

Crystallization and Anisotropic Properties of Water-Stabilized Potassium Cobalt Oxides

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A low-temperature electrochemical synthesis of water-stabilized $K_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ crystal has been demonstrated. Temperature variable X-ray diffractions display a sandwiched structure with mobile water molecules. The crystal has hexagonal characteristic with four adjustable phases $K_{0.35}\text{CoO}_2 \cdot 0.40\text{H}_2\text{O}$, $K_{0.35}\text{CoO}_2 \cdot 0.34\text{H}_2\text{O}$, $K_{0.22}\text{CoO}_2 \cdot 0.21\text{H}_2\text{O}$, and anhydrous $K_{0.15}\text{CoO}_2$. Lattice water removal in a step-by-step process with the reduction of interlayer spacing in a single crystal can be achieved. Strong anisotropic conducting at low temperature and weak interlayer coupling in the *ab* plane have been demonstrated.

Introduction

An important step toward ceramic superconductivity was taken in 1986 when Müller and Bednorz reported the observation of the onset of superconductivity near 30 K in a mixed metal oxide sample.¹ Soon, the breakthrough came when Wu and co-workers raised the T_c to 93 K.² The ability to achieve superconductivity using liquid nitrogen cooling has brought excitement to scientists trying to discover a superconductor with higher transition temperature.³ Although great efforts have been expended in the past years, why these materials are superconducting at such a high temperature and how to increase the T_c for oxide compounds unfortunately remains a puzzle.

Compounds of $A_x\text{CoO}_2$ (A = alkali) were recognized to be the potential candidates for high thermal electric power materials.⁴ The hexagonal structure contains the CoO_2 layer intercalated with alkali metal. Interlayer spacing can be further expanded by vigorous oxidation in aqueous solution and stabilized with water molecules. Superconductivity of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ compound with near 5 K T_c when $x \approx 0.35$, $y \approx 1.3$ was discovered by Tanaka et al.⁵ Fascinating electric and magnetic properties coexisting with water molecules was entitled “icy superconductivity”. High-temperature sintered powders of Na_xCoO_2 have been prepared and well studied

with liquid bromine treatment.^{6,7} Single crystal is one of the important elements in solving novel physics phenomena for anisotropy structure. However, crystal growth of alkali cobalt oxides with water molecule is a great challenge due to high water vapor pressure.⁸ Posttreatment of anhydrous Na_xCoO_2 single-crystal interacting with electrochemical oxidation in an aqueous solution, has, up to this moment, not successfully prepared a high-quality hydrous crystal.^{9–10} As with the Na_xCoO_2 system, anhydrous $K_x\text{CoO}_2$ powder had been prepared and studied in structure and physical properties.^{11,12} This work is the first report on experiments to directly grow hydrated $K_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ crystal by low-temperature technique. It provides a reaction pathway to stabilized water molecules in $A_x\text{CoO}_2$ structure while the crystal is growing. This water-intercalated crystal provides a great opportunity in adjusting the interlayer spacing step by step along the *c*-axis. The correlations between electronic structure and interlayer interaction of the *ab* plane therefore can be studied when the process of heating and removing the water molecules is observed stepwise in a multi-tiered process on one single crystal. Conductivity measurements display a metallic behavior and strong anisotropy at low temperature.

Experimental Section

The electrochemical growth of $K_x\text{CoO}_2$ crystals is carried out in a KOH molten flux cell designed by Norton.¹³ The molten flux in a 75-mL Teflon cell typically consists of 1 g of CoO dissolved in

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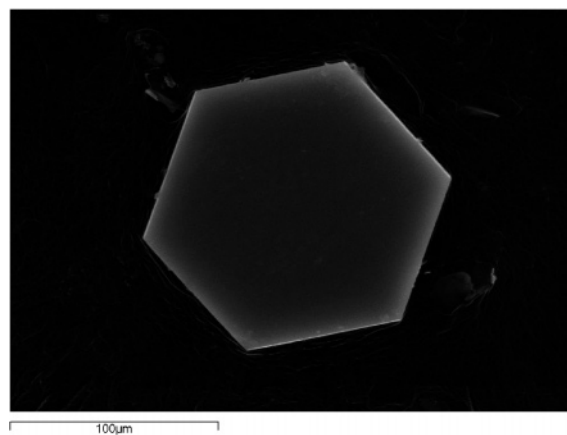


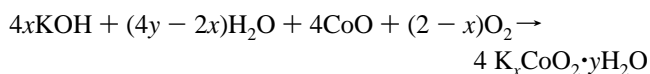
Figure 1. Scanning electron micrograph of the $K_xCoO_2 \cdot yH_2O$ crystal with hexagonal facet.

50 g of KOH. The temperature of the cell is controlled by a Eurotherm temperature controller at 260 °C. The lowered melting point of KOH flux is presumed to result from the known high water content of commercial KOH.¹⁴ The useable time is limited by the depletion of CoO from the flux through deposition of Co metal on the cathode and $K_xCoO_2 \cdot yH_2O$ on the anode. Galvanic deposition is performed utilizing two 1-mm Pt electrodes with 5-mm distance, one-compartment cell geometry. A 36-h 1 mA/cm² galvanic electrolysis for the system described above is used to grow ~1-mm hexagonal crystals.

Scanning electron microscopy and energy-dispersive X-ray analysis are performed using a JEOL model 5200 SEM equipped with a Link data acquisition system and a semiquantitative analysis program. Powder X-ray diffraction patterns of powder samples are acquired using a Shimadzu XRD-7000 (Cu) system equipped with an Anton Paar temperature variable apparatus. Resistivity is measured by a typical four-probe method. The silver paste is air-dried at room temperature and the as-grown crystal is then baked at 50 °C for 1 h. The typical contact resistance is about 30–100 Ω and when double-checked at 4.2 K continued to maintain its contact resistance.

Results and Discussion

Crystallization of $K_xCoO_2 \cdot yH_2O$ with sub-millimeter size can be synthesized by chemical reflux with O₂ at 260 °C for 24 h. Crystals are hexagonal in shape with facets along *ab* direction as shown in Figure 1. This chemical reaction can be represented as the following formula:



The crystal's color varies from dark violet to black depending upon the oxidative condition of the crystal. As-grown dark violet samples will turn black in a few days indicating the unstable properties of the hydrated crystal. SEM/EDX quantitative values for the as-grown $K_xCoO_2 \cdot yH_2O$ crystal show the potassium and cobalt elemental mole concentration ratio is close to the 0.35 to 1 ratio. Thermogravimetric analysis of the reflux crystals in Figure 2 displays four plateaus from 15 to 400 °C. Small weight loss can be observed when the temperature program is held at as low as

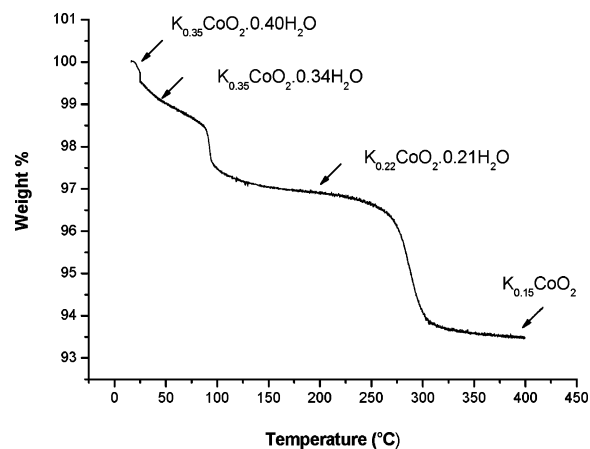


Figure 2. Thermogravimetric analysis of the as-grown $K_xCoO_2 \cdot yH_2O$. Sample is first held at 25 °C in air for 1 h and then heated at 1 °C/hr to 400 °C.

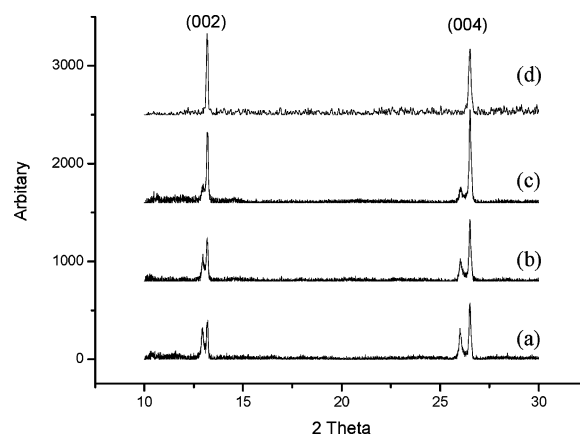


Figure 3. Powder X-ray diffraction patterns of the $K_{0.35}CoO_2 \cdot 0.40H_2O$ and $K_{0.35}CoO_2 \cdot 0.34H_2O$ mixture held isothermally at 35 °C for (a) 0, (b) 16, (c) 32, and (d) 50 h.

25 °C for 1 h. Powder X-ray diffraction patterns of the as-grown crystals in Figure 3a display two sets of (00*l*) diffraction peaks which correspond to the hydrated $K_{0.35}CoO_2 \cdot 0.40H_2O$ and $K_{0.35}CoO_2 \cdot 0.34H_2O$ structures. This increase in layer separation with intercalated water for the hydrated phase is similar to that of the $Na_xCoO_2 \cdot yH_2O$.^{6,10} Intercalated water of the hydrated $K_{0.35}CoO_2 \cdot 0.40H_2O$ phase can be readily removed and transferred into $K_{0.35}CoO_2 \cdot 0.34H_2O$ by heating the sample up to 35 °C for a few hours. In-situ X-ray measured in conjunction with a temperature variable attachment in Figure 3b–d show the low-angle diffraction peak gradually disappearing when the temperature is held at 35 °C for different time periods. In this preliminary result, water molecules in the $K_{0.35}CoO_2 \cdot 0.40H_2O$ structure seem to have vapor pressure similar to surface wetting water and hence we are not able to determine the *y* value with accuracy. The estimated value based on TGA data should be slightly lower than the actual value. The second transition, starting around 80 °C, shows the significant weight loss that is corresponding to the phase transition from $K_{0.35}CoO_2 \cdot 0.34H_2O$ to $K_{0.22}CoO_2 \cdot 0.21H_2O$. High vapor pressure during the dehydration at 80 °C indicates the high volatility and mobility of lattice water. Powder X-ray diffraction patterns of the annealed compound in Figure 4 show the lattice contraction along with the crystals' dehydration. High-

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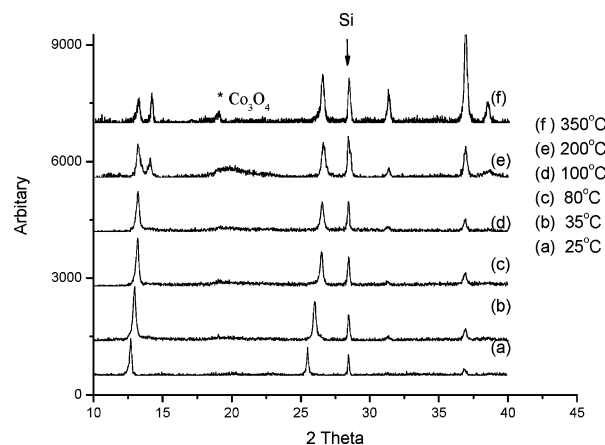


Figure 4. Powder X-ray diffraction patterns of the $\text{K}_{0.35}\text{CoO}_2 \cdot 0.40\text{H}_2\text{O}$ sample with different temperature treatments.

temperature treatment with 350 °C for 48 h results in the dehydrated $\text{K}_{0.15}\text{CoO}_2$ phase and partial structural decomposition as shown in Figure 4f. Lattice parameters of the c axis are 13.956, 13.686, 13.408, and 12.556 Å for $y = 0.40, 0.34, 0.21$, and 0, respectively. In comparison with the Na_xCoO_2 system, anhydrous K_xCoO_2 has greater interlayer spacing along c direction. Partial dehydration of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ resulting in the shrinkage of interlayer spacing and rearrangement of Na^+ ions and H_2O molecules has been reported.¹⁵ On the basis of the previous results, the edge-sharing $\text{K}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ framework there should have at least two types of arrangements for water molecule. Heating crystal concomitantly releases H_2O and K ions reflecting the electric field strength within layers correlated with water coordination. Intergrowth of crystals and resulting tails during single-crystal X-ray diffraction have not yet provided conclusive evidence. The detailed structure of intercalated water now is under investigation.

To minimize the spontaneous nucleation, electrochemical techniques can limit the crystal growth at electrode surface where the electrochemical oxidation is taking place. When constant current electrolysis is applied, $\text{K}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ crystals are formed at the anode. Crystals grown for 36 h are hexagonal and 1 mm \times 1 mm in size. The temperature dependence resistivity of $\text{K}_{0.35}\text{CoO}_2 \cdot 0.34\text{H}_2\text{O}$ crystal is shown in Figure 5. The configurations of wiring for ab -plane and c -axis measurement are shown in the inset. A metallic behavior of ab -plane is observed. The temperature dependence of resistivity can be fitted by a formula of $\rho_0 + aT^{1.6}$ at low-temperature regions. The mechanism of this unusual temperature dependence might result from the electron scattering near an itinerant to localized electronic transition.¹⁶ Dehydrated samples display the same metallic behavior

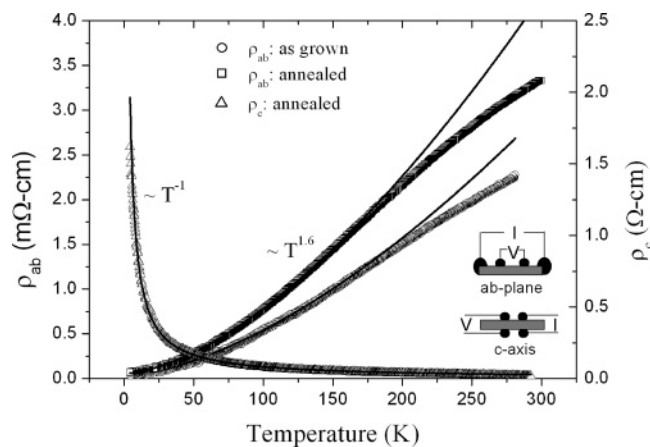


Figure 5. Temperature dependence of ρ_{ab} and ρ_c of the $\text{K}_{0.35}\text{CoO}_2 \cdot 0.34\text{H}_2\text{O}$ and dehydrated crystals. The wiring of measurement is shown in the inset.

except for having higher resistivity values. A similar resistivity behavior can be attributed to the electronic structure maintaining integrity while the c -axis lattice constant is reduced.

The resistivity along c -axis of dehydrated sample is increased as the temperature is decreased, which follows $1/T$ dependence. This behavior is different from the results of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ sample, in which a semiconductor–metal crossover around 200 K is reported.^{4,9,17} The resistivity results show a strong anisotropy in the ab -plane and along c -axis. The ratio of ρ_c/ρ_{ab} is around 10 at 300 K and goes up to 3×10^4 at 4 K. It is deduced that the majority of carriers moving in the CoO_2 plane and its inter-planar coupling become very weak at low temperature. The residual resistance ratio, $\rho_{300\text{K}}/\rho_{4\text{K}}$, is more than 50 indicating that the carriers transport is almost not scattered by impurities.

Conclusion

Crystals of $\text{K}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with four different y values have been grown. Lattice water can be removed stepwise along with the reduction of interlayer spacing. Resistivity measurements of hydrated and dehydrated crystals display similar metallic behavior in ab plane. The ρ_c/ρ_{ab} ratio around 3×10^4 at 4 K demonstrates the anisotropic conducting in the ab plane.

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