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HREM Study of the $BaCoO_{3-y}$ System: Evidence for a New 5H Phase

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Using selected area electron diffraction (SAED) and high resolution electron microscopy (HREM) results, a structural model is proposed for a new perovskite-like material in the $BaCoO_{3-y}$ system: the 5H $BaCoO_{2.74}$ polytype. According to X-ray diffraction data unit cell parameters are a = 0.566(2) and c = 1.197(4) nm (space group $P\bar{3}m1$). The structure is based on a 5-layer stacking sequence ...ccchh..., where two-fifths of the cobalt atoms are tetrahedrally coordinated by oxygen due to the presence of a cubic layer with a BaO_2 composition. The accommodation of anionic vacancies within the three remaining octahedral layers is discussed. © 1995 Academic Press, Inc.

1. INTRODUCTION

Accommodation of compositional variations in hexagonal perovskites AMO_{3-y} (A = Ba; M = Fe, Mn, Co, Ni) is strongly dependent on the ability of M cations to adopt several coordinations. For a hexagonal close packing only two layers are necessary to complete a unit cell in the ...hh... stacking sequence, leading to the ideal $BaNiO_3$ 2H hexagonal type (1). When the AO_3 layer stacking is cubic, three cubic layers are needed to describe the unit cell following a ...ccc... sequence. Between the purely cubic and hexagonal forms, several structure types can be theoretically generated (2). The site preference of the M-reduced cation determines the stacking sequence.

Previous work in our laboratory (3–7) has shown that oxygen deficiency in $BaMnO_{3-y}$ is accommodated by the introduction of $BaO_{2.5}$ cubic layers in the hexagonal close-packing of 2H $BaMnO_3$ (8). This leads to materials consisting of ordered or disordered intergrowths of octahedral MnO_6 layers and pyramidal square MnO_5 layers along the c-axis. Ordered phases are obtained when the anionic composition is $y = 0.5c/(c + h)$, c and h referring to the number of cubic and hexagonal layers per unit cell, respectively. Up to now, selected area electron diffraction (SAED) data have proved the existence of 4 rhombohedral (33R, 27R, 21R, and 15R) and 5 hexagonal (8H, 8H′, 6H, 10H and 4H) structural types within the range $0 < y \leq 0.25$.

In $BaFeO_{3-y}$, Mössbauer spectroscopy studies (9, 10) have shown that the oxygen vacancy distribution is related to the possibility of a pyramidal or tetrahedral coordination for Fe^{3+}. As a consequence, only two hexagonal types have been reported within the compositional range $0 < y < 0.5$, A 12H structural type for $0.07 \leq y \leq 0.13$ (11) and a 6H type along $0.20 \leq y \leq 0.35$ (12). According to Jacobson (13), neutron diffraction data suggest that a cubic layer has a $BaO_{2.875}$ and a hexagonal layer a $BaO_{2.5}$ composition in this system. However, since SAED studies (12, 14) indicate that this structural type allows compositional variations, it seems obvious that the composition in the stacking layers cannot remain fixed.

Powder X-ray diffraction (XRD) data in the $BaCoO_{3-y}$ system reported by several authors (15–17) suggest the existence of some phases in which the relationship between oxygen nonstoichiometry, vacancy ordering, and microstructure is not fully understood. Co^{4+} is found in both octahedral and tetrahedral sites but the reduced cation, Co^{3+}, has a strong site preference for octahedral coordination. A detailed structural study of the perovskite-like phase 12H $BaCoO_{2.6}$ by high-resolution electron microscopy (HREM) and profile analysis of powder neutron data, performed by Jacobson and Hutchison (18), shows that oxygen vacancies are nonrandom and are introduced by the replacement of some BaO_3 layers by BaO_2 layers of the type found in mixed metal oxides $A_3B_2O_8$ with the palmierite structure (19). The introduction of BaO_2 instead of BaO_3 layers has also been shown by Gibb (20) in 5H $BaCo_{0.8}Mn_{0.2}O_{2.80}$ and 12H $BaCo_{0.5}Mn_{0.5}O_{2.87}$ phases, which appear to be hexagonal perovskites with a mixture of face- and corner-sharing octahedra, although the manganese shows a strong preference for face-sharing sites, and there is evidence to suggest that some of the cobalt occupies tetrahedral sites by virtue of the introduction of BaO_2 layers.

In order to establish the relationship between compositional variations and the different structural types possibly existing in the $BaCoO_{3-y}$ system, we have undertaken a study by means of SAED and HREM of samples prepared

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with accurate control of the oxygen content. We describe in this paper the structural model proposed for a new material, the 5H $BaCoO_{2.74}$ phase.

2. EXPERIMENTAL

$BaCoO_{3-y}$ was prepared from stoichiometric amounts of $BaCO_3$ and Co_3O_4. The mixture was ground in a ball mill and fired at 750°C for 1 day. Then, the sample was heated at 1000°C in air for 20 days with intermediate grinding. After annealing, the sample remained unchanged, no variation being observed with ulterior treatments at the same temperature.

After such a treatment, a value of $y = 0.26$ was obtained as determined by thermogravimetric analysis developed on the basis of a CAHN D-200 electrobalance. The sample was reduced under H_2 at 800°C. Since the final product of the reduction process was a mixture of BaO and Co, the oxygen content was established from the weight difference between the starting $BaCoO_{3-y}$ and the final product.

Powder X-ray diffraction (XRD) was carried out on a SIEMENS D-5000 diffractometer with a graphite monocromator and using Cu$K\alpha$ radiation. SAED was carried out on a JEOL 2000FX electron microscope. HREM was performed on a JEOL 4000EX electron microscope.

3. RESULTS AND DISCUSSION

The powder XRD pattern of $BaCoO_{2.74}$ is shown in Fig. 1. This pattern does not correspond to any of the hexagonal phases up to now described in the $BaCoO_{3-y}$ system, but it can be indexed on the basis of a hexagonal cell with $a = 0.566(2)$ and $c = 1.197(4)$ nm. Since the distance between BaO_3 layers along the c axis is ~0.23 nm, the cell dimensions suggest a five-layer (5L) stacking sequence. In order to determine the anionic vacancy distribution along the crystal and to propose a structural model for this new material a SAED and HREM study was performed.

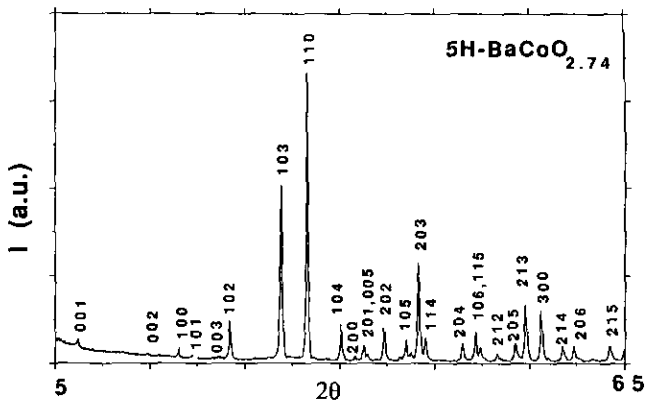

FIG. 1. Powder XRD pattern of $BaCoO_{2.74}$.

The SAED patterns along [010] and [001] zone axes are shown in Figs. 2a and 2b, respectively. A hexagonal symmetry is clearly appreciated in both patterns, all diffraction maxima being indexed on the basis of the previous unit cell.

A HREM lattice image obtained along the [010] direction is displayed in Fig. 3. All the crystals studied were apparently ordered. The columns in the image are separated by a distance consistent with the d-spacing measured using XRD and SAED. Moreover, the observed contrast pattern corresponds to a 5L unit cell with stacking sequence ...cchh... (3, 4). It may thus be concluded that a new hexagonal phase, the 5H-type, has been isolated in the $BaCoO_{3-y}$ system.

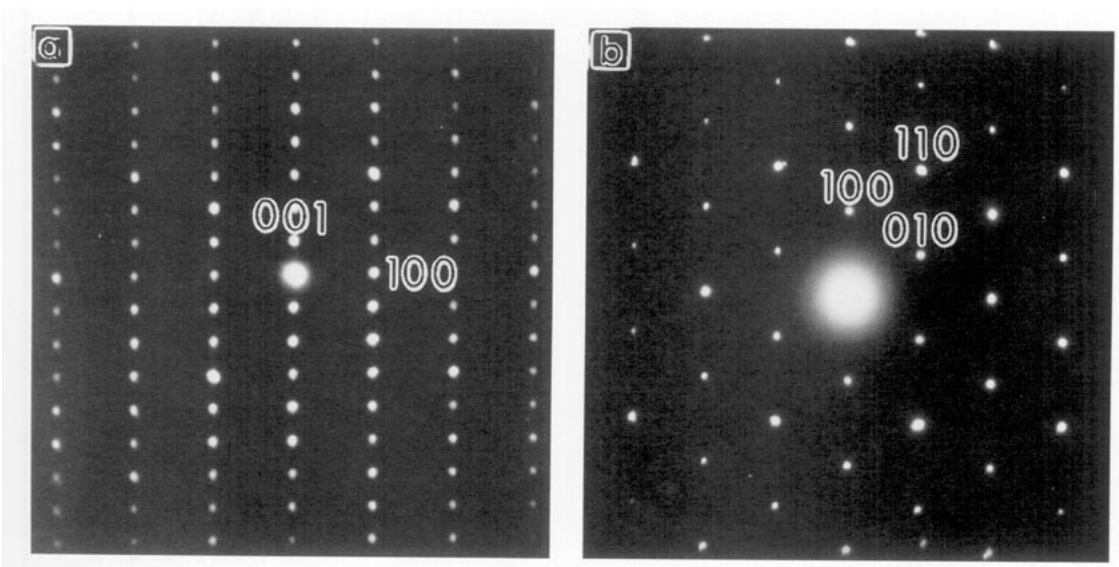

FIG. 2. (a) SAED pattern of $BaCoO_{2.74}$ along [010]. (b) Idem along [001].

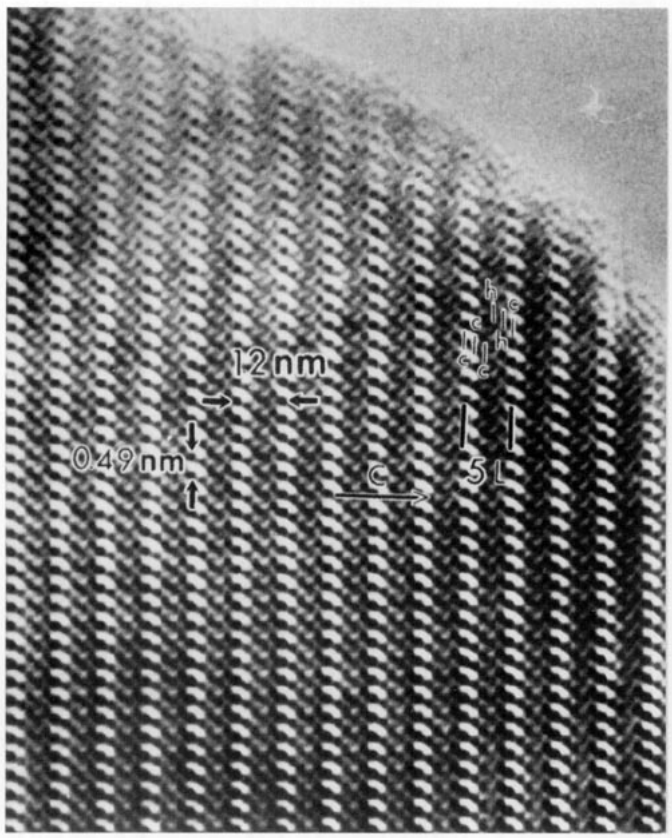

FIG. 3. High resolution image along [010] of $BaCoO_{2.74}$. The stacking sequence corresponding to the unit cell is marked.

For a 5H lattice showing hexagonal symmetry, the only possible hexagonal BaO_3-layer closest packing sequence, as shown in the International Tables for Crystallography (21) is ...ABCBC..., i.e., (4)(1) in the Zhdanov notation ($P\bar{3}m1$ space group). Assuming an ideal five-layer sequence with $P\bar{3}m1$ symmetry, the corresponding positions are: 1 Ba in (a); 2 Ba in (d), $z \approx 4/5$; 2 Ba in (d), $z \approx 2/5$; 2 Co in (d), $z \approx 1/10$; 2 Co in (c), $z \approx 3/10$; 1 Co in (b); 6 O in (i), $x \approx 1/6$, $z \approx 1/5$; 6 O in (i), $x \approx 5/6$, $z \approx 2/5$, 3 O in (e).

A structural model for such a 5H phase with composition $BaCoO_3$ is shown in Fig. 4. It consists of three face-sharing octahedra linked by two corner-sharing octahedra along the c-axis. Such a structural model is the result of an alternation of cubic and hexagonal BaO_3 layers, following the sequence ...ccchh... along the c-axis, in agreement with the sequence found in the HREM image.

The experimental composition, $BaCoO_{2.74}$, indicates a high concentration of anionic vacancies in the 5H structure. Since HREM images show apparently ordered crystals and SAED patterns do not show evidence of streaking suggesting the existence of either stacking faults or different types of disorder, it may be supposed that oxygen vacancies are randomly distributed along the crystal.

For a $BaCoO_3$ composition, a 2H-type structure, showing the stacking sequence ...hh..., has been described (15). The modification of such a structural type as a consequence of the introduction of cubic layers is associated with the appearance of anionic vacancies. It seems obvious that oxygen vacancies must be concentrated along such layers. Moreover, considering that the most probable coordination for both Co^{3+} and Co^{4+} are octahedral and/or tetrahedral, it must be assumed that introducing two layers with Co^{+4} in tetrahedral coordination entails reducing one of the cubic layers to a BaO_2 composition. Accordingly, a structural model as shown in Fig. 5 may be proposed for the 5H structural type, in which the oxygen initially in position 3(e) in $BaCoO_3$ has moved to a position 2(c) in $BaCoO_{3-y}$. As a consequence of this ordered arrangement of vacancies, two-fifths of the cobalt atoms are tetrahedrally coordinated by oxygen. The CoO_4 tetrahedra are corner-linked to strings of three face-sharing octahedra containing the remaining cobalt ions, as in 12H Ba $CoO_{2.6}$ (18).

The introduction of only one BaO_2 layer in the 5H unit cell should lead to the composition $Ba_5Co_5O_{14}$, i.e., Ba $CoO_{2.80}$, which is a composition more oxidized than the one experimentally obtained. It should then be necessary to suppose the presence of anionic vacancies randomly distributed within the BaO_3 layers.

On the other hand, if we assume that the Co^{4+} ions are tetrahedrally coordinated and Co^{3+} are in octahedral coordination, the resulting composition should be $BaCo^{3+}_{0.6}Co^{4+}_{0.4}O_{2.70}$, which is slightly reduced relative to the composition obtained by thermogravimetry.

In fact, the experimental composition practically corresponds to 50% Co^{3+} and 50% Co^{4+}. Due to the strong preference of Co^{4+} ions for fourfold coordination, the two tetrahedral sites should be occupied by two Co^{4+} ions. As a first

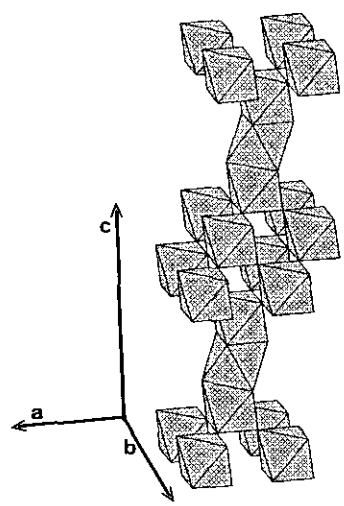

FIG. 4. Structural model corresponding to an ideal 5H-$BaCoO_3$ phase.

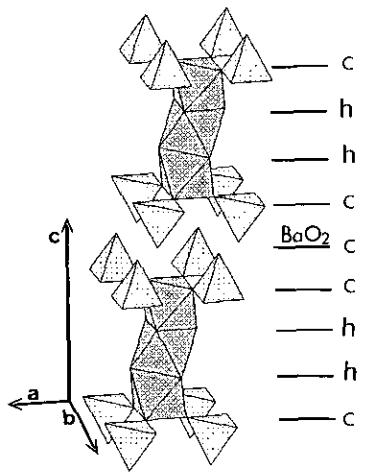

FIG. 5. Structural model proposed for the 5H-$BaCoO_{3-y}$ phase.

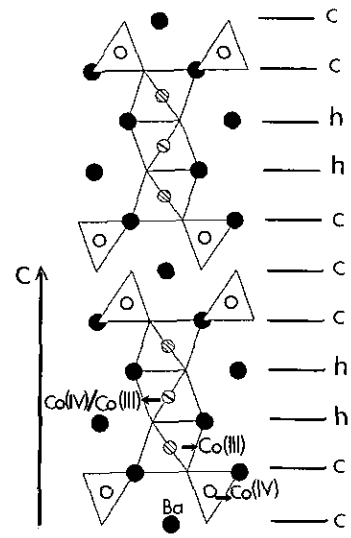

FIG. 6. Possible stacking sequence of Co ions in the 5H-Ba $CoO_{2.74}$ material.

approximation, we can then suppose that three octahedral sites of every unit cell are occupied on average by 2.5 Co^{3+} ions and the remaining 0.5 Co^{4+} ions are randomly distributed. However, regarding the 5H structural type (Fig. 5), only the central octahedron shares two triangular faces with two other octahedra. The cobalt ion situated at this central position, must be subject to stronger repulsions than the other two, since the distance to the neighboring atoms is shorter. In order to decrease such repulsions it seems more appropriate to suppose that the fraction of Co^{4+} ions occupying the octahedral sites must be situated at the central octahedron. Thus, it seems that the most stable stacking sequence of Co ions along the octahedral

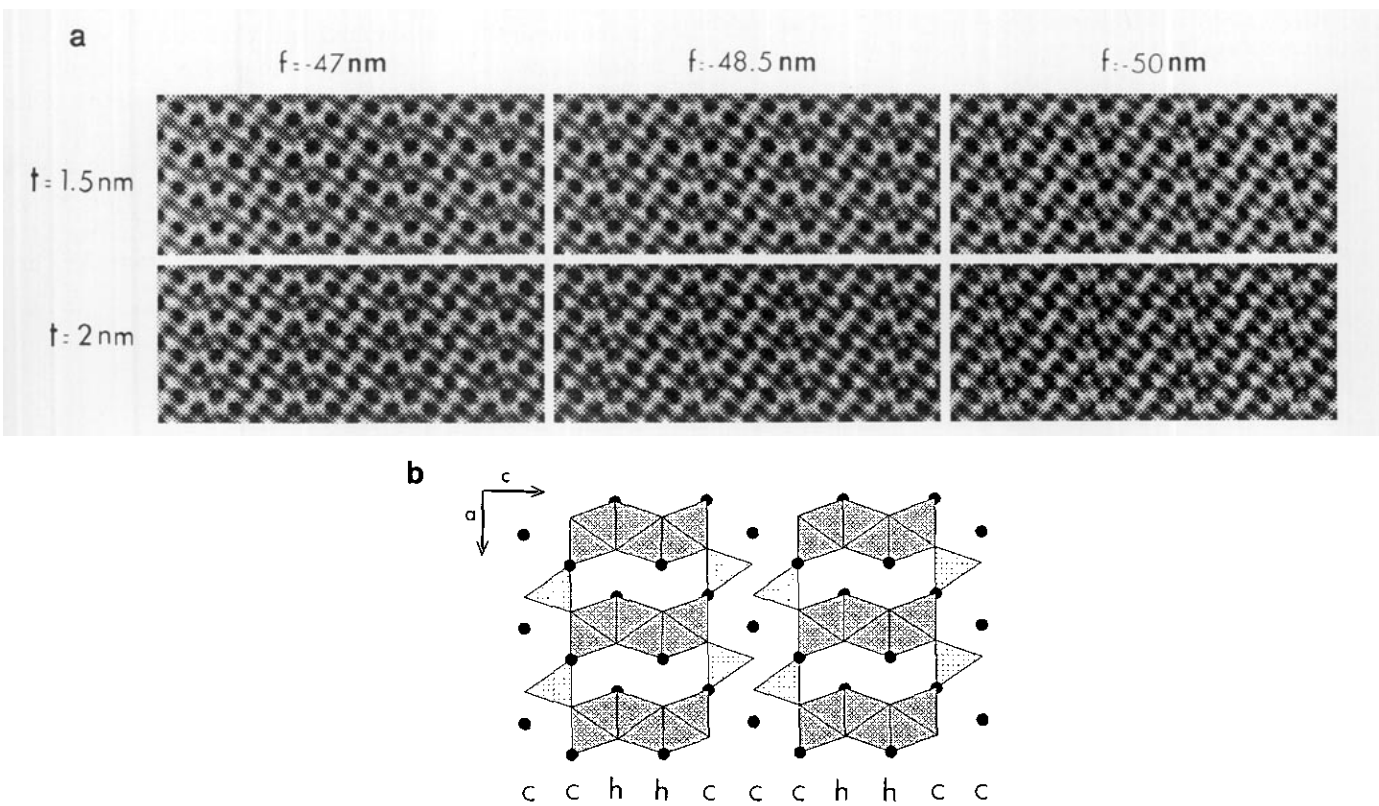

FIG. 7. (a) Calculated images on the basis of an ideal 5H structural type along the [010] projection. (b) 5H structural model along [010], with the $P\bar{3}m1$ space group. Ba atoms are represented as black dots.

sites should be ... $Co^{3+}//(Co^{4+} + Co^{3+})//Co^{3+}$ ... as shown in Fig. 6.

According to this stacking sequence, it appears that the two hexagonal layers corresponding to the 5H structural type present lower oxygen content than BaO_3. Following this reasoning, if the central cubic layer has a BaO_2 composition while the two remaining cubic layers have BaO_3, the required composition of the two hexagonal layers to get the experimental composition must be $BaO_{2.85}$. Such a small concentration of anionic vacancies suggests that they could be randomly distributed along the hexagonal layers and are not detected by SAED.

Obviously, although the above distribution of the Co ions seems to be the most favorable, we cannot discard the possibility that Co^{3+} and Co^{4+} are randomly distributed and that the anionic vacancies are also randomly distributed along the 4 BaO_3 layers per unit cell. If so, the composition corresponding to such layers would be $BaO_{2.925}$.

It is worth recalling that a structural model similar to that for the above-described $BaCoO_{3-y}$ 5H phase has been proposed by Gibb for $BaCo_{0.80}Mn_{0.20}O_{2.80}$ (20). It can be assumed that the difference observed in the anionic composition between $BaCoO_{2.74}$ and $Ba(Co, Mn)O_{2.80}$ is due to the strong preference of Mn^{4+} for octahedral sites, thus avoiding the presence of anionic vacancies along the BaO_3 layers. In any case, we cannot preclude the possibility of isolating a free-vacancy 5H $BaCoO_{2.80}$ phase although the experimental conditions used up to now lead to a mixture of both 5H and 2H-like phases for such a nominal composition.

Image calculations (Fig. 7a) of the structural model proposed (Fig. 7b) were performed using the multislice method (22), under the following conditions: $\Delta f = -47$, -48.5, and -50 nm; sample thickness (t) = 1.5 and 2.0 nm. The best fit seems to correspond to $\Delta f = -48.5$ and $t = 1.5$ nm. However, a good correspondence between calculated and experimental images is observed only for Ba atoms, since calculations have been performed considering the ideal cationic positions of an undistorted 5H-type, as shown in Fig. 4. Obviously, the introduction of a BaO_2 layer must modify, at least, the atomic positions close to such a layer. In order to obtain more accurate information on such positions, a neutron diffraction study is in progress.

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