Optical pseudogap of $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions

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Abstract. $Ag_7(Si_{1-x}Ge_x)S_5I$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) solid solutions are obtained in the form of micro-crystalline powders by grinding the substance in agate mortar. Diffuse optical reflectance spectra of $Ag_7(Si_{1-x}Ge_x)S_5I$ are studied at 293 K in the spectral range 220–1350 nm. They are analyzed using a Kubelka–Munk function. It is shown that increasing Si content in the solid solutions shifts the absorption edge towards higher photon energies. The optical pseudogap is estimated by a known Tauc method. It is demonstrated that the cationic substitution $Si^{+4} \rightarrow Ge^{+4}$ inside anionic sublattice decreases monotonically the optical pseudogap such that the corresponding compositional dependence is close to linear one.

Keywords: argyrodites, optical properties, diffuse reflection, solid solutions.

UDC: 535.3

1. Introduction

Superionic chalcohalogenides Ag_7SiS_5I and Ag_7GeS_5I belong to a large family of compounds with an argyrodite structure [1–3]. The general formula of argyrodites is $A^{m+}_{(12-n-x)/m}B^{n+}Y^{2-}_{6-x}X^{1-}_x$ $(0 \le x \le 1)$, with n and m being respectively the valences of cations A (Cu^+, Ag^+, Cd^{2+} and Hg^{2+}) and B (Ga^{3+}, Si^{4+}, Ge^{4+}, P^{5+} and As^{5+}) and Y (S^{2-}, Se^{2-} and Te^{2-}) and X (I^-, Br^- and Cl^-) denoting anions [3]. Ag_7SiS_5I and Ag_7GeS_5I are characterized by high enough ionic conductivity and intrinsic structural disorder caused by the presence of vacancies in their silver cationic sublattice [4–6].

The latter fact has drawn much attention of researchers in relation to ordering-disordering phenomena and phase transitions. In addition to the temperature disordering caused by thermal oscillations of atoms in a lattice, the structural disordering is no less significant for the superionic conductors with argyrodite structure [7]. Here the effect is caused by non-equivalence of the number of mobile ions and the positions they can occupy. It refers only to the sublattice of mobile ions, because its rigid part retains a regular structure. In this respect, superionic conductors differ from amorphous and glassy materials, for which all the structural constituents are not located regularly. It is interesting that, while the X-ray diffraction studies indicate a usual crystalline structure of superionic conductors, the Raman spectra of the latter contain broad bands characteristic of amorphous or glassy materials. Thus, superionic conductors occupy an intermediate position between crystalline and amorphous solids [7].

As a matter of fact, the optical properties of the Ag_7SiS_5I and Ag_7GeS_5I compounds and their solid solutions have not yet been studied. Therefore we will estimate the optical pseudogap of $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0. Notice that determining the band gap of semiconductors is one of the basic problems of materials science and, moreover, it is known that the band gap can be influenced notably by the structural disordering. The optical spectroscopy, including a diffuse-reflectance spectroscopy method, has been widely used to determine the band energy structure [8].

Let us explain in brief the effect of diffuse reflection. When a material consisting of many particles (e.g., crystallites or nanoparticles) is irradiated, a portion of radiation penetrates into a sample, and the rest of it is reflected from its surface. The penetrated portion of light is multiply scattered on its path and transmitted through the particles. Only that part of radiation which comes back to the input surface of sample and comes out of it is considered to correspond to diffuse reflection [9, 10]. The diffuse-reflectance spectroscopy represents a simple non-destructive method for the studies of porous and micro- or nano-crystalline materials [11]. This technique is especially useful when it is impossible to investigate a material using a specular reflection or difficult to find directly its optical transmission. Application of the diffuse-reflectance spectroscopy to the problems of estimating the optical pseudogap of superionic materials is rather complex. This is caused by the difficulties associated with interpretation of electronic transitions occurring in micro-crystallites, which can vary depending on inter-phase electronic interactions in disordered systems.

The aim of this work is to determine the optical pseudogap of the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0, following from the method of diffuse reflectance spectroscopy. Namely, the pseudogap values will be estimated in the approximation of Kubelka–Munk theory, using a standard Tauc-plot technique. As a result, we will analyze the structural disordering taking place in the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions due to cationic substitution $Si^{+4} \leftrightarrow Ge^{+4}$ in anionic sublattice.

2. Experimental

Quaternary chalcohalogenides Ag_7SiS_5I and Ag_7GeS_5I were synthesized from appropriate elementary components taken according to stoichiometric ratios. These were silver (the purity 99.995%), silicon (99.999%), germanium (99.999%), sulphur (99.999%), and pre-synthesized binary silver (I) iodide. The synthesis was performed by a direct single-temperature method in quartz ampoules evacuated down to 0.13 Pa. The regime of synthesis of Ag_7GeS_5I and Ag_7SiS_5I included a step heating up to 723 K at the rate 100 K/h, an exposure during 48 h, a further temperature increase to 1273 K at the rate 50 K/h, and an exposure at this temperature for 24 hours. A further cooling was carried out in a furnace-off mode [12, 13].

The $Ag_7(Si_{1-x}Ge_x)S_5I$ (x = 0.2, 0.4, 0.6 and 0.8) solid solutions were synthesized by the same direct single-temperature method, using the quaternary Ag_7SiS_5I and Ag_7GeS_5I compounds synthesized in advance. The synthesis mode included a heating at the rate 100 K/h up to 1273 K and an exposure for 24 h at this temperature. The annealing temperature was 873 K and the alloys thus obtained were kept for 120 h at this temperature. A cooling down to the room temperature was again carried out in the furnace-off mode [12, 13]. As a result, bulk polycrystalline samples of the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solution with x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0 were obtained.
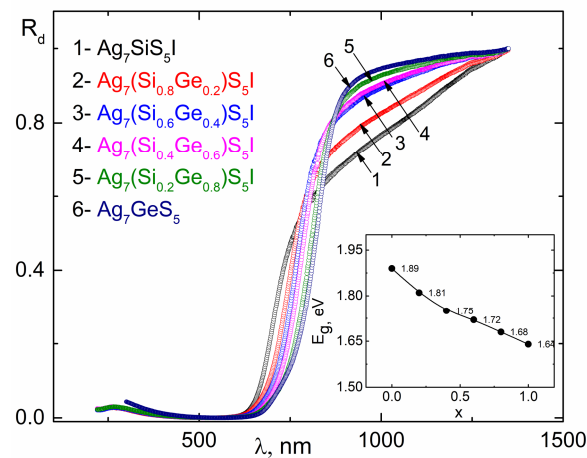
Diffuse-reflectance spectra were measured at 293 K on micro-crystalline (the sizes ~ 10–20 μm) powders of $Ag_7(Si_{1-x}Ge_x)S_5I$, which had been obtained by grinding the bulk polycrystalline samples in an agate mortar [5]. The particle-size distribution in the powders was controlled by sieving them through the sieves of appropriate porosities. The diffuse-reflectance spectra were detected using a two-beam Shimadzu UV-2600 spectrophotometer. Its main characteristics were as follows: a photomultiplier and an InGaAs semiconductor as detectors, the spectral range 220–1350 nm, and the scanning step 1 nm. UVProbe software was employed. The spectrophotometer was equipped with an integrating ISR-2600Plus sphere. A standard cuvette with a quartz window was used for the powder samples. $BaSO_4$ supplied by Shimadzu was taken as a reference material due to its ~ 100% reflectivity in the spectral range under our interest.

Finally, the diffuse reflection R_d was determined as the ratio of light intensity R_{sample} reflected by a sample to that reflected by the standard ($R_{standard}$), which is $BaSO_4$ in our case:

$$R_d = \frac{R_{sample}}{R_{standart}} \tag{1}$$

3. Results and discussion

As seen from Fig. 1, the diffuse-reflectance spectra of our $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions consist of three spectral regions. The diffuse reflection and some scattering can dominate in the low-absorption region (i.e., at the wavelengths longer than 775 nm corresponding to relatively low photon energies hv). On the other hand, in the spectral region 650–775 nm, which corresponds to sharp R_d decrease, one observes the onset of optical absorption edge. Finally, a strong optical absorption can be seen in the spectral region below 650 nm.

Fig. 1. Diffuse-reflectance spectra for $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0). The insert shows compositional dependence of E_g value calculated from the spectra (see the text).

According to the data of concentration studies (see the insert in Fig. 1), the short-wavelength limit E_g of the diffuse reflection for our $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions shifts towards longer-wavelength region when Si atoms are substituted with Ge ones. Note also that the changes in the spectral position of the reflection edge, which is observed in our case, is typical for different solid solutions [14].

It is known that the depth of penetration of incident radiation is determined by the properties of sample and its surface, as well as the incidence angles of incoming photons. Therefore, it is difficult to determine the path length and the light-absorption coefficient in a diffuse-reflection experiment. Fortunately, the above parameters are less important if one determines E_g using the spectral dependences and the method by Kubelka–Munk function. This situation differs significantly from the optical-transmission method [15].

Although there are several ways to determine the optical pseudogap E_g from diffuse-reflectance spectra [9, 16], the best one is based on comparing data fittings that correspond to different physical mechanisms, using the least-squares approach [9]. This can be done after applying the Kubelka–Munk technique for conversing the diffuse-reflectance spectra into the absorption spectra and then using the Tauc plot in order to take the band structure of a material into account.

The experimental diffuse-reflectance spectra can be converted into the absorption spectra, using the Kubelka–Munk function F_{KM}, which is known also as a re-radiation function [10]:

$$F_{KM}\left[R_d\left(h\nu\right)\right]=\frac{\left[1-R_d\left(h\nu\right)\right]^2}{2R_d\left(h\nu\right)}=\frac{K}{S}\propto\frac{\alpha}{s}. \tag{2}$$

In Eq. (2), R_d denotes the diffuse reflection, K and S are respectively the absorption and scattering coefficients of a dispersed system, and α and s the absorption and scattering coefficients of a sample. The scattering coefficient S entering in the Kubelka–Munk function remains constant at the sample thicknesses exceeding significantly the size of a micro-crystallite in this sample [17–22]. In other words, the Kubelka–Munk function can be applied for thick, endlessly densely packed samples with an arbitrary shape of particles. It represents a fairly accurate method in investigation of crystalline solids.

In the assumption of optically thick layers and a weak dependence of S, the shape of the F_{KM} function must be very close to that of the optical absorption spectrum of sample. Within the Kubelka–Munk theory, the coefficients K and S, which depend upon the absorption and scattering properties of a material, are assumed to be linear functions of the corresponding intrinsic physical parameters α and s (see Eq. (2)). In order to agree with the Kubelka–Munk theory in case of a perfectly diffused light, the K and S parameters should be defined as $K = 2\alpha$ and $S = 2s$ [23, 24].

Considering that the parameter S depends on the illumination geometry though remains constant irrespective of the light wavelength, while the K parameter is proportional to α, one arrives at the relationship

$$F_{KM}\left[R_d\left(h\nu\right)\right]\propto\alpha. \tag{3}$$

Taking into account Eq. (3), one can consider the spectral dependence $F(R_d)$ using the approaches adopted for the absorption coefficient.

Using Eq. (2) and the experimental data, we have constructed the spectral dependences in the coordinates $F(R_d)$ vs. $h\nu$ (see Fig. 2). According to Eq. (3), they are proportional to the spectral dependences of the absorption coefficient. A simple comparison of the spectral dependences shown in Fig. 2 for different $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions testifies a monotonous shift of the absorption edge towards higher photon energies, which occurs with increasing amount of Si. Concerning the nature of optical absorption edge, it can be completely understood within the quantum-mechanical
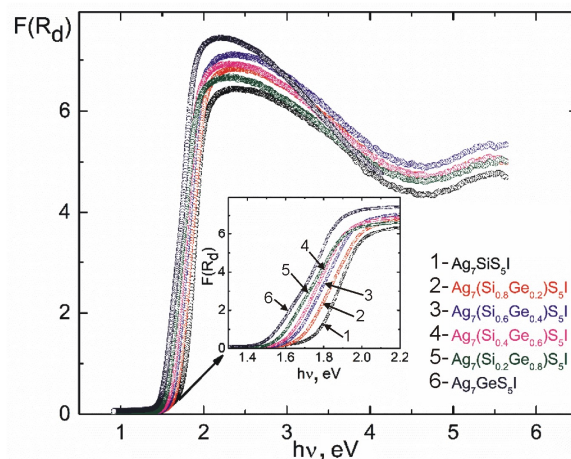
Fig. 2. Spectral dependences of Kubelka–Munk function for $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0).

theory of electron–photon interactions for different mechanisms of optical transitions. In principle, it is possible to determine the most important optical constants when studying the optical (reflection and absorption) spectra in a wide enough range of frequencies and temperatures. The main characteristics of any material determining its optical properties is the band structure [7]. In particular, it enables finding the characteristic points in the k-space of the Brillouin zone. These points correspond to certain energy gaps. The electronic transitions throughout the band gap occurring at light absorption are primarily concerned with the energy states that correspond to valence-band maximum and conduction-band minimum. They refer to $k_{min} = k_{max} = 0$ or $k_{min} \neq k_{max}$ respectively for the cases of direct or indirect transitions. Then the band gap can be evaluated using a Tauc representation:

$$(\alpha h v)^n = A(h v - E_g) \,, \qquad (4)$$

where h implies the Planck constant, v the photon frequency, α the absorption coefficient, E_g the band gap, n the coefficient, and A the proportionality constant. The exponent n depends on the nature of electronic transitions. In particular, it takes the values 2 or 2/3 in the cases of allowed or forbidden direct transitions, respectively. The interband transition is allowed or forbidden indirect one respectively when we have $n = 1/2$ or $n = 1/3$.

Combining Eqs. (2) and (4) for a real experiment, we obtain [25]

$$(F\left(R_d\right) h v)^n = A(h v - E_g) \,, \qquad (5)$$

where R_d is the absolute diffuse reflectivity at each wavelength. Basing on Eq. (5), we have attempted to elucidate the mechanism of intrinsic absorption by constructing and comparing the dependences $(F\left(R_d\right) h v)^2 = f(h v)$, $(F\left(R_d\right) h v)^{2/3} = f(h v)$, $(F\left(R_d\right) h v)^{1/3} = f(h v)$ and $(F(R_d) h v)^{1/2} = f(h v)$ with each other (see Fig. 3). Then the best linear fits of the experimental dependences performed in the widest photon-energy region would imply that the relevant electronic transitions can be ascribed to one or another type.

The fitting results for all of our solid solutions yield in rather similar goodness-of-fit values R^2. These are $R^2 = 0.9983–0.9994$ for $n = 2/3$ and $R^2 = 0.9964–0.9986$ for $n = 1/3$. Only the data shown in Fig. 3 for the $Ag_7(Si_{0.6}Ge_{0.4})S_5I$ solid solution are such that we have R^2 $(n = 1/2) > R^2$ $(n = 2/3)$. Since the R^2 values for different theoretical models are close enough, sometimes it has been difficult to draw unambiguous conclusions when comparing the models characterized by $n = 1/2$ and $n = 2/3$. In this case, we have been forced to choose the best model following from the widest region of its linear fit.

The above analysis has been performed using the Tauc plots and fitting their linear parts with different theoretical functions. In this manner we have found that our $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions belong to direct band gap semiconductors. Moreover, they are characterized by the forbidden optical transitions, i.e. the exponent n in Eq. (5) is equal to 2/3 (see Fig. 3). However, we cannot rule out completely a possibility that our materials belong to indirect band gap semiconductors (i.e., $n = 1/2$).

As a result, we have calculated the optical pseudogap for the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions using the plots of the Kubelka–Munk function in the Tauc coordinates $(F\left(R_d\right) h v)^{2/3} = f(h v)$. The corresponding concentration dependence of the optical pseudogap is displayed in Fig. 4. In particular, one can state that the cationic substitution $Si^{+4} \rightarrow Ge^{+4}$ occurring in the anionic sublattice leads to a monotonous decrease in the optical pseudogap.
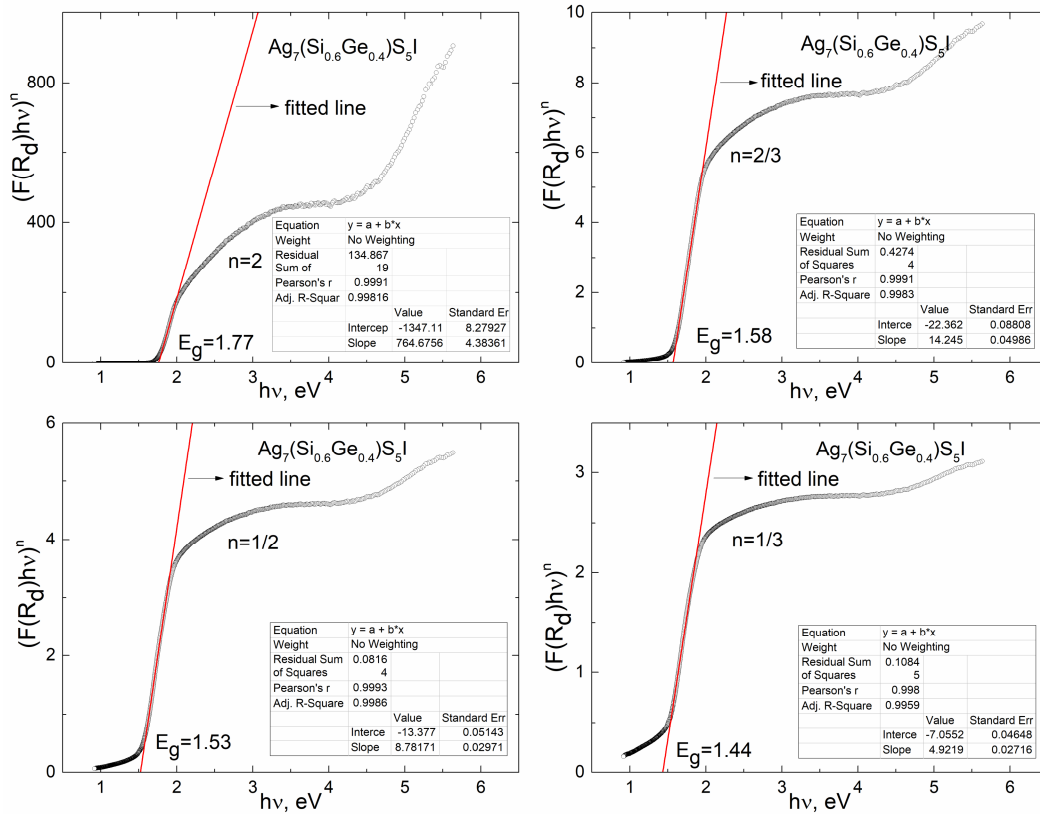
Fig. 3. Elucidation of the mechanism of intrinsic optical absorption in $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions, as illustrated on the example of $Ag_7(Si_{0.6}Ge_{0.4})S_5I$ compound.

Usually the concentration dependences of the optical pseudogap for solid solutions are described with the relation [26]

$$E_g(x) = E_g(0) + [E_g(1) - E_g(0)]x - cx(1-x),$$ (6)

where $E_g(x=0) \equiv E_g(0), E_g(x=1) \equiv E_g(1)$ are the optical pseudogaps referred respectively to the limiting compounds Ag_7SiS_5I and Ag_7GeS_5I, and c denotes a so-called 'bending parameter' (i.e., a measure of deviation of the function $E_g(x)$ from a linear dependence – see a red dashed line in Fig. 4).
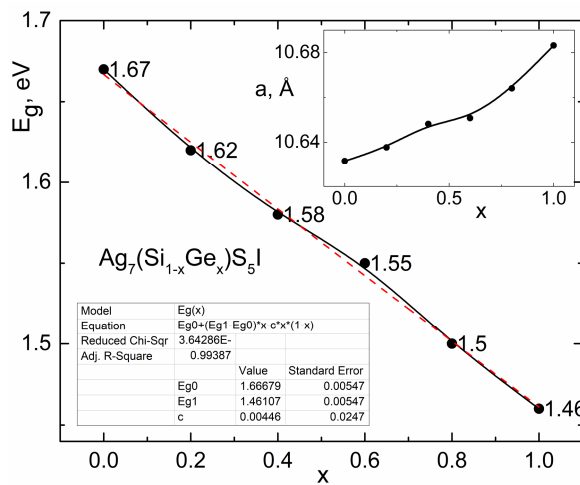
Fig. 4. Concentration dependence of optical pseudogap for $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0). The insert shows concentration changes in the lattice parameter reported for $Ag_7(Si_{1-x}Ge_x)S_5I$ in Ref. [12].

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The bending parameter c can depend on some deformation of the energy bands, e.g. due to changes in electronegativity or structural disordering. The latter can be associated with changes in the lattice parameters or deformation of the structural polyhedra that lead to changing lengths of chemical bonds. In our case, however, we have $c = 0.00446$ eV only. In other words, it would be fair to conclude that the bending parameter is close to zero. This indicates an almost linear character of the concentration dependence of the optical pseudogap. Then the cationic substitution $Si^{+4} \rightarrow Ge^{+4}$ does not lead to significant deformations of anionic framework of the argyrodite structure, which can influence the electronic structure of our solid solutions. This behaviour of the optical pseudogap can be associated only with increase in the lattice parameter, which is indeed the case (see the insert in Fig. 4) [12, 13], and a gradual increase in the electronegativity $(Si\ (1.91) \rightarrow Ge\ (2.01))$.

4. Conclusions

Micro-crystalline powders of the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 are obtained from pre-synthesized polycrystalline bulk samples by grinding them in an agate mortar. The above powders are investigated by the diffuse-reflectance spectroscopy method in the wide spectral range 220–1350 nm at the temperature 293 K. The diffuse-reflectance spectra detected for all of our solid solutions reveal a similar shape and involve three regions. The low-absorption region where the scattering reflection dominates is located at low photon energies hv (i.e., at the wavelengths longer than 775 nm). The region of strong optical absorption can be observed in the spectral region below 650 nm. Finally, a sharp decrease in the R_d characteristics is observed in the intermediate region (650–775 nm) where the onset of the optical absorption edge occurs. It is revealed that the short-wavelength limit of the diffuse reflection in our $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions shifts towards the longer-wavelength region when Si atoms are substituted by Ge ones.

The optical pseudogap of the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions is determined using the Tauc plots. The latter refer to the diffuse-reflectance spectra transformed basing on the Kubelka–Munk function. Analysis of our data indicates that the $Ag_7(Si_{1-x}Ge_x)S_5I$ solid solutions belong to direct band gap semiconductors and are characterized by the forbidden optical transitions. As a consequence, the $(F(R_d)hv)^{2/3} = f(hv)$ plots are used to calculate the optical pseudogap. It is demonstrated that the cationic substitution $Si^{+4} \rightarrow Ge^{+4}$ leads to a monotonously decreasing optical pseudogap. Moreover, the substitution $Si^{+4} \rightarrow Ge^{+4}$ does not lead to significant deformations of the anionic framework of the argyrodite structure, which can influence the electronic structure of our solid solutions. This behaviour of the optical pseudogap can be associated only with an increase of the lattice parameters and a gradual increase in the electronegativity occurring at the $Si \rightarrow Ge$ substitution.

Acknowledgment

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Анотація. *Одержано тверді розчини $Ag_7(Si_{1−x}Ge_x)S_5I$ (x = 0, 0,2, 0,4, 0,6, 0,8 і 1,0) у вигляді мікрокристалічних порошків шляхом розтирання речовини в агатовій ступці. Досліджено спектри дифузного оптичного відбивання $Ag_7(Si_{1−x}Ge_x)S_5I$ у діапазоні 220–1350 нм при 293 К. Аналіз цих спектрів виконано за допомогою функції Кубелки–Мунка. Показано, що збільшення вмісту Si у твердих розчинах зміщує край поглинання в бік вищих енергій фотонів. Оцінено оптичну псевдощілину за відомим методом Таука. Показано, що катіонне заміщення $Si^{+4} → Ge^{+4}$ всередині аніонної підгратки монотонно зменшує оптичну псевдощілину так, що відповідна композиційна залежність близька до лінійної.*