Structure and properties of the CaFe$_2$O$_4$-type cobalt oxide CaCo$_2$O$_4$

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Abstract

The calcium cobalt oxide CaCo$_2$O$_4$ was synthesized for the first time and characterized from a powder X-ray diffraction study, measuring magnetic susceptibility, specific heat, electrical resistivity, and thermoelectric power. CaCo$_2$O$_4$ crystallizes in the CaFe$_2$O$_4$ (calcium ferrite)-type structure, consisting of an edge- and corner-shared CoO$_6$ octahedral network. The structure of CaCo$_2$O$_4$ belongs to an orthorhombic system (space group: *Pnma*) with lattice parameters, $a = 8.789(2)$ Å, $b = 2.9006(7)$ Å and $c = 10.282(3)$ Å. Curie–Weiss-like behavior in magnetic susceptibility with the nearly trivalent cobalt low-spin state (Co^{3+}, $3d$ t_{2g}^6, $S = 0$), semiconductor-like temperature dependence of resistivity ($\rho = 3 \times 10^{-1}$ Ω cm at 380 K) with dominant hopping conduction at low temperature, metallic-temperature-dependent large thermoelectric power (Seebeck coefficient: $S = +147$ μV/K at 380 K), and Schottky-type specific heat with a small Sommerfeld constant ($\gamma = 4.48(7)$ mJ/Co mol K^2), were observed. These results suggest that the compound possesses a metallic electronic state with a small density of states at the Fermi level. The doped holes are localized at low temperatures due to disorder in the crystal. The carriers probably originate from slight off-stoichiometry of the phase. It was also found that S tends to increase even more beyond 380 K. The large S is possibly attributed to residual spin entropy and orbital degeneracy coupled with charges by strong electron correlation in the cobalt oxides.

1. Introduction

In the past several years, extensive studies have been carried out on the solid-state physics and chemistry of cobalt oxides because these materials possess strong electronic correlation and thus, exhibit unusual properties. Researchers have usually looked at the unconventional superconductivity observed below 5 K in hydrated Na$_{0.35}$CoO$_2 \cdot$ 1.3H$_2$O [1]. This superconductivity is quite interesting because of the unconventional Cooper pairing, possibly mediated by the magnetic fluctuations [2]. Furthermore, interest has grown in the large thermoelectric power coexisting with low electric resistivity in layered cobalt oxides, such as NaCo$_2$O$_4$ [3] and Ca$_3$Co$_4$O$_9$ [4]. This effect is considered to be attributed to the large residual entropy associated with spin frustration on the triangle lattice in the CoO$_2$ layer [5]. Lately, the search for new materials and the precise characterization of the materials have intensified, in order to further improve the understanding of the unusual physical properties and, ultimately, the essence of the electron correlation in transition-metal oxides.

In contrast, the CaFe$_2$O$_4$ (calcium ferrite)-type structure is very intriguing for solid-state chemists [6]. The prototype CaFe$_2$O$_4$ crystallizes in an orthorhombic structure with lattice constants $a = 9.217$ Å, $b = 10.702$ Å, and $c = 3.018$ Å (space group: *Pnam*), built of eight-fold-coordinated Ca atoms and distorted FeO$_6$ octahedra [7]. It has been reported that the Ca and Fe atoms can be independently replaced with different elements and resulting in the same crystallization structure. So far, a variety of related compounds having the CaFe$_2$O$_4$-type structure have been found. For instance, AB_2O$_4$ (A = Li, Na, Mg, Ca, Sr, Ba, La, and Eu; B = Ti, V, Cr, Mn, Fe, Ru, Rh, Al, Ga, In, Tl, Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, and Lu) have been reported [8–18]. Although many $3d$ elements can be substituted at the Fe site

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in $CaFe_2O_4$, the substitution of the Co, Ni and Cu elements with other elements has not been reported, to the best of the authors' knowledge.

The $CaFe_2O_4$-type structure includes edge- and corner-sharing BO_6 octahedra, constituting a very distinctive network similar to the one formed in perovskite-related compounds. This structural network suggests that interesting physical properties may exist in the $CaFe_2O_4$-type compounds, where the B-site atoms are transition-metal magnetic elements, such as high-T_C superconductivity in cuprates [19], quantum magnetic characters in ruthenates [20], strongly correlated features in manganates [21], etc. In particular, unique quantum behavior characteristic of low-dimensional systems may occur in the $CaFe_2O_4$-type compounds. This is because the edge-sharing connection of the octahedra forms a double-chain structure, which can be regarded as a part of the CdI_2-type structure observed in the layered cobalt oxides [3,4]. Thus, the t_{2g} orbital configuration of the B-site atoms in the double chain is expected to orientate towards neighboring B-site atoms and overlap, suggesting that the direct charge transfer through the t_{2g} orbitals may cause stronger intra-chain magnetic interaction between the B-site spins than inter-chain interaction.

Motivated by this hypothesis, we have searched for a new phase of the $CaFe_2O_4$-type group which has an active BO_6 network in a magnetic and electrical sense. As a result of the experiments of the new-phase search, we recently succeeded in synthesizing a new $CaFe_2O_4$-type cobalt oxide, $CaCo_2O_4$, using solid-state reaction at a condition of high temperature and high pressure. It was found that the cobalt valence of the calcium cobaltite is near to the $3+$ low-spin state with a $3d$ t_{2g}-orbital electric band almost filled with electrons (Co^{3+}, $3d$ t_{2g}^6, $S = 0$).

In this paper, we report on the synthesis, crystal structure and the magnetic and electrical transport properties of the new cobaltite, $CaCo_2O_4$. In particular, we emphasize that this novel compound can exhibit large thermoelectric power and unusual temperature dependence of the Seebeck coefficient. We discuss the electronic state of the system and origin of the unusual properties in terms of residual spin entropy and orbital degeneracy in the t_{2g} orbital.

2. Experimental

Polycrystalline samples of $CaCo_2O_4$ were prepared from a solid-state reaction using a high-pressure synthesis technique. Starting reagents, Co_3O_4 (3 N) and $(Ca_2CoO_3)_{0.62}CoO_2$ [22], were mixed in an agate mortar with a molar ratio of '0.86:3', respectively. The mixture was dried in flowing O_2 gas at 300 °C for several hours, and then placed into platinum capsules (6.8 mm in diameter, 0.2 mm in thickness, and approximately 5 mm in height) in a globe box filled with dry Ar gas. Previous to the preparation, the $(Ca_2CoO_3)_{0.62}CoO_2$ powder had been prepared from Co_3O_4 and $CaCO_3$ (3 N) by heating in O_2

at 900–950 °C for several days with intermediate grindings. The platinum capsules were heated at 1500 °C for 1 h under 6 GPa using a flat-belt-type high-pressure apparatus, and then quenched to room temperature before the pressure was released. The sintered samples were dense, black, and retained a pellet shape. The surfaces of the pellets were carefully scraped to remove any possible contaminations from chemical reactions with the platinum capsule. The typical sample weight was ∼0.4 g.

Phase purity and crystal structure of the products were studied using conventional powder X-ray diffraction (XRD). The XRD patterns were obtained using $CuK\alpha$ radiation from a diffractometer (Rigaku, RINT-ULTIMA III) equipped with Bragg–Brentano geometry with a goniometer radius of 285 mm and a conventional slit system. The crystal structure was analyzed using the X-ray Rietveld method with the software RIETAN-2000 [23]. The intensity data for the refinement were collected at room temperature in a 2θ angle range of 10–110° using a step-scan (fixed-time) mode with a 2θ step size of 0.02° and a data-collection time of 30 s per step. The slit condition was set as follows: divergence-slit width = scattering-slit width = $1/3°$ and receiving-slit width = 0.3 mm. Inter-atomic distances and bond-angles were calculated from the refined positional parameters using a computer program ORFFE [23].

The Seebeck coefficient was measured between 10 and 390 K with a four-probe configuration, using a thermal transport option (TTO) in a commercial apparatus (Quantum Design, PPMS). The sample size was $1.5 \times 2.1 \times 5.5$ mm^3, and the distance between temperature/voltage terminals was 2.9 mm. Fine copper wires (cross section: ∼0.24×0.64 mm^2) were attached onto the polished sample surface via an evaporated gold film using silver paste, in order to make a good ohmic contact. Data were collected using the continuous mode at a cooling rate of 0.3 K/min. Temperatures at the terminals were obtained from thermometers (Cernox 1050), and the temperature difference between the terminals was kept to within 3% of the measurement temperature. The electrical resistivity was measured using the conventional four-probe ac method simultaneously with the Seebeck coefficient measurement. The ac current of 0.01–0.05 mA at 60–300 Hz was applied to the sample.

The magnetic susceptibility was measured on a pulverized sample (200.97 mg) using a superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design, MPMS-XL) at a magnetic field of 1 kOe between 5 and 350 K on heating and cooling. The specific heat measurement was performed using a bulk specimen (12.34 mg) in the PPMS system with a time-relaxation method over the temperature range 2–300 K.

3. Results and discussion

Fig. 1 is the powder X-ray diffraction pattern of $CaCo_2O_4$. All the Bragg reflections can be systematically indexed with an orthorhombic system with lattice parameters,