Inorg. Chem. **2006**, *45*, 9151–9153

Inorganic Chemistry
Communication

New Barium Cobaltite Series $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$: Intergrowth Structure Containing Perovskite and CdI_2-Type Layers

Junliang Sun,[†] Min Yang,[†] Guobao Li,[†] Tao Yang,[†] Fuhui Liao,[†] Yingxia Wang,[†] Ming Xiong,[‡] and Jianhua Lin*,[†]

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, China, and X-ray Laboratory, China University of Geoscience, Beijing 100083, China

Received June 4, 2006

Single crystals of two new cobaltites, $Ba_2Co_9O_{14}$ and $Ba_3Co_{10}O_{17}$, were obtained from the flux of K_2CO_3 in the temperature range 800–890 °C. They crystallize in an intergrowth structure containing perovskite block and CdI_2-type layers and can be attributed to the $n = 1$ and 2 members in a new intergrowth series of cobaltites, $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$. Both $Ba_2Co_9O_{14}$ and $Ba_3Co_{10}O_{17}$ are metastable and transform into the known 2*H*-perovskite-related oxides at high temperature.

Recently, considerable interests have been focused on cobalt oxides largely because of their unusual structural and physical properties. One of the structure types that has been most studied is the hexagonal perovskite-related oxides with a general formula $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$. These oxides, containing one-dimensional chains formed by face-sharing octahedra and trigonal prisms, often adopt incommensurate structures.[1] Another interesting structural family is the misfit layered cobaltites,[2] which consist of CdI_2-type oxide layers (CoO_2) and rock-salt-type layers. The misfit of the crystallographic parameters of these two types of layers leads also to incommensurate structures. As typical examples, one may refer to $[M_2CoO_3][CoO_2]_{1.62}$ (M = Ca and Sr)[3] and $[Pb_{0.7}Sr_{1.9}Co_{0.4}O_3][CoO_2]_{1.8}$,[4] in which three rock-salt layers are interleaved between the CdI_2-type layers. More interestingly, many of the misfit layered cobaltites exhibit a high thermopower and low resistivity presumably because of the CdI_2-type layers and, thus, were considered as promising candidates for thermoelectric materials.[5] Noting that an ideal CdI_2-type layer has 3-fold symmetry, it is naturally assumed that replacing the rock-salt layer with a perovskite (111) layer in the misfit structure may lead to a new type of intergrowth structure. In the present Communication, we report on the synthesis and structures of two new intergrowth cobaltites, $Ba_2Co_9O_{14}$ (**1**) and $Ba_3Co_{10}O_{17}$ (**2**). These two compounds can be considered as $n = 1$ and 2 members in a cobaltite intergrowth family of $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ that contains the CdI_2-type and perovskite layers.

Single crystals of **1** and **2** were obtained in the flux of K_2CO_3. As a typical example, a total of 3 g of starting materials, preheated Co_2O_3 (analytical reagent) and $BaCO_3$ (>99.0%) in a mole ratio of 1:1, was mixed thoroughly and placed in alumina crucibles, above which about 20 g of K_2CO_3 was added. The samples were heated in a furnace (60 °C/h) to 890 °C and held for 1 week. The furnace was cooled in a rate of 6 °C/h to 800 °C and then switched off, allowing gradual cooling to room temperature. Single crystals of both **1** and **2** were isolated from the partially melted K_2CO_3 flux, of which **1** is the major phase, appearing as large single crystals (Figure 1), and **2** is the minor phase, with small crystals. Syntheses of polycrystalline samples were conducted by heating $BaCO_3$ and Co_2O_3 in a stoichiometric ratio of $Ba_2Co_9O_{14}$ and $Ba_3Co_{10}O_{17}$, respectively, at 800, 850, 890, 950, and 1000 °C in air for 2 weeks with several intermediate grindings. The experiments show that the products depend strongly on the reaction temperature. **2** can only be formed at low temperature (800 °C) together with a trace of Co_3O_4 or $BaCoO_3$. At 850−950 °C, **1** was obtained as a pure phase.

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* To whom correspondence should be addressed. E-mail: jhlin@pku.edu.cn.

[†] Peking University.

[‡] China University of Geoscience.

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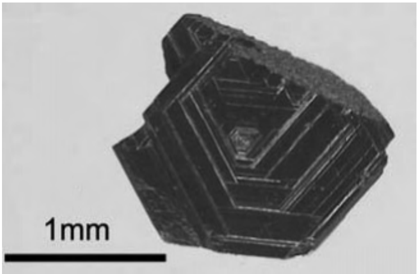

Figure 1. Single crystal of $Ba_2Co_9O_{14}$.

At higher temperature (1000 °C), a 2*H*-perovskite-related oxide in the series $(Ba_8Co_6O_{18})_\alpha(Ba_8Co_8O_{24})_\beta$[6] was formed. It seems that both **1** and **2** are not stable at high temperatures (>1000 °C). This might be the reason that these phases had not been identified in the previous high-temperature syntheses.

Both **1** and **2** crystallize in the space group $R\bar{3}m$ with the lattice parameters $a = 5.6958(4)$ Å and $c = 28.909(4)$ Å for **1** and $a = 5.6901(4)$ Å and $c = 35.937(5)$ Å for **2**. Single-crystal structure study[7] established that the structures of both **1** and **2** are related and can be described as an intergrowth structure containing the CdI_2-type layers and the perovskite layers, as shown in Figure 2. In the CdI_2-type layer, there are two close-packed oxygen layers with cobalt ions in all octahedral sites. Between the CdI_2-type layers, a perovskite (111) block with either a single-octahedral layer (**1**) or a double-octahedral layer (**2**) is interleaved. It is well-known that the perovskite can be described as a close-packing $[BaO_3]$ array and that the octahedral sites are occupied by cobalt ions. Therefore, the structures of both **1** and **2**, in fact, can be described as mixed close-packing arrays consisting of close-packed oxygen layers and $[BaO_3]$ layers, in which the octahedral and tetrahedral interstitials are occupied by cobalt ions. In Figure 2, we also show the sequences of the close-packed layers in both **1** and **2**. The two kinds of close-packed layers are nicely matched, which results in commensurate structures. It should be noted that an interface layer is present between the CdI_2-type and the perovskite blocks. As shown in Figure 3, the interface layer contains a close-packed oxygen layer and a $[BaO_3]$ layer. Therefore, there are two types of polyhedral sites, i.e., octahedral and tetrahedral sites, all of which are occupied by cobalt ions in these two structures.

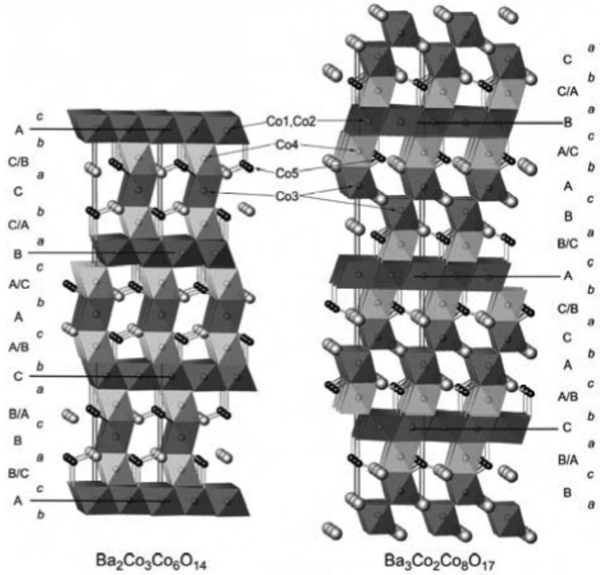

Figure 2. Structures of (a) $Ba_2Co_9O_{14}$ (**1**) and (b) $Ba_3Co_{10}O_{17}$ (**2**). The octahedra in the dark areas are those in the CdI_2 layers and perovskite layers, and the octahedra in the light areas are those in the interface layers. The tetrahedra cobalt ions are expressed as dark balls, and barium ions are expressed as light balls.

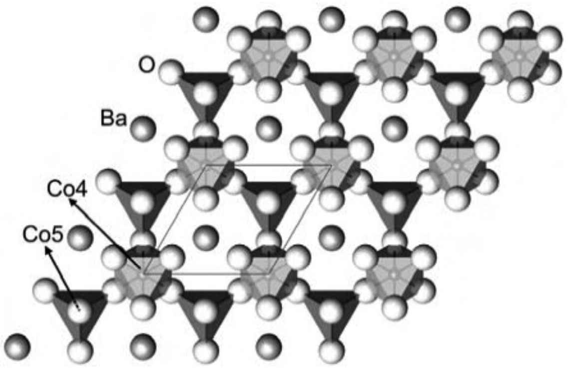

Figure 3. Interface layer in both **1** and **2** consisting of close-packed $[BaO_3]$ and oxygen layers. The octahedral and tetrahedral sites are occupied by cobalt ions, which are shown as polyhedra; barium and oxygen atoms are expressed as dark and light balls.

The composition of a perovskite (111) block with a thickness of *n* octahedral layers can be expressed as $[Ba_{n+1}Co_nO_{3n+3}]$, while the CdI_2-type layer can be expressed as $4[CoO_2]$. Further including additional cobalt ions (4Co) in the interface layer, one could obtain a general formula of $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ for this intergrowth cobaltite family. **1** is the $n = 1$ member that contains a single perovskite layer ($Ba_2Co_9O_{14}$), while **2** is the $n = 2$ member containing a double perovskite layer ($Ba_3Co_{10}O_{17}$). This general formula may help us to formulate the compositions of other high-*n* members. For instance, the $n = 3$ member may have a composition of $Ba_4Co_{11}O_{20}$ and, additionally, one could estimate its structural parameters by insertion of the perovskite layers ($a \approx 5.7$ Å and $c \approx 43.0$ Å).

In the structures of **1** and **2**, there are five crystallographically independent cobalt sites, which are coordinated in two types of coordination polyhedra, i.e., octahedron and tetrahedron. The environments of the octahedra can further be differentiated from the linkages to the neighboring polyhedra. The cobalt octahedra in the CdI_2-type layer share six edges

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(7) Structure determination: Single-crystal diffraction data of $Ba_2Co_9O_{14}$ (**1**) and $Ba_3Co_{10}O_{17}$ (**2**) were collected on an Enraf-Nonius Kappa CCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,69$ Å). Indexation of single-crystal diffraction data yielded a rhombohedral unit cell, $a = 5.6958(4)$ Å and $c = 28.909(4)$ Å for **1** and $a = 5.6901(4)$ Å and $c = 35.937(5)$ Å for **2**. Absorption correction was applied by a multiscan method. The analysis of the intensity statistics of single-crystal diffraction data for **1** suggested the possible space group of $R\bar{3}m$ ($|E^2 - 1| = 0.931$; $R_{sym} = 0.033$). All atomic positions can be identified from direct methods. The refinement with anisotropic thermal parameters for all sites leads to the residual value $R = 0.0258$ and $wR = 0.0565$. The space group of **2** is also $R\bar{3}m$, and through the relationship between **1** and **2**, one can easily establish the structure model of **2** by *SHELX97*. With anisotropic thermal parameters, the last refinement leads to $R = 0.0421$ and $wR = 0.1105$.

Table 1. Average Co−O Distance and BVS of Cobalt Ions

	$Ba_2Co_9O_{14}$			$Ba_3Co_{10}O_{17}$		
atom	site	Co−O (Å)	BVS	site	Co−O (Å)	BVS
Co1	3a	2.076	2.12	3b	2.077	2.12
Co2	9e	1.919	3.15	9d	1.916	3.20
Co3	3b	1.954	2.86	6c	2.024	2.49
Co4	6c	1.937	3.00	6c	1.942	2.96
Co5	6c	1.922	2.15	6c	1.877	2.37

with neighboring octahedra within the layer. Considering the neighboring polyhedra, the cobalt ions in the CdI_2-type layer can be divided into two groups (Co1 and Co2). The Co1 octahedron further shares six corners with the Co4 octahedron in the interface layers, whereas the Co2 octahedron shares two edges with the Co4 octahedron and two corners with the Co5 tetrahedron. The bond valance sum (BVS) calculation indicated that cobalt ions are mainly Co^{II} at the Co1 site and Co^{III} at the Co2 site in both **1** and **2** (Table 1). The charge distribution in the CdI_2-type layers is significantly different from the other known CdI_2-layer-containing compounds, such as $NaCo_2O_4$[8] and other misfit cobaltites, where the cobalt ions in CdI_2-type oxide layers are mainly Co^{III} and Co^{IV}.

The environments of the octahedral cobalt in the perovskite block (Co3) are different in **1** and **2**. The Co3 octahedron in **1** shares two triangular faces with the Co4 octahedron in the interface layer and six corners with the Co5 tetrahedron, whereas in **2**, the Co3 octahedron shares one face with the Co4 octahedron and six corners with the Co5 tetrahedron and the neighboring Co3 octahedron. This influences strongly the bond distances and, in turn, the oxidation states of cobalt ions at the Co3 site, as shown in Table 1. The larger BVS value (2.86) at the Co3 site in **1** indicates mainly Co^{III} in the perovskite block. In **2**, the BVS value at the Co3 site is significantly smaller (2.49), indicative of more Co^{II} ions at this site. Similarly, the cobalt ions at the tetrahedral site (Co5) are mainly Co^{II} (BVS = 2.15) in **1**, while in **2**, a shorter Co5−O bond and a higher BVS value (2.40) reveal the possible presence of Co^{III} at the tetrahedral site. The environment of the octahedral site in the interface layers (Co4) is rather similar in both **1** and **2**, and both can be described as Co^{III}.

Considering the overall average oxidation states of cobalt ions, which is +2.67 for **1** and +2.8 for **2**, the compounds can be described as $Ba_2Co^{II}{}_3Co^{III}{}_6O_{14}$ (**1**) and $Ba_3Co^{II}{}_2Co^{III}{}_8O_{17}$ (**2**). As far as the BVS values of the cobalt ions are concerned, the distribution of the Co^{II} ions is more or less ordered in **1** and can be assigned mainly at the Co1-octahedral and Co5-tetrahedral sites. In the compound **2**, the distribution of Co^{II} ions is not clear-cut. However, the BVS values show that the Co^{II} ions are mainly distributed in the Co1, Co3, and Co5 sites, in which the Co1 site is almost purely Co^{II} and the Co3 and Co5 sites are of mixed valance (Co^{II} + Co^{III}).

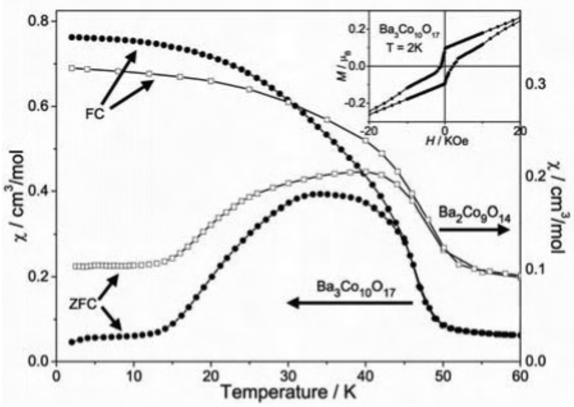

Figure 4. Field cooling and zero field cooling of **1** (open squares) and **2** (filled circles). The hysteresis loop of **2** is shown in the inset.

Unlike the other known CdI_2-containing cobalt oxides, which often exhibit metallic behavior,[2] the conductivity measurement shows that both **1** and **2** are semiconductors below 300 K. Although the mechanism of conductivity is not clear in these materials, the lower oxidation state of the cobalt ions (Co^{II} + Co^{III}) in **1** and **2**, in comparison with that in other CdI_2-containing cobalt oxides (normally Co^{III} + Co^{IV}) in the CdI_2-type layer, might be responsible for the distinct conductivity behavior. Additionally, **1** and **2** are paramagnetic at high temperature and become antiferromagnetic below about 50 K, with small canting angles as shown in Figure 4. The Curie constant C_m is about 9.7 for **1** and 8.6 for **2**, which can be understood by assuming nonmagnetic Co^{III} and strong spin−orbital coupling for Co^{II}.

In conclusion, two new cobaltites, $Ba_2Co_9O_{14}$ (**1**) and $Ba_3Co_{10}O_{17}$ (**2**), can be attributed to the $n = 1$ and 2 members of a hexagonal intergrowth family, $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$. There are several known hexagonal intergrowth families that adopt related structures. For example, the misfit layered compounds, $[M_2CoO_3][CoO_2]_{1.62}$ (M = Ca and Sr)[3] and $[Pb_{0.7}Sr_{1.9}Co_{0.4}O_3][CoO_2]_{1.8}$,[4] contain also the CdI_2-type oxide layers, but the interleaved species are the rock-salt blocks instead of perovskite. Another known hexagonal perovskite intergrowth family, $La_{n+1}Mn_nO_{3n+3}(Ca_2O)$,[9] contains hexagonal perovskite blocks that are interleaved by graphite-like $[Ca_2O]$ layers. The present series, $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$, represents a new intergrowth family consisting of the CdI_2-type layers and the perovskite (111) blocks of *n*-octahedral layers. Although both compounds exhibit antiferromagnetic semiconductor behavior, it will be interesting to see further modification of the physical properties by doping with other cations.

Acknowledgment. We thank Nature Science Foundation of China for financial support (Grants 20221101 and 20371005) and Prof. Chen at USTC and Dr. Zhang at PKU for the resistance and magnetic measurements.

Supporting Information Available: For both compounds **1** and **2**, X-ray crystallographic files in CIF format, tables for atomic positions and selected bond distances, and figures for resistance and magnetic properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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