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OPTICAL PROPERTIES OF CATION-SUBSTITUTED (Cu_{1-x}Ag_x)₇GeSe₅I MIXED CRYSTALS

(Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals were grown by the vertical zone crystallization method and are shown to crystallize in a cubic structure (F43m). The diffuse reflection spectra for the powders of (Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals were measured at room temperature. The refractive indices and extinction coefficients for (Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals were obtained from spectral ellipsometry measurements. Two anomalies of the refractive index in the spectral region from 440 nm to 1000 nm are observed. One of them corresponds to the band-to-band optical transition, while another one to the interband Van Hove–Phillips singularity. A nonlinear decrease of the energy pseudogap is revealed with an increase in the Ag content in (Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals.

Keywords: mixed crystal, spectral ellipsometry, refractive index, diffuse reflection, energy pseudogap.

1. Introduction

Cu₇GeSe₅I and Ag₇GeSe₅I crystals belong to a large family of compounds with argyrodite structure, which are united by the general formula $A_{(12-n-x)/m}^{m+1}B_n^{n+}X_{6-x}^{2-}Y^{1-}$ ($0 < x < 1$), where m is the valence of cations $A = (\text{Cu}^+, \text{Ag}^+, \text{Cd}^{2+}, \text{Hg}^{2+})$, n is the valence of cations $B = (\text{Ga}^{3+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{P}^{5+}, \text{As}^{5+})$, $X = \text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-}$ and $Y = \text{Cl}^-, \text{Br}^-, \text{I}^-$ are anions [1, 2]. Representatives of the argyrodite family are characterized by a high ionic conductivity and are promising for practical applications as solid state batteries, supercapacitors, and electrochemical sensors [2, 3]. Recently, alongside well-studied Cu- and Ag-containing argyrodites, Li- and K-containing argyrodites are being actively investigated [4–8]. In addition, a great attention is paid to the production of various types of argyrodite-based ceramic and composite materials, as well as their production in thin film form, which significantly expands the scope of their practical application [9–12].

Germanium-containing argyrodite Cu₇GeX₅I ($X = \text{S}, \text{Se}$) crystals, as well as the mixed crystals on their base, were studied in several papers [13–19]. It was shown that Cu₇GeSe₅I crystal is characterized by the highest value of electrical conductivity among the well-known copper-containing superionic conductors [16]. For Ag₇GeSe₅I crystal, a non-Arrhenius behavior of the electrical conductivity is observed and described by the Vogel–Fulcher–Taman equation. Moreover, its temperature variation is related to a “quasiliquid” sublattice of Ag⁺ ions [20–22]. The influence of the Cu⁺ → Ag⁺ cationic substitution on the electrical conductivity of (Cu_{1-x}Ag_x)₇GeS₅I and (Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals was studied in Ref. [18, 19]. It was shown that, as the content of Ag atoms increases, the ratio of ionic to electronic conductivity for (Cu_{1-x}Ag_x)₇GeSe₅I mixed crystals increases as well [19].

Optical studies have shown that the absorption edge of Cu₇GeS₅I single crystal and Cu₇Ge(S_{1-x}Se_x)₅I mixed crystals is described by the Urbach rule which is related to the electron-phonon interaction [13, 16, 17]. It was shown that the S → Se anionic substitution in the anionic sublattice of

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$\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ mixed crystals leads to a nonlinear increase of the electrical conductivity by more than one order of magnitude and a nonlinear decrease of the optical pseudogap [17]. Optical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals with the substitution of atoms in the cationic sublattice were studied in Ref. [23]. As the Ag content increases, a nonlinear decrease in the optical pseudogap, as well as a nonlinear increase in the refractive index with a maximum were observed [23].

Due to the fact that the optical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals have not been investigated so far, this paper is devoted to the study of the compositional behavior of the optical parameters for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals at the cationic $\text{Cu}^+ \rightarrow \text{Ag}^+$ substitution. In addition, in contrast to the previous studies [13, 16, 17] performed on samples obtained by the chemical vapor transport (CVT), the optical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals obtained by means of the directed crystallization from the melt, namely with the help of Bridgman–Stockbarger (B–S) method will be investigated in this paper. Finally, it is relevant to compare the optical parameters for $\text{Cu}_7\text{GeSe}_5\text{I}$ crystals obtained by CVT and B–S techniques.

2. Experimental

$\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals were grown by the directed crystallization from a melt, whereas $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals with $x = 0.25, 0.5, 0.75$ were obtained by the zone crystallization from a melt using a modified B–S method [19]. The XRD patterns measured by a DRON 4-07 diffractometer (conventional θ - 2θ scanning method, Bragg angle $2\theta \cong 10$ – 60° , Ni-filtered $\text{CuK}\alpha$ radiation) have shown that $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ (B–S) compounds were indexed as face-centered cubic with the space group $F\bar{4}3m$.

A spectroscopic ellipsometer Horiba Smart SE was used for optical constant measurements. Measurements were carried out in the spectrum region from 440 nm to 1000 nm at an incident angle of 70° . The diffuse reflection measurements of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were carried out on a Shimadzu UV-2600 spectrometer. Optical transmission spectra of $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal were measured by using a LOMO KSVU-23 grating monochromator. The absorption coefficient α was calculated on the basis of experimental values of the transmission

coefficient T_{tr} and the reflectivity r using the known formula

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-r)^2 + \sqrt{(1-r)^4 + 4T_{\text{tr}}^2 r^2}}{2T_{\text{tr}}} \right], \quad (1)$$

where d is the sample thickness. The relative error in the absorption coefficient determination $\Delta\alpha/\alpha$ did not exceed 10% for $0.3 \leq \alpha d \leq 3$ [24].

3. Results and Discussion

Diffuse reflection spectra for the powders of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals are presented in Fig. 1. The short-wavelength edge of the diffuse reflection spectra is shown to shift toward longer wavelengths with the substitution of Cu atoms by Ag atoms in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals. From the spectral position of the short-wavelength edge of the diffuse reflection spectra, the energy pseudogap value was estimated. It is revealed that, at the $\text{Cu}^+ \rightarrow \text{Ag}^+$ cationic substitution, the energy pseudogap nonlinearly decreases with the downward-bowing. The compositional dependence of the energy pseudogap can be described by the relation [25]:

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

where $E_g(x=0) \equiv E_g(0)$ and $E_g(x=1) \equiv E_g(1)$ are the energy pseudogap values for $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals, respectively; c is the bowing parameter which is the measure of a deviation from the

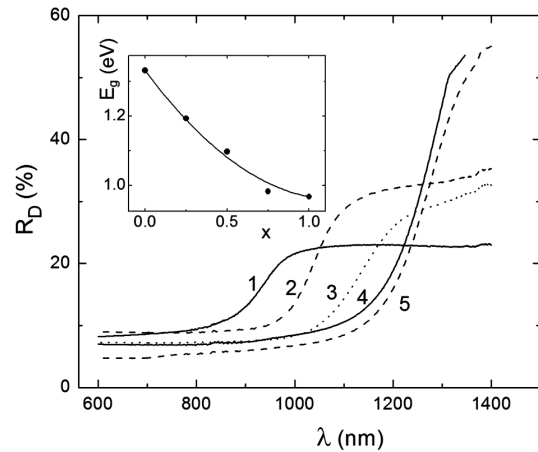


Fig. 1. Diffuse reflection spectra of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ (3), $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$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

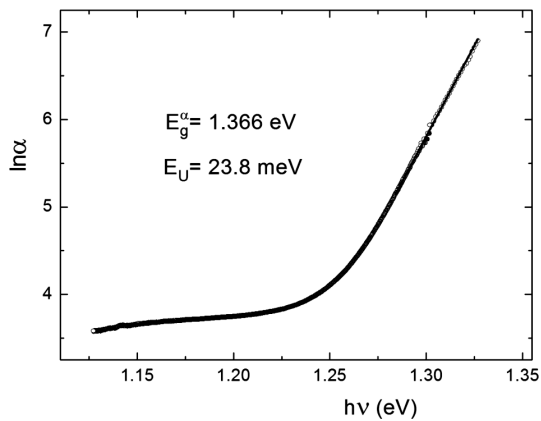


Fig. 2. Spectral dependence of the absorption coefficient for $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal at room temperature

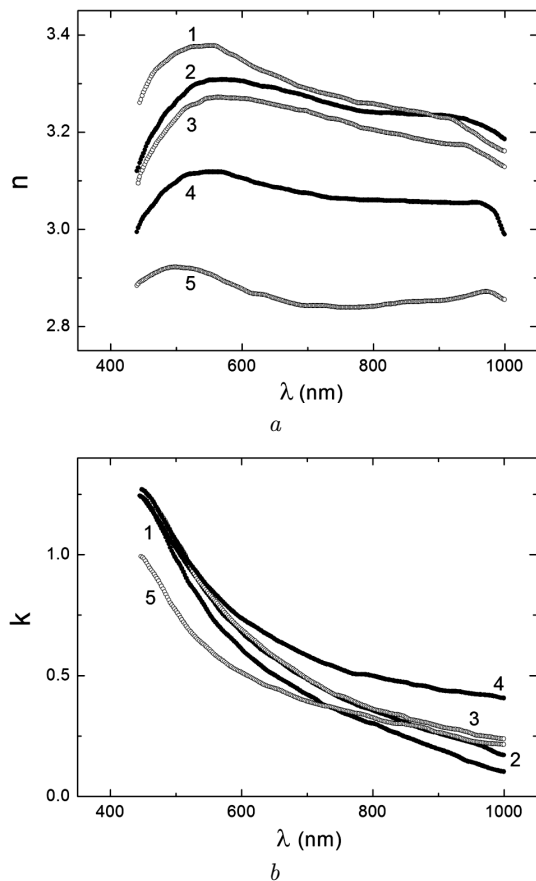


Fig. 3. Spectral dependences of the refractive index n (a) and the extinction coefficient k (b) for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$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

$E_g(x)$ function linearity. The best agreement, while describing the experimental dependence $E_g(x)$ by Eq. (2), was obtained for the c parameter equal to 0.27 eV. It should be noted that the positive value of c is the evidence of the downward-bowed compositional dependence of the energy pseudogap. According to Refs. [26, 27], the bowing of the energy pseudogap plot can be caused by an energy band deformation due to the change of lattice parameters in mixed crystals, change of electronegativity, and structural changes due to the cation bond length variation.

The comparison of the compositional dependences of the energy pseudogaps in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ and $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals [23] indicates their similarity. However, the bowing parameter for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals is more than 3 times greater than in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ mixed crystals. In addition, the substitution of S atoms by Se atoms in the anionic sublattice results in a significant decrease of the energy pseudogap. Thus, the energy pseudogaps for $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals constitute 2.173 eV and 1.678 eV [23], respectively, whereas, for $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals, they are much smaller and equal to 1.332 eV and 0.967 eV, respectively.

The optical absorption edge spectrum which has an exponential form for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B-S) is presented in Fig. 2. It should be noted that the optical absorption edge in $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) single crystal was studied in Ref. [17]. It was shown that the optical absorption edge spectra for $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) are described by the Urbach rule [28]

$$\alpha(h\nu) = \alpha_0 \exp \left[\frac{h\nu - E_0}{E_U} \right], \quad (3)$$

where E_U is the Urbach energy, α_0 and E_0 are the convergence point coordinates of the Urbach bundle. The Urbach shape of the absorption edge is, first of all, related to the exciton (electron)-phonon interaction (EPI) [29]. It was shown in Ref. [17] that the most applicable for the description of EPI in $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) crystals is the Dow-Redfield model, according to which the Urbach shape of the absorption edge is revealed as a consequence of the interaction of an exciton with microelectric fields of LO phonons. The energy of the effective phonon participating in the absorption edge formation can be estimated with regard for the temperature dependence

of the parameter $\sigma = kT/E_U$ characterizing the absorption edge slope from the known formula

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{\hbar w_p} \right) \tanh \left(\frac{\hbar w_p}{2kT} \right), \quad (4)$$

where $\hbar w_p$ is the effective phonon energy in the one-oscillator model describing EPI, σ_0 is a parameter, related to the EPI constant g as $\sigma_0 = 2/3g$ [29]. For $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) single crystal, $\sigma_0 > 1$, this is the evidence for a weak EPI in the above-mentioned crystal [17].

The Urbach energy $E_U = 23.8$ meV for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) single crystal was obtained from the exponential dependence presented in Fig. 2. It is shown that the obtained value for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) single crystal is very close to the Urbach energy $E_U = 25.0$ meV for $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) single crystal [17]. For the comparison of the spectral positions of the Urbach absorption edge in both $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) and $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) single crystals, we used the value of the energy pseudogap E_g^α (E_g^α is the energy position of an exponential absorption edge at a fixed absorption coefficient $\alpha = 10^3 \text{ cm}^{-1}$) which is 1.366 eV for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) crystal and 1.435 eV for $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) crystal [17]. It is seen that the values of the energy pseudogap of the above-mentioned crystals do not differ more than by 5%. It should be noted that the energy pseudogap E_g (1.366 eV) determined from the absorption coefficient spectrum for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) crystal is in a good agreement with E_g determined from the above-mentioned diffuse reflection spectrum (1.332 eV).

The refractive indices n and extinction coefficients k for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were obtained from spectral ellipsometry measurements which were carried out in the spectral range of 0.44–1.0 μm (Fig. 3). The two anomalous dispersion regions of the refractive index are revealed in the spectral region under investigation (Fig. 3, *a*). The weakly expressed long-wavelength (e.g., $\lambda = 973$ nm or $E = 1.274$ eV for $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal) anomaly corresponds to the band-to-band optical transition, and the spectral position of this anomaly relates to the energy pseudogap value. Another short-wavelength (e.g., $\lambda = 495$ nm or $E = 2.505$ eV for $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal) anomaly possibly corresponds to the interband Van Hove–Phillips singularity. Such type of singularity was also revealed in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals [23]. However,

both anomalies in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals are shifted, as compared to the anomalies in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals into a higher energy region (e.g., for $\text{Ag}_7\text{GeSe}_5\text{I}$, they are observed at 1.554 eV and 2.867 eV, respectively [23]). On the spectral dependences of the extinction coefficients k for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals, a monotonous decrease in its value with increasing the wavelength is observed (Fig. 3, *b*).

It should be noted that, with increasing the content of Ag atoms in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals, the long-wave anomaly corresponds to the band-to-band optical transition shifts into the low-energy region (Fig. 3, *a*), which corresponds to the compositional behavior of the energy pseudogap determined from the diffuse reflection spectra (Fig. 1). At the same time a short-wave anomaly corresponds to the interband Van Hove–Phillips singularity shifts nonlinearly into the high-energy region at the cationic $\text{Cu}^+ \rightarrow \text{Ag}^+$ substitution in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals.

4. Conclusions

$(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were obtained by means of the vertical zone crystallization method (Bridgman–Stockbarger method). The optical (diffuse reflection, transmission and spectral ellipsometry) studies were performed both on powders and single crystals in a wide spectral range. It is shown that the diffuse reflection spectra shift toward longer wavelengths with the substitution of Cu atoms by Ag atoms in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals. The energy pseudogaps determined from the diffuse reflection spectra at the $\text{Cu}^+ \rightarrow \text{Ag}^+$ cationic substitution nonlinearly decrease with the downward-bowing. Optical absorption studies have shown the exponential behavior of the absorption edge in $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal. It is revealed a good agreement between the energy pseudogaps determined from the absorption coefficient spectrum and those determined from the diffuse reflection spectrum for $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) crystal. In addition, a good proximity of values is obtained for the energy pseudogaps in $\text{Cu}_7\text{GeSe}_5\text{I}$ (CVT) and $\text{Cu}_7\text{GeSe}_5\text{I}$ (B–S) crystals. From spectral ellipsometry measurements, the two anomalous dispersion regions of the refractive index are revealed in the spectral interval 0.44–1.0 μm . The low-frequency anomaly corresponds to the band-to-band optical

transition, whereas the high-frequency anomaly corresponds to the interband Van Hove–Phillips singularity. It is observed that the low-frequency anomaly at the Cu → Ag cationic substitution shifts to the low-energy region, while the high-frequency anomaly non-linearly shifts to the high-energy region.

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ОПТИЧНІ ВЛАСТИВОСТІ
КАТІОН-ЗАМІЩЕНИХ ЗМІШАНИХ
КРИСТАЛІВ $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$

Встановлено, що змішані кристали $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$, які вирощувалися методом вертикальної зонної кристалізації, мають кубічну структуру $F\bar{4}3m$. Спектри дифузного відбивання для порошоків змішаних кристалів $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ вимірювалися при кімнатній температурі. Показники заломлення та коефіцієнти екстинкції змішаних кристалів $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ були отримані з використанням спектральної еліпсометрії. В спектральній області від 440 нм до 1000 нм спостерігаються дві аномалії показника заломлення. Одна з них відповідає зона-зонному оптичному переходу, а інша – особливості Ван Хо́ва-Філіпса. Виявлено нелінійне зменшення ширини псевдозаборононої зони при збільшенні вмісту атомів срібла у змішаних кристалах $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$.

Ключові слова: змішаний кристал, показник заломлення, дифузне відбивання, ширина псевдозаборононої зони.