Exciton absorption spectrum of thin films of $(Cs_xK_{1-x})_2CuCl_3$ solid solutions

E.N. Kovalenko[1], O.N. Yunakova[2], N.N. Yunakov[2]

[1]Kharkov National University of Radio Electronics,
14, Nauki Ave., Kharkiv 61166, Ukraine,
[2]Kharkiv National University, 4, Svobody Sq., Kharkiv 61022, Ukraine

The absorption spectra of thin films of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ (T=90K) solid solutions in the spectral range 2–6 eV were studied. According to the analysis of the spectra, the formation of two types of compounds was observed and studied: 1) compounds at x=0 and in the range of $0.4 \leq x \leq 1$ which are isostructural to Cs_2CuCl_3 and K_2CuCl_3; 2) compounds at x=0.2 which are isostructural to $CsCu_2Cl_3$. The excitonic spectra of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ compounds are caused by transitions in the Cu^+ ion. The linear concentration dependences of the spectral position of exciton bands in both types of compounds confirm the localization of excitons in sublattices containing Cu^+ ions.

Keywords: thin films, absorption spectra, excitons.

Екситонний спектр поглинання тонких плівок твердих розчинів $(Cs_xK_{1-x})_2CuCl_3$**.** *О.М. Коваленко, О.М. Юнакова, М.М. Юнаков*

Досліджено спектри поглинання тонких плівок твердих розчинів $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ (T=90К) в спектральному інтервалі 2–6 eВ. З аналізу спектрів встановлено утворення двох типів сполук: при x=0 та в інтервалі $0,4 \leq x \leq 1$ ізоструктурних Cs_2CuCl_3 та K_2CuCl_3, а при x=0,2 утворюється сполука ізоструктурна $CsCu_2Cl_3$. Екситонні спектри сполук $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ обумовлені переходами в іоні Cu^+. Лінійні концентраційні залежності спектрального положення екситонних смуг в обох типах сполук підтверджують локалізацію екситонів в підгратках, що містять іони Cu^+.

1 Introduction

Metal halide compounds with a perovskite-like structure are of interest to researchers due to their optoelectronic properties [1-6]. They are of interest as a material for solar cells, displays, lighting equipment, etc. Copper halide compounds with a perovskite structure are especially interesting [4,5], as a less toxic material compared to lead-based perovskites [1-3]. Copper perovskites with significantly different crystal lattice parameters [6] can serve as both good luminophores [4, 5] and materials for various optoelectronic devices. In this work, we study the absorption spectra of solid solutions of copper perovskites K_2CuCl_3 and Cs_2CuCl_3.

Only one compound, K_2CuCl_3, with a stable absorption spectrum is formed in the KCl – CuCl system. This compound crystallizes into a perovskite-like orthorhombic lattice with parameters (space group P_{nma}) a=12.030, b=4.148 and c=12.587 Å [6]. The structural element of the K_2CuCl_3 crystal lattice is single chains of $CuCl_4$ tetrahedra, oriented along the short axis of the crystal.

According to a study of the absorption spectra of thin films $(CsCl)_{1-x}(CuCl)_x$ $0 \leq x \leq 1$ (T=90К), the formation of two compounds with a stable spectrum, $CsCu_2Cl_3$ and Cs_2CuCl_3, was established in this concentration range [7]. Both compounds are non-hygroscopic. The

compound $CsCu_2Cl_3$ is resistant to the external environment [6-8], and Cs_2CuCl_3 is stable only in vacuum [7]. In air, Cs_2CuCl_3 apparently decomposes into $CsCu_2Cl_3$ with a disordered crystal lattice and $CsCl$ [7]. The decomposition process of Cs_2CuCl_3 is slow. In this case, the Cs_2CuCl_3 films remain optically smooth and non-scattering. In terms of the structure of the spectrum and the position of absorption bands, the spectrum of Cs_2CuCl_3 thin films is close to the spectrum of K_2CuCl_3 thin films, which indicates that both compounds are isostructural [7]. Unlike Cs_2CuCl_3, the absorption spectrum of K_2CuCl_3 thin films is stable when stored in an external environment, but the films become scattering over time.

In this work, the absorption spectra of thin films of $(Cs_xK_{1-x})_2CuCl_3$ solid solutions are studied in order to determine the possibility of obtaining compounds that are stable in the external environment.

2. Experimental

Thin films of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ were prepared using the same procedure as Cs_2CuCl_3 films [7]. A mixture of pure CsCl, KCl and CuCl powders of stoichiometric composition was preliminarily melted in a vacuum, then the melt of the mixture was evaporated at high temperature onto quartz substrates heated to 100°C, followed by annealing of the films for an hour at the same temperature. This method of producing thin films of ternary compounds is based on the fact that, as a rule, the melting point of ternary compounds is significantly lower than the melting point of the initial components [7,9]. The evaporation temperature of the melt was selected such that monophase films were obtained without admixtures of other phases of ternary compounds, for example, admixtures of the $CsCu_2Cl_3$ type phase. The evaporation temperature of the $CsCu_2Cl_3$ melt is significantly lower than the evaporation temperature of the Cs_2CuCl_3 [7], so the melt of the mixture of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ powders evaporated at a high temperature.

The phase composition of thin films $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ and their quality were controlled by absorption spectra measured at $T=90K$. Such control is possible due to the qualitative difference in the absorption spectra of various compounds and the significant difference in the spectral position of long-wave exciton bands in the ternary compounds $CsCu_2Cl_3$ (4.33 eV), Cs_2CuCl_3 (4.84 eV), K_2CuCl_3 (4.7 eV)

and the initial components CsCl (7.8 eV), KCl (7.76 eV) and CuCl (3.3 eV). To study exciton absorption spectra, films with a stable spectrum for a given concentration x, and the narrowest and most intense absorption bands were selected.

Absorption spectra were measured in the spectral range 2-6 eV at $T=90K$ on an SF-46 spectrophotometer. To measure the absorption spectra, films with a thickness of 250-300 nm were used.

The parameters of long-wave exciton bands (position E_m, half-width Γ and the value of the imaginary part of the dielectric constant at the maximum of the band $\varepsilon_{2m} = \varepsilon_2(E_m)$) were determined directly from the optical density spectrum $D = -\lg T$ by approximating the bands with two-oscillator and one-oscillator symmetrical contours, which are linear combination of Lorentzian and Gaussian contours. The parameters of the exciton bands (E_m, Γ and ε_{2m}) were found by best matching the experimental and calculated contours. During computer processing of the spectra in order to isolate excitonic bands and eliminate polariton effects, the calculated transmission T_p of samples was analyzed using the Airy formula, which takes into account Fresnel losses at the boundaries and light interference at a given film thickness t. The calculated transmittance T_p is a complex function of photon energy, thickness t, and optical constants n and k.

In the case of a Lorentz contour, the real $\varepsilon_1 = n^2 - k^2$ and imaginary $\varepsilon_2 = 2nk$ parts of the dielectric constant have the form

$$\varepsilon_1(\xi) = \varepsilon_\Phi + \varepsilon_{2m}\xi / (1 + \xi^2),$$
$$\varepsilon_2(\xi) = \varepsilon_{2m} / (1 + \xi^2). \quad (1)$$

In the case of a Gaussian contour

$$\varepsilon_1(\xi_1) = \varepsilon_\Phi + (2/\sqrt{\pi})\varepsilon_{2m}\exp(-\xi_1^2)\int_0^{\xi_1}\exp(x^2)dx,$$

$$\varepsilon_2(\xi_1) = \varepsilon_{2m}\exp(-\xi_1^2), \quad (2)$$

where $\varepsilon_{2m} = \varepsilon_2(E_m)$, $\xi = (E_m - E)/\Gamma$, $\xi_1 = 2(\ln 2)^{1/2}(E_m - E)/\Gamma$, ε_Φ, is determined by the contribution to ε_1 due to short-wave optical transitions.

For a contour intermediate between Lorentzian and Gaussian, a linear combination was used

$$\varepsilon_{1,2}(E) = (1-\alpha)\varepsilon_{1,2}{}^L(E) + \alpha\varepsilon_{1,2}{}^G(E). \quad (3)$$

With this approximation, the exciton band contour is close to the Voigt contour. The spectral position of the exciton band E_m, its half-

Table 1. Spectral position of absorption bands in compounds

Compound	E_{mA}, eV	E_{mB}, eV	E_{mB1}, eV	E_{mC}, eV
K_2CuCl_3	4.7		5.25	6,2
Cs_2CuCl_3	4.84		5.51	6.1
$(Cs_{0.2}K_{0.8})_2CuCl_3$	4.33	4.64	5.08	6.1
$CsCu_2Cl_3$	4.33	4.615	4.96	6.05

width Γ and ε_{2m} are found by matching the measured optical density spectra at the long-wavelength slope of the bands with the calculated dependences.

3. Result and discussion

The absorption spectra of thin films of $(Cs_xK_{1-x})_2CuCl_3$ $0 \le x \le 1$ (T=90К) solid solutions are shown in Fig. 1 and Fig. 2. The spectra of K_2CuCl_3 and Cs_2CuCl_3 are similar in structure and close in the position of absorption bands. The spectrum of K_2CuCl_3 thin films shows an intense long-wavelength exciton band A at 4.7 eV, a weak excitonic band B_1 at 5.25 eV, and an electronic band C at 6.2 eV. In Cs_2CuCl_3, the intense long-wavelength exciton band A is located at 4.84 eV, the weak exciton band B_1 is at 5.51 eV, and the electronic band C is at 6.1 eV. The excitonic spectrum of both compounds is interpreted based on transitions in the Cu^+ ion [7, 10]. As noted above, the structural element of the K_2CuCl_3 crystal lattice is single chains of $CuCl_4$ tetrahedra, oriented along the short axis of the crystal [6]. Cs_2CuCl_3 presumably has a similar structure [7]. Low-frequency excitations of the free Cu^+ ion correspond to the transition $^1S_0 \rightarrow {}^1D_2$. Whereas for the Cu^+ ion, which is located in the center of the tetrahedron, $^1S_0$ goes to $^1A_1$ and the 5-fold degenerate state $^1D_2$ splits into levels $^1T_2$ and ^1E. According to the selection rules for the local T_d group, optical transition to a lower level $^1T_2$ is allowed, but transition $^1A_1 \rightarrow {}^1E$ is prohibited. Since the Cu^+ ion is slightly displaced from the center of the tetrahedron in the lattices of the studied compounds [6], the local group decreases to C_{2v}. Under the influence of a weak axial intracrystalline field, the ban on $^1A_1 \rightarrow {}^1E$ transition is partially lifted, and the level $^1T_2$ is split into components. Accordingly, the intense exciton band in K_2CuCl_3 and Cs_2CuCl_3 corresponds to the transition $^1A_1 \rightarrow {}^1T_2$, and the weak B_1 band corresponds to the transition $^1A_1 \rightarrow {}^1E$ [7,10].

Despite the isostructural nature of the absorption spectra of K_2CuCl_3 and Cs_2CuCl_3, in the spectrum of $(Cs_xK_{1-x})_2CuCl_3$ (Fig. 1), even at a low impurity concentration Cs x = 0.1, a weak A^{II} band appears in the long-wavelength region of the spectrum. And at x=0.2, the absorption spectrum of a thin film $(Cs_{0.2}K_{0.8})_2CuCl_3$ (Fig. 2a) becomes similar in structure to the spectrum of $CsCu_2Cl_3$ (Fig. 2b) and is close to it in the spectral position of the absorption bands (Table 1). The spectrum of $(Cs_{0.2}K_{0.8})_2CuCl_3$ exhibits two intense long-wavelength bands A^{II} at 3.33 eV and B^{II} at 4.64 eV, a weak $B_1{}^{II}$ band at 5.08 eV, and a C^{II} band at 6.1 eV. The spectral position of absorption bands in $CsCu_2Cl_3$ is given in Table 1.

The spectrum of the compounds $CsCu_2Cl_3$ and $(Cs_{0.2}K_{0.8})_2CuCl_3$ is more complex compared to K_2CuCl_3 and Cs_2CuCl_3 due to the more complex 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 [6]. The structural element of the $CsCu_2Cl_3$ crystal lattice is double chains of $CuCl_4$ tetrahedra oriented along the short axis of the crystal [6]. Additional interaction between $CuCl_4$ tetrahedra in the double chains of the $CsCu_2Cl_3$ and $(Cs_{0.2}K_{0.8})_2CuCl_3$ crystal lattices leads to a shift of excitonic bands to the low-frequency region of the spectrum and splitting into components [7, 11]. The appearance of intense excitonic B^{II} bands in both compounds is apparently associated with Davydov splitting of excitonic bands, which occurs during the interaction of single chains of $CuCl_4$ tetrahedra in a double chain [7, 11]. In this case, the position of the exciton bands is determined by the expression $E_{ex}^{\pm} = E_{ex}^0 \pm \frac{1}{2}\Delta E_D$, where E_{ex}^0 is the exciton excitation energy in a hypothetical single chain. The value of $\Delta E_D = E_{BII} - E_{AII} = 0.285$ eV and 0.31 eV in $CsCu_2Cl_3$ and $(Cs_{0.2}K_{0.8})_2CuCl_3$, respectively.

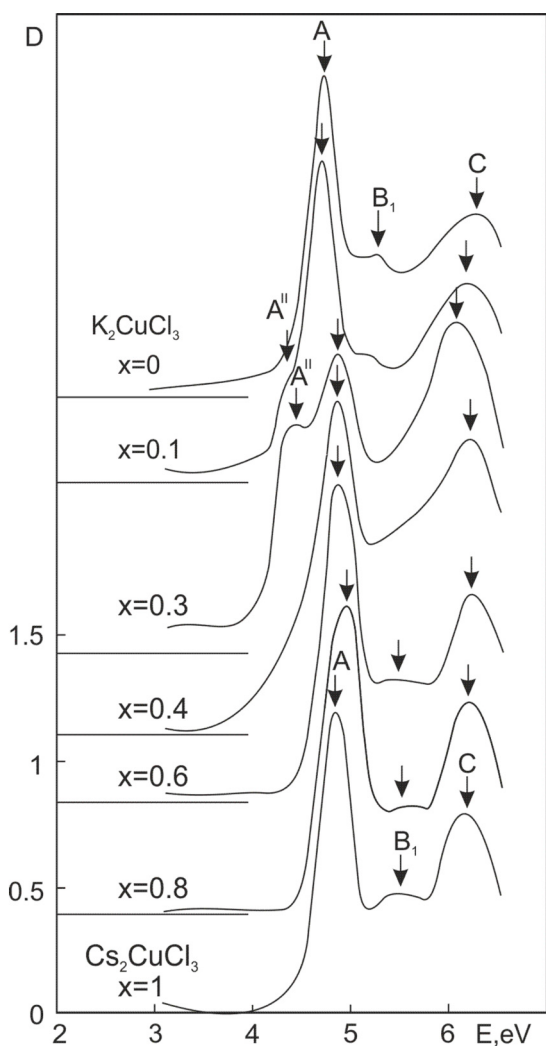It should be noted that the compound which is isostructural to $CsCu_2Cl_3$ is not formed in the

Fig.1. Absorption spectra of thin films of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ solid solutions.

Fig.2. Absorption spectrum of a thin film of $(Cs_{0.2}K_{0.8})_2CuCl_3$ (*a*) and $CsCu_2Cl_3$ (*b*).

KCl – CuCl system. The isostructural $CsCu_2Cl_3$ compound in its pure form is formed only for the composition $(Cs_{0.2}K_{0.8})_2CuCl_3$. The $CsCu_2Cl_3$ type phase dominates in the absorption spectrum of $((Cs_xK_{1-x})_2CuCl_3$ x=0.3 (Fig. 1), but an admixture of the Cs_2CuCl_3 type phase starts appearing. This is indicated by the weakening of the long-wavelength A^{II} band and the increase in the intensity of the B band. Starting from x=0.4, the absorption spectra of $(Cs_xK_{1-x})_2CuCl_3$ solid solutions are similar to the spectrum of Cs_2CuCl_3.

According to the analysis of the absorption spectra of thin films of solid solutions $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ (Fig. 1, Fig. 2), isostructural compounds Cs_2CuCl_3 and K_2CuCl_3 start forming at x=0 and in the range of $0.4 \leq x \leq 1$. Their excitonic spectra, so as the spectrum of Cs_2CuCl_3 and K_2CuCl_3, are caused by transi-
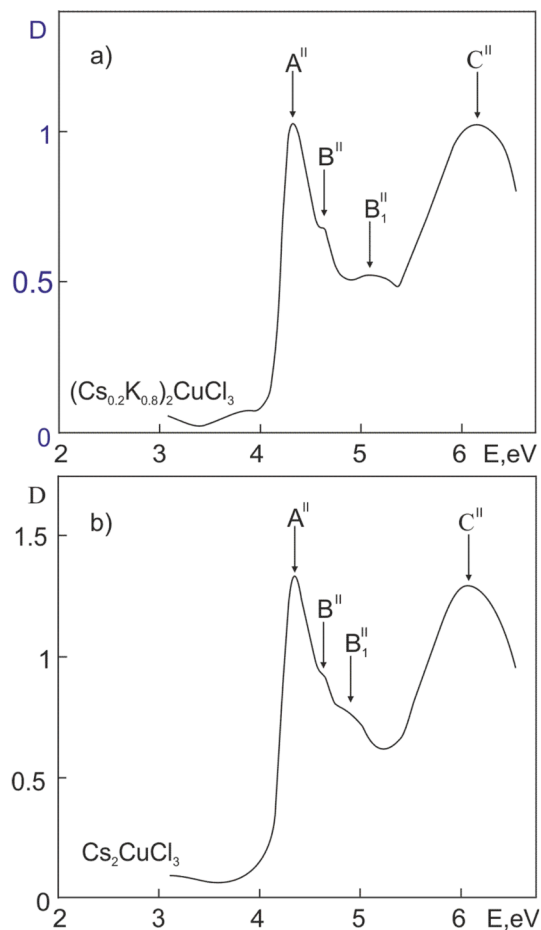
tions in the Cu^+ ion. Excitons in these compounds are localized in single chains of $CuCl_4$ tetrahedra. It should be noted that the spectra of solid solutions in the concentration range of $0.4 \leq x \leq 1$ are stable only when storing samples in a vacuum. In air, as well as in pure Cs_2CuCl_3, the compounds slowly decompose with the release of an isostructural $CsCu_2Cl_3$ phase. Unfortunately, the admixture of K ions did not lead to the stabilization of Cs_2CuCl_3 in the external environment. On the contrary, the admixture of Cs ions in K_2CuCl_3 contributes to the appearance of an impurity phase of the $CsCu_2Cl_3$-type in the samples $(Cs_xK_{1-x})_2CuCl$ with x=0.1 and x=0.3, whereas at x=0.2 a compound is formed which is isostructural to $CsCu_2Cl_3$.

Figure 3 shows the concentration dependences of the spectral position of long-wave exciton bands for different phases of compounds $(Cs_xK_{1-x})_2CuCl$ $0 \leq x \leq 1$. The concentration dependence of the spectral position of the long-wave exciton band A is linear in solid solutions $(Cs_xK_{1-x})_2CuCl_3$ (x=0 and $0.4 \leq x \leq 1$), which are
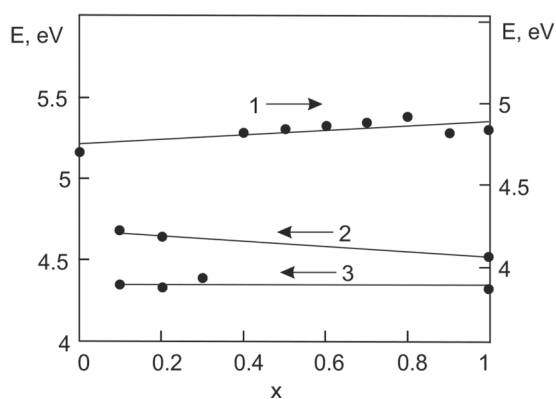
Fig.3. Concentration dependences of the spectral position of long-wave excitonic bands in thin films $(Cs_xK_{1-x})_2CuCl_3$ with a structure of the K_2CuCl_3-type ($x=0$ and $0.4 \leq x \leq 1$) $E_{mA}(x)$ (1) and with a structure of the $CsCu_2Cl_3(0.1 \leq x \leq 0.3)$ type $E_{mBII}(x)$ (2) and $E_{mAII}(x)$ (3).

isostructural to Cs_2CuCl_3 and K_2CuCl_3 (Fig. 3, section 1):

$$E_{mA}(x) = E_{mA}(0) + (dE_{mA}/dx)x, \qquad (5)$$

where $E_{mA}(0) = 4.7 \pm 0.03$ eV, $dE_{mA}/dx = 0.15 \pm 0.05$ eV.

A phase of $CsCu_2Cl_3$-type structure appears in the spectra of $(Cs_xK_{1-x})_2CuCl_3$ $0.1 \leq x \leq 0.3$. The concentration course of the spectral position of the long-wave exciton bands A^{II} and B^{II} in this concentration range linearly converges to the spectral position of the corresponding bands in $CsCu_2Cl_3$ (Fig. 3, sections 2 and 3). Linear concentration dependences of the spectral position of exciton bands in solid solutions $(Cs_xK_{1-x})_2CuCl_3$ in both phases confirms the localization of excitons in the sublattice of compounds containing Cu^+ ions.

4. Conclusions

According to the analysis of the absorption spectra of thin films of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ solid solutions, the formation of compounds of isostructural Cs_2CuCl_3 and K_2CuCl_3 at $x=0$ and in the range of $0.4 \leq x \leq 1$ was established. Thin films of solid solutions are stable only in vacuum in the range of $0.4 \leq x \leq 1$. In air however, they slowly decompose with the release of a phase of the $CsCu_2Cl_3$-type. Samples are two-phase at $x=0.1$ and $x=0.3$, whereas at $x=0.2$ the $(Cs_xK_{1-x})_2CuCl_3$ is formed which is isostructural to $CsCu_2Cl_3$.

The excitonic spectra of $(Cs_xK_{1-x})_2CuCl_3$ $0 \leq x \leq 1$ compounds are caused by transitions in the Cu^+ ion. In solid solutions of isostructural Cs_2CuCl_3 and K_2CuCl_3 ($x=0$ and $0.4 \leq x \leq 1$), excitons are localized in single chains of $CuCl_4$ tetrahedra. In $(Cs_{0.2}K_{0.8})_2CuCl_3$, excitons are localized in double chains of $CuCl_4$ tetrahedra, which causes a more complex spectrum of the compound due to Davydov splitting of excitonic bands, which occurs when single chains of $CuCl_4$ tetrahedra interact in a double chain.

Linear concentration dependences of the spectral position of exciton bands in both phases of $(Cs_xK_{1-x})_2CuCl_3$ solid solutions confirm the localization of excitons in the sublattice of compounds containing Cu^+ ions.

References

1. K. Fatima, M.I. Haider, A. Bashir, Z. Akhter, M. Sultan, *Physica E: Low-Dimensional Systems and Nanostructures*, **142,** 115265 (2022).
2. P. Gong, F. Liang, L. Kang, Z. Lin, *Chemistry of Materials*, **34**, №11, 5301(2022).
3. A.S. Sadhu, Y.-M. Huang, L.-Y. Chen, H.-C. Kuo, C.-C.Lin, *Nanomaterials*, **12**, №6, 985 (2022).
4. W. Gao, L. Yin, J.-H. Yuan, K.-H. Xue, G. Niu, B. Yang, Q. Hu, X. Liu, J. Tang, *Organic Electronics,***86**, 105903(2020).
5. R. Roccanova, A. Yangui, H. Nhalil, H. Shi, M.-H. Du, B. Saparov, *ACS Appl. Electron. Mater.*, **1**, №3, 269 (2019).
6. S. Hull, P. Berastegui, *J. Solid State Chem.*, **177**, №9, 3156 (2004).
7. E.N. Kovalenko , O. N. Yunakova, N.N. Yunakov, *Low Temperature Physics*, **49**, No. 10, 1190 (2023).
8. G. Meier, *Z. Anorg. Allg. Chem.*, **515**, 127 (1984).
9. E.N. Kovalenko , O. N. Yunakova, N.N. Yunakov, *Low Temperature Physics*, **47**, No.5, 462 (2021).
10. K. Edamatsu, T. Nanba, M. Ikezawa, *Journal of Physical Society of Japan* **58**, 301 (1989).
11. V.K. Miloslavsky, E.N. Kovalenko, O.N. Yunakova, *Opt. and Spectrosc.*, **84**, №6, 940 (1998).