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Table of Contents

2020, Volume 2

Track: Superconductivity in Nanoscale Systems

Nonlinear Proximity Effect in a Hybrid Normal Metal-Superconductor Structure <i>E.E. Zubov</i>	02SNS01
Nano Superconductivity and Quantum Processing of Information in Living Organisms <i>P. Mikheenko</i>	02SNS02
Influence of Surface Anions on the Transport Q1D Electrons in Gas Phase over Helium Film <i>V.A. Nikolaenko</i>	02SNS03

Track: Nanodevices & Sensors

Application of Nanocellulose in Humidity Sensors for Biodegradable Electronics <i>V. Koval, V. Barbash, M. Dusheyko, V. Lapshuda, O. Yashchenko, Yu. Yakimenko</i>	02NS01
Direct Laser Writing Technique for Non-enzymatic Sensors Fabrication <i>V. Andriianov, E. Khairullina, A. Smikhovskaia, M. Panov, I. Tumkin</i>	02NS02

Track: Nanomaterials for Energy & Environment

Effect of Precursor Type on Physico-Chemical and Photocatalytic Properties of TiO ₂ -SnO ₂ Nanocomposites <i>K. Bila, T. Dontsova, A. Kutuzova</i>	02NEE01
Nanocomposite Sorbents Based on TiO ₂ Containing Manganese Spinel for Concentration of Lithium Ions <i>L.N. Ponomarova, M. Chaban, L. Rozhdsvenska, Yu. Dzyazko, A. Palchik</i>	02NEE02
Electrical Conductivity of Ceramics Based on(Cu _{1-x} Ag _x) ₇ SiS ₅ I Nanocrystalline Powders <i>A. Pogodin, I. Studenyak, I. Shender, S. Bereznyuk, M. Filep, O. Kokhan</i>	02NEE03
The Influence of Nanosized Zirconium (IV) Oxide on the Catalytic Curing of Epoxy Resin ED-20 with Isomethyltetrahydrophthalic Anhydride <i>E. Bakhalova, E. Shved, Yu. Bepalko, O. Gorban, K. Yutilova</i>	02NEE04
Formation of C/Zn C/Ni Nanocomposites for Potential Application in Electrodes of LIB <i>A. Korniyushchenko, S. Shevchenko, V. Natalich, V. Perekrestov</i>	02NEE05
Charge Storage Mechanisms and Suppressing the Self-Discharge Processes of Carbon-based Supercapacitor Technology: A Review <i>J.N. Patricio, M.L.M. Budlayan, S. Del Rosario Arco</i>	02NEE06
Chemical Vapor Deposition Routes for Fluorine- and Sulfur-containing Activated Carbon Acid Catalysts: Comparison of Fluorination Methods <i>L. Grishchenko, A.N. Zaderko, S. Chernenko, A. Vakaliuk, O. Mischanchuk, G.G. Tsapyuk, A. Yatsymyrskiy, V.E. Diyuk, O. Boldyrieva, V. Lisnyak</i>	02NEE07
Quality Indicators of Ammonium Nitrate with Nanoporous Surface Structure: Final Drying Stage <i>N. Artyukhova, J. Krmela, V. Krmelova</i>	02NEE08
Technological Basis for the Production of Ammonium Nitrate with a Nanoporous Surface and Near-surface Structure in Combined Flow Motion Devices <i>A. Artyukhov, K. Berladir, J. Krmela</i>	02NEE09

Comparison of Electrical Properties of Moistured Pressboard Impregnated with New and Used Synthetic Ester <i>K. Kierczynski, M. Zenker</i>	02NEE10
Computer Simulation of Percolation in a Two-dimensional Square Network <i>P. Okal</i>	02NEE11
Study of Power Transformer Insulation Model. The X-Y Model of Oil Impregnated Pressboard - Water Nanodrops - Insulating Oil Composite <i>P. Rogalski</i>	02NEE12
Research of AC Electrical Properties of ZrC Nanocomposite Produced by Magnetron Sputtering <i>V. Bondariev, I. Lebedynskyi</i>	02NEE13
Functional Polymer Coated MoS ₂ Nanocomposites as Promising Lithium Current Sources <i>O. Balaban, N. Mitina, A. Zaichenko, O. Paiuk, Yu. Shermolovich</i>	02NEE14
Physical and Electrochemical Properties of TiO ₂ Nanotubes for Energy Storage Application <i>El-Hadi Khoumeri, H. Fraoucene</i>	02NEE15
A Comparative Study on the Stability and Degradation of Perovskite Solar Cells <i>J. Chakraborty, L. Jiao</i>	02NEE16
Track: Biomedical Applications	
Synthesis and Study of the Photodynamic Activity of Titanium Based Nanocomposites on MDA-MB-231 Cells <i>Pravena Ramachandran, Chong Yew Lee, Boon Keat Khor, Ruey-An Doong, Chern Ein Oon, Hooi Ling Lee</i>	02BA01
Sorption Composite Based on Hydroxyapatite and Biopolymers for Drainage of Purulent Cavities <i>M. Kumeda, L. Sukhodub, V. Beilai, L. Sukhodub, S. Zhdanov</i>	02BA02
Proton Beam Writing on Chitosan Films for Bionanomedicine and Microfluidics: Pilot Experiments <i>O. Kalinkevich, H. Polozhii, S. Kolinko, Y. Zinchenko, A. Kalinkevich, S.N. Danilchenko, A.G. Ponomarev, I.Yu. Protsenko</i>	02BA03
Biopolymer Composite Nanostructured Material Based on Chitosan and Brilliant Green Triarylmethane Dye <i>A. Sklyar, O. Kalinkevich, V. Holubnycha, Ye. Zinchenko, A. Kalinkevich, S. Danilchenko, Ya. Trofimenko, V. Chivanov, V. Starikov, D. Sofronov</i>	02BA04
ROS-sensitive Dyes in Lipid Nanoparticles for in vivo Imaging <i>T. Abakumova, T. Prikazchikova, I. Aparin, A. Vaneev, P. Gorelkin, A. Erofeev, T. Zatsepin</i>	02BA05
Studying Stem Cells With Iron Oxide Nanoparticles <i>V. Budnyk, L. Lukash, O. Papuga, M. Budnyk, S. Lukash, I. Uvarova</i>	02BA06
Viricidal Potential of Plasmonic and Metal Oxide Nanostructures: A Review <i>Marco Laurence Mondejar Budlayan, Jonathan Nacalaban Patricio, Susan Del Rosario Arco, Rey Yonson Capangpangan</i>	02BA07
Structural and Biological Assessment of Mg Alloy Surface after Plasma Electrolytic Oxidation in Different Solutions <i>Ye. Husak, V. Kornienko, W. Simka, O. Oleshko, T. Oleshko, B. Dryhval, Ju. Dudko, M. Pogorielov</i>	02BA08

Bio-functionalization of Electrospun Polymeric Nanofibers by Ti ₃ C ₂ T _x Mxene <i>S. Kyrylenko, O. Oleshko, V. Zahorodna, Yu. Zozulia, V. Kornienko, M. Kolesnyk, V. Buranich, V. Balitskyi, I. Baginskiy, O. Gogotsi, O. Mishchenko, A. Pogrebnyak, M. Pogorielov</i>	02BA10
Physical and Chemical Characterization of The Magnesium Surface Modified By Plasma Electrolytic Oxidation – Influence of Immersion In Simulated Body Fluid <i>O. Oleshko, Ye. Husak, T. Oleshko, V. Kornienko, S. Kyrylenko, B. Dryhval, Ju. Dudko, W. Simka, M. Pogorielov</i>	02BA11
Track: Theory & Modeling	
Shear Acoustic Phonons in AlN/GaN Nanostructures in the Presence of the Piezoelectric Effect <i>I. Boyko, H. Tsupryk, Yu. Stoianov</i>	02TM01
Effect of Interface Phonons on the Electron Spectrum in Far Infrared Range Quantum Cascade Detector at Cryogenic Temperature <i>E. Vereshko, Ju. Seti, M. Tkach</i>	02TM02
Electrical Properties of Doped Germanium Nanofilms <i>S. Luniov, O. Burban, Yu. Koval</i>	02TM03
Modelling of the Formation of p-p+ Transitions under the Influence of Pulsed Laser Irradiation in p-Ge <i>R. Peleshchak, O. Kuzyk, O. Dan'kiv</i>	02TM04
The Semi-Empirical Approach for Newtonian Nanofluids Viscosity Predicting <i>O. Khliyeva, V. Zhelezny, N. Khliiev, Ya. Hlek</i>	02TM05
Modeling the Mechanisms of Fracture Formation in Nanomodified Polymers <i>A.V. Gondlyakh, A.E. Kolosov, V.Yu. Shcherbina, A.L. Sokolskiy, A.O. Chemeris, S.I. Antonyuk</i>	02TM06
Kinetics of the Formation of Ferroelectric Regular Domain Structures upon Second Order Phase Transition <i>O.Yu. Mazur, L.I. Stefanovich</i>	02TM07
The Polarizing Phonons Influence on the Energy Shift of Electrons in the Quantum Dot <i>C. Tovstyuk</i>	02TM08
Physico-chemical Characteristics of Components as a Factor in the Formation of Nanoamorphous Structure in the Al ₈₇ RE ₅ Ni ₈ (Fe) System <i>Kh. Khrushchuk, M. Lopachak, L. Boichyshyn, N. Pandiak, B. Kotur, T. Hula</i>	02TM09
Critical Properties Study of Exactly Solved Spin Models for Ferromagnets and Ferroelectrics <i>A.N. Galdina, A.N. Turinov</i>	02TM10
Development of the Model for Describing the Electrical Conductivity of Polyether-CNT Systemse <i>E. Lysenkov, Ye. Davydenko</i>	02TM11
Track: Symposium on Additive Manufacturing and Applications	
Parts Diamond Burnishing Process Regimes Optimization Made of INCONEL 718 Alloy via Selective Laser Sintering Method <i>Ye. Vyshnepolskyi, D. Pavlenko, D. Tkach, Ya. Dvirnyk</i>	02SAMA01
Crack Arresters Design for Fatigue Strength Improvement of Additively Manufactured Components <i>P. Ferro, S. Rosso, G. Savio, R. Meneghello, F. Berto, S.M.J. Razavi</i>	02SAMA02

The Active Wave Resistance Determination of Hollow Perforated Rotor of Electromechanical Converter <i>M. Zablodskiy, O. Tymofieieva, V. Gritsyuk</i>	02SAMA03
Numerical and Experimental Analysis of Additive Manufactured Porous Regenerator for Stirling Cryocooler <i>K.V. Srinivasan, A. Mahalingam, R. Metla</i>	02SAMA04
In-situ Alloying as a Novel Methodology in Additive Manufacturing <i>A. Katz-Demyanetz, A. Koptuyug, V.V. Popov Jr.</i>	02SAMA05
Experimental Study of Aluminum Foams Thermal Conductivity. Prospects of Additive Manufacturing for Novel Heat Exchangers Production <i>A. Kovalevsky, A. Mats, M. Shmurak, A. Fleisher</i>	02SAMA06
Investigation of the Printing Parameters Influence on the Bond Lines Length in Fused Filament Fabrication <i>L. Hurina, Ye. Vyshnepolskyi, D. Pavlenko, D. Stepanov</i>	02SAMA07
Effect of Build Orientation in Electron Beam Melting of Ti-6Al-4V Specimens <i>G. Muller-Kamskii, S. Stepanov, E. Strokin, A. Kolomiets, I. Kovalevskiy, A. Popov</i>	02SAMA08
Advantages of 3D Printing for Gynecology and Obstetrics: Brief Review of Applications, Technologies, and Prospects <i>E.V. Kudryavtseva, V.V. Popov Jr., G. Muller-Kamskii, E.S. Zakurinova, V.V. Kovalev</i>	02SAMA09
3D Printed Lattice Structures: A Brief Review <i>A.H. Reddy, S. Davuluri, D. Boyina</i>	02SAMA10
Investigation of Injection Moulded UHMWPE Liner Manufacturability <i>K. Keszei, N.K. Kovács</i>	02SAMA11
Buckling Behavior of Isogrid Composite Structures Obtained by Fused Deposition Modeling Technique <i>A. Forcellese, L. Greco, T. Mancia, M. Pieralisi, M. Simoncini</i>	02SAMA12
CAD-platform-based Process Optimization Design Method by Selective Laser Melting Simulation <i>E. Dalpadulo, F. Pini, F. Leali</i>	02SAMA13
Supply Chain and Cost Evaluation for Laser Powder Bed Fusion <i>M. Schneck, M. Schmitt, G. Schlick</i>	02SAMA14
Predicting the Properties of the Refractory High-Entropy Alloys for Additive Manufacturing- Based Fabrication and Mechatronic Applications <i>V. Buranich, V. Rogoz, B. Postolnyi, A. Pogrebnjak</i>	02SAMA15
Creation of Volumetric Products Using Additive Arc Cladding with Compact and Powder Filler Materials <i>V. Kvasnytskyi, V. Korzhyk, I. Lahodzynskyi, Ye. Illiashenko, S. Peleshenko, O. Voitenko</i>	02SAMA16
Surface Polishing of Laser Powder Bed Fused Superalloy Components by Magnetic Post-treatment <i>D. Lesyk, S. Martinez, V. Dzhemelinskyi, O. Stamann, B. Mordyuk, A. Lamikiz</i>	02SAMA17
Smart Modelling of Additively Manufactured Metamaterials <i>G.F. de Vera Conrado, B.C. Daniel</i>	02SAMA18
Advanced Smoothing for Voxel-based Topologically Optimized 3D Models <i>A. Bacciaglia, A. Ceruti, A. Liverani</i>	02SAMA19

Graded Gyroid Structures for Load Bearing Orthopedic Implants <i>L. Guariento, F. Buonamici, A. Marzola, Y. Volpe, L. Governi</i>	02SAMA20
Machine-Learning Based Modelling for AM Processes <i>H. Li</i>	02SAMA21
Tracking Additive Manufacturing Using Machine Vision <i>L.A. Davis IV, J.S. Donnal, M.D.M. Kutzer</i>	02SAMA22
Producing High Precision Additive Manufacturing Parts by Direct Printing of NURBS Surfaces <i>H. Gohari, A. Barari</i>	02SAMA23
3D Printable Pneumatic Valves for Rapidly Manufacturable Mechanical Ventilator Amid Covid-19 Outbreak <i>H. Gohari, D. Bender, A. Barari</i>	02SAMA24
Track: Interdisciplinary Topics	
Structure Peculiarities of the Surface Layers of Structural Steel under Laser Alloying <i>O. Berdnikova, O. Kushmaryova, A. Bernatskyi, T. Alekseienco, Ye. Polovetskyi, M. Khokhlov</i>	02IT01
The Study of Micro - and Nanostructural Characteristics of Ostrich (<i>Struthio camelus</i>) Eggshell by the Method of Temperature-Programmable Mass Spectrometry (TPD-MS) <i>O.G. Bordunova, V.B. Loboda, R.V. Dolbanosova, P.S. Danylchenko, S.M. Danilchenko, V.D. Chivanov, V.V. Popsui, A.O. Stepanenko, O.I. Ivanova</i>	02IT02
Investigation of Surface Morphology and Shell Crystal Structure on the Mineral Fertilizer Granules <i>S. Vakal, A. Yanovska, V. Vakal, T. Yarova, A. Artyukhov, V. Shkola</i>	02IT03
Controlling the Microstructural Properties of Magnetic Iron Oxide Synthesized using Brown Seaweed (<i>Sargassum Crassifolium</i>) Extract <i>J.N. Patricio, S. Del Rosario Arco, Rey Y. Capangpangan, A.C. Alguno, M.L.M. Budlayan</i>	02IT04
Radiomodifying Effect of X-Ray Radiation on Microflora of Yogurts with Ultradisperse Powders of Beta Vulgaris <i>M.M. Samilyk, A.O. Gelih, O.V. Kalinkevich, N.V. Bolgova, I.V. Shelest, Y.V. Trofimenko, Ye.Zinchenko, V. Chivanov, A. Kalinkevich</i>	02IT05
Thermo-electric Impact of Nano-Materials on Transformer Oil and Synthetic Ester Oil <i>Rao Hasanain Muzaffar Ali, Mohd Faraz Alam, Khalid Abdullah Khan, Sughra Muzaffar</i>	02IT06

Electrical Conductivity of Ceramics Based on (Cu_{1-x}Ag_x)₇SiS₅I Nanocrystalline Powders

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Abstract—Ceramic samples based on (Cu_{1-x}Ag_x)₇SiS₅I nanocrystalline powders were manufactured by pressing them at ~ 400 MPa pressure and subsequent annealing at 973 K during 36 hours. Investigations of electrical conductivity of ceramics based on (Cu_{1-x}Ag_x)₇SiS₅I solid solutions were carried out by the method of impedance spectroscopy in the frequency range from 10 Hz to 2×10⁶ Hz and in the temperature range 292–383 K. It is established that with increasing the content of silver atoms in ceramic samples based on (Cu_{1-x}Ag_x)₇SiS₅I, the ionic component of electrical conductivity increases nonlinearly, while electronic component decreases nonlinearly, and their ratio increases nonlinearly and for Ag₇SiS₅I exceeds 60000.

Keywords—solid solutions, ceramics, electrical conductivity, activation energy, compositional dependence.

I. INTRODUCTION

Ceramic materials are widely used due to their unique properties (structural, mechanical, chemical, functional ones, etc.). High values of melting point, modulus of elasticity, hardness and low thermal expansion of ceramic materials do not limit the scope of their use by engineering problems, but also significantly expand them [1-4]. Presently, ceramic materials are actively used in medicine, biochemistry, optics, thermoelectricity, electronics and electrochemistry [5-9].

Presently, the study of electrochemical ceramic materials has received considerable development due to the study and improvement of electrochemical energy storage technologies [10, 11]. The rapid development of these technologies is caused by both the development of alternative energy sources and electric vehicles, and the increase in the number of portable electronic devices [12-14].

Electrochemical capacitors (supercapacitors), batteries and fuel cells are used as electrochemical energy storage devices [11]. Li-ion batteries containing liquid organic electrolyte received most commercial distribution [9, 15, 16]. However, the combination of chemically active lithium and flammable liquid reduces the safety of the device [15].

When using a solid electrolyte instead of liquid one, there exists a splendid opportunity to improve the safety of batteries, as well as simplify their design [14, 17-21]. Solid electrolytes that can be used in solid-state batteries are

conventionally divided into three groups: inorganic (crystal, or glass-ceramic) substances, organic polymers and hybrid materials. Oxides, phosphates and complex sulphides are used as functional solid-state inorganic materials [17-19].

Since the efficiency of batteries depends directly on the properties of the working material, the search and improvement of new materials is especially relevant. Sulphur-containing solid electrolytes, among which complex phosphorus sulphides of Li⁺ and Na⁺ are noteworthy, attract considerable attention due to the high ionic conductivity, which is ensured by the peculiarities of their crystal structure [14, 18, 22-25]. Since sulphur-containing superionic compounds with ionic conductivity on Li⁺ and Na⁺ cations are difficult to obtain in the crystalline state [24], they are obtained in glass-ceramic form [23, 24, 26, 27].

Compounds of the argyrodite family [28-31], which are characterized by high values of ionic conductivity are considered promising superionic materials. Features of their crystal structure (tetrahedral dense packaging) and high variability of compositions [32, 33] contribute to the formation of solid solutions on their basis.

The purpose of this study is to produce and carry out electrical investigation of ceramic samples based on nanocrystalline powders of (Cu_{1-x}Ag_x)₇SiS₅I solid solutions as well as to study the influence of Cu→Ag cationic substitution on their electrical parameters.

II. EXPERIMENT METHODOLOGY

Synthesis of Cu₇SiS₅I and Ag₇SiS₅I was carried out from the simple substances: copper (99.999%), silver (99.995%), silicon (99.99997%), sulfur (99.999%) and pre-synthesized binary cuprum (I) iodide and argentum (I) iodide, taken in stoichiometric ratios in vacuated to 0.13 Pa quartz ampoules. The binary cuprum (I) iodide and argentum (I) iodide were further purified by vacuum distillation and directional crystallization, respectively. The synthesis regime of Cu₇SiS₅I and Ag₇SiS₅I included step heating up to 723 K at a rate of 100 K/h (shuttering during 48 hours), further increase of temperature to 1470 K (Cu₇SiS₅I) and 1230 K for Ag₇SiS₅I at a rate of 50 K/h and shuttering at this temperature for 24 hours. Cooling was performed in the oven off mode.

Alloys of $\text{Cu}_7\text{SiS}_5\text{I}-\text{Ag}_7\text{SiS}_5\text{I}$ system were synthesized by a direct one-temperature method from pre-synthesized $\text{Cu}_7\text{SiS}_5\text{I}$ and $\text{Ag}_7\text{SiS}_5\text{I}$. The synthesis mode included step heating at a rate of 100 K/h to 1023 K and shuttering at that temperature for 24 hours, further raising the temperature to 1470 K at a rate of 50 K/h and shuttering at that temperature for 72 hours. The annealing temperature constituted 873 K, and shuttering took 120 hours. Cooling to room temperature was carried out in the oven off mode.

Synthesized solid solutions $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ ($x = 0.25, 0.5, 0.75, 1$) were used for the production of ceramic samples by solid-phase sintering of pressed nanocrystalline powders of the corresponding compositions. Nanocrystalline powders were obtained by grinding the synthesized compounds and solid solutions based on them in the planetary ball mill PQ-N04 during 30 minutes at a rate of 200 rpm to 150 nm, what is established using SEM microscopy. Pressing of samples was carried out at a pressure of ~ 400 MPa, annealing - at 973 K during 36 hours. Ceramic samples of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ solid solutions were obtained in the form of disks with a diameter of 8 mm and a thickness of 3-4 mm. To determine the size of crystallites after annealing, the ceramic samples were investigated by microstructural analysis using metallographic microscope METAM-R1 (Fig.3). According to the results of the analysis of obtained microstructures, histograms of distribution of crystallites were plotted and it was found that ceramic samples are characterized by a fairly homogeneous microstructure, which is described by distribution of crystallites in a rather narrow interval. It is established that after recrystallization, the average size of crystallites for ceramic samples obtained from nanocrystalline powders constitutes $\sim 5 \mu\text{m}$.

Measurements of electrical conductivity of ceramic samples based on $\text{Cu}_7\text{SiS}_5\text{I}$, $\text{Ag}_7\text{SiS}_5\text{I}$ and $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ ($x = 0.25, 0.5, 0.75, 1$) solid solutions were carried out by impedance spectroscopy method [34] in frequency $10-2 \times 10^6 \text{ Hz}$ and temperature 292-383 K ranges using high-precision LCR meters Keysight E4980A and AT-2818. The amplitude of the alternating current constituted 10 mV. Measurements were carried out by a two-electrode method on blocking (electronic) gold contacts. Gold contacts for measurements were applied by chemical precipitation from solutions [35, 36].

III. RESULTS AND DISCUSSION

For all ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ there is an increase in the total electrical conductivity with increasing frequency (Fig. 1), which is characteristic for the materials with ionic conductivity in the solid state [37]. On the basis of the obtained results, we constructed the compositional dependence of the total electrical conductivity at a frequency of 100 kHz, which shows that $\text{Cu}^+ \rightarrow \text{Ag}^+$ cationic substitution leads to a monotonous nonlinear increase in the total electrical conductivity that manifests itself in the presence of an insignificant minimum for the composition $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\text{I}$ (insert to Fig. 1).

For detailed studies of frequency behavior of total electrical conductivity and its separation into ionic and electronic components, a standard approach was applied including the use of electrode equivalent circuits and their analysis on Nyquist plots [34, 37, 38]. The parasitic inductance of the cell ($\sim 2 \times 10^{-8}$ H) was taken into account during the analysis of all samples.

According to the results of the analysis of impedance spectra, the temperature and compositional behavior of ionic and electronic components of electrical conductivity of ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ were studied. It is established that with an increase in the content of silver atoms, the ionic component of electrical conductivity in the process of cationic substitution during $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{SiS}_5\text{I} \rightarrow (\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\text{I} \rightarrow (\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{SiS}_5\text{I} \rightarrow \text{Ag}_7\text{SiS}_5\text{I}$ transition nonlinearly increases, while the value of the electronic component nonlinearly decreases (Fig.2).

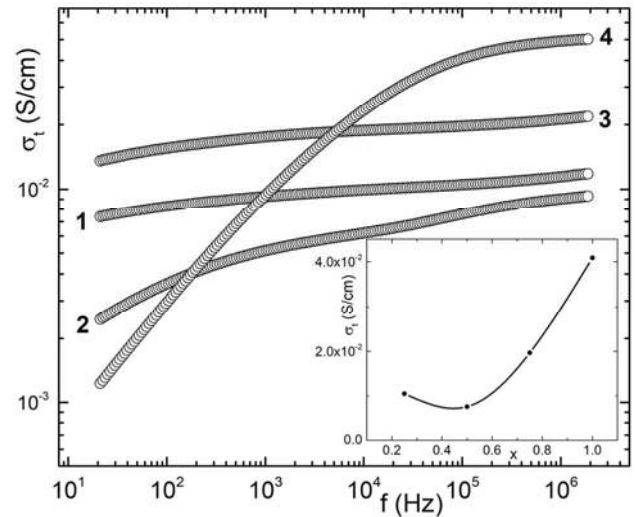


Fig. 1. Frequency dependences of total electrical conductivity at 298 K temperature for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$: $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{SiS}_5\text{I}$ (1), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{SiS}_5\text{I}$ (2), $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{SiS}_5\text{I}$ (3) and $\text{Ag}_7\text{SiS}_5\text{I}$ (4). The insert shows the compositional dependence of total electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ ceramic samples at a frequency of 100 kHz.

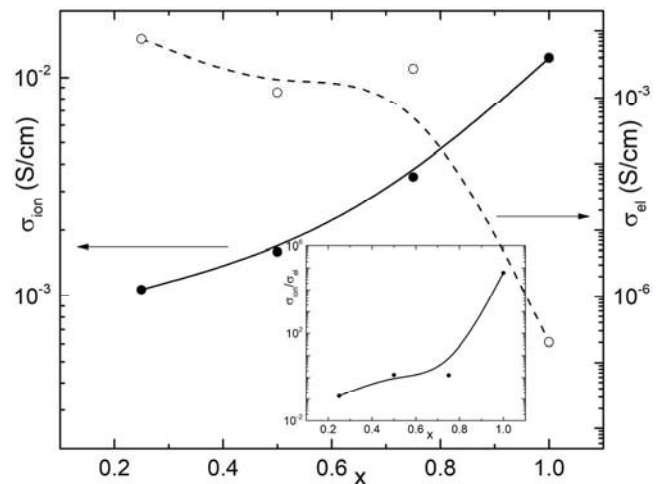


Fig. 2. Compositional dependences of ionic and electronic components of electrical conductivity at 298 K for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$. On the insert, the compositional dependence of the ratio of the ionic to electronic component of electrical conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ ceramic samples is presented.

A very important characteristic of superionic materials is represented by the ratio of the ionic component of electrical conductivity to the electronic one, the compositional dependence of which is shown on the insert to Fig. 2.

It should be noted that when copper atoms are substituted by silver atoms in ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{SiS}_5\text{I}$ the ratio $\sigma_{\text{ion}}/\sigma_{\text{el}}$ increases nonlinearly, and for

Ag₇Si₅I the ionic component of electrical conductivity exceeds the electronic one by more than 60000 times.

Fig. 3 shows the temperature dependences of ionic and electronic components of electrical conductivity in Arrhenius coordinates. It is established that they are linear and are described by the Arrhenius law, which testifies to the thermoactivating character of conductivity. With their help, the values of activation energy were determined, both for the ionic and for the electronic components of electrical conductivity (Fig. 4).

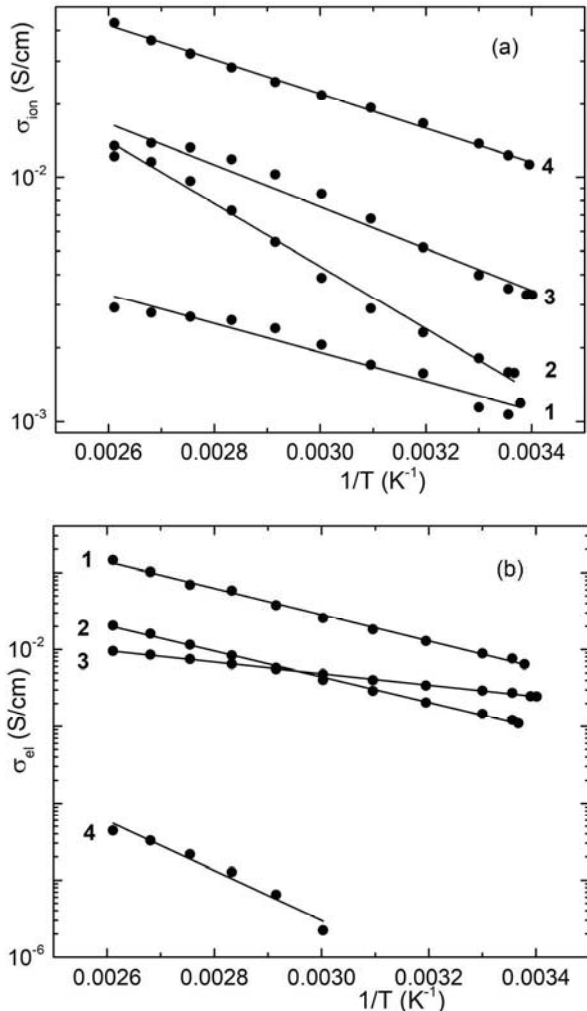


Fig. 3. Temperature dependences of ionic (a) and electronic (b) components of electrical conductivity for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$: $(\text{Cu}_{0.75}\text{Ag}_{0.25})_7\text{Si}_5\text{I}$ (1), $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{Si}_5\text{I}$ (2), $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{Si}_5\text{I}$ (3), $\text{Ag}_7\text{Si}_5\text{I}$ (4).

A nonlinear decrease of the activation energy with a maximum for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_7\text{Si}_5\text{I}$ (the value of the activation energy at the maximum is $E_{a(\text{ion})}=0.419$ eV) is revealed on the compositional dependence of activation energy of ionic components of electrical conductivity at increase of silver atoms content in ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ solid solutions. In this case, the activation energy of the electronic component of electrical conductivity during $\text{Cu}^+ \leftrightarrow \text{Ag}^+$ cationic substitution nonlinearly increases with a minimum for $(\text{Cu}_{0.25}\text{Ag}_{0.75})_7\text{Si}_5\text{I}$ (the value of the activation energy at a minimum is $E_{a(\text{el})}=0.294$ eV).

It should be noted that ceramic samples prepared on the basis of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ solid solutions are characterized by complex and disordered structure. This is caused, primarily, by the different sizes of crystallites, the nature of their

distribution and the complex process of recrystallization during the annealing of samples. Recrystallization process involves the enlargement of crystallites due to solid-phase diffusion processes, and it is accompanied by the emergence of microstructural heterogeneities that contribute to the emergence of micro- and macrodefects. This additionally leads to the appearance of internal voltage of the ceramic material. Here we should also add the processes of composite disordering of the crystal lattice of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ solid solutions caused by the cationic substitution $\text{Cu}^+ \leftrightarrow \text{Ag}^+$. The combination of the aforementioned features causes corresponding changes not only in the overall electrical conductivity, but also in the ionic and electronic components.

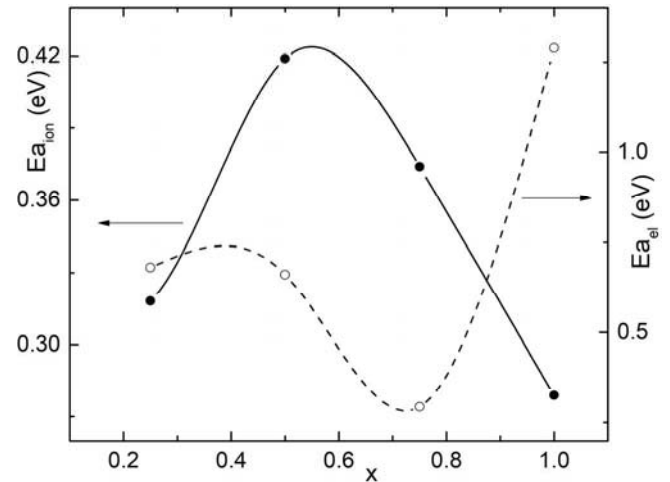


Fig. 4. Compositional dependences of the activation energy for ionic and electronic components of electrical conductivity for ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$.

IV. CONCLUSIONS

Compounds of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ solid solutions are synthesized and ceramic samples are made on their basis by pressing and sintering nanocrystalline powders. According to the results of micro-structural analysis, it was established that, as a result of recrystallization, the average size of crystallites for ceramic samples constitutes ~ 5 μm . On the obtained ceramic samples, the total electrical conductivity was measured by impedance spectroscopy method in the frequency range from 10 Hz to 2 MHz and in 292-383 K temperature range. It is found that cationic $\text{Cu}^+ \rightarrow \text{Ag}^+$ substitution leads to a monotonous nonlinear growth of total electrical conductivity of ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$.

On the basis of frequency dependences of total electrical conductivity, Nyquist diagrams were plotted, which were further analyzed using electrode equivalent circuits. Using this approach, the total electrical conductivity was divided into ionic and electronic components. It is established that an increase in the content of silver atoms in ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ leads to a nonlinear increase of the ionic component, nonlinear decrease in the electronic component, and nonlinear growth of the ratio of the ionic component to the electronic one.

It is shown that the temperature dependences of ionic and electronic components of total electrical conductivity of ceramic samples based on $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{Si}_5\text{I}$ are described by

Arrhenius law, which confirms the thermoactivation nature of electrical conductivity.

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