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M. M. Kubenova

*L.N. Gumilyov Eurasian National University, Astana, Kazakhstan, kubenova.m@yandex.kz*

M. Kh. Balapanov

*Ufa University of Science and Technology, Ufa, Russia, balapanovmk@mail.ru*

K. A. Kuterbekov

*L.N. Gumilyov Eurasian National University, Astana, Kazakhstan*

B. Akhmetgaliev

*Ufa University of Science and Technology, Ufa, Russia*

R. Kh. Ishembetov

*Ufa University of Science and Technology, Ufa, Russia*

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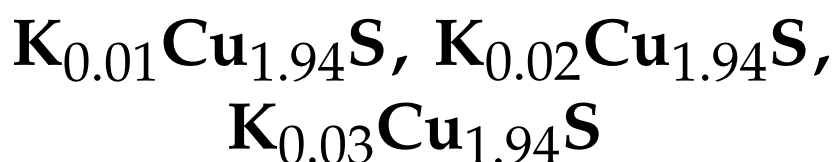
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## Concentration polarization and ionic conductivity of nanocomposite thermoelectric materials $K_{0.01}Cu_{1.94}S$ , $K_{0.02}Cu_{1.94}S$ , $K_{0.03}Cu_{1.94}S$

### Authors

M. M. Kubenova, M. Kh. Balapanov, K. A. Kuterbekov, B. Akhmetgaliev, R. Kh. Ishembetov, R. F. Almukhametov, M. Zeleev, A. M. Kabyshev, K. Zh. Bekmyrza, R. Alina, R. E. Kondakirov, and M. K. Kenzhebek

# Concentration polarization and ionic conductivity of nanocomposite thermoelectric materials



M.M. Kubenova<sup>1,\*</sup>, M.Kh. Balapanov<sup>2,\*\*</sup>, K.A. Kuterbekov<sup>1</sup>,  
B. Akhmetgaliev<sup>2</sup>, R.Kh. Ishembetov<sup>2</sup>, R.F. Almukhametov<sup>2</sup>,  
M. Zeleev<sup>3</sup>, A.M. Kabyshev<sup>1</sup>, K.Zh. Bekmyrza<sup>1</sup>,  
R. Alina<sup>1</sup>, R.E. Kondakirov<sup>1</sup>, M.K. Kenzhebek<sup>1</sup>

<sup>1</sup>L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

<sup>2</sup>Ufa University of Science and Technology, Ufa, Russia

<sup>3</sup>Bashkir State Medical University, Ufa, Russia

E-mail: kubenova.m@yandex.kz, balapanovmk@mail.ru

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The paper presents experimental results of concentration polarization and ionic conductivity of nanocomposite thermoelectric materials  $\text{K}_{0.01}\text{Cu}_{1.94}\text{S}$ ,  $\text{K}_{0.02}\text{Cu}_{1.94}\text{S}$ ,  $\text{K}_{0.03}\text{Cu}_{1.94}\text{S}$ . According to X-ray phase analysis, the synthesized samples are monoclinic jarleite  $\text{Cu}_{1.93\pm 1.97}\text{S}$  with an admixture of oxygen oxide  $\text{Cu}_2\text{S}$  and monoclinic chalcocite. High values of total ionic conductivity are observed, ranging from 0.86 to 1.5 Cm/cm. The lowest ionic conductivity (0.86 Cm/cm at 355 °C) is observed for alloy  $\text{K}_{0.02}\text{Cu}_{1.94}\text{S}$ . In addition, it was found that with an increase in the concentration of potassium in the studied materials, ionic conductivity tends to decrease, activation energy increases, but the characteristics of ion transport remain high, corresponding to superionic materials.

**Keywords:** ionic conductivity; nanocomposite; superionic semiconductors; activation energy

## Introduction

The main reasons hindering the creation of commercial thermoelectric materials competitive with copper telluride are the low stability of properties, the complexity of manufacturing technologies or the toxicity of promising materials or their high cost (or even the whole set of these reasons) with dimensionless thermoelectric efficiency  $ZT$ , much higher than the  $ZT$  of telluride [1-2]. The aim of the work is to increase the thermoelectric characteristics of a material based on superionic copper sulfide by optimizing the chemical composition of the cationic sublattice, which allows reducing the thermal conductivity of the crystal lattice to a theoretical minimum.

One of the common features of the recently synthesized thermoelectrics, which showed  $ZT > 1$ , is that most of them have a lower thermal conductivity of the lattice than that of modern commercial materials. The essence of the modern trend is that by reducing the thermal conductivity of a known thermoelectric material, we bring it closer to the state of "phonon glass" (poorly conducting phonons), while maintaining an "electronic crystal" (leaving good conditions for electron transfer). A decrease in the thermal conductivity of the lattice is achieved due to the scattering of phonons on defects and inhomogeneities of various length scales, obtained, among other things, by nanoengineering methods. The reduced thermal conductivity of the grating directly improves the thermoelectric efficiency of  $ZT$  and, under certain circumstances, makes it possible to optimize the conditions of transfer of electronic charge carriers for additional improvement of  $ZT$  [3-7].

Recently, for  $K_{0.04}Cu_{1.85}S$  nanocomposite based on non-stoichiometric copper sulfide, an extremely high thermoelectric figure of merit  $ZT = 9.67$  was obtained at a temperature of 605 K [8], which was provided by the super low thermal conductivity about  $0.2 \text{ Wm}^{-1}\text{K}^{-1}$ .

The glasses have one of the lowest values of the thermal conductivity of the lattice. In glass, thermal conductivity is a random energy wandering through the lattice, rather than rapid phonon transfer, and therefore leads to minimal thermal conductivity [9]. However, real glasses are poor thermoelectrics because they lack the necessary "electron-crystalline" properties – compared to crystalline semiconductors, they have less electronic mobility due to increased electron scattering and a lower effective mass due to wider zones. Therefore, good thermoelectrics are crystalline materials that manage to disperse phonons without significantly disrupting electrical conductivity. The heat flow in them is carried by an ensemble of phonons with widely varying wavelengths and average free path lengths (from less than 1 nm to more than 10 microns), which creates the need for phonon scatterers (inhomogeneities of the medium) with sizes of inhomogeneities corresponding to the same wide range of lengths [9].

The most common methods of obtaining thermoelectric chalcogenide superionic materials in the last decade are the SPARK, melt-solidification and mechanochemical methods [3].

Doped nonstoichiometric phases of copper sulfide (jarleite) in the nanoscale state are considered as candidates for thermoelectric materials in this work, which

can exhibit superionic properties at temperatures above  $10^3$  °C and, in addition, have a high electronic conductivity of the order of  $10^2$  ohms<sup>-1</sup>cm<sup>-1</sup>.

## Synthesis of materials

Samples of the  $K_{0.01}Cu_{1.94}S$ ,  $K_{0.02}Cu_{1.94}S$ ,  $K_{0.03}Cu_{1.94}S$  chemical compositions were synthesized in a melt of a mixture of NaOH and KOH hydroxides at about 438 K using KCl, CuCl, and  $Na_2S \cdot 9H_2O$  as reagents. The annealing time was 12 hours. The product obtained in the form of a clot was washed three times with distilled water, then with pure ethanol, and dried at a room temperature.

The nine-aqueous sodium sulfide used in the synthesis of samples is not the best source of sulfur for the reaction, since the water contained in it ultimately leads to the formation of an admixture of oxygen oxide in the final product. Oxygen oxide leads to a decrease in both the electronic and ionic conductivity of the cathode material. An attempt was made to dehydrate sodium sulfide  $Na_2S \cdot 9H_2O$  by drying in a vacuum of the order of  $10^{-3}$  mmHg at 60 °C. Sodium sulfide was placed in a quartz ampoule and then in a heated vacuum tank. After drying for more than 5 hours, the water completely evaporates, and pure  $Na_2S$  remains in the ampoule, which was confirmed by X-ray phase analysis.

Thus, using commercial  $Na_2S \cdot 9H_2O$  pre-dried in vacuum, it is possible to obtain potassium-doped copper sulfide samples with a minimum admixture of copper oxide, which reduces the conductivity of the thermoelectric material.

## Experimental part

Figure 1 shows, for example, a powder diffractogram of sample  $K_{0.01}Cu_{1.94}S$ , taken at room temperature with  $CoK_{\alpha}$  radiation ( $\lambda = 1.78892$  Å). According to X-ray phase analysis, the synthesized samples are monoclinic jarleite  $Cu_{1.93 \div 1.97}S$  (1) with an admixture of oxygen oxide  $Cu_2S$  (2) and monoclinic chalcocite (3).

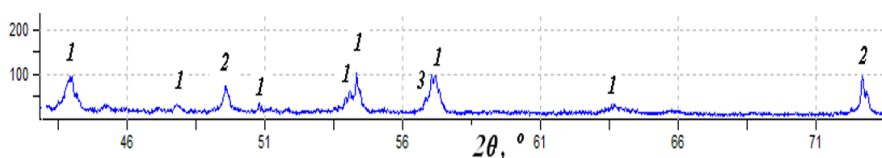


Figure 1. Powder diffractogram of sample  $K_{0.01}Cu_{1.94}S$ , taken at room temperature on  $CoK_{\alpha}$  radiation. The numbers in the figure indicate the phases of monoclinic jarleite  $Cu_{1.93 \div 1.97}S$  (1), oxygen oxide  $Cu_2S$  (2) and monoclinic chalcocite (3).

Figure 2 shows images of synthesized powder particles obtained using a Tescan scanning electron microscope. The particle sizes in the figure range from 100 to 1000 nm, the average particle size  $K_{0.01}Cu_{1.94}S$  is about 460 nm,  $K_{0.03}Cu_{1.94}S$  is about 380 nm.

The direct current method was used to measure ionic conductivity. The measurements were carried out using an electrochemical cell  $Cu/CuBr/$  Sample /

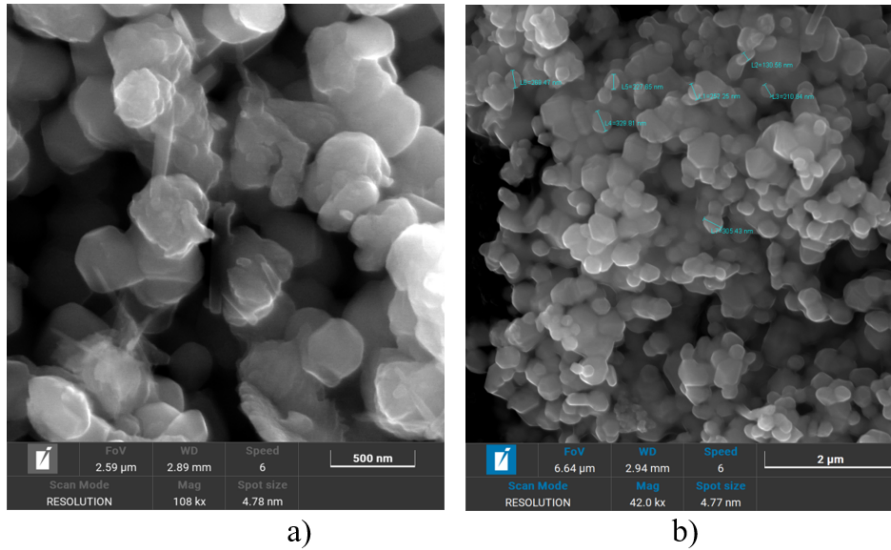


Figure 2. Images of particles of synthesized powder  $K_{0.01}Cu_{1.94}S$  (a),  $K_{0.03}Cu_{1.94}S$  (b) obtained using a Tescan scanning electron microscope.

CuBr/CuI with reversible Cu/CuBr ion electrodes. CuBr has unipolar ionic conductivity over copper ions in the temperature range 340–440 °C, and suppresses the electronic component of the current. In the case of two varieties of mobile ions (in this case,  $Cu^+$ ,  $Na^+$ ), as shown by Sh. Miyatani, the method allows you to find the total cationic conductivity. Ionic conductivity is measured by the stationary potential difference between two Cu/CuBr ion probes.

Figure 3–5 shows the curves of the establishment and decline of concentration polarization when a current of 1 mA flows through a Cu/CuBr cell/ Sample/ CuBr/Cu for samples  $K_{0.01}Cu_{1.94}S$ ,  $K_{0.02}Cu_{1.94}S$ ,  $K_{0.03}Cu_{1.94}S$  at temperatures of 355 °C, 370 °C, 380 °C and 390 °C.

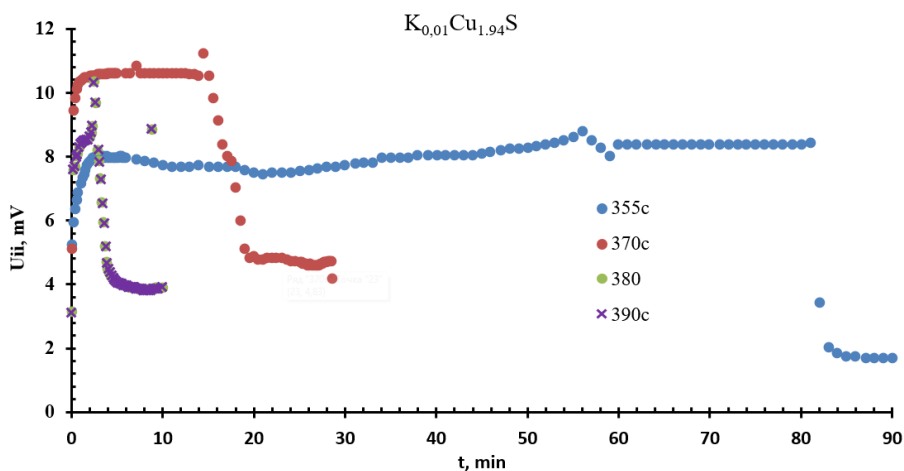


Figure 3. Concentration polarization curves of the  $K_{0.01}Cu_{1.94}S$  sample at temperatures of 355 °C, 370 °C, 380 °C and 390 °C at an ion current of 1 mA.

The results of measurements of ionic conductivity depending on temperature are shown in Figure 6

High values of total ionic conductivity are observed, ranging from 0.86 to 1.5 Cm/cm. The lowest ionic conductivity (0.86 Cm/cm at 355 °C) is observed for alloy  $K_{0.02}Cu_{1.94}S$ .

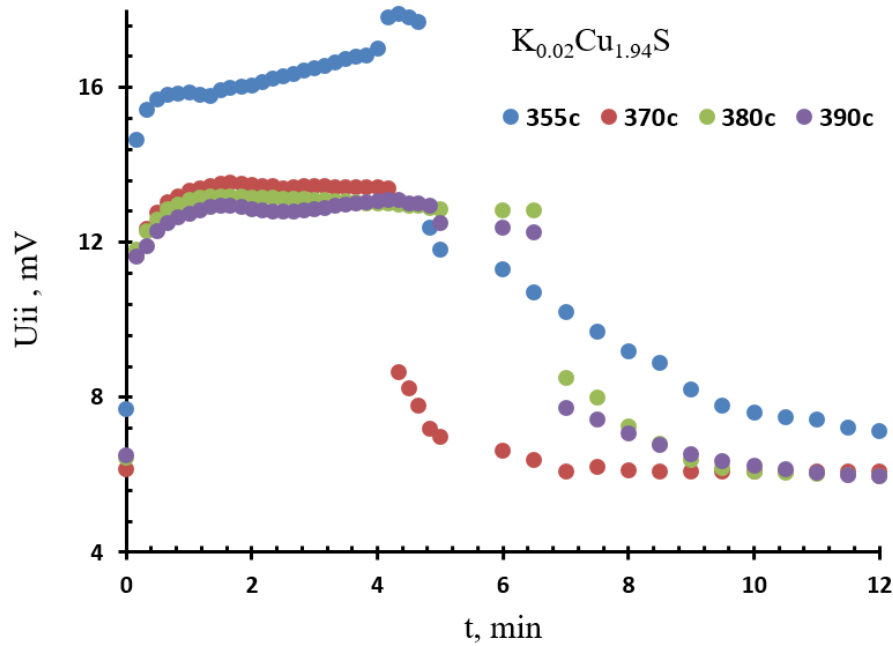


Figure 4. Installation curves and decreases in concentration polarization when a current of 1 mA flows through a Cu/CuBr/  $K_{0.02}Cu_{1.94}S$  /CuBr/Cu cell at temperatures of 355 ° C, 370 ° C, 380 ° C and 390 ° C.

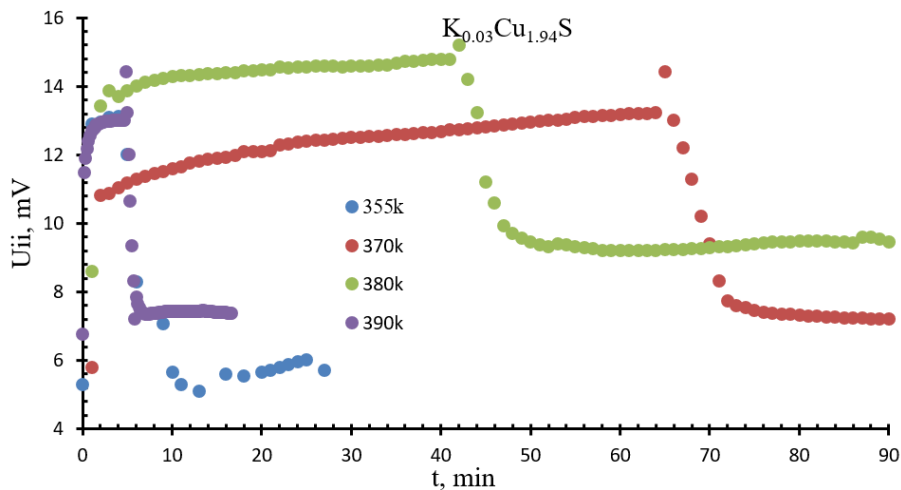


Figure 5. Installation curves and decreases in concentration polarization when a current of 1 mA flows through a Cu/CuBr/  $K_{0.03}Cu_{1.94}S$  /CuBr/Cu cell at temperatures of 355 ° C, 370 ° C, 380 ° C and 390 ° C.

To determine the activation energy of ionic conductivity, auxiliary graphs  $\sigma_i T(1/T)$  were constructed, shown in Figure 7.

The values of the activation energy of the ionic conductivity of cathode materials are given in Table 1.

Table 1.  
Ionic conductivity measurement results.

Sample	Activation energy of ionic conductivity, eV	Ionic conductivity at 370°C, cm/cm
$K_{0.01}Cu_{1.94}S$	$0.37 \pm 0.02$	$1.42 \pm 0.06$
$K_{0.02}Cu_{1.94}S$	$0.42 \pm 0.01$	$1.10 \pm 0.04$
$K_{0.03}Cu_{1.94}S$	$0.44 \pm 0.01$	$1.14 \pm 0.05$

As can be seen from Table 1, with an increase in the concentration of potassium

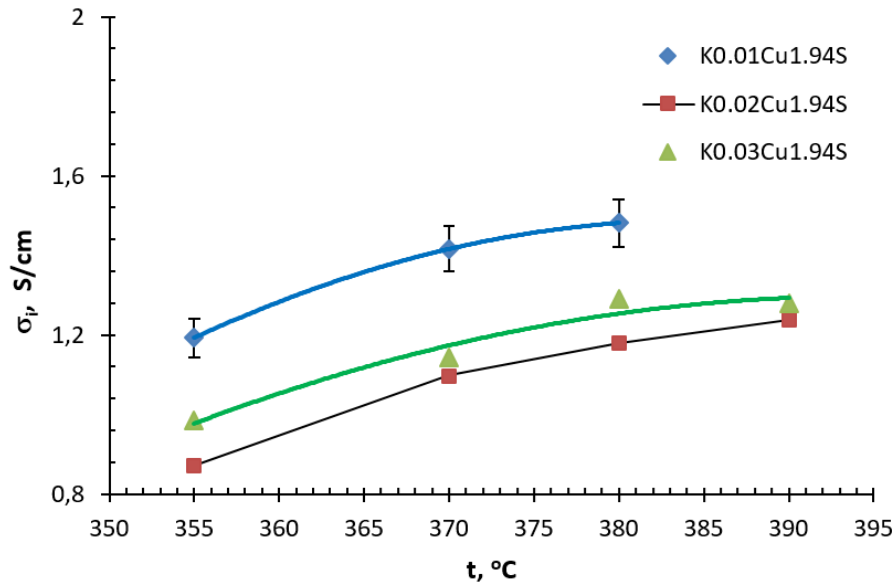


Figure 6. Temperature dependence of the ionic conductivity of the samples.

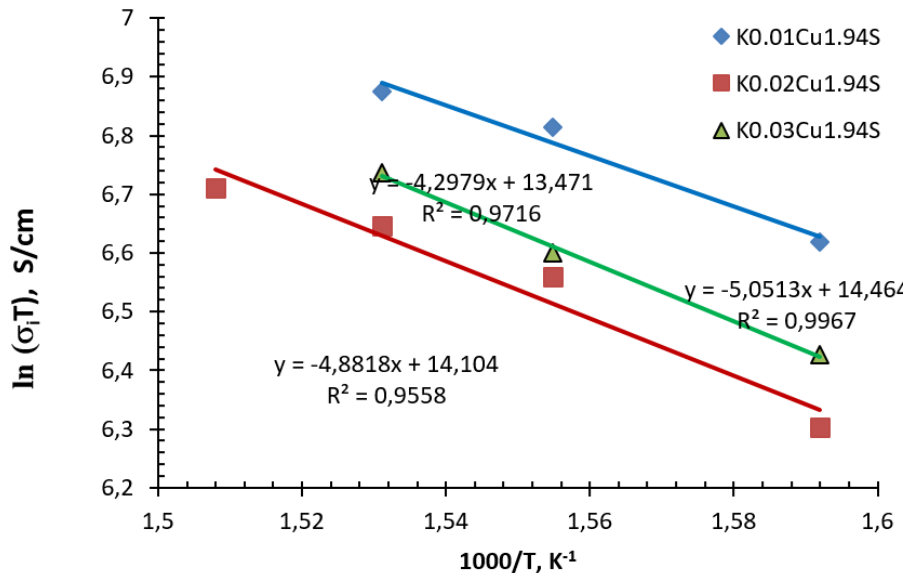


Figure 7. Temperature dependences of the ionic conductivity of samples in coordinates  $\ln \sigma_i T(1/T)$ .

in the studied material, the ionic conductivity tends to decrease, the activation energy increases, but the characteristics of ion transport remain high, corresponding to superionic materials.

In general, ionic conductivity is high and weakly depends on the content of potassium impurity, which indicates a high disorder ("melting") the cationic sublattice. The strong disordered structure ensures a low lattice component of thermal conductivity. The obtained low activation energy values are typical for good superionic conductors and also indicate a high intrinsic disorder of the crystal structure [4-6].

According to recent work [10] the  $K_{0.03}Cu_{1.94}S$  samples has the extremely low thermal conductivity. Total thermal conductivity of  $K_{0.03}Cu_{1.94}S$  does not exceed  $0.71 \text{ Wm}^{-1}\text{K}^{-1}$  in the temperature interval of 300–700 K, dropping to  $0.17 \text{ Wm}^{-1}\text{K}^{-1}$ .



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## Conclusion

Thus, in the studied samples it was found that ionic conductivity increases with increasing grain size. This can be explained by the fact that in a good superionic conductor with a low activation energy, such as these materials, the diffusion of cations throughout the volume is faster than along the grain boundaries, even at fairly low temperatures (about 100 °C). The activation energy  $E_a$  of ionic conductivity was 0.41 eV, which is higher in value  $E_a = 0.16$  eV in pure copper sulfide. The fact that ionic conductivity remains high in the range (1.10–1.42) S/cm, despite the high concentration of foreign atoms (potassium), may speak in favor of the participation of potassium in ion transfer, and also indicates high disorder (melting) of the cationic sublattices.

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