A novel route to phase formation of cobalt oxyhydrates using KMnO$_4$ as an oxidizing agent

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ABSTRACT

We have first successfully synthesized the sodium cobalt oxyhydrate superconductors using KMnO$_4$ as a de-intercalating and oxidizing agent. It is a novel route to form the superconductive phase of Na$_x$CoO$_2$·$y$H$_2$O without resort to the commonly used Br$_2$/CH$_3$CN solution. The role of KMnO$_4$ is to de-intercalate the Na$^+$ from the parent compound Na$_{0.7}$CoO$_2$ and oxidize the Co ion as a result. The higher molar ratio of KMnO$_4$ relative to the sodium content tends to remove more Na$^+$ from the parent compound and results in a slight expansion of the c-axis in the unit cell. The superconducting transition temperature is 4.6 - 3.8 K for samples treated by aqueous KMnO$_4$ solution with the molar ratio of KMnO$_4$ relative to the sodium content in the range of 0.03 and 2.29.
1. Introduction

The recent discovery of superconductivity [1] in hexagonal cobalt oxyhydrates Na$_x$CoO$_2$·yH$_2$O with $T_c = 4 – 5$ K has attracted great attention [2-7] because it is unique to have the water molecule intercalated into the parent structure of Na$_{0.7}$CoO$_2$ which is crucial for the occurrence of superconductivity. It is also a particularly interesting system for comparison with the high-$T_c$ cuprates in terms of the structure-electronic state correlations in view of the fact that both have 2D layers (triangular CoO$_2$ layers and square CuO$_2$ layers) in structure and have spin 1/2 ions ($t_{2g}^5$ for Co$^{3+}$ in low spin state and $t_{2g}^6e_{g}^3$ for Cu$^{2+}$) in electron configuration. Besides, this family of materials is of particular interest because of their magnetic and thermoelectric properties. The parent compound Na$_x$CoO$_2$ is a potential candidate for thermoelectric applications due to its high electrical conductivity, large thermopower and low thermal conductivity [8]. There exists four phases [9,10] in the related cobalt oxides: (1) α-Na$_x$CoO$_2$ (0.9 ≤ x ≤ 1, O3 phase); (2) α'-Na$_{0.75}$CoO$_2$ (O'3 phase); (3) β-Na$_x$CoO$_2$ (0.55 ≤ x ≤ 0.6, P3 phase); and (4) γ-Na$_x$Co$_y$O$_2$ (0.55 ≤ x/y ≤ 0.74, P2 phase). The O3 phase represents 3 CoO$_2$ layers in the unit cell with the Na$^+$ in the octahedral surroundings, while P2 phase represents 2 CoO$_2$ layers in the unit cell with the Na$^+$ in the trigonal prismatic surroundings. The O'3 phase is the monoclinic distortion of O3 phase.

Takada et al. obtained the superconducting phase of Na$_x$CoO$_2$·yH$_2$O by immersing Na$_{0.7}$CoO$_2$ powders in Br$_2$/CH$_3$CN solution followed by filtering and rinsing [1]. Park et al. [11] reported the alternative route to make the superconductive Na$_x$CoO$_2$·yH$_2$O. This process is generally considered as a chemical oxidation by removing Na partially before the H$_2$O is intercalated between the CoO$_2$ layers and Na layers. The purpose of this paper is to report a novel route of preparing the superconducting Na$_x$CoO$_2$·yH$_2$O phase using aqueous KMnO$_4$ solution as a de-intercalating and oxidizing agent. It is an alternative route to use oxidant rather than Br$_2$/CH$_3$CN solution to form the superconducting phase of Na$_x$CoO$_2$·yH$_2$O.

2. Experimental
The superconducting cobalt oxyhydrates Na$_x$CoO$_2$$y$H$_2$O were prepared following the procedures below: (1) Preparation of parent material Na$_{0.7}$CoO$_2$. Polycrystalline powders of Na$_{0.7}$CoO$_2$ were synthesized by quantitatively mixing high-purity powders of Na$_2$CO$_3$ and CoO. The mixed powders were ground thoroughly using a Retch MM2000 laboratory mixer mill, followed by a rapid heat-up procedure [12] at 700°C in order to avoid the loss of Na in the heating process. (2) De-intercalation of Na and Oxidation. The resulting powders (0.5 -1 g) were immersed and stirred in 50 ml of water solution with different molar ratios of KMnO$_4$/Na labeled as 0.05X – 2.29X at room temperature for 5 days. (3) Formation of superconductive phase. The products were carefully filtered and washed thoroughly with deionized water, followed by drying at ambient conditions for 10 - 20 hrs in order to remove the powders from the filter paper. The dried powders were then stored in a wet chamber with sufficient humidity for further structural and magnetic characterization. Powder x-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer equipped with Fe Kα radiation. The sodium content was determined by using a Perkin Elmer Optima 3000 DC inductively coupled plasma - atomic emission spectrometer (ICP-AES). Before the chemical analysis, samples are dehydrated by heating at 300°C in air for 12 h. Thermogravimetric analysis (TGA) was carried out by using a Perkin Elmer Pyris 1 thermogravimetric analyzer. A commercial SQUID magnetometer (Quantum Design) was used to characterize the superconducting transition temperature of the samples.

3. Results and discussion

Fig. 1 shows the powder x-ray diffraction patterns (XRD) of the products obtained by different molar ratios of KMnO$_4$ relative to Na content. The XRD patterns for ≤ 0.1X samples are a mixture of a fully-hydrated superconducting phase and a non-superconducting dehydrated phase, which is similar to bromine-treated samples with substoichiometric or stoichiometric Br$_2$/CH$_3$CN solutions [2]. Single phase of fully hydrated Na$_x$CoO$_2$$y$H$_2$O occurs for KMnO$_4$/Na = 0.3. For 0.5 ≤ KMnO$_4$/Na ≤ 2.29, there is a very tiny peak appearing at 2θ ≈ 16°, the characteristic (002) peak of so-called y = 0.6 intermediate
hydrated phase [5], in addition to the diffraction peaks of the fully hydrated phase. The sodium contents are determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and shown in Table I. Chemical analyses show that the sodium contents in \( \text{Na}_x \text{CoO}_2 \cdot y\text{H}_2\text{O} \) systematically decreases with increasing molar ratio of \( \text{KMnO}_4/\text{Na} \). The values of \( x \) are 0.38, 0.32, 0.28 for 0.3X, 0.5X, and 2.29X samples, respectively. These results confirm that the role of \( \text{KMnO}_4 \) is acting as an oxidizing agent to partially de-intercalate the Na from the structure and hence oxidize the electronically active CoO\(_2\) layers. The \( c\)-axis of the unit cell in \( \text{Na}_x \text{CoO}_2 \cdot y\text{H}_2\text{O} \) tends to increase with increasing molar ratio of \( \text{KMnO}_4/\text{Na} \) from 19.669 Å for the 0.3X sample to 19.735 Å for the 2.29X sample but with little changes in the \( a\)-axis.

The thermal stability and water content of 0.3X sample are checked and determined by heating the sample in flowing \( \text{O}_2 \) at the slowest rate of 0.1°C/min available to the Perkin Elmer Pyris 1 thermogravimetric analyzer (TGA). Fig. 2 indicates a multi-stage loss of water with relatively unstable intermediates [13], being consistent with the thermally unstable nature of the fully hydrated phase [5,14]. The water content of fully hydrated phase is estimated to contain 1.45 and 1.55 \( \text{H}_2\text{O} \) pre formula unit by taking the weight loss at 320 °C and 600 °C, respectively, as the fully dehydrated phase (\( y = 0 \)), assuming no oxygen deficiency in the sample for the present estimations.

Fig. 3 shows the zero-field cooled and field cooled magnetization data of 0.3X, 0.5X, and 2.29X samples measured in a dc field of 10 Oe. The onset superconducting transition is observed at about 4.6 K, 4.5 K, and 3.8 K for 0.3X, 0.5X, and 2.29X, respectively. The mass magnetization at 1.8 K is \(-1.28\times10^{-2}\) emu/g in the zero-field cooling measurements, which is approximately 31% of the theoretical value for perfect diamagnetism.

4. Conclusions

We have first synthesized the superconductive cobalt oxyhydrates \( \text{Na}_x \text{CoO}_2 \cdot y\text{H}_2\text{O} \) using \( \text{KMnO}_4 \) as an oxidizing agent instead of using \( \text{Br}_2/\text{CH}_3\text{CN} \) solutions. The role of \( \text{KMnO}_4 \) is to de-intercalate the
Na from the structure and hence oxidize the Co ion based on the electron neutrality. The higher molar ratio of KMnO₄ relative to Na content used to treat the samples leads to more removal of Na. The superconductive phase of NaₓCoO₂·yH₂O is commonly obtained by Br₂/CH₃CN solutions, which is highly toxic by ingestion and inhalation. This new route might also indicate that KMnO₄ has the potential to treat other layered oxide materials with similar function of de-intercalation and oxidation and to have mass production of superconducting samples.

Acknowledgment. This work is supported by National Science Council of ROC under the grant No. NSC 92-2112-M-018-005.
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Table I. Sodium content and lattice constants of Na$_x$CoO$_2$$\cdot$yH$_2$O prepared using KMnO$_4$ as oxidant

| Molar ratio of KMnO$_4$/Na | Sodium content $x^a$ | $a$ axis$^b$ A | $c$ axis$^b$ A |
|---------------------------|-----------------------|----------------|----------------|
| 0.3X                      | 0.38                  | 2.8249(1)      | 19.669(1)      |
| 0.5X                      | 0.32                  | 2.8248(1)      | 19.679(1)      |
| 2.29X                     | 0.28                  | 2.8250(2)      | 19.735(2)      |

$^a$The error in weight % of each element in ICP-AES analysis is ±3 %, which corresponds to an estimated error of ±0.02 per formula unit.

$^b$Lattice constants are determined by least squares refinement using the XRD data between 2θ of 5° and 90° based on a hexagonal lattice with space group P6$_3$/mmc.
Fig. 1. Powder x-ray diffraction (XRD) patterns for Na$_x$CoO$_2$·yH$_2$O prepared using different molar ratios of KMnO$_4$ relative to Na content. The 0.3 X and 2.29 X represent the molar ratios of KMnO$_4$ relative to Na content are 0.3 and 2.29, respectively. The asterisk indicates the tiny peak for the (002) diffraction peak for the so-called y = 0.6 intermediate hydrated phase.
Fig. 2. Thermogravimetric analysis of Na\textsubscript{x}CoO\textsubscript{2}·yH\textsubscript{2}O (0.3X) with a heating rate of 0.1 °C/min in flowing oxygen. The water content is determined by assuming a complete loss of water at 320°C.
Fig. 3. Zero-field cooled and field cooled d.c. magnetization for Na$_x$CoO$_2$·yH$_2$O (solid circle: 0.3X; open circle: 0.5X; solid diamond: 2.29X).