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Strontium ordering, structural modulation in layered hexagonal Sr_xCoO_2 and physical properties of $Sr_{0.35}CoO_2$

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Abstract

Layered $Sr_{0.35}CoO_2$ has been synthesized by means of an ion exchange reaction from $Na_{0.7}CoO_2$. Resistivity measurements show that this material can be either metallic or semiconducting depending on the annealing conditions. The magnetic susceptibility of the sample increases with decreasing temperature, showing a Curie–Weiss behavior in high temperatures. Transmission electron microscopy observations reveal the presence of two superstructures arising respectively from the intercalated Sr-ordering (a compositional modulation) with $q_2 = a^*/3 + b^*/3$ and a periodic structural distortion (a transverse structural modulation) with $q_2 = a^*/2$.

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1. Introduction

Layered deintercalatable alkali metal oxides, such as Li_xCoO_2 ($0.5 \leq x \leq 1.0$) and Na_xCoO_2 ($0.33 \leq x \leq 1.0$), have been a subject of an intense research activity in the past years owing to their potential technological applications as the battery electrodes and thermoelectric materials [1–3]. The notable structural and chemical features in this kind of materials are that the cation content can vary over a large range by deintercalation without evidently modifying the average crystallographic structure [4–6]. Recently, a rich variety of physical properties, such as superconductivity in $Na_{0.33}CoO_2{\cdot}1.3H_2O$ and charge ordering in $Na_{0.5}CoO_2$, have been observed [6–12]. Structural investigations revealed that the intercalations of either Na atoms or H_2O molecules could make the local structure very complex; the intercalated atoms can be random with high mobility or crystallized in certain ordered states [12]. For instance, Na atoms in $Na_{0.5}CoO_2$ crystallize in a well-defined zigzag ordered pattern and yield an orthorhombic structure in which low temperature charge ordering is observed [8,9,12]. Intercalation of divalent ions (Ca^{2+}, Sr^{2+}) into cobalt oxides are expected to improve the thermoelectric properties. $Sr_{0.35}CoO_2$ shows a Seebeck coefficient comparable to that of Na_xCoO_2 [13]. Partial substitution of Ca for Na in Na_xCoO_2 also gave an enhancement in both Seebeck coefficient and electric resistivity [2,14]. From structural point of view, significant questions to answer in M_xCoO_2 (M = Na, Li, Sr or

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Ca) materials are what kinds of ordered states actually exist for the intercalated M cations and whether the CoO_2 sheets show up relevant distortions depending on the M occupancy. Our recent experimental investigations on Sr_xCoO_2 ($0.25 \leq x \leq 0.4$) system demonstrated that the $Sr_{0.35}CoO_2$ material is crystallized in a well-defined Sr-ordered state yielding a superstructure of $3^{1/2}a \times 3^{1/2}a$. This specific superstructure is expected to have large effects on the charge ordered states and magnetic structures as theoretically demonstrated by first principle calculations [9,15]. In this paper, we will focus our attention on superstructure modulations in correlation with Sr ordering and local structural distortion in $Sr_{0.35}CoO_2$. Certain fundamental physical properties and defect structures in present system have also been discussed.

2. Experiment

Polycrystalline materials with nominal compositions of Sr_xCoO_2 ($x = 0.25$, 0.30, 0.35, 0.4) were prepared by the low-temperature ion exchange reaction from the γ-Na_xCoO_2 ($x = 0.50$, 0.60, 0.70, 0.8) precursor prepared by conventional solid-state reaction or by sodium deintercalation of $Na_{0.75}CoO_2$ [6]. The ion exchange process was carried out by using the modified Cushing–Wiley method [14]. An amount of γ-Na_xCoO_2 was mixed thoroughly with 10% molar excess anhydrous $Sr(NO_3)_2$ powder, then heated at 310 °C for 2 days in air, the mixture was grinded repeatedly during the process. The final products are washed by distilled water. X-ray diffraction (XRD) measurements were carried out with a diffractometer in the Bragg–Brentano geometry using Cu Kα radiation. Low-temperature magnetization measurements as a function of temperature were performed using a commercial Quantum Design SQUID. The resistivity as a function of temperature was measured by a standard four-point probe technique. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves were obtained by using a SDT Q600 V8.0 Build 95 thermal analysis system. The metal ratios in the products were determined by inductively coupled plasma (ICP) analysis, yielding Sr:Co:Na = 0.25:1.0:0.0035 for $Sr_{0.25}CoO_2$ sample, 0.30:1.0:0.0026 for $Sr_{0.30}CoO_2$ sample, 0.36:1.0:0.0043 for $Sr_{0.35}CoO_2$ sample and 0.40:1.0:0.0025 for $Sr_{0.40}CoO_2$ sample. Specimens for transmission electron microscopy (TEM) observations were polished mechanically with a Gatan polisher to a thickness of around 50 μm and then ion-milled by a Gatan-691 PIPS ion miller. The TEM investigations were performed on a TECNAI F20 operating at a voltage of 200 kV.

3. Results and discussion

Structural analysis indicated that the average structures of all the four kinds as-made Sr_xCoO_2 materials are isomorphic to the γ-Na_xCoO_2 phase with the layered hexagonal structure. The lattice parameter a (2.824 Å) remains almost unchanged for all the samples and parameter c decreases slightly with the increase of the Sr content. The c values are 11.531 Å, 11.527 Å, 11.524 Å and 11.521 Å for $Sr_{0.25}CoO_2$, $Sr_{0.30}CoO_2$, $Sr_{0.35}CoO_2$ and $Sr_{0.40}CoO_2$, respectively.

Fig. 1 shows the XRD patterns obtained from materials with nominal compositions of Sr_xCoO_2 ($x = 0.35$ and 0.25) and their precursors γ-Na_xCoO_2 ($x = 0.7$ and 0.5). Lattice parameters calculated from our experiments are given in Fig. 1. The evident change of lattice parameters is only observed along the c-axis direction, which is considered arising from the relatively larger Sr substitution for Na among the CoO_2 layers. For instance, the $Sr_{0.35}CoO_2$ has the lattice parameter of $c = 1.15$ nm with a notable 7% increase in comparison with that of $Na_{0.7}CoO_2$ ($c = 1.08$ nm). The structural transition from orthorhombic $Na_{0.5}CoO_2$ to hexagonal $Sr_{0.25}CoO_2$ can be also seen in Fig. 1(b). This fact directly suggests that the orthorhombic structural distortion in $Na_{0.5}CoO_2$ which arises from the zigzag Na ordering is totally destroyed in the $Sr_{0.25}CoO_2$ sample. It is also noted that the reflection peaks for $Sr_{0.25}CoO_2$ are somewhat broader than that of $Sr_{0.35}CoO_2$. Further TEM investigation reveals that $Sr_{0.35}CoO_2$ is crystallized in a well-defined Sr ordered phase, while $Sr_{0.25}CoO_2$ in general contains notable structural inhomogeneity and defects.

In order to understand the thermal stability of the $Sr_{0.35}CoO_2$ compound, the DSC, TG and DTA experiments were performed on several typical samples. The experimental results demonstrated that some changes correspond to the structural phase transformations and some other changes arise from partial thermal decomposition. Fig. 2(a) shows the experimental results of TGA, DSC and DTG as the functions of temperature for $Sr_{0.35}CoO_2$ in the oxygen atmosphere. The appreciable weight loss in the wide temperature range below 200 °C as shown in the TGA and DTG data is quite possibly caused by losing the substance absorbed on the sample surface. Above 400 °C, it can be easily recognized that there are four clear endothermic peaks in the DSC curve, which are companied with evident weight loss as illustrated