Thermal and electrical properties of nanocrystalline superionic $Na_xCu_{1.75}S$ (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 $Na_xCu_{1.75}S$ (x = 0.1, 0.15, 0.2, 0.25) compositions, and preliminary results of $Na_{0.1}Cu_{1.75}S$ 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 $Cu_{1.75}S$, triclinic roxbyite $Cu_{1.74\div1.82}S$, also the compositions can contain monoclinic $Na_2Cu_4S_3$, 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 $Na_{0.1}Cu_{1.75}S$ the endothermic thermal effects with critical temperatures near 123 ºC, 422 ºC and 442 ºC, caused by structural transitions in copper sulfide. Fourth endothermic peak at 323 ºC 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 $Cu/CuBr/Na_{0.10}Cu_{1.75}S/Pt$, which corresponds to minimum for the carrier concentration. This conclusion correlates well with the observed conductivity minimum at about 410°C. Electrode material $Na_{0.10}Cu_{1.75}S$ 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 $Na_{0.15}Cu_{1.75}S$, $Na_{0.20}Cu_{1.75}S$ and $Na_{0.25}Cu_{1.75}S$ samples were described in our recent work [1-3], except for the $Na_{0.10}Cu_{1.75}S$ sample. For example, the powder X-ray diffraction pattern of the $Na_{0.15}Cu_{1.75}S$ sample taken at room temperature is shown in Figure 1 a. This alloy contains next phases: triclinic roxbyite, orthorhombic anilite, monoclinic $Na_2Cu_4S_3$, cubic Cu_2O. Analysis of the spectrum of Figure 1 a revealed that the main phase of $Na_{0.15}Cu_{1.75}S$ sample is the triclinic roxbyite $Cu_{1.8125}S$ with space group *P* and cell parameters, a =13.4051(9) Å, b=13.4090(8), c=15.4852(3) Å, α = 90.022(2)°, β = 90.021(2)°, γ =90.020(3)°.

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References

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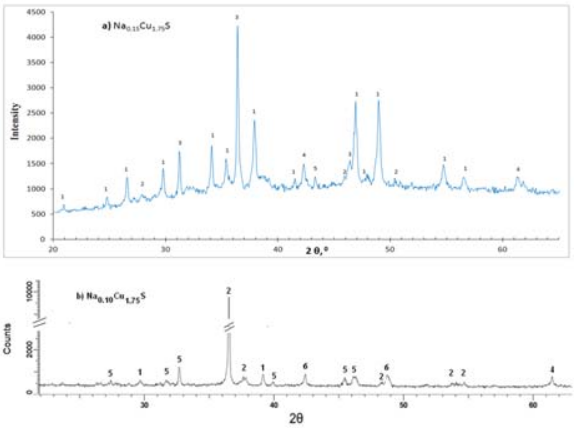

Figure 1. Powder diffraction pattern of the $Na_{0.15}Cu_{1.75}S$ (a), $Na_{0.10}Cu_{1.75}S$ (b) samples taken at room temperature. Digits above pikes denotes: 1-triclinic roxbyite, 2–orthorhombic anilite, 3-monoclinic $Na_2Cu_4S_3$, 4-cubic Cu_2O, 5-monoclinic chalcocite Cu_2S, 6-orthorhombic Na_2S.