Communication

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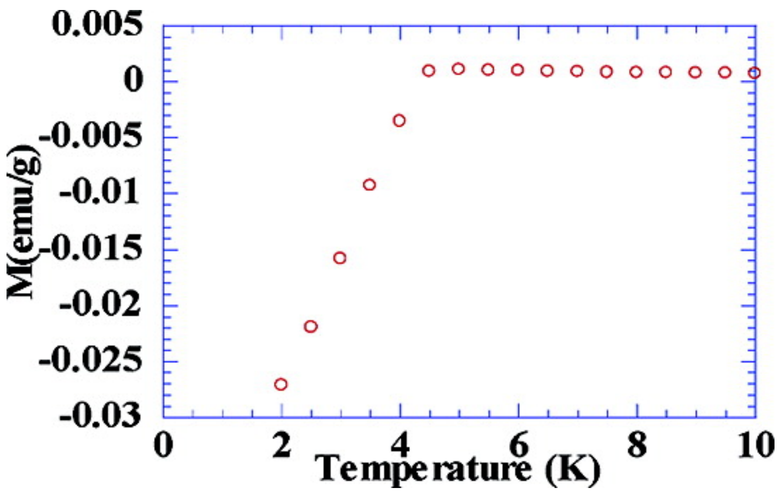

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COMMUNICATIONS

Preparation of Superconducting $Na_x(H_2O)_yCoO_2$ using $NaMnO_4$ as the Deintercalation and Oxidation Agent

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The layered ternary sulfides, A_xMS_2 (A = group 1A or 2A metal, M = Ti, Nb, or Ta), undergo spontaneous intercalating hydration to take up water and form $A_x(H_2O)_yMS_2$ through a topotactic transformation process when exposed to water vapor or liquid water.[1] These ternary sulfides exhibit low dimensional properties due to their anisotropic structures as a result of covalent bonding character between transition metal and sulfur as well as the ionic bonding of 1A or 2A elements. Takada and co-workers recently discovered the superconducting sodium cobalt oxyhydrates, $Na_x(H_2O)_yCoO_2$, with $T_c \approx 4.6$ K using Br_2/CH_3CN solution.[2] Both systems share much similarity with respect to the structure and bonding character of constituting atoms, except that the formation of $Na_x(H_2O)_yCoO_2$ requires partial deintercalation of Na^+ from the parent material, γ-$Na_{0.7}CoO_2$, which is generally considered as a deintercalation and oxidation process, followed by a hydration reaction. As a result of intercalation of water, both systems lead to interlayer expansion of the *c*-axis and enhanced two-dimensional character.

We have recently reported a novel route to prepare sodium potassium cobalt oxyhydrates, $(Na,K)_x(H_2O)_yCoO_2$ ($0.28 \leq x \leq 0.38$), using aqueous potassium permanganate ($KMnO_4$) solution.[3,4] We found that two distinct phases form when using different molar ratios of $KMnO_4$/Na to treat the parent material, γ-$Na_{0.7}CoO_2$. At a low molar ratio of $KMnO_4$/Na, the resulting product is superconducting $(Na,K)_x(H_2O)_yCoO_2$ with a larger *c*-axis ($c \approx 19.6$ Å), whereas at a high molar ratio of $KMnO_4$/Na (≥ 4.286), the resulting product is nonsuperconducting $(Na,K)_x(H_2O)_yCoO_2$ with a smaller *c*-axis ($c \approx 13.9$ Å). Moreover, a higher molar ratio of $KMnO_4$/Na leads to more substitution or even nearly complete substitution of K^+ for Na^+ in the sodium layers. The structure of parent material γ-$Na_{0.7}CoO_2$ is composed of two CoO_2 layers with the Na ions located between, and it crystallizes in a hexagonal lattice with the space group of $P6_3/mmc$ (#194). The *c*-axis is ca. 10.9 Å and, therefore, has an interlayer spacing of ca. 5.45 Å between the two CoO_2 layers. Intercalation of water molecules into the host γ-$Na_{0.7}CoO_2$ results in an expansion of the *c*-axis. It has been found that the value of the interlayer expansion of MS_2 in $A_x(H_2O)_yMS_2$ is 2.9−3.2 Å for monolayers of water and 5.6−5.8 Å for bilayers of water, which corresponds well to the size of a water molecule with a van der Waals diameter of ca. 2.8 Å.[1] The interlayer expansion is ca. 5.7 and 3 Å for A = Na^+ and K^+, respectively. The two distinct interlayer distances are ascribed to the size of the cation A, that is, a larger size of cation A leads to a monolayer of water. This phenomenon is also found in $(Na,K)_x(H_2O)_yCoO_2$. The $c \approx 13.9$ Å phase having more K^+ content has an interlayer expansion of ca. 1.5 Å, whereas the $c \approx 19.6$ Å phase having less K^+ content has an interlayer expansion of ca. 4.35 Å. The former has the hydration water content of $y \approx 0.7$, while the latter has $y \approx 1.33$. Note that the water content was found to be $y \approx 0.5-0.7$ for A = K and $y \approx 1.6-1.8$ for A = Na in $A_x(H_2O)_yMS_2$. Therefore, the water content seems to be closely associated with the interlayer spacing and the *c*-axis in both systems.

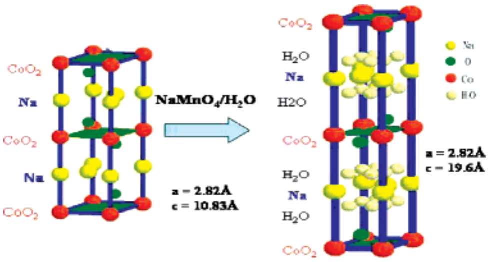

Figure 1. γ-$Na_{0.7}CoO_2$ undergoes a topotactic transformation process to form $Na_x(H_2O)_yCoO_2$ when γ-$Na_{0.7}CoO_2$ is immersed in aqueous $NaMnO_4$ solution.

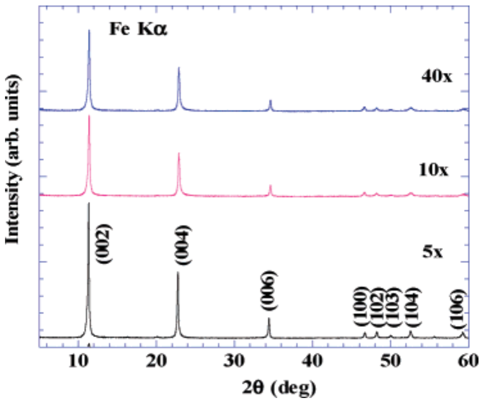

Figure 2. Powder X-ray diffraction patterns of $Na_x(H_2O)_yCoO_2$ prepared by immersing γ-$Na_{0.7}CoO_2$ in aqueous $NaMnO_4$ solution. The label 5X refers to the molar ratio of $NaMnO_4$ relative to the Na in the parent compound (5) (i.e., 3.5 mol of $NaMnO_4$ is used for 1 mol of γ-$Na_{0.7}CoO_2$). All the samples indicate the fully hydrated phase with $c \approx 19.6$ Å.

Besides the potassium permanganate, sodium permanganate ($NaMnO_4$) is another common form of permanganates. Both forms have similar chemical reactivity. Sodium permanganate has about 10 times the solubility in water that potassium permanganate has. This fact would be an advantage for producing superconducting potassium-free cobalt oxyhydrates in large quantities using $NaMnO_4$ as the deintercalation and oxidation agent without resorting to highly toxic Br_2/CH_3CN solution. In this paper, we report successful preparation of superconducting $Na_x(H_2O)_yCoO_2$ using aqueous $NaMnO_4$ solution for the first time. We also find that the sodium content *x* decreases with increasing concentration of $NaMnO_4$ solution. Unlike using a high concentration of aqueous $KMnO_4$ solution, all the resulting hydrated products are the $c \approx 19.6$ Å phase with bilayers of water molecules intercalated between two CoO_2 layers, as shown in Figure 1.

Figure 2 shows the powder X-ray diffraction patterns of sodium cobalt oxyhydrates, $Na_x(H_2O)_yCoO_2$, prepared by using various concentrations of aqueous $NaMnO_4$ solutions. Samples are labeled

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Table 1. Chemical Compositions of $Na_x(H_2O)_yCoO_2$ Prepared Using Aqueous $NaMnO_4$ Solution with Different Molar Ratios of $NaMnO_4$/Na Analyzed by ICP-AES Techniques

sample	Na content (x)
2X	0.429(2)
5X	0.417(5)
10X	0.280(4)

by the molar ratio of $NaMnO_4$ relative to the sodium content in the parent material, that is, 5X−40X ($5 \le NaMnO_4/Na \le 40$). All samples exhibit the characteristic (002) reflection at $2\theta \approx 11.3°$, which corresponds to the superconducting $c \approx 19.6$ Å phase. All the reflection peaks are able to be indexed based on a hexagonal lattice with the space group of $P6_3/mmc$ (#194). When a high molar ratio of $NaMnO_4/Na = 40$ is used, the $c \approx 19.6$ Å phase still remains, which is very different from using the aqueous $KMnO_4$ solution because of no substitution of K^+ for Na^+ in the sodium layers in the case of $NaMnO_4$. Note that a shorter $c \approx 13.9$ Å phase forms at a molar ratio of $KMnO_4/Na \ge 4.286$ when using aqueous $KMnO_4$ solution to prepare $(Na,K)_x(H_2O)_yCoO_2$, presumably due to the larger size of K^+, being reminiscent of the situation in $A_x(H_2O)_yMS_2$, where alkali metal cation A with ionic radii >1 Å in the parent compound A_xMS_2 would lead to hydration of monolayers of water and a shorter c-axis.

In the deintercalation and oxidation process of γ-$Na_{0.7}CoO_2$ using aqueous $KMnO_4$ or $NaMnO_4$ solution, the proposed half-reaction of reduction could be given as

$$4\,\mathrm{MnO_4}^- + \left(2+\frac{z}{2}\right)\mathrm{H_2O} + ze^- \rightleftarrows 4\,\mathrm{MnO_2}(s) + \left(3-\frac{z}{4}\right)\mathrm{O_2}(g) + (4+z)\mathrm{OH}^- \quad (1)$$

which is evidenced by the immediate and significant increase of pH value (ca. 2−3) upon loading the parent compound into aqueous permanganate solution due to the production of OH^-. We realize that aqueous permanganate solution tends to oxidize water and produce the basic hydroxide ion OH^-.[5] The above test was carried out after the aqueous permanganate solution reaches a certain pH value followed by addition of γ-$Na_{0.7}CoO_2$ powders to make sure that the increase of pH value is due to deintercalation and oxidation of γ-$Na_{0.7}CoO_2$ accompanied by the production of the basic hydroxide ion OH^- according to eq 1. As seen in Table 1, a higher concentration of aqueous $NaMnO_4$ solution (larger molar ratio of $NaMnO_4$/Na) leads to lower sodium content. This could be ascribed to the higher redox potential for higher $NaMnO_4$ concentration, according to the Nernst equation, since chemical potential[6] increases with increasing removal of Na^+ and, therefore, requires a higher redox potential to deintercalate more Na^+. Figure 3 shows the dc zero-field-cooled (ZFC) mass susceptibility the 5X sample measured in an applied field of 10 Oe. The onset superconducting transition temperature is $T_c \approx 4.6$ K, and the ZFC mass magnetization at 2 K is -2.71×10^{-2} emu/g, which is much greater than that of the sample prepared using aqueous $Na_2S_2O_8$ solution[7] and corresponds to 65.5% of the theoretical value for perfect diamagnetism. It should be noted that the highest T_c so far is ca. 4.6 K in the system of cobalt oxyhydrate superconductors.

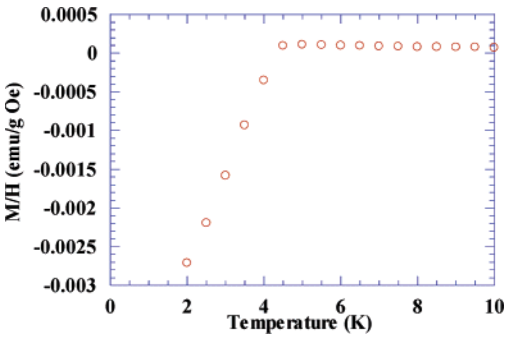

Figure 3. Zero-field-cooled dc mass susceptibility of the 5X sample in a magnetic field of 10 Oe. The onset superconducting transition temperature is $T_c \approx 4.6$ K, and the ZFC mass magnetization at 2 K is -2.71×10^{-2} emu/g. The water content in this sample is 1.33, estimated from the thermogravimetric analysis (TGA).

In conclusion, we have successfully prepared superconducting potassium-free cobalt oxyhydrates, $Na_x(H_2O)_yCoO_2$, using aqueous $NaMnO_4$ solution for the first time. We also find that the sodium content x decreases with increasing concentration of $NaMnO_4$ solution and depends slightly on the immersion time. Even with high concentration of aqueous $NaMnO_4$ solution, all the resulting hydrated products are the $c \approx 19.6$ Å phase with bilayers of water molecules inserted into the host structure.

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Supporting Information Available: Experimental preparations. This material is available free of charge via the Internet at http://pubs.acs.org.

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