Comments

Comment on “Characterization of Sodium Cobalt Oxides Related to P3-Phase Superconductor”

In a recent article, Takada et al.[1] reported characterization of P3 phase-related sodium cobalt oxides and stated that the superconducting bilayer-hydrate phase was obtained by the ion exchange between Na^+ and H_3O^+, which resulted in the insertion of H_3O^+ in the host lattice on the basis of their Raman spectra data. They claimed that the lower-than-expected oxidation state of Co was due to the reductive insertion of H_3O^+ by using the same argument for the P2 phase superconductor.[2] However, careful Co K-edge X-ray absorption spectroscopy measurements on the $Na_{0.3}CoO_2 \cdot yH_2O$ ($y = 0$, 0.6, 1.2) materials indicate that there is no Co valence change upon hydration.[3] These results undermine the postulation of H_3O^+ participating in the charge balance of the system.

In addition, to transform 0.5 g of α-$Na_{0.7}CoO_2$ (4.389×10^{-3} mol) into P3 anhydrous $Na_{0.42}CoO_2$ and P3 bilayer-hydrate phase $Na_{0.35}(H_3O)_{0.17}(H_2O)_{1.22}CoO_2$ would require 7.461×10^{-4} mol (calculated from 0.17 mol in 1 mol of P3 bilayer-hydrate phase) of H_3O^+ ions to get into the lattice or 3.072×10^{-4} mol (calculated from a 0.07 mol decrease of Na^+) of H_3O^+ ions to exchange with Na^+. However, the concentration of H_3O^+ in pure water is 1.0×10^{-7} mol/L at 25 °C, and the mole number of the H^+ would be 10^{-8} mol if using a volume of 100 mL of pure water in the immersion step. To obtain the superconducting bilayer-hydrate phase by ion exchange between H_3O^+ and Na^+ at least 3072 L of pure water would be needed to do the job!

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