



Impedance studies and electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals



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ABSTRACT

Synthesis and growth of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were performed. $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals were grown by the method of directed crystallization from the melt as well as $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were grown by zone crystallization from the melt. Electrical measurements were carried out in the frequency range from 20 Hz to 2×10^6 Hz and in the temperature interval 292–378 K. Temperature and frequency dependences of electrical conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals were studied. The compositional behavior of ionic and electronic conductivity as well as the compositional behavior of their activation energies are discussed. The ratio of ionic and electronic components of conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals was analyzed.

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1. Introduction

$\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals belong to the superionic compounds with argyrodite structure [1,2]. Representatives of the argyrodite family are widely investigated for applications as solid state batteries, supercapacitors and electrochemical sensors [2,3]. In the recent decade, besides copper- and silver-containing argyrodites, Li-containing argyrodites are actively studied as one of the most promising solid electrolyte materials [4–8]. Besides, in the recent year they appear interesting as new materials for thermo-electric applications [9,10].

Growth as well as physical and chemical properties of $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Cu}_7\text{GeSe}_5\text{I}$ crystals and mixed $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals on their base were studied in several papers [11–13]. Electrical, electrochemical and optical properties of the above mentioned crystals were investigated in Refs. [14–16]. It was shown that $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal is characterized by the highest value of electrical conductivity among the well-known copper-containing superionic conductors (0.64 S/cm at the frequency of 10^6 Hz at 300 K) [15]. Besides, for $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal as well as for $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ mixed crystals an increase of electrical conductivity with temperature

according to the Arrhenius law was revealed, this being an evidence for their thermoactivation nature.

Optical studies have shown that the absorption edge of the $\text{Cu}_7\text{GeSe}_5\text{I}$ single crystal and mixed $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals exhibits an Urbach behavior in a wide temperature range [14–16]. The Urbach absorption edge is related to the manifestation of electron-phonon interaction. Besides, it was shown that the temperature-related, structural and compositional disordering affect the Urbach absorption edge shape in mixed $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals [14–16]. Finally, at S→Se anionic substitution in the mixed $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ crystals a nonlinear increase of electrical conductivity by more than an order of magnitude, a nonlinear decrease of the optical pseudogap and a typical for mixed crystals behavior of the Urbach energy were observed [14–16]. The influence of $\text{Cu}^+ \rightarrow \text{Ag}^+$ 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. [17].

For $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal a non-Arrhenius behavior of the electrical conductivity is observed and the electrical conductivity value at 298 K is 7.96×10^{-2} S/cm [18–21]. The non-Arrhenius behavior of the electrical conductivity in Ref. [19] is described by the Vogel-Fulcher-Taman equation, and its temperature variation in $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal is related to a “quasi-liquid” sublattice of Ag^+ ions.

The aim of this paper is synthesis and growth as well as

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investigation of frequency-dependent, temperature-dependent and compositional behavior of the electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals.

2. Materials and methods

$\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$ crystals were obtained by directed crystallization from the melt while mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ ($x = 0, 0.25, 0.5, 0.75, 1$) crystals on their base were obtained by zone crystallization from the melt using a modified method. Specificity of the modified method for the crystal growth in the case of individual compounds is that in the growth ampoule the initial elemental Ag (99.999%), Cu (99.999%), Ge (99.9999%), Se (99.9999%) and pre-synthesized CuI (AgI) are loaded in the corresponding stoichiometric ratios, further purified by vacuum distillation (CuI) and by directed melt crystallization (AgI). As a starting material for the growth of mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals we used previously synthesized $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$.

Growth of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals includes forming a monocrystalline nucleating seed by accumulative recrystallization in the lower conical part of the growth container (48 h). The crystallization front rate was 0.4 mm/h. After moving the ampoule with the crystal into the annealing region, it is annealed for homogenizing for 3 days, which is required to remove thermal stresses in the crystals. Thus, $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals with $x = 0, 0.25, 0.5, 0.75$ and 1 of 20–40 mm in length and 10–15 mm in diameter were obtained.

The electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals with $x = 0, 0.25, 0.5, 0.75$ and 1 was investigated by impedance spectroscopy [22] in the frequency range of 20 Hz– 2×10^6 Hz and temperature interval 292–378 K, using a high-precision Keysight E4980A LCR meter. The amplitude of the alternating current was 10 mV. Measurement was carried out by a two-electrode method, with blocking gold contacts. The gold contacts were deposited by chemical precipitation from solutions. As starting solutions, 0.02 M sodium tetrachloroaurate $\text{Na}[\text{AuCl}_4]$ 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 an increasing recovery rate.

3. Results and discussion

Fig. 1 presents frequency dependences of the total electrical conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals with $x = 0, 0.25, 0.5, 0.75$ and 1. It is shown that for all crystals under investigation the total electrical conductivity increases with frequency (Fig. 1). However, for $\text{Cu}_7\text{GeSe}_5\text{I}$ (Fig. 1, curve 1) and $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (Fig. 1, curve 2) crystals, in the frequency range of 10^5 Hz– 10^6 Hz there is a decrease in the total electrical conductivity due to the effect of a parasitic inductance caused by the high electrical conductivity values [23]. For the detailed studies of the frequency behavior of the electrical conductivity and its separation into ionic and electronic components, a standard approach using electrode equivalent circuits (EECs) [24] and their analysis at Nyquist plots was used. In the analysis of all samples the parasitic inductance of the cell ($\sim 4 \times 10^{-7}$ H) is taken into account.

For the analysis of $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal an EEC is chosen, which is characterized by the presence of an electronic resistance R_e , parallelly to which a capacity of the double diffusion layer C_d is connected as well as the ionic resistance of the sample R_{ion} (Fig. 2). As can be seen from the dependence in the Nyquist plot and according to the results of description of the experimental data (solid symbols) by the ones calculated according to the EEC (open symbols),

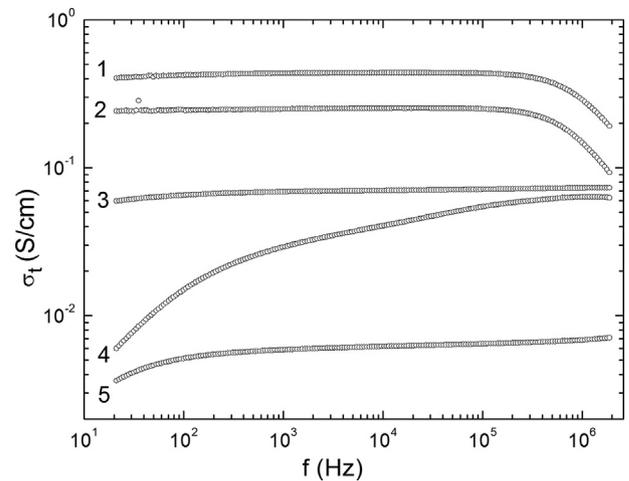


Fig. 1. Frequency dependences of total electrical conductivity at $T = 298$ K for mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$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

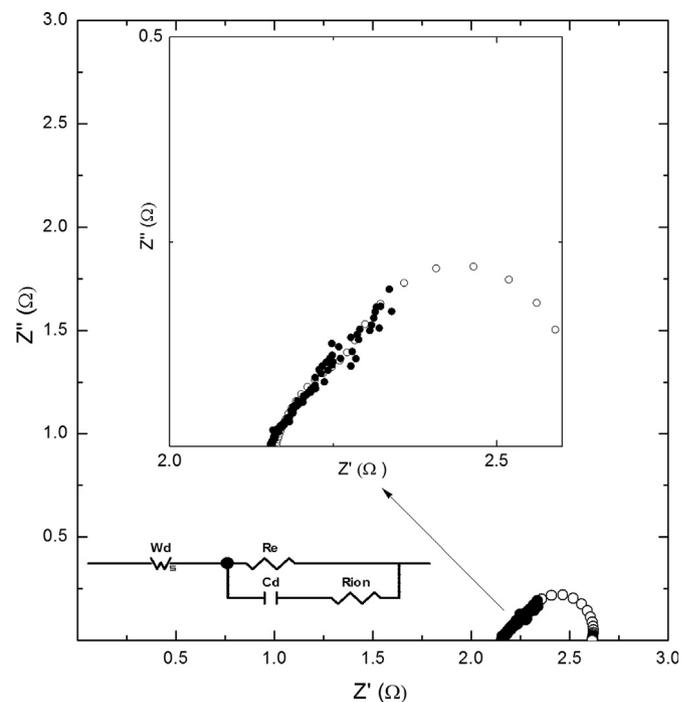


Fig. 2. Nyquist plot at $T = 298$ K for $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal: experimental data (solid symbols), calculated data (open symbols) and EEC.

$\sigma_{\text{ion}} < \sigma_{\text{el}}$, but along with the very high value of electronic conductivity ($\sigma_{\text{el}} = 0.429$ S/cm), the ionic conductivity is also quite high ($\sigma_{\text{ion}} = 0.011$ S/cm). This indicates the possibility of existence of diffusion processes that occur across the boundary of the double diffusion layer, which can be described using the Warburg element W_d (Fig. 2). We can assume that there is a certain diffusion “boundary” between the ionic and electronic conductivity.

In the Nyquist plot for the mixed $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ crystal, like for the $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal, one semicircle is observed, but the diffusion processes at the interface of the double diffusion layer could not be described using the Warburg element W_d . Thus, a capacitance $C_{\text{ion/el}}$ is included in the EEC, which corresponds probably to the appearance of an additional ionic barrier within the double diffusion layer related to the influence of domain

boundaries, which together with the high electronic conductivity ($\sigma_{el} = 0.25$ S/cm) prevent the diffusion processes.

For the $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ and $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ crystals two semicircles are observed: a low-frequency one, which is responsible for diffusion and relaxation processes, and a high-frequency one, associated with the processes at the domain boundaries and the bulk of the mixed crystal. The Nyquist plots, typical for these mixed crystals, are presented in Fig. 3 (curve 1). It is shown for the mixed $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ crystal that $\sigma_{ion} > \sigma_{el}$, and the ionic conductivity increases compared to Cu_7GeSe_5I ($\sigma_{ion} = 0.016$ S/cm for $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ and $\sigma_{ion} = 0.011$ S/cm for Cu_7GeSe_5I), while the electronic component of the conductivity decreases ($\sigma_{el} = 0.048$ S/cm for $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ and $\sigma_{el} = 0.429$ S/cm for Cu_7GeSe_5I). This increases the influence of diffusion and relaxation ionic processes, as a result, the low-frequency semicircle corresponds to the diffusion processes at the boundary of the double diffusion layer C_d , and the crystal/electrode boundary, responsible for which is a series-connected Warburg element W_d with a parallel-connected electronic resistance R_e (Fig. 3). The high-frequency semicircle corresponds, in turn, to the processes at the boundaries of domains expressed by the resistance R_{db} and the capacitance C_{db} of the domain boundaries, in parallel with the electronic resistance R_e , which is responsible for the electronic component of the conductivity. The ionic conductivity is determined by the sum of the resistance of the domain boundaries R_{db} and the resistance of the diffusion boundary $W_d - R$.

As the temperature increases, the increase of the electronic conductivity gradually reduces the effect of diffusion ionic processes, at the boundaries of the domains of the crystal, as evidenced by "blurring" of the high-frequency semicircle at a temperature of 323 K (Fig. 3, curve 2). However, with a further increase in temperature to 378 K (Fig. 3, curve 3), a further reduction of the influence of diffusion ionic processes in the mixed $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ crystal together with a decrease in the thickness of the double diffusion layer, ultimately leads to the complete disappearance of

the high-frequency semicircle.

For the $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ crystal, a decrease of ionic conductivity ($\sigma_{ion} = 0.008$ S/cm) was revealed. Despite this, due to the decrease of the electronic component of conductivity, $\sigma_{ion} > \sigma_{el}$ ($\sigma_{ion}/\sigma_{el} = 6$), which caused the displacement of the low-frequency semicircle even more to the low-frequency region.

Ag_7GeSe_5I crystal is characterized with the lowest value of the electronic conductivity ($\sigma_{el} = 7.51 \times 10^{-4}$ S/cm) among all the samples, the ionic conductivity is also reduced ($\sigma_{ion} = 3.36 \times 10^{-3}$ S/cm), despite that $\sigma_{ion} > \sigma_{el}$, which caused an even greater shift of the low-frequency semicircle further to the low-frequency region, which leads to an increase in the influence of the diffusion and relaxation processes. In the Nyquist plot, like in the previous case, two semicircles are observed, but due to **reduction** of both ionic and electronic conductivity, the high-frequency semicircle is revealed more clearly (Fig. 4). The low-frequency semicircle is described by parameters responsible for the ion resistance, the capacitance of the double diffusion layer and the ion diffusion W_d at the boundary of the double diffusion layer (Fig. 4). The high-frequency semicircle, in turn, is described by R_{db}/C_{db} . Parallely to the diffusion processes of the double diffusion layer and processes at the domain boundaries, the electronic resistance R_e is connected, which is the crucial factor for the electronic component of the conductivity.

The analysis of the impedance spectra by means of the **EECs**, described above, was carried out for all the crystals and throughout the whole range of the temperatures investigated. The temperature behavior for the mixed $(Cu_{0.25}Ag_{0.75})_7GeSe_5I$ crystal and Ag_7GeSe_5I crystal is similar to that of the mixed $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ crystal. The compositional dependences of both the ionic and the electronic conductivity are presented in Fig. 5a. It is shown that the compositional dependence of the ionic conductivity is nonlinear with a maximum for the mixed $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ crystal (Fig. 5). Such compositional behavior of the ionic conductivity is obviously related to the processes of ordering/disordering of the cationic sublattice in the mixed crystals under investigations. Ag_7GeSe_5I

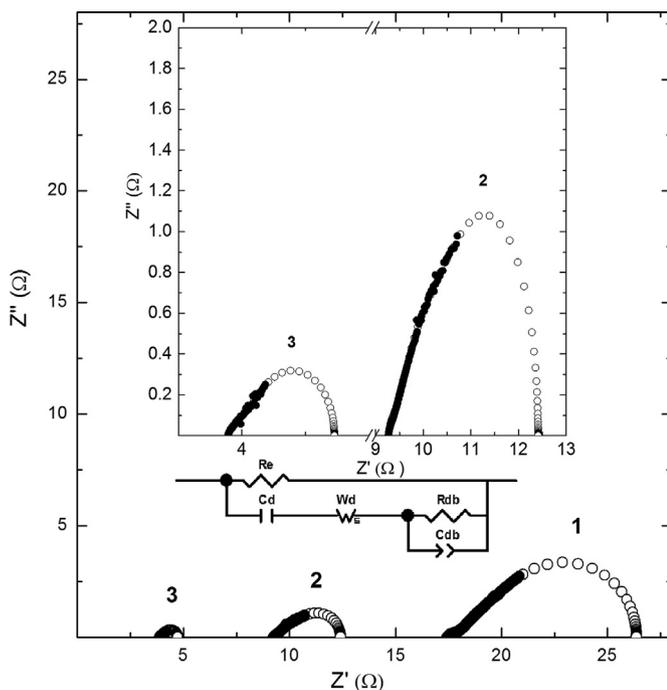


Fig. 3. Nyquist plots for mixed $(Cu_{0.5}Ag_{0.5})_7GeSe_5I$ crystal at 298 K (1), 323 K (2) and 378 K (3): experimental data (solid symbols), modelled (calculated) data (open symbols).

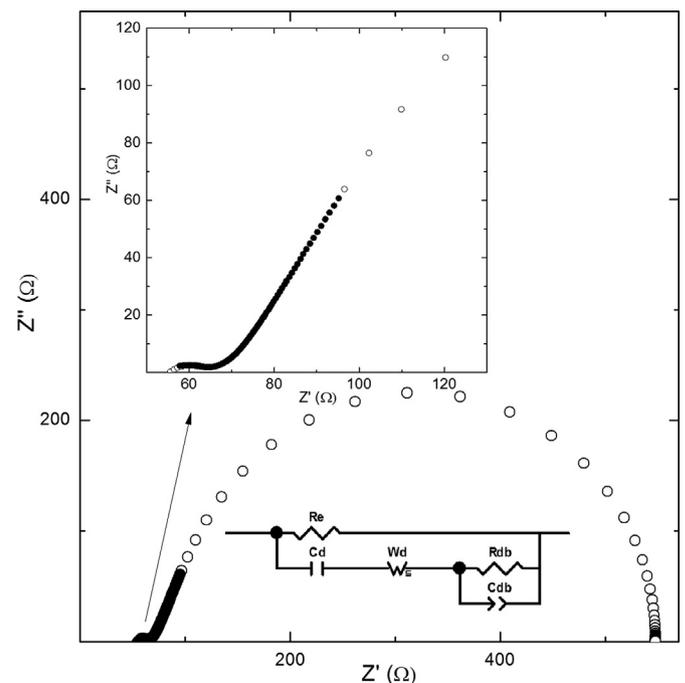


Fig. 4. Nyquist plot at $T = 298$ K for Ag_7GeSe_5I crystal: experimental data (solid symbols), modelled (calculated) data (open symbols) and EEC.

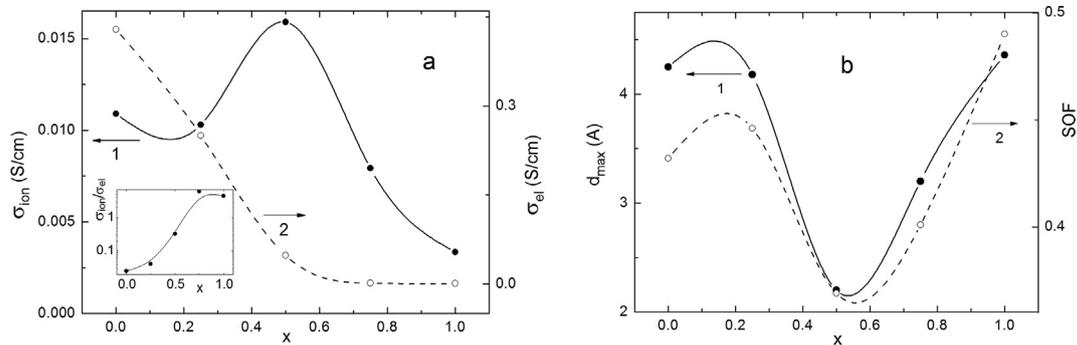


Fig. 5. (a): Compositional dependences of the ionic and electronic conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals at $T = 298\text{ K}$. The inset shows the compositional dependence of the ionic-to-electronic conductivity ratio for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals at $T = 298\text{ K}$. **(b):** Compositional dependences of d_{max} (1) and SOF (2) for the movable atom positions in the crystal lattice.

crystal is characterized by a slightly lower ionic conductivity than $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal, which is associated with a higher ordering of Ag movable atom positions compared to Cu positions in the crystal lattice. The site occupation factors (SOF) for Ag and Cu positions are $\text{SOF}(\text{Ag}) = 0.490$ and $\text{SOF}(\text{Cu}) = 0.432$. It should be noted that the movable atom positions are Ag1 and Cu1, which are in the triangular coordination of selenium atoms. The compositional dependence of the ionic conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals (Fig. 5a) is in a good agreement with the values of SOF of Cu(Ag) movable atom positions in the crystal lattice and the values of maximum distances d_{max} between the above mentioned positions (Fig. 5b). The movable atom positions for the mixed crystals are the Ag1+Cu1 positions (triangular coordination of selenium atoms for $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$) and Ag2+Cu2 positions (tetrahedral coordination with a displacement to the plane of the triangle [Se2I] for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ and $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$), which are obviously related to the order-disorder processes in the cationic sublattice.

In contrast, the value of the electronic conductivity monotonously decreases at the $\text{Cu}^+ \rightarrow \text{Ag}^+$ cationic substitution (Fig. 5a). The inset to Fig. 5 shows the compositional dependence of the ratio of ionic to electronic conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals. At the transition from the $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal, where the electronic conductivity is 39 times greater than the ionic one, to the $\text{Ag}_7\text{GeSe}_5\text{I}$, the ratio $\sigma_{\text{ion}}/\sigma_{\text{el}}$ tends to increase and for $\text{Ag}_7\text{GeSe}_5\text{I}$ the ionic conductivity is 4.5 times greater than the electronic one. It is noteworthy that for the mixed $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ crystal the ionic conductivity is 6 times greater than the electronic one, which

is higher than the one for $\text{Ag}_7\text{GeSe}_5\text{I}$ (Fig. 5a).

For a more detailed analysis of the temperature behavior of the electrical conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals, the temperature dependences of the electrical conductivity are constructed (Fig. 6). It is shown that the dependences of the ionic (Fig. 6a) and the electronic (Fig. 6b) components of the electrical conductivity $1/T$ are linear and obey the Arrhenius equation, which enabled us to determine the activation energy of both the ionic and the electronic components of the electrical conductivity (Fig. 7). The increase of the activation energy of the ionic conductivity at the cationic substitution, which for the mixed $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ crystal is maximal (Fig. 7) and reaches 0.45 eV, compared with the $\text{Cu}_7\text{GeSe}_5\text{I}$ ($E_{\text{a(ion)}} = 0.066\text{ eV}$) and $\text{Ag}_7\text{GeSe}_5\text{I}$ ($E_{\text{a(ion)}} = 0.165\text{ eV}$) crystals, is related to an increasing influence of the domain boundaries and compositional disordering of crystalline structures that cause significant difficulties in the process of ion transport. Instead, the activation energy of the electronic conductivity at the cationic substitution in the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals nonlinearly increases with the transition from $\text{Cu}_7\text{GeSe}_5\text{I}$ ($E_{\text{a(el)}} = 0.17\text{ eV}$) to $\text{Ag}_7\text{GeSe}_5\text{I}$ ($E_{\text{a(el)}} = 0.619\text{ eV}$) (Fig. 7).

4. Conclusions

Synthesis and growth of the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals were performed. The growth was carried out by directed crystallization (for $\text{Cu}_7\text{GeSe}_5\text{I}$ and $\text{Ag}_7\text{GeSe}_5\text{I}$) as well as zone crystallization (for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$) from the melt. Electrical measurements were performed in the range of frequencies from of 20 Hz to

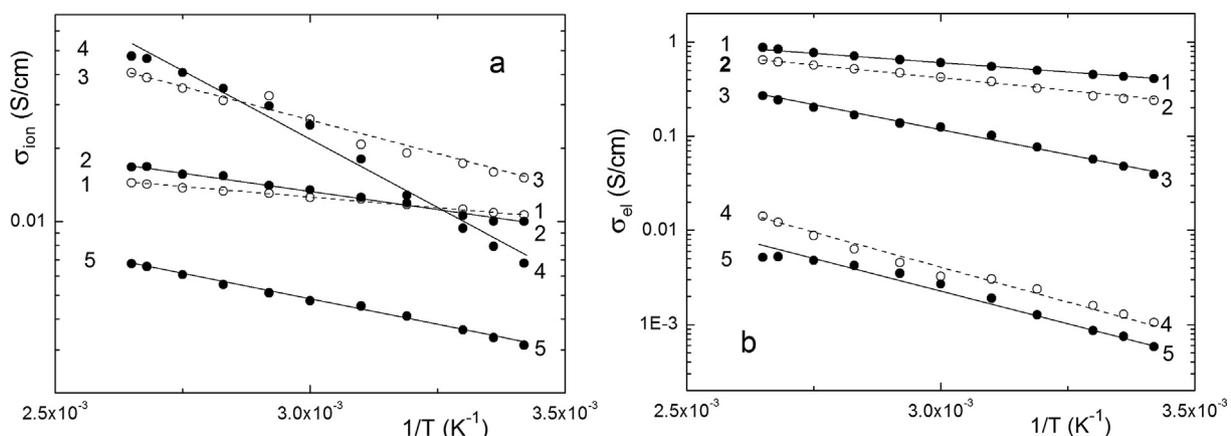


Fig. 6. Temperature dependences of the ionic (a) and electronic (b) conductivities for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals: $\text{Cu}_7\text{GeSe}_5\text{I}$ (1), $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{GeSe}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{GeSe}_5\text{I}$ (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).

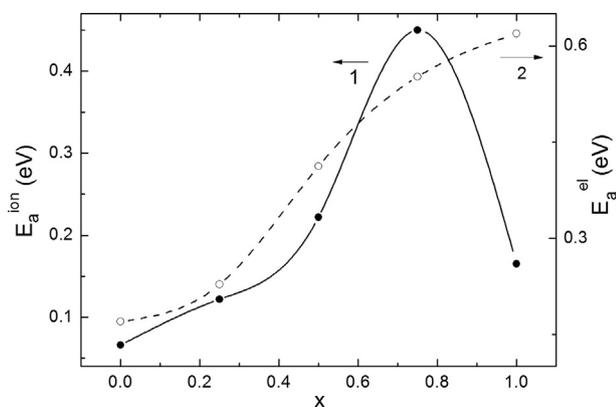


Fig. 7. Compositional dependences of the activation energy of the ionic and electronic components of conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals.

2×10^6 Hz and in the temperature interval 292–378 K. Temperature and frequency dependences of the electrical conductivity were analyzed. For the detailed studies of the frequency behavior of the electrical conductivity and its separation into ionic and electronic components, a standard approach using electrode equivalent circuits and their analysis with Nyquist plots was used. The electric conductivity of the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals follows the Arrhenius law. The compositional dependence of the ionic conductivity is nonlinear with a maximum, whereas the electronic conductivity for the mixed $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ crystals nonlinearly decreases without any anomalies with silver content increase. Simultaneously, the nonlinear compositional dependence of the activation energy of the ionic conductivity reveals a maximum for the $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{GeSe}_5\text{I}$ crystal and the activation energy of the electronic conductivity nonlinearly grows with silver content increase. It should be noted that at the transition from the $\text{Cu}_7\text{GeSe}_5\text{I}$ crystal where the electronic conductivity is 39 times greater than the ionic one, to $\text{Ag}_7\text{GeSe}_5\text{I}$, the ratio $\sigma_{\text{ion}}/\sigma_{\text{el}}$ tends to increase and in $\text{Ag}_7\text{GeSe}_5\text{I}$ crystal the ionic conductivity is 4.5 times greater than the electronic one.

Declaration of competing interest

The authors of manuscript entitled “Impedance studies and electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeSe}_5\text{I}$ mixed crystals” declare no conflicts of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jallcom.2019.152792>.

References

- [1] W.F. Kuhs, R. Nitsche, K. Scheunemann, The argyrodites – a new family of the tetrahedrally close-packed structures, *Mater. Res. Bull.* 14 (1979) 241–248.
- [2] T. Nilges, A. Pfitzner, A structural differentiation of quaternary copper

- argyrodites: structure – property relations of high temperature ion conductors, *Z. Krist.* 220 (2005) 281–294.
- [3] I.P. Studenyak, M. Kranjčec, M.V. Kurik, Urbach rule and disordering processes in $\text{Cu}_6\text{P}(\text{S}_{1-x}\text{Se}_x)_5\text{Br}_{1-y}\text{I}_y$ superionic conductors, *J. Phys. Chem. Solids* 67 (2006) 807–817.
- [4] J. Auvergniot, A. Cassel, D. Foix, V. Viallet, V. Seznec, R. Dedryvère, Redox activity of argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte in all-solid-state Li-ion battery: an XPS study, *Solid State Ion.* 300 (2017) 78–85.
- [5] N.C. Rosero-Navarro, T. Kinoshita, A. Miura, M. Higuchi, K. Tadanaga, Effect of the binder content on the electrochemical performance of composite cathode using $\text{Li}_6\text{PS}_5\text{Cl}$ precursor solution in an all-solid-state lithium battery, *Ionics* 23 (2017) 1619–1624.
- [6] S. Wenzel, S.J. Seldmaier, C. Dietrich, W.G. Zeier, J. Janek, Interfacial reactivity and interphase growth of argyrodite solid electrolytes at lithium metal electrodes, *Solid State Ion.* 318 (2018) 102–112.
- [7] S. Yubuchi, M. Uematsu, C. Hotehama, A. Sakuda, A. Hayashi, M. Tatsumisago, An argyrodite sulfide-based superionic conductor synthesized by a liquid-phase technique with tetrahydrofuran and ethanol, *J. Mater. Chem.* 7 (2019) 558–566.
- [8] Z. Zhang, L. Zhang, X. Yan, H. Wang, Y. Liu, C. Yu, X. Cao, L. van Eijck, B. Wen, All-in-one improvement toward $\text{Li}_6\text{PS}_5\text{Br}$ -based solid electrolytes triggered by compositional tune, *J. Power Sources* 410–411 (2019) 162–170.
- [9] S. Schwarzmüller, D. Souchay, D. Günther, A. Gocke, I. Dovgaliuk, S.A. Miller, G.J. Snyder, O. Oeckler, Argyrodite-Type $\text{Cu}_8\text{GeSe}_{6-x}\text{Te}_x$ ($0 \leq x \leq 2$): temperature-dependent crystal structure and thermoelectric properties, *Z. Anorg. Allg. Chem.* 644 (2018) 1915–1922.
- [10] X. Shen, C.-C. Yang, Y. Liu, G. Wang, H. Tan, Y.-H. Tung, G. Wang, X. Lu, J.n He, X. Zhou, High-temperature structural and thermoelectric study of argyrodite Ag_5GeSe_6 , *ACS Appl. Mater. Interfaces* 11 (2019) 2168–2176.
- [11] I.P. Studenyak, M. Kranjčec, GySh Kovacs, I.D. Desnica-Frankovic, A.A. Molnar, V.V. Panko, V.Yu Slivka, Electrical and optical absorption studies of $\text{Cu}_7\text{GeS}_5\text{I}$ fast-ion conductor, *J. Phys. Chem. Solids* 63 (2002) 267–271.
- [12] Y. Tomm, S. Schorr, S. Fiechter, Crystal growth of argyrodite-type phases $\text{Cu}_{8-x}\text{GeSe}_{6-x}\text{I}_x$ and $\text{Cu}_{8-x}\text{GeSe}_{6-x}\text{I}_x$ ($0 \leq x \leq 0.8$), *J. Cryst. Growth* 310 (2008) 2215–2221.
- [13] I.P. Studenyak, O.P. Kokhan, M. Kranjčec, V.V. Bilanchuk, V.V. Panko, Influence of S → Se substitution on chemical and physical properties of $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ superionic solid solutions, *J. Phys. Chem. Solids* 68 (2007) 1881–1884.
- [14] I.P. Studenyak, V.V. Bilanchuk, O.P. Kokhan, YuM. Stasyuk, A.F. Orliukas, A. Kezionis, E. Kazakevicius, T. Šalkus, Electrical conductivity, electrochemical and optical properties of $\text{Cu}_7\text{GeS}_5\text{I-Cu}_7\text{GeSe}_5\text{I}$ superionic solid solutions, *Lit. J. Phys.* 49 (2009) 203–208.
- [15] I.P. Studenyak, M. Kranjec, V.V. Bilanchuk, O.P. Kokhan, A.F. Orliukas, E. Kazakevicius, A. Kezionis, T. Šalkus, Temperature variation of electrical conductivity and absorption edge in $\text{Cu}_7\text{GeSe}_5\text{I}$ advanced superionic conductor, *J. Phys. Chem. Solids* 70 (2009) 1478–1481.
- [16] I.P. Studenyak, M. Kranjčec, V.V. Bilanchuk, O.P. Kokhan, A.F. Orliukas, A. Kezionis, E. Kazakevicius, T. Šalkus, Temperature and compositional behaviour of electrical conductivity and optical absorption edge in $\text{Cu}_7\text{Ge}(\text{S}_{1-x}\text{Se}_x)_5\text{I}$ mixed superionic crystals, *Solid State Ion.* 181 (2010) 1596–1600.
- [17] I.P. Studenyak, A.I. Pogodin, O.P. Kokhan, V. Kavaliukė, T. Šalkus, A. Kezionis, A.F. Orliukas, Crystal growth, structural and electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ superionic solid solutions, *Solid State Ion.* 329 (2019) 119–123.
- [18] M. Laqibi, B. Cros, S. Peytavin, M. Ribes, New silver superionic conductors $\text{Ag}_7\text{XY}_5\text{Z}$ (X = Si, Ge, Sn; Y = S, Se; Z = Cl, Br, I) – synthesis and electrical studies, *Solid State Ion.* 23 (1987) 21–26.
- [19] A. Zerouale, B. Cros, B. Deroide, M. Ribes, Electrical properties of $\text{Ag}_7\text{GeSe}_5\text{I}$, *Solid State Ion.* 28–30 (1988) 1317–1318.
- [20] R. Belin, A. Zerouale, A. Pradel, M. Ribes, Ion dynamics in the argyrodite compound $\text{Ag}_7\text{GeSe}_5\text{I}$: non-Arrhenius behavior and complete conductivity spectra, *Solid State Ion.* 143 (2001) 445–455.
- [21] R. Belin, L. Aldon, A. Zerouale, C. Belin, M. Ribes, Crystal structure of the non-stoichiometric argyrodite compound $\text{Ag}_{7-x}\text{GeSe}_5\text{I}_{1-x}$ ($x=0.31$). A highly disordered silver superionic conducting material, *Solid State Sci.* 3 (2001) 251–265.
- [22] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, John Wiley & Sons, New Jersey, 2008.
- [23] A.K. Ivanov-Schitz, I.V. Murin, *Solid State Ionics*, vol. 1, Univ. Press, S.-Petersburg, 2000 (in Russian).
- [24] R.A. Huggins, Simple method to determine electronic and ionic components of the conductivity in mixed conductors: a review, *Ionics* 8 (2002) 300–313.