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## Investigation of thermoelectric properties of nanocrystalline copper chalcogenides

Modern research efforts are aimed at developing fuel cells characterized by high efficiency, low cost and environmental friendliness, which largely depend on the properties of the corresponding catalyst materials — the most important components of the fuel cell. Catalysts based on metal chalcogenides, predominantly S based, have activity in accelerating the oxygen reduction reaction comparable to the activity of Pt in H<sub>2</sub>SO<sub>4</sub>. The work uses the technique of compacting powder materials and obtained volumetric samples. Nanodisperse powder fractions with an average particle size of (50–100) nm were obtained. The values of the thermo-emf coefficient (about 0.08 mV/K) were obtained for the studied alloy with low defects in the cation sublattice of the Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub> type. It was found that a decrease in grain size leads to a significant decrease in electronic conductivity for all studied samples. The paper presents the results of a study of the thermoelectric properties of the Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub> triple alloy. For the studied composition, a decrease in thermal conductivity by (25–30)% and a slight increase in the thermal emf coefficient compared with large-crystal samples were obtained. Low thermal conductivity was found in the range (0.3–1.1) W m<sup>-1</sup> K<sup>-1</sup> with a conductivity above 1000 ohms-1cm-1. For the studied sample Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub> — thermoelectric efficiency (ZT = 0.25) at 400 °C, which allows us to hope for the possibility of improving the characteristics of samples of this composition to acceptable values for practical thermoelectric devices by selecting the optimal alloying.

*Keywords:* thermoelectric materials; copper sulfide; crystal structure; conductivity; diffusion; thermal conductivity; Seebeck coefficient; superionic conductors.

### Introduction

The current efforts of researchers are aimed at developing fuel cells characterized by high efficiency, low cost and environmental compatibility, which largely depend on the properties of the corresponding catalyst materials (the most important components of the fuel cell) [1]. Currently, the best and most commonly used catalysts for fuel cells are still noble metal nanocomposites (catalysts (the most important components of a fuel cell), especially Pt), if we take into account their comparable catalytic characteristics relative to ORR and much lower cost [1].

Metal chalcogenide-based catalysts, mainly based on Se and S, again attracted considerable attention after Alonso-Vante and Tributsch [2] found that Ru<sub>2</sub>Mo<sub>4</sub>Se<sub>8</sub> has an activity in accelerating the oxygen reduction reaction comparable to the activity of Pt in H<sub>2</sub>SO<sub>4</sub> [3, 4]. Many metals forming chalcogenides with S, Se and Te have shown good activity of the oxygen reduction reaction (ORR) [1–4].

### Experimental part

The method of synthesis of thermoelectric materials

Due to the high reactivity of tellurium, the synthesis of the required Cu<sub>2-x</sub>Te<sub>x</sub>S samples took place in two stages:

1. First, non-stoichiometric compositions of Cu<sub>2-x</sub>S were obtained.

2. The second stage of the preparation of Cu<sub>2-x</sub>Te<sub>x</sub>S samples consisted in the introduction of tellurium instead of the copper missing to the stoichiometric composition in such a way that for the metal as a whole. The binary alloy obtained after homogenization was ground in an agate mortar and placed in quartz ampoules filled with argon, pieces of lithium were placed inside the ampoules of the powder so that they did not come into contact with the walls of the ampoule.

The synthesis temperature was reached within three days with a gradual increase in temperature. The furnace was slowly heated to melt lithium and held for several hours until it dissolved in reagents. The final stage of the synthesis of the substance took place at a temperature of 450 °C for three days.

### Results and discussion

#### The results of alloy synthesis $\text{Cu}_2\text{S}_y\text{Te}_{1-y}$

Triple  $\text{Cu}_2\text{S}_y\text{Te}_{1-y}$  alloys were synthesized. Strong alloying or substitution is in line with the modern strategy of optimizing the thermoelectric properties of materials [5–8].

Table shows the results of X-ray spectral analysis of the chemical composition of the  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$  alloy. The chemical composition was determined by averaging measurements at three different points on the surface. The sample was in the form of a fine powder.

The presence of a noticeable amount of oxygen in the sample indicates a significant oxidation of the surface. Taking into account the formation of an oxide film, the chalcogenide composition on the surface corresponds to the chemical formula  $\text{Cu}_{1.84}\text{S}_{0.37}\text{Te}_{0.63}$ . The lack of copper in the composition compared to the charge composition is caused by the action of oxygen. The excess of tellurium and the lack of tellurium relative to the composition of the charge can be explained by significant evaporation of sulfur during synthesis, which took place in a loosely closed ampoule in the presence of argon.

T a b l e

**Results of X-ray spectral analysis of the chemical composition  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$**

| Atom %  | S   | Cu   | Se | Fe   | O     | Te    | Sum    |
|---|-----|------|----|------|-------|-------|--------|
| $\text{Cu}_{1.84}\text{S}_{0.37}\text{Te}_{0.63}$ | 9.9 | 60.1 | 0  | 0.94 | 12.11 | 16.94 | 100.00 |

When replacing tellurium with sulfur in copper telluride, the band gap gradually changes. This leads to a change in both the equilibrium concentration of charge carriers and the values of the the Seebeck coefficient.

Figure 1 shows the results of a study of the Seebeck coefficient of the sample  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$ . In general, with increasing temperature, the thermo-EMF coefficient increases, but there are small steps in the temperature dependence at 540 K, 620 K and 700 K. The  $\alpha$  values are significantly higher than in  $\text{Cu}_2\text{Te}$ , but slightly lower than in  $\text{Cu}_2\text{Te}$ .

The thermo-EMF coefficient, as is known, directly depends on the position of the Fermi level and on the scattering factor of charge carriers. In the materials under study, it is possible to determine electrochemically the relative height of the Fermi electron level directly during the experiment on measuring thermo-EMF.

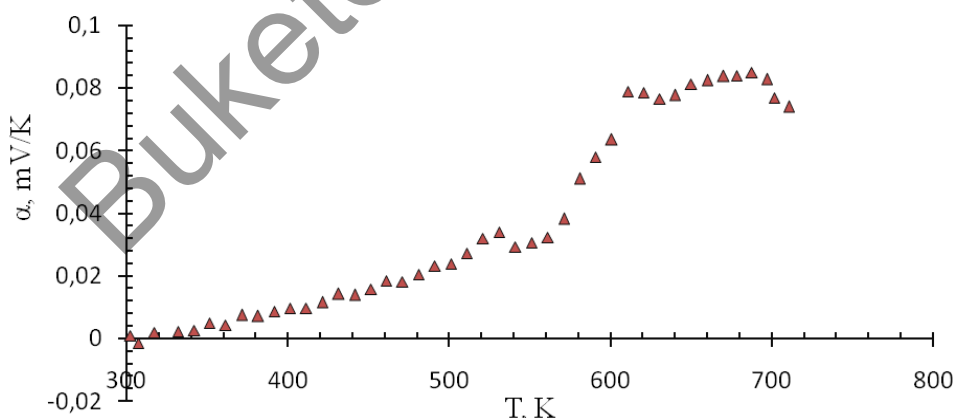


Figure 1. Temperature dependence of the coefficient of electronic thermo-emf of a coarse-grained sample  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$

Figure 2 shows the temperature dependence of the EMF ( $E$ ) of the electrochemical cell  $\text{Cu}/\text{CuBr}/\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}/\text{Pt}$ , which essentially shows the movement of the Fermi electron level in the studied phase  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$  relative to the Fermi level of electrons in the copper electrode with increasing temperature.

The break in the dependence  $E(T)$  at 620 K is associated with a phase transition in  $\text{CuBr}$ , since at (600–620) K it completes the transition to a high-temperature superionic phase. Above 630 K, a linear dependence  $E(T)$  is observed, which makes it possible to determine the entropy of copper atoms in a sample by the slope of the graph according to the method described in [9].

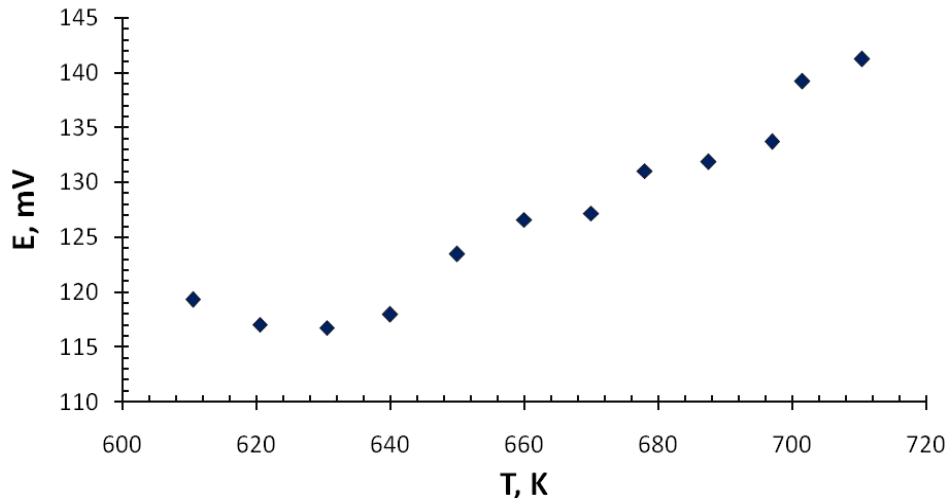


Figure 2. Temperature dependence of the EMF of an electrochemical cell Cu/CuBr/Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub>/Pt

Figure 3 shows the dependence of the coefficient of thermal EMF of the alloy Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub> on the EMF Cu/CuBr/Cu<sub>2</sub>S<sub>0</sub>. Figure 3 — Dependence of the thermo-EMF coefficient of coarse-grained 5Te<sub>0.5</sub>/Pt. The dependence has a break at 130 mV, which corresponds to a temperature of about 680 K (according to Figure 2). From Figure 1 it can be seen that the temperature dependence of the Seebeck coefficient also has a break at 680 K.

In general, the investigated triple compounds of the Cu<sub>2</sub>S<sub>y</sub>Te<sub>1-y</sub> type show the values of the thermal EMF coefficient significantly lower than those of pure copper sulfide and lithium-doped copper sulfide.

Electronic conductivity and thermal EMF of Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub>.

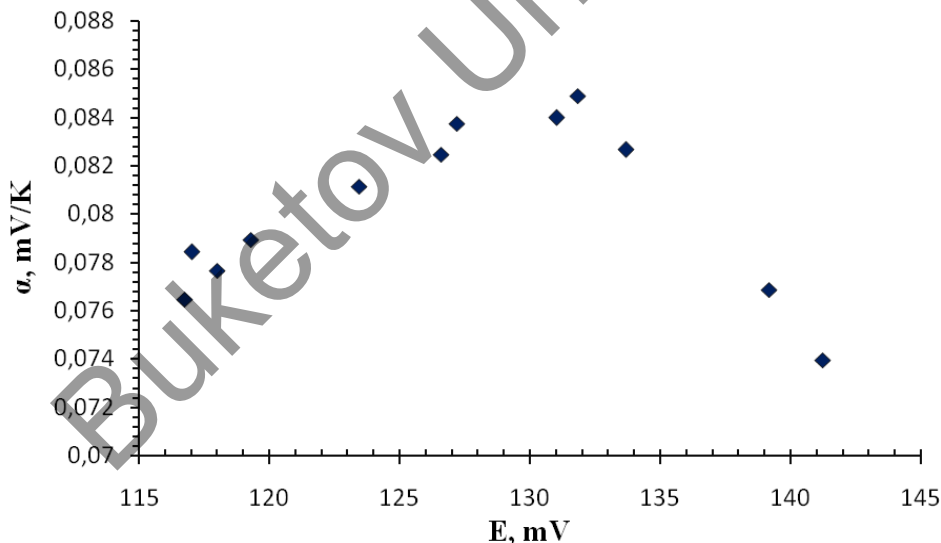


Figure 3. Dependence of the thermo-EMF coefficient of coarse-grained Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub> from the EMF of an electrochemical cell Cu/ CuBr/Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub>/Pt

Figure 4 shows the temperature dependence of the electron conductivity of coarse-grained Cu<sub>2</sub>S<sub>0.5</sub>Te<sub>0.5</sub>.

In general, the investigated triple compounds of Cu<sub>2</sub>S<sub>y</sub>Te<sub>1-y</sub> type show the values of the thermal EMF coefficient significantly lower than those of pure copper sulfide and lithium-doped copper sulfide.

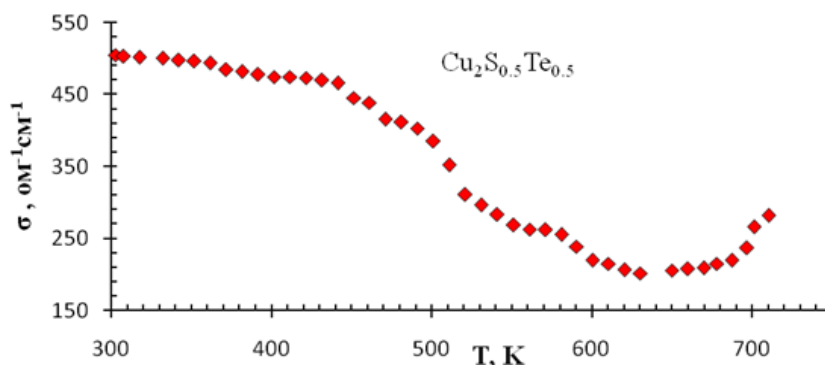


Figure 4. Temperature dependence of the electron conductivity of coarse-grained  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$

The thermal conductivity of  $\text{Cu}_2\text{S}_y\text{Te}_{1-y}$ . Figure 5 shows the thermal conductivity results of three alloys of the  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$  triple system. Low thermal conductivity values were found (from 0.4 to 0.6  $\text{W m}^{-1} \text{K}^{-1}$ ).

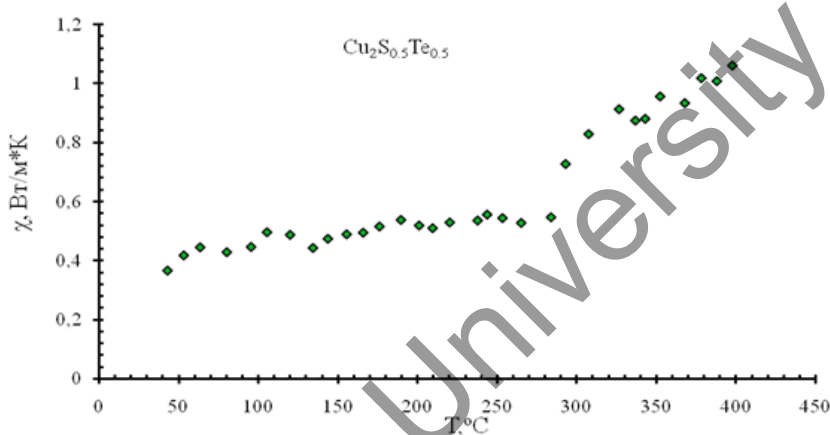


Figure 5. Temperature dependence of the thermal conductivity coefficient of a solid solution  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$

#### Thermoelectric efficiency of $\text{Cu}_2\text{S}_y\text{Te}_{1-y}$ .

Figure 6 shows the temperature dependence of the thermoelectric efficiency  $ZT$  of coarse-grained  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$ . The observed values of thermoelectric efficiency — 0.25 at 400° C allow us to hope for the possibility of improving the characteristics of samples of this composition to acceptable values for practical thermoelectric devices by selecting the optimal alloying.

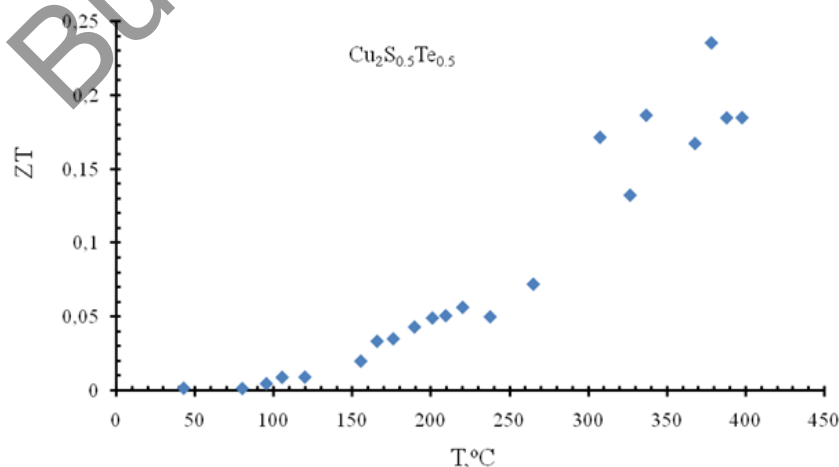


Figure 6. Temperature dependence of the thermoelectric efficiency of a coarse-grained alloy sample  $\text{Cu}_2\text{S}_{0.5}\text{Te}_{0.5}$

### Conclusion

To optimize the thermoelectric properties of the materials, the substitution of tellurium with nonstoichiometric copper sulfide was used.

The materials obtained are of particular interest for use as a catalyst (the most important components of a fuel cell).

Nanostructuring was used to reduce the thermal conductivity of materials, which has a positive effect on the thermoelectric efficiency of the material. For the studied composition, nanostructured samples showed a decrease in thermal conductivity by (25–30) % and a slight increase in the thermal emf coefficient compared with large-crystal samples. Low thermal conductivity was found in the range (0.3–1.1) W m<sup>-1</sup> K<sup>-1</sup> with a conductivity above 1000 ohm<sup>-1</sup>cm<sup>-1</sup>. However, it was not possible to obtain simultaneously high values of the Seebeck coefficient for the non-stoichiometric composition studied by us. Since the thermoelectric, electrical and thermal properties of chalcogenides are very sensitive to non-stoichiometry of the composition, it is possible that higher indicators of thermoelectric efficiency can be achieved by selecting the optimal degree of non-stoichiometry of the composition [10–12].

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## Нанокристалды мыс халькогенидтерінің термоэлектрлік қасиеттерін зерттеу

Зерттеушілердің заманауи күш-жігері катализаторлардың тиісті материалдарының қасиеттеріне, яғни отын элементінің маңызды компоненттеріне байланысты жоғары тиімділікпен, төмен бағамен және экологиялық таза болуымен сипатталатын отын элементтерін дамытуға бағытталған. Металл халькогенидтеріне негізделген, негізінен S сипатындағы катализаторлар  $\text{H}_2\text{SO}_4$ -тегі Pt белсенділігімен салыстырылатын оттегінің тотықсыздану реакциясын жеделдету белсенділігіне ие. Жұмыста ұнтақты материалдарды ықшамдау әдісі қолданылған және көлемді үлгілер алынған. Бөлшектердің орташа мөлшері (50–100) нм болатын нанодисперсті ұнтақ фракциялары алынды. Термо-экс коэффициентінің мәндері (шамамен 0,08 м В/К)  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$  типті катиондық тор бойынша ақауы аз зерттелетін қорытпа үшін алынған. Түйіршіктер мөлшерінің азаюы барлық зерттелетін үлгілер үшін электронды өткізгіштіктің айтарлықтай төмендеуіне әкелетіні анықталды. Мақалада  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$  үштік қорытпасының термоэлектрлік қасиеттерін зерттеу нәтижелері келтірілген. Зерттелген құрам үшін жылу өткізгіштіктің 25–30%-ға төмендеуі және ірі кристалды үлгілермен салыстырғанда термо-экс коэффициентінің шамалы өсуі алынды.  $1000 \text{ Ом}^{-1}\text{см}^{-1}$  -ден жоғары өткізгіштік кезінде (0,3–1,1) Вт  $\text{м}^{-1} \text{К}^{-1}$  диапазонында төмен жылу өткізгіштік анықталды. Зерттелетін үлгі үшін  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$ – 400 °С температурада термоэлектрлік тиімділік (ZT= 0,25), бұл оңтайлы легирлеуді таңдау арқылы практикалық термоэлектрлік құрылғылар үшін осы құрамның үлгілерінің өнімділігін қолайлы шамаларға дейін жақсарту мүмкіндігіне үміттенуге мүмкіндік береді.

*Кілт сөздер:* термоэлектрлік материалдар, мыс сульфиді, кристалдық құрылым, өткізгіштік, диффузия, жылу өткізгіштік, Зеебек коэффициенті, суперионды өткізгіштер.

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## Исследование термоэлектрических свойств нанокристаллических халькогенидов меди

Современные усилия исследователей направлены на разработку топливных элементов, характеризующихся высокой эффективностью, низкой стоимостью и экологичностью, которые во многом зависят от свойств соответствующих материалов катализаторов — важнейших компонентов топливного элемента. Катализаторы на основе халькогенидов металлов, преимущественно на основе S, обладают активностью в ускорении реакции восстановления кислорода, сравнимой с активностью Pt в  $\text{H}_2\text{SO}_4$ . В статье использована методика компактирования порошковых материалов и получены объемные образцы. Получены фракции нанодисперсного порошка со средним размером частиц (50–100) нм. Значения коэффициента термо-эдс (порядка 0,08 мВ/К) получены для исследуемого сплава с малой дефектностью по катионной подрешетке типа  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$ . Установлено, что уменьшение размеров зерен приводит к значительному снижению электронной проводимости для всех исследуемых образцов. Авторами представлены результаты исследования термоэлектрических свойств тройного сплава  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$ . Для исследованного состава было получено снижение теплопроводности на 25–30 % и небольшое возрастание коэффициента термо-эдс по сравнению с крупнокристаллическими образцами. Обнаружена низкая теплопроводность в диапазоне 0,3–1,1 Вт  $\text{м}^{-1}\text{К}^{-1}$  при проводимости выше  $1000 \text{ Ом}^{-1}\text{см}^{-1}$ . Для исследуемого образца  $\text{Cu}_2\text{S}_{0,5}\text{Te}_{0,5}$  — термоэлектрическая эффективность ZT = 0,25 при 400 °С, что позволяет надеяться на возможность улучшения характеристики образцов этого состава до приемлемых величин для практических термоэлектрических устройств за счет подбора оптимального легирования.

*Ключевые слова:* термоэлектрические материалы, сульфид меди, кристаллическая структура, проводимость, диффузия, теплопроводность, коэффициент Зеебека, суперионные проводники.

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