ISSN 1027-5495. Functional Materials, 22, No.2 (2015), p. 175-180.
doi:http://dx.doi.org/10.15407/fm22.02.175

Exciton absorption spectrum of Cs_4PbCl_6 thin films

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

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

Received February 20, 2015

Absorption spectrum of Cs_4PbCl_6 thin films was studied in the spectral range of 2–6 eV within the temperature interval 90–500 K. Localization of low-frequency excitonic states in sublattice of the compound containing Pb^{2+} ions was established. Excitons have intermediate bond and two-dimensional (2D) nature.
Keywords: thin films, absorption spectra, excitons.

Исследован спектр поглощения тонких пленок Cs_4PbCl_6 в области спектра 2–6 эВ и температурном интервале 90–500 К. Установлено, что низкочастотные экситонные возбуждения локализованы в подрешетке соединения, содержащей ионы Pb^{2+}, относятся к экситонам промежуточной связи и носят двухмерный характер.

Екситонний спектр поглинання тонких плівок Cs_4PbCl_6. *О.Н.Юнакова, В.К.Милославський, Е.Н.Коваленко, В.В.Коваленко*
Досліджено спектр поглинання тонких плівок Cs_4PbCl_6 в області спектра 2–6 еВ и температурному інтервалі 90–500 К. Установлено, що низькочастотні екситонні збудження локалізовані у підгратці сполуки, яка містить іони Pb^{2+}, відносяться до екситонів проміжного зв'язку та мають двомірний характер.

1. Introduction

Two compounds $CsPbCl_3$ and Cs_4PbCl are formed in $CsCl–PbCl_2$ system according to researches of the phase diagram [1, 2]. The first compound is studied in detail including the absorption spectra of [3–5], but the compound Cs_4PbCl_6 is little investigated. According to [6] Cs_4PbCl_6 crystallizes in monoclinic structure with the lattice parameters a = 13.449, b = 9.417, c = 13.181 Å, γ = 91.61°. According to the later researches [2], Cs_4PbCl_6 has the hexagonal lattice with unit cell parameters a = 13.155, c = 16.604 Å, space group R–3c. The octahedron $(PbCl_6)^{4-}$ of almost correct form with the interatomic distances Pb–Cl 2.876 Å is structural element of the crystal lattice in the both cases [2, 6].

Cs_4PbCl_6 absorption spectrum was measured in [2, 7] on single crystals in the range of long-wavelength excitonic band and in [8] on thin films. The difficulty of making Cs_4PbCl_6 without $CsPbCl_3$ impurity was noted in the both cases. In the studied single crystals [2, 7] small $CsPbCl_3$ impurity was present, and thin films without $CsPbCl_3$ impurity could only be received at deposition of $(CsCl)_{1-x}(PbCl_2)_x$ mix with excess CsCl (x = 0.1) [8]. The mixture was evaporated by explosion on substrates cooled to 77 K with their subsequent annealing and slow temperature increase to 500 K. CsCl impurity in the thin films of

Cs_4PbCl_6 complicates analysis of the spectrum in the short-wave range [8].

In this research thin films Cs_4PbCl_6 of stoichiometric composition were obtained and it was investigated their excitonic spectrum in the region of 2–6 eV and in broad temperature range of 90–500 K.

2. Experimental

Cs_4PbCl_6 thin films were prepared by evaporation of CsCl and $PbCl_2$ pure powders mixture of stoichiometric molar composition on heated to 453 K quartz substrates with their subsequent annealing during two hours at the same temperature. The powder mixture was preliminarily melted under the screen which was located between an evaporator and a substrate. This method was used previously to prepare Cs_4PbI_6 [9] and Rb_4PbI_6 [10] thin films. It based on the fact that, as a rule, melting temperature of ternary compounds is significantly lower than that of the initial binary compounds. Some difficulties occurred during preparation of the Cs_4PbCl_6 films from the melt due to $CsPbCl_3$ impurity phases in the films. Cs_4PbCl_6 melting point (493°C) is lower than $CsPbCl_3$ (615°C) [1]. It is also known that two-phase M_4PbI_6 films with $MPbI_3$ (M = Cs, Rb) impurity transform into monophase M_4PbI_6 at the high-temperature annealing [9, 10]. Considering these two facts, the Cs_4PbCl_6 monophasic film was obtained with minimized evaporation temperature of the melt mixture of the powders and increased substrate temperature to a value at which no light scattering appears in the film (it's 453 K).

The phase structure of the films was controlled by absorption spectra measured at T = 90 K. Such control is possible due to significant differences in the spectral position of the long-wavelength excitonic bands in $CsPbCl_3$ (3.04 eV [5]), Cs_4PbCl_6 (4.345 eV), $PbCl_2$ (4.6 eV) and CsCl (5.8 eV).

The films of 100–120 nm thick were used for the absorption spectra measurement, the films of 400–500 nm thick were used for determining dispersion of the refractive index. The absorption spectra were measured in the spectral interval of 2–6 eV at T = 90 and 290 K on a spectrophotometer SF-46. In a narrower spectral interval of 3.4–4.8 eV, which is the region of the long-wavelength excitonic band, the absorption spectrum was measured in a wide temperature band 90–500 K.

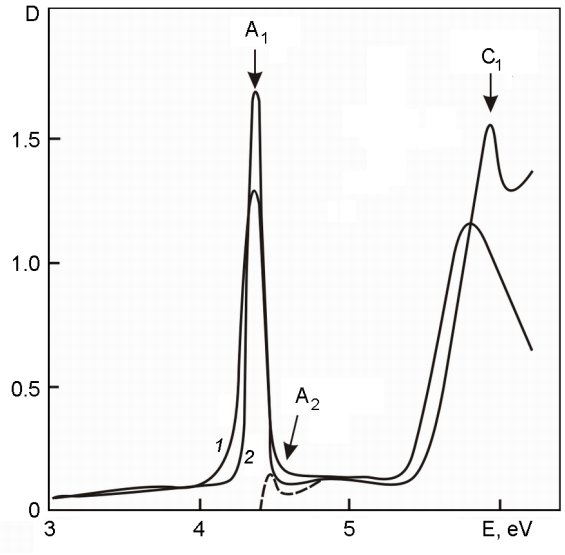

Fig. 1. Absorption spectrum of Cs_4PbCl_6 thin film (t = 120 nm) at T = 90 K (*2*) and 290 K (*1*).

Dispersion of refractive index $n(\lambda)$ in thin films of Cs_4PbCl_6 in the transparence region was determined by the interference method [11].

The long-wavelength A-band parameters (position E_m, half-width Γ and $\varepsilon_{2m} = \varepsilon_2(E_m)$ — the value of imaginary part of dielectric constant in the band maximum) were determined by the technique [12], using approximation of A_1-band by symmetric single-oscillator profile representing the linear combination of the Lorentzian and Gaussian profiles. The excitonic band parameters (E_m, Γ and ε_{2m}) were chosen to obtain the best fit of the calculated profile to the measured spectrum at long-wavelength slope of the band.

3. Results and discussion

3.1. Absorption spectrum of Cs_4PbCl_6 thin films

The narrow intensive A_1-band at 4.345 eV (90 K) and the short-wave C_1-band at 5.904 eV (90 K) were observed in the absorption spectrum of Cs_4PbCl_6 thin film (Fig. 1). The A_1-band spectral position is consistent with the data [8], but in the short wavelength spectral range, unlike to the spectrum in [8], only one narrow C_1-band was observed. With temperature increase, both bands are shifted to the longer wavelengths, broadened and weakened due to exciton-phonon interaction, which indicates to their connection with the excitonic states. The ledge A_2, which we associate

with the excitation of 2*s* exciton, observed in background of interband transitions at 4.46 eV (Fig. 1) after separation of the long-wavelength exciton A_1-band by the symmetrical contour. The exciton binding energy was estimated as $R_{ex} = 4/3\ (E_{A2} - E_{A1}) = 0.153$ eV and the band gap $E_g = E_{A1} + R_{ex} = 4.5$ eV, considering that A_1- and A_2-bands belong to the exciton series with head A_1-band by their spectral position.

The dispersion of the refractive index $n(\lambda)$ in Cs_4PbCl_6 thin films (Fig. 2) in the transparency region is well described by the one-oscillator Vemple model [13]:

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

where $E = \hbar\omega$, E_0 and E_d are parameters of the one-oscillator model. E_0 determines spectral position of the effective oscillator associated with interband optical transitions, the value of $E_0 > E_g$ [13], E_d is dispersion energy that characterizes intensity of the interband transitions.

The dependence of $(n^2 - 1)^{-1}$ on E^2 (1) is linear. Processing of the experimental data of $n(\lambda)$ using dependence $(n^2 - 1)^{-1}$ on E^2 by the least squares method allowed to determine the value $(E_0E_d)^{-1} = 0.012 \pm 0.0002$ by slope of the line, the value $E_0/E_d = 0.467 \pm 0.0015$ by intersection with y-axis and therefore $E_0 = 6.238$ eV and $E_d = 13.358$ eV. Calculated dependence of $n(\lambda)$ with Eq.(1) (Fig. 2, solid line) with the above given values E_0 and E_d has a good match with the experimental dependence $n(\lambda)$ (Fig. 2, dots). Approximation of the dependence $n(\lambda)$ to a low-energy limit gives the value of optical dielectric permittivity $\varepsilon_\infty = 1 + E_d/E_0 = 3.141$. Using received ε_∞ value we can estimate the exciton radius as

$$a_{ex} = a_B \frac{R}{R_{ex}\varepsilon_{eff}}, \qquad (2)$$

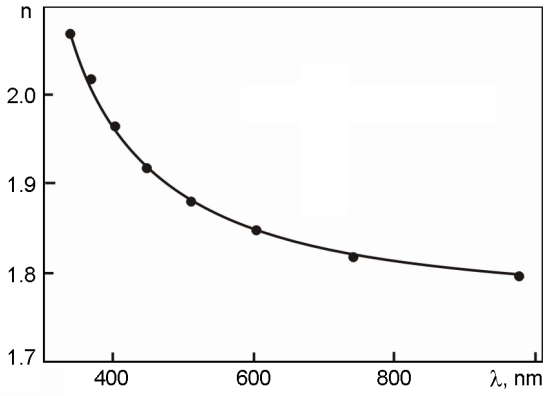

Fig. 2. Spectral dependence of the refractive index $n(\lambda)$ of Cs_4PbCl_6 thin films: dots — experiment, solid lines — calculation by Eq.(1).

where $a_B = 0.529 \cdot 10^{-8}$ cm is the Bohr radius, $R = 13.6$ eV is the Rydberg constant, ε_{eff} is effective dielectric permittivity, $\varepsilon_\infty < \varepsilon_{eff} < \varepsilon_0$, ε_0 is static dielectric permittivity, $R_{ex} = 0.153$ eV is the value of excitonic binding energy in Cs_4PbCl_6. We used the ε_{eff} lower limit to assess a_{ex} as the main contribution to ε_{eff} determined by the value of ε_∞ in the low-frequency region of the excitonic band. The obtained value $a_{ex} = 14.97$ Å indicates excitation of excitons of intermediate coupling in Cs_4PbCl_6 similar to that of the exciton in alkali halide crystals.

For interpretation of the Cs_4PbCl_6 spectrum it is compared with the spectra of impurity bands of Pb^{2+} in CsCl [14] and also with the spectra of previously studied compounds Cs_4PbI_6 [9] and Rb_4PbI_6 [10]. Spectral positions of A_1 and C_1 excitonic bands are close to the positions of impurity bands of Pb^{2+} in CsCl (see Table) which indicates the cationic nature of the exciton states in Cs_4PbCl_6. Spectra of Cs_4PbI_6 [9] and Rb_4PbI_6 [10] are also close to the impurity spectrum $CsI:Pb^{2+}$ by the spectral position of the excitonic bands and the spec-

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

Compound	E_{A1}, eV	E_{C1}, eV	E_{C2}, eV	E_{C3}, eV	E_D, eV	R_{ex}, eV	E_g, eV
Cs_4PbCl_6	4.345	5.904				0.153	4.5
Cs_4PbI_6 [9]	3.41	4.19	4.36	4.73	5.2	0.149	3.56
Rb_4PbI_6 [10]	3.41	4.1	4.43	4.73	5.28	0.133	3.543
$CsCl:Pb^{2+}$ [14]	4.42	6.08	6.2	6.32	4.87		
$CsI:Pb^{2+}$ [14]	3.38	4.77	4.9	5.04	5.77		

trum structure (Table). And although the spectra of Cs_4PbCl_6 and Cs_4PbI_6, Rb_4PbI_6 differ significantly in the spectral position of the excitonic bands [9, 10, 15, 16], they are similar in the spectrum structure in the region of A_1 and C_1-bands. Previously it was found that the excitons in Cs_4PbI_6 and Rb_4PbI_6 have cationic nature, and their absorption spectra and spectra of $CsI:Pb^{2+}$ and $RbI:Pb^{2+}$ are conditioned by electronic transitions in $(PbI_6)^{4-}$ octahedrons [9, 10, 15, 16].

The cationic nature of exciton states is typical for halogen compounds of lead. Spectra of binary compounds PbI_2, $PbBr_2$ and $PbCl_2$ are also interpreted based on the cationic exciton model [17, 18]. In the cationic exciton model the long-wave excitonic absorption bands in $PbCl_2$ are associated with the transition $^1S_0 \rightarrow {}^3P_1$ in Pb^{2+} ion. Apparently, the Cs_4PbCl_6 absorption spectrum, as well as $CsCl:Pb^{2+}$ spectrum, is also conditioned by electronic transitions in the lead ion.

It should be noted that in isomorphic series of compounds PbI_2, $PbBr_2$, $PbCl_2$ the absorption edge of two last compounds (3.98 eV and 4.68 eV, respectively) [18, 19] is significantly shifted to the shorter wavelengths relatively, as compared to PbI_2 (2.5 eV) [17]. The same pattern is observed in the impurity spectra of $CsI:Pb^{2+}$, $CsBr:Pb^{2+}$, $CsCl:Pb^{2+}$ [14], and in ternary compounds Cs_4PbI_6 and Cs_4PbCl_6 (see Table). Excitons in all above given compounds have cationic nature, the absorption spectrum of the compounds is treated as electronic transitions in Pb^{2+} ion, and significant difference in the spectral position of the long-wave excitonic bands in iodine, bromine and chlorine compounds, apparently, is conditioned by different number of halogen ions that surround the Pb^{2+} ion, due to differences in the crystal structures of the compounds. So each Pb^{2+} ion is surrounded by 6 I^- ions in PbI_2, and its spectrum is conditioned by the electronic transitions in $(PbI_6)^{4-}$ octahedron [17], and each Pb^{2+} ion is surrounded by 9 Br^- (Cl^-) ions in $PbBr_2$ and $PbCl_2$, that causes a lot larger ionicity of the compounds and therefore the short-wave shift of the absorption edge. Apparently, the same pattern retains in the impurity spectra and in the complex compounds spectra.

Crystalline structure of Cs_4PbCl_6 is insufficiently studied and, as noted above, there are contradictions in the studies of various authors. So the authors of [6] note, that Cs_4PbCl_6 structure belongs to the new structural type. In the monoclinic lattice given in [6], each Pb^{2+} ion is surrounded by 8 Cl^- ions, although the authors identify octahedrons $[PbCl_6]$ as structural elements of the lattice. Apparently, more short-wave spectral position of the long-wavelength excitonic A_1-band in Cs_4PbCl_6, compared with the position of A_1-bands in Cs_4PbI_6 and Rb_4PbI_6 is conditioned by a large coordination number of Cl^- ions in environment of Pb^{2+} ion. The spectra of two other compounds $CsPbCl_3$ and $CsPbI_3$ [5, 9] prove this conclusion. The spectra of isostructural compounds $CsPbCl_3$ and $CsPbI_3$ are close to the spectral position of the band and the spectrum structure, and they are conditioned by electronic transitions in octahedrons $(PbHal_6)^{4-}$ $Hal = Cl,I$, which are the structural elements of the compound crystal lattices [5, 9]. Replacement of Cl^- ions in the environment of Pb^{2+} ions by I^- ions does not lead to significant shift of the excitonic bands in the compounds (spectral position of the long-wavelength excitonic A_1-band is 3.04 eV and 3.013 eV at $T = 90$ K in $CsPbCl_3$ and $CsPbI_3$, respectively).

Besides, the long-wavelength A_1-band spectral position (4.345 eV, 90 K) of the studied compound Cs_4PbCl_6 is close to the long-wavelength excitonic band (4.45 eV, 8 K) of KPb_2Cl_5, which crystallizes in monoclinic lattice where each Pb^{2+} ion is surrounded by 8.5 Cl^- ions [20], the absorption spectrum is also conditioned by the electronic transitions in Pb^{2+} ion [21].

Thus, significant difference in the spectral positions of the excitonic bands in Cs_4PbCl_6 and Cs_4PbI_6, apparently, is conditioned by the difference in their crystalline structures, particularly by a larger number of Cl^- ions in the environment of Pb^{2+}.

3.2. Temperature dependence of parameters of the long-wavelength excitonic band in Cs_4PbCl_6.

Absorption spectra of Cs_4PbCl_6 thin films in the region of long-wavelength excitonic band (3.4–4.8 eV) were measured in the interval of temperatures 90–500 K.

With the temperature increase, A_1-band linearly shifted to the longer wavelengths with $dE_m/dT = -7.1 \cdot 10^{-5}$ eV/K (Fig. 3a). Such shift is typical for majority of ionic crystals, which include currently studied compound, and is due to exciton-phonon interaction. It should be noted as a normal "red" shift of the excitonic band occurs with the temperature increase in Cs_4PbCl_6,

as in pure $PbCl_2$ [22], unlike $CsPbCl_3$, where there was observed the short-wave ("violet") excitonic band shift with T increase [5]. Different types of the temperature dependences of spectral position of the excitonic bands can be explained by the model of exciton-phonon system, that takes into account not only linear but also quadratic interaction by the phonon operators in the Hamiltonian of the exciton-phonon system [23].

Interaction of the excitons with longitudinal optical (LO) phonons dominates in the ionic crystals, and the largest temperature change of the excitonic bands parameters occurs at $\hbar\omega_{LO} \le kT$. Unknown value $\hbar\omega_{LO}$ in Cs_4PbCl_6 was estimated by the linear interpolation from the values $\hbar\omega_{LO} = 21.08$ meV in CsCl and $\hbar\omega_{LO} = 38.93$ meV in $PbCl_2$: $\hbar\omega_{LO} = 24.65$ meV. $\hbar\omega_{LO}$ values in CsCl and $PbCl_2$ were found using known frequencies of asymmetric molecular vibrations of Cs_2Cl_2 and $PbCl_2$ [24]. With the temperature increase, half-width of the A_1-band increases nonlinearly (Fig. 3b). Broadening of the excitonic band due to the exciton-phonon interaction $\Gamma(T)$ for excitons of different dimension d ($d = 1, 2, 3$) in the theory [25] is defined as

$$\Gamma(T) \approx \left[\frac{\pi D^2}{\gamma(d/2)(2\pi B)^{d/2}}\right]^{\frac{2}{4-d}}, \qquad (3)$$

where $\gamma(d/2)$ is gamma function, which depends on d, B is width of excitonic zone and $D^2 = 0.5C^2\hbar\omega_{LO}\mathrm{cth}(\hbar\omega_{LO}/2kT)$, $C^2/2$ is the energy of the lattice relaxation in the exciton state. The contribution of the residual broadening $\Gamma(0)$ due to the lattice defects to the total half-width of the exciton band Γ should be also taken into account. The form of excitonic A_1-band at the temperatures is close to the Gaussian, and at high is the complete Gaussian, so the total half-width Γ can be represented as

$$\Gamma = [\Gamma^2(0) + \Gamma^2(T)]^{1/2}, \qquad (4)$$

where $\Gamma(T)$ is due to Eq.(3) with unknown factor N, that does not depend on T. Processing of the experimental dependence $\Gamma(T)$ using Eq.(3) with different d gives the best match of the theory and experiment with $d = 2$. In this case

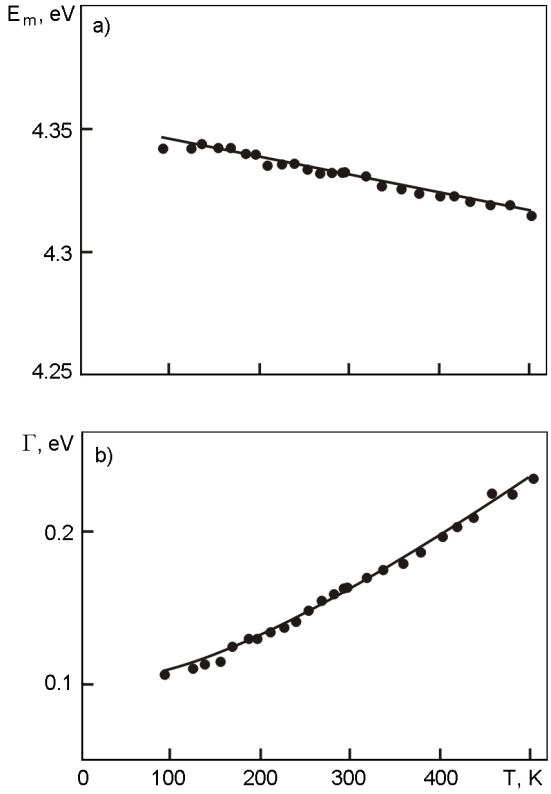

Fig. 3. Temperature dependences of spectral position $E_m(T)$ (a) and half-widths $\Gamma(T)$ (b) of the long-wavelength exciton A_1-band in Cs_4PbCl_6. Fig. 3b: dots — experiment, solid lines — calculation by Eq.(4), Eq(5).

$$\Gamma(T) = N\mathrm{cth}(\hbar\omega_{LO}/2kT) \qquad (5)$$

and dependence $\Gamma(T)$ in Γ^2 on $\mathrm{cth}^2(\hbar\omega_{LO}/2kT)$ is linear. Processing of this dependence by the least squares method gives the values $\Gamma(0) = 0.082\pm0.002$ eV and $N = 0.069\pm0.0005$ eV. Calculated temperature dependence $\Gamma(T)$ by Eq.(4, 5) with found $\Gamma(0)$ and N values has a good match with the experimental one (Fig. 3b). The excitons in Cs_4PbCl_6 have two dimensional character as appears from the analysis of the temperature dependence $\Gamma(T)$.

4. Conclusions

Cs_4PbCl_6 thin films of stoichiometric composition were synthesized. Absorption spectrum of the Cs_4PbCl_6 thin films was studied in the spectral range of 2–6 eV and temperature range 90–500 K. Observed in the spectrum A_1- and C_1-bands correspond to excitonic states localized in sublattice of the compound containing Pb^{2+} ions. The ex-

citons in Cs_4PbCl_6 have cationic nature and relate to the excitons of intermediate coupling.

2D nature of the excitonic states in Cs_4PbCl_6 was established from the analysis of the $\Gamma(T)$ temperature dependence.

References

1. I.I.Ilyasov, *Mag. Inorg. Chem.*, **8**, 1230 (1963).
2. K.Nitsch, A.Cihlar, M.Dusek et al., *Phys. Stat. Sol. (a)*, **135**, 565 (1993).
3. K.Heidrich, H.Kunzel, J.Treusch, *Solid State Commun.*, **25**, 887 (1978).
4. H.Ito, H.Onuki, R.Onaka, *J. Phys. Soc. Japan*, **45**, 2043 (1978).
5. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, V.V.Kovalenko, *Fizika Nizkikh Temp.*, **40**, 882 (2014).
6. V.V.Petrov, A.A.Bogdanova, M.A.Bagina et al., *Crystallography*, **32**, 495 (1987).
7. M.Nikl, E.Mihokova, K.Nitsch, *Solid State Commun.*, **84**, 1089 (1992).
8. S.Kondo, K.Amaya, S.Higuchi et al., *Solid State Commun*, **120**, 141(2001).
9. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, *Optika i Spektr.*, **112**, 95 (2012).
10. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, E.V.Ksenofontova, *Fizika Nizkikh Temp.*, **38**, 1191 (2012).
11. S.P.Liashengko, V.K.Miloslavsky, *Optika i Spektr.*, **16**, 151 (1964).
12. O.N.Yunakova, V.K.Miloslavsky, E.N.Kovalenko, *Optika i Spektr.*, **104**, 631 (2008).
13. S.H.Wemple, *Phys. Rev. B*, **7**, 3767 (1973).
14. S.Radhakrishna, K.P.Pande, *Phys. Rev. B*, **7**, 424 (1973).
15. S.Kondo, A.Masaki, T.Saito, H.Asada, *Solid State Commun*, **124**, 211 (2002).
16. S.Kondo, K.Amaya, T.Saito, *J. Phys.:Condens. Matter.*, **15**, 971 (2003).
17. I.Ch.Schluter, M.Schluter, *Phys. Rev. B*, **9**, 1652 (1974).
18. G.G.Liydya, V.G.Plekhanov, *Optika i Spektr.*, **32**, 86 (1972).
19. A.F.Malysheva, V.G.Plekhanov, *Optika i Spektr.*, **34**, 527 (1973).
20. H.P.Beck, G.Clicque, H.Nau, *Z.Anorg.Allg. Chem.*, **536**, 35 (1986).
21. V.A.Pustovarov, I.N.Ogorodnikov, N.S.Bastrikova et al., *Optika i Spektr.*, **101**, 247 (2006).
22. N.L.Kramarenko, V.K.Miloslavsky, Yu.V.Naboykin, *Ukr. Fiz. Zh.*, **15**, 416 (1970).
23. N.V.Tkach, V.M.Nitsovich, Ya.M.Voronyak, *Ukr. Fiz. Zh.*, **24**, 67 (1979).
24. K.S.Krasnov, Molecular Constants of Inorganic Connections, Chemistry, Leningrad (1979) [in Russian].
25. M.Schreiber, Y.Toyasawa, *J. Phys. Soc. Japan*, **51**, 1528 (1982).