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## ELECTRICAL CONDUCTIVITY STUDIES OF COMPOSITES BASED ON $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ SOLID SOLUTIONS

*Polymer composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions are produced. The electrical conductivity of the composites is measured by impedance spectroscopy in the frequency range from 20 Hz to  $2 \times 10^6$  Hz and in the temperature interval 292–338 K. The frequency dependences of the total electrical conductivity are obtained, the Nyquist plots are constructed, and their analysis is performed. The effect of  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution on the total electrical conductivity and the activation energy, as well as on the electronic and ionic components of the electrical conductivity of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions is studied on the basis of compositional dependences.*

*Keywords:* solid solutions, composites, cation substitution, electrical conductivity, activation energy, compositional dependence.

### 1. Introduction

$\text{Cu}_7\text{GeSe}_5\text{I}$  and  $\text{Ag}_7\text{GeSe}_5\text{I}$  compounds belong to the argyrodites with the general chemical formula  $\text{A}_{12-n-x/m}^{m+1}\text{B}^{n+}\text{X}_{6-x}^{2-}\text{Y}^{1-}$  ( $0 < x < 1$ ), where  $m$  and  $n$  are the valences of cations  $\text{A} = (\text{Cu}^+, \text{Ag}^+, \text{Cd}^{2+}, \text{Hg}^{2+})$  and  $\text{B} = (\text{Ga}^{3+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{P}^{5+}, \text{As}^{5+})$ , respectively, with  $\text{X} = (\text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-})$  and  $\text{Y} = (\text{Cl}^-, \text{Br}^-, \text{I}^-)$  anions [1]. The wide potential for the substitution of atoms makes them promising for obtaining the solid solutions based on them, which are, in turn, a prospect for the purposeful search of materials with predetermined parameters. The representatives of the argyrodite family are well known as superionic conductors and widely used for the applications as the solid-state batteries, su-

percapacitors, and other electrochemical devices [2–6]. The growth processes and physical and chemical properties of  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Cu}_7\text{GeSe}_5\text{I}$  crystals, as well as  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals on their base, were studied in several papers [7–9]. Electrical, electrochemical and optical properties of the above-mentioned crystals were investigated in Refs. [10–12]. It was shown that a  $\text{Cu}_7\text{GeSe}_5\text{I}$  crystal is characterized by the highest electrical conductivity among the well-known copper-containing superionic conductors (0.64 S/cm at a frequency of  $10^6$  Hz and at a temperature of 300 K) [11]. Optical studies have shown that the absorption edges of a  $\text{Cu}_7\text{GeS}_5\text{I}$  single crystal and  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals exhibit the Urbach behavior in a wide temperature range [10–12]. It is shown that, at the  $\text{S} \rightarrow \text{Se}$  anionic substitution in  $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$  mixed crystals, a nonlinear increase of the electrical conductivity by more than an order of magnitude, nonlinear decrease of the op-

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tical pseudogap, and behavior of the Urbach energy typical of mixed crystals were observed [10–12]. The influence of the  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution on the electrical conductivity of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions was studied in Ref. [13]. For an  $\text{Ag}_7\text{GeSe}_5\text{I}$  crystal, the non-Arrhenius behavior of the electrical conductivity is observed and described by the Vogel–Fulcher–Taman equation. Moreover, their temperature changes are related to a “quasiliquid” sublattice of  $\text{Ag}^+$  ions [14–17]. In the last decade, we had actively investigated the polymer composites based on argyrodites [18–21]. The purpose of this work was the preparation of composites, the study of their frequency and temperature dependences of the electrical conductivity, as well as the study of the compositional behavior of the total conductivity, ionic and electronic components of the conductivity, and activation energy of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions.

## 2. Experimental

The synthesis of  $\text{Cu}_7\text{GeSe}_5\text{I}$  and  $\text{Ag}_7\text{GeSe}_5\text{I}$  compounds was carried out from the simple substances Ag (99.999%), Cu (99.999%), Ge (99.9999%), Se (99.9999%) and pre-synthesized CuI (AgI) loaded in the corresponding stoichiometric ratios, further purified by the vacuum distillation (CuI) and by the directed melt crystallization (AgI). As the starting materials for the synthesis of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions, we used pre-synthesized  $\text{Cu}_7\text{GeSe}_5\text{I}$  and  $\text{Ag}_7\text{GeSe}_5\text{I}$  compounds. In the first stage, the temperature is being risen to 873 K for 6 hours. After that, a 24-hour ageing is carried out, which is due to the need for the complete binding of selenium (for  $\text{Cu}_7\text{GeSe}_5\text{I}$  and  $\text{Ag}_7\text{GeSe}_5\text{I}$ ). A rapid increase in the temperature can lead to the depressurization of an ampoule. Further, the temperature is being risen during the day to maximum temperature values, which are 50 K above the melting point  $T_{\text{melt}}$ , following by a 24-hour ageing at which the complete homogenization of the melt occurs. The subsequent lowering to the temperature of homogenizing annealing constituting  $2/3T_{\text{melt}}$  (72 h) occurs at a speed of 100 K/h. The cooling to room temperature is carried out in the oven off mode. The obtained samples were investigated by differential thermal methods (chromel–alumel thermocouples, fast heating and cooling at 700 K/h) and X-ray (DRON 4-07,  $\text{CuK}\alpha$  radiation, angle scanning speed  $2\theta - 0.02$  deg, exposure – 1 s)

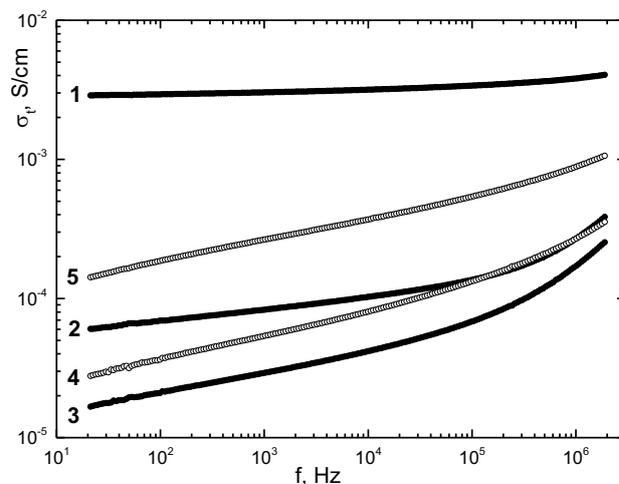
analyses. For the production of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions with  $x = 0, 0.25, 0.5, 0.75,$  and  $1$ , the powders (10–50  $\mu\text{m}$ ) of the latter were mixed with ethylene-vinyl acetate polymer dissolved in ethyl acetate in the ratio: 90 wt.%  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  and 10 wt.% EVA (ethylene-vinyl acetate). The stirring was being performed for 10–15 min using ultrasound (50 W, 40 kHz) to obtain homogeneous suspensions, which were subsequently dried at 333 K. The pressing of the samples was carried out at a pressure of 400 MPa, resulting in obtaining disks of composites with a diameter of 8 mm and a thickness of 3–4 mm. Studies of the electrical conductivity of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions with  $x = 0, 0.25, 0.5, 0.75, 1$  were carried out by impedance spectroscopy [22, 23] in the frequency range 20 Hz– $2 \times 10^6$  Hz and in the temperature interval 292–338 K, using a high-precision LCR meter Keysight E4980A. The amplitude of the alternating current was 10 mV. Measurements were carried out by the two-electrode method on blocking gold contacts. Gold contacts were deposited by the chemical precipitation from solutions. As starting solutions, 0.02M tetrachloroaurat (III) sodium  $\text{Na}[\text{AuCl}_4]$  and formalin solution (40% $\text{CH}_2\text{O} + 8\%\text{CH}_3\text{OH} + 52\%\text{H}_2\text{O}$ ) (deoxidant) were used in the ratio of 5/1 (selected experimentally). The precipitation was carried out at a temperature of not more than 293 K. Increasing the temperature negatively affects the quality of the deposited film due to the growth of the recovery rate.

## 3. Results and Discussion

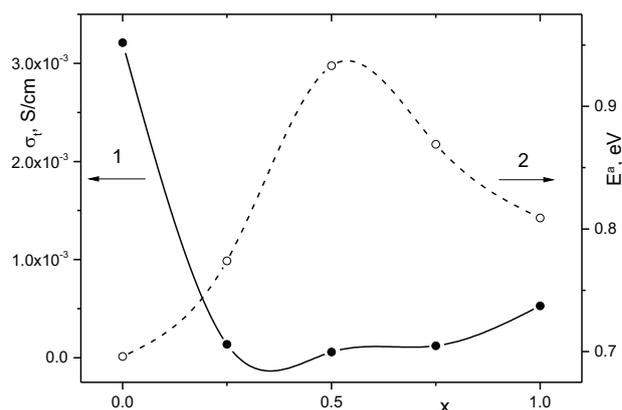
It is shown that, for all composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions, the total electrical conductivity is increased with the frequency (Fig. 1). Based on the obtained results, a compositional dependence of the total conductivity at a frequency of 100 kHz was constructed (Fig. 2). Apparently, the dependence of the total conductivity on the composition is nonlinear (Fig. 2). The conductivity of the composite based on  $\text{Cu}_7\text{GeSe}_5\text{I}$  at 298 K is  $3.21 \times 10^{-3}$  S/cm, while the composite based on  $\text{Ag}_7\text{GeSe}_5\text{I}$  is characterized by a slightly lower value of the total electrical conductivity,  $5.29 \times 10^{-4}$  S/cm. Composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  ( $x = 0.25, 0.5, 0.75$ ) solid solutions are characterized by lower conductivity values than the starting individual  $\text{Cu}_7\text{GeSe}_5\text{I}$  and

$\text{Ag}_7\text{GeSe}_5\text{I}$  compounds, which is obviously associated with their considerable compositional disordering.

According to the results of temperature studies, the temperature dependences of the electrical conductivity for the composites were measured. They are found to be well described by the Arrhenius law and are linear in the Arrhenius coordinates. This made it possible to determine the activation energies of the total conductivity, which are shown in Fig. 2. It is revealed that the compositional dependence of the activation energy of the composites has nonlinear character with a maximum for  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$  ( $E_a = 0.933$  eV) compared to the values for the individual  $\text{Cu}_7\text{GeSe}_5\text{I}$  ( $E_a = 0.696$  eV) and  $\text{Ag}_7\text{GeSe}_5\text{I}$  ( $E_a = 0.809$  eV) compounds. A standard approach using electrode equivalent circuits (EEC) [24] and their analysis on Nyquist plots were used for detailed studies of the frequency dependences of the electrical conductivity determining the electrochemical processes and the separation into ionic and electronic components. The parasitic inductance of the cell ( $\approx 4 \times 10^{-7}$  H) was taken into account in the analysis of all the samples. For composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions, two semicircles which correspond to the ion processes are observed in Nyquist plots (Fig. 3, *a-e*). The low-frequency semicircle corresponds to the capacitance of the double diffusion layer  $C_d$  with the subsequently included resistance  $R_{gb}$  and capacity  $C_{gb}$  of the grain boundary. The high-frequency semicircle, in turn, corresponds to the resistance  $R_g$  and capacity  $C_g$  of the grain for the composite material. Parallel to the ion processes, the electronic resistance  $R_e$  is included into EEC. It is responsible for the electronic conductivity and makes its appropriate contribution to the representation of both low- and high-frequency semicircles. As can be seen (Fig. 3), in the process of  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution, there is a change in the ratio of the semicircle sizes, which is manifested in an increase in the low-frequency semicircle radius and a decrease in the radius of the high-frequency semicircle, respectively. Alongside, the low-frequency semicircle gradually shifts further into the low-frequency region, as can be seen from the calculated data (open dots). This is obviously caused by a change in the ratio of the conductivity components. Thus, for a composite based on  $\text{Cu}_7\text{GeSe}_5\text{I}$ ,  $\sigma_{\text{ion}} < \sigma_{\text{el}}$  (Fig. 3, *a*); in the process of cation substitution for a composite based on  $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ ,

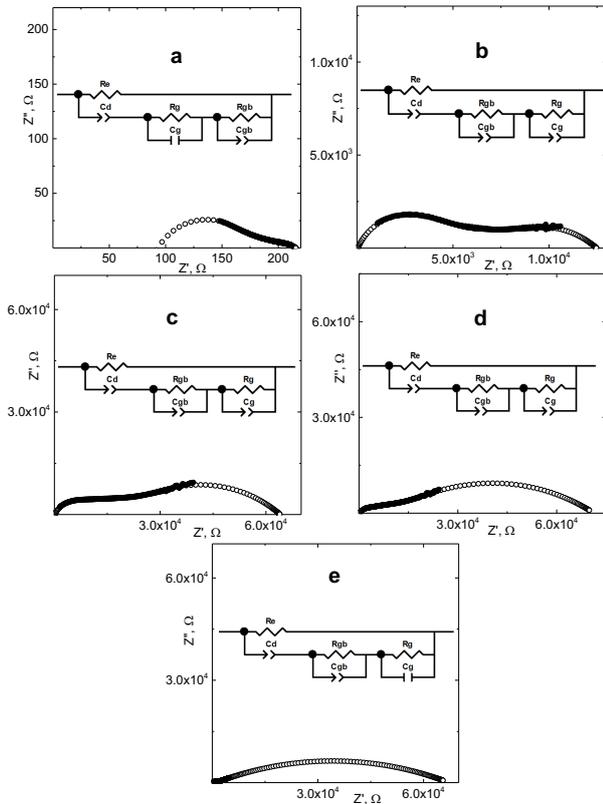


**Fig. 1.** Frequency dependences of the total electrical conductivity at  $T = 298$  K for the composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions:  $\text{Cu}_7\text{GeSe}_5\text{I}$  (1),  $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$  (2),  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$  (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)

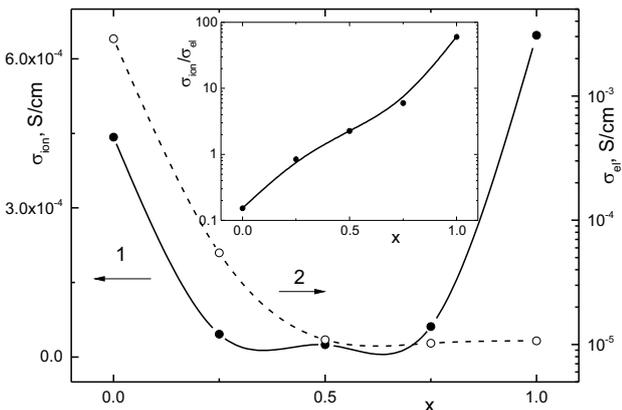


**Fig. 2.** Compositional dependences of the total electrical conductivity (1) at  $T = 298$  K and 100 kHz and the activation energy (2) for the composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions

$\sigma_{\text{ion}} \approx \sigma_{\text{el}}$  (Fig. 3, *b*); and, for the composite based on  $\text{Ag}_7\text{GeSe}_5\text{I}$ ,  $\sigma_{\text{ion}} \gg \sigma_{\text{el}}$  (Fig. 3, *e*), respectively. Therefore, such dynamics of changes in the semicircle shape on Nyquist plots (Fig. 3) in the process of  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution is explained by a decrease in the electronic component of the conductivity, resulting in the increasing influence of the diffusion and relaxation processes within the double diffusion layer. The ionic conductivity of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions consists of the sum of the conductivities of grains and the boundaries



**Fig. 3.** Nyquist plots at  $T = 298$  K of the composites based of  $\text{Cu}_7\text{GeSe}_5\text{I}$  (a),  $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$  (b),  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$  (c),  $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$  (d) and  $\text{Ag}_7\text{GeSe}_5\text{I}$  (e): experimental data (solid dots), calculated data (open dots), and EEC



**Fig. 4.** Compositional dependences of ionic (1) and electronic (2) conductivities for the composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions at  $T = 298$  K. The inset shows the compositional dependence of the ratio of the ionic to electronic conductivity for the composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions at  $T = 298$  K

of grains. It should be noted that the ionic conductivity of grain boundaries is smaller than the conductivity of grains themselves.

The carried out analysis of the frequency dependences made it possible to investigate the compositional behavior of the ionic and electronic components of the total electrical conductivity of the composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions (Fig. 4). Apparently, the dependence of the ionic component on the composition is nonlinear with a minimum for  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$  (Fig. 4). The ionic conductivity of the composite based on  $\text{Cu}_7\text{GeSe}_5\text{I}$  at 298 K is  $4.42 \times 10^{-4}$  S/cm, whereas the composite based on  $\text{Ag}_7\text{GeSe}_5\text{I}$  is characterized by a slightly higher ionic conductivity of  $6.47 \times 10^{-4}$  S/cm due to the greater mobility of Ag positions compared to Cu positions. In the process of  $\text{Cu}^+ \leftrightarrow \text{Ag}^+$  cationic substitution, the ionic component of the conductivity decreases and, for a composite based on  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ , has a minimum value of  $2.48 \times 10^{-5}$  S/cm. Instead, the electronic component, which is  $2.89 \times 10^{-3}$  S/cm for a composite based on  $\text{Cu}_7\text{GeSe}_5\text{I}$ , decreases in the process of  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution without any anomalies. For a composite based on  $\text{Ag}_7\text{GeSe}_5\text{I}$ , its value is  $1.07 \times 10^{-5}$  S/cm (Fig. 4). Thus, one of the main characteristics of the superionic materials is the ratio of ionic and electronic conductivities. In the inset in Fig. 4, its compositional dependence is shown. As can be seen from the transition from  $\text{Cu}_7\text{GeSe}_5\text{I}$  composite, where the electronic conductivity component is 6.5 times greater than the ionic one, to the  $\text{Ag}_7\text{GeSe}_5\text{I}$ , the  $\sigma_{\text{ion}}/\sigma_{\text{el}}$  ratio tends to increase. For  $\text{Ag}_7\text{GeSe}_5\text{I}$  composite, the ionic conductivity component is 60 times greater than the electronic one.

#### 4. Conclusions

$(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  compounds with  $x = 0, 0.25, 0.5, 0.75,$  and  $1$  are synthesized for the preparation of composites on their base. The composites are prepared by mixing the powders of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions with ethylene-vinyl acetate in a 9:1 ratio, the mixture of which was further dried and pressed. The conductivity studies of composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions are performed by impedance spectroscopy in the frequency range from 20 Hz to  $2 \times 10^6$  Hz and in the temperature interval 292–338 K. The measurements are performed

by a two-electrode method on blocking gold contacts. For all composites, an increase in the conductivity with the frequency is detected on the frequency dependences of the total electrical conductivity. It is found that, with increasing the Ag content in composites based on  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$  solid solutions, the total electrical conductivity decreases nonlinearly with the downward bowing, whereas the activation energy increases nonlinearly with the maximum for  $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$  solid solution. Nyquist plots are constructed, and their detailed analysis is performed using an electrode-equivalent circuit, which allowed us to separate the contributions of the ionic and electronic components into the total electrical conductivity. The dependence of the ionic conductivity on the composition is found to be nonlinear with a minimum, and the ionic conductivity for the composite based on  $\text{Ag}_7\text{GeSe}_5\text{I}$  ( $6.47 \times 10^{-4}$  S/cm) is greater than for  $\text{Cu}_7\text{GeSe}_5\text{I}$  ( $4.42 \times 10^{-4}$  S/cm). The electronic conductivity with increasing the silver content decreases nonlinearly, and its value for  $\text{Cu}_7\text{GeSe}_5\text{I}$  is more than two orders of magnitude greater than for  $\text{Ag}_7\text{GeSe}_5\text{I}$ . The analysis of the compositional dependence of the ratio of the ionic conductivity to the electronic one shows that, due to the  $\text{Cu}^+ \rightarrow \text{Ag}^+$  cationic substitution, it is nonlinearly increasing by more than two orders of magnitude.

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ДОСЛІДЖЕННЯ ПРОВІДНОСТІ КОМПОЗИТІВ  
НА ОСНОВІ ТВЕРДИХ РОЗЧИНІВ  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$

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Виготовлені полімерні композити на основі твердих розчинів  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ . Виміряно їх провідність методом імпедансної спектроскопії на частотах від 20 до  $2 \cdot 10^6$  Гц при температурах 292–338 К. Отримано частотну залежність загальної провідності, побудовані графіки Найквіста і дано їх аналіз. З урахуванням залежності від композиції вивчено дію заміни  $\text{Cu}^+ \rightarrow \text{Ag}^+$  на загальну провідність, енергію активації і на електронну та іонну компоненти провідності композитів на основі твердих розчинів  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ .