

## Electrical and dielectrical properties of composites based on $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$ mixed crystals

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**Abstract.** Polymer composites were prepared from  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals grown using Bridgman–Stockbarger method. The impedance measurements were performed at room temperature in the frequency range  $10^{-3}$ – $2 \cdot 10^6$  Hz. The frequency dependences of electrical conductivity and dielectric permittivity for composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals were obtained. The Nyquist plots for  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$ -based composite has been analyzed. The influence of cation  $\text{Ag} \rightarrow \text{Cu}$  substitution on electrical conductivity of composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals has been studied.

**Keywords:** mixed crystals, composites, cation substitution, impedance measurements, electrical conductivity, dielectric permittivity.

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### 1. Introduction

$\text{Ag}_7\text{GeS}_5\text{I}$  and  $\text{Cu}_7\text{GeS}_5\text{I}$  crystals belong to the argyrodite-type superionic conductors and demonstrate high values of electrical conductivity [1-3]. At room temperature, they crystallize in the face-centered cubic lattice ( $F\bar{4}3m$  space group,  $Z=4$ ); no phase transitions within the temperature range 77...373 K were observed [1-3]. Investigations of the influence of cationic substitution on the physical properties of solid solutions based on  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  crystals are only started. Mechanical properties of  $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$  mixed crystals studied by micro-indentation method were presented in Ref. [4]. Crystal growth technology, electrical and optical properties of other  $\text{Cu}_7\text{GeS}_5\text{I}$ -based solid solutions were studied in Refs. [5-10].

It should be noted that the crystalline material itself is very brittle and, thus, not enough applicable in practice. Solid electrolytes are widely used in the form of polymer composites in secondary power sources. Polymer composite form enhances the mechanical properties of such materials (flexibility, adhesion to electrodes, etc.). It is expected that at high pressures that overcome the yield strength of polymer the last one is pushed out from space between grains and fills the hollow space. As a result, a better contact between grains, higher density and better internal adhesion are achieved.

The paper is aimed at the development of preparation technology, production of the composites and study of the electrical and dielectrical properties of composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals.

### 2. Experimental

$\text{Cu}_7\text{GeS}_5\text{I}$ - $\text{Ag}_7\text{GeS}_5\text{I}$  superionic mixed crystals were obtained by the solid state reaction between finely grinded and mixed crystalline powders of pure  $\text{Cu}_7\text{GeS}_5\text{I}$  and  $\text{Ag}_7\text{GeS}_5\text{I}$  taken in corresponding proportions. The mixtures were sintered at temperature 1173 K during 120 h. As a result, an intensive recrystallization of material was observed. XRD studies confirmed formation of continuous series of solid solutions. The changes of lattice parameter follow the Vegard law.

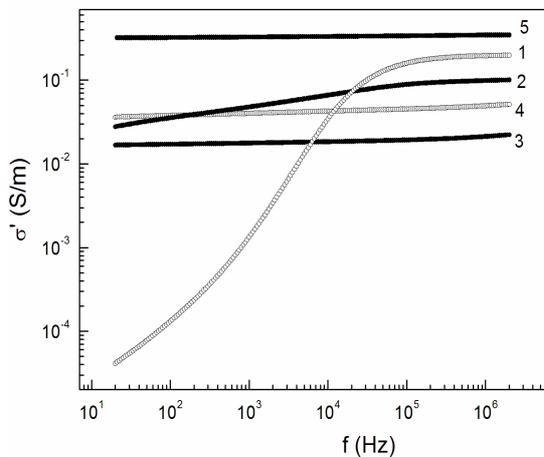
Polymer composites based on  $\text{Cu}_7\text{GeS}_5\text{I}$ - $\text{Ag}_7\text{GeS}_5\text{I}$  mixed crystals were prepared from polycrystalline powders previously finely grinded in agate mortar. The obtained powders were ultrasonically dispersed in ethyl acetate. The solution of EVA bonding polymer (ethylene-vinyl-acetate copolymer) in ethyl acetate was added to powder dispersion in amount of 1:9 by mass and further dispersed in ultrasonic bath for 10 min. Thus, the composite consisted of 10% of EVA binder and 90% of superionic active material. The obtained mixture was

evaporated in air with continuous mixing to prevent sedimentation and enhance the homogeneity of particles. Then it was dried at 60 °C for 24 h. The dry cake was grinded in agate mortar and pressed to 8-mm diameter and hardened with steel mold at room temperature. The calculated pressure inside the mold was around 7800 bar. As a result, hard tablets of 8 mm in diameter were obtained. The electrodes were spray deposited onto both disk faces by using Cramolin Graphite conductive paint based on colloidal graphite. Thus, the obtained electrodes were expected to demonstrate ion blocking effect at DC.

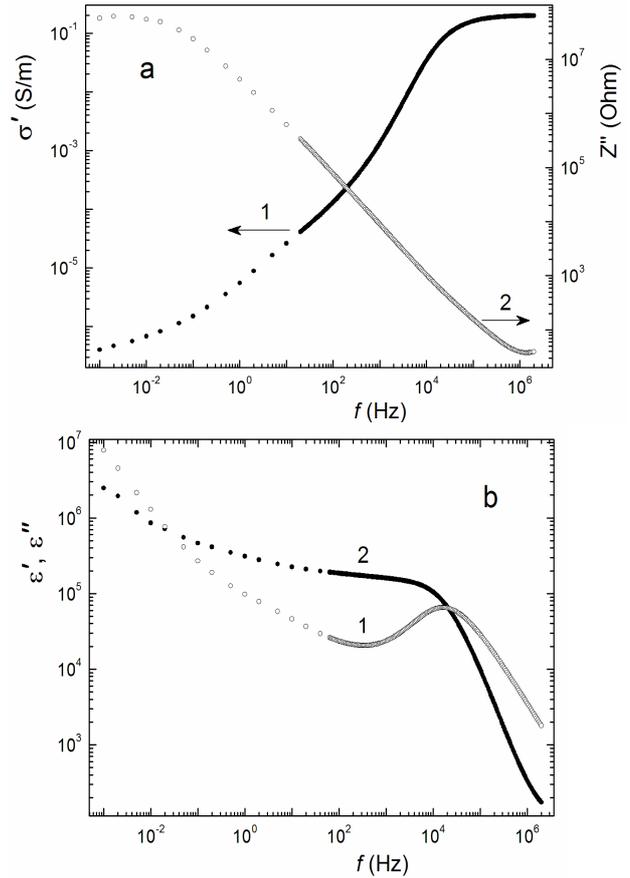
The impedance measurements were performed within the wide frequency range  $10^{-3} \dots 2 \cdot 10^6$  Hz with no DC bias and 10 mV AC voltage, applied to the samples. Agilent E4980A Precision LCR Meter was used for  $20 \dots 2 \cdot 10^6$  Hz frequency range. The measurements in  $10^{-3} \dots 20$  Hz were performed on the lab-scale system. The analysis of obtained frequency dependences was made using Scribner ZView software.

### 3. Results and discussion

The single dispersion region is observed on the frequency dependences of the real part of electrical conductivity  $\sigma'$  for composites based on  $(Ag_{1-x}Cu_x)_7GeS_5I$  mixed crystals (Fig. 1). The low-frequency part is associated with ion current blocking effect at the “graphite electrode / superionic composite” interface, while the high-frequency part of the spectra is defined predominantly by the charge transfer across the grain boundaries, as will be shown later. The high-frequency part that is mostly affected by the internal ionic conductivity of grains isn't observed in the frequency range under investigation. Nevertheless, it demonstrates significant contribution into frequency behavior in megahertz region and has to be taken into consideration during fitting. With the copper content increase, significant attenuation of dispersion in the low-frequency region can be observed (Fig. 1), which is caused by the rapid increase of electronic conductivity as will be shown further.



**Fig. 1.** Frequency dependences of the real part of electrical conductivity for composites based on  $(Ag_{1-x}Cu_x)_7GeS_5I$  mixed crystals:  $Ag_7GeS_5I$  (1),  $(Ag_{0.75}Cu_{0.25})_7GeS_5I$  (2),  $(Ag_{0.5}Cu_{0.5})_7GeS_5I$  (3),  $(Ag_{0.25}Cu_{0.75})_7GeS_5I$  (4) and  $Cu_7GeS_5I$  (5).

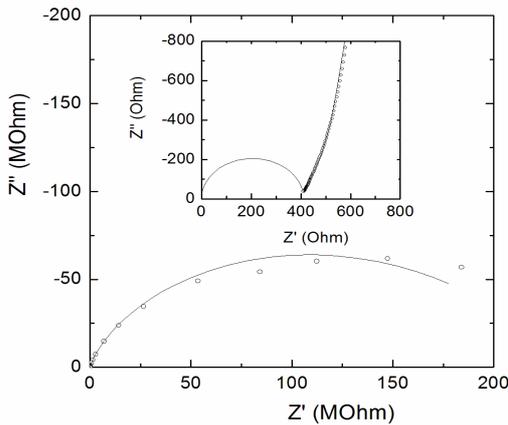


**Fig. 2.** Frequency dependences of the real part of electrical conductivity (1a), imaginary part of impedance (2a), real (1b) and imaginary (2b) parts of dielectric permittivity for  $Ag_7GeS_5I$ -based composite.

The sharp increase of imaginary part of impedance  $Z''$  in the low-frequency region together with the decrease of real part of electrical conductivity  $\sigma'$  (Fig. 2a) is the evidence of high ionic to electronic conductivity ratio in composites based on  $Ag_7GeS_5I$  superionic crystals. This behavior is typical for good solid electrolytes. Two dispersions can be observed on the frequency dependences of the real and imaginary parts of dielectric permittivity for  $Ag_7GeS_5I$ -based composite (Fig. 2b). The low-frequency dispersion can be associated with capacitance of the near-electrode layer, while the high-frequency one can be caused by the capacitance of grain boundaries.

One large semicircle can be observed in the Nyquist plot for  $Ag_7GeS_5I$ -based composite (Fig. 3). Its low-frequency part is defined by the shunt resistance caused by the electronic conductivity of the sample and capacitance of the double electric layer capacitor formed at the interface between the solid electrolyte and graphite electrode that is irreversible in respect to silver ions. The high-frequency part of the semicircle is deformed due to its overlapping with small middle-frequency semicircle caused by the resistance and capacity of the grain boundaries. The high-frequency semicircle related to the internal grain resistivity and bulk capacity of the grains isn't observed in the experimental data due to frequency limitations of the impedance analyzer. Thus, it is shown only for demonstration purposes as a calculated line

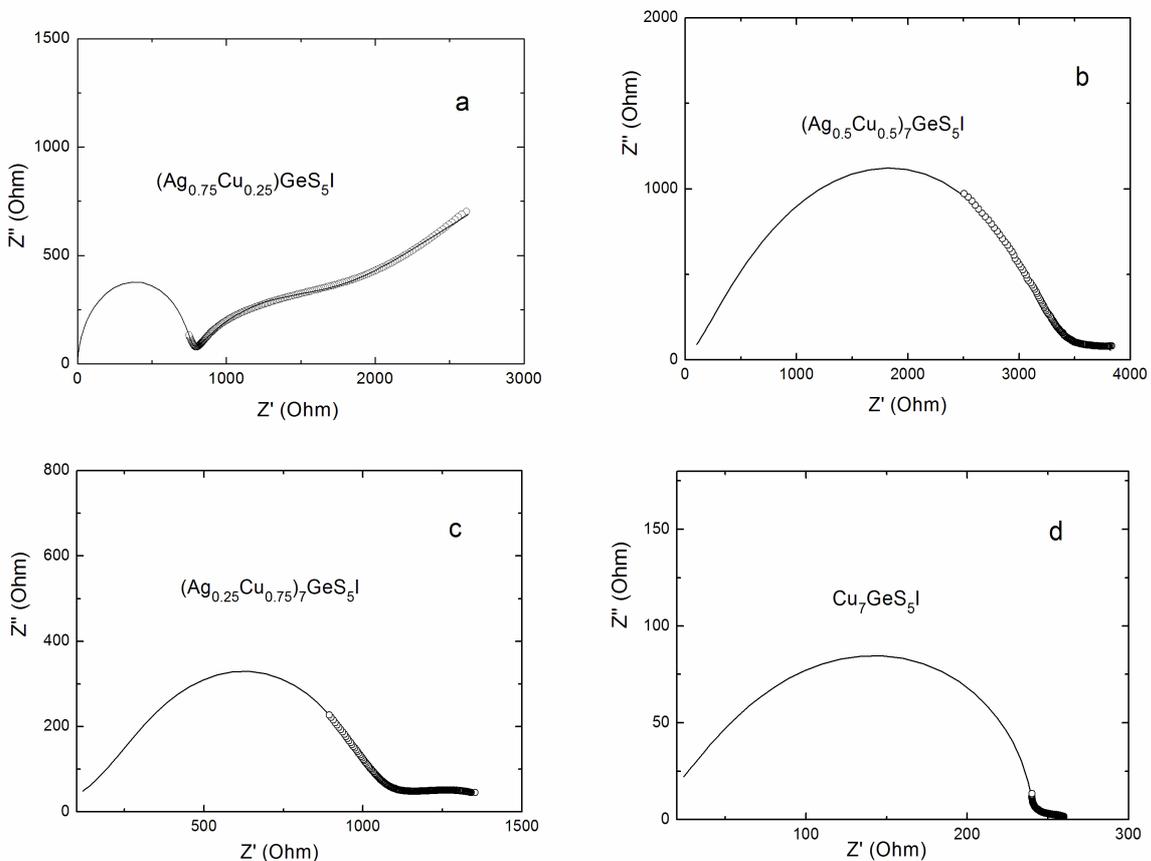
generated by the equivalent circuit used for fitting and shown in Fig. 3. It is responsible for the high-impedance shift of the Nyquist plot along  $Z'$  axis. From the viewpoint of practical interest, the value of the total ionic conductivity limited by the grain boundary transfer process can be more interesting in comparison to pure internal grain conductivity. Thus, the value of resistance consisting from internal grain and grain boundary resistances connected in series was used for further evaluation of the total ionic conductivity of the whole sample.



**Fig. 3.** Nyquist plot for  $\text{Ag}_7\text{GeS}_5\text{I}$ -based composite with the fitting result. A high-frequency magnified part of the plot is shown in the inset.

In Fig. 4 an evolution of impedance frequency behavior with increase of copper content in composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals is shown. Even a small increase in copper content leads to significant change in proportions of semicircles caused by sharp increase of parasitic electronic component of conductivity and moderate decrease of ionic contribution. The further increase of copper content leads to degeneration of low-frequency semicircle into the low-frequency tail that is rather complicate for fitting. The same equivalent circuit was used for modeling of the impedance spectra of composite samples with various copper content. The results of such fitting are summarized in the table.

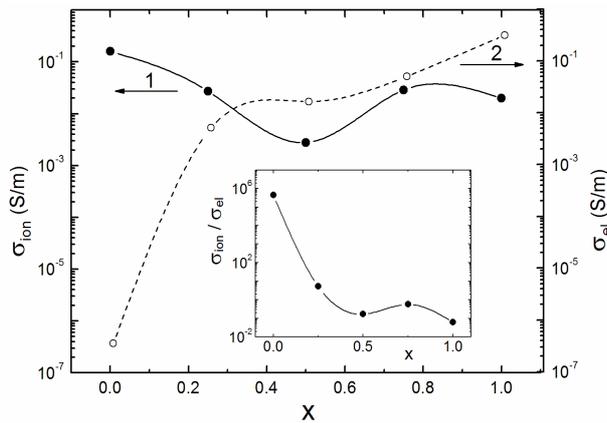
Substitution of Ag atoms with Cu ones leads to sharp increase of electronic component of conductivity (Fig. 5). The most significant increase is observed at low copper concentrations that can be considered from the technological viewpoint as a poisoning effect caused by Cu impurities in Ag-conducting argyrodite-based solid electrolytes. Thus, a great attention must be paid to the traces amount of copper in the silver used in synthesis of superionic material with high ionic to electronic conductivity ratio. The decrease of ionic component of conductivity together with the copper content increase can be observed in composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals (Fig. 5). The minimum on the compositional dependence of ionic conductivity



**Fig. 4.** Nyquist plots for  $(\text{Ag}_{0.75}\text{Cu}_{0.25})_7\text{GeS}_5\text{I}$  (a),  $(\text{Ag}_{0.5}\text{Cu}_{0.5})_7\text{GeS}_5\text{I}$  (b),  $(\text{Ag}_{0.25}\text{Cu}_{0.75})_7\text{GeS}_5\text{I}$  (c) and  $\text{Cu}_7\text{GeS}_5\text{I}$  (d) based composites with fitting results.

**Table.** Results of Nyquist plots fitting for composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals ( $R_g$  and  $R_{gb}$  are grain and grain boundary resistances;  $R_i$  and  $R_e$  are ionic and electronic resistances;  $\sigma_i$  and  $\sigma_e$  are ionic and electronic conductivity;  $C_g$ ,  $C_{gb}$  and  $C_{dl}$  are capacitance of the grains, grain boundaries and double electric layer, respectively).

$(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$	$R_g$ , Ohm	$R_{gb}$ , Ohm	$R_i$ , Ohm	$\sigma_i$ , S/m	$R_e$ , Ohm	$\sigma_e$ , S/m	$C_{gb}$ , nF	$C_{dl}$ , $\mu\text{F}$	$C_g$ , pF
$x = 0$	407	116	523	$1.6 \cdot 10^{-1}$	$2.4 \cdot 10^8$	$3.6 \cdot 10^{-7}$	285	0.29	13
$x = 0.25$	793	1029	1822	$2.7 \cdot 10^{-2}$	9707	$5.1 \cdot 10^{-3}$	4280	0.69	16
$x = 0.5$	5357	17794	23151	$2.8 \cdot 10^{-3}$	3933	$1.7 \cdot 10^{-2}$	3.1	1.54	29
$x = 0.75$	1272	1438	2710	$2.9 \cdot 10^{-2}$	1535	$5.1 \cdot 10^{-2}$	16.3	42	46
$x = 1$	2092	2053	4145	$2.0 \cdot 10^{-2}$	262.5	$3.2 \cdot 10^{-1}$	251	8.3	24



**Fig. 5.** Compositional dependences of ionic (1) and electronic (2) contributions to electrical conductivity for polymer composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals. The inset shows the compositional dependence of ionic to electronic conductivity ratio for polymer composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals.

can be explained by the effect of compositional disordering usually observed in solid solutions [9, 10]. The break of ion conductivity channels caused by the compositional disordering in crystal lattice leads to the decrease of ion transport efficiency. It should be noted that the ratio of ionic to electronic conductivity also decreases significantly with the increase of copper content in composites under investigation (inset in Fig. 5).

#### 4. Conclusions

$\text{Cu}_7\text{GeS}_5\text{I}-\text{Ag}_7\text{GeS}_5\text{I}$  superionic mixed crystals were obtained using the solid state reaction. Polymer composites based on  $\text{Cu}_7\text{GeS}_5\text{I}-\text{Ag}_7\text{GeS}_5\text{I}$  mixed crystals were prepared from the polycrystalline powders and ethylene-vinyl-acetate binder in proportion 9:1. The impedance measurements were carried out within the frequency range  $10^{-3} \dots 2 \cdot 10^6$  Hz.

In the frequency range under investigation, the single dispersion region in the frequency dependences of electrical conductivity for composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals has been observed. It has been shown that the copper content increase leads to significant attenuation of dispersion in the low-frequency region, which is caused by the rapid increase of electronic conductivity. Two dispersions can be observed

in the frequency dependences of dielectric permittivity, the low-frequency dispersion can be associated with the capacitance of the near-electrode layer, while the high-frequency one can be caused by the capacitance of grain boundaries.

The analysis of obtained frequency dependences was performed in Scribner ZView software, the Nyquist plots for composites based on  $(\text{Ag}_{1-x}\text{Cu}_x)_7\text{GeS}_5\text{I}$  mixed crystals were constructed as well as the compositional dependences of ionic and electronic contributions to electrical conductivity were discussed. It has been shown that substitution of Ag atoms with Cu ones leads to a sharp increase of electronic conductivity, decrease of ionic conductivity as well as decrease of the ratio of ionic to electronic conductivity.

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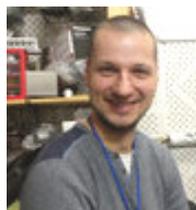
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