Electron thermal EMF for $Na_xCu_{2-x}S$

Kairat Kuterbekov[1,*], *Malik* Balapanov[2], *Rais* Ishembetov [2], *Marzhan* Kubenova [1], *Talgat* Baitasov [1], *Asset* Kabyshev[1], *Aidos* Azhibekov[1], *Bekmyrza* Kenzhebatyr[1], and *Temirulan* Alibay[1]

[1]L.N. Gumilyov Eurasian National University, Astana, Kazakhstan
[2] Bashkir State University, Ufa, Russia

Abstract. In the present study, the temperature dependences of the thermoelectromotive force (thermo-emf) in copper selenide, substituted in a small concentration, were studied. The results of the measurements showed that the thermo-emf coefficient of the samples increases, and the conductivity decreases with increasing silver concentration in its composition. These results allow - with optimal selection of the doping regime and protective coatings - to develop on the basis of nanostructured copper selenide an effective thermoelectric for use at temperatures of 20–500°C as p-type semiconductors suitable for increasing the efficiency of thermoelectric generators.

1 Introduction

Modern thermoelectric converters have a number of advantages over traditional electric generators: simplicity of design, absence of moving parts, noiselessness of operation, high reliability, possibility of miniaturization without loss of efficiency.

In order for thermoelectric generators to become more competitive than conventional power sources, thermoelectric materials should achieve high performance ZT ≥ 4 [1]. This indicator is a guide in the search and synthesis of new promising materials that can become the basis for industrially produced thermoelectric devices in the foreseeable future (20 to 25 years).

The dimensionless thermoelectric figure of merit, characterizing the efficiency of materials in thermoelectric devices, is determined by the formula

$$ZT = \alpha^2 \sigma T / \chi \qquad (1)$$

where α – is the coefficient of thermal emf (Seebeck coefficient); σ – is electrical conductivity; χ – is the thermal conductivity of the material.

Achieving the optimal combination of all three properties at the same time to obtain a high thermoelectric figure of merit is a complex task.

At present, among the industrially produced thermoelectric materials, the most common is doped bismuth telluride $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$, which has a Q-factor of about 1 (ZT≈1) at

* Corresponding author: kkuterbekov@gmail.com

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room temperature [2]. The highest values of Z are strongly doped semiconductors or semimetals with an electron concentration of the order of 10^{19}–10^{20} см$^{-3}$ [2].

2 Experiment

The results of experimental studies of the dependence of the Thermo-electromotive force (emf) of nanocomposite and microcrystalline copper and silver chalcogenides differing in chemical composition, the synthesis method and the particle size, as well as thermo-emf of nanocomposite and microcrystalline copper and silver chalcogenides in the temperature range 20–500°C are presented.

The choice of the objects of research $Na_xCu_{2-x}S$ (x = 0.05, 0.1, 0.15, 0.2) is due to their use as p-type semiconductors suitable for increasing the efficiency of thermoelectric generators [1].

To study the thermoelectric properties of solid alloys of copper selenides, they were prepared by solid-state synthesis in an inert atmosphere and by low-temperature chemical synthesis. To obtain nanocrystalline powders, a technique was used, described in detail in a number of papers [3, 4].

The registration of thermoelectric properties was carried out with the aid of an experimental setup for studying the Seebeck coefficient and electrical resistance (Model ZEM-3) shown in Fig. 1.

Fig. 1. Experimental setup for studying the Seebeck coefficient and electrical resistance.

The values of the electronic thermal-emf coefficient for the solid solution $Na_xCu_{2-x}S$ (x = 0.05, 0.1, 0.15, 0.2) were measured as a function of temperature. The sign of the coefficient e is positive, which, taking into account the rule of choice of the sign for all samples, corresponds to the motion of electron holes from the hot end of the sample to the cold one.

Figures 2–5 show the dependence of the coefficient α_e of the electronic thermo-emf for the composition $Na_{0,05}Cu_{1,95}S$, $Na_{0,1}Cu_{1,9}S$, $Na_{0,15}Cu_{1,85}S$ and $Na_{0,2}Cu_{1,8}S$ in the range from room temperature to 750 K. For all samples, With an increase in temperature, an increase in the electronic thermal-emf coefficient α_e is observed.

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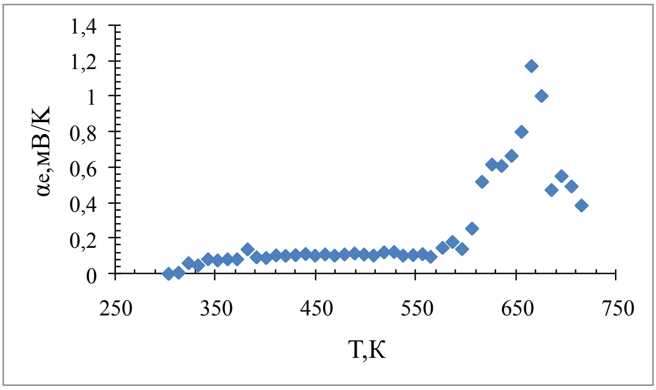

Fig. 2. Temperature dependence of the coefficient of electron thermal emf $Na_{0,05}Cu_{1,95}S$.

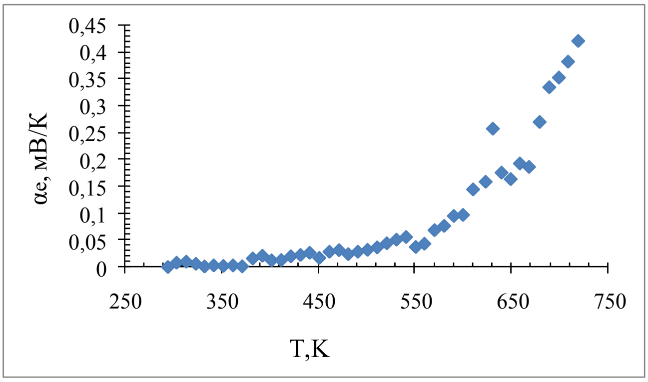

Fig. 3. Temperature dependence of the coefficient of electron thermal emf $Na_{0,1}Cu_{1,9}S$.

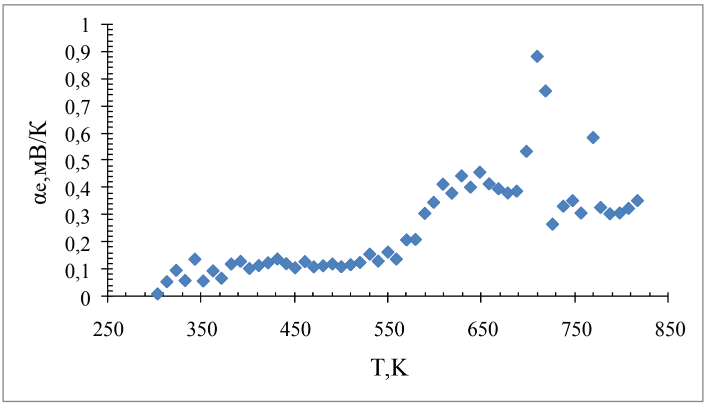

Fig. 4. Temperature dependence of the coefficient of electron thermal emf $Na_{0,15}Cu_{1,85}S$.

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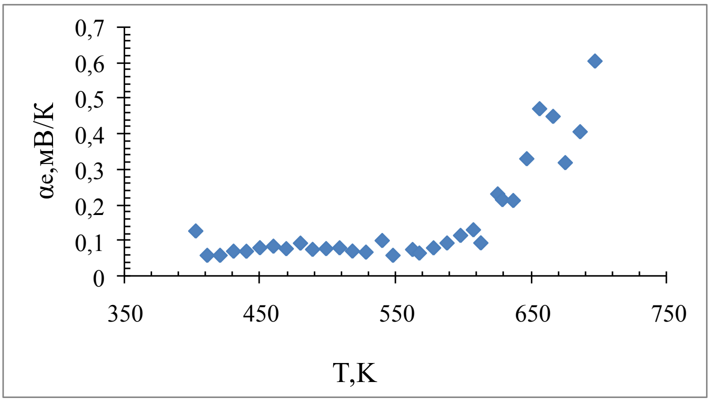

Fig. 5. Temperature dependence of the coefficient of electron thermal emf $Na_{0,2}Cu_{1,8}S$.

Fig. 6 shows the temperature dependence of the emf of the electrochemical cell $Cu/CuBr/Na_{0.2}Cu_{1.8}S/C$. The observed dependence is linear in nature, which indicates the constancy of the entropy of the metal atoms in the compound within the temperature range 630–680 K. From the values of the cell emf, one can judge the degree of non-stoichiometry of the compound, in this case the deviation from the stoichiometric composition is $\delta \approx 0.01$ in the chemical formula of the sample $Na_{0.2}Cu_{1.8-\delta}S$.

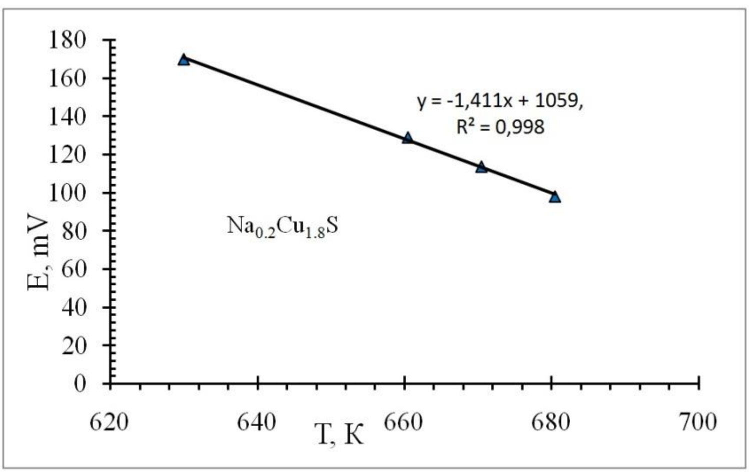

Fig. 6. Temperature dependence of the emf of an electrochemical cell $Cu/CuBr/Na_{0.2}Cu_{1.8}S/C$.

3 Conclusion

Thus, results of measurements have shown that temperature dependences of coefficient of electronic copper of thermo-eds nanocrystal sulfides which cationic sublattice has been alloyed by sodium, with the general chemical formula $Na_xCu_{2-x}S$ (x = 0.05; 0.1; 0.15; 0.2) in the field of temperatures from 20°C to 500°C. The sign of coefficient thermo-eds α_e for all samples was positive that taking into account the rule of the choice of a sign for all samples corresponds to the movement of electronic holes since the hot end of a sample on cold. In general, the coefficient thermo-eds with temperature increase from room temperature to about 650–660 To grows. In the neighborhood of temperature 660 K there is a maximum, probably, the nature of which, probably, is connected with the happening phase transition. The highest values of coefficient electronic thermo-eds in 1.2 mV/To are reached at the same time at structure of $Na_{0,05}Cu_{1,95}S$.

The results of the measurements showed that the thermo-emf coefficient of the samples increases, and the conductivity decreases with increasing silver concentration in its composition. These results allow – with optimal selection of the doping regime and protective coatings – to develop an effective thermoelectric on the basis of nanostructured copper selenide for use at temperatures (400–600) K as p-type semiconductors suitable for increasing the efficiency of thermoelectric generators.

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