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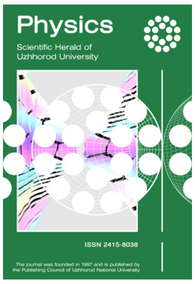

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Influence of the Cation Substitution upon the Electrical Conductivity of the Superionic Ceramics on the Basis of Microcrystalline Powders of $(Cu_{1-x}Ag_x)_7SiS_5I$

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Abstract

Purpose. The purpose of this study was to prepare the superionic ceramics, to study the frequency and temperature dependences of electrical conductivity as well as to investigate the compositional behavior of the total electrical conductivity, the ionic and electronic components of the electrical conductivity, and their activation energies for ceramics based on $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions.

Methods. For preparing the ceramic samples the compounds on the basis of Cu_7SiS_5I, Ag_7SiS_5I and $(Cu_{1-x}Ag_x)_7SiS_5I$ ($x = 0.25, 0.5, 0.75$) solid solutions were synthesised. Then, microcrystalline powders have been manufactured with the help of grinding/disintegration of the synthesised compounds within the agate mortar down to the sizes approximately from 10 up to 50 μm. Pressing of the samples was performed at the pressure of approximately 400 MPa, while annealing was carried out at the temperature of 973°K during 36 hours. Ceramic samples [which were manufactured on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ solid solutions] were manufactured in the form of disks having diameters at the level of 8 mm and thicknesses at the level from 3 mm up to 4 mm. Investigations of the electrical conductivity of the ceramics on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ ($x=0.25, 0.5, 0.75, 1$) were performed with the help of the impedance spectroscopy method within the range of frequencies from 10 Hz up to 2×106 Hz, as well as within the range of temperatures from 292°K up to 383°K with the help of the following highly-precision LCR meters: Keysight E4980A and AT-2818. Measurements were performed in accordance with the two-electrode method on the blocking golden contacts, which have been applied with the help of the method of chemical precipitation from the relevant solutions.

Results. Frequency dependences of the total electrical conductivity have demonstrated an increase in the conductivity in the course of increase in frequency for all ceramic samples. It was established that in the course of increase in the silver content in the ceramics on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$, general electrical conductivity increases nonlinearly at 100 kHz. Nyquist diagrams were constructed and their detailed analysis was carried out using the electrode equivalent circuits. With the help of the Nyquist diagrams and the electrode equivalent circuits, contributions of the ionic and electronic components to the general electrical conductivity were determined. It was demonstrated that in the course of the increase in silver content, the ionic conductivity increases nonlinearly, while the electronic conductivity nonlinearly decreases. Analysis of the concentration dependence of the ratio of the ionic conductivity to the electronic one has shown that in the case of the cation substitution ($Cu^+ \rightarrow Ag^+$), this ratio nonlinearly increases.

Conclusions. Superionic ceramics on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ were prepared. Measurements of electrical conductivity of the ceramic samples with the help of the impedance spectroscopy method within the range of frequencies from 10 Hz to 2×106 Hz, as well as within the range of temperatures from 292°K up to 383°K were performed. Frequency dependences of general electrical conductivity were obtained. Influence of the cation substitution ($Cu^+ \rightarrow Ag^+$) upon the general electrical conductivity and upon the electronic and ionic components of the conductivity of ceramics on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5$ was studied on the basis of concentration dependences

Keywords: solid solutions, ceramics, electrical conductivity, energy of activation, concentration dependence

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Introduction

Ceramic materials are widely used due to their unique properties (structural, mechanical, chemical, functional etc.). High values of hardness, melting temperature, and modulus of elasticity, as well as low coefficient of thermal expansion of the ceramic materials do not limit sphere of their application by the engineering problems, but they expand this sphere essentially [1-4]. As of today, ceramic materials are extensively used in the following spheres and branches of industry: medical industry, biochemistry, optics, thermoelectricity, electronics, and electrochemistry [5-9].

Presently, there is essential development of investigations of electrochemical ceramic materials. This fact is connected with the studies and improvements of the technologies for the electrochemical storage of energy [10; 11]. Rapid development of the above-listed technologies is connected both with development of the alternative power sources (electric cars), and with growth of quantity of the portable electronic devices [12-14].

Electrochemical capacitors (supercapacitors), accumulators, and fuel elements [11] are utilized as the electrochemical energy storage devices. The widest commercial distribution was reached by the lithiumion batteries, which contain liquid organic electrolyte [9, 15, and 16]. However, combination of the chemically active lithium and the highly flammable liquid decreases safety of this device [15].

In the case of utilization of the solid electrolyte instead of the liquid one, it is possible to increase safety of accumulators, as well as to simplify design and structure of the entire accumulator [14; 17-21]. The solid electrolytes, which can be used in the solid-state accumulators, are conventionally separated in three groups in accordance with their origination: inorganic (crystalline or glass-ceramic) substances, organic polymers, and hybrid materials. Oxides, phosphates, and complex sulphides are utilised as functional solid-state inorganic materials [17-19].

Because of efficiency of accumulators is in direct dependence on properties of the working material, searches and improvement of new materials are highly topical problems. Sulphur-containing solid-state electrolytes (among which it is worth to note complex phosphorus-containing sulphides Li^+ and Na^+) attract essential attention due to their high ionic conductivity, which is ensured by the specific features of their crystallographic structure [14; 18; 22-25]. Because of it is difficult to obtain the sulphur-containing superionic compounds with ionic conductivity in respect of the cations Li^+ and Na^+ in the crystalline state [24], therefore these substances are usually obtained in the glass-ceramic form [23; 24; 26; 27].

Compounds of the argyrodite family [28-31], which are characterised by high values of the ionic conductivity, are considered as prospective superionic materials. Specific features of their crystallographic structure (close-packed tetrahedral structure) and high variability of chemical compositions [32; 33] promote manufacture of the solid solutions on the basis of these compounds.

Purposes of this study are as follows: preparation and electrical investigations of the ceramic samples on the basis of microcrystalline powders of the solid solutions of $(Cu_{1-x}Ag_x)_7SiS_5I$, as well as study of influence of the cation substitution ($Cu^+ \rightarrow Ag^+$) upon electrical parameters of these samples.

Techniques of the Experiments

Synthesis of Cu_7SiS_5I and Ag_7SiS_5I has been performed with the help of simple substances: copper (99.999%), silver (99.995%), silicon/silicium (99.99997%), sulphur (99.999%), as well as with the help of the previously synthesised binary copper (I) iodide and silver (I) iodide (which were taken in accordance with their stoichiometric relationships) in the vacuumised (down to 0.13 Pa) quartz vessels/vials. The binary copper (I) iodide and binary silver (I) iodide were additionally cleaned with the help of the methods of vacuum distillation and of directional crystallisation, respectively. The mode of synthesis of the Cu_7SiS_5I and Ag_7SiS_5I has been included the stepped heating up to 723°K with the heating rate at the level of 100°K/hour (soak during 48 hours), subsequent increase in the temperature up to 1470°K (for the Cu_7SiS_5I) and up to 1230°K (for the Ag_7SiS_5I) with the heating rate at the level of 50°K/hour and soak at this temperature during 24 hours. Cooling has been performed in the mode of the de-energised oven.

Alloys of the "Cu_7SiS_5I – Ag_7SiS_5I" system have been synthesised with the help of the direct single-temperature method from the previously synthesised tetrary Cu_7SiS_5I and Ag_7SiS_5I samples. The mode of synthesis has been included the stepped heating with the heating rate at the level of 100°K/hour up to 1023°K and soak at this temperature during 24 hours, subsequent increase in temperature up to 1470°K with the heating rate at the level of 50°K/hour and soak at this temperature during 72 hours. The annealing temperature was equal to 873°K; soak during 120 hours. Cooling down to the room temperature has been performed in the mode of the de-energised oven.

The synthesised compounds of the solid solutions of $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0.25, 0.5, 0.75, and 1) have been used for manufacture of the ceramic samples with the help of the method of solid-phase sintering of the pressed microcrystalline powders having relevant chemical compositions. Microcrystalline powders have been manufactured with the help of grinding/disintegration of the synthesised compounds within the agate mortar down to the sizes approximately from 10 up to 50 μm. Pressing of the samples has been performed at the pressure of approximately 400 MPa, while annealing was carried out at the temperature of 973°K during 36 hours. Ceramic samples of the solid solutions of $(Cu_{1-x}Agx)_7SiS_5I$ were manufactured in the form of disks with diameters at the level of 8 mm and thickness at the level of 3-4 mm. In order to determine sizes of the crystalline particles upon completion of the annealing process, ceramic samples have been investigated with the help of the method of the microstructure analysis with the help of the METAM-R1 metallographic microscope. In accordance with results of the analysis of the obtained microstructures, histograms of distribution of the crystalline particles by sizes were constructed, and it was established that the ceramic samples are characterised by the sufficiently uniform microstructure, which is described with the help of distribution of the crystalline particles within the sufficiently narrow interval. It was established that upon completion of the re-crystallisation, average size of the crystalline particles within the ceramic samples, which were manufactured from the microcrystalline powders, is equal to 12 μm.

Measurements of the electrical conductivity of the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0.25, 0.5, 0.75, 1) have been performed with the help of the method of the impedance spectroscopy [34] within the range of frequencies from 10 Hz up to 2×10^6 Hz, as well as within the range of temperatures from 292°K up to 383°K, as well as with the help of the following highly-precision LCR meters: Keysight E4980A and AT-2818. Amplitude of the alternating current was equal to 10 mV. Measurements were performed in accordance with the two-electrode method on the blocking (electronic) golden contacts. These golden contacts have been applied with the help of the method of chemical precipitation from the relevant solutions [35; 36].

Results and Discussion

As concerns all ceramic samples on the basis of the "$(Cu_{1-x}Ag_x)_7SiS_5I$" compounds, it was established that growth of the general electrical conductivity is observed in the course of increase in frequency (Fig. 1). It was also established that it is the characteristic feature of the materials with ionic conductivity in the solid-state condition [37]. On the basis of the obtained results, the concentration dependence of the general electrical conductivity was constructed at the frequency of 100 kHz. It is obvious from this concentration dependence, that the cation substitution ($Cu^+ \rightarrow Ag^+$) causes monotone nonlinear growth of the general electrical conductivity (Fig. 1).

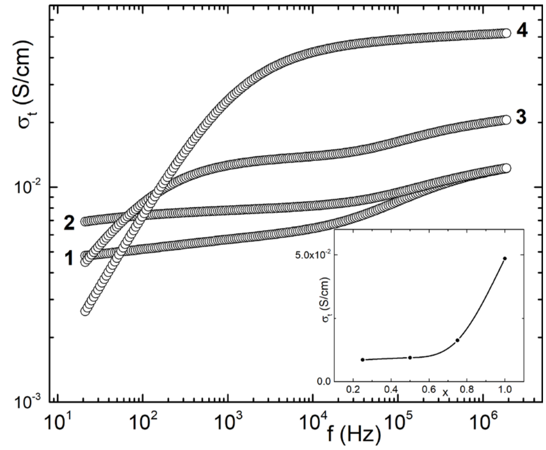

Figure 1. Frequency dependences of the general electrical conductivity at the temperature of 298°K within the ceramic samples on the basis of the following $(Cu_{1-x}Ag_x)_7SiS_5I$ compounds: $(Cu_{0.75}Ag_{0.25})_7SiS_5I$ (1); $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ (2); $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ (3), and Ag_7SiS_5I (4). The insertion within the Figure presents the concentration dependence of the general electrical conductivity of the ceramic $(Cu_{1-x}Ag_x)_7SiS_5I$ samples at the frequency of 100 kHz

In order to perform detailed investigations of the frequency behaviour of the general electrical conductivity, as well as investigations of the ionic and electronic components of the general electrical conductivity, the standard approach was used with the help of the electrode equivalent circuits [34; 37; 38], as well as with the help of their analysis at the Nyquist diagrams. In the course of the analysis of all these samples, the parasitic inductance of the relevant cell (which is approximately equal to 2×10^{-8} henry) has been taken into account.

In accordance with results of the performed analysis of the impedance spectra, the temperature behaviour and concentration behaviour of the ionic and electronic components of the electrical conductivity of the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ were studied. It was established that in the course of increase in the quantity of the silver atoms, the ionic component of the electrical conductivity in the course of the cation substitution [in the course of the following transition/transformation: $(Cu_{0.75}Ag_{0.25})_7SiS_5I \rightarrow (Cu_{0.5}Ag_{0.5})_7SiS_5I \rightarrow (Cu_{0.25}Ag_{0.75})_7SiS_5I \rightarrow Ag_7SiS_5I$) increases nonlinearly, while values of the electronic component decreases nonlinearly (Fig. 2). Ratio of the ionic component of the electrical conductivity to the electronic component is very important characteristic of the superionic materials. Concentration dependence of this ratio is presented at the insertion within Figure 2.

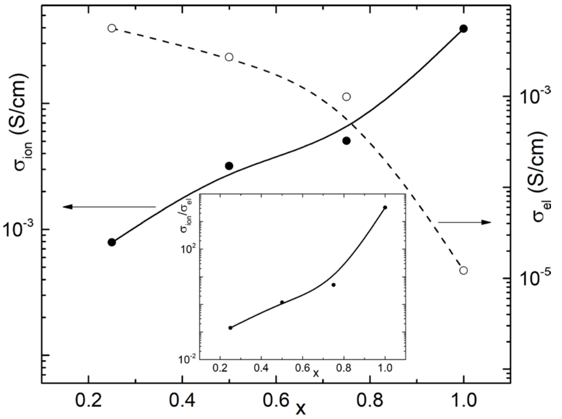

Figure 2. Concentration dependences of the ionic and electronic components of the electrical conductivity at the temperature of 298°K within the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$. Insertion within this Figure presents the concentration dependence of the ratio of the ionic component of the electrical conductivity to the electronic component within the ceramic samples $(Cu_{1-x}Ag_x)_7SiS_5I$

It is worth to note that in the case of substitution of the copper atoms by atoms of silver within the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$, ratio σ_{ion}/σ_{el} increases nonlinearly, while for the Ag_7SiS_5I compound, the ionic component of the electrical conductivity exceeds the electronic component by more than 3000 times.

Figure 3 presents temperature dependences of the ionic and electronic components of the electrical conductivity in the Arrhenius coordinates. It was established that these dependences are dependences of the linear character, as well as that they are described by the Arrhenius law, and this fact demonstrates the thermoactivation nature of the electrical conductivity. With the help of these dependences, it was possible to calculate values of the energy of activation both for the ionic component, and for the electronic component of the electrical conductivity (Fig. 4).

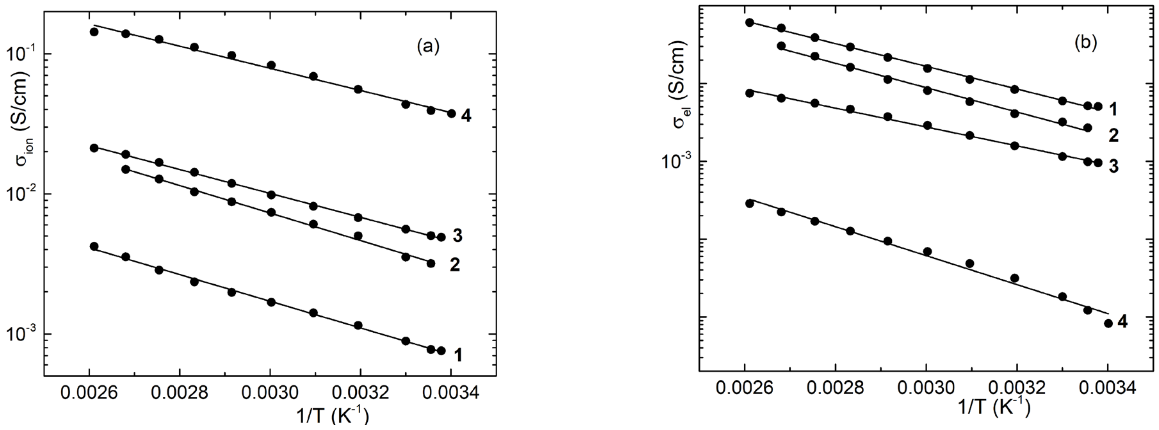

Figure 3. Fig. 3: Temperature dependences of the ionic (a) and electronic (b) components of the electrical conductivity within the ceramic samples on the basis of the following $(Cu_{1-x}Ag_x)_7SiS_5I$ samples: $(Cu_{0.75}Ag_{0.25})_7SiS_5I$ (1), $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ (2), $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ (3), and Ag_7SiS_5I (4)

In the case of increase in the quantity of the silver atoms in the ceramic samples which were manufactured on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$, nonlinear decrease in the activation energy of the $(Cu_{0.5}Ag_{0.5})_7SiS_5I$ compound was found at the concentration dependence of the energy of activation of the ionic component of the electrical conductivity (maximum value of the activation energy $E_{a(ion)}$ is equal to 0.389 electronvolt). At the same time, activation energy of the electronic component of the electrical conductivity in the course of the cation substitution ($Cu^+ \leftrightarrow Ag^+$) increases nonlinearly at the concentration dependence of the $(Cu_{0.25}Ag_{0.75})_7SiS_5I$ compound (minimum value of the activation energy $E_{a(el)}$ is equal to 0.481 eV)).

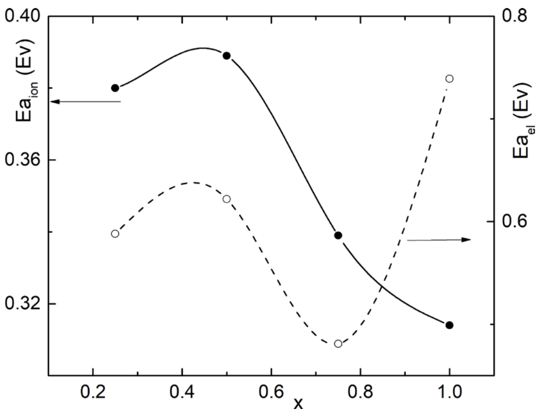

Figure 4. Concentration dependences the activation energy of the ionic and electronic components of the electrical conductivity within the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$

It is worth to note that the ceramic samples, which were manufactured on the basis of the solid solutions of $(Cu_{1-x}Ag_x)_7SiS_5I$, are characterised by the complex and disordered micro- and macrocrystalline structure. In the first turn, this fact is connected with different sizes of the crystalline particles, with the nature of their distribution, as well as with the complicated process of the re-crystallisation in the course of annealing of these samples. The process of the re-crystallisation includes the stage of coarsening and agglomeration of the crystalline particles due to the processes of the solid-phase diffusion, and this re-crystallisation process is accompanied by the process of occurrence of the microstructure non-uniformities, which promote occurrence of the micro- and macrodefects. This fact causes additional events of occurrence of the internal stresses within the ceramic material. In addition, it is also necessary to take into account the processes of the compositional disordering of the crystal lattice within solid solutions of $(Cu_{1-x}Ag_x)_7SiS_5I$, which were caused by the cation substitution ($Cu^+ \rightarrow Ag^+$). Combination of the above-mentioned specific features is responsible for the relevant changes not only in the general electrical conductivity, but in the ionic and electronic components as well.

Conclusions

Compounds of the solid solutions of $(Cu_{1-x}Ag_x)_7SiS_5I$ were synthesised and relevant ceramic samples were manufactured on the basis of these compounds with the help of the pressing and sintering of the microcrystalline powders. In accordance with the results of the microstructure analysis, it was established that due to the re-crystallisation processes, average size of the crystalline particles within the ceramic samples is equal to approximately 12 μm. Measurements of the general electrical conductivity were performed on the manufactured ceramic samples with the help of the impedance spectroscopy method within the range of frequencies from 10 Hz up to 2 MHz, as well as within the range of temperatures from 292°K up to 383°K. It was established that the cation substitution ($Cu^+ \rightarrow Ag^+$) causes monotone nonlinear growth of the general electrical conductivity of the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ compounds.

On the basis of the frequency dependences of the general electrical conductivity, the Nyquist diagrams were constructed. Subsequently these diagrams have been analysed with the help of the electrode equivalent circuits. With the help of this approach, general electrical conductivity was separated into the ionic and electronic components. It was established that increase in the quantity of the silver atoms (argentum) within the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ compounds causes nonlinear increase in the ionic component, nonlinear decrease in the electronic component and nonlinear growth of the ratio of the ionic component to the electronic component.

It was demonstrated that temperature dependences of the ionic and electronic components of the general electrical conductivity of the ceramic samples on the basis of the $(Cu_{1-x}Ag_x)_7SiS_5I$ compounds are described by the Arrhenius law, and this fact confirms the thermoactivation nature of the electrical conductivity.

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Вплив катіонного заміщення на електричну провідність суперіонної кераміки на основі мікрокристалічних порошків $(Cu_{1-x}Ag_x)_7SiS_5I$

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Анотація

Мета. Метою цього дослідження було підготувати суперіонну кераміку, вивчити частотні та температурні залежності електропровідності, а також дослідити поведінку складу загальної електропровідності, іонної та електронної складових електропровідності та енергії їх активації для кераміки на основі твердих розчинів $(Cu_{1-x}Ag_x)_7SiS_5I$.

Методи. Для приготування керамічних зразків синтезовано сполуки на основі твердих розчинів Cu_7SiS_5I, Ag_7SiS_5I та $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0,25, 0,5, 0,75). Потім за допомогою подрібнення/дезінтеграції синтезованих сполук у агатовому розчині виготовляли мікрокристалічні порошки до розмірів приблизно від 10 до 50 мкм. Пресування зразків проводили під тиском приблизно 400 МПа, а відпал – за температури 973°К протягом 36 годин. Керамічні зразки [виготовлені на основі твердих розчинів $(Cu_{1-x}Ag_x)_7SiS_5I$] виготовляли у вигляді дисків діаметром на рівні 8 мм і товщиною на рівні від 3 мм до 4 мм. Дослідження електропровідності кераміки на основі $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0,25, 0,5, 0,75, 1) проводили за допомогою методу імпедансної спектроскопії в діапазоні частот від 10 Гц до 2×10^6 Гц, а також в діапазоні температур від 292°К до 383°К за допомогою таких високоточних вимірювачів LCR: Keysight E4980A і AT-2818. Вимірювання проводили за двоелектродним методом на блокуючих золотих контактах, що наносили за допомогою методу хімічного осадження з відповідних розчинів.

Результати. Частотні залежності сумарної електропровідності продемонстрували збільшення провідності пыд час збільшення частоти для всіх керамічних зразків. Встановлено, що у процесі збільшення вмісту срібла в кераміці на основі $(Cu_{1-x}Ag_x)_7SiS_5I$ загальна електропровідність нелінійно зростає на частоті 100 кГц. Побудовано діаграми Найквіста та проведено їх детальний аналіз за допомогою схем заміщення електродів. За допомогою діаграм Найквіста та схем заміщення електродів визначено внески іонної та електронної складових у загальну електропровідність. Показано, що у процесі збільшення вмісту срібла іонна провідність зростає нелінійно, а електронна – нелінійно зменшується. Аналіз концентраційної залежності відношення іонної провідності до електронної показав, що у випадку катіонного заміщення ($Cu^+ \rightarrow Ag^+$) це співвідношення нелінійно зростає.

Висновки. Отримано суперіонну кераміку на основі $(Cu_{1-x}Ag_x)_7SiS_5I$. Проведено вимірювання електропровідності керамічних зразків методом імпедансної спектроскопії в діапазоні частот від 10 Гц до 2×10^6 Гц, а також в діапазоні температур від 292°К до 383°К. Отримано частотні залежності загальної електропровідності. На основі концентраційних залежностей досліджено вплив катіонного заміщення ($Cu^+ \rightarrow Ag^+$) на загальну електропровідність, електронну та йонну складові провідності кераміки на основі $(Cu_{1-x}Ag_x)_7SiS_5$

Ключові слова: тверді розчини, кераміка, електрична провідність, енергія активації, концентраційна залежність

Влияние катионного замещения на электрическую проводимость суперионной керамики на основе микрокристаллических порошков$(Cu_{1-x}Ag_x)_7SiS_5I$

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Аннотация

Цель. Целью этого исследования было подготовить суперионную керамику, изучить частотные и температурные зависимости электропроводности, а также исследовать поведение состава общей электропроводности, ионной и электронной составляющих электропроводности и энергии их активации для керамики на основе твердых растворов $(Cu_{1-x}Ag_x)_7SiS_5I$.

Методы. Для приготовления керамических образцов синтезированы соединения на основе твердых растворов Cu_7SiS_5I, Ag_7SiS_5I и $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0,25, 0,5, 0,75). Затем посредством измельчения/дезинтеграции синтезированных соединений в агатовом растворе изготовляли микрокристаллические порошки до размеров приблизительно от 10 до 50 мкм. Прессование образцов проводили под давлением примерно 400 МПа, а отжиг – при температуре 973°K в течение 36 часов. Керамические образцы [изготовленные на основе твердых растворов $(Cu_{1-x}Ag_x)_7SiS_5I$] изготовляли в виде дисков диаметром на уровне 8 мм и толщиной от 3 мм до 4 мм. Исследование электропроводности керамики на основе $(Cu_{1-x}Ag_x)_7SiS_5I$ (x=0,25, 0,5, 0,75, 1) проводили посредством метода импедансной спектроскопии в диапазоне частот от 10 Гц до 2×10^6 Гц, а также в диапазоне температур от 292°K до 383°K с помощью таких высокоточных измерителей LCR: Keysight E4980A и AT-2818. Измерение проводили по двухэлектродному методу на блокирующих золотых контактах, которые наносили с помощью метода химического осаждения из соответствующих растворов.

Результаты. Частотные зависимости суммарной электропроводности продемонстрировали увеличение проводимости во время увеличения частоты для всех керамических образцов. Установлено, что при увеличении содержания серебра в керамике на основе $(Cu_{1-x}Ag_x)_7SiS_5I$ общая электропроводность нелинейно возрастает на частоте 100 кГц. Построены диаграммы Найквиста и проведен их детальный анализ с помощью схем замещения электродов. С помощью диаграмм Найквиста и схем замещения электродов определены вклады ионной и электронной составляющих в общую электропроводность. Показано, что в процессе увеличения содержания серебра ионная проводимость растет нелинейно, а электронная нелинейно уменьшается. Анализ концентрационной зависимости отношения ионной проводимости к электронной показал, что в случае катионного замещения ($Cu^+ \rightarrow Ag^+$) это соотношение нелинейно возрастает.

Выводы. Получено суперионную керамику на основе $(Cu_{1-x}Ag_x)_7SiS_5I$. Произведено измерение электропроводности керамических образцов методом импедансной спектроскопии в диапазоне частот от 10 Гц до 2×10^6 Гц, а также в диапазоне температур от 292°K до 383°K. Получены частотные зависимости общей электропроводности. На основе концентрационных зависимостей исследовано влияние катионного замещения ($Cu^+\rightarrow Ag^+$) на общую электропроводность, электронную и ионную составляющие проводимости керамики на основе $(Cu_{1-x}Ag_x)_7SiS_5$

Ключевые слова: твердые растворы, керамика, электрическая проводимость, енергия активации, концентрационная зависимость