Diffuse reflectance spectroscopy of solid solutions in the Ag$_{7}$PS$_{6}$-Ag$_{8}$GeS$_{6}$ system

T.O. Malakhovska$^a$, A.I. Pogodin$^b$, M.J. Filep$^{1,2}$, Ya.I. Studenyak$^1$, O.P. Kokhan$^1$, O.V. Zubaka$^1$, V.Yu. Izaî$^1$, P. Kúš$^3$

$^1$Uzhhorod National University, 46, Pidhirna str., 88000 Uzhhorod, Ukraine
$^2$Ferenc Rakoczi II Transcarpathian Hungarian College of Higher Education, 6, Kossuth Sq., 90200 Beregovo, Ukraine
$^3$Comenius University, Mlynska dolina, Bratislava 84248, Slovakia

Abstract. Samples of Ag$_{7+x}$(P$_{1-x}$Ge$_x$)$_6$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 Ag$_{7+x}$(P$_{1-x}$Ge$_x$)$_6$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 Ag$_{7+x}$(P$_{1-x}$Ge$_x$)$_6$S$_6$ solid solutions, a red shift of the reflection edge beginning is observed with increasing Ge content. The pseudo-gap values of Ag$_{7+x}$(P$_{1-x}$Ge$_x$)$_6$S$_6$ solid solutions was estimated by the Tauc method. It was found that the heterovalent cationic substitution P$^{5+}$ → 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, 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$_8$SnS$_6$, which is a structural analogue [5] of the initial argyrodite Ag$_4$GeS$_6$. The reported bandgap $E_g$ for Ag$_8$SnS$_6$ nanocrystals is 1.24...1.41 eV [3, 4]. The use of Ag$_8$SnS$_6$-based heterostructures as photoanodes [6, 7] and photocatalysts [9] has been reported. The quaternary representatives of the argyrodites, Ag$_4$PS$_4$I and Ag$_2$Si(Ge)S$_4$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$_8$GeS$_6$ and Ag$_8$PS$_6$ and solid solutions based on them were chosen. Both ternary sulfides Ag$_8$GeS$_6$ and Ag$_8$PS$_6$ melt congruently at 958 °C [14, 15] and 801 °C [15, 16], respectively. The structural phase transition in the Ag$_8$GeS$_6$ (271 °C) and Ag$_8$PS$_6$ (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$_8$GeS$_6$ crystallizes in SG Pna$_2$1 with lattice parameters:
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]:

\[ f(R_d) = \frac{(1 - R_d)^2}{2R_d} = K/S. \]

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 \( \text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge})\text{S}_6 \) 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 \( \text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge})\text{S}_6 \) 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 \( \text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge})\text{S}_6 \) 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 °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 \( \text{Ag}_{7+x}(\text{P}_{1-x}\text{Ge})\text{S}_6 \) (\( x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0 \)) 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...20 $\mu$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 ($\lambda$, 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 $h\nu$,

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]:

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

where $R_d$ is the diffuse reflectance at each wavelength, $h$ is the Planck constant, $\nu$ is the photon frequency, $\alpha$ is the absorption coefficient, $E_g$ is the band gap, and $A$ is the proportionality constant.

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.)

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 $\text{Ag}_6\text{GeS}_6$ crystal [20], an attempt to determine the intrinsic absorption mechanism was made by constructing only two dependences: $[F(R_g)h\nu]^2 = f(h\nu)$, $[F(R_g)h\nu]^2/3 = f(h\nu)$, 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 $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ 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 $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions was plotted (Fig. 3).

An analysis of the compositional dependence of the pseudo-gap energy of $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ 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]:

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

where $E_g(x = 0) = E_g(0)$, $E_g(x = 1) = E_g(1)$ are the values of the pseudo-gap for individual ternary sulfides $\text{Ag}_6\text{PS}_6$ and $\text{Ag}_6\text{GeS}_6$, 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 $P$ ($2.19 \rightarrow \text{Ge} (2.01)$) 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 $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ 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 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 $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ ($x = 0, 0.1, 0.25, 0.33, 0.5, 0.75, 1.0$) solid solutions were synthesized using the one-temperature method. By mechanical grinding in an agate mortar, microcrystalline powders of $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ with a crystallite size of ~10...20 $\mu$m 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 monotonic nonlinear decrease in the pseudo-gap energies, which confirms the presence of structural disorder in $\text{Ag}_7\text{Ge}(\text{P}_{1-x}\text{Ge}_x)\text{S}_6$ solid solutions.

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References


Authors and CV

Tetyana O. Malakhovska, born in 1983, defended her PhD thesis in inorganic chemistry in 2010. Senior researcher at the Uzhhorod National University. Authored 70 scientific publications and 10 patents. The area of her scientific interests includes solid state chemistry and materials science.

https://orcid.org/0000-0001-7309-4894

Artem I. Pogodin, defended his PhD thesis in Inorganic Chemistry in 2016. Senior Researcher at the Uzhhorod National University. Authored over 100 scientific publications and 100 patents. The area of his scientific interests includes solid state chemistry, crystal growth and materials science.

E-mail: artempogodin88@gmail.com, https://orcid.org/0000-0002-2430-3220

Mykhailo J. Filep, born in 1987, defended his PhD thesis in Inorganic Chemistry in 2015. Senior Researcher at the Uzhhorod National University. Authored over 100 articles and 50 patents. The area of his scientific interests includes solid state chemistry and materials science.

E-mail: mfilee23@gmail.com, http://orcid.org/0000-0001-7017-5437

Yaroslav I. Studenyak, PhD, Associate Professor at the Department of Analytical Chemistry, Uzhhorod National University. Author of over 20 scientific publications indexed in the Scopus and Web of Science databases as well as 9 patents.

E-mail: yaroslav.studenyak@uzhnu.edu.ua, https://orcid.org/0000-0002-8970-2222

Oleksandr P. Kokhan, PhD, Associate professor of Inorganic Chemistry department, Uzhhorod National University. Authored over 80 scientific publications and 95 patents. The area of his interests includes inorganic chemistry, solid state chemistry, crystal growth, materials science.

E-mail: aleksandr.kokh@gmail.com, http://orcid.org/0000-0003-1534-6779

Oksana V. Zubaka, PhD, Associate professor of Inorganic Chemistry department, Uzhhorod National University. Authored over 40 scientific publications. The area of her scientific interests includes solid state chemistry and materials science.

E-mail: oksana.zubaka@uzhnu.edu.ua, https://orcid.org/0009-0004-1175-2723

Vitalii Yu. Izai, born in 1985, defended his PhD thesis in Physics of Semiconductors and Dielectrics in 2013. Senior Researcher at the Department of Applied Physics, Uzhhorod National University till 2017. Scientific associate at the Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava from 2017. Authored 40 scientific publications in the Scopus and Web of Science databases as well as more than 20 patents (1 in EU database). The area of his interests includes materials science, superionic materials for solid-state ionicics, deposition and physical properties of thin films obtained using various plasma enhanced PVD and CVD techniques (magnetron sputtering, plasma beam sputtering, cathodic vacuum arc evaporation, HiPIMS, RF PECVD and their combination), design of artificial materials and interfaces.

E-mail: vitalii.izai@fmph.uniba.sk https://orcid.org/0000-0001-7512-3388

Peter Kúš, DrSc, Professor of the Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava. Authored 135 scientific publications in the Scopus and Web of Science databases and 18 patents (1 in EU database). The area of his interests includes materials science, superhard coatings for tool industry obtained using various PVD techniques, high-temperature superconducting films, materials for energy storage.

E-mail: peter.kus@fmph.uniba.sk, https://orcid.org/0000-0001-9153-5622
Authors’ contributions

Malakhovska T.O.: investigation, writing – original draft.
Pogodin A.I.: supervision, conceptualization, investigation, writing – original draft.
Filep M.J.: investigation, writing – original draft.
Kokhan O.P.: methodology, writing – review & editing.
Zubaka O.V.: investigation.
Izai V.Yu.: investigation, visualization.
Kúš P.: methodology, writing – review & editing.

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Спектроскопія дифузного відбиття твердих розчинів у системі Ag₇⁺²⁺Ag₈GeS₆

Т.О. Малаховська, А.І. Погодін, М.Й. Філеп, Я.І. Студеняк, О.П. Кохан, О.В. Зубака, В.Ю. Ізай, Р. Кúš

Анотація. Зразки твердих розчинів Ag₇+x(P₁−xGeₓ)S₆ (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 Ag₇+x(P₁−xGeₓ)S₆ 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 Ag₇+x(P₁−xGeₓ)S₆ при збільшенні вмісту Ge спостерігається червоний зсув початку краю відбиття. Графічним методом Таука оцінено псевдоширину забороненої зони твердих розчинів Ag₇+x(P₁−xGeₓ)S₆. Установлено, що гетеровалентне катіонне заміщення P⁵⁺ → Ge⁴⁺ у межах анонної підгратки приводить до монотонного нелінійного зменшення псевдоширини забороненої зони.

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