Rapid communication

Low temperature synthesis of bilayer hydrated cesium cobalt oxide

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Abstract

Bilayer hydrated \(\text{Na}_{0.35}\text{CoO}_2\cdot\text{H}_2\text{O}\) structure has re-directed superconductivity research in recent years. Here, we develop a low temperature synthesis method to prepare a novel hydrous \(\text{Cs}_{0.2}\text{CoO}_2\cdot\text{H}_2\text{O}\) compound in one step. The bilayer-hydrate of \(\text{Cs}_{0.2}\text{CoO}_2\cdot\text{H}_2\text{O}\) with a greatest interlayer spacing \(d = 10.0(2)\,\text{Å}\) among alkali cobalt oxides has been grown in crystal form. Magnetic susceptibility measurement of \(\text{Cs}_{0.2}\text{CoO}_2\cdot\text{H}_2\text{O}\) displays a paramagnetic behavior down to 1.9 K. With the assistance of low temperature molten CsOH solvent, crystals of \(\text{Rb}_{0.30}\text{CoO}_2\cdot\text{H}_2\text{O}\) and \(\text{K}_{0.35}\text{CoO}_2\cdot\text{H}_2\text{O}\) 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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1. Introduction

Anhydrous metal cobalt oxides with layered structure have been attracting wide attention for the past two decades. \(\text{Li}_x\text{CoO}_2\) is one of the most important intercalation compounds for secondary lithium ion batteries [1]. \(\text{Na}_x\text{CoO}_2\) is recognized to be a potential candidate for thermal electric power materials [2]. \(\text{A}_x\text{CoO}_2\) compounds have a layered structure, with the \(\text{CoO}_2\) layers consisting of \(\text{CoO}_6\) octahedra sharing common edges and forming a triangular \(\text{Co}–\text{O}\) sublattice. Open and polarizable framework structure makes the compounds adaptable by chemical modification. Tanaka and his co-workers found the superconductivity of hydrated \(\text{Na}_{0.35}\text{CoO}_2\cdot\text{H}_2\text{O}\) in 2003 [3]. Hydrated \(\text{Na}_{0.35}\text{CoO}_2\cdot\text{H}_2\text{O}\) oxide was immediately targeted by research scientists owing to its unusual bilayer-hydrate (BLH) structure [4]. The anisotropy in transport properties of hydrated \(\text{Na}_{0.35}\text{CoO}_2\cdot\text{H}_2\text{O}\), strong inverse correlation between the \(\text{CoO}_2\) 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 \(\text{CuO}_2\) layers play an essential role in high-temperature superconductivity [7–9]. In hydrated \(\text{A}_x\text{CoO}_2\cdot\text{yH}_2\text{O}\) compounds, the coupling strength of \(\text{CoO}_2\) 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 \(\text{CoO}_2\) 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...
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-Cs0.2CoO2·0.63H2O compound in one step, which will assist both in exploring novel compounds and fundamental physical study.

2. Experimental

The synthesis of Cs0.2CoO2·0.63H2O 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 moistened 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·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_2O⁺ 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 ¹³³Cs 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 hydroscopic property of CsOH and external wetted atmosphere. The oxygen oxidation and slow cooling processes can crystallize novel BLH Cs0.2CoO2·0.63H2O compound in one step. Crystals of Cs0.2CoO2·0.63H2O with about 80 μm size grown in a reflux system is shown in Fig. 1. Selected area electron diffraction (SAED) pattern of the vacuum-dried Cs0.2CoO2·0.63H2O 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 Cs0.2CoO2·0.63H2O indicates the coordination of intercalated water to be a bilayer hydrated structure. The magnetic susceptibility measurement of BLH Cs0.2CoO2·0.63H2O 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 Cs0.2CoO2·0.63H2O 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 20 shifting. It indicates a high volatility of lattice water, which is quite different from the multi-tiered behavior of K_{0.35}CoO_2·0.4H_2O MLH compounds [14]. The structure is collapsed at 350 °C and identified to have Co_3O_4 formula. In comparison to the ¹³³Cs-SSNMR results, only...
measured at different temperature. Sample is first held at 25 °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 CoO₂ layers, which is due to the decrease in the space of the CoO₂ 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 Na₄CoO₂ [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 the hydroxide molten salt are self-generated upon contact with O₂ gas as the following reactions:

\[ 4\text{OH}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{O}_2^{2-}, \]

\[ 4\text{OH}^- + 3\text{O}_2 \rightarrow 2\text{H}_2\text{O} + 4\text{O}_2^- . \]

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 Cs₀.2CoO₂·1.5H₂O 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) Rb₀.30CoO₂·0.36H₂O, K₀.35CoO₂·0.4H₂O and the anhydrous Na₀.33CoO₂, Li₀.36CoO₂ were harvested and identified by XRD as shown in Fig. 4. The CoO₂ interlayer spacing along c-axis is reduced from 10.0(2) for Cs₀.2CoO₂·0.63H₂O to 7.0(1) and 6.8(4) Å for the MLH Rb₀.30CoO₂·0.36H₂O and K₀.35CoO₂·0.4H₂O, respectively. Shrinking of the BLH Cs₀.2CoO₂·0.63H₂O structure when a different cation is added reflects a possible competition between lattice energy of Cs₀.2CoO₂·0.63H₂O and cation-assisted electrostatic attraction force within layers. Magnetic susceptibility measurements of the novel MLH Rb₀.36CoO₂·0.36H₂O and K₀.36CoO₂·0.4H₂O 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 CoO₂ 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 CoO₂ structure in the as-grown BLH Cs₀.2CoO₂·0.63H₂O. 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 CoO₂ layers, which is due to the decrease in the space of the CoO₂ 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 Na₄CoO₂ [15–17].

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temperature reaction. In conclusion, a low temperature CsOH–HOH molten solvent system is developed. One-step synthesis of novel BLH-Cs$_x$CoO$_2$$\cdot$$y$H$_2$O and MLH-Rb$_x$CoO$_2$$\cdot$$y$H$_2$O 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.

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