

CRYSTAL GROWTH, STRUCTURAL AND OPTICAL PARAMETERS OF $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ SUPERIONIC CONDUCTORS

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Single crystals of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ solid solutions are obtained by chemical transport reactions. The crystals are investigated by X-ray and spectrometric techniques at room temperature. The effect of $\text{Br} \rightarrow \text{I}$ anionic substitution upon the absorption edge energy position and refractive index dispersion in $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals is studied. The compositional variation of the cubic lattice parameter, density, optical pseudogap and refractive index are analyzed.

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1. Introduction

$\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{I}$ crystals belong to the family of compounds with argyrodite structure [1,2]. They are characterized by high concentration of disordered vacancies and reveal both superionic and ferroelastic properties. High ionic conductivity at room temperature [3] enables their possible applications as solid-electrolyte energy sources and sensors. Besides, they are of interest as nonlinear optical materials [1], and the synthesis of solid solutions of this family enables their parameters to be varied in a broad range.

At room temperature $\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{I}$ crystals belong to cubic syngony ($F\bar{4}3m$ space group) [1]. At low temperatures in $\text{Cu}_6\text{PS}_5\text{Br(I)}$ crystals two phase transitions (PTs) are realized: a ferroelastic one at $T_c=(269\pm 2)$ K for $\text{Cu}_6\text{PS}_5\text{I}$ and $T_c=(268\pm 2)$ K for $\text{Cu}_6\text{PS}_5\text{Br}$; a superionic one at $T_s=(165-175)$ K for $\text{Cu}_6\text{PS}_5\text{I}$ and $T_s=(166-180)$ K for $\text{Cu}_6\text{PS}_5\text{Br}$ [2]. $\text{Cu}_6\text{PS}_5\text{Br}$ crystals below the ferroelastic PT temperature belong to monoclinic syngony (Cc space group), and the superionic PT possesses the features of an isostructural transformation [4]. The symmetry of the low-temperature phases in $\text{Cu}_6\text{PS}_5\text{I}$ remains undetermined yet. Calorimetric, acoustic and optical properties of $\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{I}$ crystals were studied in a number of papers (Refs. [2–10]).

The optical absorption edge of $\text{Cu}_6\text{PS}_5\text{Br}$ and $\text{Cu}_6\text{PS}_5\text{I}$ crystals was studied in Refs. [7–9]. At low temperatures in the range of direct optical transitions exciton absorption bands are observed, broadening with the temperature increase and smearing at $T > T_s$. Besides, at $T \geq T_s$ at the absorption edge exponential sections appear, whose temperature behaviour is described by the Urbach rule. As shown in [8], the absorption edge is essentially affected by dynamic structural disordering, caused by the cation sublattice disordering due to Cu^+ ion migration, as well as static structural disordering, caused by the difference in the crystal growth procedure.

This paper is aimed at studying the compositional behaviour of the lattice parameter, density, optical pseudogap and refractive index in $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ ($0 \leq x \leq 1$) solid solutions, as well as the effect of $\text{Br} \rightarrow \text{I}$ anionic substitution upon the optical absorption edge shape and refractive index dispersion.

2. Experimental

Single crystals of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ solid solutions were grown by chemical transport reactions. High-purity Cu, P, S and copper monohalides, obtained by precipitation from aqueous solutions and distilled in vacuum, were used as initial components for synthesis. The growth was carried out from the Cu_2S -enriched mixture; copper monohalides being used as transport agents (10–20 mg per 1 cm^3 of the ampoule free volume). The temperature zones were kept in the interval 950–1100 K. The difference between the temperature zones was 30–50 K. The single crystals were grown in the shape of reddish orange $5 \times 5 \times 2 \text{ mm}^3$ -size plates or $4 \times 4 \times 4 \text{ mm}^3$ -size distorted tetrahedra.

Transmission and reflection measurements were carried out for the samples, oriented in the cubic phase, the incident light propagating along [100] crystallographic direction. The experimental setup and technique for the absorption edge studies are described in [8]. The samples of different thickness ($d \approx 20\text{--}200 \mu\text{m}$) were used for the measurements, the absorption coefficient error $\Delta\alpha/\alpha$ did not exceed 10%. For X-ray studies of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals DRON-3 diffractometer was used (conventional θ - 2θ scanning method, Bragg angle $2\theta \approx 10\text{--}60^\circ$, Ni-filtered $\text{CuK}\alpha$ radiation).

3. Results and discussion

The performed X-ray studies have shown a continuous row of substitutive solid solutions with $F\bar{4}3m$ cubic symmetry at room temperature to be formed in $\text{Cu}_6\text{PS}_5\text{Br} - \text{Cu}_6\text{PS}_5\text{I}$ system. The lattice parameter a increases from $a = 9.723 \text{ \AA}$ for $\text{Cu}_6\text{PS}_5\text{Br}$ crystal to $a = 9.792 \text{ \AA}$ for $\text{Cu}_6\text{PS}_5\text{I}$ crystal (Fig. 1a), positive deviation from the Végard law being observed. From the experimental values $a(x)$ in accordance with the known formula the compositional dependence of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystal density was calculated (Fig. 1a):

$$\rho(x) = \frac{Z \cdot \mu(x)}{N_A \cdot a^3(x)}, \quad (1)$$

where $\mu(x)$ is molecular mass, N_A – Avogadro constant, $Z=4$. The linear dependence $\mu(x)$ was assumed at the calculations of $\rho(x)$. The density of the solid solution crystals is shown to increase with x , the plot being nonlinear, downward-bowed.

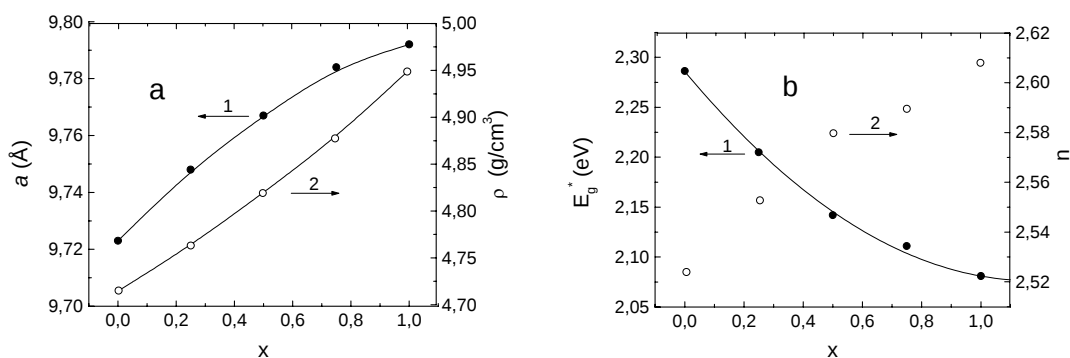


Fig. 1. (a) Compositional dependences of cubic crystal lattice parameter a (1) and the calculated density ρ (2) at room temperature for $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals; (b) Compositional dependences of optical pseudogap E_g^* (1) and refractive index n (2) at room temperature for $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$. The experimental values of E_g^* are represented by dark circles, and the calculated dependence, obtained from Eq. (2), – by solid line.

Optical absorption edge studies for $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ solid solution crystals at $T=300$ K have shown that in the range of direct optical transitions the absorption edge is of exponential shape (Fig.2). At the substitution of bromine by iodine atoms the low-energy shift of the absorption edge is observed. The energy width of the exponential absorption edge (the value, inverse to the absorption edge slope) nonlinearly decreases from 23.8 meV for $\text{Cu}_6\text{PS}_5\text{Br}$ to 19.3 meV for $\text{Cu}_6\text{PS}_5\text{I}$. The variation of the absorption edge energy position and energy width at the Br→I anion substitution is determined by the effect of compositional disordering which is typically observed for crystalline solid solutions [11].

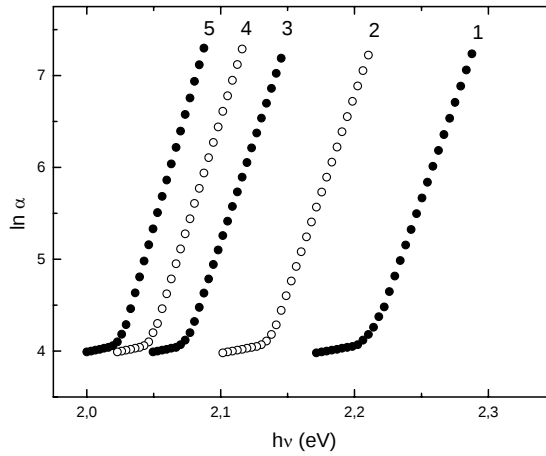


Fig. 2. Absorption coefficient spectral dependences for $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals at $T=300$ K and various values of x : 1 – 0.0; 2 – 0.25; 3 – 0.5; 4 – 0.75; 5 – 1.0

Due to the direct optical transitions being masked by long-wavelength Urbach absorption tails, the true value of the direct energy gap cannot be determined. It is shown [9] that in such case optical pseudogap value E_g^* is often used, corresponding to the absorption edge energy position at fixed absorption level $\alpha=10^3 \text{ cm}^{-1}$. The compositional dependence of $E_g^*(x)$, shown in Fig. 1b, is nonlinear, downward-bowed. The compositional variation of optical energy gap can be described by [12]:

$$E_g(x) = E_g(0) + [E_g(1) - E_g(0)]x - cx(1-x), \quad (2)$$

where $E_g(x=0) \equiv E_g(0)$ and $E_g(x=1) \equiv E_g(1)$ are the energy gap values for the pure crystals in the solid solutions row, c – a so-called bowing parameter, being the measure of deviation from linearity for the $E_g(x)$ function. The best agreement at the description of the experimental dependence $E_g^*(x)$ by Eq. (2) is obtained at the parameter values $E_g^*(0)=2.286$ eV, $E_g^*(1)=2.081$ eV and $c = 0.15$ eV (the positive value of c indicated downward bowing in the $E_g^*(x)$ plot).

In the literature a number of empirical formulae (Moss, Ravindra, Wemple–DiDomenico etc.) are available, relating the energy gap value E_g to refractive index n [13–17]. They differ in fitting parameters and rather accurately describe the relation between E_g and n . Here we use the optical-refractometric relation [16, 17], since its reliability has been shown for over 150 various nonmetallic materials, including $\text{Cu}_6\text{PS}_5\text{I}$ and $\text{Cu}_6\text{PS}_5\text{Br}$ crystals [10]:

$$\frac{1}{3} \frac{n^2(h\nu) + 2}{n^2(h\nu) - 1} = \left(\frac{\eta_s}{2} \right)^s \left(1 + \frac{E_g^*}{E_{pv}} \right)^s - \left(\frac{h\nu}{E_s} \right)^s, \quad (3)$$

where $s=2$ for the medium part of the transparency range and $s=3$ for its high-energy part, η_s and E_s are fitting parameters. The energy of the valence electron plasma vibrations E_{pv} is determined as [10]

$$E_{pv} = 28.82 \sqrt{\frac{n_v \rho}{\mu}} \text{ (eV)}, \quad (4)$$

where n_v is the number of valence electrons per formula unit. Taking into account the fact that the experimental dependences $n(\lambda)$ for $\text{Cu}_6\text{PS}_5\text{I}$ and $\text{Cu}_6\text{PS}_5\text{Br}$ are well described by Eq. (3), we used the latter for the calculations of $n(\lambda)$ dependences for the solid solution crystals, shown in Fig. 3. The experimental values of $E_g^*(x)$ (Fig. 1b) were used, $E_{pv}(x)$ values were calculated from Eq. (4), and the linearity of the compositional dependence of the fitting parameters η_s and E_s was taken into account (the values of the above parameters used for the $n(\lambda)$ dispersion calculations are listed in Table 1). Based on the calculated dispersion $n(\lambda)$ the compositional dependence $n(x)$ at $\lambda=5 \mu\text{m}$, shown in Fig. 1b, was obtained. The refractive index $n(x)$ is shown to increase nonlinearly with x with upward bowing.

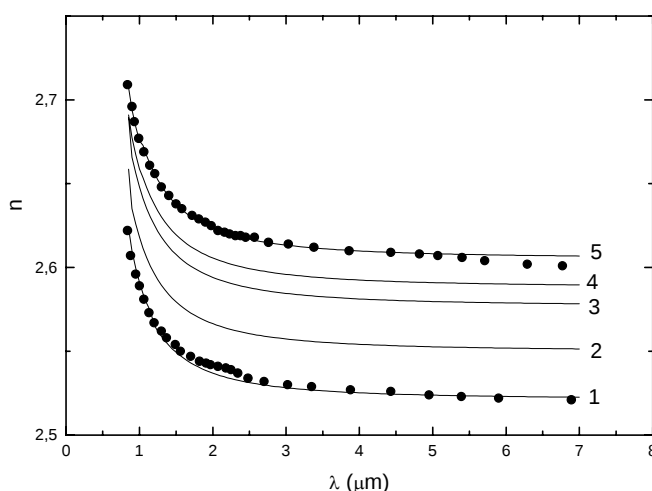


Fig. 3. Dispersion dependences of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystal refractive indices at room temperature for various x values: 1 – 0.0; 2 – 0.25; 3 – 0.5; 4 – 0.75; 5 – 1.0. The experimental values of the refractive indices are shown by dark circles, and the calculated plots, obtained from Eq. (3), by solid lines.

Table 1. Optical and refractometric parameters of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals

Crystal	E_g^* (eV)	$n(\lambda=5 \mu\text{m})$	E_{pv} (eV)	E_2 (eV)	E_3 (eV)	η_2	η_3
$\text{Cu}_6\text{PS}_5\text{Br}$	2.286	2.524	16.97	11.90	6.21	1.271	1.4140
$\text{Cu}_6\text{PS}_5(\text{Br}_{0.75}\text{I}_{0.25})$	2.205	2.553	16.91	11.88	6.28	1.270	1.4142
$\text{Cu}_6\text{PS}_5(\text{Br}_{0.5}\text{I}_{0.5})$	2.142	2.580	16.86	11.85	6.35	1.269	1.4145
$\text{Cu}_6\text{PS}_5(\text{Br}_{0.25}\text{I}_{0.75})$	2.111	2.590	16.82	11.83	6.41	1.267	1.4148
$\text{Cu}_6\text{PS}_5\text{I}$	2.081	2.608	16.80	11.80	6.48	1.266	1.4150

Now compare the specific features of the compositional behaviour of structural and optical-refractometric parameters in $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ crystals and $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals, having been studied earlier [18]. The common feature at the anionic substitution of S and Br atoms by heavier Se and I atoms, respectively, is the increase of the lattice parameter, density and refractive index and the decrease of the optical pseudogap. However, the character of the nonlinearity (downward or upward bowing) is different for these substitutions, e. g. at $\text{S} \rightarrow \text{Se}$ anionic substitution the optical pseudogap value decreases with the upward bowing, while at $\text{Br} \rightarrow \text{I}$ substitution it decreases with the downward bowing. According to [12], the bowing of the $E_g^*(x)$ plot can result from the following factors: (i) energy band deformation due to the solid solution lattice parameter variation; (ii) electronegativity variation; (iii) structural changes due to the anion bond length variation. Note that $\text{S} \rightarrow \text{Se}$ and $\text{Br} \rightarrow \text{I}$ substitution results in the same character of electronegativity variation, namely to its decrease [19]. Besides, substitution of S by Se atoms with bigger radius results in the increase of Se–Se and Se–I anion bond lengths with respect to S–S and S–I bond length. Similarly, substitution of Br by I atoms with bigger radius also results in the increase of S–I bond length with respect to S–Br. Thus, the difference in the $E_g^*(x)$ plot nonlinearity character should be determined by the difference in the energy band deformation in the solid solutions at $\text{S} \rightarrow \text{Se}$ and $\text{Br} \rightarrow \text{I}$ due to the different nonlinearity character of the lattice parameter compositional dependence $a(x)$. The downward-bowing increase of the cubic lattice parameter at $\text{S} \rightarrow \text{Se}$ substitution in $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals [18] is the evidence for the fact that at small concentrations of Se atoms ($x < 0.5$) the crystal lattice deformation due to the statistical substitution of atoms takes place slowly, and at $x > 0.5$ – much faster. For the crystals under investigation the increase of $a(x)$ (Fig. 1a) is upward-bowed. This is evidently related to the specific features of argyrodite crystal structure, resulting in the following: at the initial stage (at small concentrations of Se atoms) $\text{S} \rightarrow \text{Se}$ substitution is less favoured than $\text{Br} \rightarrow \text{I}$ substitution, since S atoms are more rigidly bound to their sites in the crystal lattice. Besides, the equivalent isotropic displacement parameter U_{eq} is smaller for S atoms than for Br atoms [4].

4. Conclusions

The performed investigations have enabled us to study the compositional behaviour of the absorption edge spectra, refractive index dispersion, cubic lattice parameter and the calculated density of $\text{Cu}_6\text{PS}_5(\text{Br}_{1-x}\text{I}_x)$ solid solution crystals. The comparative analysis of the results of $\text{Br} \rightarrow \text{I}$ anionic substitution with those for $\text{S} \rightarrow \text{Se}$ substitution in $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals enabled us to unveil the reasons of the compositional behaviour of these parameters.

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