Optics

Optical characteristics of microcrystalline powders of Ag$_{7+x}$(P$_{1-x}$Si$_x$)S$_6$ solid solutions

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Abstract. Optical characteristics of microcrystalline powders of solid solutions formed in an Ag$_7$PS$_6$-Ag$_8$SiS$_6$ system were studied. The optical characteristics were determined by the diffuse reflectance spectroscopy. The diffuse reflectance spectra were analyzed using the Kubelka–Munk function and the Tauc method. The latter was used to take into account the energy structure of the studied materials. As a result, pseudo-gap values of the Ag$_{7+x}$(P$_{1-x}$Si$_x$)S$_6$ solid solutions were estimated. It was found out that heterovalent P^{+5} → Si^{+4} cationic substitution within the anionic sublattice leads to a monotonic nonlinear decrease in the pseudo-gap values, which confirms the presence of a structural disorder.

1. Introduction

Continuously increasing energy demand viewed in the context of natural energy resource depletion has led to an intensive search for alternative energy sources that would be environmentally friendly, cheaper, stable in different environments, and resistant to external factors. The search for new, less toxic, narrow-bandgap semi-conductor materials has incepted the study of ternary and tetrahedral chalcogenide semiconductor compounds [1–4]. In this aspect, study of multifunctional materials, including superionic conductors, which are characterized by high ionic conductivity in solid state due to the polyhedral crystal structure and a large number of possible equivalent crystallographic positions with partial occupancy that provides efficient ion migration and diffusion, is of great interest [1, 6–9]. Recently, the optical properties of ternary and quaternary silver chalcogenides with an argyrodite structure have been actively studied for photovoltaic technologies for solar cell applications [3, 10–12]. In this aspect, the most studied representative of argyrodites is canfieldite Ag$_8$SnS$_6$, which is a structural analog of the initial argyrodite Ag$_8$GeS$_6$. The band gap E_g of Ag$_8$SnS$_6$ nanocrystals is 1.24…1.41 eV, and a long-term photo-electrochemical activity is also observed [13].

Study of optical properties of ternary compounds Ag$_8$GeS$_6$, Ag$_7$PS$_6$ and solid solutions based on them has demonstrated that they belong to direct-band semiconductors. Heterovalent cationic substitution P^{+5} → Ge^{+4} leads to a decrease in the pseudo-gap value in the range of 1.68 to 1.34 eV [14]. Quaternary representatives of argyrodites Ag$_6$PS$_5$I and Ag$_7$Si(Ge)S$_5$I are characterized by higher values of the optical pseudo-gap in the range of 1.55 to 2.03 eV [15, 16].

The properties of solid solutions depend on the influence of the compositional disorder of the structure. Study of order-disorder phenomena is required to understand in detail the physical properties and the influence of structural features on them. This will allow more efficient use of multi-component silver chalcogenides for practical purposes.

For this study, ternary compounds Ag$_8$SiS$_6$, Ag$_7$PS$_6$ and solid solutions based on them were chosen [15–17]. The aim of this work is to study the optical characteristics of microcrystalline powders of Ag$_{7+x}$(P$_{1-x}$Si$_x$)S$_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions. Analysis of the changes in the optical pseudo-gap allows us to determine the effect of cationic substitution P^{+5} → Si^{+4} on the anionic framework disorder. In its turn, the latter causes disorder of the mobile cationic Ag$^+$ lattice and are directly related to the mechanism of ionic conductivity.

2. Experimental

The initial components for synthesizing ternary sulfides Ag_7PS_6 and Ag_8SiS_6 were silver (99.995%), phosphorus (99.999%), silicon (99.9999%), and sulfur (99.999%) taken in stoichiometric ratios. The synthesis was carried out by a direct one-temperature method in quartz ampoules evacuated to 0.13 Pa. The synthesis regime included heating to a maximum temperature of 1125 K (Ag_7PS_6) or 1300 K (Ag_8SiS_6) at a rate of 50 K/h and keeping at this temperature for 24 hours. The polycrystalline alloys were homogenized by annealing at 800 K (Ag_7PS_6) and 913 K (Ag_8SiS_6) for 120 hours. Cooling to the annealing temperature was carried out at a rate of 50 K/h. A further decrease to the room temperature was carried out in the furnace off mode. $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.1, 0.25, 0.5, 0.75) solid solutions were obtained by a direct one-temperature method from the previously synthesized ternary compounds. The synthesis regime included heating at a rate of 100 to 1300 K (with regard of the component with the highest melting point) and keeping at this temperature for 24 h. The annealing temperature was in the range of 800 to 913 K depending on the composition of the solid solution. The annealing time was 120 h. Cooling down to the room temperature was carried out in the furnace off mode [18].

The obtained $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions were ground in an agate mortar, followed by sieving through sieves of appropriate porosity. As a result, micropowders of $Ag_{7+x}(P_{1-x}Si_x)S_6$ solid solutions with the crystallite size of ~10 to 20 μm were obtained.

Optical characteristics were obtained using diffuse reflectance spectroscopy, which is a non-destructive and simple method for studying microcrystalline solid solutions. Diffuse reflectance spectra were collected by a Shimadzu UV-2600 double-beam spectrophotometer (detectors: photomultiplier tube and semiconductor InGaAs, spectral range: 220…1400 nm), equipped with an ISR-2600Plus integrating sphere. The scanning step was 1 nm. A standard cuvette with a quartz window was used to study the powdered samples. Diffuse reflectance (R_d) is defined as the ratio of the radiation intensity reflected by a sample R_{sample} to the standard value R_{BaSO4}. $BaSO_4$, provided by Shimadzu and characterized by ~100% reflectivity in the studied spectral range, was used as a reference material. The diffuse reflectance spectra (Fig. 1) for further processing were obtained by automatic fixation using the UVProbe software.

Three spectral ranges in the diffuse reflectance spectra of $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions can be distinguished, namely: (i) a strong optical absorption region below 640 nm, (ii) a region at 640…1100 nm, where R_d sharply decreases and optical absorption edge appears, and (iii) a low optical absorption region above 1100 nm. Considering the region of the sharp decrease in R_d in the concentration dependence of the solid solutions, a typical shift (for solid solutions) of the short-wave edge of diffuse reflection towards long-waves when P atoms were replaced by Si was found out [14–16].
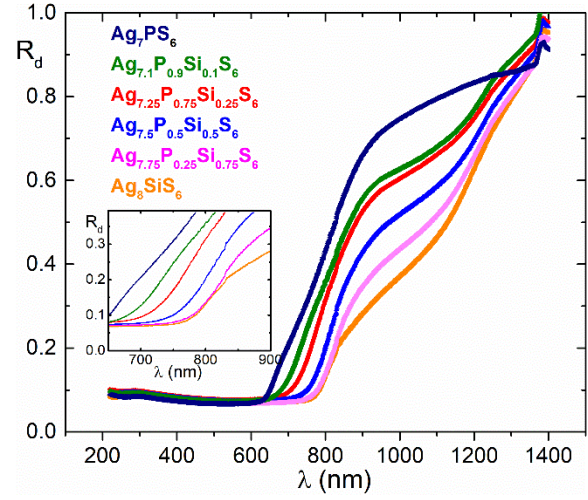

Fig. 1. Diffuse reflectance spectra of the $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions.

3. Results and discussion

3.1. Processing of spectra

To estimate the optical transition energy values from the spectral dependences of diffuse reflection, the Kubelka–Munk function should be applied. This is one of the fundamental principles used in the analysis of diffuse reflection spectra for weakly absorbing samples [14–17]. In our case, the Kubelka–Munk function was used to transform the diffuse reflectance spectrum into the absorption spectrum according to Eq. (1):

$$F\left[R_d\left(h\nu\right)\right] = \frac{\left[1 - R_d\left(h\nu\right)\right]^2}{2R_d\left(h\nu\right)} \propto \frac{\alpha}{s} \propto \alpha, \qquad (1)$$

where α is the absorption coefficient and s is the scattering coefficient, respectively, the latter being constant at a sample thickness much larger than the size of a single crystallite [20].

It is well known that direct and indirect optical transitions are possible in semiconductor materials. The value of the optical transition energy E_g can be calculated using the fundamental absorption, which corresponds to electronic excitation from the valence band to the conduction band. For a detailed optical characterization of the $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions by diffuse reflectance spectroscopy, the Kubelka–Munk function was applied using the Tauc plot method (Eq. (2)) to take into account the band structure of the materials under study [19, 20]:

$$\left[F\left(R_d\right)h\nu\right]^n = A\left(h\nu - E_g\right). \qquad (2)$$

Here, R_d is the wavelength dependent absolute diffuse reflectivity, h is the Planck constant, ν is the photon frequency, A is the proportionality constant, and the power n indicates the nature of optical electronic transitions, respectively. The value $n = 2$ or 2/3 points to direct allowed or forbidden transitions, while $n = 1/2$ or 1/3 means indirect allowed or forbidden interband transitions [20]. Taking into account the previous studies
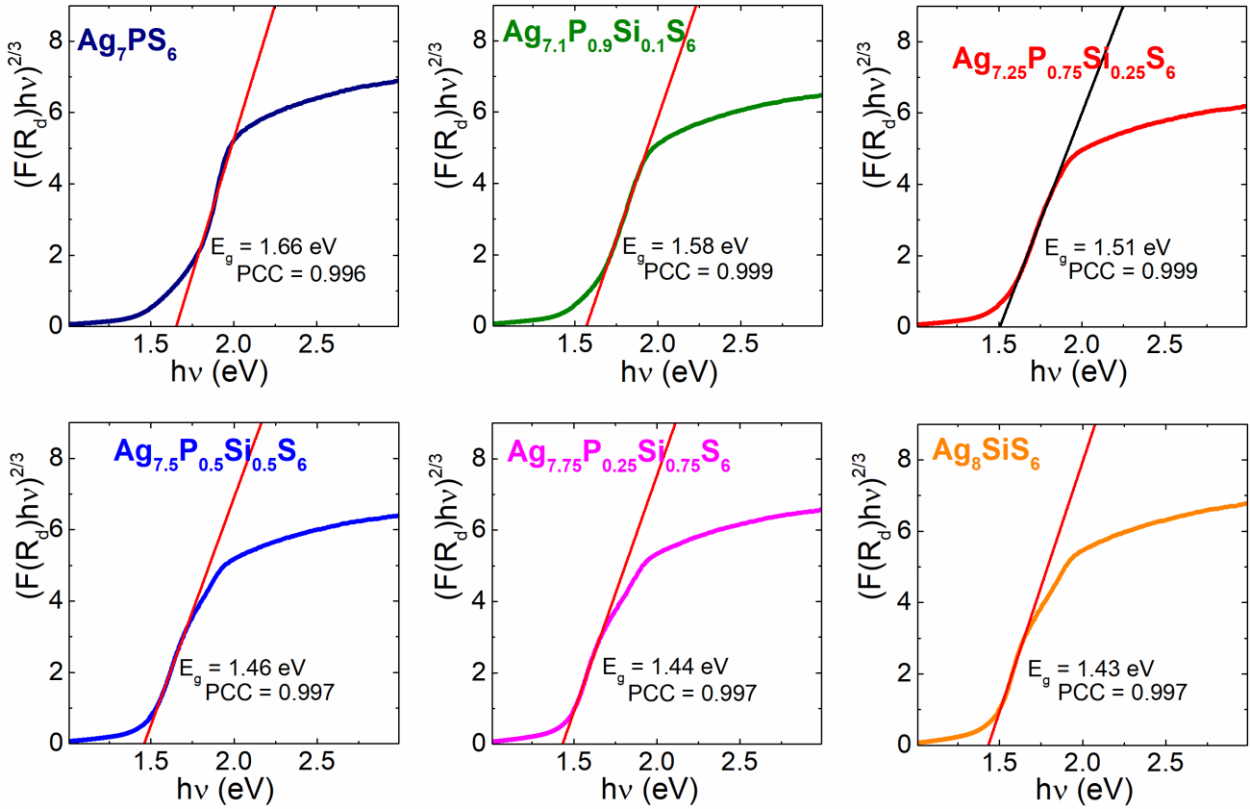
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Fig. 2. Tauc plots for the $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions for direct forbidden transitions.

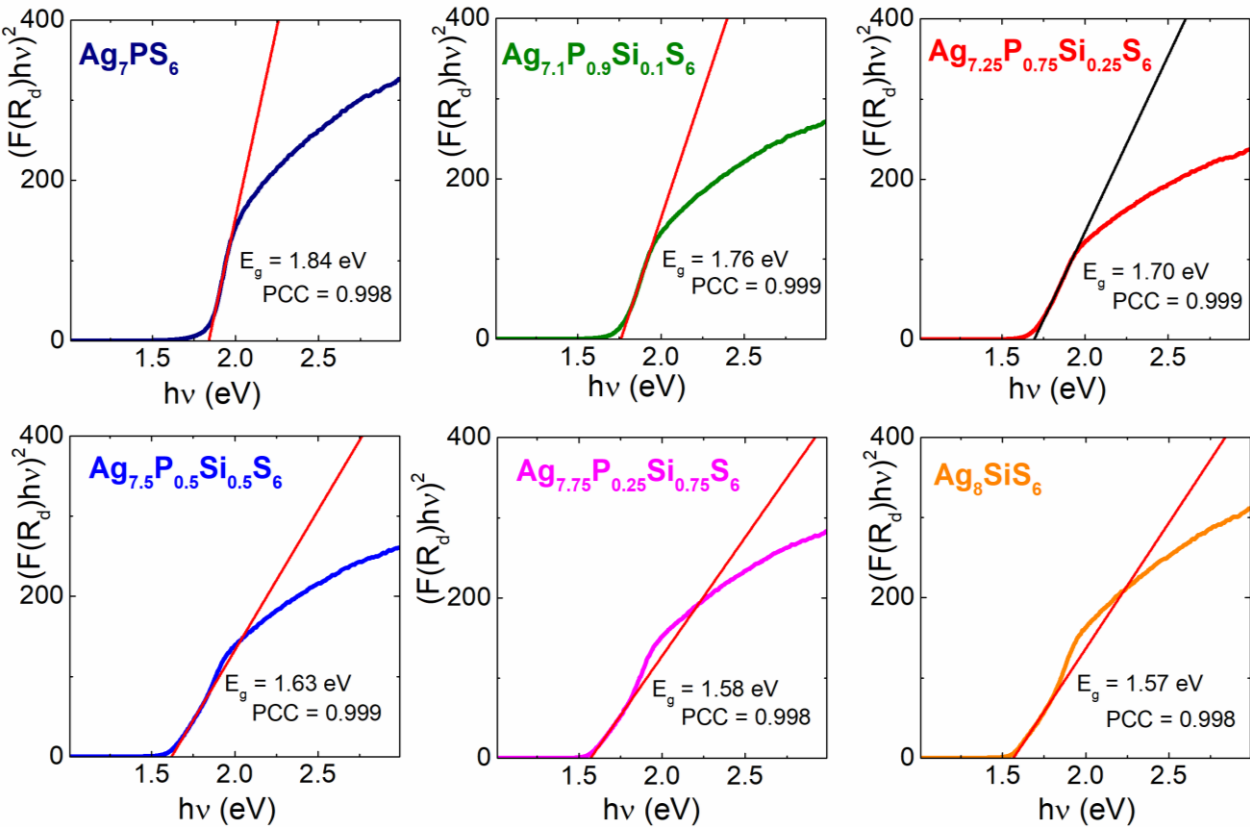**Fig. 3**. Tauc plots for the $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions for direct allowed transitions.

of the band structure of Ag_7PS_6, Ag_8GeS_6, and Ag_8SnS_6 argyrodites [14, 21], it was concluded that these argyrodites belong to direct-band semiconductors. Therefore, to determine the intrinsic absorption mechanism, two dependences, namely with $n = 2$ and $n = 2/3$ (Eq. (2)), were constructed [14]. Attribution of an optical electronic transition to a particular type is defined by the most linear dependence, *i.e.*, the closer value of the Pearson correlation coefficient (PCC) to unity [16].

Fig. 2 shows the graphical dependence of the Tauc equation of the Kubelka–Munk function for determining the intrinsic absorption mechanism in the $Ag_{7+x}(P_{1-x}Si_x)S_6$ ($x = 0.0, 0.1, 0.25, 0.5, 0.75$, and 1.0) solid solutions for direct forbidden transitions. Fig. 3 shows the Tauc plot for direct allowed transitions.

To determine the values of the optical pseudo-gap of the $Ag_{7+x}(P_{1-x}Si_x)S_6$ ($x = 0.0, 0.1, 0.25, 0.5, 0.75$, and 1.0) solid solutions, the linear parts of the spectra in the range of 1.5 to 2 eV obtained using Eq. (2) were processed by the least-squares method (Figs 2 and 3). The optical pseudo-gap values were found to decrease in both cases ($n = 2$ and $n = 2/3$) with a decrease in the electronegativity of the structure-forming element, namely P ($\chi = 2.19$) and Si ($\chi = 1.90$) [22], in the $[ES_4]$ tetrahedra, which are the basis of the anionic framework.

Thus, by combining the Kubelka–Munk function (to transform the diffuse reflection spectra into the absorption ones) with the Tauc plot method (to take into account the band structure) and the multilevel least-squares approximation, the compositional dependences of the energies of direct allowed (Fig. 2) and forbidden (Fig. 3) transitions for the $Ag_{7+x}(P_{1-x}Si_x)S_6$ ($x = 0.0, 0.1, 0.25, 0.5, 0.75$, and 1.0) solid solutions were obtained (Fig. 4) [16].

Analysis of the compositional dependence of the optical pseudo-gap values for the $Ag_{7+x}(P_{1-x}Si_x)S_6$ ($x = 0.0, 0.1, 0.25, 0.5, 0.75$, and 1.0) solid solutions demonstrates that a decrease in the electronegativity of a tetrahedra-forming element (P^{+5} and Si^{+4}), *i.e.*, heterovalent

cationic $P^{+5} \rightarrow Si^{+4}$ substitution within the anionic sublattice, leads to a monotonic nonlinear decrease in the optical pseudo-gap in both $n = 2$ and $n = 2/3$ cases (Fig. 4).

Deviation of the compositional dependences for the studied solid solutions from linear ones is described by the following relation [16]:

$$E_g(x) = E_g(0) + [E_g(1) - E_g(0)]x - cx(1-x), \qquad (3)$$

where $E_g(x = 0) \equiv E_g(0)$ and $E_g(x = 1) \equiv E_g(1)$ are the optical pseudo-gap values for individual ternary sulfides Ag_7PS_6 and Ag_8SiS_6, respectively, and c is the "bending" parameter, which is a measure of deviation from linearity of the function $E_g(x)$ (Fig. 4, dashed lines).

The value of the "bending" parameter c may depend on the deformation of the energy bands. Such changes in the band structure may occur due to a change in the electronegativity at the P (2.19) $\rightarrow$ Si (1.90) substitution as well as due to structural disorder associated with the change in the lattice parameters, but with certain peculiarities. It should be noted that since the initial sulfides Ag_7PS_6 and Ag_8SiS_6 crystallize in different space groups, $P2_13$ and $Pna2_1$, respectively, the $Ag_{7+x}(P_{1-x}Si_x)S_6$ solid solutions with x = 0. 0, 0.1, and 0.25 crystallize in a cubic cell, while the solid solutions with x = 0.5, 0.75, and 0.9 crystallize in an orthorhombic cell. Within these space groups, the lattice parameters in the heterovalent cationic $P^{+5} \rightarrow Si^{+4}$ substitution process are characterized by a tendency to monotonous nonlinear growth. Since an orthorhombic cell may be considered as a deformed cubic cell, the lattice parameters of both cells monotonously change in the entire compositional range [18]. Thus, the cationic heterovalent $P^{+5} \rightarrow Si^{+4}$ substitution leads to deformations of the anionic framework of the argyrodite structure that may affect the electronic structure of the solid solutions. At different n values in the Tauc equation the values of "bending" parameter c are close, regardless of the nature of electronic transitions (Fig. 4). Therefore, determining the most linear dependence (PCC value) is quite controversial (Figs 2, 3), and it is impossible to clearly identify the nature of electronic transitions. However, in accordance with the theoretical basis of the electronic band structure, at $E_g(n = 2/3) < E_g(n = 2)$, the solid solutions most likely belong to direct-band semiconductors characterized by forbidden optical transitions [21].

4. Conclusions

The pseudo-gap energies E_g for microcrystalline powders (the crystallite size of ~10…20 μm) of pure Ag_7PS_6, Ag_8SiS_6 and $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.1, 0.25, 0.5, and 0.75) solid solutions with argyrodite structure were determined by diffuse reflectance spectroscopy. The E_g values were determined using the Tauc plot method applied to the diffuse reflectance spectra transformed using the Kubelka–Munk function. As a result of the studies, the disorder of the crystal structure of the $Ag_{7+x}(P_{1-x}Si_x)S_6$ solid solutions induced by heterovalent cationic $P^{+5} \rightarrow Si^{+4}$ substitution within the anionic sublattice was confirmed.
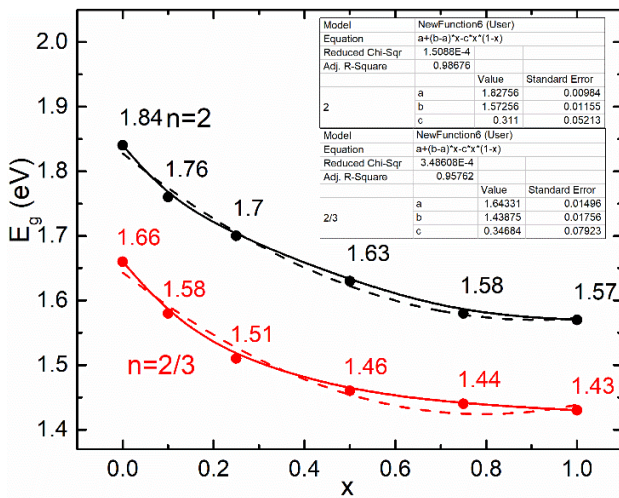
Fig. 4. Compositional dependences of the optical pseudo-gap of the $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions for direct forbidden and allowed transitions.

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The $Ag_{7+x}(P_{1-x}Si_x)S_6$ (x = 0.0, 0.1, 0.25, 0.5, 0.75, and 1.0) solid solutions were found to belong to direct-bandgap semiconductors and are characterized by forbidden optical transitions.

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Studenyak Ya.I.: investigation, writing – original draft.

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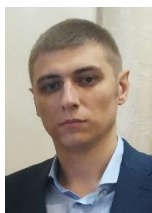
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Оптичні характеристики мікрокристалічних порошків твердих розчинів $Ag_{7+x}(P_{1-x}Si_x)S_6$

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Анотація. Досліджено оптичні характеристики мікрокристалічних порошків твердих розчинів, утворених в системі Ag_7PS_6-Ag_8SiS_6. Оптичні характеристики визначено методом дифузного відбиття. Спектри дифузного відбиття проаналізовано за допомогою функції Кубелки–Мунка та методу Тауца. Метод Тауца використано для врахування зонної структури досліджуваних матеріалів. У результаті оцінено значення оптичної ширини забороненої зони твердих розчинів $Ag_{7+x}(P_{1-x}Si_x)S_6$ і встановлено, що гетеровалентне катіонне заміщення $P^{+5} \rightarrow Si^{+4}$ в аніонній підгратці приводить до монотонного нелінійного зменшення значень оптичної ширини забороненої зони, що підтверджує наявність структурного розупорядкування.

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

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