Electrophysical and thermal properties of $\text{Na}_x\text{Cu}_{2-x}\text{S}$ ($x = 0.05, 0.075, 0.10$) and $\text{Na}_{0.125}\text{Cu}_{1.75}\text{S}$ semiconductor alloys

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Abstract. The results of measurements of electronic conductivity and the Seebeck coefficient, as well as X-ray phase analysis, electron microscopy, differential scanning calorimetry (DSC) and studies of the heat capacity of nanocrystalline $\text{Na}_x\text{Cu}_{2-x}\text{S}$ ($x = 0.05, 0.075, 0.10$) and $\text{Na}_{0.125}\text{Cu}_{1.75}\text{S}$ semiconducting alloys in the temperature interval of 300 - 600 K are presented. At ambient temperature, the alloys under study consist of three phases: monoclinic $\text{Na}_2\text{Cu}_4\text{S}_3$, hexagonal chalcocite $\text{Cu}_2\text{S}$ and rhombohedral digenite $\text{Cu}_9\text{S}_5$. Measurements show that the Seebeck coefficient increases, and the conductivity decreases with increasing sodium concentration in the alloys. Thermal effects near the temperatures of 360 K, 450 K and 640 K have been observed by the DSC method.

1. Introduction

In nature, copper and sulfur form chemical compounds of a wide variety of compositions, ranging from chalcocite ($\text{Cu}_2\text{S}$) to villamaninite ($\text{Cu}_5\text{S}_3$) with various intermediates: covellite ($\text{CuS}$), jurleite ($\text{Cu}_{1.96}\text{S}$) and anilite ($\text{Cu}_{1.75}\text{S}$) [1]. Copper sulfides exhibit mixed electronic-ionic conductivity and possess high potential for practical applications as p-branches of solar cells, thermoelectric devices, superionic materials, cathode materials with high energy density for lithium batteries, nanosized switches, catalysts, and nonlinear optical materials [2-5].

We have previously studied the effect of lithium substitution on the electronic and ionic transport in $\text{Cu}_{2-\delta}\text{S}$ and $\text{Cu}_{2-\delta}\text{Se}$ [6-8]. The substitution resulted in a decrease in both the ionic and electronic conductivities of the compounds. The $\text{Li}_x\text{Cu}_{2-\delta}\text{S}$ and $\text{Li}_x\text{Cu}_{2-\delta}\text{Se}$ alloys are mixtures of two or three phases at ambient temperature and exhibit transition to a single phase state at elevated temperatures forming solid solutions on the base of nonstoichiometric copper sulfide (selenide) or an individual chemical substance as, for example, $\text{Li}_{0.25}\text{Cu}_{1.75}\text{Se}$ [7]. As a rule, copper sulfide and selenide are chemically unstable in air. Insertion of lithium decreases the temperatures of phase transformations and increases the chemical stability of copper sulfide and copper selenide. For example, the high temperature f.c.c. cubic phase of copper sulfide becomes stable at ambient temperature for $\text{Li}_{0.15}\text{Cu}_{1.85}\text{S}$ [6]. Shannon effective ionic radii of $\text{Li}^+$ and $\text{Cu}^+$ ions are near 0.59 and 0.60 Å in tetrahedral coordination correspondingly [9]) and this fact favors the formation of a solid solution in $\text{Li}_x\text{Cu}_{2-\delta}\text{S}$. The ionic radii of $\text{Na}^+$ ions are significantly larger (0.99 Å) than the ionic radii of $\text{Li}^+$ ions, so, in our opinion, ordering effects are probable in sodium doped copper sulfides. Na-containing copper sulfides are investigated rather poorly. As an example, the existence of a quasi-one-
dimensional Na$_2$Cu$_5$S$_3$ compound is known [10]. Along with this fact, the crystal structure of copper sulfide does not change after light sodium doping. The authors of [11] obtained homogeneous Na$_x$Cu$_y$S$_z$ samples with $x = 0.025$, 0.05, 0.15 and achieved the maximal thermoelectric figure of merit $ZT = 1.1$ at 773 K for the composition $x = 0.05$ (in our terminology it corresponds to the Na$_{0.15}$Cu$_{1.85}$S composition).

Nanocrystalline alloys of the Na$_{0.15}$Cu$_{1.85}$S, Na$_{0.17}$Cu$_{1.80}$S and Na$_{0.20}$Cu$_{1.75}$S compositions were synthesized in recent work [12]. A quasi-one-dimensional monoclinic phase of Na$_2$Cu$_4$S$_3$ and two ordinary sulfide phases, the hexagonal Cu$_9$S$_4$ and the cubic Cu$_6$S$_3$ ones, were observed at ambient temperature. A very low heat conductivity in the interval of 0.1-0.7 W m$^{-1}$K$^{-1}$ was found. The achieved thermoelectric figure of merit $ZT \approx 0.28$ for the Na$_{0.15}$Cu$_{1.85}$S composition at 590 K is comparable with the result [11] for the Na$_{0.0}$Cu$_{1.80}$S composition at the same temperature. In other recent paper [13], high ionic conductivity values of 1.5-2.3 S/cm in the temperature interval of 620 K – 680 K and low heat conductivity about 0.3-0.4 W m$^{-1}$K$^{-1}$ in the temperature interval of 620 K – 680 K were observed for Na$_{0.2}$Cu$_{1.85}$S and good semiconducting electron properties for the Na$_{0.1}$Cu$_{1.95}$S and Na$_{0.2}$Cu$_{1.75}$S compositions were found. In this paper we present the results of more detailed investigations of the Na$_x$Cu$_y$S$_z$ ($x = 0.05$, 0.075, 0.10) and Na$_{0.125}$Cu$_{1.75}$S compositions including phase analysis, electron microscopy, differential scanning calorimetry and heat capacity studies with in order to obtain a better understanding of the transport phenomena in these multiphase alloys.

2. Experimental methods

Materials for investigations were synthesized at temperatures of about 165 °C. The reaction was performed in a mixed medium of NaOH and KOH hydroxides. All reagents (CuCl, NaCl, NaS+9H$_2$O) were simultaneously placed in a heated Teflon vessel. A nanocrystalline powder was formed inside the vessel in 8 hours. The resulting product was washed with distilled hot water and then with pure ethanol. The particle sizes of the obtained powder were in the range from 20 to 600 nm. X-ray phase analysis was performed with a D8 ADVANCE ECO diffractometer (Bruker, Germany) using the CuK$_\alpha$ radiation. The international database ICDD PDF-2 was used to identify the phases. Images of the surfaces of the samples were taken using scanning electron microscopes (SEM) MIRA3 (TESCAN) and JSM 7500F (JEOL). For differential scanning calorimetry of the samples and measurements of the heat capacity in the temperature range from 300 to 700 K, the DSC404 F1 Pegasus device (NETZSCH, Germany) was used. The heating rate was 10 K/min, a slow argon flow was applied (30 ml/min). Electronic conductivities and the Seebeck coefficients were measured simultaneously in an argon atmosphere with ZEM-3 equipment (ULVAC Inc., Japan).

3. Results of X-ray phase analysis, electron microscopy and differential scanning calorimetry

Figure 1 shows the X-ray diffraction patterns of the samples obtained at room temperature. Analysis of diffraction lines using the Rietveld method shows that the samples consist of the following phases: Na$_3$Cu$_2$S$_3$ (PDF – 01-082-6340), the lattice type is monoclinic, space group is C2/m (12); chalcocite Cu$_2$S (PDF – 00-026-1116), the lattice type is hexagonal, space group is P6$_3$/mmc (194); and digenite Cu$_6$S$_3$ (PDF - 00-047-1748), the lattice type is rhombohedral, space group is R-3m (166).

It is known [1] that chalcocite Cu$_2$S has a hexagonal structure with the space group P6$_3$/mmc with $a_0 = 3.95$ Å, $c_0 = 6.75$ Å between 377 K and 708 K only, so the presence of this structure at ambient temperature is very unusual and probably could be caused by the influence of introducing Na into the crystal lattice. The hexagonal modification of the chalcocite exhibits superionic properties and, therefore, high ionic conductivity can be expected in the alloys under study even at room temperature.

Figure 2 shows a SEM image of the etched surface of a Na$_{0.05}$Cu$_{1.95}$S sample. On this image, the porous surface structure can be seen. Individual grains predominate in the form of melted cubes or parallelepipeds with dimensions of 100-200 nm, and larger blocks with an unresolved substructure are also visible. Figure 2 also presents SEM images of powder particles of Na$_{0.075}$Cu$_{1.925}$S (b), Na$_{0.1}$Cu$_{1.90}$S (c) and Na$_{0.125}$Cu$_{1.75}$S (d) samples. The synthesized powder consists of irregularly shaped plates, having a granular substructure with sizes from 20 nm to several hundred nanometers.
Figure 1. X-ray diffraction patterns of the samples at ambient temperature (1- Na$_{0.05}$Cu$_{1.95}$S, 2- Na$_{0.075}$Cu$_{1.925}$S, 3- Na$_{0.10}$Cu$_{1.90}$S, 4- Na$_{0.125}$Cu$_{1.75}$S).

Figure 2. Image of the etched surface of Na$_{0.05}$Cu$_{1.95}$S (a), obtained on a scanning electron microscope and SEM images of powder particles of Na$_{0.075}$Cu$_{1.925}$S (b), Na$_{0.10}$Cu$_{1.90}$S (c), Na$_{0.125}$Cu$_{1.75}$S (d) samples.

Differential scanning calorimetry curves and temperature dependences of specific heat are presented on figure 3. According to G. Will et al. [14], two modifications of digenite exist, low-temperature (below 364 K) and high-temperature (above 364 K). Sharp endothermic peaks about 370 K recorded on all DSC and heat capacity curves in figure 3 confirm the X-ray phase analysis data on
the presence of the digenite phase in the studied samples. As is known, the high-temperature cubic phase of digenite exhibits superionic conductivity, carried by copper $\text{Cu}^{+}$ ions [5, 6].

![DSC curves and temperature dependencies of specific heat of Na$_{0.05}$Cu$_{1.95}$S (a), Na$_{0.075}$Cu$_{1.925}$S (b), Na$_{0.10}$Cu$_{1.90}$S (c), Na$_{0.125}$Cu$_{1.75}$S (d) samples.](image)

The temperature of the peak tip increases with increasing sodium content from 371 K to 382 K in the Na$_{0.05}$Cu$_{1.95}$S, Na$_{0.075}$Cu$_{1.925}$S, Na$_{0.10}$Cu$_{1.90}$S row. The Na$_{0.125}$Cu$_{1.75}$S alloy deviates from the general trend exhibiting the peak tip temperature of 370 K. The value of the enthalpy of phase transformation, measured by the peak area in figure 3, increases with increasing sodium content for all samples from 3398 J/kg*K for Na$_{0.05}$Cu$_{1.95}$S up to 8366 J/kg*K for Na$_{0.125}$Cu$_{1.75}$S. It is possible that sodium partially dissolves in the structure of the digenite or accumulates at the grain boundaries, and its presence leads to an increase of thermal costs during structural transformation in the digenite.

In the range of 440-460 K, the curves in figure 3 exhibit an anomaly in the form of a stepped fall, the origin of which is unclear. There is no data on phase transitions in Na$_2$Cu$_4$S$_3$ above room temperature in the literature. Since digenite has the phase transition temperature of 364 K, at 440 K it is already in the high-temperature cubic phase [14]. The hexagonal chalcocite of Cu$_2$S composition is transformed into the f.c.c. modification above 713 K [1].

It is possible that the substitution by sodium in the Cu$_2$S lattice reduces the temperature of the phase transition to the cubic phase to 440-460 K or the phase transformation takes place in Na$_2$Cu$_4$S$_3$ phase.

For all samples, the exothermic effect is exhibited around 630-640 K. For the Na$_{0.075}$Cu$_{1.925}$S sample, this effect is shifted to 580 K. Also a weak endothermic peak is observed for the Na$_{0.05}$Cu$_{1.925}$S and Na$_{0.125}$Cu$_{1.75}$S samples at 677 K and 653 K, respectively. High temperature X-ray structural studies are needed to shed light on the nature of all these thermal effects.

4. Electronic conductivity and the Seebeck coefficient

Figure 4 shows the temperature dependences of the electronic conductivity and the Seebeck coefficients of nanocrystalline Na$_{0.05}$Cu$_{1.95}$S, Na$_{0.075}$Cu$_{1.925}$S, Na$_{0.1}$Cu$_{1.90}$S, Na$_{0.125}$Cu$_{1.75}$S samples in the range from 300 to 600 K. All the presented curves show several extrema at the points of phase transitions assumed on the basis of figure 3. The conductivity of all samples is small. The conductivities of Na$_{0.05}$Cu$_{1.95}$S and Na$_{0.125}$Cu$_{1.75}$S samples is significantly higher than that of others.
The Na_{0.05}Cu_{1.95}S sample contains less impurity (Na), scattering on which usually reduces the mobility of carriers. The Na_{0.125}Cu_{1.75}S sample contains more sodium than the Na_{0.075}Cu_{1.925}S and Na_{0.1}Cu_{1.9}S samples, and this should lead to a decrease in charge carrier mobility, but the chemical composition of the Na_{0.125}Cu_{1.75}S sample also has a large metal deficiency, which, according to the electroneutrality rule, should greatly increase the concentration of electron holes, and, consequently, increase the conductivity. We believe that as a result of the compromise of these two factors, the conductivity of the non-stoichiometric Na_{0.125}Cu_{1.75}S sample is higher than that of the stoichiometric Na_{0.075}Cu_{1.925}S and Na_{0.1}Cu_{1.9}S compositions.

In the low-temperature phase of the samples, the semiconductor character of conductivity is observed with the same impurity activation energy of 0.057 ± 0.001 eV, as shown in figure 4, only for the Na_{0.075}Cu_{1.925}S alloy, the impurity activation energy is slightly higher and equal to 0.067 ± 0.001 eV. The Seebeck coefficient of the samples is positive over the entire temperature range studied. This fact is characteristic for copper sulfides, which usually exist with a deficiency of copper in the crystal lattice. Figure 4 shows that the Seebeck coefficients increase with increasing sodium content. An exception is the Na_{0.125}Cu_{1.75}S composition, which exhibits the lowest Seebeck coefficient, which can be explained by a strong deficiency of cations and, consequently, a high concentration of holes, at which carrier degeneracy most likely occurs.

![Figure 4. Temperature dependencies of electronic conductivities](image)

5. Conclusions
At ambient temperature, the studied alloys consist of three phases: monoclinic Na_{2}Cu_{4}S_{3}, hexagonal chalcocite Cu_{2}S and rhombohedral digenite Cu_{9}S_{5}. The complex phase composition of the mixture is confirmed by differential scanning calorimetry, which recorded a number of thermal effects at temperatures of 370–382 K, 440–460 K, 630–640 K, 653 K, and 677 K. The first heat effect occurring at 370–382 K, in our opinion, is associated with the superionic phase transition in digenite. The enthalpy of phase transformation for the studied samples increases with increasing sodium content in the samples. Since the superionic transition is associated with the disordering of the structure, it can be assumed that the presence of sodium in the lattice hampers the disordering and retards the rearrangement of the lattice. This assumption is confirmed by an increase in the temperature of phase transitions with increasing sodium content. The chalcocite Cu_{2}S phase in the studied alloys has a hexagonal structure at room temperature and can be a superionic conductor already at room temperature.

The electronic conductivity of the alloys is small, it has a tendency to decrease with increasing sodium content in the alloy, while the Seebeck coefficient increases. The analysis of a three-phase system is comprehensive and cannot give unambiguous conclusions. It is clear that sodium atoms play the role of a compensating impurity when doping non-stoichiometric copper sulfide, reducing the concentration of holes. At the same time, the carrier mobility should also decrease due to scattering by...
impurity sodium atoms. Nano-dimension of the grains also usually reduces conductivity due to the increasing role of scattering on the grain boundaries. X-ray structural studies at high temperatures are necessary to verify the possibility of obtaining a single-phase state of the alloys under study.

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