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Electric conductivity studies of composites based on $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ superionic conductors

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Abstract. The composites based on superionic $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ solid solutions were prepared by mixing of microcrystalline powder with polyvinylacetate glue. The temperature and frequency behaviour of the total electric conductivity of composites within the frequency range $1.0 \cdot 10^6$ – $1.2 \cdot 10^9$ Hz and temperature range 300 to 420 K were investigated. The linear increase of the total electric conductivity with temperature increase was revealed, as well as the influence of Cu→Ag cation substitution on electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites was studied.

Keywords: superionic conductor, composite, electric conductivity, cation substitution, compositional behavior.

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1. Introduction

Superionic conductors $\text{Cu}_6\text{PS}_5\text{I}$ and $\text{Ag}_6\text{PS}_5\text{I}$ belong to the family of compounds with argyrodite structure [1, 2]. They are chemical and structural analogues (at room temperature they crystallize in cubic system). Studying the electrical properties of $\text{Cu}_6\text{PS}_5\text{I}$ crystals shows that they possess high value of electric conductivity at room temperature, which is comparable with the conductivity of the best superionic conductors [3, 4]. Thus, the electrical conductivity of mono- and polycrystalline superionic conductor $\text{Cu}_6\text{PS}_5\text{I}$ is equal to $1.3 \cdot 10^{-3}$ and $2.0 \cdot 10^{-4}$ S/cm, while the electrical conductivity of polycrystalline $\text{Ag}_6\text{PS}_5\text{I}$ is equal to $7.4 \cdot 10^{-4}$ S/cm [5].

Among argyrodite-type superionic conductors, the most intensively studied is $\text{Cu}_6\text{PS}_5\text{I}$ crystal. At low temperatures, in $\text{Cu}_6\text{PS}_5\text{I}$ crystal two phase transitions (PTs) occur: structural second-order PT at $T_{II} = (269 \pm 2)$ K, which is accompanied by the symmetry change $F\bar{4}3m \rightarrow F\bar{4}3c$ as well as superionic and ferroelastic first-order PT at $T_I = (144 \pm 1)$ K accompanied by the symmetry change $F\bar{4}3c \rightarrow Cc$ [6, 7]. Optical absorption edge studies of $\text{Cu}_6\text{PS}_5\text{I}$ crystal have shown the existence of bound and free excitons at high absorption levels at temperatures below the first-order PT, while in the superionic state the temperature behaviour of the exponential parts of the absorption edge is described by the empirical Urbach rule [8, 9]. Some

electrical, thermodynamic and optical properties of Ag-containing argyrodite-type superionic conductors are studied in Refs. [5, 10, 11].

Thus, the presence of high ionic conductivity in superionic phase determines the prospects of practical application of argyrodite-type superionic conductors as electrochemical power sources and sensors. The aim of this paper is to prepare and investigate the electric conductivity of composites based on $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ superionic conductors.

2. Experimental

To synthesize the polycrystalline samples of the $\text{Cu}_6\text{PS}_5\text{I}$ – $\text{Ag}_6\text{PS}_5\text{I}$ system, the powders of $\text{Cu}_6\text{PS}_5\text{I}$ and $\text{Ag}_6\text{PS}_5\text{I}$ compounds were used. The maximal temperature of synthesis was 580 °C, duration of the process was 145 hours, cooling was carried out in the mode of the eliminated stove. The composite samples were obtained by mixing the microcrystalline powder, the average size of particles in which was 50 μm , with polyvinylacetate glue. Mixing was carried out in the mechanical way in wet medium at room temperature; the microcrystalline powder and polyvinylacetate glue was mixed in proportion 90 and 10 wt.%, respectively. After mixing, the pellets of 8 mm in diameter and 0.2–2 mm thick were pressed at 150 MPa from as-prepared viscous samples. The pressed samples were dried at room temperature for 15 hours.

Measurements of the complex electric conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites were carried out within the frequency range $1.0 \cdot 10^6$ – $1.2 \cdot 10^9$ Hz and at the temperatures from 300 to 420 K by using the coaxial impedance spectrometer [12].

3. Results and discussion

Frequency dependences of the real part of complex conductivity σ' for composites based on solid solutions under investigation are shown in Fig. 1. In the studied temperature and frequency ranges, two dispersion regions, caused by the ion transport in the intercrystallite regions and in the bulk of composite microcrystals, are observed. These frequency and temperature dependences of σ' indicate that two types of relaxation processes caused by ion transport in superionic composites take place. The high frequency parts of the spectra correspond to relaxation in the bulk, while the lower parts correspond to grain boundary processes. Both dispersion areas are shifted into the high-frequency range with the temperature increase. The observed dispersions of relaxation type are confirmed by the impedance frequency dependences plotted in the complex plane. Typical impedance spectrum consists of two semicircles superposition, which centers lie below the real axis. Relaxation process in the bulk leads to the high frequency arc, while the low-frequency arc illustrates the relaxation process in the grain boundary areas of the composites.

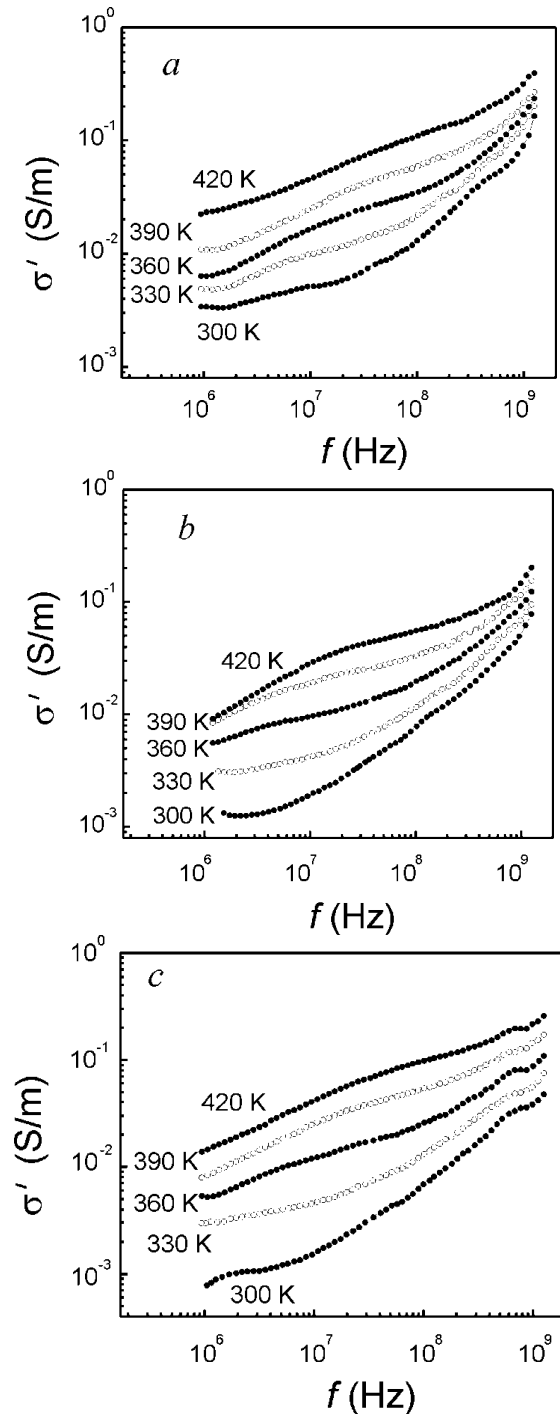


Fig. 1. Frequency dependences of the real part of complex conductivity σ' for composites based on solid solutions: $(\text{Cu}_{0.3}\text{Ag}_{0.7})_6\text{PS}_5\text{I}$ (a), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_6\text{PS}_5\text{I}$ (b), and $(\text{Cu}_{0.7}\text{Ag}_{0.3})_6\text{PS}_5\text{I}$ (c) at various temperatures.

Shown in Fig. 2 are the temperature dependences of the real part of complex conductivity σ' for composites based on $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ solid solutions measured at various frequencies. It was revealed that at temperature increase the σ' value increases linearly according to the Arrhenius law:

$$\sigma' = \frac{\sigma_0}{T} \exp\left(-\frac{\Delta E_a}{kT}\right), \quad (1)$$

where ΔE_a is the activation energy of total electrical conductivity, σ_0 – constant value, k – Boltzmann constant, T – temperature. From $\sigma'(T)$ dependences, the activation energy ΔE_a for $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites was determined.

It should be noted that the above mentioned frequency regions are observed as maxima on the spectra of imaginary part of complex impedance Z'' (Fig. 3). From the frequency position of the high-frequency peak of Z'' the relaxation frequencies f_b of the relaxation process in the bulk of composites were determined. It was shown that the temperature dependences of f_b (Fig. 4) are well described by the equation:

$$f_b = f_0 \exp\left(-\frac{\Delta E_b}{kT}\right), \quad (2)$$

where ΔE_b is the activation energy of f_b , f_0 – attempt frequency related to the lattice vibrations. The obtained from Eq.(2) values of ΔE_b as well as ΔE_a for $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites are presented in Fig. 5. It was shown that the activation energy of total conductivity ΔE_a and bulk conductivity ΔE_b in the superionic phase with increasing the silver atoms content in $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites nonlinearly increases in the compositional range $x=0\dots0.7$, at $x=0.7$ they reach maxima and then nonlinearly decreases. Besides, the bulk activation energy ΔE_b is lower than ΔE_a .

It should be noted that substitution of Cu atoms by the Ag ones leads to a nonlinear decrease of the real part of complex conductivity σ' within the compositional interval $x = 0\dots0.6$, at $x=0.6$ the minimum on the compositional dependence is observed, at $x>0.6$ the electric conductivity increases.

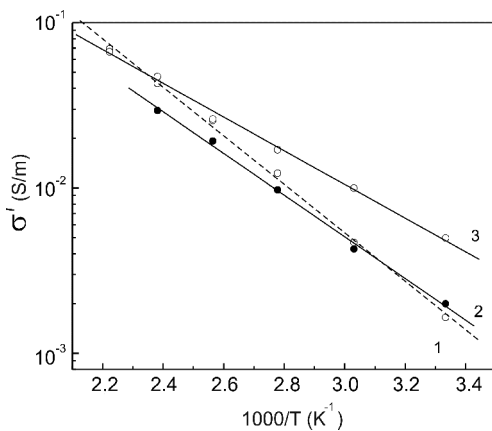


Fig. 2. Temperature dependences of the real part of complex conductivity σ' for $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites at the frequency 10 MHz: $(\text{Cu}_{0.3}\text{Ag}_{0.7})_6\text{PS}_5\text{I}$ (1), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_6\text{PS}_5\text{I}$ (2) and $(\text{Cu}_{0.7}\text{Ag}_{0.3})_6\text{PS}_5\text{I}$ (3).

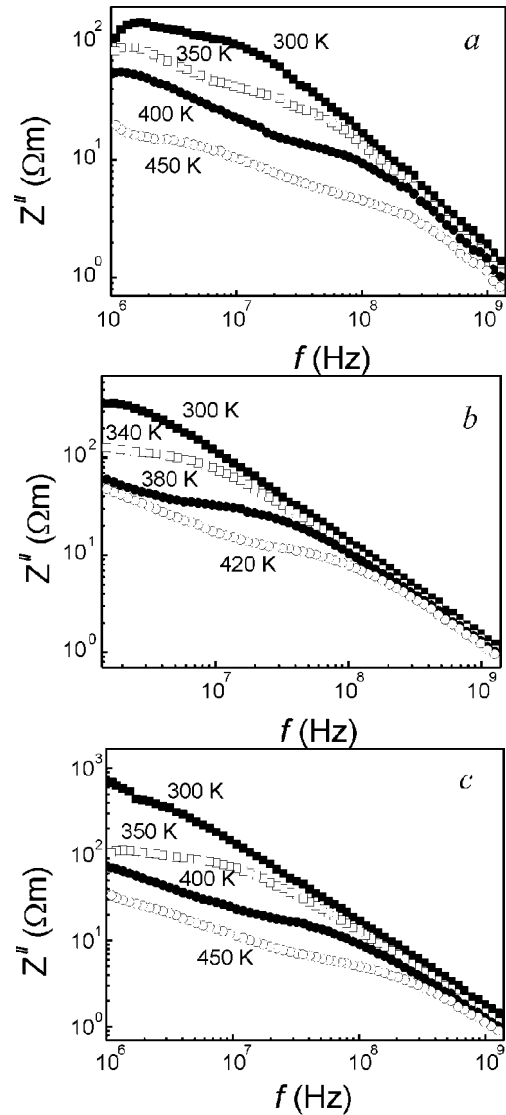


Fig. 3. Frequency dependences of the imaginary part of impedance Z'' for $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites at various temperatures: $(\text{Cu}_{0.3}\text{Ag}_{0.7})_6\text{PS}_5\text{I}$ (a), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_6\text{PS}_5\text{I}$ (b), and $(\text{Cu}_{0.7}\text{Ag}_{0.3})_6\text{PS}_5\text{I}$ (c).

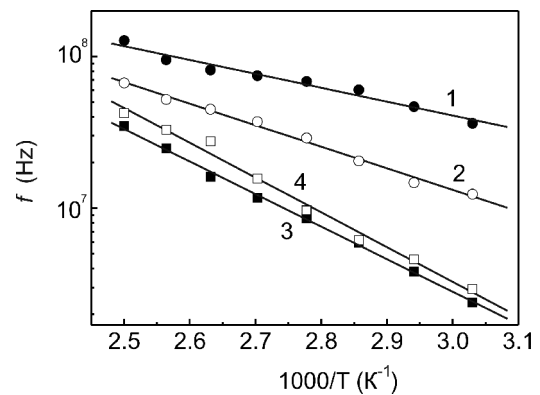


Fig. 4. Temperature dependences of the relaxation frequency f_b for $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites: $(\text{Cu}_{0.1}\text{Ag}_{0.9})_6\text{PS}_5\text{I}$ (1), $(\text{Cu}_{0.3}\text{Ag}_{0.7})_6\text{PS}_5\text{I}$ (2), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_6\text{PS}_5\text{I}$ (3) and $(\text{Cu}_{0.7}\text{Ag}_{0.3})_6\text{PS}_5\text{I}$ (4).

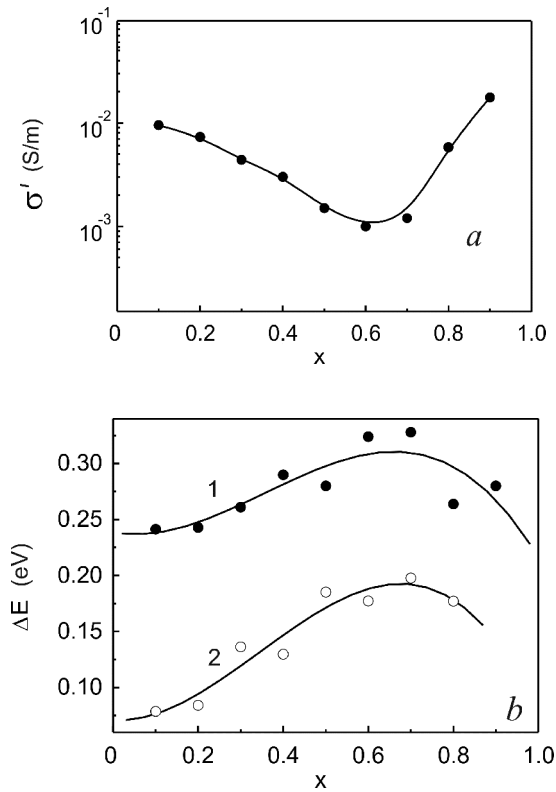


Fig. 5. Compositional dependences of the real part of complex conductivity σ' at the frequency 10 MHz (a) and activation energy (b) of the total electric conductivity ΔE_a (1) as well as the bulk activation energy ΔE_b (2) of $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites at the temperature $T = 300\text{ K}$.

4. Conclusions

Composites based on $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ superionic conductors were prepared by mixing the microcrystalline powder with polyvinylacetate glue. The complex electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_6\text{PS}_5\text{I}$ composites was measured within the temperature range 300 to 420 K and frequency one from 1 MHz to 1.2 GHz. The results have shown that substitution of Cu atoms by the Ag ones leads to a nonlinear, with downward bowing, increase of the real part of complex conductivity σ' . It has been observed that with the temperature growth the σ' value increases linearly according to the Arrhenius law. It has been revealed that, with increasing the frequency, the conductivity value increases. Moreover, two dispersion areas, caused by the ion transport at the grain boundaries and in the bulk, are observed. With the temperature, both parts are shifted to the high frequency range due to the thermally activated mechanism of the above mentioned processes.

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