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Effect of oxygen content on transport and magnetic properties of $PrBaCo_2O_{5.50+\delta}$

Xue Zhang [a], Xiao-Ming Wang [a], Heng-Wei Wei [a], Xiao-Huan Lin [a], Chun-Hai Wang [a], Yan Zhang [b], Chinping Chen [b,*], Xi-Ping Jing [a,*]

[a] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China
[b] School of Physics, Peking University, Beijing 100871, PR China

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ABSTRACT

Samples of $PrBaCo_2O_{5.50+\delta}$ ($\delta = -0.15$–0.14), synthesized by solid-state reactions, were investigated to ascertain oxygen compositional effects on transport/magnetic properties. Resistivity decreases with increasing oxygen content, indicative of *p*-type conduction. A metal-insulator transition was observed at 330 K only for sample $PrBaCo_2O_{5.52}$, coinciding with phase transition and spin-state transition of Co^{3+}. When δ deviates from zero, samples show insulator–insulator transitions, although for sample $\delta = 0.14$, no transition occurs but only semi-conductive behavior appears. Electronic transport is governed by the hopping mechanism at lower temperatures and thermal activation at higher temperatures. All samples underwent paramagnetic–ferromagnetic–antiferromagnetic transitions, except $PrBaCo_2O_{5.64}$, which only went through a paramagnetic–ferromagnetic transition. The ferromagnetic state for $\delta < 0$ originates with the Co^{3+}/Co^{2+} super-exchange interaction; for $\delta > 0$, it stems from the Co^{3+}/Co^{4+} double exchange interaction.

1. Introduction

Because of the metal–insulator (M–I) transition at around room temperature and the multiple magnetic transitions, the ordered oxygen-deficient '112' perovskite phases $RBaCo_2O_{5.50}$ (R = rare-earth elements) have attracted considerable interest in recent years [1–4]. The crystal structure of $RBaCo_2O_{5.50+\delta}$ was first determined from X-ray diffraction and high-resolution electron microscopy by Maignan et al. in 1999 [5]. The detailed structure of the Pr phase with $\delta = 0$ ($PrBaCo_2O_{5.50}$) was given by Frontera [6]; the phase has a orthorhombic unit cell at room temperature with space group *Pmmm* and cell parameters $a = 3.9049(1)$ Å, $b = 7.8733(2)$ Å, and $c = 7.6084(2)$ Å. The structure (see Fig. 1) can be described as a stacking of sequence [CoO_2–BaO–CoO_2–$PrO_{0.5}$] along the *c* direction, in which oxygen vacancies are adopted in the [$PrO_{0.5}$] planes. Because of the partial absence of oxygen in the [$PrO_{0.5}$] planes, half of the Co ions form CoO_6 octahedrons and the other half form CoO_5 square pyramids [6]. The structures of the $RBaCo_2O_{5.50}$ phases for other rare-earth elements (R = Y, La, Nd, Sm, Eu, Gd, Tb, Dy, and Ho) have the same perovskite framework, but their cell symmetries can differ slightly. At room temperature, most of the phases have orthorhombic unit cells, but a tetragonal cell was reported for the Y phase [7–9]. The structural phase transitions around room temperature were reported for some phases [9,10]. During the transition, the unit cells have only minor deformation between the high-temperature and low-temperature polymorphs; for example, the low-temperature polymorph of the Ho phase has a monoclinic cell that transforms to orthorhombic at 290 K, but the perovskite framework persists [10]. M–I transitions were reported for the Y, Eu, Nd, Sm, Gd, and Ho phases [10–12]. However, for the La phase [3], the transition cannot be considered as a typical M–I transition; nevertheless this can be considered as an insulator–insulator (I–I) transition. The complex magnetic properties of the Gd phase were initially studied by Troyanchuck et al. [13] and a paramagnetic–ferromagnetic–antiferromagnetic (PM–FM–AFM) transition was observed. Subsequently, the magnetic properties in consideration of spin transitions, charge and orbital orderings, and magnetic phase separations have been thoroughly explored for other rare-earth phases [5,14–16].

These '112' perovskite cobaltates have a wide range of oxygen nonstoichiometry and their formulae can be represented as $RBaCo_2O_{5.50+\delta}$. As δ-value varies from −0.5 to +0.5, the Co valence varies from +2.5 (a mixture of +2 and +3) to +3.5 (a mixture of +3 and +4). The transport and magnetic properties of these phases

* Corresponding authors. Tel.: +86 10 62754188.
E-mail addresses: cpchen@pku.edu.cn (C. Chen), xpjing@pku.edu.cn (X.-P. Jing).

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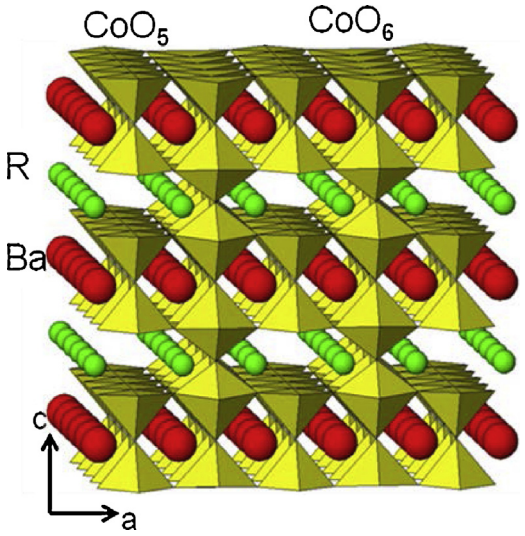

Fig. 1. Oxygen-deficient perovskite structure of $RBaCo_2O_{5.50}$ (R = rare-earth elements). The structure is described as stacking sequence [CoO_2–BaO–CoO_2–$PrO_{0.5}$] along the *c* direction.

are strongly affected by the oxygen content. Such effects were investigated for the Sm, Eu, Y, Gd and Ho phases [7,10,17,18]. In particular, for the Eu and Sm phases, the temperatures for the M–I transition and the PM–FM transition were shown largely unaffected by variation in δ, although the temperature of the FM–AFM transition did vary significantly; magnetization values also changed.

Although much research has been reported on the $RBaCo_2O_{5.50+\delta}$ phases, its particular transport and magnetic behavior is still a subject of controversy [19–22]. To further understand the complex properties of these phases, we conducted comprehensive studies on the transport and magnetic properties of the Pr phase. Correlations between the transport/magnetic properties and the Co valence, which are affected by the δ-value, are discussed. Consequently, a phase diagram of the Pr phase was compiled for the '*T* (temperature) ~δ ' spaces. For samples with near-zero δ, the M–I transition and the PM–FM–AFM transition were observed, whereas samples with δ far from 0 (whether positive or negative) underwent PM–FM transitions; in the latter, FM–AFM and M–I transition were less obvious. The results indicated that a structural phase transition (at ~350 K) was correlated with M–I transitions, but not to PM–FM transitions.

2. Experimental

Polycrystalline samples in the $PrBaCo_2O_{5.50+\delta}$ system were prepared by conventional solid-state reactions. Stoichiometric amounts of raw materials Pr_6O_{11} (99.9%), $BaCO_3$ (AR), and Co_3O_4 (AR) were weighed and mixed by grinding in an agate mortar with a few drops of ethanol. To compensate volatilization during heating, 2% excess Co_3O_4 was added. The mixed powders were initially fired at 1000 °C for 24 h. After grinding, the fired powders were pressed into pellets, and then heated at 1150 °C in air for 3 days with intermediate grindings every day. The as-prepared samples were obtained by cooling in air.

Various thermal treatments were applied to the as-prepared samples to modify the oxygen content of the samples, which were determined by iodometric titration. Samples with δ = 0.02, −0.08, and −0.15 (within uncertainties of ±0.02) were obtained by annealing the samples at 600 °C for 20 min, 180 min, and 330 min, respectively, in a tube furnace with a N_2 atmosphere. After annealing, samples were then cooled to room temperature at rate 100 °C/h. Samples with δ = 0.09 were obtained by quenching the pellet in air from 1150 °C to room temperature. A sample of relatively high oxygen content (δ = 0.14) was obtained if the sample is slowly cooled from 1150 °C to room temperature (*e.g.*, at the rate of 100 °C/h) after firing.

X-ray diffraction (XRD) patterns of $PrBaCo_2O_{5.52}$ (δ = 0.02) at various temperatures from 123 K to 473 K were recorded on a Bruker AXS D8 Discover X-ray powder diffractometer (Germany) containing a temperature accessory. Data were collected at 40 kV and 40 mA in a 2θ range from 20° to 50° (scan speed 0.4°/min) using Cu$K\alpha$ radiation, λ = 1.5418 Å. To confirm the lattice symmetry at different temperatures, patterns with a wide 2θ range from 10° to 100° at selected temperatures were collected using a slow scan speed (0.12°/min). Room temperature XRD patterns of the samples with various δ-values were collected on a PANalytical B.V. Empyrean X-ray powder diffractometer (Netherlands) from 5° to 100° at a slow scan speed of 0.04°/min. The data were recorded at 40 kV and 40 mA using Cu$K\alpha$ radiation. Rietveld refinements on the above patterns, collected using a slow scan speed, were conducted using TOPAS [23].

Transport measurements were conducted in the temperature range 80 K–673 K in the four-wire configuration. The low-temperature environment below 500 K was provided by a closed cycle refrigerator (VPF-100, Janis Research Co., USA) regulated using a temperature controller (LakeShore M331); the high-temperature environment above 500 K was provided by a tube furnace controlled by GB/T7676-98 temperature controller (Dalian Huaxia Instrument and Meter Complete Plant Equipment, China). A SB118 current source and a PZ158A voltmeter (Shanghai Qianfeng Electronic Instruments Co., China) were used for data collection. During measurements, Pt wire-electrodes were cemented to the pellet samples with Ag paste. Magnetization measurements were performed from 5 K–350 K using a superconducting quantum interference device magnetometer (MPMSXL-7, Quantum Design, USA). Diffusive reflection spectra were recorded using an ultraviolet–visible–near infrared (UV–vis–NIR) spectrophotometer (Shimadzu UV-3100, Japan).

3. Results and discussion

3.1. Structure analysis

The XRD patterns of the sample $PrBaCo_2O_{5.52}$ (not shown) measured at temperatures from 123 K to 473 K coincide with those of $EuBaCo_2O_{5.52}$ (JCPDS 53-136) and can be fully indexed in

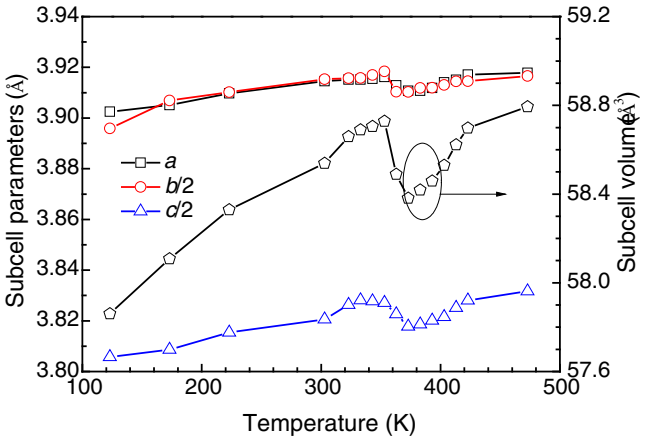

Fig. 2. Variation in subcell parameters and volume with temperature for $PrBaCo_2O_{5.52}$. Discontinuous parameters and volume at 350 K indicate a structural phase transition.