_2Cl_3 .

Investigation of the absorption spectra of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions will make it possible to establish the degree of disorder in the sublattice of alkali halide compounds and to determine the formula of a compound with a high copper content in the RbCl-CuCl system.

2. Experimental

Thin films $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ were prepared by vacuum evaporating a molten mixture of pure CsCl , RbCl and CuCl powders of a given molar composition and deposition onto quartz substrates heated to 373 K, followed by annealing the films for an hour at a constant temperature. This method was previously used to obtain thin films of CsCu_2Cl_3 [8] and is based on the fact that the melting point of ternary compounds is significantly lower than that of the initial components. The evaporated melt of CsCl , RbCl , and CuCl powders had a stoichiometric composition of the compounds MeCu_2Cl_3 ($\text{Me} = \text{Cs}, \text{Rb}$ ($x_{\text{CuCl}} = 0.66$)).

The quality of the films and their phase composition were monitored using the absorption spectra measured at $T = 90$ K. Such control of the phase composition is possible due to a significant shift in the spectral positions of the long-wavelength exciton bands in solid solutions $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ (4.21–4.35 eV) and in the initial components CuCl

(3.3 eV), CsCl (7.8 eV) and RbCl (7.52 eV). In the studied $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ films, there were no impurities of the initial components and ternary compounds of a different molar composition.

The absorption spectra were measured for films with a thickness of 150–200 nm in the spectral range of 2–6 eV at $T = 90$ K using a SF-46 spectrophotometer. The parameters of the long-wavelength exciton bands A and B (the position E_m , the half-width (FWHM) Γ and the value of the imaginary part of the permittivity at the maximum of the band $\varepsilon_{2m} = \varepsilon_2(E_m)$) were determined by the method proposed in [15]. The bands A and B were approximated by a two-oscillator symmetric contour, which is a linear combination of the Lorentzian and Gaussian contours. The parameters of the exciton bands (E_m , Γ and ε_{2m}) were found according to the best agreement between the experimental and calculated contours.

3. Results and discussion

The absorption spectra of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ $0 \leq x \leq 1$ solid solutions (Fig. 1) are similar in structure. The intense long-wavelength bands A and B , a weaker band B_1 and a band C can be observed in these spectra. When the temperature increases, the A and B bands shift to the long-wavelength part of the spectrum, become wider and weaker due to the exciton-phonon interaction, which indicates their relationship with excitons. The C band is not very sensitive to temperature and, apparently, corresponds to interband transitions.

To interpret the absorption spectra of solid solutions $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ $0 \leq x \leq 1$, let us turn to the structure of their crystal lattices. CsCu_2Cl_3 crystallizes into an orthorhombic lattice (space group C_{mcm}) with parameters $a = 9.5$, $b = 11.89$ and $c = 5.6$ Å, $z = 4$ [1, 3]. The double chains of CuCl_4 tetrahedra, oriented along the short axis of the crystal, are the structural elements of the crystal lattice of CsCu_2Cl_3 [3]. The crystal structure of RbCu_2Cl_3 was studied in [16], but the authors were unable to determine the type of the lattice. The crystal structure of the compound $\text{Rb}_4\text{Cu}_9\text{Cl}_{13}$, close by molar composition, is described in detail in [17, 18]. $\text{Rb}_4\text{Cu}_9\text{Cl}_{13}$ has rhombohedral symmetry (space group $R\bar{3}c$) with lattice parameters $a = 19.541$ Å, $\alpha = 84.43^\circ$ (hexagonal lattice parameters $a = 26.26$ Å, $c = 36.98$ Å) and 12 molecules per unit cell.

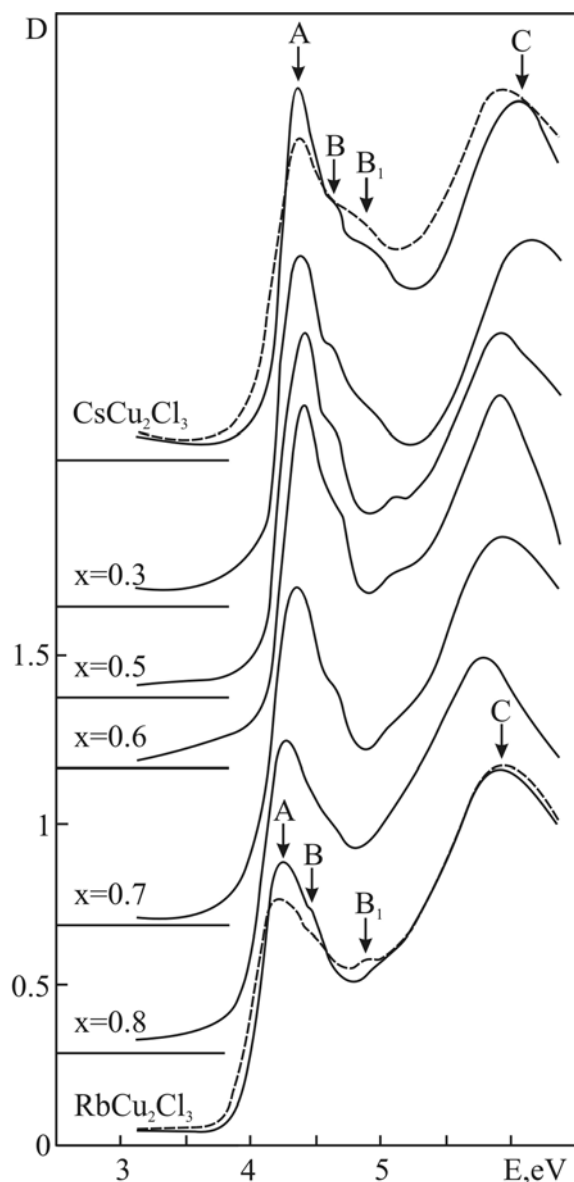


Fig. 1. Absorption spectra of thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 < x < 1$) solid solutions thin films at $T = 90$ K and CsCu_2Cl_3 and RbCu_2Cl_3 thin films at $T = 90$ K (solid line) and 290 K (dotted line).

In the $\text{Rb}_4\text{Cu}_9\text{Cl}_{13}$ lattice, Cu^+ ions are distributed over 11 sets of tetrahedral positions surrounded by Cl^- and one set of positions with 3-fold coordination with respect to Cl^- . The previously described lattice type can apparently be attributed to RbCu_2Cl_3 , since only RbCu_2Cl_3 crystallizes at a high copper content in the RbCl-CuCl system [11]. Common to the crystal lattices of CsCu_2Cl_3 and RbCu_2Cl_3 is the arrangement of Cu^+ ions in a tetrahedral environment by Cl^- ions with a slight shift of Cu^+ from the center of the tetrahedron [3, 16–18].

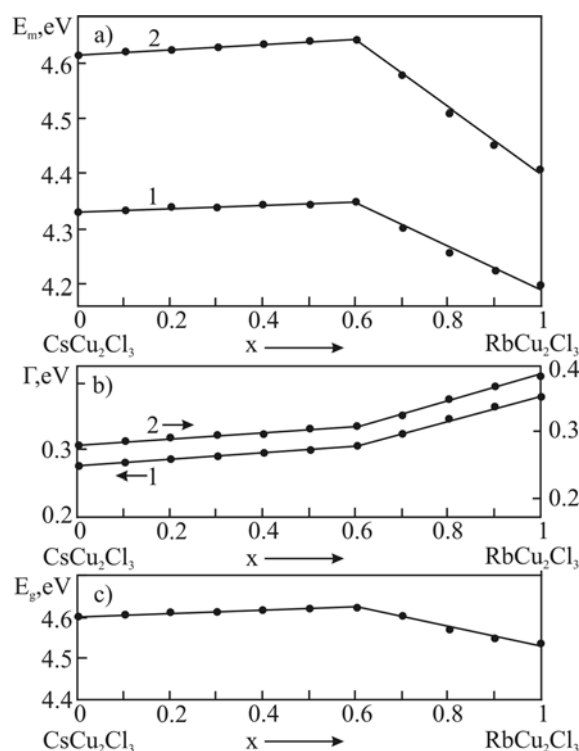


Fig. 2. The concentration dependences (a) of the spectral position $E_m(x)$; (b) of half-width $\Gamma(x)$; (c) of the long-wavelength exciton bands A(1) and B(2) and the bandgap width $E_g(x)$.

As noted above, excitons in CsCu_2Cl_3 are cationic. The exciton spectrum of CsCu_2Cl_3 thin films is due to transitions in Cu^+ ions [8]. Low-frequency excitations of free Cu^+ ions correspond to the transition $^1S_0 \rightarrow ^1D_2$. The Cu^+ ion, located in the center of the tetrahedron 1S_0 , transforms into 1A_1 , and the fivefold degenerate state 1D_2 splits into levels 1T_2 and 1E . According to the selection rules for the local group T_d , the optical transition to a lower level 1T_2 is allowed, but the transition $^1A_1 \rightarrow ^1E$ is forbidden. Since the Cu^+ ion is slightly displaced from the center of the tetrahedron in the CsCu_2Cl_3 lattice [3], the local group decreases to C_{2v} . Under the impact of a weak axial intracrystalline field, the forbiddance on the transition $^1A_1 \rightarrow ^1E$ is partially lifted, and the level 1T_2 is split into components. Accordingly, the intense exciton bands A and B in CsCu_2Cl_3 correspond to the transition $^1A_1 \rightarrow ^1T_2$, and the weak band B_1 corresponds to the transition $^1A_1 \rightarrow ^1E$ [8].

Apparently, in solid solutions $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 \leq x \leq 1$), as in CsCu_2Cl_3 , excitons are localized in the structural elements CuCl_4^{3-} of the crystal lattice, and their exciton absorption spectrum is due to transitions in

the Cu^+ ion. This assumption is supported by the similarity in structure of exciton absorption spectra of thin films $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 \leq x \leq 1$) (Fig. 1). However, there is no complete similarity of the absorption spectra in the entire range $0 \leq x \leq 1$.

In the concentration range $0 \leq x \leq 0.6$, the absorption spectra of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ thin films are similar in the structure and close in the spectral positions of the absorption bands (Fig. 1, Fig. 2a). The exciton bands A and B are slightly shifted to the short-wavelength region of the spectrum with an increase in x , with $dE_m/dx = 0.03$ eV and 0.045 eV, respectively. In the interval $0.6 < x \leq 1$; on the contrary, there is a noticeable linear long-wavelength shift of exciton bands A and B with increasing x with $dE_m/dx = -0.43$ eV and -0.59 eV. The half-width $\Gamma(x)$ of exciton bands A and B (Fig. 2b) slightly increases in the range $0 \leq x \leq 0.6$ with $d\Gamma_A/dx = 0.05$ eV and $d\Gamma_B/dx = 0.049$ eV. The half-width $\Gamma(x)$ grows with $d\Gamma_A/dx = 0.19$ eV and $d\Gamma_B/dx = 0.185$ eV in the range $0.6 < x \leq 1$.

A nonlinear concentration dependence of the spectral position $E_m(x)$ of exciton bands with a deviation to the long wavelength region and a nonlinear growth of $\Gamma(x)$ with a maximum at $x = 0.5$ are characteristic of solid solutions of compounds with a mixed spectrum [19, 20]. Linear concentration dependences of the spectral position $E_m(x)$ (Fig. 2a) and the half-width $\Gamma(x)$ (Fig. 2b) of the long-wavelength exciton bands A and B confirm the localization of excitons in the sublattice of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 \leq x \leq 1$) compounds containing Cu^+ ions. In the studied compounds, for a given localization, the top of the valence band, as in CuCl , is formed by the $3d$ states of the Cu^+ ion and the $3p$ states of the Cl^- ion, and the conduction band is formed by the $4s$ states of the Cu^+ ion.

The presence of two concentration ranges with different concentration dependences $E_m(x)$ and $\Gamma(x)$ of exciton bands A and B is possibly due to the varying crystal structures of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ compounds in the ranges $0 \leq x \leq 0.6$ and $0.6 < x \leq 1$. In the first concentration range, apparently, $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions are isostructural with CsCu_2Cl_3 , since their exciton spectra are similar by structure and close by spectral positions of the bands. An insignificant short-wavelength shift of the A and B bands in the range $0 \leq x \leq 0.6$ indicates a slight

increase in the ionicity of the compounds and the bandgap width E_g . In this concentration range, $E_g(x)$ grows linearly (Fig. 2c):

$$E_g(x) = E_g(0) + ax, \quad (1)$$

where $E_g(0) = 4.605 \pm 0.001$ eV, $a = dE_g/dx = 0.03 \pm 0.003$ eV.

In the range $0.6 < x \leq 1$, apparently, $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions are isostructural with RbCu_2Cl_3 . A significant long-wavelength shift of the spectral position $E_m(x)$ of exciton bands A and B in this concentration range indicates a decrease in the ionicity and in E_g of solid solutions $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$. Apparently, the lower ionicity of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0.6 < x \leq 1$) is due to the presence of Cu^+ ions positions with a threefold coordination relative to Cl^- in crystal lattice [17, 18]. In this concentration range, the bandgap width $E_g(x)$ decreases linearly (Fig. 2c) with $dE_g/dx = -0.23$ eV. Linear concentration dependences of the bandgap width $E_g(x)$ in $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ solid solutions also confirm the localization of excitons in the sublattice of compounds containing Cu^+ ions.

The analysis of the absorption spectra of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ thin films has shown a formation of solid solutions in the entire concentration range $0 \leq x \leq 1$; the solid solutions are isostructural with CsCu_2Cl_3 in the range $0 \leq x \leq 0.6$ and RbCu_2Cl_3 in the range $0.6 < x \leq 1$.

4. Conclusions

The absorption spectra obtained at $T = 90$ K for thin films of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 \leq x \leq 1$) solid solutions were studied in the spectral range of 2 to 6 eV. The formation of the solid solutions isostructural with CsCu_2Cl_3 in the concentration range $0 \leq x \leq 0.6$ was found. In the range $0.6 < x \leq 1$, the solid solutions are apparently isostructural with RbCu_2Cl_3 .

The localization of excitons in the structural elements CuCl_4^{3-} of the crystal lattice of the compounds was revealed from an analysis of the absorption spectra of the solid solutions. The linear concentration dependences of $E_m(x)$, $\Gamma(x)$ and $E_g(x)$ confirm the localization of excitons in the sublattice containing Cu^+ ions.

Exciton absorption spectra of $\text{Cs}_{1-x}\text{Rb}_x\text{Cu}_2\text{Cl}_3$ ($0 \leq x \leq 1$) solid solutions were interpreted on the basis of transitions in the Cu^+ ions.

References

1. S.Hull, P.Berastegui, *J.Solid State Chem.*, **177**, 3156 (2004).
2. S.Geller, J.R.Akridge, S.A.Wilber, *Phys. Rev. B*, **5396** (1979).
3. G.Meier, Z.Anorg, *Allg.Chem.*, **515**, 127 (1984).
4. A.K.Ivanov-Shits, I.V.Murin, Ionics of the Solid State, vol. 1, St. Petersburg (2000) [in Russian].
5. V.K.Miloslavsky, O.N.Yunakova, Sun Jia-Lin, *Opt. Spectrosc.*, **78**, 436 (1995).
6. V.K.Miloslavsky, O.N.Yunakova, E.N.Kovalenko, *Functional Materials*, **4**, 12 (1997).
7. R.Rocanova, A.Yangui, H.Nhalil et al., *ACS Appl. Electron. Mater.*, **1**, 269 (2019).
8. V.K.Miloslavsky, E.N.Kovalenko, O.N.Yunakova, *Opt. Spectrosc.*, **84**, 940 (1998).
9. E.N. Kovalenko, O. N. Yunakova, N.N. Yunakov, *Low Temper. Phys.*, **47**, No. 5, 462 (2021)
10. G.M.Lescano, Maria E.F.de Rapp, J.A.Schmidt, N.W.de Reça, *Mater. Lett.*, **45**, 269 (2000).
11. V.F.Vybornov, V.S.Shvetsov, V.V.Ivanov, A.M.Kolomoets, *Izv.USSR Academy of Sciences Inorganic Materials*, **20**, 1413 (1984).
12. V.S.Shvetsov, V.F.Vybornov, *Electrochemistry*, **19**, 942 (1983).
13. R.Kanno, Y.Takeda, Y.Masuyama et al., *Solid State Ionics*, **11**, 221 (1983).
14. J.M.Gaines, S.Geller, *Phys. Rev. B*, **34**, 8963 (1986).
15. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, *Opt. i Spec.*, **104**, 631 (2008).
16. V.S.Shvetsov, V.F.Vybornov, V.V.Ivanov, *Electrochemistry*, **18**, 986 (1982).
17. J.M.Gaines, S.Geller, *Phys. Rev. B*, **34**, 8963 (1986).
18. J.M.Gaines, S.Geller, *J.Electrochem Soc.*, **133**, 1501 (1986).
19. V.K.Miloslavsky, E.N.Kovalenko, O.N.Yunakova, N.N.Yunakov, *Low Temper. Phys.*, **43**, 1532 (2017).
20. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, *Functional Materials*, **11**, 761 (2004).