Preparation and electrical conductivity of (Cu0.5Ag0.5)7SiS5I-based superionic ceramics

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Abstract

The ceramics based on (Cu0.5Ag0.5)7SiS5I solid solution of superionic conductor with argyrodite structure were prepared by using the powders with different particles size. The structural studies of powders were performed by XRD technique, while the ceramic samples with different average size of the crystallites were investigated by microstructural analysis. The total electrical conductivity of ceramic samples was measured by impedance spectroscopy in the frequency range from 10 Hz to 2×106 Hz and temperature interval from 292 K to 383 K. The contributions of ionic and electronic components into the total electrical conductivity were separated as well as their temperature behavior was studied. The dependences of ionic and electronic conductivity and their activation energies on average size of the crystallites in (Cu0.5Ag0.5)7SiS5I-based ceramic samples were investigated.

1 Introduction

Among ceramic materials, electrochemical ceramics have recently been widely studied in order to develop the latest technologies of electrochemical energy storage, which is caused by the rapid development of alternative energy sources, electric vehicles and portable electronic devices [1–5]. Electrochemical capacitors (supercapacitors), batteries and fuel cells are usually used as electrochemical energy storage devices [2]. The most promising materials in this regard are solid electrolytes used in all-solid-state batteries. It should be noted that the use of solid electrolyte instead of liquid one not only increases the safety of batteries, but also simplifies the design of the battery itself [5–8].

Since the efficiency of batteries directly depends on the properties of the working material, so the search for and improvement of new materials is relevant. Sulfur-containing solid electrolytes attract considerable attention due to the high ionic conductivity, which is provided by the peculiarities of their crystal structure [5, 6, 9–12], among which it is worth noting complex phosphorus sulfides with Li+ and Na+. Usually sulfur-containing superionic compounds with ionic conductivity of Li+ and Na+ are difficult to obtain in the crystalline state [11], so they are obtained in glass-ceramic form [10, 11, 13, 14].

It should be noted that promising superionic materials in this regard are presented by compounds with the structure of argyrodite [15–18], which have high values of ionic conductivity. They are characterized by a similar crystalline structure (tetrahedral dense packaging) and high variability of compositions [19, 20], which favors the formation of solid solutions. In addition, in recent years they have been obtained in the forms of composites, ceramics and thin films [21–24]. Copper-containing argyrodites in ceramic form were studied in Ref. [23]. In this paper, we will focus on investigating new ceramic material (Cu0.5Ag0.5)7SiS5I based on argyrodites, in which half of the copper atoms are replaced by silver atoms. As far as we know nowadays, such studies have not been conducted. The electrical properties of (Cu0.5Ag0.5)7SiS5I mixed crystals were studied by impedance spectroscopy in Ref. [25].

Thus, the aim of this paper is to prepare ceramic samples based on (Cu0.5Ag0.5)7SiS5I solid solution, study their structural and electrical properties, separate the contributions of ionic and electronic
conductivity components, and compare the electrical parameters of the obtained ceramic samples with the parameters of crystals. It should be noted that the production and study of argyrodites in the form of ceramic samples is relevant because they can successfully replace crystalline materials.

2 Materials And Methods

\((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) solid solution was synthesised from pre-synthesized \(\text{Cu}_7\text{SiS}_5\text{I}\) and \(\text{Ag}_7\text{SiS}_5\text{I}\) compounds in vacuumized quartz ampoules. The process of \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) synthesis included step heating up to 1023 K at a rate of 100 K/h and ageing during 48 hours, further increase of temperature to 1470 K at a rate of 50 K/h and ageing at this temperature for 72 hours. The annealing temperature was 873 K, ageing at this temperature for 120 hours. Cooling to room temperature was performed in the oven off mode.

The ceramic samples were prepared from powders of different dispersion: 1) powders obtained by grinding in an agate mortar with an average particle size of \(\sim 10—50\ \text{µm}\); 2) powders obtained by grinding in a planetary ball mill PQ-N04 for 30 min and 60 min with a speed of 200 rpm. Then the powders were pressed at \(\sim 400\ \text{MPa}\) and were annealed at 973 K during 36 hours. In such a way the polycrystalline ceramic samples were fabricated in the form of disks with a diameter of 8 mm and a thickness of 3—4 mm.

The structural properties of \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) powders and ceramic samples were studied by XRD technique and microstructural analysis. The XRD measurements were performed be the diffractometer DRON 4–07 with CuKα radiation, angle scanning speed \(2\theta\) was 0.02 degree, exposure was 1 s. The ceramic samples were investigated by microstructural analysis using metallographic microscope METAM - R1.

Electrical conductivity measurements were carried out by impedance spectroscopy [26] in frequency range from 10 Hz to \(2 \times 10^6\ \text{Hz}\) and temperature interval from 292 to 383 K ranges with combination of high-precision LCR meters: Keysight E4980A and AT-2818. The amplitude of the alternating current constituted 10 mV. Measurement was carried out by a two-electrode method, on blocking (electronic) gold contacts. Gold contacts for measurements were applied by chemical precipitation from solutions [25].

3 Results And Discussion

Figure 1 shows the XRD patterns for \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) powders with different average particle size. It is shown that XRD patterns for \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) powders are similar to diffractogram for \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\) solid solution crystal [25]. Comparison of diffractograms indicates that the lines broadening occurs with particle size decrease (Fig. 1). The results of microstructural analysis for prepared \((\text{Cu}_{0.5}\text{Ag}_{0.5})\text{_7SiS}_5\text{I}\)-based ceramics are presented in Fig. 2. From histograms of crystallites size distribution for different ceramic samples, obtained from powders which grinding in agate mortar and planetary ball mill for 30 min and 60 min, the size of crystallites after annealing was determined (Fig. 2).
It is shown that the ceramic samples prepared by sintering powders obtained by grinding in a planetary ball mill are characterized by a more homogeneous microstructure, characterized by the distribution of particles in a narrower range, in contrast to the samples obtained by sintering a microcrystalline powder with a particle size of 10–50 µm (Fig. 2). As a result of recrystallization process, the average size of crystallites for samples obtained from powders grinding in an agate mortar is ~12 µm, while for samples obtained from powders grinding in a planetary ball mill for 30 min and 60 min is ~5 µm and ~3 µm, respectively.

Figure 3 presents the frequency dependences of total electrical conductivity for (Cu$_{0.5}$Ag$_{0.5}$)$_7$SiS$_5$I-based ceramics. With frequency increase the electrical conductivity grows which is typical for materials with ionic conductivity in solid state [27]. The insert to Fig. 3 shows the dependence of the total electrical conductivity on the size of crystallites. It is revealed that at decrease of size of crystallites from 12 µm to 3 µm the decrease of total electrical conductivity for (Cu$_{0.5}$Ag$_{0.5}$)$_7$SiS$_5$I-based ceramic samples is observed.

For separation of the total electrical conductivity into ionic and electronic components, a standard approach using electrode equivalent circuits (EEC) [27, 28] and their analysis on Nyquist plots was used. The parasitic inductance of the cell (~2 × 10$^{-8}$ H) is taken into account during the analysis of all ceramic samples. It is shown that ceramic samples prepared on the basis of (Cu$_{0.5}$Ag$_{0.5}$)$_7$SiS$_5$I, are characterized by equal values of electronic and ionic components of electrical conductivity (σ$_{ion}$ ~ σ$_{el}$). At Z'-Z" dependences for (Cu$_{0.5}$Ag$_{0.5}$)$_7$SiS$_5$I-based ceramics with average crystallites size of 12 µm, 5 µm, and 3 µm two semicircles are observed.

The EEC, which described the Nyquist plots, can be divided in two parts: one of them relates to ionic processes, another one to electronic processes. Low-frequency semicircles on the Nyquist plots correspond to the diffusion relaxation processes at the electrode/crystal boundary which is described by the capacity of the double diffusion layer C$_{dl}$ and Warburg element of W$_{dl}$, responsible for diffusion within the latter (Fig. 4). Serial to them were included the elements with R$_{gb}$/C$_{gb}$ parameters which related to resistance and capacity of the grain boundaries of ceramic samples (the end of low-frequency semicircles) (Fig. 4). High-frequency semicircles correspond to the conductivity processes determined by the resistance of intra-grain boundaries, which is marked by R$_{db}$ on the EEC (Fig. 4). Thus, the ionic conductivity of (Cu$_{0.5}$Ag$_{0.5}$)$_7$SiS$_5$I-based ceramic samples is determined by the sum of the resistance of grain boundaries R$_{gb}$ and the resistance limiting the ion diffusion W$_R$. It should be noted that on EEC parallelly to the elements responsible for ion processes the electronic resistance R$_e$ is included and determined electronic conductivity of the samples (Fig. 4). With crystallites size decrease (12 µm → 5 µm → 3 µm) the low-frequency shift of low-frequency semicircle on EEC is observed. It may be related to the increasing of influence of diffusion ionic processes as well as increasing of ionic relaxation time due to the electronic conductivity decreasing.
Temperature studies have shown that with increasing temperature, the increase of electronic conductivity gradually eliminates the influence of diffusion ionic processes at the boundaries of ceramics crystallites, as evidenced by the decrease of the high-frequency semicircle at 323 K (Fig. 4, curve 2). With further increase of temperature up to 373 K (Fig. 4, curve 3) there is a further reduction of the influence of diffusion ionic processes, which, together with the decrease in the thickness of the double diffusion layer, and the complete disappearance of the high-frequency semicircle.

Figure 5a shows the dependences of the ionic and electronic components of electrical conductivity on the size of crystallites in (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I-based ceramic samples. It is revealed that the decrease in the size of crystallites leads to monotonous decrease of ionic and electronic components of electrical conductivity, while their ratio remains unchanged ($$\sigma_{\text{ion}} \sim \sigma_{\text{el}}$$).

The temperature dependences of the ionic and electronic components of electrical conductivity in the Arrhenius coordinates presents on Fig. 6. The linear behavior of above mentioned dependences was confirmed the thermoactivating character of electrical conductivity. From the presented temperature dependences of the ionic and electronic conductivity the activation energies were determined (Fig. 5b). It is shown that the activation energies of both components of electrical conductivity for (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I-based ceramic samples nonlinearly depend on the size of crystallites (рис.5b). Thus, at the transition of the size of crystallites from 12 µm to 5 µm the slight increase of the activation energies of both components of electrical conductivity is observed, whereas at the transition of the size of crystallites from 5 µm to 3 µm the tendency to decrease of the activation energies of both components of electrical conductivity is revealed.

It should be noted that (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I-based ceramics are characterized by disordered structure, which is associated with different reasons: (i) structural disordering, caused by the different size of crystallites; (ii) structural disordering, caused by the recrystallization process during annealing; (iii) compositional disordering, caused by the Cu$^+$ ↔ Ag$^+$ cationic substitution. The combination of the above features in the final case leads to a change of the Nyquist plots for samples with different size of crystallites (Fig. 4) and causes the corresponding behavior of the total electrical conductivity (Fig. 3), its ionic and electronic components (Fig. 5), and its thermoactivation behavior (Figs. 6 and 7) for (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I-based ceramics.

Comparison of the values of ionic and electronic conductivities, as well as their ratio for crystal and ceramic samples of (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I solid solution have shown that the ionic conductivity and the ratio $$\sigma_{\text{ion}} / \sigma_{\text{el}}$$ of ceramic sample with an average crystallite size of 12 µm is slightly greater than that of crystal ones ($$\sigma_{\text{ion}} = 2.2 \times 10^{-3} \text{ S/cm}$$ and $$\sigma_{\text{ion}} / \sigma_{\text{el}} = 0.9$$ for crystal) [25]. Thus, studies show that (Cu_{0.5}Ag_{0.5})_{7}SiS_{5}I-based ceramics is characterized by high electrical parameters, comparable or even higher than in the corresponding crystals. This, in turn, makes their use in solid ionic devices more promising due to their greater manufacturability and ease of production compared to crystals.
4 Conclusions

The compound of \((\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\) solid solution with the same content of copper and silver atoms was synthesized and three types of ceramic samples were made on its basis by pressing and sintering. Powders of different dispersion were obtained by grinding in an agate mortar as well as in a planetary ball mill. X-ray diffraction spectra showed that during grinding the structure of the argyrodite type is preserved, however, as the particle size decreases, the diffraction bands expand. The obtained ceramic samples were investigated by microstructural analysis, which resulted in the dependences of size distribution and average crystallites size for \((\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\) ceramic samples.

Impedance studies of the total electrical conductivity for \((\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\) ceramic samples were performed in the frequency range from 10 Hz to \(2 \times 10^6\) Hz and temperature interval from 292 K to 383 K. With increasing frequency, an increase of the total electrical conductivity and its decrease with decreasing crystallite size were observed. Using Nyquist plots the electrical conductivity of \((\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\)-based ceramics was separated into ionic and electronic components. It is revealed that in the studied ceramic samples the values of ionic and electronic components are almost equal \((\sigma_{\text{ion}} \sim \sigma_{\text{el}})\), with decreasing crystallites size they decrease, and their ratio \(\sigma_{\text{ion}}/\sigma_{\text{el}}\) remains unchanged. Temperature studies have shown that the temperature dependences of ionic and electronic components are described by the Arrhenius law, which confirms the thermoactivating character of conductivity. Revealed high values of electrical parameters for ceramic samples of \((\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\) solid solution, which are comparable to the values for crystals, make them promising to develop on their basis electrochemical devices.

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Figures
Figure 1

Diffractograms of (Cu0.5Ag0.5)7SiS5I powders obtained by grinding in agate mortar (1) and planetary ball mill for 30 min (2) and 60 min (3).
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Diffractograms of (Cu0.5Ag0.5)7Si5S5I powders obtained by grinding in agate mortar (1) and planetary ball mill for 30 min (2) and 60 min (3).
Dependences of size distribution for crystallites of (Cu0.5Ag0.5)7SiS5I ceramic samples, obtained from powders which were milled in agate mortar (a) and planetary ball mill for 30 min (b) and 60 min (c). The inserts show the microstructure images for different (Cu0.5Ag0.5)7SiS5I ceramic samples.
Figure 2

Dependences of size distribution for crystallites of (Cu0.5Ag0.5)7SiS5I ceramic samples, obtained from powders which were milled in agate mortar (a) and planetary ball mill for 30 min (b) and 60 min (c). The inserts show the microstructure images for different (Cu0.5Ag0.5)7SiS5I ceramic samples.
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Figure 3

Frequency dependences of total electrical conductivity at T=298 K for (Cu0.5Ag0.5)7SiS5I ceramic samples with different sizes of crystallites: (1) 12 µm; (2) 5 µm; (3) 3 µm. The insert shows the dependence of the total electrical conductivity on the size of crystallites at 100 kHz.
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Frequency dependences of total electrical conductivity at T=298 K for (Cu0.5Ag0.5)7SiS5I ceramic samples with different sizes of crystallites: (1) 12 µm; (2) 5 µm; (3) 3 µm. The insert shows the dependence of the total electrical conductivity on the size of crystallites at 100 kHz.
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Frequency dependences of total electrical conductivity at $T=298$ K for $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ ceramic samples with different sizes of crystallites: (1) 12 µm; (2) 5 µm; (3) 3 µm. The insert shows the dependence of the total electrical conductivity on the size of crystallites at 100 kHz.
Figure 4

EEC and Nyquist plots for (Cu0.5Ag0.5)7SiS5I ceramic samples with different crystallite sizes: (a) 12 µm; (b) 5 µm; (c) 3 µm for temperatures (1) 298 K, (2) 323 K, (3) 373 K. Experimental data correspond to the solid dots, calculated data correspond to the open dots.
Figure 4

EEC and Nyquist plots for (Cu0.5Ag0.5)7SiS5I ceramic samples with different crystallite sizes: (a) 12 µm; (b) 5 µm; (c) 3 µm for temperatures (1) 298 K, (2) 323 K, (3) 373 K. Experimental data correspond to the solid dots, calculated data correspond to the open dots.

Figure 5

(a) Dependences of ionic (1) and electronic (2) components of electrical conductivity at T=298 K on the size of crystallites for (Cu0.5Ag0.5)7SiS5I ceramic samples, the insert shows the dependence of the ratio of the conductivity components on the size of the crystallites; (b) Dependences of the activation energy of ionic (1) and electronic (2) components of electrical conductivity on the size of crystallites for (Cu0.5Ag0.5)7SiS5I ceramic samples.
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Temperature dependences of ionic (a) and electronic (b) components of electrical conductivity for \((\text{Cu0.5Ag0.5})_7\text{SiS}_5\text{I}\) ceramic samples with different crystallite sizes: (1) 12 µm; (2) 5 µm; (3) 3 µm.

Figure 6
Figure 6

Temperature dependences of ionic (a) and electronic (b) components of electrical conductivity for (Cu0.5Ag0.5)7SiS5I ceramic samples with different crystallite sizes: (1) 12 µm; (2) 5 µm; (3) 3 µm.