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Synthesis of Cobalt Oxyhydrate Superconductor through a Disproportionation Reaction Route

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A cobalt oxyhydrate superconductor with very low content of sodium and relatively high content of hydronium was synthesized through a disproportionation route in hydrochloric acid. The disproportionation reaction was accompanied by ion exchange between Na^+ and H_3O^+. By using the Na^+ ion-selective electrode (ISE) method, energy-dispersive X-ray (EDX) spectroscopy, and thermogravimetric analysis, the composition of the superconductor was determined as $Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$. Magnetic susceptibility measurement indicated the bulk superconductivity below 4.1 K. The new synthetic method is expected to be employed in fabricating the superconducting cobalt oxyhydrate crystals.

Introduction

The recent discovery[1] of the first cobalt oxide superconductor $Na_xCoO_2 \cdot yH_2O$ ($x \approx 0.33$, $y \approx 1.3$) has received much attention due to the unconventional superconductivity induced in a planar triangular lattice.[2−9] The material is built up by the conducting triangular CoO_2 layers sandwiched with insulating block layers that consist of two layers of water molecules and one layer of the sodium ions.[1,10,11] Contrasts and similarities between the cobalt oxide superconductor and the copper oxide ones in view of structural and electronic correlations may shed light on the challenging issue of high-T_c superconductivity.[12]

The experimental study of this new superconductor encounters difficulties because the compound was shown to be rather unstable—extremely sensitive to the environmental temperature and humidity.[13] This challenge happens in each process of synthesis, characterization, and the physical property measurement. For this reason, inconsistent experimental results often appear in the literature. Therefore, it is meaningful to pursue an optimal synthetic method for this intriguing material.

Synthesis of the cobalt oxyhydrate superconductor generally comprises three steps,[1,4,5] including (1) preparation of the parent compound of γ-Na_xCoO_2 with $x = 0.5−0.75$,[14] (2) oxidation of γ-Na_xCoO_2, and (3) the hydration process. Among them, the second step was demonstrated necessary because the intercalation of bilayer water for the non-hydrous Na_xCoO_2 could be realized only when $x < 0.35$.[4] Therefore, the previous preparation method inevitably involved an oxidation process for the parent compound either by the chemical oxidation at low temperatures using Br_2,[1] $Na_2S_2O_8$,[15] and $KMnO_4$[16] as the oxidizing agents or by electrochemical oxidation.[6] In the oxidation process, sodium ions are partially deintercalated, without modifying the two-dimensional CoO_2 building layers.

As we know, some 3*d* transition metal oxides with the intermediate valence state undergo disproportionation reactions in acid solutions. A relevant example is the layered lithium cobalt oxide. It was shown that the disproportionation reaction $2Co(III) \rightarrow Co(II) + Co(IV)$ took place accompanied by the ion exchange between Li^+ ions and protons in acid solutions.[17] Even in the bare solid state of γ-Na_xCoO_2, charge disproportionation was predicted by the correlated band theory.[18] So, it is probable to utilize the disproportionation reaction rather than the direct oxidation for preparing the cobalt oxide superconductor. The ion exchange between Na^+ ions and protons has been demonstrated in the cobalt oxyhydrate superconductor very recently.[19,20] The result shows that the incorporation of protons does not destroy the

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superconductivity. Therefore, one would expect that the cobalt oxyhydrate superconductor with high content of protons can be obtained through the disproportionation reaction route because the ion exchange between Na^+ ions and protons takes place more easily in acid solutions than it does in neutral solutions. Here we report the new synthesis and characterization of the cobalt oxyhydrate superconductor.

Experimental Section

Sample Preparation. There are also three steps in the present synthesis. In the first procedure, parent material γ-Na_xCoO_2 was prepared by a solid-state reaction. High-purity Na_2CO_3 and Co_3O_4 powders with the nominal stoichiometric ratio of $Na_{0.74}CoO_2$ were mixed thoroughly and then pressed into pellets under a pressure of 2000 kg/cm^2. The pellets were rapidly heated to 1073 K in flowing oxygen, and held at that temperature for 12 h. This process was repeated twice with an intermediate grinding. As a result, the single-phase Na_xCoO_2 was obtained (hereafter called Sample A). The sodium content in Sample A was measured to be 0.70(1), slightly lower than the initial one, which is due to volatilization of sodium oxide during the very beginning of the solid-state reaction.

The second procedure of the synthesis is the disproportionation reaction of Sample A in an acid solution. About 0.5 g of $Na_{0.7}CoO_2$ was immersed in 100 mL of 1 M HCl solution for 2 days at room temperature. It was observed that the color of the solution gradually turned pale red due to the release of $[Co(H_2O)_6]^{2+}$. The resulting black solid was filtered, washed with deionized water, and dried in air at room temperature; it is hereafter referred to as Sample B. Finally, Sample B was placed in a chamber with the relative humidity of 100% at room temperature for several days for the water intercalation. The resultant is referred to as Sample C.

Sample Characterizations. Samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TA), and magnetic susceptibility measurement. XRD experiments were carried out using a D/Max-γA diffractometer with Cu Kα radiation. Lattice parameters were refined by a least-squares fit with the consideration of the zero shifts. SEM images were taken on a SIRON scanning electron microscope. The ground sample powders were placed directly on the copper sample holder for making the SEM specimen. Energy-dispersive X-ray (EDX) spectra were obtained by using the Phoenix EDAX equipment attached to the electron microscope. The TA experiment was carried out on a WCT-2 differential thermal microbalance, operating at a heating rate of 10 K/min from 298 to 1373 K. The system is able to record the thermogravimetric (TG) signal and the differiential thermal analysis (DTA) one simultaneously. The temperature dependence of ac magnetization (M_{ac}) was measured on a Quantum Design PPMS facility. The applied ac magnetic field is $H_{ac} = 10$ Oe, thus the ac susceptibility can be obtained: $\chi_{ac} = M_{ac}/H_{ac}$.

Sodium content of the sample was determined by the Na^+ ion-selective electrode (ISE) method[19] as well as by the EDX spectra. Weighted samples (dried whenever necessary) were dissolved in a mixture of H_2O_2 and HNO_3 solution. The pH value of the solution was then neutralized to 9−10 by adding isopropylamine to eliminate the disturbance of H_3O^+. Blank data were measured and then subtracted. The measured precision of the sodium content achieves 0.01 when the fluctuation of the environmental temperature is controlled within ±0.3 K.

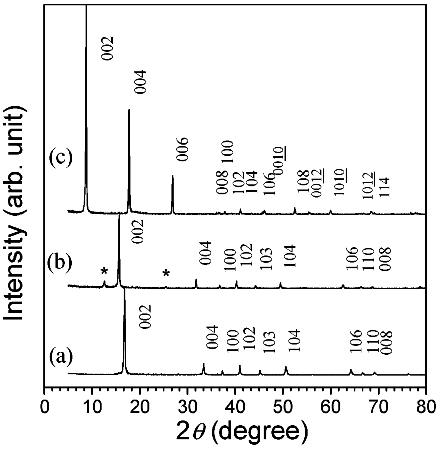

Figure 1. X-ray diffraction patterns for Sample A ($Na_{0.7}CoO_2$), Sample B ($Na_{0.15}(H_3O)_{0.2}CoO_2$), and Sample C ($Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$). The peaks marked by the star indicate the formation of small amount of the monolayer hydrate.

Results and Discussion

Crystal Structure and Morphology. Figure 1 shows the XRD patterns of the Samples A, B, and C. Sample A contains a single hexagonal γ-Na_xCoO_2 phase, whose structure consists of edge-sharing CoO_6 octahedral layers separated by the sodium ions in trigonal prismatic coordination.[21] The lattice parameters are $a = 2.834$ Å and $c = 10.90$ Å, in good agreement with the previous report.[14,21]

After the treatment in the HCl solution, the a-axis of the main phase shrinks to 2.811 Å and the c-axis expands to 11.24 Å. The shrinkage of a-axis is attributed to the increase of the oxidation state of cobalt, shortening the Co−O bond length. Meanwhile, the elongation of the c-axis is due to the weakening of the interlayer Coulomb interaction as a consequence of the deintercalation of Na^+ ions. The sodium ion exchange with the hydronium ions may also result in the elongation of the c-axis. It should be noticed that the XRD pattern of Sample B shows two minor peaks at $2\theta \approx 13°$ and 26°, indicating the formation of a small amount of the monolayer hydrate.[13,22]

As can be seen from the XRD pattern, the fully hydrated Sample C becomes single phase again. The hexagonal cell parameters are $a = 2.820$ Å and $c = 19.82$ Å, indicating that bilayer water molecules are intercalated into the adjacent CoO_2 layers. One notes that the c-axis is particularly longer than the values of the previous reports.[1,4,5] We argue that it is due to the incorporation of the hydronium ion, the size of which is larger than that of the sodium ion.

Figure 2 shows the typical SEM images of Sample A and Sample C that had been preserved in air with humidity of 20% and 100%, respectively, at room temperature for two weeks. The low-resolution image for the Sample A shows platelike grains with the size ranging from 20−50 μm in irregular shapes. The surface of the grains looks coarse. The high-magnification image shows that there are small particles with size below 1 μm on the surface of the grains. In comparison, the grain size of Sample C becomes smaller on

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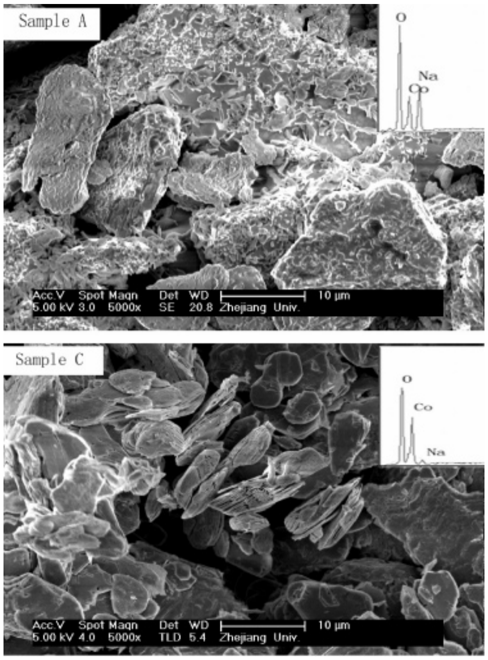

Figure 2. SEM images of Sample A ($Na_{0.7}CoO_2$) and Sample C ($Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$). Note that Sample A had been preserved in air with humidity of 20% at room temperature for two weeks. The insets show the corresponding representative EDX spectra. The small peak at the low energy side (ascribed to carbon) can be observed for Sample A.

average, and the platelike grains tend to be hexagon-shaped and have smooth surfaces. By further magnifying, no such small particles can be seen on the surface. The striking feature of the morphology is the booklet-like structure in each "grain", which has also been observed earlier.[23] The thickness of the "page" is as thin as 20 nm from the high-resolution image. Obviously, the formation of the "booklet" is due to the release of the intercalated water when the sample was in the SEM vacuum chamber.

The EDX spectra, as shown in the inset of Figure 2, determined that the atomic ratio of Na, Co, and O for the Sample A was 1.3:1:2.6. The element carbon was also detected. The result was very similar while probing the different particles or collective particles. Obviously, the measured sodium content is too much higher than the expected value 0.70. This let us conclude that the small particles on the grain surfaces are probably sodium carbonate. The formation of Na_2CO_3 on the surface of Na_xCoO_2 crystals was also suggested by the Raman spectroscopy measurement.[24] What is more, when Sample A was immersed in the acid solution, some bubbles (carbon dioxide) could be observed on the surface of the sample by the naked eye, which further confirms the formation of sodium carbonate. The mechanism is likely to be involved in the formation of NaOH when the sodium ions exchange with hydrated protons in humid air. Consequently, the sodium carbonate appears on the grain surface due to the reaction with CO_2 (from air).

Chemical Composition Analysis. The EDX spectra determined that the atomic ratio of Na, Co, and O for Sample C was 0.17:1:2.3. This result is in good agreement with the Na^+ ISE measurement, which gives the sodium content of 0.15(1).

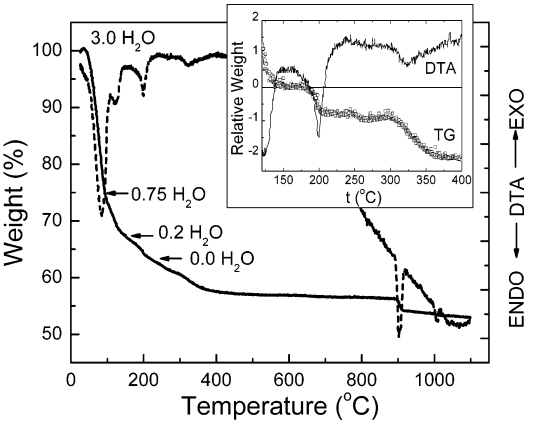

Figure 3. Thermal analysis result for Sample C ($Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$). The inset shows the enlarged plot, where the original TG data (in %) have been subtracted by an empirical quadratic "background" of $76.85 - 0.0767 \times t + 8.42 \times 10^{-5} \times t^2$ (t denotes the temperature in °C) that is primarily due to the kinetic process of water loss.

The thermal analysis result of Sample C is shown in Figure 3. As can be seen, the TG curve shows steplike weight-loss corresponding to the endothermal peaks in the DTA curve. According to our previous analysis,[19] we explain each step as follows. The first heavy weight loss below 100 °C is attributed to both the crystal water and the absorbed free water because the calculated water content for the pristine sample is as high as 3.0, which is too much for occupying two water layers. At about 100 °C, the water content is 0.75, where the sample mainly contains the monolayer hydrated phases with the *c*-axis of 13.9 Å.[13,22] The second weight loss indicates further loss of water in the monolayer hydrated phase. Compared with the above crystal water, the water in the hydronium is not easily released. Therefore, the loss of the last crystal water accompanied by the sharp DTA peak at 200 °C is associated with the decomposition of the incorporated hydronium. The fourth weight loss around 330 °C is ascribed to the decomposition of $Na_xH_yCoO_2$ into $Na_{0.7}CoO_2$ and Co_3O_4, releasing oxygen and water vapor. The weight losses in the third and the fourth steps can be more explicitly seen in the inset of Figure 3. The last two weight losses at high temperatures are assigned to the decomposition of Co_3O_4 and $Na_{0.7}CoO_2$, respectively. All the steps with increasing temperature can be illustrated as follows:

$$Na_xH_yCoO_2 \cdot wH_2O \xrightarrow{40-100\ ^\circ C} Na_xH_yCoO_2 \cdot w'H_2O \xrightarrow{100-150\ ^\circ C}$$
$$Na_xH_yCoO_2 \cdot yH_2O \xrightarrow{200\ ^\circ C} Na_xH_yCoO_2 \xrightarrow{200-350\ ^\circ C}$$
$$Na_{0.7}CoO_2 + Co_3O_4 \xrightarrow{900\ ^\circ C} Na_{0.7}CoO_2 + CoO \xrightarrow{1010\ ^\circ C}$$
$$\text{Melt } (Na_2O + CoO)$$

Since x is given to be 0.15(1), y value can be independently calculated from the weight loss in the third or the fourth step. For example, the weight loss in the third step was determined to be 3.6(2)%, which gives the y value of 0.20(2). Once y is settled, the fourth weight loss can be described by the equation $Na_{0.15}H_{0.2}CoO_2 \rightarrow 0.214\ Na_{0.7}CoO_2 + 0.262$

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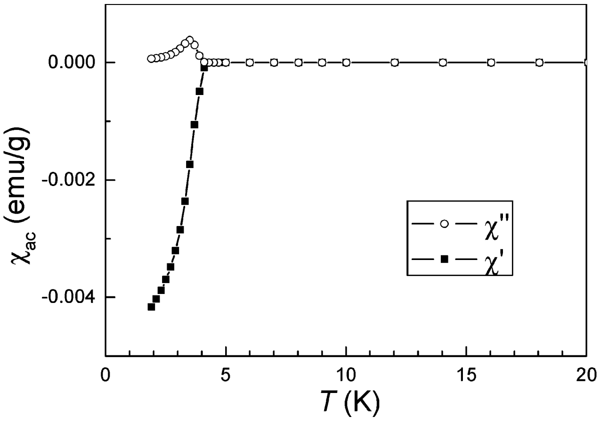

Figure 4. Temperature dependence of ac magnetic susceptibility for powdered Sample C ($Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$). χ' and χ'' denote the real and imaginary parts, respectively.

$Co_3O_4 + 0.1H_2O$ (↑) + 0.212 O_2 (↑). This process will have the weight loss of 5.77% (compared with the initial hydrated compound), which is in very good agreement with the experimental value 5.8(2)%. Moreover, the calculated weight-loss in the fifth step also satisfies the experimental data quite well. Therefore, the chemical formula of the superconductor can be written as $Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$, where the content of the crystal water cannot be exactly determined due to the existence of free water.

Recently, it was proposed that the oxidation of Na_xCoO_2 by Br_2/CH_3CN produced the oxygen deficiency,[25] which was supported by the chemical titration.[26] However, when sintered the $Na_{0.7}CoO_2$ sample in flowing oxygen, the oxygen deficiency can be eliminated.[27] It is argued that the oxygen deficiency is not likely to happen in the process of the disproportionation reaction in acid solutions. Actually, we also carried out the iodometric titration[26] for Sample C, however, the uncertainty of free water (as indicated above) prevented us from obtaining a definite the oxidation state of cobalt.

Superconductivity. Figure 4 shows the temperature dependence of ac magnetic susceptibility for the powdered Sample C. The real part of the susceptibility indicates a sharp diamagnetic transition at 4.1 K, while the imaginary part gives a complete dissipation peak, suggesting good homogeneity for the sample. The magnetic shielding at 2 K for the powdered sample corresponds to the superconducting volume fraction of 12%, comparable to or better than the values measured on the previous powdered samples.[1,5,19,26] The value of T_c is slightly lower than that of the cobalt oxyhydrate superconductor containing less hydronium.[19] Note that the sodium content is beyond the range exhibiting superconductivity in the electronic phase diagram established by Schaak et al.[4] Nevertheless, the oxidation state of cobalt is estimated as +3.65(3) due to the incorporation of hydronium, provided the oxygen deficiency is absent. This indicates, as expected, that it is the carrier concentration (or the oxidation state of cobalt) rather than the sodium content that controls the appearance of superconductivity in the cobalt oxyhydrate system.

Disproportionation Reaction. Now let us discuss the disproportionation reaction of $Na_{0.7}CoO_2$ in acid solutions. The main chemical reactions of $Na_{0.7}CoO_2$ in acid solutions should be (1) disproportionation reaction and (2) ion exchange reaction, similar to the case in the $LiCoO_2$ system.[17] The disproportionation reaction involves the electron transfer between equivalent portions of the cobalt ions. One portion of cobalt ions dissolves in the solution forming divalent hydrous cations and the other portion of cobalt ions in the solid is oxidized. At the same time, partial sodium ions also dissolved into the aqueous phase to balance the charge. These chemical processes will erode the parent material, which can be seen from eq 1 as follows:

$$Na_xCoO_2 + \frac{4\delta}{2-x+\delta}H^+ \xrightarrow{\text{disproportionation}} \frac{2-x}{2-x+\delta}Na_{x-\delta}CoO_2 + \frac{2\delta}{2-x+\delta}Na^+ + \frac{\delta}{2-x+\delta}Co^{2+} + \frac{2\delta}{2-x+\delta}H_2O \quad (1)$$

The above SEM images give the information on the disproportionation reaction. The parent material has larger grain size (in the *ab* plane) than that of Sample C, giving the evidence of eroding due to the disproportionation reaction. In addition, Sample C tends to have a regular (hexagonal) shape. This observation suggests that the disproportionation reaction takes place on the verge of the crystal grains. One may make use of this property for preparing the cobalt oxyhydrate crystals.

In the ion exchange reaction, Na^+ ions exchange with hydronium while the oxidation state of cobalt remains unchanged. This is a competitive reaction described below

$$Na_xCoO_2 + yH_3O^+ \xrightarrow{\text{ion-exchange}} Na_{x-y}(H_3O)_yCoO_2 + yNa^+ \quad (2)$$

So, combining eqs 1 and 2 with the water intercalation, and using the realistic composition, we may write the total chemical reaction as follows:

$$Na_{0.7}CoO_2 + 1.006H^+ + (w - 0.267)H_2O \rightarrow 0.788Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O + 0.582Na^+ + 0.212Co^{2+} \quad (3)$$

Conclusion

We succeeded in synthesizing a cobalt oxyhydrate superconductor $Na_{0.15}(H_3O)_{0.2}CoO_2 \cdot wH_2O$ through a disproportionation reaction route. The superconductor contains a very low content of sodium and a relatively high content of hydronium but it is still superconducting below 4.1 K. Since the disproportionation reaction takes place on the verge of the crystal grains, we expect that this synthesis method can be employed in obtaining superconducting crystals of the cobalt oxyhydrate.

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