



A novel route to phase formation of superconductive 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 cobalt oxyhydrates without resort to the commonly used $\text{Br}_2/\text{CH}_3\text{CN}$ solution. The role of KMnO_4 is to de-intercalate the Na^+ from the parent compound $\text{Na}_{0.7}\text{CoO}_2$ 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 the 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.

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1. Introduction

The recent discovery of superconductivity [1] in hexagonal cobalt oxyhydrates $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with $T_c = 4\text{--}5\text{K}$ has attracted great attention [2–7] because it is unique to intercalate the water molecule into the parent structure of $\text{Na}_{0.7}\text{CoO}_2$ and 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^{4+} in low spin state and $t_{2g}^6 e_g^3$ 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 of γ -phase

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Na_xCoO_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) $\alpha\text{-Na}_x\text{CoO}_2$ ($0.9 \leq x \leq 1$, O3 phase); (2) $\alpha'\text{-Na}_{0.75}\text{CoO}_2$ (O'3 phase); (3) $\beta\text{-Na}_x\text{CoO}_2$ ($0.55 \leq x \leq 0.6$, P3 phase); and (4) $\gamma\text{-Na}_x\text{Co}_y\text{O}_2$ ($0.55 \leq x/y \leq 0.74$, 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 $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ by immersing $\text{Na}_{0.7}\text{CoO}_2$ powders in $\text{Br}_2/\text{CH}_3\text{CN}$ solution followed by filtering and rinsing with acetonitrile and distilled water [1]. Park et al. [11] reported the alternative route to make the superconductive $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. This process is generally considered as a chemical oxidation by removing Na^+ partially before intercalating the H_2O between the CoO_2 layers and Na layers. The purpose of this paper is to report a novel route of preparing the superconducting cobalt oxyhydrate phase using an aqueous KMnO_4 solution as a deintercalating and oxidizing agent. It is an alternative route to use oxidant rather than $\text{Br}_2/\text{CH}_3\text{CN}$ solution to form the superconducting phase of cobalt oxyhydrates.

2. Experimental

The superconducting cobalt oxyhydrates were prepared following the procedures below: (1) Preparation of parent material $\text{Na}_{0.7}\text{CoO}_2$. Polycrystalline powders of $\text{Na}_{0.7}\text{CoO}_2$ were synthesized by quantitatively mixing high-purity powders of Na_2CO_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 800°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 $\text{KMnO}_4/$

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 several times with de-ionized water, followed by drying at ambient conditions for 10–20 h 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 $\text{FeK}\alpha$ 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 $\leq 0.1\text{X}$ 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 $\text{Br}_2/\text{CH}_3\text{CN}$ solutions [2]. Single phase of fully hydrated cobalt oxyhydrate occurs for $\text{KMnO}_4/\text{Na} = 0.3$. All reflection peaks are indexable based on a hexagonal lattice with space group $\text{P6}_3/\text{mmc}$ (# 194). For $0.5 \leq \text{KMnO}_4/\text{Na} \leq 2.29$, there is a very tiny peak appearing at $2\theta \approx 16^\circ$, the characteristic (002) reflection peak of so-called $y = 0.6$ intermediate hydrated phase [5], in addition to the reflection 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 1. Chemical analyses show that the sodium contents systematically decreases with increasing molar ratio of

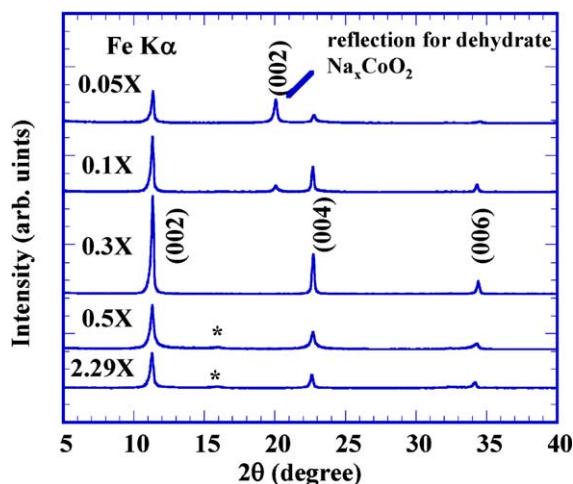


Fig. 1. Powder X-ray diffraction (XRD) patterns for $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ prepared using different molar ratios of KMnO_4 relative to Na content. The 0.3X and 2.29X represent the molar ratios of KMnO_4 relative to Na content are 0.3 and 2.29, respectively. The asterisk indicates the tiny peak for the (002) diffraction peak for the so-called $y = 0.6$ intermediate hydrated phase.

Table 1

Sodium content and lattice constants of cobalt oxyhydrates prepared using KMnO_4 as oxidant

Molar ratio of KMnO_4/Na	Sodium content x^a	a axis ^b (Å)	c axis ^b (Å)
0.3X	0.37	2.8249(1)	19.669(1)
0.5X	0.37	2.8248(1)	19.679(1)
2.29X	0.30	2.8250(2)	19.735(2)

^a The error in wt% of each element in ICP-AES analysis is $\pm 3\%$, 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 $\text{P6}_3/\text{mmc}$.

KMnO_4/Na . The values of x are 0.37, 0.37, 0.30 for 0.3X, 0.5X, and 2.29X samples, respectively. These results confirm that the role of 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 tends to increase with increasing molar ratio of KMnO_4/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.

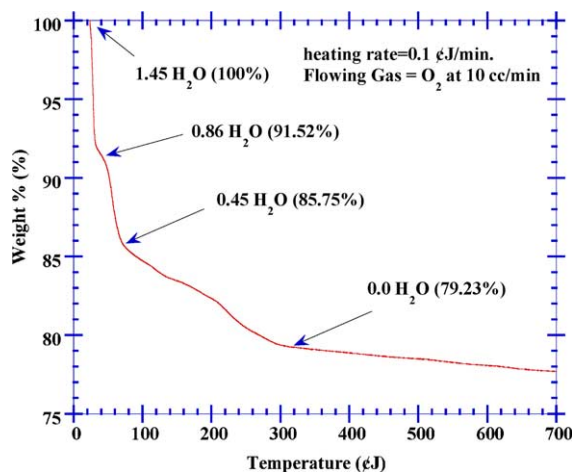


Fig. 2. Thermogravimetric analysis of KMnO_4 -treated cobalt oxyhydrate (0.3X) at a heating rate of $0.1^\circ\text{C}/\text{min}$ in flowing oxygen. The water content is determined by assuming a complete loss of water at 320°C .

The thermal stability and water content of 0.3X sample are checked and determined by heating the sample in flowing O_2 at the slowest rate of $0.1^\circ\text{C}/\text{min}$ 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 H_2O per formula unit by taking the weight loss at 320°C and 600°C as the fully dehydrated phase ($y = 0$), assuming no oxygen deficiency in the sample for the present estimations. The former seems to be more reliable because the impurity phase of Co_3O_4 begins to appear at the temperature above 320°C .

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 of the 0.3X sample at 1.8 K is -1.28×10^{-2} emu/g in the zero-field cooling measurements, which is approximately 31% of the theoretical value for perfect diamagnetism.

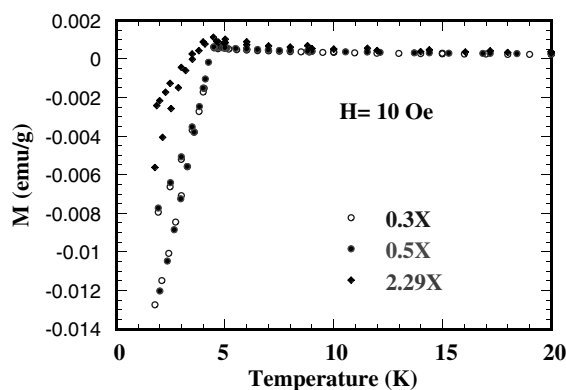


Fig. 3. Zero-field cooled and field cooled dc magnetization of KMnO_4 -treated cobalt oxyhydrates (\circ : 0.3X; \bullet : 0.5X; \blacklozenge : 2.29X).

4. Conclusions

We have first synthesized the superconductive cobalt oxyhydrates using an aqueous KMnO_4 solution as an oxidizing agent instead of using $\text{Br}_2/\text{CH}_3\text{CN}$ solution. The role of KMnO_4 is to deintercalate the Na from the structure and hence oxidize the Co ion based on the electron neutrality. The higher molar ratio of KMnO_4 relative to Na content used to treat the samples leads to more removal of Na. The superconductive phase of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is commonly obtained by $\text{Br}_2/\text{CH}_3\text{CN}$ solutions, which is highly toxic by ingestion and inhalation. This new route might also indicate that KMnO_4 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.

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