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## Interrelations between structural and optical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals

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**Abstract.**  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals grown with a vertical-zone crystallization technique are described by the cubic structure  $F\bar{4}3m$ . We analyze compositional dependences of their lattice parameter and crystal density. Diffuse-reflection spectra for the powders of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  are measured at the room temperature. Refractive indices and extinction coefficients are obtained from spectral ellipsometry measurements. When Ag content increases, we observe a nonlinear decrease in the pseudogap and a nonlinear increase in the refractive index, with a maximum. Interrelations between the structural and optical properties of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  are discussed.

**Keywords:** mixed crystals, X-ray diffraction, spectral ellipsometry, diffuse reflection, energy pseudogap

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### 1. Introduction

$\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  crystals belong to the family of compounds with an argyrodite structure [1, 2]. They are crystallized in the cubic symmetry at room temperature, with the space group  $F\bar{4}3m$ . Rather high electrical conductivity of  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  has been found at the room temperature, which is typical for advanced superionic conductors [3, 4]. Due to high ionic conductivity, the above crystals represent attractive materials for many applications, e.g. solid electrolytes for a new generation of power sources. Moreover,  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  are interesting for the studies of order–disorder processes. Note that the structural, electrical and optical properties of the mixed crystals based on  $\text{Cu}_7\text{GeS}_5\text{I}$  have been studied in Refs. [5, 6].

A method of chemical transport reactions (CTR) is most commonly used for growing single crystals with argyrodite structure. Unfortunately, this method cannot obtain the  $\text{Ag}_7\text{GeS}_5\text{I}$  crystals due to its slight carryover, whereas the  $\text{Cu}_7\text{GeS}_5\text{I}$  crystals are small-sized. Moreover, the CTR method is lengthy and has a disadvantage lying in inclusion of carrier admixtures in the lattice. For these reasons, we have chosen crystallization from a melt of stoichiometric composition as our working method for the crystal growth.

The present article studies the growth process, the structural parameters and the optical properties of the mixed crystals  $\text{Cu}_7\text{GeS}_5\text{I}$ – $\text{Ag}_7\text{GeS}_5\text{I}$  grown by means of a directed crystallization from melt (i.e., a so-called Bridgman–Stockbarger method). Besides, we aim at studying interrelations between the structural and optical properties of the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  crystals, namely those concerned with the lattice parameter, the density, the energy pseudogap and the refractive index.

## 2. Experimental

The process of crystals growth was performed for the both individual chemical compounds and for their solid solutions. The growth was done using a method of directed crystallization from melt (i.e., zonal crystallization). As in the case when the individual compounds are obtained, the growth method applied to the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals had a peculiar feature. This was the fact that the synthesis and growth were performed in the same ampoule, without overloading its charge. This allows one to obtain the crystalline solid solutions of predefined compositions, with no deviations from stoichiometry in the whole concentration interval.

The  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  crystals were synthesized according to the following procedures. The temperature of the both zones increased up to 673 K within 6 h, hereupon a 24 h exposure was performed. Then the temperature increased during a day to its maximal values 1323 K for the ‘hot’ upper zone and 973 K for the ‘cold’ lower zone. The temperature in the melt zone was kept to be 50 K higher than the melting point, in order to prevent partial thermal dissociation of the substances. After that a 24 h long exposure took place at which the melt was completely homogenized.

A vertical-zone crystallization method was used to obtain homogeneous single-crystalline solid solutions. After moving the ampoule with the crystal into the annealing zone, a homogenizing annealing, which is required for thermal stress relaxing, was carried out for 3 days. In this way, we obtained the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals with the length 30–40 mm and the diameter 10–15 cm (see Fig. 1).

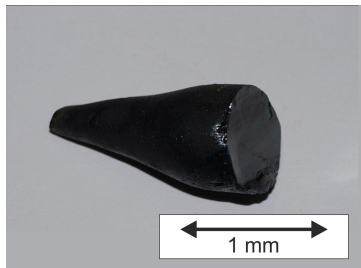
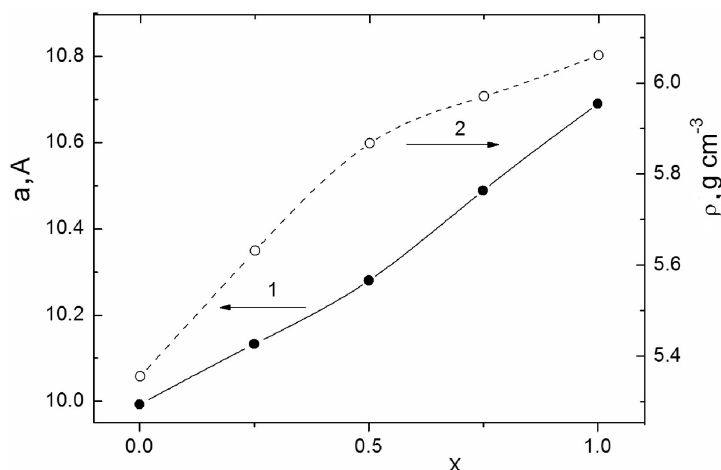


Fig. 1. Image of  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$  single crystal.

The structural studies of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  were carried out with a powder method, using the diffraction patterns obtained with a DRON 4-07 diffractometer (the conventional  $\theta$ - $2\theta$  scanning method, the Bragg angle  $2\theta \cong 10$ – $60^\circ$ , and the Ni-filtered  $\text{CuK}_\alpha$  radiation). The lattice parameters were calculated using a DICVOL 04 software [7]. A spectroscopic ellipsometer M-2000V was used for measuring the optical constants. Finally, diffuse-reflection measurements for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals were carried out using a LOMO MDR-3 spectrometer.

## 3. Results and discussion

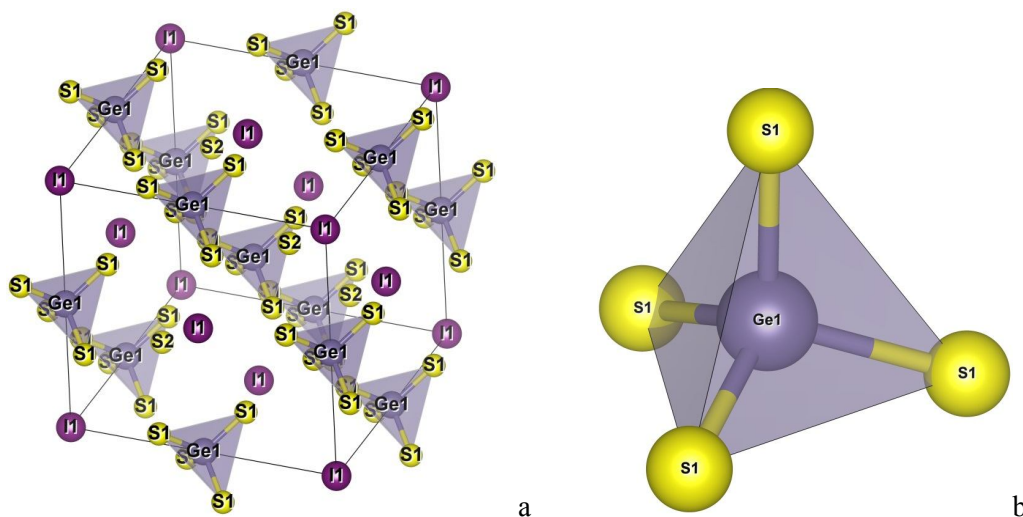
Our X-ray diffraction studies have shown that the both compounds and their solid solutions in  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  crystallize in a cubic system, with the space group  $F\bar{4}3m$  and  $Z=4$ . Compositional dependences of the cubic-lattice parameter and the density at  $\text{Cu}\leftrightarrow\text{Ag}$  cation substitution are obtained on this basis, as shown in Fig. 2. The increase in the Ag content leads to nonlinear increase in the lattice parameter. Besides, the compositional dependence of lattice parameter is described by a Vegard law. It has a monotonous concave character, which is associated with disordering (distortion) of the anion sublattice due to different crystallochemical radii of  $\text{Ag}^+$  and  $\text{Cu}^+$ , and changes in the filling ratio of equivalent positions during cation replacement. The crystal density increases also nonlinearly with increasing Ag content, although the curve 2 in Fig. 2 is convex.



**Fig. 2.** Compositional dependences of cubic-lattice parameter (1) and density (2) for  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals.

Since our compounds are iso-structural and the appropriate ionic radii are close to each other ( $0.98\text{\AA}$  for  $\text{Cu}^+$  and  $1.13\text{\AA}$  for  $\text{Ag}^+$ ), a continuous series of solid solutions can be created in the  $\text{Cu}_7\text{GeS}_5\text{I} - \text{Ag}_7\text{GeS}_5\text{I}$  system by means of  $\text{Cu}^+ \leftrightarrow \text{Ag}^+$  substitution. The mechanism of the  $\text{Cu}^+ \leftrightarrow \text{Ag}^+$  substitution and the coordinates of atoms in the lattice have been clarified basing on the refined initial-structure models found using a Rietveld method [8, 9]. Calculations and refinement of the model have been carried out using an EXPO 2014 program [10].

Let us consider the main peculiarities of the structure of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals. The basis of the anionic frame is represented by tetrahedra  $[\text{GeS}_4]$ ,  $[\text{S}_3\text{I}]$  and  $[\text{SI}_4]$ , on the sides and in the middle of which there are copper and silver atoms (see Fig. 3). Notice that, during the formation of solid solutions, the  $[\text{GeS}_4]$  tetrahedra keep their symmetry peculiar for the individual compounds. The Ge–S bond lengths, the S–S distances and the tetrahedral volumes for the mixed crystals with  $x = 0.75, 0.5$  and  $0.25$  are listed in Table 1.



**Fig. 3.** Illustration of elementary lattice (a) and tetrahedron  $[\text{GeS}_4]$  (b) for the  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$  structure.

Fig. 4 shows the diffuse-reflection spectra for the powders of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals. The short-wavelength edge of the spectra for the powders shifts towards longer

wavelengths when Cu atoms are substituted with Ag. It should be noted that a change in the reflectance-edge spectral position is typically observed for various solid solution with Cu→Ag substituting [11, 12]. Issuing from the spectral position of the short-wavelength edge of the diffuse-reflection spectra, one can estimate the energy pseudogap value. We have revealed that the compositional dependence of the pseudogap has a nonlinear concave behaviour. It can be described using the relation [13]

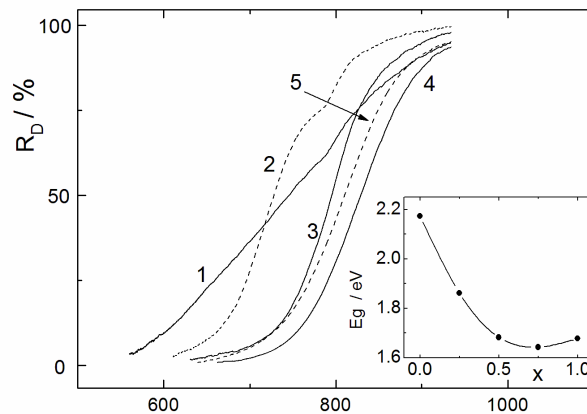
$$E_g(x) = E_g(0) + [E_g(1) - E_g(0)]x - cx(1-x), \quad (1)$$

where  $E_g(x=0) \equiv E_g(0)$  and  $E_g(x=1) \equiv E_g(1)$  are respectively the pseudogap values for  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$ , and  $c$  is a ‘concavity’ (or ‘convexity’) parameter which represents a measure of deviation of the function  $E_g(x)$  from linearity. The experimental dependence  $E_g^*(x)$  is best fitted with Eq. (1) when the corresponding parameters are equal to  $E_g^*(0) = 2.173$  eV,  $E_g^*(1) = 1.678$  eV and  $c = 0.95$  eV. The positive  $c$  value evidences a concave-like compositional dependence of the energy pseudogap.

**Table 1.** Ge–S bond lengths, S–S distances and tetrahedral volumes (denoted as V) for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals.

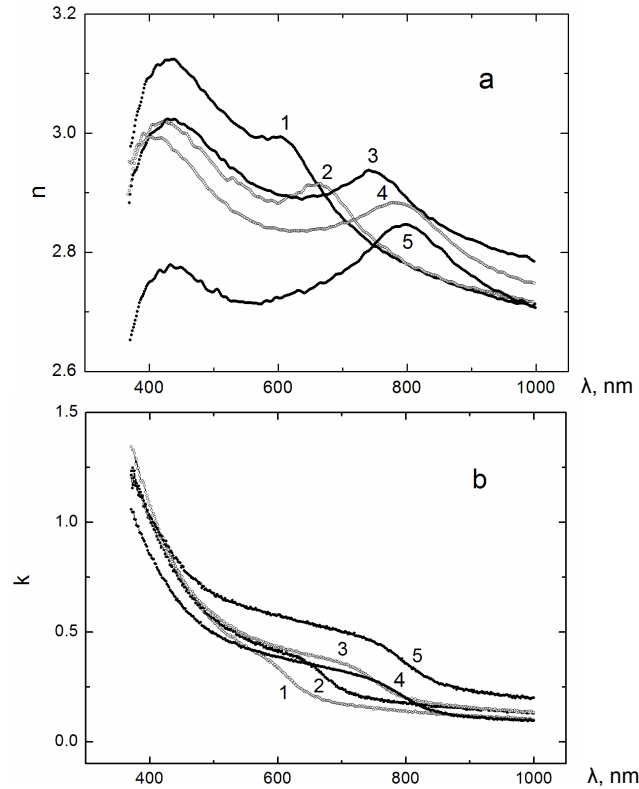
Composition	Ge–S, Å	S–S, Å	V, Å <sup>3</sup>
$\text{Cu}_7\text{GeS}_5\text{I}$	2.063	3.369	4.51
$(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeS}_5\text{I}$	2.097	3.425	4.74
$(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$	2.058	3.361	4.48
$(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeS}_5\text{I}$	2.007	3.278	4.15
$\text{Ag}_7\text{GeS}_5\text{I}$	1.822	2.975	3.1

It has been shown in Refs. [13–15] that concavity of the pseudogap plot can result from the following factors: (i) energy-band deformation due to changing lattice parameters in solid solutions, (ii) changes in electronegativity, and (iii) structural changes due to varying cation-bond length.



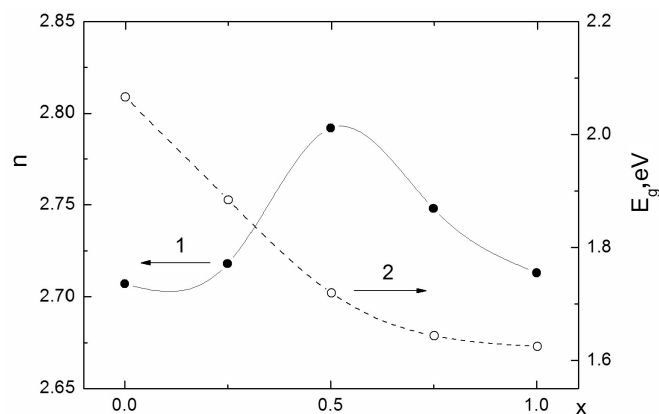
**Fig. 4.** Diffuse-reflection spectra obtained for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals:  $\text{Cu}_7\text{GeS}_5\text{I}$  (1),  $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeS}_5\text{I}$  (2),  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$  (3),  $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeS}_5\text{I}$  (4), and  $\text{Ag}_7\text{GeS}_5\text{I}$  (5). The inset shows compositional dependence of the energy pseudogap.

The refractive indices  $n$  and the extinction coefficients  $k$  of the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals have been obtained from the spectral ellipsometry measurements carried out in the spectral range 0.3–1.0  $\mu\text{m}$  (see Fig. 5). In the region of optical transparency, we observe normal refractive-index dispersion. The refractive index increases with approaching the absorption edge. The two



**Fig. 5.** Spectral dependences of refractive index  $n$  (a) and extinction coefficient  $k$  (b) for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals:  $\text{Cu}_7\text{GeS}_5\text{I}$  (1),  $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeS}_5\text{I}$  (2),  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeS}_5\text{I}$  (3),  $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeS}_5\text{I}$  (4), and  $\text{Ag}_7\text{GeS}_5\text{I}$  (5).

regions of anomalous refractive-index dispersion are observed where the extinction coefficient increases (see Fig. 5). The long-wavelength anomaly, which is detected at the light wavelength  $\lambda = 599$  nm (or the photon energy  $E = 2.070$  eV) for  $\text{Cu}_7\text{GeS}_5\text{I}$ , corresponds to the band-to-band optical transition. The spectral position of this anomaly is associated with the pseudogap value. Perhaps, the short-wavelength anomaly detected at  $\lambda = 433$  nm (or  $E = 2.864$  eV) for  $\text{Cu}_7\text{GeS}_5\text{I}$  corresponds to an inter-band Van Hove–Phillips singularity. This type of singularity has earlier been observed for the other  $\text{Cu}_6\text{PS}_5\text{I}$  argyrodites [16, 17].



**Fig. 6.** Compositional dependences of refractive index  $n$  (1) and energy pseudogap  $E_g$  (2) for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals.

Fig. 6 presents the compositional dependences of the refractive index at the light wavelength  $\lambda = 1 \mu\text{m}$  and the energy pseudogap  $E_g$ , which are obtained from the spectral ellipsometry measurements for the  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals. Note that the  $E_g$  values have been determined as the positions of a ‘knee’ observed in the spectral dependence of the extinction coefficient  $k$  (see Fig. 5b).

It is important that the pseudogap  $E_g$  values obtained from the diffuse-reflection spectra (see inset in Fig. 4) and the spectral dependences of extinction coefficient (see Fig. 5b) differ by no more than 5%. Moreover, the  $E_g$  value found from the spectra of absorption coefficient [3] for  $\text{Cu}_7\text{GeS}_5\text{I}$  crystal agrees well with the values derived from the diffuse reflection and the extinction coefficient mentioned above.

#### 4. Conclusions

$(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals have been obtained using the vertical-zone crystallization method. The structural studies are carried out by means of the powder method. The diffraction patterns are indexed following from the face-centred cubic cell of the space group  $F\bar{4}3m$ . The number of formula units per unit cell is equal to  $Z = 4$ . Basing on the Rietveld method, we have refined the mechanism of cationic substitution and the atomic lattice coordinates. A nonlinear increase in both the lattice parameter and the density of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  is observed with increasing Ag content.

The optical studies, including diffuse reflection and spectral ellipsometry, have been performed on both the powders and the single crystals. The diffuse-reflection spectra, and the spectral dependences of the refractive index and the extinction coefficient have been measured for our mixed crystals in a wide spectral region. We have revealed a nonlinear decrease of the pseudogap energy and a nonlinear increase for the refractive index, with occurrence of a maximum.

We have witnessed good interrelations of the structural and optical properties of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ . In particular, the compositional behaviours of the lattice parameter and the crystal density derived from the X-ray diffraction data correlate well with the compositional dependences of the pseudogap and the refractive index.

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**Анотація.** Змішані кристали  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ , вирошені за методом вертикальної зонної кристалізації, описуються кубічною структурою  $F\bar{4}3m$ . У цій праці проаналізовано концентраційні залежності їхніх параметра ґратки та густини. Вивчено спектри дифузного відбивання для порошків  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  за кімнатної температури. Показники заломлення та коефіцієнти екстинкції одержано з даних спектральної еліпсометрії. Зі зростанням вмісту Ag спостерігаємо нелінійне зменшення псевдоцілини та нелінійне зростання показника заломлення, із наявністю максимуму. Обговорено взаємозв'язки структурних та оптичних властивостей  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ .