Glass-Ceramic Formation Tendency for System $LiCoPO_4$-$NaCoPO_4$

I. Zatovsky[1], N. Klyui[1], J. Li[1], N. Strutynska[2], W. Han[1], N. Slobodyanik[2], O. Marchenko[2]

[1]*College of Physics, Jilin University, 2699 Qianjin Str., 130012 Changchun, P.R. China*
[2]*Taras Shevchenko National University, 64/13 Volodymyrska Str., 01601 Kyiv, Ukraine*

Complex phosphates of $LiCoPO_4$ and $NaCoPO_4$ are well known as cobalt redox-active electrode materials in rechargeable lithium or sodium batteries [1]. In addition, this compounds is efficient water oxidation catalyst [2]. The possibilities of formation of solid solutions of general compositions $Li_{1-x}Na_xCoPO_4$ have not been reported so far. Herein, we report glass-ceramic formation tendency and electrical conductivity of lithium-sodium cobalt phosphates are examined for Li/Na-ion batteries.

Starting the melt compositions in this study is $(1-x)Li_2O$-xNa_2O-$2CoO$-P_2O_5 (x = 0, 0.25, 0.5, 0.75 and 1.0). Reagents Li_2CO_3, Na_2CO_3, Co_3O_4 and $(NH_4)_2HPO_4$ in appropriate stoichiometric ratios were melted in a platinum crucible at 1000 °C. The melts were exposed during 1 h at the temperature, and then were poured onto a copper sheet to freeze processes. The glass transition and crystallization temperatures were determined by differential thermal analysis (DTA). Obtained samples were subsequently annealed at 600 °C (1 h). Obtained glass-ceramics were characterized by XRD, FTIR, SEM, TEM and impedance spectroscopy method.

Crystalline phases have been obtained in all cases. In particular, XRD pattern revealed low- and high-temperature forms for $NaCoPO_4$, the estimated ratio α-$NaCoPO_4$ (space group *Pnma*) : β-$NaCoPO_4$ (space group $P6_5$) was approximately 1:1. For this sample the phase transition β-$NaCoPO_4$ → α-$NaCoPO_4$ was observed when heated to 600 °C. For the system $(1-x)Li_2O$-xNa_2O-$2CoO$-P_2O_5 (x = 0-1.0) the formation of solid solutions $Li_{1-x}Na_xCoPO_4$ was not happening. Two types of general compositions have been obtained, namely: $LiCoPO_4$ + $NaCoPO_4$ (α- and β- polymorphs) at fast cooling or $LiCoPO_4$ + β-$NaCoPO_4$ (samples were annealed at 600 °C). Thus, although crystal structures of $LiCoPO_4$ (space group *Pnmb*, a = 5.922, b = 10.206, c = 4.701 Å) and β-$NaCoPO_4$ (space group *Pnma*, a = 8.896, b = 6.8007, c = 5.0341 Å) are very similar, but these compounds do not form solid solutions. The report discussed the conductive properties of the obtained composites also.

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