УДК 537.32 + 537.312 + 544.034
DOI: 10.33184/bulletin-bsu-2026.2.8

SYNTHESIS AND THERMOELECTRIC PROPERTIES OF CESIUM-DOPED $Cs_xCu_{2-x}S$ (x = 0.04, 0.075, 0.125) COPPER SULFIDES

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Cesium-containing semiconductor copper sulfides have been synthesized. Temperature dependences of electron conductivity, electron Seebeck coefficient, thermal conductivity, and e.m.f. of the Cu/CuBr/Sample/C electrochemical cell in the range of 300–700 K have been obtained. An increase in the electrical conductivity of the alloys with increasing cesium content has been detected. The found activation energies of conductivity in the range from 300 to 370 K are 0.076 eV, 0.064 eV, and 0.036 eV for the compositions $Cs_{0.04}Cu_{1.96}S$, $Cs_{0.075}Cu_{1.925}S$, and $Cs_{0.125}Cu_{1.875}S$, respectively. A sharp drop in conductivity is observed when heated above 600 K, which is associated with the transition of the main phase of the alloy to a cubic modification based on copper sulfide. For the $Cs_{0.125}Cu_{1.875}S$ composition, a high dimensionless thermoelectric figure of merit ZT = 0.76 at 684 K was obtained.

***Keywords**: copper sulfide, phase transitions, entropy, thermoelectric materials, conductivity.*

Introduction

Copper sulfide $Cu_{2-\delta}S$ has long been known as a mixed electron-ion semiconductor [1–3]. Recently, there has been increased interest in it due to its potential for use in thermoelectric devices, solar cells, catalysts, sensors, optical filters, medical devices, batteries, and fuel cells [4–10]. The potential of the material for use in thermoelectric devices can be conveniently assessed by the dimensionless thermoelectric efficiency $ZT = \sigma\alpha^2T/k$, determined by three main parameters of the semiconductor: conductivity σ, Seebeck coefficient α, and thermal conductivity k.

Previously, we investigated the electrophysical properties of copper sulfide doped with lithium, sodium, and potassium [11–15]. In a recent study [16], a low thermal conductivity of 0.18 $W\,m^{-1}K^{-1}$ and a very high value of the thermoelectric figure of merit ZT = 1.76, about 673 K, were achieved for the $Li_{0.11}Cu_{1.89}S – Cu_2O$ nanocomposite. Doping copper sulfide with sodium improves the thermoelectric properties, reducing the thermal conductivity; limit of solid solubility of sodium in Cu_9S_5 is about 5 at. % of the sulfur content [17].

In the work [18], for the $K_{0.2}Cu_{1.8}S$ nanocomposite alloy, consisting of a mixture of cubic phases $Cu_{1.84}S$ and Cu_2S, rhombohedral $Cu_{17}S_9$ phase, and metastable tetragonal $P4_32_12$ phase Cu_2S, ultra-high peak value of the dimensionless thermoelectric figure of merit ZT = 3.5 at 653 K was achieved. For nanocrystalline $K_xCu_{1.85}S$ ($0 < x < 0.05$) at x = 0.04, 0.05 the thermal conductivity decreased to $0.16 \div 0.25\ WK^{-1}m^{-1}$ in the temperature range of 450–600 K [19]. This resulted in a record peak of ZT = 9.67 for the $K_{0.04}Cu_{1.85}S$ composition at 620 K [20]. For the $K_{0.04}Cu_{1.93}S$ nanocomposite alloy, an even lower thermal conductivity of 0.09–0.16 $WK^{-1}m^{-1}$ above 670 K was recently achieved [21].

There are no publications in the literature on the physical properties of cesium-doped copper sulfide. In this work, semiconductor alloys with different cesium contents – $Cs_xCu_{2-x}S$ (x = 0.04, 0.075, 0.125) – are synthesized and studied.

Research methods

Semiconducting $Cs_xCu_{2-x}S$ (x = 0.04, 0.075, 0.125) alloys were synthesized in a melt of a mixture of NaOH and KOH hydroxides at a temperature of about 438 K. All reagents (CuCl, CsCl, Na_2S*9H_2O) were placed in a heated Teflon vessel simultaneously. The nanostructure was formed for about 16 hours. The resulting product was washed with distilled heated water, then with pure ethanol, and dried at 333 K.

For electrical conductivity measurements, a four-probe method was used with direct current, the Seebeck coefficient was studied in the same measuring cell in the absence of current at a gradient of about 10 degrees per 1 cm. When measuring conductivity, the contribution of the thermo-e.m.f. was subtracted from the potential difference between the probes. Thermal conductivity was measured by comparison with a standard, which was a fused quartz plate. The measurement error for electrical conductivity and the Seebeck coefficient was within 3–5%, and for thermal conductivity it was within 7–10%.

Experimental results and discussion

Fig. 1 shows images of four conglomerates of $Cs_{0.125}Cu_{1.875}S$ powder particles taken on a Tescan scanning electron microscope: loose “snow” of nanoparticles (a), a pile of nanoplatelets and nanorods (b), a ball of nanoplatelets (c), and a bundle of nanorods (d). The thickness of the plates varied within 100–200 nm, the diameter of the nanorods was

within 150–300 nm, and their length was several microns. All these types of nanoparticles were previously observed in pure and doped copper sulfides [22–23].

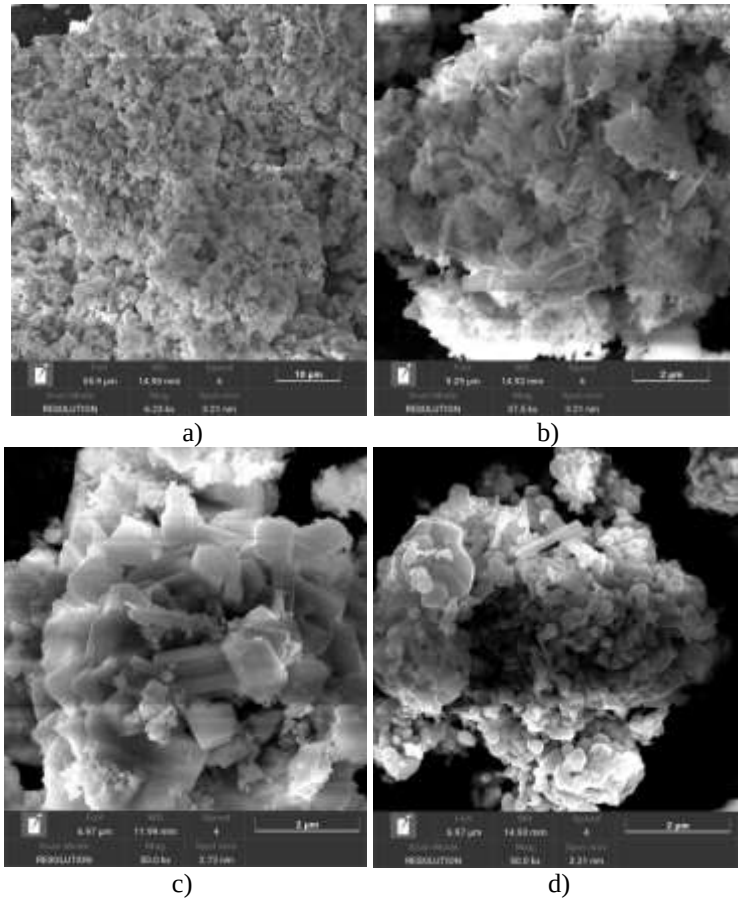
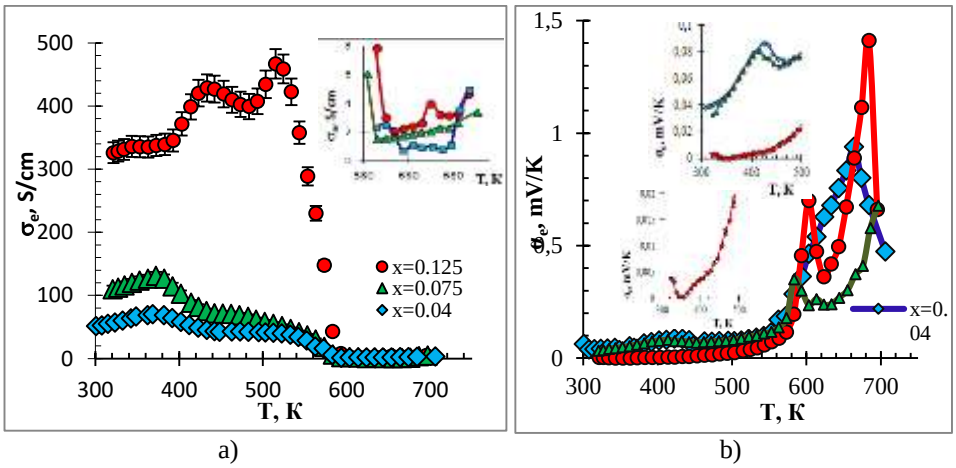
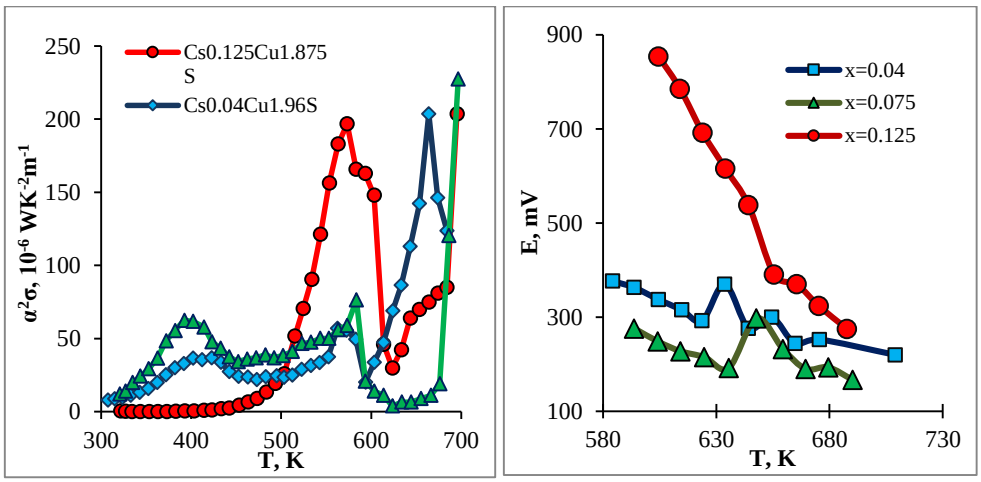


Fig. 1. Scanning electron microscope images of $Cs_{0.125}Cu_{1.875}S$ powder particles: loose “snow” of nanoparticles (a), a pile of nanoplatelets and nanorods (b), nanoplatelets (c), a ball of a bundle of nanorods (d).

Fig. 2 presents the temperature dependences of: electron conductivity σ (a), Seebeck coefficient α (b), thermoelectric power $P = \alpha^2\sigma$ (c), and e.m.f. of the Cu/CuBr/Sample/C electrochemical cell (d). We associate the jumps in the dependences a) and b) around 364 K with the structural transition from the monoclinic to the superionic hexagonal phase in copper sulfide (the transition temperature is 376.5 K in pristine Cu_2S [1; 24; 25]). The presence of cesium, apparently insignificantly, but still lowered the phase transition temperature in doped copper sulfide.





c) d)

Fig. 2. Temperature dependences: electron conductivity (a), Seebeck coefficient (b), thermoelectric power (c), temperature dependence of e.m.f. of the electrochemical cell Cu/CuBr/Sample/C (d) of the $Cs_xCu_{2-x}S$ alloys (x = 0.04, 0.075, 0.125). The inset in *Fig.* 2a shows the region from 580 to 700 K on a larger scale, the two insets in *Fig.* 2b show the region from 300 to 500 K on an enlarged scale (in the lower inset – separately for the $Cs_{0.125}Cu_{1.875}S$ composition).

For the $Cs_{0.125}Cu_{1.875}S$ composition, an unusual behavior of the temperature dependence of conductivity for stoichiometric (Cu_2S composition) copper sulfide is observed in Fig. 2a: a barely noticeable phase transition at 343 K in the form of a flat local maximum and then two peaks with an increase in conductivity, followed by a sharp drop in conductivity from 466 to 2 S/cm. The conductivity anomaly at 343 K is not accidental; it also corresponds to a sharp minimum of the Seebeck coefficient of $Cs_{0.125}Cu_{1.875}S$ in *Fig.* 2b (lower inset to the figure).

The second phase transition from the hexagonal to the cubic phase in Cu_2S occurs at 710 K [24, 25]. However, in the temperature dependences of Fig. 2 between 400 and 700 K we see not one, but two anomalies. The anomaly near 590 K is accompanied by a sharp drop in electron conductivity to 1–2 S/cm and an increase in the Seebeck coefficient to 0.35–0.7 mV/K, which is similar to the transition to the cubic phase of Cu_2S, which is characterized by the same low intrinsic conductivity caused by the transfer of electrons across a wide band gap [1]. It is possible that doping with cesium reduces the temperature of this phase transition from 710 K to 590 K. At least, no other anomalies are observed in the temperature dependences of conductivity (*Fig.* 2a).

When interpreting the results, the temperature dependence of the Fermi level of electrons measured by the e.m.f. of the Cu/CuBr/Sample/C electrochemical cell (*Fig.* 2d) can be taken into account. The strong peak near 670 K on the Seebeck coefficient curves (*Fig.* 2b) approximately coincides with the point of change in the slope of the temperature dependences E(T), which is associated with a change in the entropy of copper atoms. The entropy of copper atoms can be estimated from the temperature dependence E(T) of the e.m.f. of the Cu/CuBr/Sample/C electrochemical cell using the formula

$$S_{Cu} - S^o_{Cu} = e\frac{\partial E}{\partial T}\ [26]. \qquad (1)$$

The entropies of copper atoms in the $Cs_xCu_{2-x}S$ (x = 0.04, 0.075, 0.125) samples calculated from the E(T) dependences in *Fig.* 2d using formula *(1)* and given relative to the entropy S^o_{Cu} of copper atoms in metallic copper in the states before and after the second phase transition are presented in *Table*.

Table

Entropy of copper atoms in the $Cs_xCu_{2-x}S$ (x = 0.04, 0.075, 0.125) samples, calculated relative to the entropy of copper atoms in metallic copper in the states before and after the second phase transition

$S_{Cu} - S^o_{Cu}$, kJ/(mol·K)	$Cs_{0.04}Cu_{1.96}S$	$Cs_{0.075}Cu_{1.925}S$	$Cs_{0.125}Cu_{1.875}S$
Before the transition	−209	−186	−851
After the transition	−99.2	−181	−408

From *Table* it is evident that for $Cs_{0.04}Cu_{1.96}S$ and $Cs_{0.04}Cu_{1.96}S$, during the phase transition, there is a twofold change in the entropy of copper, associated with the increase in the disordering of copper atoms in the interstices of the anionic framework of the lattice.

In mixed electron-ion conductors with a wide homogeneity region, the e.m.f. of an electrochemical cell of the Cu/CuBr/Sample/C type is the relative height of the Fermi level of electrons (holes). The theory of the method was developed by C. Wagner [27]. Wagner, taking into account that diffusion in a mixed electron-ion conductor occurs much faster than in a CuBr electrolyte, obtained the expression for the e.m.f. of an electrochemical cell of Pt/Cu/CuBr/Sample/Pt

$$E = -\frac{\mu_{Cu} - \mu_{Cu}^0}{e}, \quad (2)$$

where μ_{Cu} is the chemical potential of a copper atom in the sample, μ_{Cu}^0 is the chemical potential of a copper atom in metallic copper.

Due to the strong disordering of the cation sublattice of the studied objects, the chemical potential of copper ions depends weakly on the small redistribution of copper in the sample with a change in temperature, then, according to formula *(2)*, the e.m.f. E of the electrochemical cell is determined only by the change in the chemical potential of electrons, representing the height of the Fermi level in the sample relative to the Fermi level in the copper electrode [15; 27]. This made it possible to relate the temperature dependence of the properties of these materials to the change in the position of the Fermi level.

Fig. 3 shows the dependences of the electron conductivity (a) and the Seebeck coefficient (b) of the $Cs_{0.04}Cu_{1.96}S$ sample on the e.m.f. of the Cu/CuBr/ $Cs_{0.04}Cu_{1.96}S$ /C electrochemical cell. It is evident that the course of the dependence changes sharply as a result of the phase transition. The phase transition occurs at an e.m.f. E ≈ 230 mV, which corresponds to a temperature of about 664 K. The maximum of the Seebeck coefficient for $Cs_{0.04}Cu_{1.96}S$ in Figure 2d corresponds exactly to this temperature.

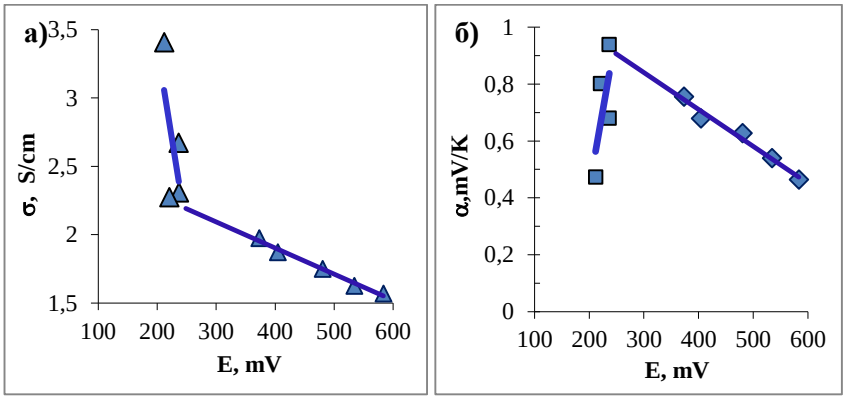


Fig. 3. Dependences of the electron conductivity (a) and the Seebeck coefficient (b) of the $Cs_{0.04}Cu_{1.96}S$ sample on the e.m.f. of the electrochemical cell Cu/CuBr/ $Cs_{0.04}Cu_{1.96}S$.

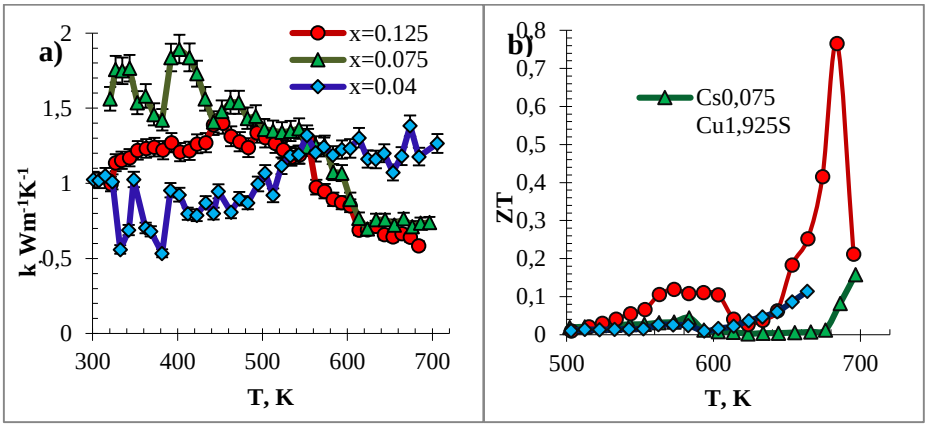


Fig. 4. Temperature dependences of thermal conductivity (a) and dimensionless thermoelectric figure of merit (b) of $Cs_xCu_{2-x}S$ alloys (x = 0.04, 0.075, 0.125).

Above 650 K there is also a region of semiconductor dependence of conductivity, in which the activation energy of carriers is significantly higher – 0.257 eV for the $Cs_{0.04}Cu_{1.96}S$ composition, 1.4 eV for $Cs_{0.075}Cu_{1.925}S$, and 0.273 eV for $Cs_{0.125}Cu_{1.875}S$. It is possible that this energy characterizes the difference in Fermi levels in the spatial region of the phase transition from the hexagonal to the cubic modification of copper sulfide in the sample.

The temperature dependences of the thermoelectric power P of the samples are shown in *Fig.* 2c. The dependence P (T) was affected by all the anomalies noted for the behavior of electrical conductivity (*Fig.* 2a) and the Seebeck coefficient (*Fig.* 2b), so it has a complicated character.

The thermal conductivity of the samples (*Fig*. 4a) has low values between 0.5 and 1.9 W m^{-1} K^{-1}, which is typical for a highly disordered structure of superionic conductors, suppressing the propagation of phonons [15; 28]. For the composition with a cesium content of x = 0.04, the thermal conductivity increases with increasing temperature after the phase transition, whereas for the other two compositions, with a cesium content above the solid solubility limit,

the thermal conductivity decreases. Figure 4b shows the temperature dependences of the dimensionless thermoelectric figure of merit ZT of the samples. In general, the studied series of samples showed insufficiently high ZT values for practical application, with the exception of the 550–600 K region for the $Cs_{0.125}Cu_{1.875}S$ composition and the region around the phase transition in the same sample, where a significant peak of ZT = 0.76 is achieved at a temperature of 684 K. We believe that optimization of the vacancy concentration in the metal sublattice will significantly improve the achieved indicators.

Conclusion

Synthesized submicrocrystalline cesium-containing copper sulfides of the $Cs_{0.04}Cu_{1.96}S$, $Cs_{0.075}Cu_{1.925}S$, and $Cs_{0.125}Cu_{1.875}S$ compositions have semiconductor properties. An increase in the electrical conductivity of the alloys with an increase in the cesium content was found, while the Seebeck coefficient, accordingly, decreases. The found activation energies of conductivity up to 370 K are 0.076 eV, 0.064 eV, and 0.036 eV for the $Cs_{0.04}Cu_{1.96}S$, $Cs_{0.075}Cu_{1.925}S$, and $Cs_{0.125}Cu_{1.875}S$ compositions, respectively. For all compositions, a sharp drop in conductivity is noted when heated above 600 K, which is associated with the transition of the alloys to the cubic phase based on copper sulfide, which is characterized by low conductivity.

Above 650 K there is also a region of semiconductor dependence of conductivity, in which the activation energy of carriers is significantly higher – 0.257 eV for the composition $Cs_{0.04}Cu_{1.96}S$, 1.4 eV for $Cs_{0.075}Cu_{1.925}S$, and 0.273 eV for $Cs_{0.125}Cu_{1.875}S$. High values of Seebeck coefficient from 0.10 to 1.4 mV/K are observed in the temperature range above 560 K, which is important for possible thermoelectric applications. For the composition $Cs_{0.125}Cu_{1.875}S$ the high thermoelectric figure of merit ZT = 0.76 at 684 K was obtained.

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Received 26.04.2026.

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