

## Ellipsometric studies of $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$ and $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$ mixed crystals

I.P. Studenyak<sup>1</sup>, M.M. Luchynets<sup>1</sup>, M.M. Pop<sup>1</sup>, V.I. Studenyak<sup>1</sup>,  
A.I. Pogodin<sup>1</sup>, O.P. Kokhan<sup>1</sup>, B. Grančič<sup>2</sup>, P. Kúš<sup>2</sup>

<sup>1</sup>*Uzhhorod National University, Faculty of Physics,  
3, Narodna Sq., 88000 Uzhhorod, Ukraine*

<sup>2</sup>*Faculty of Mathematics, Physics and Informatics, Comenius University,  
Mlynska dolina, 84248 Bratislava, Slovakia  
E-mail: studenyak@dr.com*

**Abstract.**  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals were grown using a direct crystallization technique from the melt. Refractive indices and extinction coefficients for mixed crystals were obtained from the spectral ellipsometry measurements. A nonlinear increase of the refractive indices is revealed with increase of  $\text{Cu}_7\text{PS}_6$  content. The dispersion of refractive indices is described in the framework of Wemple–DiDomenico model. The compositional dependences of optical parameters for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals are analyzed.

**Keywords:** superionic conductors, mixed crystals, spectral ellipsometry, refractive index, extinction coefficient.

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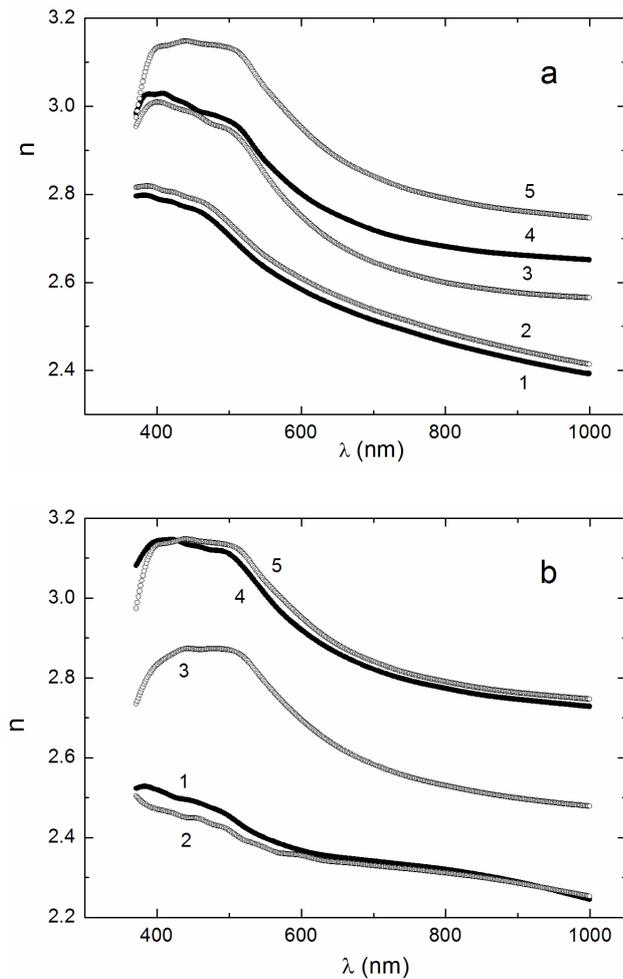
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### 1. Introduction

$\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$  compounds belong to the argyrodite-type superionic conductors [1]. They are promising materials for applications in solid state ionics as the materials for solid state batteries, supercapacitors and electrochemical sensors. At room temperature  $\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$  and  $\text{Cu}_7\text{PS}_6$  crystallize in the cubic crystal system ( $F\bar{4}3m$  and  $P2_13$  space groups, respectively) [1, 2]. The most investigated in this family are  $\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$  crystals that show a high value of electric conductivity at room temperature, comparable with the conductivity of the best solid electrolytes [1]. At low temperatures  $\text{Cu}_6\text{PS}_5\text{I}$  crystal undergoes two phase transitions (PTs), one of them being a first-order superionic and ferroelastic PT at  $T_I = 144\dots 169$  K, the other is a second-order structural PT at  $T_{II} = (269 \pm 2)$  K [3]. Another situation is realized in  $\text{Cu}_6\text{PS}_5\text{Br}$  crystal: with decreasing temperature it undergoes two phase transitions – the ferroelastic one at  $T_{II} = (268 \pm 2)$  K and superionic transition at  $T_I = (166\dots 180)$  K [4, 5].

It is shown that  $\text{Cu}_7\text{PS}_6$  compound is formed with a large excess of  $\text{S}^{2-}$  anions and in a simplified case its structure can be viewed as a  $\text{Cu}_2\text{S}$  matrix containing isolated  $[\text{PS}_4]^{3-}$  ions [2]. In  $\text{Cu}_7\text{PS}_6$  the PT is observed at

515 K from the high-temperature phase with  $F\bar{4}3m$  symmetry to the low-temperature phase with  $P2_13$  symmetry. Calorimetric studies of  $\text{Cu}_7\text{PS}_6$  showed no phase transitions within the temperature range of 100 to 400 K [6]. Electrical properties of  $\text{Cu}_7\text{PS}_6$  crystal grown using direct crystallization were studied in the frequency range  $10\dots 10^{10}$  Hz and temperature interval 296...351 K in Ref. [7]. The main feature of argyrodites is ability to create solid solution rows on their base [8, 9]. The halogen-substituted  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals were investigated in Refs. [10, 11]. In Ref. [10], the structural peculiarities of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  are studied and discussed. The crystal structure, as being based on the X-ray diffraction data, shows the face-centred cubic lattice for  $\text{Cu}_6\text{PS}_5\text{I}$ -rich solid solutions ( $x < 0.12$ ) and primitive cubic lattice for  $\text{Cu}_7\text{PS}_6$ -rich ( $0.84 < x < 1$ ) solid solutions [10]. Structural studies of  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals reveal a face-centred cubic lattice ( $F\bar{4}3m$  space group) for  $\text{Cu}_6\text{PS}_5\text{Br}$ -rich crystals ( $0 < x < 0.4$ ) and a primitive cubic lattice ( $P2_13$  space group) for  $\text{Cu}_7\text{PS}_6$ -rich ( $0.4 < x < 1$ ) crystals [11]. These structural data correlate with the Raman spectra and compositional dependence of the energy gap in the mixed crystals under investigations [10, 11].

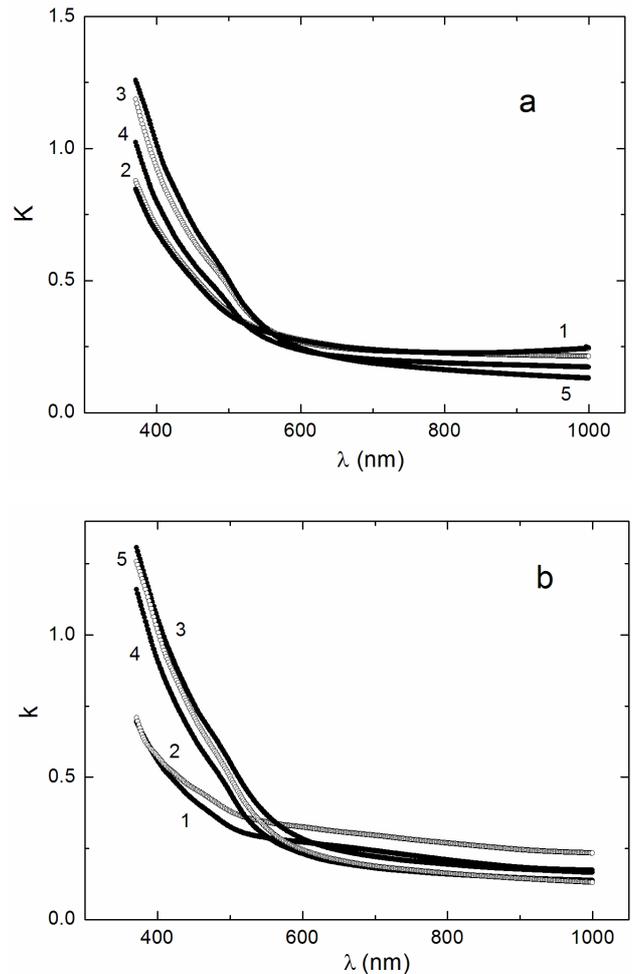


**Fig. 1.** Spectral dependences of the refractive index  $n$  for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (a) and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (b) mixed crystals: a)  $\text{Cu}_6\text{PS}_5\text{I}$  (1),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$  (2),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$  (3),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$  (4),  $\text{Cu}_7\text{PS}_6$  (5); b)  $\text{Cu}_6\text{PS}_5\text{Br}$  (1),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$  (2),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$  (3),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$  (4),  $\text{Cu}_7\text{PS}_6$  (5).

In this paper, we report on the ellipsometric studies of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals obtained by means of directed crystallization from the melt. Besides, the paper is aimed at the analysis of refractometric data in the framework of Wemple–DiDomenico model.

## 2. Experimental

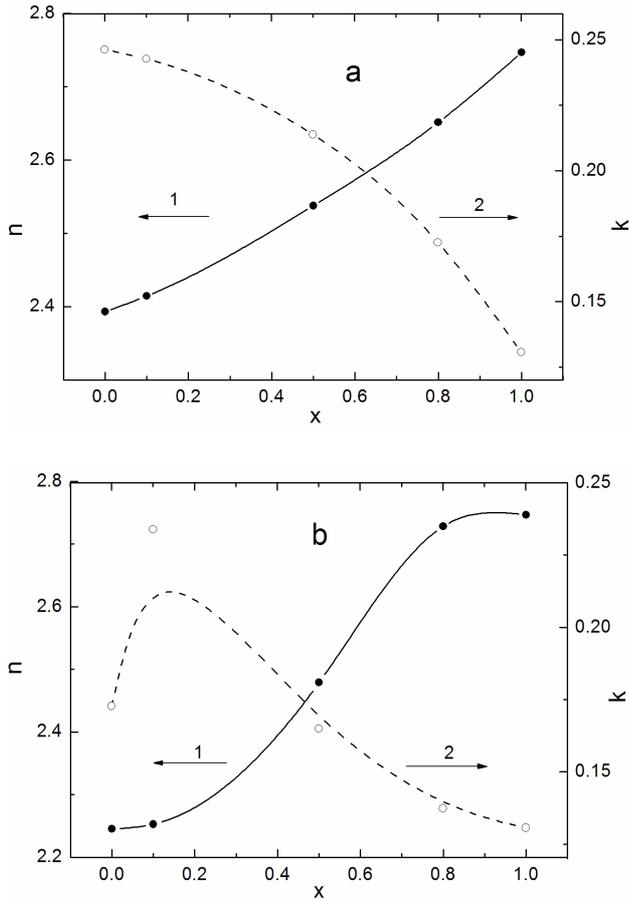
$(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals were grown using a direct crystallization technique from the melt. Synthesis of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  compounds was performed using the following procedure: heating at the rate close to 50 K/h up to  $(673 \pm 5)$  K, ageing at this temperature for 24 h, then heating the “hot” zone to  $(1330 \pm 5)$  K as well as the “cold” zone to



**Fig. 2.** Spectral dependences of the extinction coefficient  $k$  for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (a) and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (b) mixed crystals: a)  $\text{Cu}_6\text{PS}_5\text{I}$  (1),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$  (2),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$  (3),  $(\text{Cu}_6\text{PS}_5\text{I})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$  (4),  $\text{Cu}_7\text{PS}_6$  (5); b)  $\text{Cu}_6\text{PS}_5\text{Br}$  (1),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$  (2),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$  (3),  $(\text{Cu}_6\text{PS}_5\text{Br})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$  (4),  $\text{Cu}_7\text{PS}_6$  (5).

$(973 \pm 5)$  K. At the temperature of  $(1330 \pm 5)$  K the mixture was kept for 72 h and then the melting zone was heated up to  $(1380 \pm 5)$  K (which is 50 K above the melting point) and kept at this temperature for 24 h. Seeding was performed for 48 h in the lower part of the container. The crystallization front rate was 3 mm/day. Subsequent annealing of the silica glass ampoule with the crystal was performed in the “cold” zone at  $(973 \pm 5)$  K for 48 h. The procedure resulted in  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals, 45...50 mm long with the diameter of 10...12 mm.

Spectroscopic ellipsometer M-2000V was used for the measurements of the optical constants of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals. Measurements were carried out in the spectral range 370...1000 nm at the angle of incidence close to  $70^\circ$ .

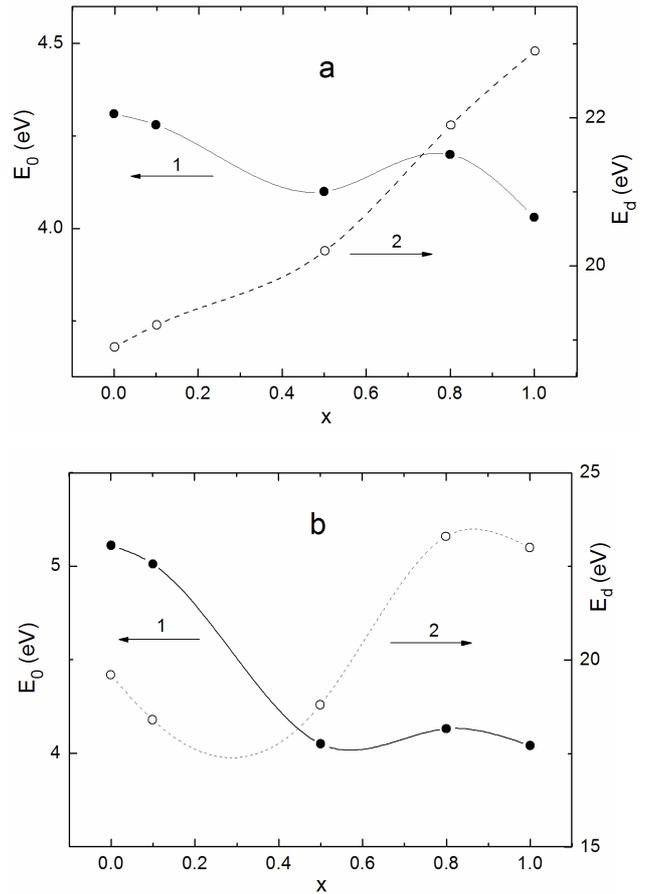


**Fig. 3.** Compositional dependences of the refractive index  $n$  (1) and extinction coefficient  $k$  (2) for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (a) and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (b) mixed crystals.

### 3. Results and discussion

Refractive indices  $n$  and extinction coefficients  $k$  for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals were obtained from the spectral ellipsometry measurements which were carried out within the spectral range 370 to 1000 nm (Figs. 1 and 2). In the region of transparency, the refractive index dispersion is observed, besides, the refractive index increases when approaching to the absorption edge. The one anomaly (in the form of broader and smeared maximum) of refractive index is revealed in the region of the extinction coefficient increase (Figs. 1 and 2). The observed anomaly corresponds to the band-to-band optical transition, and the spectral position of this anomaly relates to the energy gap value. It should be noted that in the region of extinction coefficient  $k$  increase, the knee was observed in the spectral dependences of  $k$ , the spectral position of which is related with the value of band gap energy.

Fig. 3 presents the compositional dependences of the refractive index and extinction coefficient at  $\lambda = 1 \mu\text{m}$  obtained from spectral ellipsometry measurements for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals. With increasing the  $\text{Cu}_7\text{PS}_6$  content the non-linear increase of refractive index as well as the non-linear



**Fig. 4.** Compositional dependences of Wemple and DiDomenico parameters  $E_0$  (1) and  $E_d$  (2) for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (a) and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  (b) mixed crystals.

decrease of extinction coefficient are also observed, moreover, the above mentioned compositional dependences in  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals, contrary to those in  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals, is monotonous without any peculiarities.

A number of models which described the refractive index dispersion are based on the relationship between the refractive index and the energy gap [12–14]. Among them one should, first of all, mention the well-known Wemple–DiDomenico (WDD) model [13]. Wemple and DiDomenico have proposed the model where the refractive index dispersion is studied in the transparency region below the gap, using the single-oscillator approximation [13].

In this paper, the dispersion dependences of refractive indices were analyzed in the framework of the WDD model [13]. In this case, the energy dependence of refractive index can be described using the relationship [13]

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

where  $E_0$  is the single-oscillator energy, and  $E_d$  is the

**Table 1.** Wemple and DiDomenico parameters, optical band gap, static refractive index and ionicity for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals.

Crystal	$E_0$ (eV)	$E_d$ (eV)	$E_g^{opt}$ (eV)	$n_0$	$f_i$
$\text{Cu}_6\text{PS}_5\text{I}$	4.31	18.9	2.16	2.321	0.48
$(\text{Cu}_6\text{PS}_5\text{I})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$	4.28	19.2	2.14	2.340	0.47
$(\text{Cu}_6\text{PS}_5\text{I})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$	4.10	20.2	2.05	2.433	0.45
$(\text{Cu}_6\text{PS}_5\text{I})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$	4.20	21.9	2.10	2.490	0.44
$\text{Cu}_7\text{PS}_6$	4.03	22.9	2.02	2.587	0.42

**Table 2.** Wemple and DiDomenico parameters, optical band gap, static refractive index and ionicity for  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals.

Crystal	$E_0$ (eV)	$E_d$ (eV)	$E_g^{opt}$ (eV)	$n_0$	$f_i$
$\text{Cu}_6\text{PS}_5\text{Br}$	5.11	19.6	2.56	2.199	0.52
$(\text{Cu}_6\text{PS}_5\text{Br})_{0.9}(\text{Cu}_7\text{PS}_6)_{0.1}$	5.01	18.4	2.51	2.160	0.52
$(\text{Cu}_6\text{PS}_5\text{Br})_{0.5}(\text{Cu}_7\text{PS}_6)_{0.5}$	4.05	18.8	2.03	2.375	0.46
$(\text{Cu}_6\text{PS}_5\text{Br})_{0.2}(\text{Cu}_7\text{PS}_6)_{0.8}$	4.13	23.3	2.06	2.579	0.42
$\text{Cu}_7\text{PS}_6$	4.04	23.0	2.02	2.587	0.42

dispersion energy. The dispersion energy  $E_d$  characterizes the average strength of interband optical transitions and relates with the changes in the structural ordering of the material (ionicity, anion valency and coordination number of the material). From the dependences  $(n^2 - 1)^{-1}$  on  $E^2$  by using Eq. (1) the  $E_0$  and  $E_d$  values were determined. The above mentioned parameters of the WDD model for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals are listed in Tables 1 and 2. It is shown that with the increase of  $\text{Cu}_7\text{PS}_6$  content the single-oscillator energy  $E_0$  nonlinearly decreases as well as the dispersion energy  $E_d$  nonlinearly increases for both  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals (Fig. 4). The nonlinear and nonmonotonous compositional behaviour of the parameters of the WDD model (Fig. 4) and optical constants (Fig. 3b) is explained by the structural transformation during the transition from  $\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$  compound to  $\text{Cu}_7\text{PS}_6$  compound [10, 11] as well as the compositional disordering of crystal lattice typical for argyrodite-type mixed crystals [8, 9].

According to the relation  $E_0 \approx 2E_g^{opt}$  [15], the optical band gap values  $E_g^{opt}$  were estimated and presented in Tables 1 and 2. It should be noted that  $E_g^{opt}$  values and the energy pseudogap  $E_g$  ones obtained from the analysis of diffuse reflection spectra for  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals do not differ more than 10% [11]. The transition from halogen-containing  $\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$  to halogen-free  $\text{Cu}_7\text{PS}_6$  argyrodites leads to the optical band gap  $E_g^{opt}$  decrease in  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals.

The static refractive index  $n_0$  for the mixed crystals under investigations was calculated using the equation

$$n_0 = \left[ 1 + \frac{E_d}{E_0} \right]^{1/2}. \quad (2)$$

The variation of the static refractive index  $n_0$  on the composition of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals is presented in

Tables 1 and 2. It is revealed that with the increase of  $\text{Cu}_7\text{PS}_6$  content, the static refractive indices  $n_0$  increase for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals.

By using the parameters of the WDD model, one can calculate this important parameter for superionic conductors as the ionicity [16]

$$f_i = \left[ \frac{E_0}{E_d} \right]^{1/2}. \quad (3)$$

The values of ionicity for  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals are presented in Tables 1 and 2. It is shown that, with increase of the  $\text{Cu}_7\text{PS}_6$  content, the ionicity of mixed crystals under investigation is decreased. This fact is in a good agreement with the recent studies of electrical conductivity in  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$ -based composites [17]. It is shown in Ref. [17] that the ratio of ionic to electronic components of electrical conductivity decreases at the transition from halogen-containing  $\text{Cu}_6\text{PS}_5\text{I}$  compound to halogen-free  $\text{Cu}_7\text{PS}_6$  compound.

#### 4. Conclusions

$(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals were obtained using a direct crystallization technique from the melt. The ellipsometric studies were performed in the spectral range 370 to 1000 nm. Optical constants (refractive indices and extinction coefficients) for mixed crystals were obtained from the spectral ellipsometry measurements. In the region of transparency, the refractive indices dispersion is observed, the refractive indices increase when approaching to the absorption edge, and the one anomaly of refractive indices is revealed in the range of the extinction coefficients increase. The refractive indices anomaly corresponds to the band-to-band optical transition, and the spectral position of this anomaly relates to the energy gap value.

The dispersion of refractive indices is described in the framework of the Wemple–DiDomenico model. The nonlinear increase of the refractive indices and the nonlinear decrease of the optical band gap  $E_g^{opt}$ , the nonlinear decrease of the single-oscillator energy  $E_0$  and the nonlinear increase of the dispersion energy  $E_d$  as well as the ionicity decrease are revealed with increase of  $\text{Cu}_7\text{PS}_6$  content in  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  and  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals.

## References

1. Nilges T., Pfitzner A. A structural differentiation of quaternary copper argyrodites: Structure – property relations of high temperature ion conductors. *Z. Kristallogr.* 2005. **220**. P. 281–294.
2. Andrae H., Blachnik R. Metal sulphide-tetraphosphorusdecasulphide phase diagrams. *J. Alloys and Compounds.* 1992. **189**. P. 209–215. [https://doi.org/10.1016/0925-8388\(92\)90709-I](https://doi.org/10.1016/0925-8388(92)90709-I).
3. Gagor A., Pietraszko A., Kaynts D. Diffusion paths formation for  $\text{Cu}^+$  ions in superionic  $\text{Cu}_6\text{PS}_5\text{I}$  single crystals studied in terms of structural phase transition. *J. Solid State Chem.* 2005. **178**, Issue 11. P. 3366–3375. <https://doi.org/10.1016/j.jssc.2005.08.015>.
4. Haznar A., Pietraszko A., Studenyak I.P. X-ray study of the superionic phase transition in  $\text{Cu}_6\text{PS}_5\text{Br}$ . *Solid State Ionics.* 1999. **119**. P. 31–36. [https://doi.org/10.1016/S0167-2738\(98\)00479-2](https://doi.org/10.1016/S0167-2738(98)00479-2).
5. Studenyak I.P., Kranjčec M., Kovacs Gy.Sh., Panko V.V., Azhnyuk Yu.M., Desnica I.D., Borets O.M., Voroshilov Yu.V. Fundamental optical absorption edge and exciton-phonon interaction in of  $\text{Cu}_6\text{PS}_5\text{Br}$  superionic ferroelastic. *Mat. Sci. Eng. B.* 1998. **52**, Issue 2-3. P. 202–207. [https://doi.org/10.1016/S0921-5107\(97\)00278-X](https://doi.org/10.1016/S0921-5107(97)00278-X).
6. Fiechter S., Gmelin E. Thermochemical data and phase transition of argyrodite-type ionic conductors  $\text{Me}_6\text{PS}_5\text{Hal}$  and  $\text{Me}_7\text{PS}_6$  (Me = Cu, Ag; Hal = Cl, Br, I). *Thermochimica Acta.* 1985. **87**. P. 319–334. [https://doi.org/10.1016/0040-6031\(85\)85351-X](https://doi.org/10.1016/0040-6031(85)85351-X).
7. Šalkus T., Kežionis A., Banyš J., Izai V.Yu., Pogodin A.I., Kokhan O.P., Sidey V.I., Sabov M.Yu., Studenyak I.P. Structural and electrical properties of argyrodite-type  $\text{Cu}_7\text{PS}_6$  crystal. *Lithuanian Journal of Physics.* 2017. **57**. P. 243–251.
8. Kranjčec M., Studenyak I.P., Bilanchuk V.V., Dyordyay V.S., Panko V.V. Compositional behaviour of Urbach absorption edge and exciton-phonon interaction parameters in  $\text{Cu}_6\text{PS}_5\text{I}_{1-x}\text{Br}_x$  superionic mixed crystals. *J. Phys. Chem. Solids.* 2004. **65**, Issue 5. P. 1015–1020. <https://doi.org/10.1016/j.jpcs.2003.10.061>.
9. Studenyak I.P., Kranjčec M., Kurik M.V. Urbach rule and disordering processes in  $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{Br}_{1-y}\text{I}_y$  superionic conductors. *J. Phys. Chem. Solids.* 2006. **67**. P. 807–817. <https://doi.org/10.1016/j.jpcs.2005.10.184>.
10. Studenyak I.P., Luchynets M.M., Izai V.Yu., Pogodin A.I. *et al.* Structure and Raman spectra of  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals. *SPQEO.* 2017. **20**. P. 369–374. <https://doi.org/10.15407/spqeo20.03.369>.
11. Studenyak I.P., Luchynets M.M., Izai V.Yu., Pogodin A.I., Kokhan O.P., Azhniuk Yu.M., Zahn D.R.T. Structural and optical properties of  $(\text{Cu}_6\text{PS}_5\text{Br})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals. *J. Alloys and Compounds.* 2018. **782**. P. 586–591. <https://doi.org/10.1016/j.jallcom.2018.12.214>.
12. Moss T.S. Relations between the refractive index and energy gap of semiconductors. *phys. status solidi (b).* 1985. **131**, Issue 2. P. 415–427. <https://doi.org/10.1002/pssb.2221310202>.
13. Wemple S.H., DiDomenico M., Jr. Behaviour of the dielectric constant in covalent and ionic materials. *Phys. Rev. B.* 1971. **3**. P. 1338–1352. <http://dx.doi.org/10.1103/PhysRevB.3.1338>.
14. Gupta V.P., Ravindra N.M. Comments on the Moss formula. *phys. status solidi (b).* 1980. **100**, No 2. P. 715–719. <https://doi.org/10.1002/pssb.2221000240>.
15. Tanaka K. Optical properties and photoinduced changes in amorphous As-S films. *Thin Solid Films.* 1980. **66**, Issue 3. P. 271–279. [https://doi.org/10.1016/0040-6090\(80\)90381-8](https://doi.org/10.1016/0040-6090(80)90381-8).
16. Tubbs M.S. A spectroscopic interpretation of crystalline ionicity. *phys. status solidi (b).* 1970. **41**, Issue 1. P. K61–K64. <https://doi.org/10.1002/pssb.19700410164>.
17. Izai V.Yu., Luchynets M.M., Studenyak I.P. *et al.* Preparation and electrical properties of composites based on  $(\text{Cu}_6\text{PS}_5\text{I})_{1-x}(\text{Cu}_7\text{PS}_6)_x$  mixed crystals. *Semiconductor Physics, Quantum Electronics & Optoelectronics.* 2019. **22**. P. 182–187. <https://doi.org/10.15407/spqeo22.02.182>.

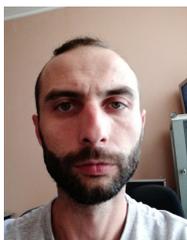
## Authors and CV



**Ihor P. Studenyak**, born in 1960, defended his Dr. Sc. degree in Physics and Mathematics in 2003 and became full professor in 2004. Vice-rector for research at the Uzhhorod National University, Ukraine. Authored over 200 publications, 120 patents, 15 textbooks. The area of his scientific interests includes physical properties of semiconductors, ferroics and superionic conductors.



**Mykhailo M. Luchynets**, born in 1994. Currently he is PhD student of the Uzhhorod National University, Faculty of Physics. Authored 17 scientific publications and 2 patents. The area of scientific interests is electrical and optical properties of superionic conductors.



**Mykhailo M. Pop**, born in 1982, defended his PhD thesis in Physics and Mathematics in 2016. Lecturer and Researcher at the Uzhhorod National University, Ukraine. Authored over 40 publications. The area of his scientific interests includes physical properties of semiconductors, chalcogenide glasses and films.



**Viktor I. Studenyak**, born in 1997. At present he is a master student at the Faculty of Physics, Uzhhorod National University. Authored 7 articles and 5 patents. The area of his scientific interests includes optical properties of superionic conductors.



**Artem I. Pogodin**, born in 1988, defended his PhD thesis in inorganic chemistry in 2016. Senior researcher at the Uzhhorod National University. Authored over 35 articles and 25 patents. The area of his scientific interests includes solid state chemistry, crystal growth, and materials science.



**Oleksandr P. Kokhan**, born in 1958, defended his PhD thesis in inorganic chemistry in 1996 and became docent in 2002. Associate professor of Inorganic Chemistry department at the Uzhhorod National University. Authored over 80 articles and 40 patents. The area of his scientific interests includes inorganic chemistry, solid state chemistry, crystal growth, materials science.



**Branislav Grančič**, born in 1978, defended his PhD thesis in solid state physics in 2008. Scientific researcher at the Department of experimental physics at Comenius University in Bratislava (Slovakia). Authored over 30 articles in referred journals. The area of his scientific interests includes thin film deposition and materials science.



**Peter Kúš**, born in 1959, defended his Dr. Sc. degree in 2004 and became full professor in 2005. Professor of Department of experimental physics at Comenius University in Bratislava (Slovakia). Authored over 100 articles in refereed journals. The area of scientific interests includes solid state physics, superconductivity and materials science.