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ELECTRICAL CONDUCTIVITY, ELECTROCHEMICAL AND OPTICAL PROPERTIES OF Cu_7GeS_5I–Cu_7GeSe_5I SUPERIONIC SOLID SOLUTIONS

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Single crystals of Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions were grown by chemical transport. Their electrical conductivity in the frequency range $1.0{\cdot}10^6$–$1.2{\cdot}10^9$ Hz and in the temperature range 100–300 K was measured; the compositional dependences of the electrical conductivity and activation energy were obtained. Electrochemical studies of Cu_7GeS_5I–Cu_7GeSe_5I solid solutions were performed, the character of compositional variation of the electrode potential and the range of the electrochemical stability at S→Se substitution were determined. The optical absorption edge of Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions in the temperature range 77–300 K were studied; the compositional dependences of the optical pseudogap and Urbach energy were obtained.

Keywords: superionic conductors, electrical conductivity, electrochemical properties, optical absorption edge

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1. Introduction

Cu_7GeS_5I compounds belong to argyrodite family and are known as superionic conductors [1]. They exhibit rather high electrical conductivity and low activation energy [2]. Optical studies have shown that the absorption edge of Cu_7GeS_5I crystals exhibits Urbach behaviour in a wide temperature range [2]. Some electrochemical properties of Cu_7GeS_5I crystals are reported in [3]. A comparative analysis has shown that P→Ge and Cu→Ag cation substitution in argyrodite-type superionic conductors results in an increase of electrical conductivity and a decrease of activation energy [4–6].

The compositional dependence of the lattice parameter of the alloys and single crystals of Cu_7GeS_5I–Cu_7GeSe_5I system was shown to be linear, described by Vegard law that is the evidence for the formation of a continuous row of substitutive solid solutions [7]. At room temperature $Cu_7GeS(Se)_5I$-based solid solutions crystallize in the cubic symmetry (space group $F\bar{4}3m$). The short-wavelength edge of the diffuse reflection spectra of $Cu_7Ge(S_{1-x}Se_x)_5I$ solid solutions is shown to shift towards longer wavelengths with the substitution of S atoms by Se [7].

The present work is aimed at electrical, electrochemical, and optical studies in Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions, which can find applications as solid electrolyte batteries and electrochemical sensors.

2. Experimental procedure

Single crystals of Cu_7GeS_5I–Cu_7GeSe_5I system were grown by chemical transport. Pure $Cu_7GeS(Se)_5I$ compounds and $Cu_7GeS(Se)_5I$-based solid solutions were synthesized from extra pure Cu, Ge, S(Se), and CuI compounds, additionally purified by distillation in vacuum. To avoid contamination and deviations from stoichiometry, the single crystals were synthesized and grown in the same evacuated (down to 0.13 Pa) quartz ampoules. The temperature of the evaporation zone was kept within 1023–1073 K, and that of the crystallization zone within 983–1023 K. 10–20 mg of CuI per 1 cm^3 of the ampoule free volume were used as a transport agent. Thus, the as-grown crystals had the shape of plane-parallel platelets or distorted tetrahedra $5{\times}3{\times}3(2.5)$ mm^3 in size with colour from dark red to black.

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The measurements of complex electrical conductivity were carried out in the frequency range $1.0{\cdot}10^6$–$1.2{\cdot}10^9$ Hz in the temperature range 100–300 K using a coaxial impedance spectrometer set-up [8]. Potentiometric studies of the electrode characteristics were performed using a two-electrode scheme for a series of solutions containing 10^{-1}–10^{-6} mol/l of the main ion with respect to which the electrode selectivity was studied [3]. The electrode potentials were determined with respect to the Ag / AgCl electrode at 293 K.

Spectral dependence of the absorption coefficient α was studied in the temperature range 77–300 K using the set-up described in Ref. [5]. For the transmittance and reflectance measurements the samples were oriented at room temperature, while in cubic phase. The orientation was chosen such that the unpolarized light beam was propagating along the [100] crystallographic direction. The reflectance measurements were performed on separate samples in which reflection from the rear surface could be neglected. The absorption coefficient α as a function of transmittance, T, and reflection of the surface, R, was calculated using the well-known formula, which takes into account multiple internal reflections [5]. To be within the accepted level of accuracy of $\Delta\alpha/\alpha < 10\%$, the product αd has to be between 1 and 3, where d is the sample thickness. Isoabsorption temperature studies consisted in measuring the absorption edge energy position E_g^α at the fixed absorption level.

3. Results and discussion

3.1. Electrical conductivity

The obtained results show that substitution of S atoms by Se leads to an increase of the total electrical conductivity σ. In comparison with Cu_7GeS_5I, in Cu_7GeSe_5I crystals the σ value increases by more than an order of magnitude. However, the character of the compositional dependence of the electric conductivity is rather complicated (Fig. 1(a)). With the increase of Se atom content the σ value increases and reaches the value $\sigma_{295} = 52.3$ S/m at $3.0{\cdot}10^6$ Hz and 295 K for the composition $0.7Cu_7GeS_5I$–$0.3Cu_7GeSe_5I$. Then, with the further increase of selenium concentration, the σ value decreases to 12.8 S/m for $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ and again increases up to 64.0 S/m for Cu_7GeSe_5I. The activation energy E_a in the solid solutions under consideration has a general trend to increase with Se atom content from 0.092 eV for Cu_7GeS_5I to 0.125 eV for Cu_7GeSe_5I. In its compositional dependence two distinct minima are observed for the compositions $0.7Cu_7GeS_5I$–$0.3Cu_7GeSe_5I$ and $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$, for which the E_a values are 0.035 and 0.049 eV, respectively (Fig. 1(a)). The studies of electric conductivity have shown that the Cu_7GeS_5I–Cu_7GeSe_5I solid solution crystals are characterized by rather high electric conductivity and low activation energy that puts them in line with the most efficient solid electrolytes.

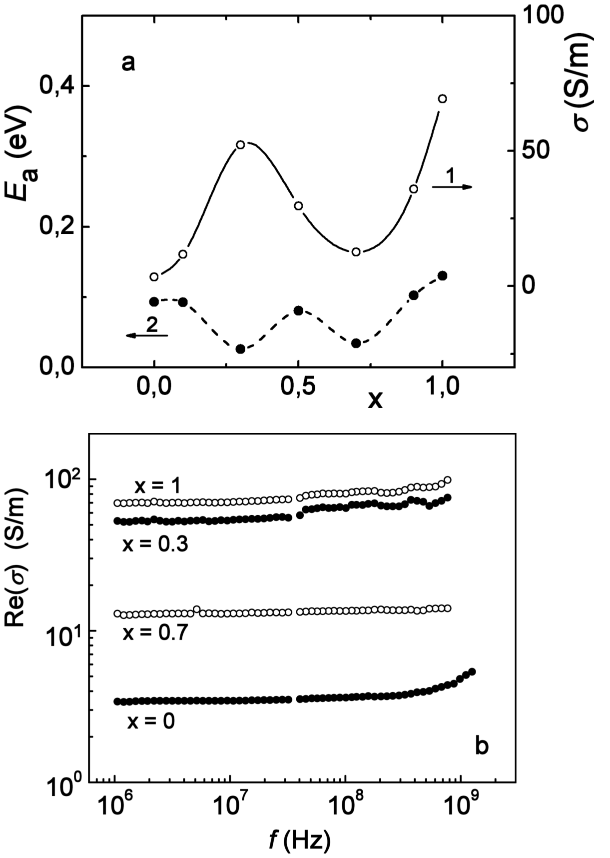

Fig. 1. (a) Compositional dependences of electrical conductivity (*1*), measured at 295 K and $3.0{\cdot}10^6$ Hz, and activation energy (*2*) for Cu_7GeS_5I–Cu_7GeSe_5I solid solutions. (b) Frequency dependences of real part of electrical conductivity in $(1-x)Cu_7GeS_5I$–xCu_7GeSe_5I solid solutions, measured at 295 K.

The spectra of real part of complex conductivity exhibit constant values up to 10^8 Hz at room temperature (Fig. 1(b)). At higher frequencies the relaxation dispersion of conductivity was observed and the part of typical semicircle was seen in the complex impedance plots.

3.2. Electrochemical properties

For electrodes prepared from Cu_7GeS_5I–Cu_7GeSe_5I solid solutions, electrochemical behaviour in ion-containing solutions was studied (Fig. 2). Results of mea-

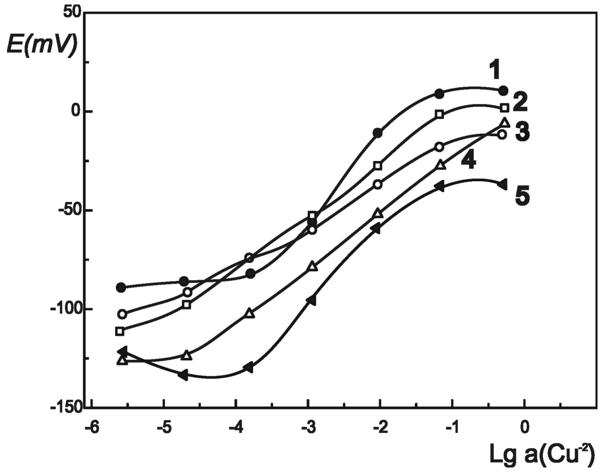

Fig. 2. Concentrational dependence of the electrode potential in Cu_7GeS_5I–Cu_7GeSe_5I solid solutions: *1* for Cu_7GeS_5I, *2* for $0.8Cu_7GeS_5I$–$0.2Cu_7GeSe_5I$, *3* for $0.6Cu_7GeS_5I$–$0.4Cu_7GeSe_5I$, *4* for $0.4Cu_7GeS_5I$–$0.6Cu_7GeSe_5I$, *5* for $0.2Cu_7GeS_5I$–$0.8Cu_7GeSe_5I$.

surements show that for the majority of solid solutions the concentrational dependence of the potential is nonlinear and the Nernst equation for the divalent Cu^{2+} ion is not fulfilled. Only for the $0.4Cu_7GeS_5I$–$0.6Cu_7GeSe_5I$ sample a linear dependence of the potential versus concentration with a slope of 27.8 mV/decade is observed within the Cu^{2+} concentration interval 10^{-5}–100 mol/l (curve *4*, Fig. 2).

With the increase of selenium content in the sample, a monotonous shift of potentials towards negative values is observed, which can be explained by the decrease of the bond polarity at S→Se substitution. Besides, stationary potentials, especially for Cu_7GeSe_5I electrodes, are unstable with time and even after a slight polarization of the electrode. Therefore, though a certain equilibrium between copper ions in the solid phase and in the working solution can be established, this process is still durable.

Current–voltage (*I*–*V*) characteristics were studied in a standard three-electrode cell with an Ag/AgCl comparing electrode. The electrochemical studies were carried out in working solutions with various concentrations of copper ions. The *I*–*V* characteristics were measured at different potential scanning rates (from 4 to 80 mV/s) with or without stirring the solution.

Figure 3(a) shows an *I*–*V* characteristic for an electrode prepared from $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ solid solution. With the polarization of the $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ electrode above +50 mV and below −600 mV (with respect to the chlorine-silver electrode, c. s. e.), both the anode and the cathode current sharply increase. With further polarization the current grows

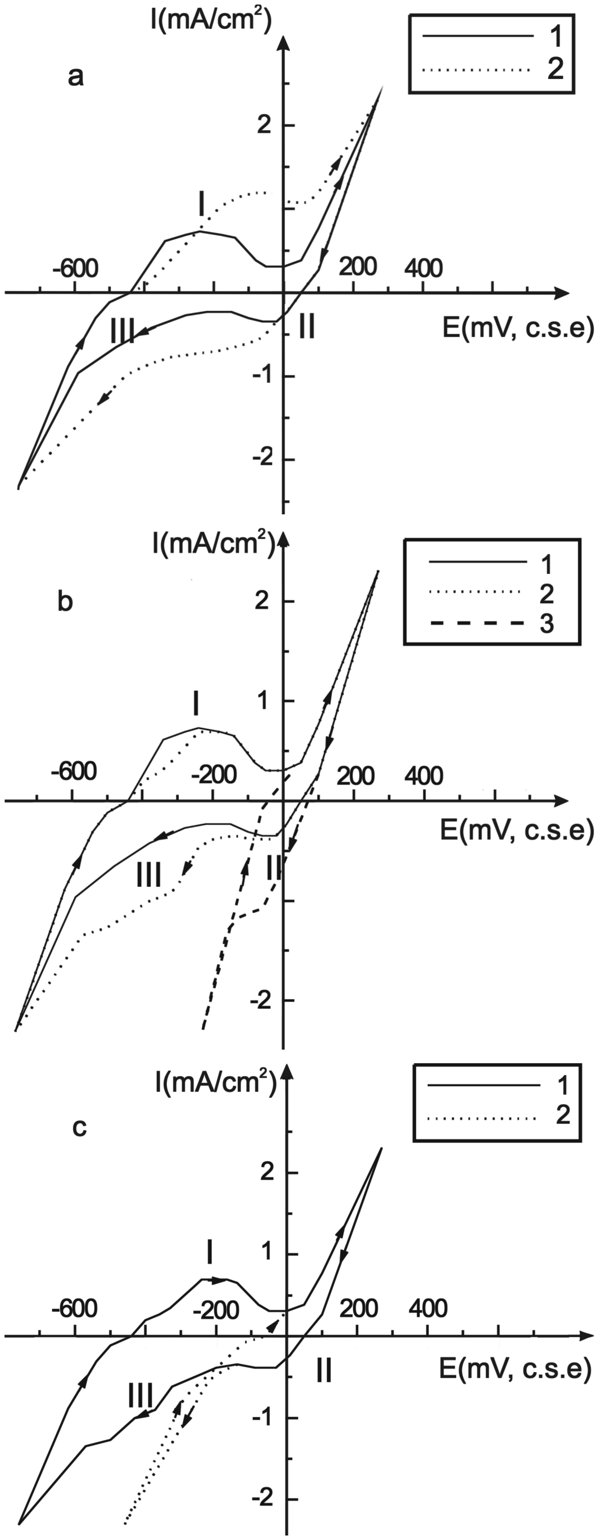

Fig. 3. *I*–*V* characteristic for $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ electrode: (a) at the potential scanning rate of 4 mV/s (*1*) and 40 mV/s (*2*) in 10^{-3} mol/l $CuSO_4$/0.1 mol/l H_2SO_4; (b) at $V_{sc} = 4$ mV/s in 10^{-3} (*1*), 10^{-2} (*2*), 10^{-1} mol/l $CuSO_4$/0.1 mol/l H_2SO_4 (*3*); (c) at $V_{sc} = 4$ mV/s, in 10^{-2} mol/l $CuSO_4$/0.1 mol/l H_2SO_4 without (*1*) and with (*2*) stirring the working solution.

unlimitedly till the complete electrochemical destruction of the sample. At such potential the process of forced motion of Cu^+ ions from the crystal lattice occurs which in the anode range of the I–V characteristic is superimposed by the processes of Cu^+ ion deintercalation, oxidation $Cu^+ \to Cu^{2+} + e^-$, and desorption of Cu^{2+} to the solution; in the cathode range the process of ion reduction to free copper $Cu^+ + e^- \to Cu^0$ occurs at the rear contact. In the range of $(-450 - +50)$ mV a range of relative electrochemical stability with small (<0.75 mA/cm^2) currents exists. In a cyclic I–V characteristic one anode (I) and two cathode (II, III) maxima are observed. With the increase of the potential scanning rate from 4 to 40 mV/s the values of all the maxima increase and their potentials shift (for I towards the anode range, for II and III towards the cathode range). If these processes are not restricted, they result in a complete electrochemical destruction of the structure.

Both I and II maxima are independent of copper ion concentration in the working solution or its stirring, but considerably increase due to preceding cathode (for I) and anode (for II) polarization. These facts are the evidence for the peaks to correspond to the ionic transport of Cu^+ ions in the solid phase of $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$. The cathode maximum III, on the contrary, entirely depends on the working solution concentration. Below 10^{-3} mol/l copper ions in the working solution, this peak is hardly revealed (Fig. 3(b), cyclic curve *1*), at 10^{-2} mol/l it considerably increases (Fig. 3(b), cyclic curve *2*), and at 10^{-1} mol/l it increases so high that it cannot be registered at the I–V characteristic at the given conditions (Fig. 3(b), cyclic curve *3*). Stirring of the working solution also results in an increase of the maximum III (Fig. 3(c)). It is shown that peak III depends on the Cu^+ concentration in the near-surface layer of the $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ electrode and corresponds to the process of copper ion intercalation from the solution to the solid phase.

Figure 4 shows I–V characteristics for electrodes of the system under investigation with different sulphur-to-selenium ratio: $0.9Cu_7GeS_5I$–$0.1Cu_7GeSe_5I$ (cyclic curve *1*), $0.5Cu_7GeS_5I$–$0.5Cu_7GeSe_5I$ (cyclic curve *2*), and $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ (cyclic curve *3*). All the I–V characteristics are measured at the same conditions $T = 293$ K, $V_{sc} = 4$ mV/s, $C = 10^{-3}$ mol/l $CuSO_4$/0.1 mol/l H_2SO_4. The character of the processes is much the same as in the case of the $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ electrode (Fig. 3). One anode peak and two cathode peaks are observed. However, these peaks increase with selenium content in the solid solution. Simultaneously the range of the anode and cathode polarization potentials becomes narrower. Therefore, it can be concluded that monocrystalline $0.9Cu_7GeS_5I$–$0.1Cu_7GeSe_5I$ exhibits higher electrochemical stability in comparison with $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ single crystals. Thus, it should be noted that the decrease of electrochemical stability with substitution of sulphur by selenium is accompanied by the increase of ionic conductivity of Cu_7GeS_5I–Cu_7GeSe_5I solid solutions.

3.3. Optical absorption edge

The temperature dependences of the absorption edge energy position E_g^α, obtained as a result of isoabsorption studies, have confirmed that within the temperature interval of 77–300 K any anomalies in $E_g^\alpha(T)$ dependences and correspondingly phase transitions in the abovementioned temperature interval are not observed. It should be noted that in Cu_7GeS_5I–Cu_7GeSe_5I solid solutions at 77 K the excitonic bands have not been found and the optical absorption edge in the range of direct allowed interband transitions has an exponential Urbach's shape. It is investigated that the exponential shape and Urbach behaviour of the long-wavelength absorption edge are related to the manifestation of electron–phonon interaction which is strong for Cu_7GeS_5I–Cu_7GeSe_5I solid solutions. The temperature dependences of optical pseudogap and Urbach energy obtained by absorption edge analysis are well described in the framework of Einstein model. The influence of S→Se anionic substitution on optical absorption edge parameters such as the optical pseudogap E_g^* and Urbach energy E_U are studied for Cu_7GeS_5I–Cu_7GeSe_5I solid solutions (Fig. 5). The increase of selenium content in Cu_7GeS_5I–Cu_7GeSe_5I solid solutions leads to the nonlinear decrease of the optical pseudogap. The complicated compositional dependence of Urbach energy is determined by the influence of different types of crystal lattice disordering (Fig. 5).

4. Conclusions

Single crystals of Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions were grown by chemical transport reactions. The electrical conductivity measurements in the frequency range $1.0\cdot10^6$–$1.2\cdot10^9$ Hz and in the temperature range 100–300 K were carried out. With the increase of Se content in Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions the σ value is shown to increase, a maximum in the compositional dependence being observed for the composition $0.7Cu_7GeS_5I$–

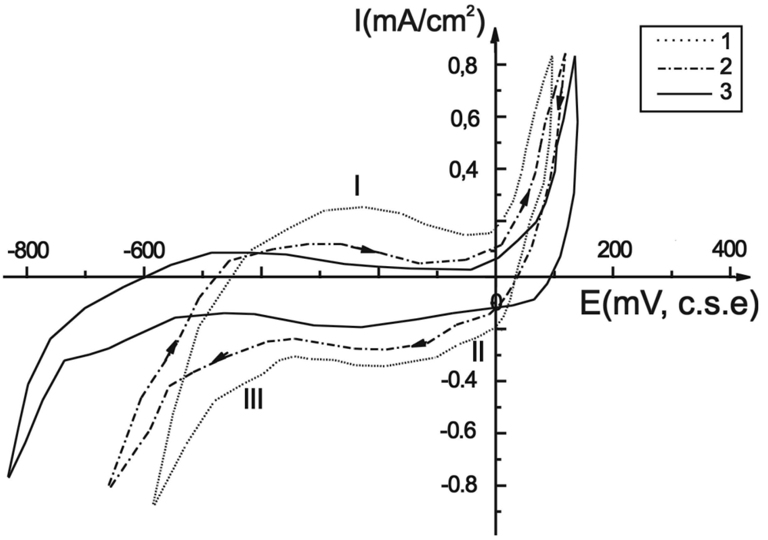

Fig. 4. Dependence of I–V characteristics on the composition of Cu_7GeS_5I–Cu_7GeSe_5I solid solutions at $V_{sc} = 4$ mV/s, in 10^{-3} mol/l $CuSO_4$ / 0.1 mol/l H_2SO_4: *1* for $0.9Cu_7GeS_5I$–$0.1Cu_7GeSe_5I$, *2* for $0.5Cu_7GeS_5I$–$0.5Cu_7GeSe_5I$, *3* for $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$.

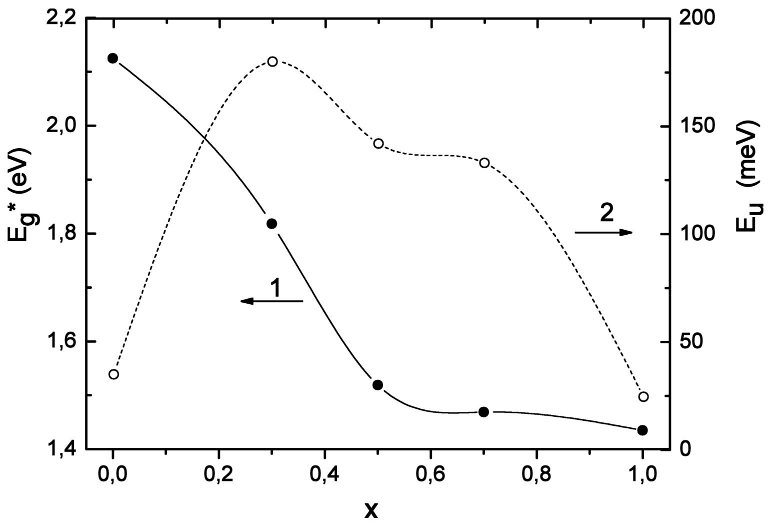

Fig. 5. Compositional dependences of optical pseudogap E_g^* (*1*) and Urbach energy E_U (*2*) at 300 K for Cu_7GeS_5I–Cu_7GeSe_5I solid solutions.

$0.3Cu_7GeSe_5I$. Though the activation energy has a general trend to increase with Se content in the solid solutions under study, two clear minima are observed in its compositional dependence: for the $0.7Cu_7GeS_5I$–$0.3Cu_7GeSe_5I$ and $0.3Cu_7GeS_5I$–$0.7Cu_7GeSe_5I$ compositions.

Electrochemical studies have shown that with the increase of selenium content in the sample a monotonous shift of electrode potentials towards negative values is observed that can be explained by the decrease of the bond polarity at S→Se substitution. In the I–V characteristics, in the range of polarization from -450 to $+50$ mV, a range of relative electrochemical stability with small currents exists. In this range one anode and two cathode maxima are observed, these peaks increasing with selenium content in the solid solution. Besides, at S→Se substitution the range of the anode and cathode polarization potentials gets narrower and electrochemical stability becomes lower.

The isoabsorption studies do not reveal any phase transitions for Cu_7GeS_5I–Cu_7GeSe_5I superionic solid solutions in the temperature interval 77–300 K. A nonlinear decrease of the optical pseudogap in the Cu_7GeS_5I–Cu_7GeSe_5I solid solutions at S→Se anionic substitution is observed, the compositional dependence of Urbach energy exhibits the typical behaviour for solid solution crystals.

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References

[1] W.F. Kuhs, R. Nitsche, and K. Scheunemann, The argyrodites – A new family of tetrahedrally close-packed structures, Mater. Res. Bull. **14**, 241–248 (1979).

[2] I.P. Studenyak, M. Kranjčec, Gy.Sh. Kovács, I.D. Desnica-Franković, A.A. Molnar, V.V. Panko, and V.Yu. Slivka, Electrical and optical absorption studies of Cu_7GeS_5I fast-ion conductor, J. Phys. Chem. Solids **63**, 267–271 (2002).

[3] Yu.M. Stasyuk, O.P. Kokhan, V.V. Panko, and S.K. Kovach, Obtaining and some properties of Cu_7GeS_5I and Cu_7GeSe_5I compounds, Visnyk UzhDU: Ser. Khim. **4**, 9–12 (1999) [in Ukrainian].

[4] I.P. Studenyak, V.O. Stefanovich, M. Kranjčec, D.I. Desnica, Yu.M. Azhnyuk, Gy.Sh. Kovacs, and V.V. Panko, Raman scattering studies of Cu_6PS_5Hal (Hal = Cl, Br and I) fast-ion conductors, Solid State Ionics **95**, 221–225 (1997).

[5] I.P. Studenyak, M. Kranjčec, Gy.S. Kovács, V.V. Pan'ko, D.I. Desnica, A.G. Slivka, and P.P. Guranich, The effect of temperature and pressure on the optical absorption edge in Cu_6PS_5X (X = Cl, Br, I) crystals, J. Phys. Chem. Solids **60**, 1897–1904 (1999).

[6] M. Laqibi, B. Cros, S. Peytavin, and M. Ribes, New silver superionic conductors Ag_7XY_5Z (X = Si, Ge, Sn; Y = S, Se; Z = Cl, Br, I) – synthesis and electrical studies, Solid State Ionics **23**, 21–26 (1987).

[7] I.P. Studenyak, O.P. Kokhan, M. Kranjčec, V.V. Bilanchuk, and V.V. Panko, Influence of S→Se substitution on chemical and physical properties of $Cu_7Ge(S_{1-x}Se_x)_5I$ superionic solid solutions, J. Phys. Chem. Solids **68**, 1881–1884 (2007).

[8] A.F. Orliukas, A. Kezionis, and E. Kazakevicius, Impedance spectroscopy of solid electrolytes in the radio frequency range, Solid State Ionics **176**, 2037–2043 (2005).

Cu_7GeS_5I–Cu_7GeSe_5I SUPERJONINIŲ KIETŲJŲ TIRPALŲ ELEKTRINIS LAIDUMAS BEI ELEKTROCHEMINĖS IR OPTINĖS SAVYBĖS

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Santrauka

Cu_7GeS_5I–Cu_7GeSe_5I superjoninių kietųjų tirpalų monokristalai buvo užauginti cheminės pernašos metodu. Jų elektrinis laidumas išmatuotas $1.0 \cdot 10^6$–$1.2 \cdot 10^9$ Hz dažnių ir 100–300 K temperatūros intervaluose ir nustatytos elektrinio laidumo bei aktyvacijos energijos priklausmybės nuo cheminės sudėties parametro. Atlikti Cu_7GeS_5I–Cu_7GeSe_5I kietųjų tirpalų elektrocheminiai tyrimai, nustatyti elektrodų sudėties kitimo įtakos jų potencialui pobūdis ir elektrocheminio stabilumo sritis keičiant S→Se. Cu_7GeS_5I–Cu_7GeSe_5I superjoninių kietųjų tirpalų optinė sugerties riba ištirta 77–300 K temperatūros intervale, nustatyta cheminės sudėties įtaka optiniam pseudotarpui ir Urbacho energijos vertei.