

Thermal and electrical properties of nanocrystalline superionic $\text{Na}_x\text{Cu}_{1.75}\text{S}$ ($x=0.1, 0.15, 0.2, 0.25$) compounds

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The paper presents the results of the studies of thermal properties of nanocrystalline superionic $\text{Na}_x\text{Cu}_{1.75}\text{S}$ ($x = 0.1, 0.15, 0.2, 0.25$) compositions, and preliminary results of $\text{Na}_{0.1}\text{Cu}_{1.75}\text{S}$ using as energy stored cathode material in Na-ion half-cell with NaPF_6 electrolyte and Na anode. The compositions contain a few copper sulfide phases: monoclinic chalcocite Cu_2S , orthorhombic anilite $\text{Cu}_{1.75}\text{S}$, triclinic roxbyite $\text{Cu}_{1.74\pm 1.82}\text{S}$, also the compositions can contain monoclinic $\text{Na}_2\text{Cu}_4\text{S}_3$, orthorhombic Na_2S , cubic Cu_2O as inclusion phases. The sizes of powder particles lie in the range from 10 to 113 nm. Differential scanning calorimetry revealed in $\text{Na}_{0.1}\text{Cu}_{1.75}\text{S}$ the endothermic thermal effects with critical temperatures near 123 °C, 422 °C and 442 °C, caused by structural transitions in copper sulfide. Fourth endothermic peak at 323 °C presumably belongs to Na_2S phase. The minimum for the Fermi level at about 420 °C is found with using of the e.m.f. E of the electrochemical cell of the $\text{Cu}/\text{CuBr}/\text{Na}_{0.10}\text{Cu}_{1.75}\text{S}/\text{Pt}$, which corresponds to minimum for the carrier concentration. This conclusion correlates well with the observed conductivity minimum at about 410 °C. Electrode material $\text{Na}_{0.10}\text{Cu}_{1.75}\text{S}$ achieved a significant specific energy density 146.5 mAh/g in half-cell assembled from the cathode active material, electrolyte (NaPF_6 in 0.5 mol PC) and Na anode.

The results of X-ray phase analysis of the $\text{Na}_{0.15}\text{Cu}_{1.75}\text{S}$, $\text{Na}_{0.20}\text{Cu}_{1.75}\text{S}$ and $\text{Na}_{0.25}\text{Cu}_{1.75}\text{S}$ samples were described in our recent work [1-3], except for the $\text{Na}_{0.10}\text{Cu}_{1.75}\text{S}$ sample. For example, the powder X-ray diffraction pattern of the $\text{Na}_{0.15}\text{Cu}_{1.75}\text{S}$ sample taken at room temperature is shown in Figure 1 a. This alloy contains next phases: triclinic roxbyite, orthorhombic anilite, monoclinic $\text{Na}_2\text{Cu}_4\text{S}_3$, cubic Cu_2O . Analysis of the

spectrum of Figure 1 a revealed that the main phase of $\text{Na}_{0.15}\text{Cu}_{1.75}\text{S}$ sample is the triclinic roxbyite $\text{Cu}_{1.8125}\text{S}$ with space group P and cell parameters, $a = 13.4051(9)$ Å, $b = 13.4090(8)$, $c = 15.4852(3)$ Å, $\alpha = 90.022(2)^\circ$, $\beta = 90.021(2)^\circ$, $\gamma = 90.020(3)^\circ$.

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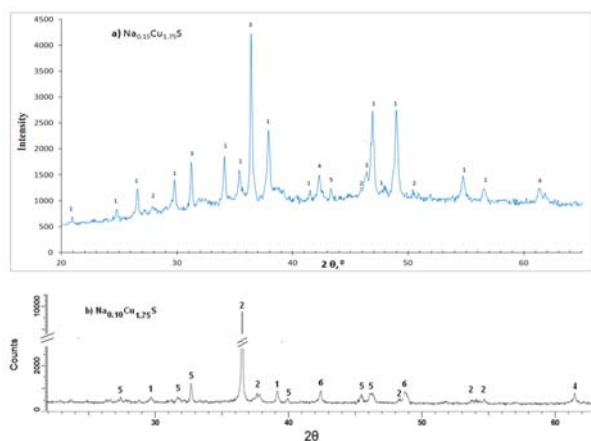


Figure 1. Powder diffraction pattern of the $\text{Na}_{0.15}\text{Cu}_{1.75}\text{S}$ (a), $\text{Na}_{0.10}\text{Cu}_{1.75}\text{S}$ (b) samples taken at room temperature. Digits above pikes denotes: 1- triclinic roxbyite, 2-orthorhombic anilite, 3- monoclinic $\text{Na}_2\text{Cu}_4\text{S}_3$, 4-cubic Cu_2O , 5-monoclinic chalcocite Cu_2S , 6-orthorhombic Na_2S .