Rapid communication

Low temperature synthesis of bilayer hydrated cesium cobalt oxide

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Abstract

Bilayer hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ structure has re-directed superconductivity research in recent years. Here, we develop a low temperature synthesis method to prepare a novel hydrous $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ compound in one step. The bilayer-hydrate of $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ with a greatest interlayer spacing $d = 10.0(2)$ Å among alkali cobalt oxides has been grown in crystal form. Magnetic susceptibility measurement of $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ displays a paramagnetic behavior down to 1.9 K. With the assistance of low temperature molten CsOH solvent, crystals of $Rb_{0.30}CoO_2 \cdot 0.36H_2O$ and $K_{0.35}CoO_2 \cdot 0.4H_2O$ can be grown. The results provide the capability for preparing a novel hydrous structure and the systematic investigation of interlayer coupling effect of alkali ion insertion compounds.

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Keywords: Hydrous cobalt oxide; Bilayer hydrate; Cesium hydroxide; Rubidium cobalt oxide; Magnetic susceptibility

1. Introduction

Anhydrous metal cobalt oxides with layered structure have been attracting wide attention for the past two decades. Li_xCoO_2 is one of the most important intercalation compounds for secondary lithium ion batteries [1]. Na_xCoO_2 is recognized to be a potential candidate for thermal electric power materials [2]. A_xCoO_2 compounds have a layered structure, with the CoO_2 layers consisting of CoO_6 octahedra sharing common edges and forming a triangular Co–O sublattice. Open and polarizable framework structure makes the compounds adaptable by chemical modification. Tanaka and his co-workers found the superconductivity of hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ in 2003 [3]. Hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$ oxide was im-

mediately targeted by research scientists owing to its unusual bilayer-hydrate (BLH) structure [4]. The anisotropy in transport properties of hydrated $Na_{0.35}CoO_2 \cdot 1.3H_2O$, strong inverse correlation between the CoO_2 layer thickness, and the superconducting transition temperature, reveal the similarities to the cuprate superconductor [5,6]. Furthermore, Anderson et al. has revealed that the interlayer coupling between CuO_2 layers play an essential role in high-temperature superconductivity [7–9]. In hydrated $A_xCoO_2 \cdot yH_2O$ compounds, the coupling strength of CoO_2 layers might be varied by the replacement of different ionic size alkalis resulting in the change of c-axis lattice constant. The influence of coupling strength between CoO_2 layers on superconductivity, therefore, can be possibly studied when the process of controlling the interlayer spacing is developed.

Great efforts in growing hydrous crystal and preparing novel cobaltate compound have been approached by different techniques [5,10]. However, the conflict of high temperature sintering and water preservation for hydrous

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compound has restricted the progress of material preparation and fundamental study [11]. In this work, we develop a low temperature molten salt reaction to crystallize a novel BLH-$Cs_{0.2}CoO_2 \cdot 0.63H_2O$ compound in one step, which will assist both in exploring novel compounds and fundamental physical study.

2. Experimental

The synthesis of $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ is carried out in a CsOH molten flux. The molten flux in a 75-mL Teflon cell typically consists of 1 g of CoO dissolved in 50 g CsOH. To grow hexagonal crystals, crystallization by a slow cooling process is normally in a moisturized oxygen atmosphere. A highly moisturized environment at low temperature is required to maintain water vapor pressure in preparing BLH compound. The temperature is controlled within $0.1\,°C$ precision by a Eurotherm temperature controller at $260\,°C$. The temperature program for crystal growth is held at $260\,°C$ for 24 h followed by $0.5\,°C/h$ cooling rate to $160\,°C$. Samples are harvested from solidified hydroxide salts at room temperature by de-ionized water rinsing and filtration.

Scanning electron microscopy and energy dispersive X-ray analysis are performed using a Jeol model 5200 SEM/EDX equipped with a Link data acquisition system and a semi-quantitative analysis program. Elemental analysis is performed with a GBC 902 atomic absorption spectrometry (AAS). For $A_xCoO_2 \cdot yH_2O$ meta-stable compounds, chemical stoichiometry determined with accuracy is an extremely difficult work. The interferences may come from the trace of solidified salt sandwiched in defects, high vapor pressure of lattice water and/or ion-exchange with H_3O^+ during processing [12]. The x, y values in this work are typically obtained by averaging the values of three separate test. Powder X-ray diffraction patterns of powder samples are acquired using a Shimadzu XRD-7000 (Cu) system. Solid-state NMR (SSNMR) experiments are carried by Varian INOVA 300 MHz spectrometer with Chemagnetics 4.0 mm MAS probe at room temperature. All ^{133}Cs chemical shifts are referenced to 1 M solution of cesium nitride. Magnetic properties are characterized by a DC SQUID, Quantum Design model MPMS2. The applied magnetic field is 50 G and measured temperature starting from 1.9 K.

3. Results and discussion

High temperature sintered powders of layered A_xCoO_2 ($A =$ Li, Na) have been prepared and well studied [1,2]. Post-treatment of anhydrous Na_xCoO_2 powder interacting with liquid bromine and oxidation in an aqueous solution, has, up to this moment had the most success in preparing hydrous compound [3]. However, crystal growth of hydrous alkali cobalt oxides without post-treatment is a great challenge due to high temperature vaporization of lattice water. To overcome the high temperature problems

in directly preparing hydrous compound, molten cesium hydroxide solvent provides advantages in its low melting point and high solubility for the oxide precursor [13]. In addition, molten CsOH can form a moisturized (CsOH–HOH) solution with H_2O molecules carried by flowing oxygen. The moisturized environment can be preserved and balanced by the intrinsic hygroscopic property of CsOH and external wetted atmosphere. The oxygen oxidation and slow cooling processes can crystallize novel BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ compound in one step. Crystals of $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ with about $80\,\mu m$ size grown in a reflux system is shown in Fig. 1. Selected area electron diffraction (SAED) pattern of the vacuum-dried $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ crystal in Fig. 1 displays a characteristic hexagonal structure with $a = 2.8(3)$ Å. Powder X-ray diffraction in Fig. 2 displays a hydrous interlayer spacing $d = 10.0(2)$ Å. The widely extended c-axis of the $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ indicates the coordination of intercalated water to be a bilayer hydrated structure. The magnetic susceptibility measurement of BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ displays a paramagnetic behavior. Though not exhibiting superconductive behavior, several interesting features can be further studied from this novel structure with its large interlayer spacing among alkali cobalt oxides.

TGA/DTA analysis of BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ in Fig. 3 displays high vapor pressure of intercalated water and low temperature phase transition. As shown in Fig. 2, dehydration at $40\,°C$ results in the crystal structure shifting ambiguously from BLH into anhydrous phase detected by in situ XRD apparatus. Heat treatments at 100 and $200\,°C$ for 2 h display an anhydrous phase with no detectable 2θ shifting. It indicates a high volatility of lattice water, which is quite different from the multi-tiered behavior of $K_{0.35}CoO_2 \cdot 0.4H_2O$ MLH compounds [14]. The structure is collapsed at $350\,°C$ and identified to have Co_3O_4 formula. In comparison to the ^{133}Cs-SSNMR results, only
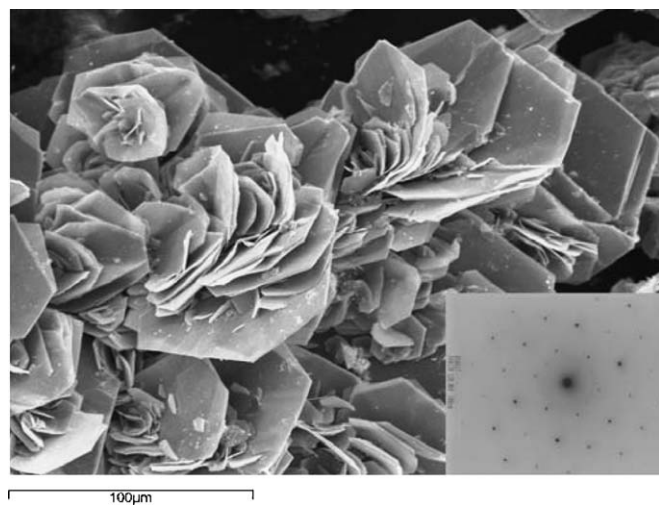

Fig. 1. Scanning electron micrograph of BLH $Cs_{0.2}CoO2 \cdot 0.63H_2O$ crystals grown from low temperature molten salt. (Inset: SAED pattern is taken along (00l) incident direction.)

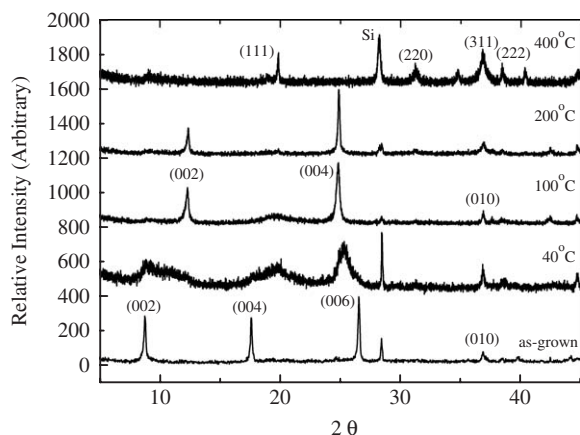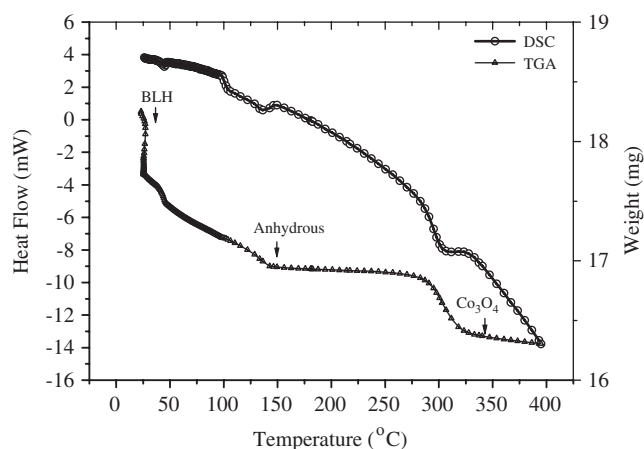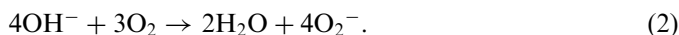Fig. 2. In situ powder XRD patterns of BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ sample measured at different temperature.
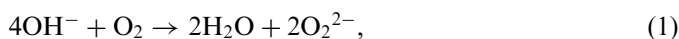

Fig. 3. Thermogravimetric analysis of the as-grown $Cs_{0.2}CoO_2 \cdot 0.63H_2O$. Sample is first held at 25 °C in air for 1 h and then heated at 1 °C/h to 400 °C.

the following reactions:

$$4OH^- + O_2 \rightarrow 2H_2O + 2O_2^{2-}, \qquad (1)$$

$$4OH^- + 3O_2 \rightarrow 2H_2O + 4O_2^-. \qquad (2)$$

Chemical oxidation by peroxide and/or superoxide initiates the crystal growth while accompanied with a polymerization reaction of cobalt hydroxyl complex ions. The polymerization process results in a three-dimensional (3D) framework simultaneously stuffed with alkali cations and coordinated water molecules. The extra stability of the BLH $Cs_xCoO_2 \cdot yH_2O$ structure may benefit from the moisturized environment preserved in the system. To test the cation-specific effect in the CsOH–HOH solvent, experiments were performed in a series of molten salt combinations using cesium hydroxide to mix with alkali hydroxide in a 75/25 wt% ratio. Using the CsOH–AOH (A = Rb, K, Na or Li) molten salts, single-phase compounds of the monolayer-hydrate (MLH) $Rb_{0.30}CoO_2 \cdot 0.36H_2O$, $K_{0.35}CoO_2 \cdot 0.4H_2O$ and the anhydrous $Na_{0.35}CoO_2$, $Li_{0.36}CoO_2$ were harvested and identified by XRD as shown in Fig. 4. The CoO_2 interlayer spacing along c-axis is reduced from 10.0(2) for $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ to 7.0(1) and 6.8(4) Å for the MLH $Rb_{0.30}CoO_2 \cdot 0.36H_2O$ and $K_{0.35}CoO_2 \cdot 0.4H_2O$, respectively. Shrinkage of the BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ structure when a different cation is added reflects a possible competition between lattice energy of $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ and cation-assisted electrostatic attraction force within layers. Magnetic susceptibility measurements of the novel MLH $Rb_{0.30}CoO_2 \cdot 0.36H_2O$ and $K_{0.35}CoO_2 \cdot 0.4H_2O$ samples do not show the superconductivity at current stage. The physical properties of anisotropic structure are sensitive to alkaline cation and the valence state at CoO_2 layer. It would be interesting to modify the chemical stoichiometry by changing synthesis parameters of the low
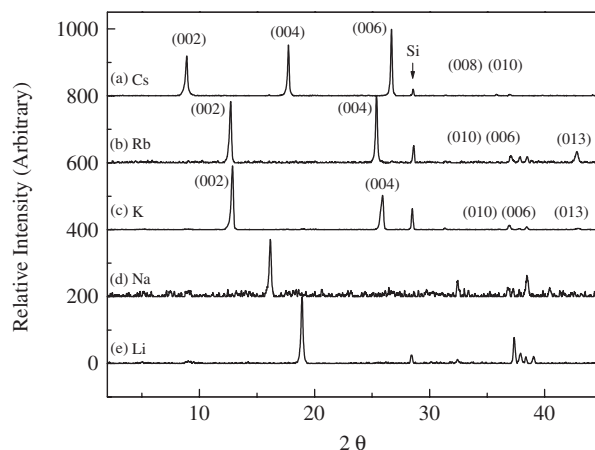
one isotropic chemical shift is observed at 560 ppm corresponding to the cesium ions intercalated between the layers of CoO_2 structure in the as-grown BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$. Sample measured at 40 °C results slow and complicates downfield shifts. It is in agreement with the ambiguous phase transition observed in XRD measurement. When the sample is dehydrated at 100 °C for 2 h, the isotropic chemical shift is completely shifted to 870 ppm. The larger downfield shift indicates stronger interaction between the cesium ion and the CoO_2 layers, which is due to the decrease in the space of the CoO_2 layers. Both hydrated and dehydrated samples presenting large downfield shifts are probably due to the hyperfine interaction between unpaired electrons and nuclei as in the case of Na_xCoO_2 [15–17].

Crystal growth process is considered to be a chemical oxidation reaction. Cobalt (II) oxide precursor dissolved in the hydroxide molten salt is transformed to the cobalt hydroxyl complex ion. Peroxide and superoxide oxidants in molten salt are self-generated upon contact with O_2 gas as

Fig. 4. XRD patterns of water-stabilized compound synthesized by molten salt: (a) BLH $Cs_{0.2}CoO_2 \cdot 0.63H_2O$ grown from CsOH melt. (b–c) MLH $Rb_{0.3}CoO_2 \cdot 0.36H_2O$ and $K_{0.35}CoO_2 \cdot 0.4H_2O$ from the CsOH–AOH (A = Rb or K) melt. (d–e) anhydrous Na_xCoO_2 and Li_xCoO_2 harvested from the CsOH–AOH (A = Na or Li) molten solution individually.

temperature reaction. In conclusion, a low temperature CsOH–HOH molten solvent system is developed. One-step synthesis of novel BLH-$Cs_xCoO_2 \cdot yH_2O$ and MLH-$Rb_xCoO_2 \cdot yH_2O$ crystals have been demonstrated in this work. It can synthesize compounds with different interlayer spacing and proper crystallinity. By exploring more of these layered cobalt oxides, the correlations of magnetism, interlayer coupling, superconductivity and its structure dependence can be further understood.

Acknowledgments

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