

Influence of cation substitution on electrical conductivity of microcrystalline ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions

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Abstract. Ceramic samples based on the microcrystalline powders $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) were prepared by pressing them at the pressure close to 400 MPa and subsequent annealing at 873 K for 36 hours. Using the microstructural analysis, the average size of microcrystallites of these samples was determined. Investigation of electrical conductivity of ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions was carried out using the method of impedance spectroscopy in the frequency range from 10 Hz to 3×10^5 Hz and within the temperature range 293...383 K. Analysis of the Nyquist plots allowed determining the contributions of ionic and electronic components to the total electrical conductivity. The temperature dependence of ionic and electronic conductivity in Arrhenius coordinates is linear, which indicates their thermoactivation character. The compositional behaviour of ionic and electronic conductivity, as well as their activation energies have been studied. Their nonlinear character can be explained by the complex process of recrystallization and $\text{Cu}^+ \leftrightarrow \text{Ag}^+$ cation substitution within the cationic sublattice.

Keywords: argyrodite, superionic conductor, solid solution, ceramic, impedance spectroscopy.

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1. Introduction

$\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ compounds are representatives of a wide family of argyrodites, united by a similar structural motive [1–4]. A characteristic feature of compounds with argyrodite structure is the simultaneous coexistence of rigid anionic and disordered cationic sublattices. This is caused by the peculiarities of the crystal lattice: interpenetrating icosahedra (rigid sublattice) form tetrahedral voids that can be filled with cations (disordered sublattice). The same type phases with the structure of argyrodite [1–4] have close parameters of the crystal lattice, which causes the presence of a significant amount of solid solutions [5–11] and represents the ability to change their parameters within a wide range.

Argyrodites exhibit a wide range of properties: thermoelectric [12–14], ferroelastic [9, 15] and superionic [6, 7, 16–19], among which the most studied are Cu^+ , Ag^+ , Li^+ -containing argyrodites. However,

nowadays the main focus of the study of argyrodites is their use as solid electrolytes. It should be noted that solid electrolytes increase battery safety and are an alternative to modern liquid electrolytes. The use of polycrystalline, ceramic, composite materials and films also makes it possible to simplify the design of batteries [20–24].

$\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystallize in cubic syngony, SG $F\bar{4}3m$ with lattice parameters 10.012 and 11.016 Å, respectively [1]. The temperature behaviour of $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal structure is investigated in Ref. [25]. It is ascertained that within the temperature range from 15 up to 475 K, the lattice parameters increase linearly. $\text{Cu}_7\text{GeSe}_5\text{I}$ has significant ionic conductivity. Thus, in accord with Ref. [26], the electrical conductivity of $\text{Cu}_7\text{GeSe}_5\text{I}$ single-crystal samples at 295 K is 0.64 S/cm (at 10^6 Hz) with the activation energy 0.125 eV. The authors of the paper [17] investigated the frequency dependence of electrical conductivity of $\text{Ag}_7\text{GeSe}_5\text{I}$

polycrystalline sample and found out that it equals $7.96 \times 10^{-2} \text{ S/cm}$ (298 K). However, according to the papers [27, 28] conductivity of $\text{Ag}_7\text{GeSe}_5\text{I}$ is $2.77 \times 10^{-2} \text{ S/cm}$ (298 K) and is characterized by non-Arrhenius behavior of electrical conductivity. The authors of Ref. [29] revealed that with increasing the pressure from 0.1 MPa up to 1.5 GPa results in a monotonous decrease in the values of electrical conductivity of $\text{Ag}_7\text{GeSe}_5\text{I}$. The studies of electrical and mechanical properties of monocrystalline and polymeric composites (based on ethylene vinyl acetate polymer) of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions were performed in the papers [30–34].

The aim of this paper was to carry out the frequency and temperature studies of the electrical conductivity of microcrystalline ceramics, prepared using $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions as well as to study compositional behavior of ionic and electronic components of electrical conductivity and influence of cationic substitution on their electrical parameters.

2. Experimental

Synthesis of quaternary $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ compounds was performed from elementary Ag (99.999%), Cu (99.999%), Ge (99.9999%), Se (99.9999%) and pre-synthesized CuI (AgI) in the appropriate stoichiometric ratios, further purified using the vacuum distillation method (CuI) and directional crystallization from the melt (AgI). Pre-synthesized $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ compositions were used as initial substances to synthesize $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions.

The synthesizing mode of both individual $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ as well as $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions consists of several stages. First, the temperature should be increased up to 873 K for 6 hours. Thereafter, 24-hour exposure is performed, which is related with the need for full selenium binding (in the case of $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ compounds) and a rapid temperature increase can cause the ampoule to leak out. Then there is an increase in temperature for one day to the maximum value of 1163 K, which is $\sim 50 \text{ K}$ above the melting point of the most high-melting component ($\text{Ag}_7\text{GeSe}_5\text{I}$). To fully homogenize the melt of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0.25, 0.5, 0.75, 1$) solid solutions were exposed at the maximum temperature for 24 hours. The homogenizing temperature of annealing is 873 K (72 hours). Cooling to room temperature is carried out in the oven-off mode.

From the synthesized $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions, the ceramics of the corresponding compositions were prepared by the method of solid-phase sintering of the pressed samples. Microcrystalline powders obtained by grinding in agate mortar to the sizes between 10 to 50 μm were used for preparation of ceramic samples.

Pressing the samples was performed at the pressure close to 400 MPa, annealing was carried out at the temperature 873 K (heating/cooling rate was close to 20 K/h)

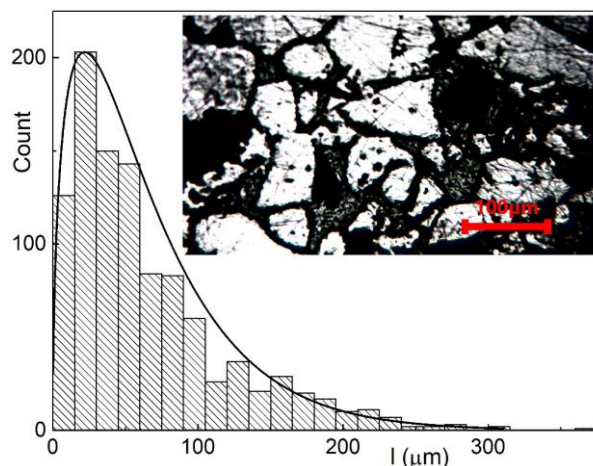


Fig. 1. Histogram of size distribution for crystallites of ceramics prepared on the basis of $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ solid solution. The insert shows the microstructure of ceramic material.

for 36 hours. As a result, microcrystalline samples of ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions with the diameter 10 mm and thickness 3-4 mm were obtained. To determine the size of crystallites after annealing, the obtained ceramic samples were investigated using the microstructural analysis with metallographic microscope METAM-R1. Based on the analysis of obtained microstructures, histograms of particle size distribution were constructed, and it was ascertained that the ceramics obtained by sintering of micropowders are characterized by a rather heterogeneous microstructure, which can be concluded looking at the distribution of particles in a wide range (Fig. 1). It was determined that as a result of recrystallization, the average size of ceramic crystallites obtained from microcrystalline powders is close to 22 μm .

Investigations of electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -based ceramic samples were performed by impedance spectroscopy [35] at the frequency from 10 to $3 \times 10^5 \text{ Hz}$ and in the temperature range 293...383 K by using high-precision LCR-meter 2818. The amplitude of the alternating voltage was 10 mV. The measurements were carried out using the two-electrode method with blocking (electronic) graphite contacts, which were applied in the form of a suspension.

3. Results and discussion

Fig. 2a shows the frequency dependences of the total electrical conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -based ceramics. For all the ceramics under investigation, there observed was the increase in electrical conductivity with the frequency, which is typical for ion-conductive solids [36].

Being based on the obtained results, the compositional dependence of the total conductivity at the frequency 100 kHz (Fig. 2b, curve 1) was plotted. It was

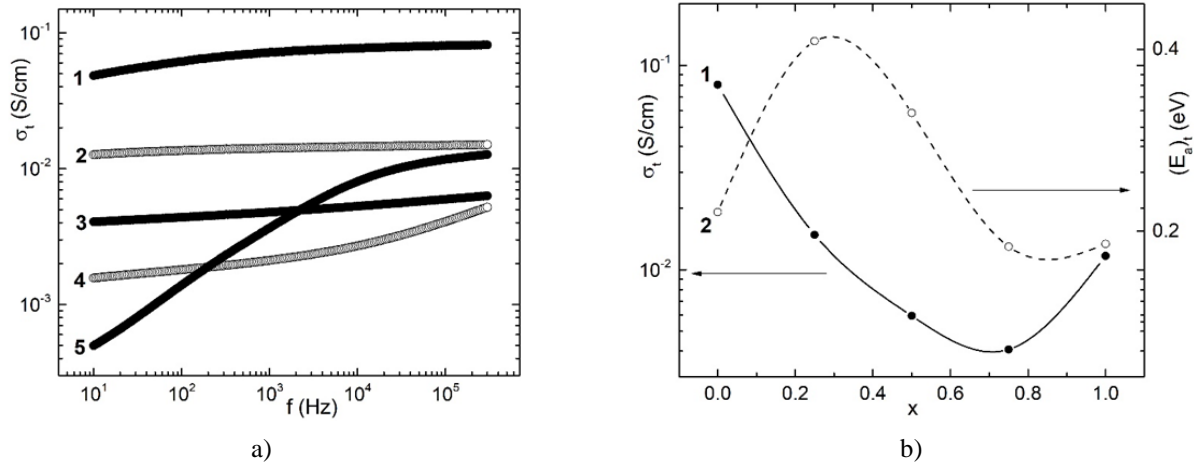


Fig. 2. (a) Frequency dependences of the total electrical conductivity of ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ at 298 K: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ (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); (b) Compositional dependences of total electrical conductivity (1) and activation energy (2) at 298 K and 100 kHz.

ascertained that the compositional dependence of the total electrical conductivity is nonlinear, which manifests itself in the presence of a minimum for $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ -based ceramic. The dependences of electrical conductivity on the inverse temperature show a linear character and are described by the Arrhenius equation, which enabled to determine their activation energies (Fig. 2b, curve 2). The compositional dependence of the latter is characterized by the presence of a maximum observed for $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ -based ceramic.

For detailed studies of the frequency dependences of electrical conductivity and its separation by ionic and electronic components, the electrode equivalent circuits were used [35–37] and their analysis by using the Nyquist plots was carried out. The parasitic inductance of the cell ($\sim 2 \times 10^{-8}$ H) was taken into account during the analysis of all the samples.

The character of the frequency dependence of the total electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75$) ceramic samples (Fig. 2a) indicates the prevailing effect of the electronic component of electrical conductivity over the ionic one ($\sigma_{\text{ion}} < \sigma_{\text{el}}$). At the same time, ceramics prepared on the basis of $\text{Ag}_7\text{GeSe}_5\text{I}$, refers to ionic-electronic conductors with a slight predominance of the ionic component of electrical conductivity ($\sigma_{\text{ion}} > \sigma_{\text{el}}$). On Z' - Z'' dependences for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -based ceramics, two semicircles are observed (Fig. 3). However, for $\text{Cu}_7\text{GeSe}_5\text{I}$ -based and $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ -based ceramics, we can distinguish a weakly expressed mid-frequency semicircle, which is especially noticeable at the temperature 298 K (Figs 3a and 3c).

The electrode equivalent circuit (EEC), selected for the description of the Nyquist plots (Fig. 3), can be separated into two parts: ionic, describing the processes associated with the ionic component of conductivity, and electronic, describing the processes associated with the electronic component of conductivity. Low-frequency semicircles for ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$

($x = 0, 0.25, 0.5, 0.75$) in the Nyquist plots correspond to diffusion relaxation processes at the boundary of the electrode/crystal, which is expressed by the included capacitance of the double diffusion layer C_{dl} (Figs 3a to 3d) with a sequentially included Warburg element responsible for ionic diffusion within the latter. For $\text{Ag}_7\text{GeSe}_5\text{I}$ the low-frequency semicircle is described by the capacitance of the double diffusion layer C_{dl} with sequentially included elements R_{gb}/C_{gb} , responsible for the resistance and capacitance of the crystallite boundaries of ceramics (Fig. 3e). The high-frequency semicircles for ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75$), in their turn, are characterized by conductivity processes at inter-crystallite boundaries, which correspond to the sequentially included resistance R_{gb} on EEC with the capacitance C_{gb} included in parallel (Figs 3a to 3d). In the case of $\text{Ag}_7\text{GeSe}_5\text{I}$, the high-frequency semicircle corresponds to the sequentially included resistance of microcrystallites (intercrystallite boundaries), which, in its turn, corresponds to the resistance R_d , and possibly to the above mentioned elements R_{gb}/C_{gb} (Fig. 3e).

Thus, the ionic component of electrical conductivity of ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75$) is defined by the sum of the resistance of the crystallite boundaries R_{gb} with resistance limiting ionic diffusion W_R , and in the case of $\text{Ag}_7\text{GeSe}_5\text{I}$, is defined as the sum of R_{gb} and R_d (inter-crystallite boundaries). In parallel to the elements, corresponding to the ionic processes, the electronic resistance R_e is included in EEC, which contributes to the representation of both available semicircles in the Nyquist plots and defines the electronic component of the electrical conductivity of ceramic samples (Fig. 5).

The analysis of the impedance spectra by means of EEC (Fig. 3) was carried out for all the ceramic samples and throughout the whole range of investigated temperatures. There is a good coordination of experimental and calculated data by using the parameters

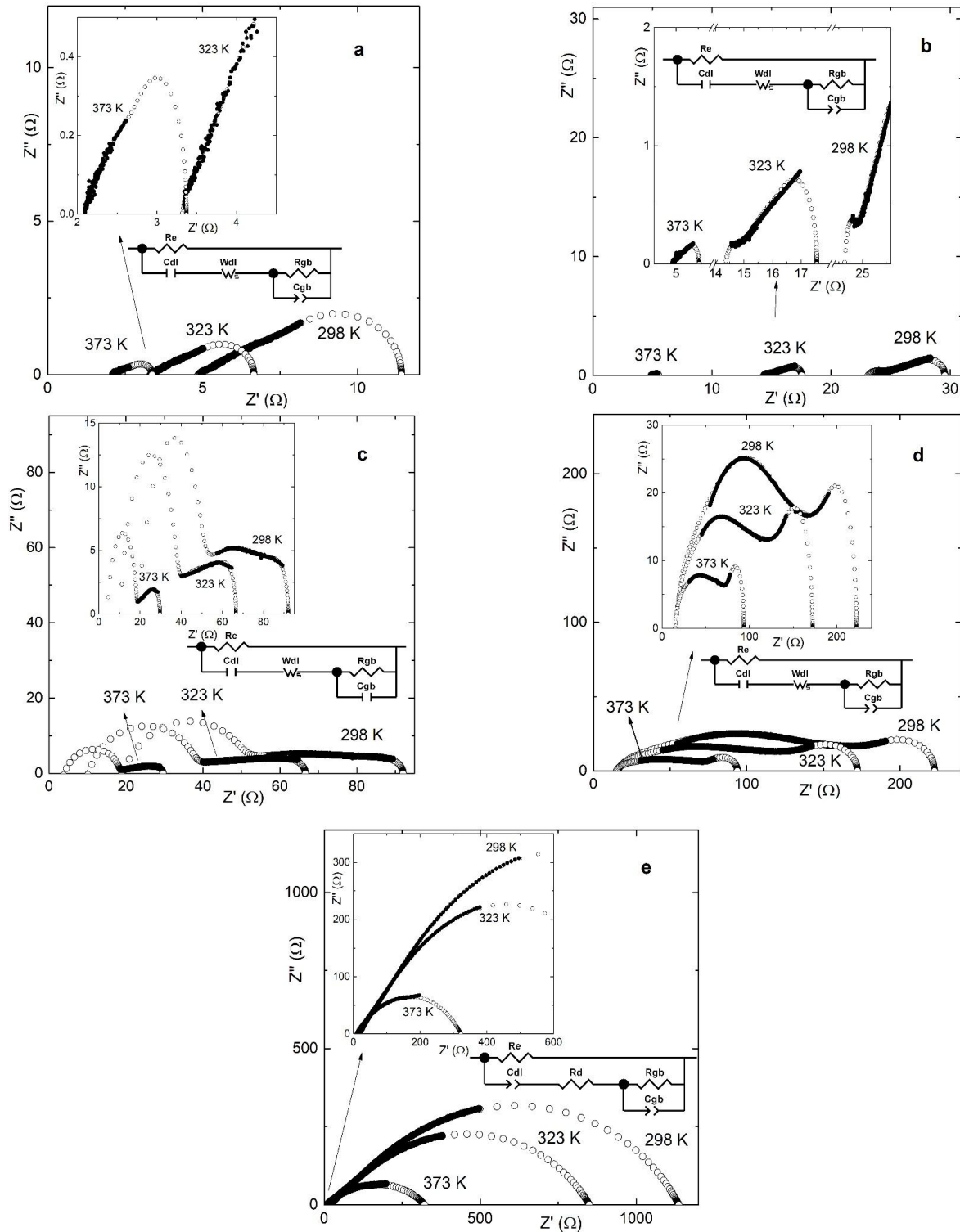


Fig. 3. EEC and Nyquist plots for ceramic samples prepared on the basis of $\text{Cu}_7\text{GeSe}_5\text{I}$ (a), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (b), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ (c), $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ (d) and $\text{Ag}_7\text{GeSe}_5\text{I}$ (e). Experimental data correspond to the solid dots, calculated data correspond to the open dots.

of EEC (Fig. 3). In addition, the analysis of impedance spectra enabled to investigate the temperature and compositional dependences of ionic and electronic components of electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -based ceramics.

Fig. 4 shows the compositional dependences of components of electrical conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -

based ceramics. It was ascertained that the compositional dependence of the ionic component of electrical conductivity σ_{ion} (Fig. 4, curve 1) has a nonlinear character, which manifests itself in the presence of the minimum for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ -based ceramic. Instead, the value of electronic component of electrical conductivity σ_{el} (Fig. 4, curve 2) in the process of $\text{Cu}^+ \rightarrow \text{Ag}^+$

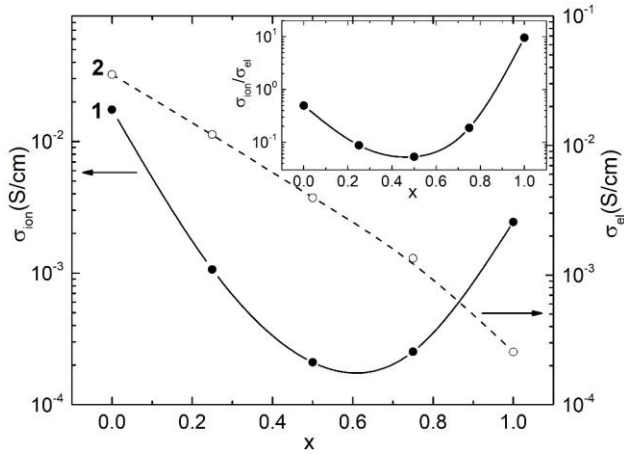


Fig. 4. Compositional dependences of ionic (1) and electronic (2) components of electrical conductivity (a) at 298 K for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$). The insert shows the compositional dependence of the ratio of the ionic component of electrical conductivity to the electronic one for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions.

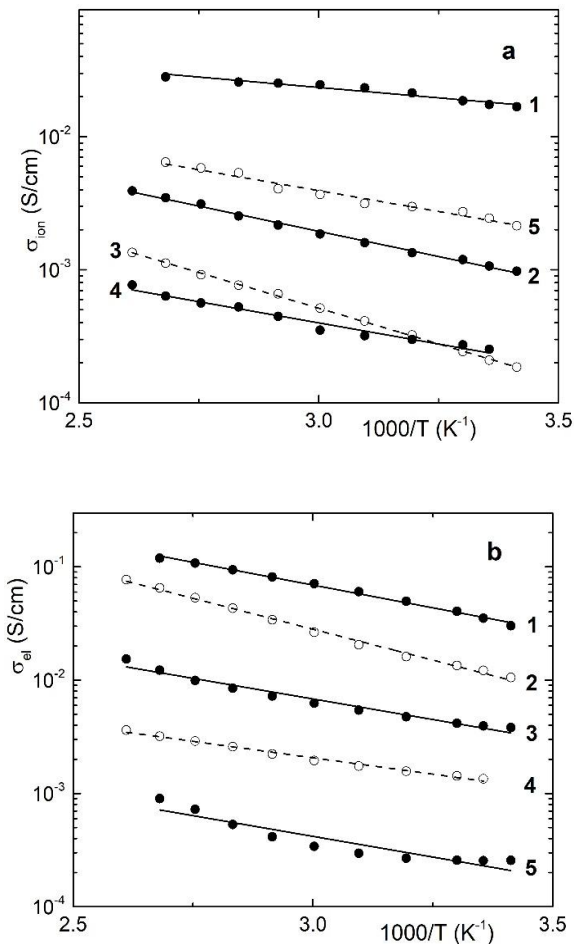


Fig. 5. Temperature dependences of ionic (a) and electronic (b) components of electrical conductivity for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ (3), $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ (4) and $\text{Ag}_7\text{GeSe}_5\text{I}$ (5).

cationic substitution decreases without any features. Such compositional behaviour of electrical conductivity components leads to the nonlinear behaviour of the ratio $\sigma_{\text{ion}}/\sigma_{\text{el}}$ with the minimum for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ -based ceramic (insert to Fig. 4). The maximum value of the ratio $\sigma_{\text{ion}}/\sigma_{\text{el}}$ is observed for $\text{Ag}_7\text{GeSe}_5\text{I}$ -based ceramic ($\sigma_{\text{ion}}/\sigma_{\text{el}} \sim 10$), whereas for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75$) the electronic component of electrical conductivity exceeds the ionic one (insert to Fig. 4).

In Fig. 5, the temperature dependences of ionic and electronic components of electrical conductivity in Arrhenius coordinates are shown. It was ascertained that they are linear and described by the Arrhenius law, which is the evidence of the thermoactivation character of conductivity. Using them, the activation energies of ionic and electronic components of electrical conductivity (Fig. 4) were determined. It was ascertained that the compositional dependences of the activation energies of both the ionic (Fig. 6, curve 1) and electronic (Fig. 6, curve 2) components of electrical conductivity are nonlinear, which manifests itself in the presence of maxima $(E_a)_{\text{ion}}$ for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ -based and $(E_a)_{\text{el}}$ for $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ -based ceramics, as well as the minimum $(E_a)_{\text{el}}$ for $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ -based ceramic.

It should be noted that ceramics based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions are characterized by a complex and disordered micro- and macrostructure. This is primarily caused by the different size of crystallites (Fig. 1) and the complex process of recrystallization during the annealing of microcrystalline samples. This process, first of all, includes consolidation of crystallites related to the processes of solid-phase diffusion and, as a result, “dissolution” of smaller particles by larger ones – recrystallization, which is clearly visible according to the particle size distribution curve and results of microstructural research. In the process of recrystallization,

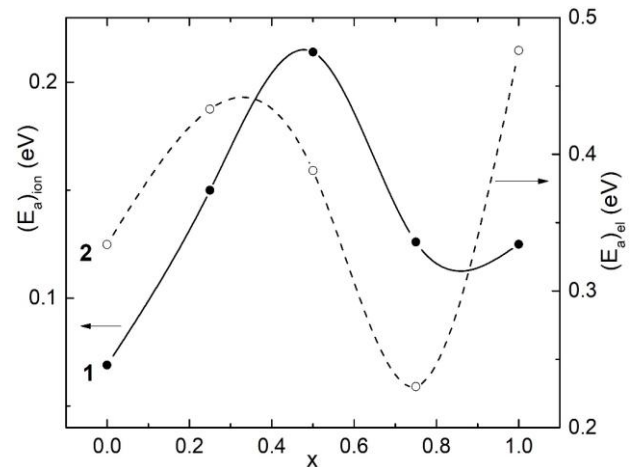


Fig. 6. Compositional dependences of activation energy of ionic (1) and electronic (2) components of electrical conductivity for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ solid solutions.

the emergence of microstructural inhomogeneities is inevitable, which contributes to the emergence of micro- and macrodefects. This additionally leads to the appearance of internal stresses of the ceramic material. Additionally, important here is a complex and disordered crystal structure of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) solid solutions, caused by $\text{Cu}^+ \leftrightarrow \text{Ag}^+$ substitution in a cationic sublattice [32]. The combination of the above features ultimately causes the corresponding behaviour of total electrical conductivity (Fig. 2), its ionic and electronic components (Fig. 4) of the ceramic samples under study. This is especially evident in the compositional dependences of activation energies of total and both components of electrical conductivity. They differ from the compositional behaviour of the activation energies of ionic and electronic components of electrical conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) crystals, for which the compositional dependence of the activation energy of the ionic component is nonlinear, then $(E_a)_{\text{el}}$ grows monotonously without any features [32].

4. Conclusions

$(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) compounds have been synthesized and ceramic samples prepared on their basis by pressing and sintering of microcrystalline (grain sizes from 10 up to 50 μm) powders. According to the results of microstructural analysis, it has been ascertained that, as a result of recrystallization, the average size of crystallites for ceramic samples is close to 22 μm . In the obtained ceramic samples, the total electrical conductivity was measured using the impedance spectroscopy method within the frequency range from 10 Hz up to 300 kHz and within the temperature range 293...383 K. It has been found that the $\text{Cu}^+ \rightarrow \text{Ag}^+$ cationic substitution leads to a nonlinear decrease in the total electrical conductivity of ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0.25, 0.5, 0.75$) solid solutions.

Based on frequency dependences of total electrical conductivity, the Nyquist diagrams were plotted, which were further analyzed using electrode equivalent circuits. Using this approach, the total electrical conductivity was separated by ionic and electronic components. It has been ascertained that the increase in the content of silver atoms in ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0.25, 0.5, 0.75$) solid solutions leads to a nonlinear reduction of the ionic component and a monotonous reduction of the electronic component, which results in the presence of a minimum on the compositional dependence of their ratio.

It has been shown that the temperature dependences of ionic and electronic components of electrical conductivity inherent to $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ -based ceramics are described by the Arrhenius law, which confirms the thermoactivation mechanism of electrical conductivity. Activation energies of ionic and electronic components of electrical conductivity have been calculated and their compositional dependences analyzed.

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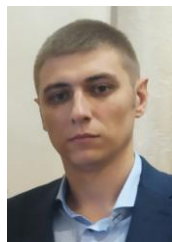
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Вплив катіонного заміщення на електричну провідність мікрокристалічної кераміки на основі твердих розчинів $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$

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Анотація. Керамічні зразки на основі мікрокристалічних порошоків $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) виготовлено шляхом їх пресування при тиску ~ 400 МПа з наступним відпалом при температурі 873 К протягом 36 годин. Методом мікроструктурного аналізу визначено розміри кристалітів одержаних керамік. Дослідження електропровідності керамічних матеріалів $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ проведено методом імпедансної спектроскопії у частотному діапазоні $10 - 3 \cdot 10^5$ Гц та у температурному інтервалі 293–383 К. За результатами аналізу частотної залежності електропровідності на діаграмах Найквіста визначено внески іонної та електронної компонент електропровідності, а також їх співвідношення. Термоактиваційний характер електропровідності підтверджено на основі лінійності температурних залежностей її компонент в арреніусівських координатах. Побудовано відповідні концентраційні залежності іонної та електронної компонент електропровідності та їх енергій активації. Встановлено, що вони носять нелінійний характер, який пояснюється складним процесом рекристалізації та заміщенням $\text{Cu}^+ \leftrightarrow \text{Ag}^+$ у межах катіонної підґратки.

Ключові слова: аргіродит, суперіонний провідник, твердий розчин, кераміка, імпедансна спектроскопія.