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Preparation and electrical properties of composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals

V.Yu. Izai[1], M.M. Luchynets[1], I.P. Studenyak[1], A.I. Pogodin[1], O.P. Kokhan[1], M. Rajňák[2], M. Timko[2], P. Kopčanský[2]

[1]Uzhhorod National University, Faculty of Physics,
3, Narodna Sq., 88000 Uzhhorod, Ukraine
[2]Institute of Experimental Physics, Slovak Academy of Sciences,
Watsonova 47, 040 01 Košice, Slovakia
E-mail: studenyak@dr.com

Abstract. $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were grown using the direct crystallization technique from melt (Bridgman–Stockbarger technique). The polymer composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were prepared. Electrical properties of composites were studied in the frequency range from 10^{-3} Hz to $2\cdot10^6$ Hz at room temperature. The parallel equivalent circuit with double electric layer assumed at the electrode interface was applied to analyze the frequency dependences of electrical conductivity. It has been shown that the highest value of total electric conductivity is observed for the $(Cu_6PS_5I)_{0.75}(Cu_7PS_6)_{0.25}$-based composite. The further increase of Cu_7PS_6 content leads to the monotonically decreasing values of total electric conductivity. The ratio of total ionic to electronic components demonstrates the highest value for Cu_6PS_5I-based composite.

Keywords: mixed crystals, polymer composites, electrical conductivity, Nyquist plot, compositional dependence.

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1. Introduction

Mixed crystals in Cu_6PS_5I-Cu_7PS_6 system belong to the argyrodite family of superionic conductors and demonstrate high values of conductivity at room temperature [1, 2]. The representatives of this family are promising materials for applications in solid state ionics as the materials for solid state batteries, supercapacitors and electrochemical sensors. At room temperature, pure Cu_6PS_5I and Cu_7PS_6 crystallize in the cubic crystal system ($F\bar{4}3m$ and $P2_13$ space groups, respectively). The most investigated in this family are Cu_6PS_5I crystals, showing a high value of electric conductivity at room temperature, comparable with the conductivity of the best solid electrolytes [2]. At low temperatures, the Cu_6PS_5I crystal undergoes two phase transitions (PTs), one of them being the first-order superionic and ferroelastic PT at T_I = 144…169 K, while another is the second-order structural PT at T_{II} = (269±2) K [3, 4].

The phase diagram of a quasi-binary Cu_2S–P_4S_{10} system was studied in Ref. [5]. Cu_7PS_6 compound is formed with a large excess of S^{2-} anions and in a simplified case its structure can be viewed as the Cu_2S matrix containing isolated $[PS_4]^{3-}$ ions. In Cu_7PS_6, PT is observed at 515 K from the high-temperature phase with $F\bar{4}3m$ symmetry to the low-temperature phase with $P2_13$ symmetry. Calorimetric studies of Cu_7PS_6 showed no phase transitions within the temperature range 100...400 K [6]. Electrical properties of Cu_7PS_6 crystal grown using direct crystallization were studied in the frequency range 10…10^{10} Hz and temperature interval 296…351 K in Ref. [7]. Two processes were observed, which cause two conductivity dispersions and a dielectric dispersion. At room temperature and at 1 kHz frequency, the conductivity value is $1.77\cdot10^{-3}$ S/m, while at high frequency of 1 GHz the conductivity reaches 5 S/m.

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Argyrodite-based composites were studied in several works (*e.g.*, [8-10]). It was shown that for Cu_6PS_5I-based composites with polyvinylacetate, the electric conductivity value was $7.2 \cdot 10^{-2}$ S/m at 10^6 Hz [8], while for the composites of Cu_6PS_5I nanoparticles in the 6CB liquid crystal it was increased up to $4.8 \cdot 10^{-6}$ S/m at 10^6 Hz [9]. The polymer composites based on $(Ag_{1-x}Cu_x)_7GeS_5I$ mixed crystals were recently prepared from the above mentioned mixed crystals grown using the Bridgman–Stockbarger method [10]. It should be noted that substitution of Ag atoms with the Cu ones leads to a sharp increase of electronic conductivity, decrease of ionic conductivity as well as decrease of the ratio of ionic to electronic conductivities [10].

In this paper, we report on the technology development for new polymer composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ superionic conductors with argyrodite structure as well as their electrical properties.

2. Experimental

Cu_6PS_5I-Cu_7PS_6 superionic mixed crystals were obtained by the solid state reaction between finely grinded and mixed crystalline powders of pure Cu_6PS_5I and Cu_7PS_6 taken in corresponding proportions. The mixtures were sintered at the temperature 1173 K for 120 h. As a result, intense recrystallization of material was observed.

$(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were grown using the direct crystallization technique from the melt (Bridgman–Stockbarger method). Synthesis of $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ compounds was performed by the following procedure: heating at a rate of 50 K/h to (673 ± 5) K, ageing at this temperature for 24 h, then heating of the "hot" zone to (1330 ± 5) K and the "cold" zone to (973 ± 5) K, ageing at this temperature for 72 h and further heating of the melting zone up to (1380 ± 5) K (50 K above the melting point) with 24-h ageing. Seeding was performed for 48 h in the lower part of the container. The crystallization front rate was 3 mm/day. The ampoule with the crystal was subsequently annealed in the "cold" zone at (973 ± 5) K for 48 h.

XRD studies confirmed formation of continuous series of $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ solid solutions. The changes of lattice parameter follow the Vegard law. Polymer composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were prepared from polycrystalline powders previously finely grinded in agate mortar. The obtained powders were ultrasonically dispersed in ethyl acetate. The solution of EVA bonding polymer (ethylene-vinyl-acetate copolymer) in ethyl acetate was added to powder dispersion in amount of 1:9 by mass and further dispersed in ultrasonic bath for 10 min. Thus, the composite consisted of 10% of EVA binder and 90% of superionic active material. The obtained mixture was evaporated in air with continuous mixing to prevent sedimentation and enhance homogeneity of particles and dried at 60 °C for 24 h. Dry cake was grinded in agate mortar and pressed in 8 mm in diameter hardened steel mold at room temperature. The calculated pressure inside the mold was around 7800 bar. As a result hard tablets 8 mm in diameter have been obtained. The electrodes were spray deposited onto both disk faces using Cramolin Graphite conductive paint based on colloidal graphite. Thus, the obtained electrodes were expected to demonstrate ion blocking effect at DC.

The impedance measurements were performed in the wide frequency range from 10^{-3} Hz to $2 \cdot 10^6$ Hz with no DC bias and 10 mV AC voltage, applied to the samples. Agilent E4980A Precision LCR Meter was used for $20 \ldots 2 \cdot 10^6$ Hz frequency range. The measurements within the frequency range $10^{-3} \ldots 20$ Hz were performed using the lab-scale system. The analysis of obtained frequency dependences was carried out in Scribner ZView software.

3. Results and discussion

On the frequency dependence of electrical conductivity for Cu_7PS_6-based composite, the single dispersion region is observed (Fig. 1). It results in a broadened semicircle in the Nyquist plot that cannot be fitted with one single RC-circuit (Fig. 2a). The fitting can be performed using the equivalent circuit (Fig. 2a) composed on the assumption that Cu_7PS_6 have both ionic and electronic (hole) components of conductivity. Thus, the low-frequency part of the semicircle is defined generally by electronic conductivity and capacitance of double layer capacitor formed at the interface of irreversible electrode and solid electrolyte. The high-frequency part is affected by the ion transfer across the grain boundaries. The frequency relaxation associated with bulk conductivity and capacitance of the grains is expected in the high-frequency region above 100 MHz and can't be observed on the plots under investigation. The capacity value obtained for the double electric layer is too low, but it can be explained by the poor contact area between graphite and Cu_7PS_6 particles. This approach leads us to comparable values of electronic and ionic component and indicates the mixed character of conductivity in the samples under investigations.

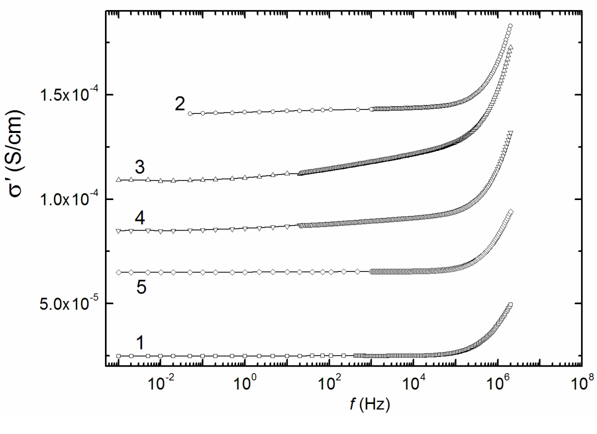

Fig. 1. Frequency dependences of the real part of electric conductivity σ′ for $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$-based polymer composites with the various content of Cu_7PS_6: (*1*) $x = 0$, (*2*) 0.25, (*3*) 0.5, (*4*) 0.75, (*5*) 1.

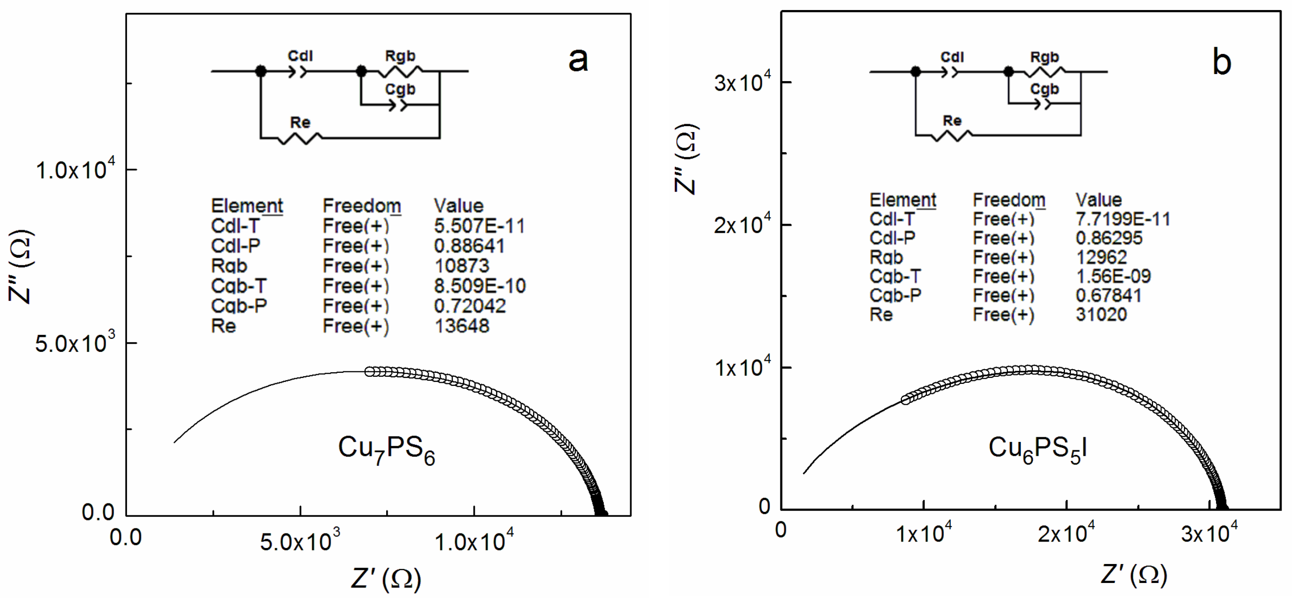

Fig. 2. Nyquist plots for Cu_7PS_6-based polymer composite (a) and Cu_6PS_5I-based polymer composite (b) demonstrate results of fitting the used parallel equivalent circuit with double electric layer assumed at the electrode interface.

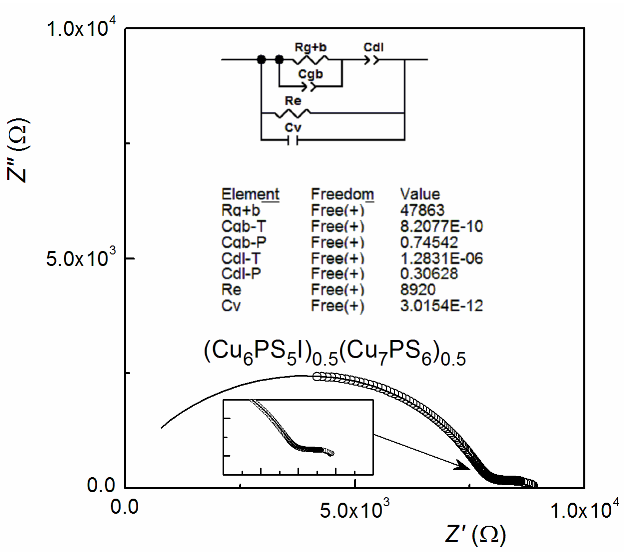

Fig. 3. Nyquist plot for $(Cu_6PS_5I)_{0.5}(Cu_7PS_6)_{0.5}$-based polymer composite and results of fitting made by using the parallel equivalent circuit with a double electric layer assumed at the electrode interface.

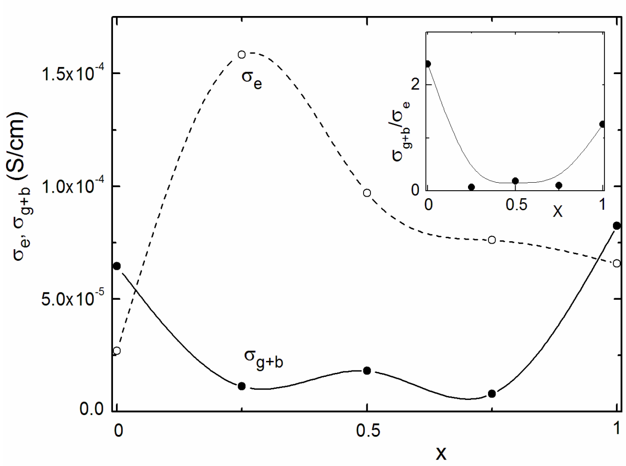

Fig. 4. Compositional dependences of electronic σ_e and total (grains with grain boundaries) ionic σ_{g+b} components of electric conductivity for $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$-based polymer composites. Inset shows the compositional dependence of total ionic to electronic components ratio σ_{g+b}/σ_e.

The similar analysis can be also performed for pure Cu_6PS_5I-based composite, though the frequency behavior of electric conductivity (Fig. 1) as well as the impedance (Fig. 2b) is almost the same with only difference in higher values of impedance and, thus, lower values of electric conductivity and dielectric permittivity obtained. On the frequency dependences of electric conductivity of composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals, one more dispersion in the low-frequency region appears (Fig. 1). It results in a small additional semicircle observed to the right in the low-frequency part of the Nyquist plot after the main semicircle (Fig. 3). Taking into account the low frequencies corresponding to the observed semicircle, the latter is associated with a double electric layer capacitance and electronic conductivity that is comparatively large in the objects under investigation. The equivalent circuit shown in Fig. 3 gives adequate values of fitted parameters and, thus, was used for further analysis. It should be emphasized that only the total ionic conductivity value (including both grains and grain boundaries) can be obtained from the analyzed plots due to the upper frequency limit of the measurements.

Table. Values of fitted parameters and conductivities for $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$-based polymer composites with various content of Cu_7PS_6.

Composite	R_e (Ω)	σ_e (S/cm)	C_{dl} (F)	R_{g+b} (Ω)	σ_{g+b} (S/cm)	C_{gb} (F)
Cu_6PS_5I	31020	$2.70\cdot10^{-5}$	$7.72\cdot10^{-11}$	12962	$6.45\cdot10^{-5}$	$1.56\cdot10^{-9}$
$(Cu_6PS_5I)_{0.75}(Cu_7PS_6)_{0.25}$	6163	$1.58\cdot10^{-4}$	$1.82\cdot10^{-5}$	87406	$1.12\cdot10^{-5}$	$1.69\cdot10^{-10}$
$(Cu_6PS_5I)_{0.5}(Cu_7PS_6)_{0.5}$	8920	$9.70\cdot10^{-5}$	$1.28\cdot10^{-6}$	47863	$1.81\cdot10^{-5}$	$8.21\cdot10^{-10}$
$(Cu_6PS_5I)_{0.25}(Cu_7PS_6)_{0.75}$	10110	$7.62\cdot10^{-5}$	$1.31\cdot10^{-6}$	97552	$7.89\cdot10^{-6}$	$2.79\cdot10^{-10}$
Cu_7PS_6	13648	$6.56\cdot10^{-5}$	$5.51\cdot10^{-11}$	10873	$8.24\cdot10^{-5}$	$8.51\cdot10^{-10}$

Note. R_e – electronic resistance, σ_e – electronic component of conductivity, C_{dl} – double electric layer capacitance, R_{g+b} – total ionic resistance (assuming grains and grain boundaries connected in series), σ_{g+b} – total ionic conductivity, C_{gb} – capacitance of grain boundaries.

Anyway, this value is more important for practical applications than internal conductivity of grains itself and should be used in further comparison.

As can be seen from Fig. 1, the highest values of total electric conductivity are observed for the $(Cu_6PS_5I)_{0.75}(Cu_7PS_6)_{0.25}$ (it rises rapidly with increase of Cu_7PS_6 content). The further increase of Cu_7PS_6 content leads to the monotonically decreasing values of total electric conductivity. While the frequency dependences of electric conductivity are not sufficiently informative or quantative analysis (only low-frequency plateau is observed), our comparison was performed between parameters obtained from fitting the used equivalent circuit with a double electric layer assumed at the electrode interface to hold the equal approach for all the samples under investigation. The results of fitting are given in Table, where R_e, σ_e, C_{dl}, R_{g+b}, σ_{g+b}, C_{gb} are the values of electronic resistance, electronic component of conductivity, double electric layer capacitance, total ionic resistance (assuming grains and grain boundaries connected in series), total ionic conductivity and capacitance of grain boundaries, respectively.

A sharp increase of electronic component of conductivity at the concentration $x = 0.25$ of Cu_7PS_6 is changed with its monotonous decrease together with further increase of Cu_7PS_6 content (Fig. 4). Nevertheless, the electronic conductivity of pure Cu_7PS_6 based composite remains at higher level comparing to pure Cu_6PS_5I based composite. From the other hand, the value of total ionic conductivity decreases for composites based on mixed crystals in comparison with those based on pure Cu_6PS_5I and Cu_7PS_6. In spite of the fact that the total ionic conductivity of Cu_7PS_6-based composite ($8.24\cdot10^{-5}$ S/cm) is somewhat greater than that of Cu_6PS_5I-based composite ($6.45\cdot10^{-5}$ S/cm), the ratio of total ionic to electronic components demonstrates the highest value for Cu_6PS_5I-based composite. A sharp decrease of ionic component and increase of the electronic one can be explained by the compositional disordering effects usually observed in solid solutions. Thus, the break of ionic conductivity channels and enhanced overlapping of electron density functions may occur due to compositional disordering in crystal lattice resulting in domination of electronic component of conductivity in composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals. As a result, pure Cu_6PS_5I and Cu_7PS_6 superionic composites remain the best materials from the chosen series of mixed crystals for possible electrochemical applications.

4. Conclusions

$Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were grown using the direct crystallization technique. Polymer composites based on $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$ mixed crystals were prepared from the polycrystalline powders and consisted of 10% of EVA (ethylene-vinyl-acetate copolymer) binder and 90% of superionic active material. The impedance measurements for $(Cu_6PS_5I)_{1-x}(Cu_7PS_6)_x$-based composites were carried out in the wide frequency range from 10^{-3} Hz to $2\cdot10^6$ Hz. The parallel equivalent circuit with double electric layer assumed at the electrode interface was applied to analyze the frequency dependences of electrical conductivity. This approach leads us to comparable values of electronic and ionic components and indicates the mixed character of conductivity in the samples under investigations.

The highest value of total electric conductivity is observed for the $(Cu_6PS_5I)_{0.75}(Cu_7PS_6)_{0.25}$-based composite (it rises rapidly with increase of Cu_7PS_6 content). The further increase of Cu_7PS_6 content leads to the monotonically decreasing values of total electric conductivity. The comparison was performed between parameters obtained from fitting the used equivalent circuit with double electric layer assumed at the electrode interface.

In spite of the fact that the total ionic conductivity of Cu_7PS_6-based composite ($8.24\cdot10^{-5}$ S/cm) is somewhat higher than that of Cu_6PS_5I-based composite ($6.45\cdot10^{-5}$ S/cm), the ratio of total ionic to electronic components demonstrates the highest value for Cu_6PS_5I-based composite. A sharp decrease of ionic component and increase of the electronic can be explained by compositional disordering effects usually observed in solid solutions.

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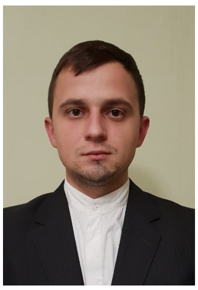
Authors and CV

Ihor P. Studenyak, born in 1960, defended his Dr. Sc. degree in Physics and Mathematics in 2003 and became full professor in 2004. Vice-rector for research at the Uzhhorod National University, Ukraine. Authored over 200 publications, 120 patents, 15 textbooks. The area of his scientific interests includes physical properties of semiconductors, ferroics and superionic conductors.

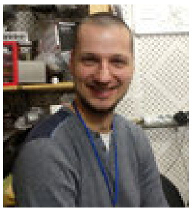
Artem I. Pogodin, born in 1988, defended his PhD thesis in inorganic chemistry in 2016. Senior researcher at the Uzhhorod National University. Authored over 35 articles and 25 patents. The area of his scientific interests includes solid state chemistry, crystal growth, and materials science.

Oleksandr P. Kokhan, born in 1958, defended his PhD thesis in inorganic chemistry in 1996 and became docent in 2002. Associate professor of Inorganic Chemistry department at the Uzhhorod National University. Authored over 80 articles and 40 patents. The area of his scientific interests includes inorganic chemistry, solid state chemistry, crystal growth, materials science.

Vitaliy Yu. Izai, defended his PhD thesis in Physics and Mathematics in 2013. Senior researcher at Uzhhorod National University. Authored over 35 articles and 20 patents. The area of scientific interests is electrical and optical properties of semiconductors and superionic conductors.



Mykhailo M. Luchynets, born in 1994. Currently he is PhD student of the Uzhhorod National University on Faculty of Physics. Authored 17 scientific publications and 2 patents. The area of scientific interests is electrical and optical properties of superionic conductors.



Michal Rajňák, defended his PhD thesis in Physics of Condensed Matter in 2015. Currently he is working as a senior researcher at Institute of Experimental Physics, Slovak Academy of Science. He focused on dielectric properties of nanocomposite systems.

Milan Timko, PhD in solid state physics. Senior researcher of Institute of Experimental Physics, Slovak Academy of Science. Authored over 220 articles, 4 patents and 3 textbooks. The area of his scientific interests includes solid state physics, magnetic fluids and their magnetic, dielectric and hyperthermia properties.

Peter Kopčanský, Professor in solid state physics. Director of Institute of Experimental Physics, Slovak Academy of Science. Authored over 250 articles, 6 patents and 5 textbooks. The area of his scientific interests includes solid state physics, especially magnetism, transport properties in disordered systems, magnetic fluids, their magnetic and dielectric properties and composite systems with liquid crystals.