

Diffuse reflectance spectroscopy of solid solutions in the $\text{Ag}_7\text{PS}_6\text{-Ag}_8\text{GeS}_6$ system

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Abstract. Samples of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions were obtained in the form of microcrystalline powders by grinding in an agate mortar. The diffuse reflectance spectra of the obtained $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ samples were studied in the spectral range 200 to 1400 nm at 293 K. The spectral dependences were analyzed using multilevel approximation by applying the Kubelka–Munk function and the Tauc method. It has been found that for $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions, a red shift of the reflection edge beginning is observed with increasing the Ge content. The pseudo-gap values of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions was estimated by the Tauc method. It was found that the heterovalent cationic substitution $\text{P}^{5+} \rightarrow \text{Ge}^{4+}$ within the anionic sublattice leads to a monotonic nonlinear decrease in the pseudo-gap values.

Keywords: optical properties, diffuse reflectance spectroscopy, microcrystalline powder, Tauc method, solid solution.

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1. Introduction

Complex chalcogenides are a class of semiconductor materials that belong to different structural types (diamond-like, perovskites, argyrodites, *etc.*) and are characterized by low band gap values and are suitable for use as light-harvesting materials in a wide spectral range [1, 2]. Recently, investigation of the optical properties of ternary and quaternary silver chalcogenides with an argyrodite structure has been actively developed in the area of photovoltaic technologies for solar cell and photocatalytic applications [3, 4].

In this aspect, the most studied representative of argyrodites is canfieldite Ag_8SnS_6 , which is a structural analogue [5] of the initial argyrodite Ag_8GeS_6 . The reported bandgap E_g for Ag_8SnS_6 nanocrystals is 1.24...1.41 eV [3, 4]. The use of Ag_8SnS_6 -based heterostructures as photoanodes [6, 7] for photoelectrochemical splitting of water [8] and photocatalysts [9] has been reported. The quaternary representatives of the argyrodites, $\text{Ag}_6\text{PS}_5\text{I}$ and $\text{Ag}_7\text{Si}(\text{Ge})\text{S}_5\text{I}$ compounds, are characterized by higher optical pseudo-gap values within

the range of 1.554 to 2.030 eV [10, 11]. The structural motif of argyrodites is a tetrahedral close packing formed on the basis of a multi-charged cation (Si^{4+} , Ge^{4+} , Sn^{4+} , P^{5+}), in which the voids are occupied by single-charged cations [5]. Multi-charged cations are characterized by full occupation of the position, and single-charged cations by partial occupation. The result is formation of a rigid anionic framework formed on the basis of anions and multivalent cations and a disordered cationic sublattice. This structural disorder significantly affects the electrophysical parameters of argyrodites [10–13].

For the present study, the ternary compounds Ag_8GeS_6 and Ag_7PS_6 and solid solutions based on them were chosen. Both ternary sulfides Ag_8GeS_6 and Ag_7PS_6 melt congruently at 958 °C [14, 15] and 801 °C [15, 16], respectively. The structural phase transition in the Ag_8GeS_6 (271 °C) and Ag_7PS_6 (227 °C) phases is accompanied by the transition from the cubic crystal system of the space group (SG) F-43m [14, 16] to the primitive orthorhombic and cubic cells, respectively. The low-temperature modification of Ag_8GeS_6 crystallizes in SG Pna2₁ with lattice parameters:

$a = 15.1469 \text{ \AA}$, $b = 7.4694 \text{ \AA}$, $c = 10.5842 \text{ \AA}$, $Z = 4$ [15, 17], and Ag_7PS_6 in SG $P2_13$ with parameters $a = 10.3917 \text{ \AA}$, $Z = 4$ [15, 18]. The $\text{Ag}_7\text{PS}_6\text{-Ag}_8\text{GeS}_6$ system is characterized by formation of a continuous series of solid solutions based on high-temperature modifications. Upon cooling, the solubility gap is observed with formation of two regions of boundary solid solutions [19]. According to the LDA+U approximation calculations [20], Ag_8GeS_6 is a direct-gap semiconductor with the band gap $E_g = 1.46 \text{ eV}$.

Due to the considerable interest in searching for new materials for energy-saving technologies, it was decided to estimate the pseudo-gap value of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions by diffuse reflectance spectroscopy. Also, the influence of heterovalent substitution $\text{P}^{5+} \leftrightarrow \text{Ge}^{4+}$ on the optical properties of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions was determined.

2. Experimental

2.1. Sample preparation

Polycrystalline ternary halogen-free compounds Ag_7PS_6 , Ag_8GeS_6 were prepared from high purity elemental components: Ag (99.995%), P (99.9999%), Ge (99.999%), and S (99.999%) in evacuated (0.13 Pa) silica ampoules. The synthesis procedure of initial compounds was performed in a two-stage by using the single-temperature method. The first stage consisted of heating to $450 \text{ }^\circ\text{C}$ at a rate of $100 \text{ }^\circ\text{C/h}$ (exposure for 30 h), and the second stage – heating to $1000 \text{ }^\circ\text{C}$ at a rate of $50 \text{ }^\circ\text{C/h}$ (exposure for 60 h), followed by cooling to room temperature (rate $50 \text{ }^\circ\text{C/h}$) [15]. Thus, Ag_7PS_6 and Ag_8GeS_6 were obtained in the form of polycrystalline alloys, which were further used to obtain solid solutions based on them.

The solid solutions of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) composition were synthesized using the one-stage one-temperature method from previously synthesized ternary compounds. The synthesis regime consisted of heating stoichiometric amounts of ternary sulfides at the rate close to $50 \text{ }^\circ\text{C/h}$ up to $1000 \text{ }^\circ\text{C}$ and holding the melt at this temperature for 24 hours. Cooling to the annealing temperature ($530 \text{ }^\circ\text{C}$) was carried out at the rate approximately $50 \text{ }^\circ\text{C/h}$. The annealing of polycrystalline alloys was performed for 72 h, and cooling to the room temperature was carried out in the furnace off mode.

The obtained polycrystalline samples of individual Ag_7PS_6 and Ag_8GeS_6 compounds and $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions were grinded in an agate mortar to fine powders with a crystallite size within the range $\sim 10\text{--}20 \text{ }\mu\text{m}$. The dispersion of the obtained powders was controlled by sieving through sieves of appropriate porosity.

2.2. Methods

The diffuse reflectance spectroscopy was used to study the optical properties of powders. The diffuse reflectance

spectroscopy method is suitable for the optical characterization of powdered material [21]. The diffuse reflectance spectroscopy method takes into account the absorption and scattering capability of the polycrystalline sample. The relationship between the diffuse scattering and absorption of a sample is described by the mathematical Kubelka–Munk transformation [22, 23]:

$$f(R_d) = (1 - R_d)^2 / 2R_d = K/S.$$

The Kubelka–Munk function connects the reflectance R_d with the absorption coefficient K and the scattering coefficient S [22, 23].

The diffuse reflectance spectra of the $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ micropowders were obtained using a Shimadzu UV-2600 double-beam spectrophotometer with the measuring range of 200 to 1400 nm. The Shimadzu UV-2600 is equipped with the ISR-2600Plus integrating sphere, which provides a wider analytical system for its application (measuring range: 220 to 1400 nm). The ISR-2600Plus integrating sphere allows obtaining diffuse reflectance spectra for semiconductor materials by using standard silica window cuvettes for powdered samples (P/N 206-89065-41). The measurements were performed using the Shimadzu UV-2600 double-beam spectrophotometer with an ISR-2600Plus integrating sphere, which allows for clear observation of the absorption edges where the reflection wavelength decreases. The obtained spectra, thanks to automatic fixation with the UVProbe software, after multilevel processing enabled to determine the value of optical pseudo-bandwidth for the investigated samples [13, 24]. Estimation of the pseudo-gap inherent to $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solution samples ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) can be carried out using multilevel approximation with the graphical Tauc method applied to the transformed diffuse reflectance spectra with account of the Kubelka–Munk function [13, 24].

Optical characterization of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ micropowders were performed using the Shimadzu UV-2600 double-beam spectrophotometer equipped with an ISR-2600Plus integrating sphere, which allows for clear observation of the absorption edges where the reflection wavelength decreases. The diffuse reflectance spectra were obtained within the spectral range 200...1400 nm at the temperature $293 \text{ }^\circ\text{C}$. Measurements were performed in standard cuvettes for powdered samples with silica windows (P/N 206-89065-41). All the spectra were recorded using the UVProbe software (Shimadzu).

The obtained spectra enabled to determine the value of the optical pseudo-gap for the studied samples. Estimation of the pseudo-gap values for $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solution was carried out by multilevel approximation using the Tauc method applied to the transformed diffuse reflectance spectra with account of the Kubelka–Munk function [13, 24].

3. Results and discussion

3.1. Optical properties

Diffuse reflectance R_d spectra of the $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions were obtained on micropowders (crystallite size $\sim 10\text{--}20\ \mu\text{m}$) relative to the BaSO_4 standard (provided by Shimadzu). Shown in Fig. 1 are the UV-VIS reflectance spectra as a function of wavelength (λ , nm) for the studied solid solutions.

The spectral dependence of the diffuse reflectance of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions (Fig. 1) was considered in three spectral ranges. In the region of low absorption (over 950 nm) at low photon energies $h\nu$,

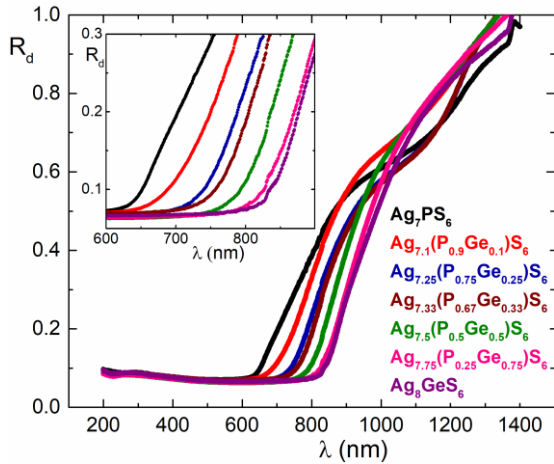


Fig. 1. Diffuse reflectance spectra of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions. Curves are arranged in ascending order of x value. (Color online.)

reflection with scattering may predominate, while in the spectral range 640...950 nm, corresponding to the region of sharp decrease in R_d , the appearance of the beginning of the optical absorption edge is observed. In the spectral range below 640 nm, a region of strong optical absorption is detected.

The analysis of the compositional spectral dependence (Fig. 1) revealed that for $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions, a red shift of the short-wave diffuse reflection edge was observed with increasing the Ge content, which is a characteristic property of solid solutions [24].

To estimate the values of the pseudo-gap E_g according to the obtained spectral dependence, it is necessary to apply multilevel processing of spectra with the Kubelka–Munk function, followed by the use of the Tauc method and application of the least squares function (as a method for determining E_g). The Kubelka–Munk function is used to convert the diffuse reflection spectrum into the absorption spectrum, and the Tauc method takes into account the band structure of material [21, 22, 24–26]:

$$[F(R_d(h\nu))]^n = \left(\frac{[1 - R_d(h\nu)]^2}{2R_d(h\nu)} \right)^n = A(h\nu - E_g),$$

where R_d is the diffuse reflectance at each wavelength, h is the Planck constant, ν is the photon frequency, $\frac{[1 - R_d(h\nu)]^2}{2R_d(h\nu)} \propto \alpha$ is the absorption coefficient, E_g is the band gap, and A is the proportionality constant.

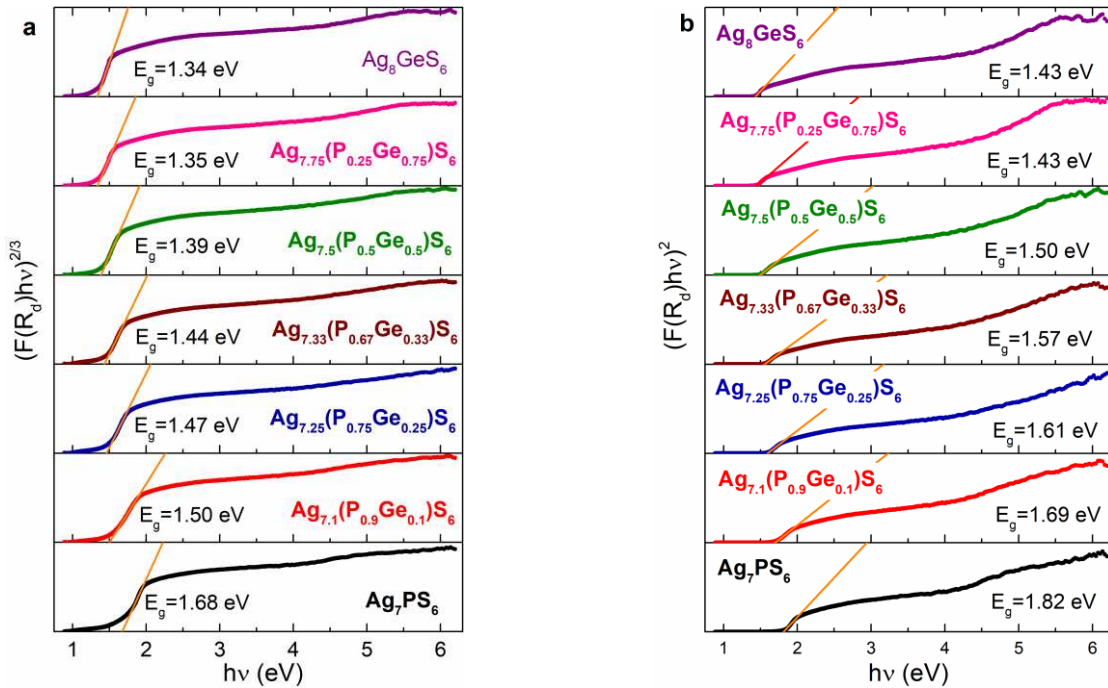


Fig. 2. Determination of the mechanism of self-absorption in $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions.

The coefficient n depends on the nature of the electronic transition and takes the values 2 or 2/3, indicating a direct allowed or forbidden transition, respectively, at $n = 1/2$ or $1/3$, the interband transition is indirect allowed or forbidden, respectively. In accord with calculations of the energy band structure inherent to the Ag_8GeS_6 crystal [20], an attempt to determine the intrinsic absorption mechanism was made by constructing only two dependences: $[F(R_d)h\nu]^2 = f(h\nu)$, $[F(R_d)h\nu]^{2/3} = f(h\nu)$, corresponding to a direct band semiconductor [20, 26]. As a result of the analysis based on the Tauc method, the graphical dependences in Fig. 2 were plotted for the processed diffuse reflection spectra with the Kubelka–Munk function.

To determine the pseudo-gap values of the $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions, the linear part of the spectrum was processed using the least-squares function. The decrease in the pseudo-gap E_g at the heterovalent cationic substitution of $\text{P}^{+5} \rightarrow \text{Ge}^{+4}$ was established for the both direct allowed and direct forbidden optical transitions ($n = 2$ and $2/3$) (Fig. 2). Accordingly, the compositional dependence of the pseudo-gap E_g for $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions was plotted (Fig. 3).

An analysis of the compositional dependence of the pseudo-gap energy of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions shows that heterovalent cationic substitution $\text{P}^{+5} \rightarrow \text{Ge}^{+4}$ within the anionic sublattice leads to a monotonic nonlinear decrease in the pseudo-gap (Fig. 3), in both cases ($n = 2$ and $2/3$).

Typically, the compositional dependence of the pseudo-gap for solid solutions is described by the relation [24, 27]:

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

where $E_g(x=0) \equiv E_g(0)$, $E_g(x=1) \equiv E_g(1)$ are the values of the pseudo-gap for individual ternary sulfides Ag_7PS_6 and Ag_8GeS_6 , respectively; c is the bowing parameter that is a measure of deviation from the linearity of the function $E_g(x)$ (Fig. 3, orange dashed lines).

The value of the bowing parameter c may depend on the deformation of the energy bands. These changes in the band structure can occur as a result of changes in the electronegativity $\text{P} (2.19) \rightarrow \text{Ge} (2.01)$ and as a result of structural disorder [19]. The latter is associated with a change in lattice parameters, deformation of the structure-forming polyhedra leading to a change in the bonds.

As a result, it was ascertained that the value of bowing parameter, when describing the compositional dependence of the E_g values for $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions (Fig. 3), is $c = 0.519$ eV at $n = 2$ and $c = 0.465$ eV at $n = 2/3$. It indicates the non-linear nature of the compositional behavior of the pseudo-gap energies. Therefore, cationic heterovalent cationic

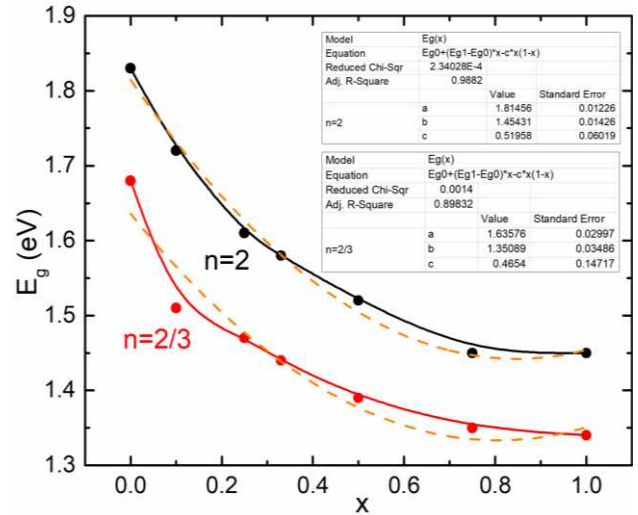


Fig. 3. Compositional dependence of the pseudo-gap energy of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions.

substitution $\text{P}^{+5} \rightarrow \text{Ge}^{+4}$ leads to deformations of the anionic framework of the argyrodite structure, which can affect the electronic structure of solid solutions. Since the bowing parameters at different values of the coefficient n that depends on the nature of the electronic transition are close (Fig. 3), and the determination of the most linear dependence is a rather controversial factor (Fig. 2), it is impossible to clearly determine the nature of the electronic transition, and requires more complex studies of the band structure.

4. Conclusions

Polycrystalline bulks of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions were synthesized using the one-temperature method. By mechanical grinding in an agate mortar, microcrystalline powders of $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ with a crystallite size of $\sim 10 \dots 20$ μm were obtained. Determination of the pseudo-gap E_g values was carried out by multilevel approximation. Applied approximation included the conversion of diffuse reflectance spectra into absorption spectra by using the Kubelka–Munk function. The transformed diffuse reflectance spectra were processed using the Tauc method. As a result, it was established that the heterovalent cationic substitution $\text{P}^{+5} \rightarrow \text{Ge}^{+4}$ within the anionic sublattice leads to a monotonous nonlinear decrease in the pseudo-gap energies, which confirms the presence of structural disorder in $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions.

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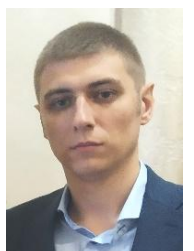
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Спектроскопія дифузного відбиття твердих розчинів у системі $\text{Ag}_7\text{PS}_6\text{-Ag}_8\text{GeS}_6$

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Анотація. Зразки твердих розчинів $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) одержано у формі мікрокристалічних порошків шляхом розмелювання в агатовій ступці. Спектри дифузного відбиття отриманих зразків твердих розчинів $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ досліджено у спектральному діапазоні 200...1400 нм при температурі 293 К. Спектральні залежності проаналізовано багаторівневою апроксимацією з використанням функції Кубелки–Мунка та графічного методу Таука. Встановлено, що для твердих розчинів $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ при збільшенні вмісту Ge спостерігається червоний зсув початку краю відбиття. Графічним методом Таука оцінено псевдоширину забороненої зони твердих розчинів $\text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$. Установлено, що гетеровалентне катіонне заміщення $\text{P}^{+5} \rightarrow \text{Ge}^{+4}$ у межах аніонної підґратки приводить до монотонного нелінійного зменшення псевдоширини забороненої зони.

Ключові слова: оптичні властивості, спектроскопія дифузного відбиття, мікрокристалічні порошки, метод Таука, тверді розчини.