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THERMAL CONDUCTIVITY AND THERMAL EMF OF NANOCRYSTALLINE COPPER SULFIDES $K_{0,01}CU_{1,85}S$ AND $K_{0,04}CU_{1,85}S$

Utilization of the thermoelectric materials in cooling/heating, converting used heat into electrical energy becomes the crucial phenomenal investigation, which new thermoelectric materials have been discovered every day. Thermoelectric materials often require a description of the electrical conductivity and thermoelectric power of the sample from room temperature to 900 K. This paper is presented the study results in thermal conductivity and heat capacity of nanocrystalline copper sulfides $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$ at the temperature range between 300 K and 700 K. As well as, this work shows the figures of X-ray phase analysis, differential scanning calorimetry (DSC) and differential thermal analysis of alloys. In the investigated temperature range Zeebeck coefficient α for $K_{0,01}Cu_{1,85}S$ fluctuate all around the period, but the figures for $K_{0.04}Cu_{1.85}S$ increase to reaching a pick of around 1.96 mV/K, before falling to around 0.32 mV/K. For the studied alloys, a strong contrast in electronic conductivity in both components of the alloy was observed and a dramatic decrease in thermal conductivity (from 2.0 to 0.5 W · m^{-1} · K^{-1}), leading to the very high local peak value of the dimensionless thermoelectric figure of merit ZT = 9.67, which is important for possible technical applications. We compared and analyzed obtained data with previous materials and focused on the estimation of the thermoelectric figure of merit of the nanocrystalline copper sulfides.

Key words: nanocrystalline copper sulfides, thermal conductivity, X-ray phase analysis, differential scanning calorimeter, differential thermal analysis, heat capacity, Zeebeck coefficient, electronic conductivity, thermoelectric figure of merit ZT.

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$K_{0,01}Cu_{1,85}S$ және $K_{0,04}Cu_{1,85}S$ нанокристалды мыс сульфидтерінің термоэффект және жылуөткізгіштігі

Термоэлектрлік материалдарды салқындату / жылыту кезінде пайдалану, пайдаланылған жылуды электр энергиясына айналдыру күн сайын жаңа термоэлектрлік материалдарды ашатын маңызды феноменальды зерттеуге айналады. Бұл мақалада $K_{0,01}Cu_{1,85}S$ және $K_{0,04}Cu_{1,85}S$ нанокристалды мыс сульфидтерінің жылу өткізгіштігі мен жылу ЭҚК-ін 300 к-ден 700 К-ге дейінгі температура диапазонында зерттеу нәтижелері келтірілген. Сондай-ақ, бұл жұмыста рентгендік фазалық талдау, дифференциалды сканерлеу калориметрі (ДСК), қорытпалардың дифференциалды термиялық талдауы көрсетілген. Зерттелетін температура диапазонында $K_{0,01}Cu_{1,85}S$ үшін Зеебек коэффициенті α бүкіл кезең ішінде өзгереді, бірақ $K_{0,04}Cu_{1,85}S$ көрсет-кіштері шамамен 0,32 мВ/К мәніне түскенге дейін шамамен 1,96 мВ/К-ға дейін артады. Зерттелетін қорытпалар үшін қорытпаның екі қосылысында да электронды өткізгіштікте күшті контраст және жылу өткізгіштіктің күрт төмендеуі (2,0-ден 0,5 Вт-қа дейін m^{-1} · K^{-1}) байқалды, бұл ZT = 9,67 өлшемсіз термоэлектрлік сапа индикаторының өте жоғары шыңына әкеледі, бұл мүмкін техникалық құрылғылар үшін маңызды. Біз алынған деректерді алдыңғы материалдармен салыстырып, талдадық және нанокристалды мыс сульфидтерінің термоэлектрлік сипаттамаларын бағалауға назар аудардық.

Түйін сөздер: нанокристалды мыс сульфидтері, жылу өткізгіштік, рентгендік фазалық талдау, дифференциалды сканерлеу калориметрі, дифференциалды жылу анализі, жылу сыйымдылығы, Зеебек коэффициенті, электронды өткізгіштік, ZT термоэлектрлік сипаттамасы.

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Теплопроводность и термо-ЭДС нанокристаллических сульфидов меди $K_{0,01}Cu_{1,85}S$ и $K_{0,04}Cu_{1,85}S$

Использование термоэлектрических материалов для охлаждения/нагрева и преобразования использованного тепла в электрическую энергию становится важнейшим феноменальным исследованием, в котором каждый день обнаруживаются новые термоэлектрические материалы. Термоэлектрические материалы часто требуют описания электропроводности и термоэлектрической мощности образца в пределах от комнатной температуры до 900 К. В данной статье представлены результаты исследования теплопроводности и термо-ЭДС нанокристаллических сульфидов меди $K_{0,01}Cu_{1,85}S$ и $K_{0,04}Cu_{1,85}S$ в диапазоне температур от 300 К до 700 К. Также в этой работе представлены показатели рентгенофазового анализа, дифференциального сканирующего калориметра (DSC), дифференциального термического анализа сплавов. В исследуемом диапазоне температур коэффициент Зеебека α для $K_{0,01}Cu_{1,85}S$ колеблется в течение всего периода, но показатели для $K_{0,04}Cu_{1,85}S$ увеличиваются до значения около 1,96 мВ/К, прежде чем упасть примерно до 0,32 мВ/К. Для исследуемых сплавов получен сильный контраст в электронной проводимости в обоих соединениях сплава и резкое снижение теплопроводности (с 2,0 до 0,5 Вт $\cdot м^{-1}К^{-1}$), что приводит к очень высокому пиковому значению безразмерного термоэлектрического показателя качества ZT = 9,67, что важно для возможных технических устройств. Мы сравнили и проанализировали полученные данные с предыдущими материалами и сосредоточились на оценке термоэлектрических характеристик нанокристаллических сульфидов меди.

Ключевые слова: нанокристаллические сульфиды меди, теплопроводность, рентгенофазовый анализ, дифференциальный сканирующий калориметр, дифференциальный термический анализ, теплоемкость, коэффициент Зеебека, электронная проводимость, термоэлектрическая характеристика ZT.

Introduction

Today, with limited fossil fuel reserves, as well as climate change, people's demand for energy is increasing day by day. in this regard, it is very important to find clean renewable energy sources while preserving the environment. Currently, most energy production/conversion techniques are based on thermal processes that produce a large amount of residual/waste heat released into the environment [1-2]. The use of this residual heat for energy increases the efficiency of all these processes. In this sense, thermoelectric devices encourage a unique opportunity with significant advantages in comparison with other types of transformations [3-4]. For the region in thermoelectric materials, it is necessary to identify many properties, such as maximizing the thermoelectric characteristics (ZT) of the material, a large thermal capacity, high electrical conductivity, and low thermal conductivity. Since these transport characteristics depend on the properties of the material, to determine several parameters to increase the ZT is essential [5-6]. The figure of merit, ZT, is determined by

$$ZT = \alpha^2 \sigma T / k, \quad (1)$$

where, α is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature.

Copper sulfides ($Cu_{2-x}S$ ($0 \le x \le 1$)) are used continuously in superionic materials, optical filters, nanoparticles, solar cells, high-capacity cathode materials for lithium batteries, catalysts, and nonlinear optical materials [7]. It ranges from chalcocite (Ch) Cu_2S to covellite (Cv) Cu-poor Cu,which corresponds to the stoichiometric number (2−x), as well as, many intermediate stages have also been reported, such as djurleite (Dj) $Cu_{1.96}S$, digenite (Dg) $Cu_{1.8}S$, and anilite (an) Cu_7S_4 [8-9].

The work [10] presented the obtained results on the $K_xCu_{1.97-x}S$ alloys in the temperature range between 300 and 700 K. According to the results of X-ray phase analysis, a mixture of different phases of copper sulfide was found, such as $Cu_{1.96}S$ (tetragonal djurleite) and Cu_2S (monocline chalcocyte) for the $K_{0.01}Cu_{1.96}S$, and $Cu_{1.97}S$ (monocline djurleite), Cu_2S (monocline chalcocite) for the $K_{0.05}Cu_{1.94}S$ alloy. As for the DSC curves of all alloys, it was shown that all compositions have an endothermic thermal effect in the temperature range of 722-743 K. For binary Cu_2S, the thermal peak in [10] corresponds to 737 K, while according to the literature data analyses, it occurs at 710 K according to the latest data [11], but there are also Hirahara data on the transition temperature of ≈ 740 K [12]. It is possible also that the K doping and nanoscale of grains affects the phase transition temperatures in [10].

The scope of research on the replenishment of copper sulfide with alkali metals is rapidly developing, in this work we present the study results on the phase composition and electrical properties of potassium-doped copper sulfide ($K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$).

Materials and methods

Preparation and certification of samples

In this paper, a simple and convenient method for synthesizing nanocrystalline copper sulfide, characterized by the chemical formula $K_xCu_{1.85}S$ (x=0.01, 0.04), were developed. Initially, semiconductor alloys $K_{0,01}Cu_{1,85}S$ and $K_{0\ 04}Cu_{1,85}S$ were synthesized in a melt of a mixture of NaOH and KOH hydroxides at a temperature of about 165 ^oC. All reagents (CuCl, KCl, Na2S*9H2O) were placed in a heated teflon vessel simultaneously. The nanostructure was formed within a few hours. Then the resulting product was washed with distilled heated water, then with pure ethanol, finally, dried at 60 °C [13].

The phase composition of the samples was studied using X-ray diffractometry at room temperature, additionally, phase transitions were studied by differential scanning calorimetry (DSC). The chemical composition was determined by the ratio of the reagents incorporated in the synthesis and controlled by X-ray fluorescence analysis. Differential scanning calorimetry (DSC) of materials was performed on the NETZSCH STA 449 F1 Jupiter device. The heating rate was 10 K/min. The measurements were carried out in an inert argon medium [14-15].

Method of measuring kinetic parameters

To measure the transport characteristics, tablets in the form of parallelepipeds with dimensions of 2 ×5 ×20 mm were compressed from the powder under a pressure of 3-5 t/cm^2. Annealing of the tablets was carried out in an argon medium at 400 ^oC for 8 hours. The electronic conductivity was measured at direct current by a four-probe method with two current directions to exclude the contribution of thermal EMF. The measurement error did not exceed 4-5%. Measurements of thermal conductivity and thermal conductivity were carried out by heating with a powerful light pulse on the LFA 467 HT HyperFlash device (NETZSCH, Germany) [16].

Results and Discussion

X-ray phase analysis

Figure 1 shows the XRD pattern of the nanocrystalline copper sulfides $K_{0,01}Cu_{1,85}S$ and $K_{0.04}Cu_{1.85}S$.

According to the results of X-ray phase analysis, the results of X-ray phase analysis show that the $K_xCu_{1.85}S$ samples at room temperature consist of a mixture of different phases of copper sulfide. In fact, X-ray lines of $Cu_{1.85}S$ cubic phase, Cu_2S cubic phase, $Cu_{17}S_9$ ($Cu_{1.89}S$) rhombohedral phase, Cu_2S tetragonal phase and traces of metallic potassium can be seen in both samples. The crystallite sizes were estimated by the width of the X-ray lines.

Differential Scanning Calorimetry

Figure 2 shows the DSC curves of the $K_xCu_{1.85}S$ (x = 0.01, 0.04) samples in temperature range of 300 – 700 K.

Endothermic peaks at 369.9 K and 371.6 K are seen for $K_{0.01}Cu_{1.85}S$ (a) and $K_{0.04}Cu_{1.85}S$ correspondingly on DSC curves on Figure 2.

Between phase transitions known in Cu-S system in range of these temperatures, a superionic phase transition from monoclinic to hexagonal chalcocite Cu_2S which occurs at 376 K [11] can be take into account. At 364 K, a transition from the low-temperature rhombohedral modification of $Cu_{1.89}S$ to the medium-temperature hexagonal modification also occurs [11]. Thus, considering the results of X-ray phase analysis, the endothermic thermal effect at about 370 K most likely reflects the structural transformation of monoclinic chalcocite Cu_2S into the hexagonal superionic modification.

As it is seen in Figure 2, the alloy with a higher potassium content ($K_{0.04}Cu_{1.85}S$) has a strong thermal effect at about 465 K, which is absent for pure $Cu_{1.85}S$, but this effect is slightly visible for $K_{0.01}Cu_{1.85}S$ near 485 K (Figure 2a). Okamoto and Kawai [17] observed a phase transition from the metastable tetragonal $Cu_{1.96}S$ phase to the hexagonal one at about 453 K. In the work [18], endothermic DSC peaks at 448 K and 451 K were obtained for $K_{0.25}Cu_{1.70}S$ and $Cu_{1.75}S$ nanocrystals. We believe that this thermal effect at about 465 K in $K_{0.04}Cu_{1.85}S$ is caused by the transition of the metastable tetragonal phase Cu_2S, revealed by X-ray phase analysis at room temperature, into the hexagonal phase Cu_2S.

In figure 2 we also see the thermal effect at 643.7 K for $K_{0.04}Cu_{1.85}S$. Its origin is not clear since it was not observed for copper sulfides earlier. Perhaps it is associated with the dissolution of existing sodium residues in the crystal lattice of the alloy.

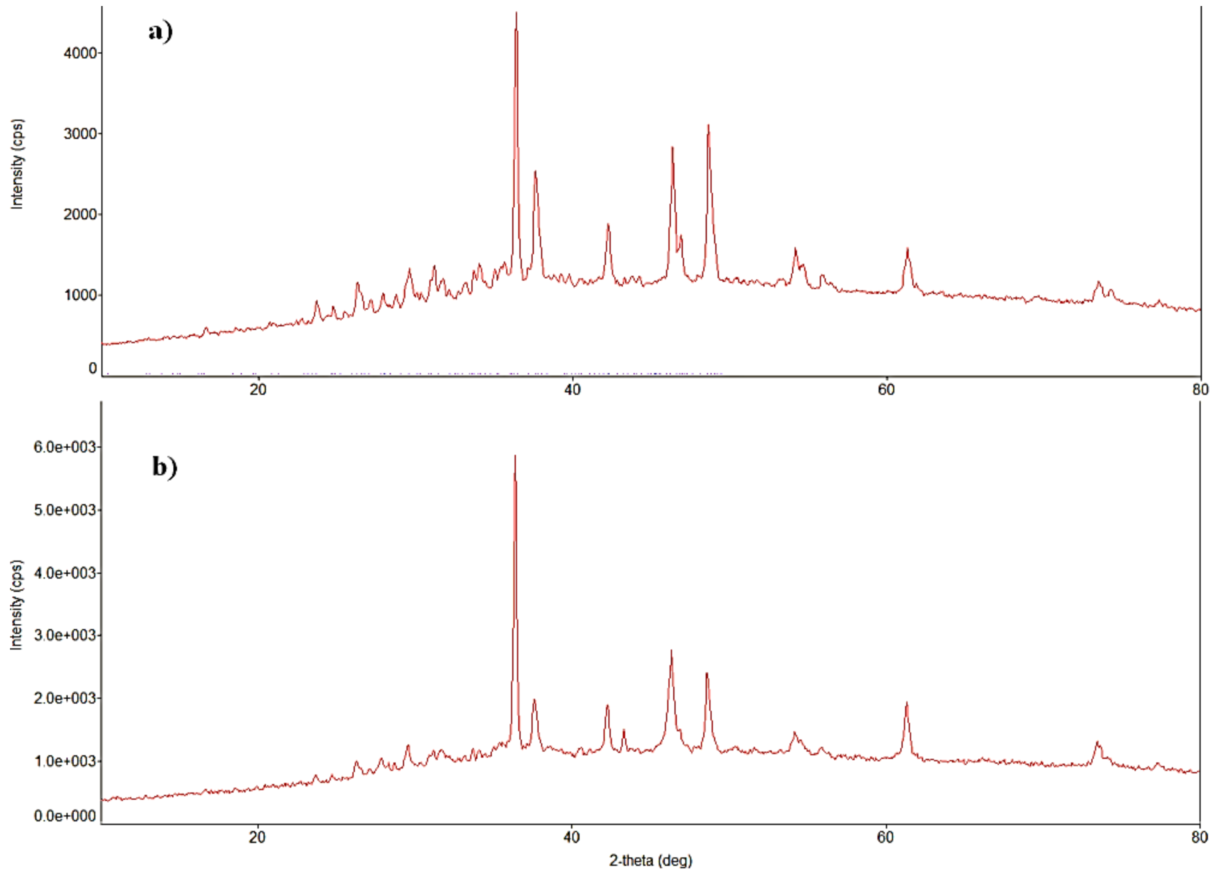

Figure 1 – X-ray spectra of samples $K_{0.01}Cu_{1.85}S$ (a) and $K_{0.04}Cu_{1.85}S$ (b)

For both samples, an endothermic thermal effect is observed near 690 K. In copper sulfide at 710 K, the phase transition occurs from the hexagonal to the cubic Cu_2S phase [11], and it is known that the lack of copper in the lattice reduces the phase transition temperature. Obviously, the observed thermal effect near 690 K in Figure 2 is caused by this phase transition.

The temperature dependences of the heat capacity in Figure 2 demonstrate the same thermal effects discussed above. It is noticeable in Figure 2 that the heat capacity initially decreases to about 525 K and then increases if to ignore thermal effects at phase transformations. Minimal value of the heat capacity is about 0.1 J $g^{-1}K^{-1}$ for both samples.

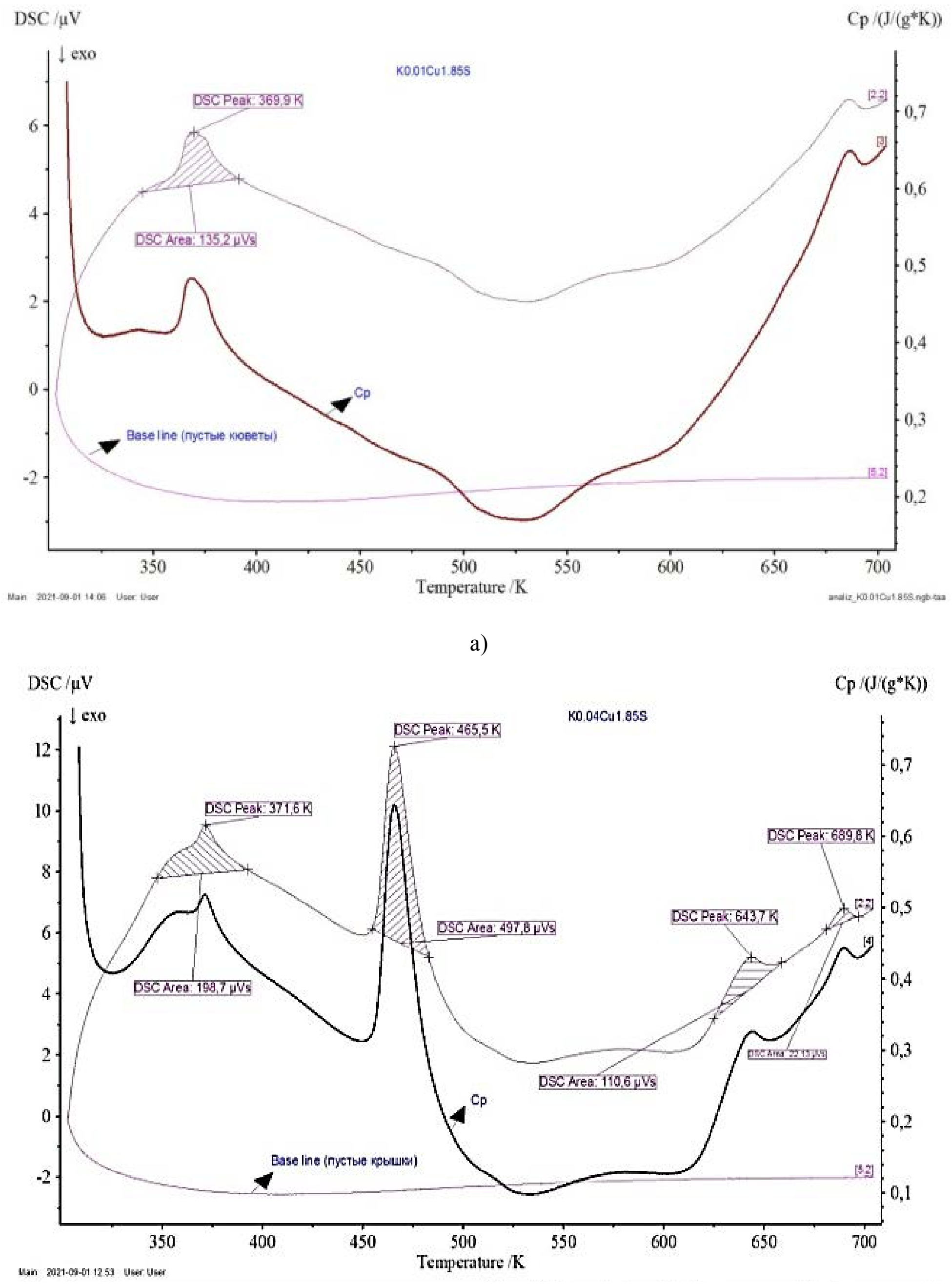

Figure 2 – DSC curves and thermal capacities of samples $K_{0.01}Cu_{1.85}S$ (a) and $K_{0.04}Cu_{1.85}S$ (b)

Thermal conductivity

The temperature-dependent graph of the thermal conductivity of the alloy is presented in Figure 3. In all measurements, the value of thermal conductivity in the temperature zone initially began with k ≈ 2 W $K^{-1}m^{-1}$, and then gradually approached (or dropped below) the value of 0.2 W $K^{-1}m^{-1}$, which is close to the glass limit (0.3 W $K^{-1}m^{-1}$). Low *k* values in the superionic Cu_2S phase caused by absence of long-range order in the cation sublattice, which suppresses the propagation of phonons. The decrease in thermal conductivity below the "glass" limit is due to numerous defects in the nanoscale material, which create additional obstacles to the movement of phonons.

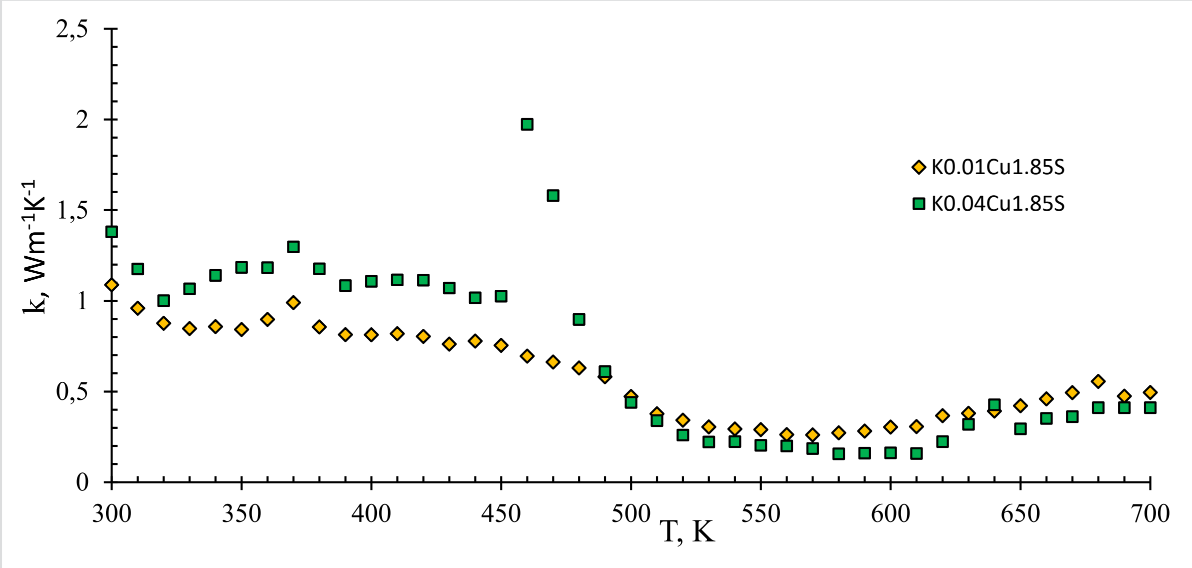

Figure 3 – Temperature dependences of the thermal conductivity coefficient of $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$ samples

In the work [19] the thermal conductivity of $Cu_{1.8}S$+3 wt% In_2S_3 bulk sample was reduced from 1.2 $Wm^{-1}K^{-1}$ to 0.65 $Wm^{-1}K^{-1}$ at 773 K due to superionic state and presence numerous nano-sized defects. This information is in a good agreement with our data analyses that the thermal conductivity of the alloys decreased to 0.2 W $K^{-1}m^{-1}$ approximately with increasing temperature.

Electronic conductivity and Zeebeck coefficient.

Figures 4 and 5 demonstrate temperature dependences of the electronic Zeebeck coefficient and electronic conductivity.

Zeebeck coefficient of $K_{0.01}Cu_{1.85}S$ was about 0.65 mV/K at room temperature, being higher than $K_{0.04}Cu_{1.85}S$ by approximately 30 times. Then, it increases to almost 1.96 mV/K at 620 K while $K_{0.04}Cu_{1.85}S$ exhibits very low Zeebeck coefficient and demonstrates a sharp increase after 470 K. At 466 K we see the thermal effect for $K_{0.04}Cu_{1.85}S$ on DSC curve (Figure 2b), the sharp jump of the thermal conductivity in Figure 3, and the sharp transition from semiconducting type of conductivity to metallic one near the same temperature in Figure 5.

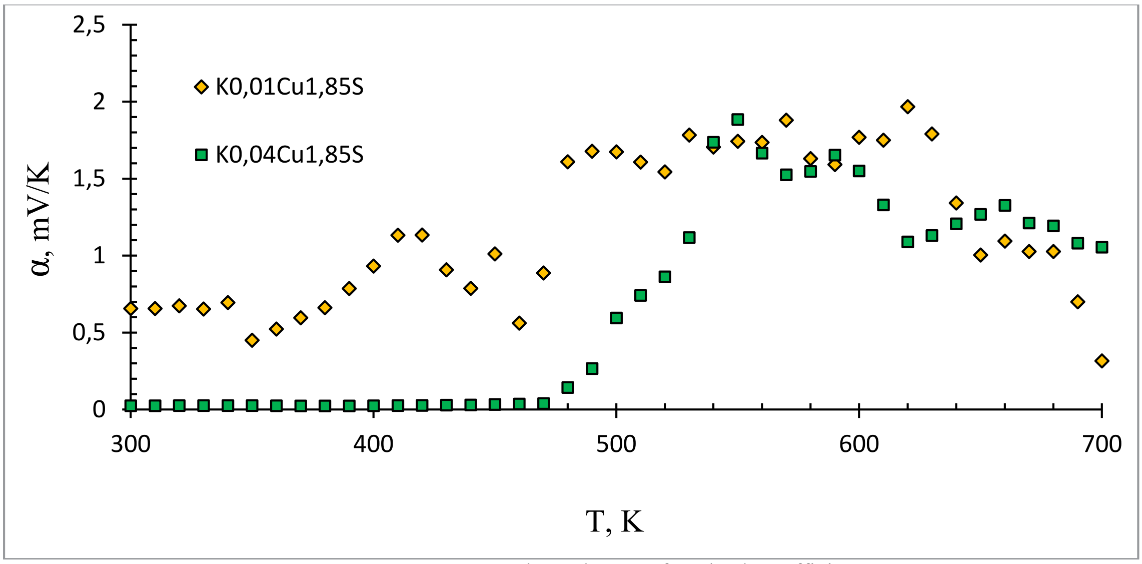

Figure 4 – Temperature dependences of Seebeck coefficient for $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$

The activation energy of the conductivity in the range of 360–400 K for $K_{0.04}Cu_{1.85}S$ alloy was 0.15 ± 0.01 eV, which is in satisfactory agreement with the value of 0.20 ± 0.02 eV for the $K_{0.2}Cu_{1.8}S$ alloy [13].

The phase transition at 643.7 K in the $K_{0.04}Cu_{1.85}S$ alloy (Figure 2b) also manifests itself in the temperature dependence of the conductivity in the form of a sharp jump, which is clearly seen in the inset in Figure 5.

Both compounds exhibit a good performance for semiconductor materials.

The dimensionless thermoelectric efficiency ZT.

Figure 6 shows the behavior of dimensionless thermoelectric efficiency ZT of nanocrystalline $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$ copper sulfides at the temperature range between 300 K and 700 K.

To achieve high ZT values, the electrical and thermal transfer properties of the materials must have a certain relevance: low electrical resistance, high Zeebeck coefficient and low thermal conductivity [22] simultaneously. In general, the best thermoelectric materials with an optimal Zeebeck coefficient and electrical conductivity are solid-alloy semiconductors with a charge carrier of 10^{19}-10^{20} per cubic centimeter [23].

According to the graphic information in figure 6, we see that thermoelectric figure of merit ZT changes irregularly due to few phase transitions at all the temperature range, reaching extremely high ZT = 9.68 for the $K_{0.04}Cu_{1.85}S$ sample near phase transition point. ZT values of $K_{0.01}Cu_{1.85}S$ sample is much higher than ones of $K_{0.04}Cu_{1.85}S$ at temperatures below 480 K. Note the very high values ZT > 1 for $K_{0.01}Cu_{1.85}S$ near room temperature. Averaged over the entire temperature range, the value of ZT for the $K_{0.01}Cu_{1.85}S$ sample is significantly higher than for $K_{0.04}Cu_{1.85}S$ sample, although the maximum value of ZT for it is lower (4.83 at 620 K).

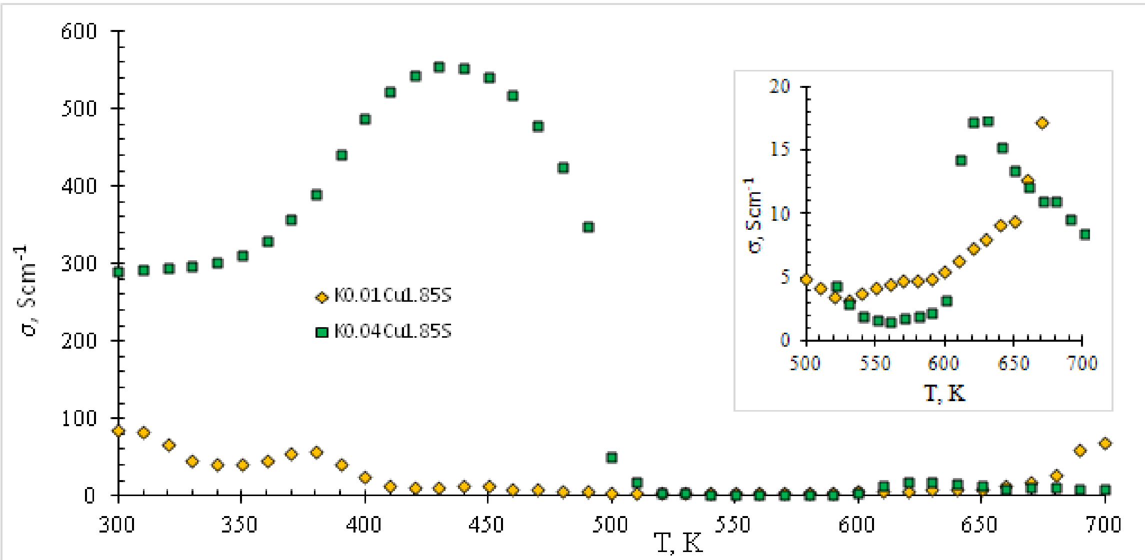

Figure 5 – Temperature dependences of the electronic conductivity for $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$. The inset shows in more detail the conductivity behavior in the temperature range of 500 – 700 K

In the work [24], ZT = 1.3 reached a high peak value in the temperature range of 348 K and 373 K. It is also noted that this process is more economical and environmentally friendly than the use of alloyed bulk crystal ingots. In our paper, the maximum value of dimensionless thermoelectric efficiency ZT was observed in a relatively large amount of potassium alloy $K_{0,04}Cu_{1,85}S$ in the upper temperature zone 610-630 K. In addition, in comparison with the work [25], the value of the thermoelectric figure of merit ZT has a much more satisfactory value, which provides greater opportunities in many cooling systems and in the production of electricity, which helps to solve the global energy dilemma [26].

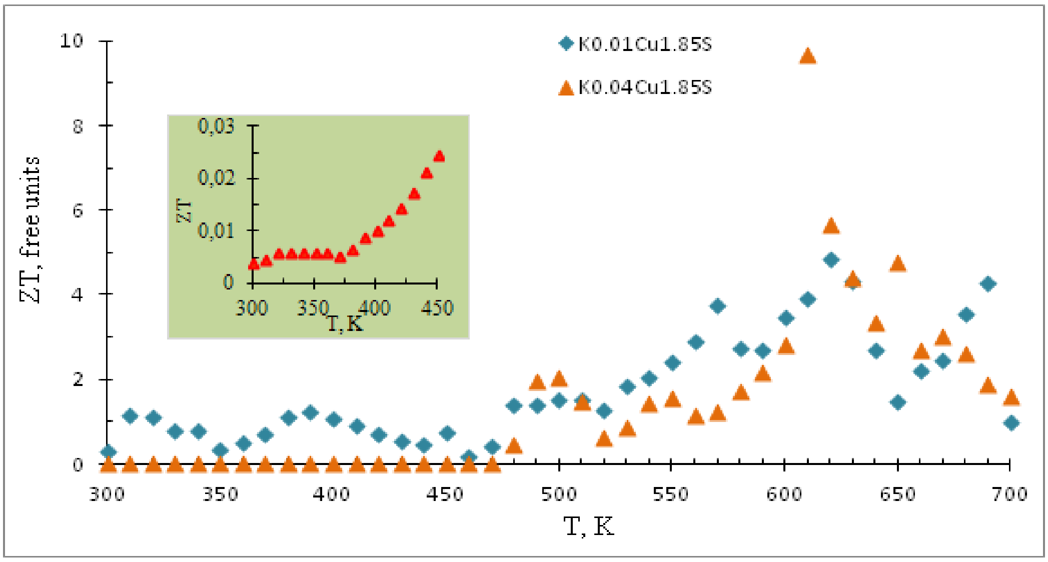

Figure 6 – Temperature dependences of the dimensionless thermoelectric efficiency ZT for samples $K_{0.01}Cu_{1.85}S$ and $K_{0.04}Cu_{1.85}S$. Fragment of the curve for $K_{0.04}Cu_{1.85}S$ is shown in inset of the figure

Conclusion

This paper studied multiphased nanocomposites $K_{0,01}Cu_{1,85}S$ and $K_{0,04}Cu_{1,85}S$. Although obtained data give us lattice thermal conductivity reduction in these materials, improvement in ZT will likely require optimization of high Zeebeck coefficient, low thermal conductivity, and other variables. High-temperature treatment is also an essential post synthesis step to create high ZT materials. In our study, it was investigated at temperature range from 300 k to 700 K, as well as we obtained good data on the results that correspond to the production conditions of devices used in renewable energy technologies. The results of X-ray phase analysis of the alloys show that the alloy consist of a mixture different phase. Using the Differential Scanning Calorimetry, we have defined alloys with a higher potassium compound $K_{0.04}Cu_{1.85}S$ have a strong thermal effect, which leads to local ZT increasing. We also took excellent figures in thermal conductivity, which it is close to the value of glass limit that is crucial in large-scale energy-conversion applications.

At temperatures up to 650 K, there is a strong increase in the Zeebeck coefficient just under 2 mV/K and a decrease in thermal conductivity to 0.5 $Wm^{-1}K^{-1}$, leading to a very high peak value of dimensionless thermoelectric efficiency ZT = 9.67 at 620 K. Thus, the experience shows that by observing and forming the synthesis of nanocrystalline copper sulfide materials based on the modification of known semiconductor chalcogenides, it is possible to obtain many properties necessary for various applications, as evidenced by numerous works of recent times.

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References

1 Caballero-Calero O., Ares J.R., Martнn-Gonzбlez M. Environmentally Friendly Thermoelectric Materials: High Performance from Inorganic Components with Low Toxicity and Abundance in the Earth // Adv. Sustainable Syst. – 2021, – 2100095. – P. 1-19.

2 Snyder J.G. Toberer. E.S. Complex thermoelectric materials // Nature materials. – 2008. – Vol. 7. – P. 105-114.

3 Zhen-Hua Ge, Xiaoye L., Dan F., Jingyang L., Jiaqing He. High-Performance Thermoelectricity in Nanostructured Earth-Abundant Copper Sulfides Bulk Materials // Adv. Energy Mater. – 2016. – P. 600-607.

4 Finefrock S.W., Haoran Y., Haiyu F., Yue Wu. Thermoelectric Properties of Solution Synthesized Nanostructured Materials // Annu. Rev. Chem. Biomol. Eng. – 2015. – P. 6:11.1–11.20.

5 Kauzlarich Susan M., Brown Shawna R., Jeffrey Snyder G. Zintl phases for thermoelectric devices // Dalton Trans. – 2007. – P. 2099–2107.

6 Bin Liu, Jizhu Hu, Jun Zhou, Ronggui Yang. Thermoelectric Transport in Nanocomposites // Materials. 2017, – Vol. 10, P. 3390-3418.

7 Balapanov M. Kh., Ishembetov R.Kh., Kuterbekov K.A., Kubenova M.M., Almukhametov R.F., Yakshibaev R.A. Transport phenomena in superionic NaxCu2-xS (x = 0,05; 0,1; 0,15; 0,2) compounds // Ionics. – 2018. – Vol. 24 (5). – P. 1349–1356.

8 JIANG J. Z. Phase transformations in nanocrystals // Journal of materials science. – 2004. – Vol. 39. – P. 5103 – 5110.

9 Balapanov M. Kh., Ishembetov R.Kh., Kuterbekov K.A., Baisheva A. Kh., Palymbetov R. Sh., Sakhabaeva S.M., Kubenova M.M., Yakshibaev R. A. Electrical and thermal properties of superionic $K_xCu_{2-x}S$ (x=0.1, 0.2, 0.25) alloys // Letters on materials. – 2020. – Vol. 10 (4). – P. 439 – 444.

10 Балапанов М.Х., Ишембетов Р.Х., Кубенова М.М., Кутербеков К.А., Сахабаева С.М., Ахметгалиев Б.М., Якшибаев Р.А. Фазовый состав и термоэлектрические свойства нанокристаллических сульфидов меди KxCu1.97-xS (0<x <0.05) // сборник трудов V Междунар. науч.-практ. конф., Республика Башкортостан, г. Стерлитамак, 16–18 сентября 2021. – 2021. – С. 34–40.

11 Gronvold F., Westrum E.F. Thermodynamics of copper sulfides I. Heat capacity and thermodynamic properties of copper(I) sulfide, Cu2S, from 5 to 950 K // J. Chem. Thermodyn. – 1987. – Vol. 19. – P. 1183–1198.

12 Hirahara E. The physical properties of cuprous sulfides – semiconductors // J. Phys. Soc. Japan. – 1951. – Vol. 6. – P. 422-427.

13 Balapanov M. Kh., Ishembetov R.Kh., Akhmetgaliev B. M., Kuterbekov K.A., Palymbetov R. Sh., Sakhabaeva S.M., Yakshibaev R. A. Transport phenomena in the superionic $K_{0.2}CU_{1.8}S$ alloy //Vestnik Bashkirskogo Universiteta. – 2020. – Vol. 25. No. 4. – Pp. 794-801.

14 Balapanov M. Kh., Yakshibaev R.A. and Mukhamed'yanov KH. Ion transfer in solid solutions of Cu2Se and Ag2Se superionic conductors // physics of the solid state. – 2003. – Vol.45 (4). – P. 634-638.

15 Balapanov M.Kh., Ishembetov R.Kh., Kuterbekov K.A., Kubenova M.M., Danilenko V.N., Nazarov K.S., Yakshibaev R.A. Thermoelectric and thermal properties of superionic Ag***x***Cu***2−x***Se (x = 0.01, 0.02, 0.03, 0.04, 0.25) compounds // Letters on materials – 2016. – 6 (4), – P. 360-365.

16 Балапанов М.Х., Зиннуров И.Б., Кутербеков К.А., Ишембетов Р.Х., Кубенова М.М., Якшибаев Р.А. Влияние концентрации меди на электронную проводимость и коэффициент электронной термо-э.д.с. сплавов LixCu1.75–δSe (x ≤ 0.25) // Вестник Башкирского университета. – 2017. – Vol. 22 (1). – С. 41–47.

17 Okamoto K. and Kawai Sh. Electrical Conduction and Phase Transition of Copper Sulfides // Japan Journal Appl. Phys. – 1973. – 12, 1130, DOI: 10.1143/JJAP.12.1130.

18 Xiaoyan Li, Chenguo Hu, Xueliang Kang,b Qiang Len,a Yi Xi,a Kaiyou Zhang, Hong Liu. Introducing kalium into copper sulfide for the enhancement of thermoelectric properties // The Royal Society of Chemistry. – 2013. – Vol. 1. – P. 13721–13726.

19 Ge Z.-H., Chong X., Feng D., Zhang Y.-X., Qiu Y., Xie L., Guan P.-W., Feng J., He J. Achieving an excellent thermoelectric performance in nanostructured copper sulfide bulk via a fast doping strategy // Materials Today Physics. – 2019. Vol. 8. – P. 71-77.

20 Kubenova M.M., Balapanov M.Kh., Kuterbekov K.A., Ishembetov R.Kh., Kabyshev A.M., Yulaeva Y.Kh. Phase composition and thermoelectric properties of the nanocomposite alloys NaxCu2−x−yS// Eurasian Journal of Physics and Functional Materials. – 2020. – Vol. 4(1). – P. 67-85.

21 Li-Jun Zheng, Bo-Ping Zhang, He-zhang Li, Jun Pei, Jia-Bing Yu. CuxS superionic compounds: Electronic structure and thermoelectric performance enhancement // Journal of Alloys and Compounds. – 2017. – Vol. 722. – P. 17-24.

22 Sabah K. Bux, Jean-Pierre Fleurial, Richard B. Kaner. Nanostructured materials for thermoelectric applications // Chem. Commun. – 2010. – Vol.46. – P. 8311–8324.

23 In Liu, Jizhu Hu, Jun Zhou, Ronggui Yang. Thermoelectric Transport in Nanocomposites // Materials. – 2017. – 10. P.1-31

24 Yi Ma, Qing Hao, Bed Poudel, Yucheng Lan, Bo Yu, Dezhi Wang, Gang Chen, Zhifeng Ren. Enhanced Thermoelectric Figure-of-Merit in p-Type Nanostructured Bismuth Antimony Tellurium Alloys Made from Elemental Chunks // Nano Lett. – 2008. Vol.8 (8). – P. 2580-2584.

25 Кутербеков К.А., Балапанов Х.М., Кубенова М.М., Сахабаева С.М., Палымбетов Р.Ш., Кабышев А.М., Бекмырза К.Ж., Куланова К.К. $K_XCu_{2-X}S$ супериондық қорытпаларығын электрлік және физикалық қасиеттері // Вестник ЕНУ. – 2020. – №4. – С. 39-48.

26 Pengfei Q., Xun Shi, Lidong Ch. Cu-based thermoelectric materials // Energy Storage Materials. – 2016. – Vol. 3. – P. 85–97.

References

1 O. Caballero-Calero, J.R. Ares, M. Martнn-Gonzбlez. Adv. Sustainable Syst., 2100095, 1-19 (2021).
2 G.J. Snyder, E.S. Toberer. nature materials, 7, 105-114 (2008).
3 Ge Zhen-Hua, et al. Adv. Energy Mater. 600-607 (2016).
4 S.W. Finefrock, et al, Annu. Rev. Chem. Biomol. Eng. 6:11.1–11.20 (2015).
5 S.M. Kauzlarich, Sh.R. Brown, G.J. Snyder. Dalton Trans., 2099-2107 (2007).
6 B. Liu, J. Hu, J. Zhou, R. Yang. Materials, 10, 3390-3418 (2017).
7 J.Z. JIANG, Journal of materials science, 39, 5103-5110 (2004).
8 M.Kh. Balapanov, et al, Ionics, 24 (5), 1349-1356 (2018).
9 M.Kh. Balapanov, et al, Letters on materials, 10, 4 (40), 439–444 (2020).
10 M.KH. Balapanov, et al, Sbornik trudov V Mezhdunar. nauch.-prakt. konf., Respublika Bashkortostan, 34–40 (2021). (in Russ).
11 F. Gronvold, E.F. Westrum, J. Chem. Thermodyn, 19, 1183–1198 (1987).
12 E. Hirahara, J. Phys. Soc. Japan, 6, 422-427 (1951).
13 M. Kh. Balapanov, et al, Vestnik Bashkirskogo Universiteta, 25 (4), 794–801 (2020).
14 M. Kh. Balapanov, et al, Physics of the Solid State, 45 (4), 634-638 (2003).
15 M.Kh. Balapanov, et al, Letters on materials, 6 (4), 360-365 (2016).
16 M. KH. Balapanov, et al, Vestnik Bashkirskogo universiteta, 22 (1), 41-47 (2017). (in Russ).
17 K. Okamoto and Sh. Kawai. Japan Journal Appl. Phys. **12**, 1130 (1973), DOI: 10.1143/JJAP.12.1130.
18 Li Xiaoyan, Hu Chenguo, Kang Xueliang, Len Qiang, Xi Yi, Zhang Kaiyou, Liu Hong, The Royal Society of Chemistry, 1, 13721–13726 (2013).
19 Z.-H. Ge, X. Chong, D. Feng, Y.-X. Zhang, Y. Qiu, L. Xie, P.-W. Guan, J. Feng, J. He. Materials Today Physics, 8, 71-77 (2019).
20 M.M. Kubenova, M.Kh. Balapanov, K.A. Kuterbekov, R.Kh. Ishembetov, A.M. Kabyshev, Y.Kh. Yulaeva, Eurasian Journal of Physics & Functional Materials, 4(1), 67-85 (2020).
21 Li-Jun Zheng, Bo-Ping Zhang, He-zhang Li, Jun Pei, Jia-Bing Yu. Journal of Alloys and Compounds, 722, 17-24 (2017).
22 Sabah K. Bux, Jean-Pierre Fleurial, Richard B. Kaner. Chem. Commun, 46, 8311–8324 (2010).
23 In Liu, Jizhu Hu, Jun Zhou, Ronggui Yang, Materials, 10, 1-31 (2017).
24 Yi Ma, Qing Hao, Bed Poudel, Yucheng Lan, Bo Yu, Dezhi Wang, Gang Chen, Zhifeng Ren. Nano Lett., 8 (8), 2580-2584 (2008).
25 S.M. Sakhabayeva, et al, Vestnik YENU, 4, 39-48 (2020). (in Russ).
26 Q. Pengfei, Xun Shi, Ch. Lidong, Energy Storage Materials, 3, 85–97 (2016).