Precise Control of Na Content in the Layered Cobaltate γ-NaxCoO2

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We have developed a preparation method for precisely controlling the Na content x of a γ-NaxCoO2 precursor by a halogen oxidation technique in the range 0.50 ≤ x ≤ 0.70. The Na content of the precursor was reduced in a concentration-controlled I2-CH3CN solution. The magnetic susceptibility of γ-NaxCoO2 shows Curie–Weiss (CW)-type paramagnetism (x ≈ 0.70) or Pauli-type paramagnetism (x ≈ 0.50). The boundary of the CW and Pauli paramagnetic phases was identified at x ≈ 0.61. The content and temperature for a disorder–order transition from the γ phase to a √7a0 × √7a0 superstructure were accurately elucidated by differential scanning calorimetry (DSC) measurement. A phase transition for the 0.52 ≤ x ≤ 0.54 sample was observed at 250 K by DSC measurements. The heat absorption of the 0.52 ≤ x ≤ 0.54 samples was of the same order of magnitude as that of the transition from the γ phase to the √7a0 × √7a0 phase.

Key words: NaNaxCoO2, Na ordering, phase transition, phase diagram

INTRODUCTION

Since the discovery of the high thermoelectric performance of NaCo2O4,1 the layered cobalt oxides γ-NaxCoO2 have attracted considerable attention from researchers. Takada et al.2 discovered superconductivity at Tc ≈ 4 K for x ≈ 0.35 samples, by introducing hydrate molecules in the structure. Subsequently, Foo et al.3 carefully measured the transport properties of γ-NaxCoO2 samples and established a phase diagram. The γ phase is described as the P2-type NaNaxCoO2 compound by Delmas et al.4 In this system, the valence state of Co ions, which is altered with changing x, plays a key role in the structural and physical properties of the compound.

In the system, Na atoms were considered to be randomly distributed at two sites in the hexagonal unit cell. However, at a particular x, Na atoms form an ordered arrangement. Such ordering of the Na distribution changes the electronic states of the CoO2 layers via its periodic Coulomb potential, as described by Roger et al.5 We previously reported the presence of two ordered phases in the γ-NaxCoO2 system, namely Na0.50CoO2,6 and Na0.58CoO2,7 which exhibit different types of Na ordering. The Na atoms of Na0.5CoO2 form a zigzag chain parallel to the a-axis, and the space symmetry of the crystal structure changes from hexagonal (P63/mmc) to (3 + 1)-dimensional orthorhombic [Ccmm(1p000)].6 The Na0.5CoO2 sample undergoes two-step phase transitions at TC01 = 87 K and TC02 = 53 K.3 The magnetic susceptibility χ(T) exhibits two cusps at TC01 and TC02, and the electrical resistivity increases rapidly at T < TC01 in a cooling process. By means of detailed structural analysis on the basis of the (3 + 1) superspace group approach, we rationalized that the charge ordering (CO) transition at TC01 = 87 K is triggered by the cooperative shift of Co and O atoms. The [Na] and [CoO2] layers were defined as “subsystems” with different periods, and fluctuations of the Co–O distances and the Co
charge ordering at $T < T_{\text{CO1}}$ were well described. Na$_{0.58}$CoO$_2$, in contrast, exhibits order–disorder transitions at $T_1 = 235$ K and $T_2 = 288$ K. $^7$ The Na atoms form a $\sqrt{7}a_0 \times \sqrt{7}a_0$ superstructure (where $a_0$ denotes the $a$-axis length of the basic hexagonal structure) at $T_1 < T < T_2$ and change its symmetry from $P6_3/mmc$ to $P6_3/m$. In this temperature range, $\chi(T)$ decreases slightly and the lengths of the $a$- and $c$-axes increase. At $T < T_1$, the $\sqrt{7}a_0 \times \sqrt{7}a_0$ superstructure disappears again and the lattice parameters and $\chi(T)$ exhibit behaviors similar to that of the $\gamma$ phase at $T > T_2$. However, the enthalpies of the two phases are obviously different. A reasonable description for the lower temperature range has not yet been provided.

To further understand the effect of Na distribution on the transport properties of Na$_x$CoO$_2$ and the possibility of the occurrence of another type of Na ordering, it is essential to conduct a detailed study that focuses on precise control of the Na content. In this study, we report a preparation method to control the Na content, $x$ dependence of $\chi(T)$, and specific heat for Na$_x$CoO$_2$ with $x$ in the range 0.50 $\leq x \leq 0.70$.

**EXPERIMENTAL PROCEDURES**

The parent $\gamma$-Na$_{0.70}$CoO$_2$ sample was synthesized by the standard solid-state reaction method using Na$_2$CO$_3$ and Co$_3$O$_4$ powders. The powders were mixed, and the mixture was pelletized and heated twice at 800°C for 12 h in flowing oxygen with intermediate grinding. The obtained single-phase powders were then immersed in I$_2$ (or Br$_2$)–CH$_3$CN intermediate grinding. The obtained single-phase powders were washed several times from 0.01 mol/L to 0.10 mol/L in increments of 0.01 mol/L; the I$_2$ concentrations were also fixed to higher values of 0.20 mol/L and 0.40 mol/L. The Br$_2$ concentration was fixed at 1.00 mol/L. After extraction, the powders were washed several times with dehydrated CH$_3$CN at room temperature to remove excess I$_2$ and NaI (Br$_2$ and NaBr). Then, the resultant samples were placed in an auto-dry dessicator for further treatment. Powder x-ray diffraction (XRD) measurement was performed to verify the purity of the $\gamma$-Na$_x$CoO$_2$ phase.

Powder neutron diffraction (ND) data were collected by using the high-resolution powder diffractometer HERMES$^8$ of the Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3 reactor at the Japan Atomic Energy Agency (JAEA), Tokai. ND and XRD data were analyzed using the Rietveld refinement program RIETAN2000$^9$ and JANA2000. $^{10}$ The magnetic susceptibility of the samples was determined using a Quantum Design MPMS-5 magnetometer under a magnetic field of $H = 8000$ Oe. The specific heat of each sample was measured by differential scanning calorimetry (DSC) by using an SII EXSTAR6000 system from 173 K up to 323 K.

**RESULTS AND DISCUSSION**

**Relationship Between Halogen Concentration and Na Content**

Figure 1 shows the relationship between the concentration of I$_2$ (Br$_2$) and the Na content $x$ of the samples. These $x$ values are evaluated based on the results of Rietveld analysis. Because of the stronger reactivity, more Na was extracted in Br$_2$ (1.0 mol/L) solution than in I$_2$ solution. The $x \approx 0.38$ sample was obtained in the Br$_2$ solution. On the other hand, for extraction in the I$_2$ solution, the minimum Na content was $x = 0.50$ (0.2 mol/L). Even at a higher concentration (0.40 mol/L) of I$_2$ solution, an $x < 0.5$ sample was not obtained.

By changing the I$_2$ concentration, we succeeded in controlling $x$ in the range 0.50 $\leq x \leq 0.70$ with an accuracy of approximately $\pm 0.02$. Samples with $x = 0.70, 0.58, 0.54,$ and 0.50$^{11,12}$ were synthesized by using this method. For these samples, Rietveld fitting with ND patterns was carried out, and $x$ values were evaluated precisely. In addition, for the $x = 0.58$ sample, results of electron probe microanalysis (EPMA) and Rietveld fitting were in reasonable agreement. Figure 2 shows the relationship between $x$ and the lattice parameter $c$ at 296 K. With decreasing $x$, the $c$-axis length increases linearly from 10.9227(5) Å ($x = 0.70$) to 11.2187(5) Å ($x = 0.38$), following Vegard’s law.

**Relationship Between Na Content and Magnetic Susceptibility**

Figure 3 shows $\chi(T)$ of Na$_x$CoO$_2$ samples in the range 0.50 $\leq x \leq 0.70$. For 0.64 $\leq x \leq 0.70$, Na$_x$CoO$_2$ samples showed a gradual increase in $\chi(T)$ at lower $T$, which is typical of Curie–Weiss (CW) compounds.