The Oxycarbonate $Ba_3Co_2O_6(CO_3)_{0.60}$ with a 2H−ABO_3-Related Structure

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The crystal structure of $Ba_3Co_2O_6(CO_3)_{0.60}$ has been determined by means of X-ray, neutron and electron diffraction, and high-resolution electron microscopy. This compound has a hexagonal symmetry (space group $P\bar{6}$) and lattice parameters $a = 0.9683(1)$ and $c = 0.95180(8)$ nm related to the 2H−ABO_3 by means of the expression $a = a_{2H}(3)^{1/2}$ and $c = 2c_{2H}$. It can be described from the ordered intergrowth of two blocks, $[Ba_2Co_2O_6]^{\delta-}$ and $[Ba(CO_3)_{0.60}]^{\delta+}$, alternating along the *a*-axis. The first block corresponds to two 2H-like rods and the second one can be related to the $BaCO_3$ aragonite-type structure. Neutron diffraction data elucidate the relative orientation of carbonate groups along *c*-axis in the aragonite-like blocks.

Introduction

The 2H−ABO_3 hexagonal perovskite[1] (A = Ba, B=Mn, Co, and Ni) can be described as a hexagonal close packing (*hcp*) of BaO_3 layers with B cations occupying octahedral sites, leading to isolated chains of octahedra sharing faces running parallel to the *c*-axis (Figure 1a). The structures of some oxides with different A:B stoichiometry (A/B >1) can be considered within the same framework either by varying the layer composition forming the *hcp* sequence or by the formation of B cationic vacancies in the oxygen octahedra defined between BaO_3 layers.

For an A:B = 3:2 ratio, several structures, all of them closely related to the 2H type, can be established depending on the nature of both A and B cations. Thus, the crystal structure of $Ca_3Co_2O_6$[2] is built up from infinite CoO_3 chains running along the *c*-axis. The Co atoms form alternating face-sharing coordination polyhedra of trigonal prisms and octahedra (Figure 1b). Their structural relationships with the 2H type have been described[3] in terms of a hexagonal stacking of Ca_3CoO_6 layers. This phase crystallizes in space group $R\bar{3}c$, the a parameter being related to the 2H subcell by a $(3)^{1/2}$ factor.

2H *hcp*-BaO_3 can be only maintained for the 3:2 cationic ratio if the octahedral positions are not fully occupied. This is the case of $Ba_3B_2O_9$ (B = Te, W) which can be described from the *hcp* packing of BaO_3 layers, with B cations occupying $^2/_3$ of the octahedral sites, leading to chains formed by two $[BO_6]$-sharing-faces octahedra alternating with one cation vacancy, along the *c*-axis. Depending on the spatial arrangement between chains, a hexagonal ($P\bar{6}m2$) or rhombohedral ($R\bar{3}c$) symmetry results for $Ba_3Te_2O_9$[4] and $Ba_3W_2O_9$[5] (Figure 1c), respectively. In the latter case, the *a*-axis is related to the 2H one by a $(3)^{1/2}$ factor. The fact that $^2/_3$ of the octahedra sites between all layers are filled, minimizing the repulsions between B cations and the high oxidation state of W(VI) and Te(VI) ensure that charge balance is achieved. When B cations present a lower oxidation state, this framework structure can be

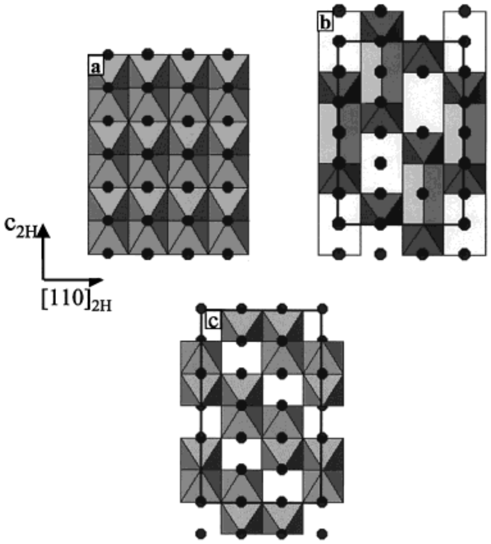

Figure 1. Idealized crystal structures projected along the $[1\bar{1}0]_{2H}$ direction of (a) 2H−ABO_3, (b) $Ca_3Co_2O_6$, and (c) $Ba_3W_2O_9$.

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maintained if an additional component is incorporated in order to compensate for the negative charge excess. In this way, Negas et al.[6,7] reported the existence of phases with the composition $Ba_3NiC_xO_{9-y}$ and $Ba_3B_2C_xO_{9-y}$ (B = Co, Ni). In all these phases, a carbonate group is present as a constituent of the structure. These materials show hexagonal symmetry, again with the a-axis related to the 2H subcell by $(3)^{1/2}$. The samples seem to be not completely ordered, and consequently their crystal structures were not established. Therefore, the carbon and oxygen content were not determined.

The presence of carbonate groups in perovskite-related structures is not unusual. It is well-established that carbonate groups successfully substitute copper polyhedra in the perovskite-related blocks leading to a high number of superconducting cuprates.[8,9] Very recently, Slater et al.[10] have reported a new copper oxide carbonate, $Ba_4ScCu_2O_{7-x}(CO_3)$, in which an ordering between Sc, Cu, and (CO_3) groups seems to be established.

In this paper, we report a structural study of a compound with the composition $Ba_3Co_2O_6(CO_3)_{0.60}$. To fully determine the structural details, X-ray diffraction (XRD), selected area electron diffraction (SAED), high-resolution electron microscopy (HREM), and neutron powder diffraction have been used.

Experimental Section

The Ba:Co = 3:2 compound was prepared from $BaCO_3$ (Merck, 99.99%) and Co_3O_4 (Aldrich, 99.995%) as starting materials. The synthesis was carried out by heating in air stoichiometric amounts of both reagents in a Pt crucible at 750 °C for 14 h. A black homogeneous product was obtained. The average cationic composition was determined by inductive coupling plasma. Also, the local composition was determined on many crystals by energy dispersive spectroscopy (EDS) on a JEOL 2000FX electron microscope, also used to perform SAED experiments, equipped with an EDS system LINK AN10000. In addition, elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer; the sample is first oxidized in a pure oxygen environment, and the resulting gases (CO_2 and H_2O) are separated under steady-state conditions and measured as a function of thermal conductivity. Infrared spectra were recorded as KBr pellets on a Nicolet Magna-550 FT-IR spectrometer.

Powder XRD was carried out on a Phillips X'Pert diffractometer with a graphite monochromator using Cu Kα radiation. Neutron powder diffraction data were collected at room temperature on the D1B powder diffractometer at the Institut Laue Langevin, working in the high-intensity mode. About 8 g of the powdered sample were contained in a cylindrical vanadium cell of 8 mm diameter. The pattern was obtained in the angular range 10°−120° (2θ°) with a step size of 0.1° (2θ) using neutrons of wavelength 1.3 Å. Both the X-ray and the neutron diffraction data were analyzed by the Rietveld method[11] using the Fullprof program.[12]

SAED was carried out on a JEOL 2000 FX electron microscope. HREM was performed on a JEOL 4000 EX electron microscope. Simulated images were calculated by the multislice method using the MacTempas software package.

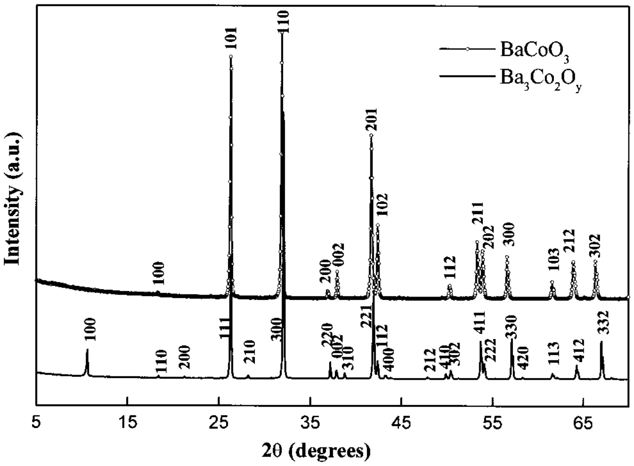

Figure 2. X-ray diffraction patterns of $Ba_3Co_2O_x(CO_3)_y$ and 2H−$BaCoO_3$.

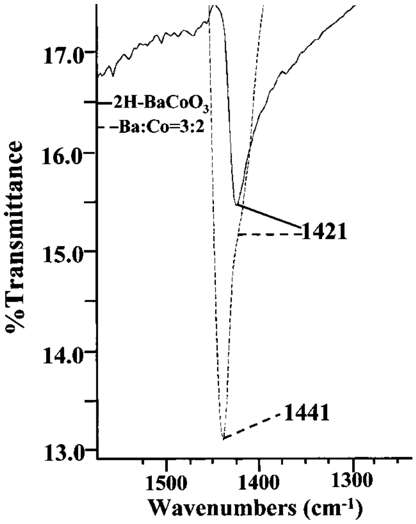

Figure 3. IR spectra corresponding to 2H−$BaCoO_3$ (continuous line) and Ba:Co = 3:2 phase (dashed line).

Results and Discussion

The sample of nominal composition $Ba_3Co_2O_x$ was confirmed to be single phase by XRD (Figure 2). The Ba:Co ratio was confirmed to be 3:2 both at the average (by wet chemical analysis) and at the microscopic (EDS) levels.

Figure 2 shows the XRD patterns of $Ba_3Co_2O_y$ and 2H−$BaCoO_3$[13] for comparison. Both patterns are very similar: the most intense peaks of the Ba:Co = 3:2 phase correspond to those of the 2H subcell, suggesting that the frameworks of both phases are the same. Together with the 2H-maxima, a set of weaker peaks appears, suggesting the existence of a 3-fold superstructure along $[110]_{2H}$. The whole pattern can be indexed on the basis of a hexagonal unit cell with parameters a = 0.97 nm ($a_{2H}(3)^{1/2}$) and c = 0.48 nm (c_{2H}). Subindex 2H will hereinafter be used to denote the 2H−ABO_3 subcell, and subindex 3:2 will stand for the Ba:Co = 3:2 cell. The value of the c parameter indicates that the distances between neighboring metallic atoms along [001] are very close to those found in the 2H structure. This result discards the presence of Ba_3CoO_6 layers in

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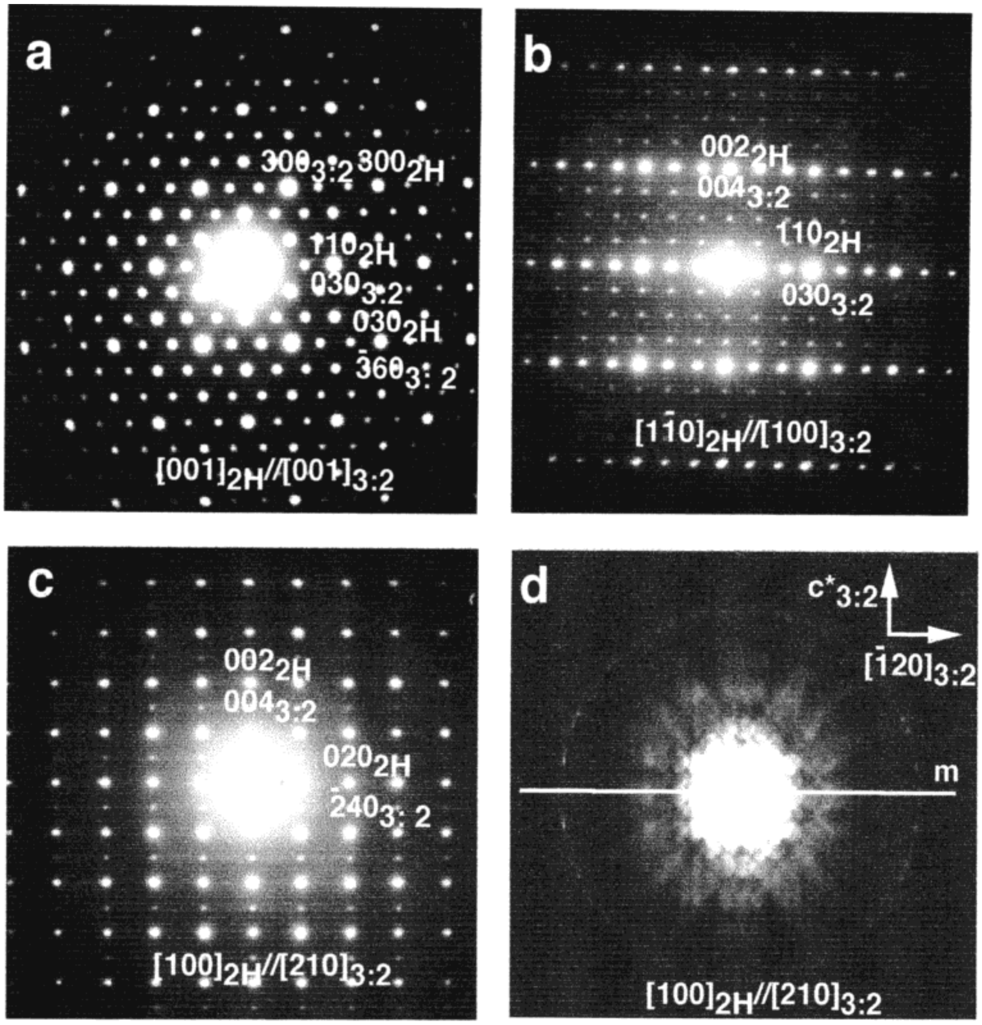

Figure 4. Electron diffraction patterns of $Ba_3Co_2O_6(CO_3)_x$, along the following zone axis: (a) $[001]_{2H}//[001]_{3:2}$, (b) $[1\bar{1}0]_{2H}//[100]_{3:2}$, (c) $[100]_{2H}//[210]_{3:2}$, and (d) CBED pattern along $[100]_{2H}//[210]_{3:2}$.

the Ba:Co = 3:2 phase. In fact, as previously reported,[2] a stacking of Ba_3CoO_6 layers in a hexagonal sequence originates both the shortening of the c_{2H}-axis and the change of the symmetry from hexagonal to rhombohedral. Therefore, the Ba:Co = 3:2 phase seems not to be isostructural with $Ca_3Co_2O_6$.

The strikingly similarity of both hexagonal phases, 2H−$BaCoO_3$ and Ba:Co = 3:2, suggests that the latter should be formed only by BaO_3-like layers (in an *hcp* sequence); thus, Co atoms fill $^2/_3$ of the octahedral sites. In this point, it is worth mentioning that the 3:2 sample contains about 1.38% (weight) of carbon, as determined by elemental analysis, and the 2H sample only shows around 0.2%. Moreover, in the 3:2 sample, IR spectroscopy suggests the presence of carbonate groups in the structure. Figure 3 shows the spectra between 1600 and 1200 cm^{-1} corresponding to the Ba:Co = 3:2 sample and 2H−$BaCoO_3$. The ν_3 vibration at 1441 cm^{-1} characteristic of carbonate groups[14] (1430 cm^{-1} in calcite and 1440 cm^{-1} in $BaCO_3$) is apparent in our sample but not in 2H−$BaCoO_3$. A band or a shoulder at 1421 cm^{-1} observed in both spectra can be associated with carbonate adsorbed at the surface. Therefore, the 1.38% weight of carbon in the Ba:Co = 3:2 phase should correspond to both structural and adsorbed carbonate. According to that, the composition of this sample could be formulated as $Ba_3Co_2O_6(CO_3)_x$.[6,7]

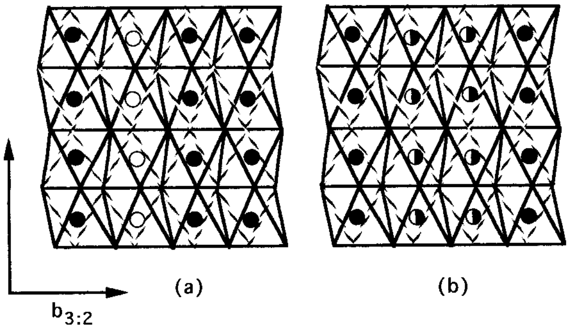

Figure 5. Schematic representations of possible cobalt arrangement for a 3:2 Ba:Co ratio in the 2H-type. Black circles, middle empty circles, and open circles represent fully, unoccupied, and half occupied Co atom positions, respectively.

SAED and HREM can provide further insight into the structure of this material. The most relevant SAED patterns for a hexagonal symmetry are shown in Figure 4. The first one (Figure 4a) corresponds to the $[001]_{2H}$ zone axis. Besides the characteristic spots of the 2H subcell, a 3-fold superstructure along $[110]_{2H}$ is observed, in agreement with that suggested by XRD results. The SAED pattern shown in Figure 4b, taken

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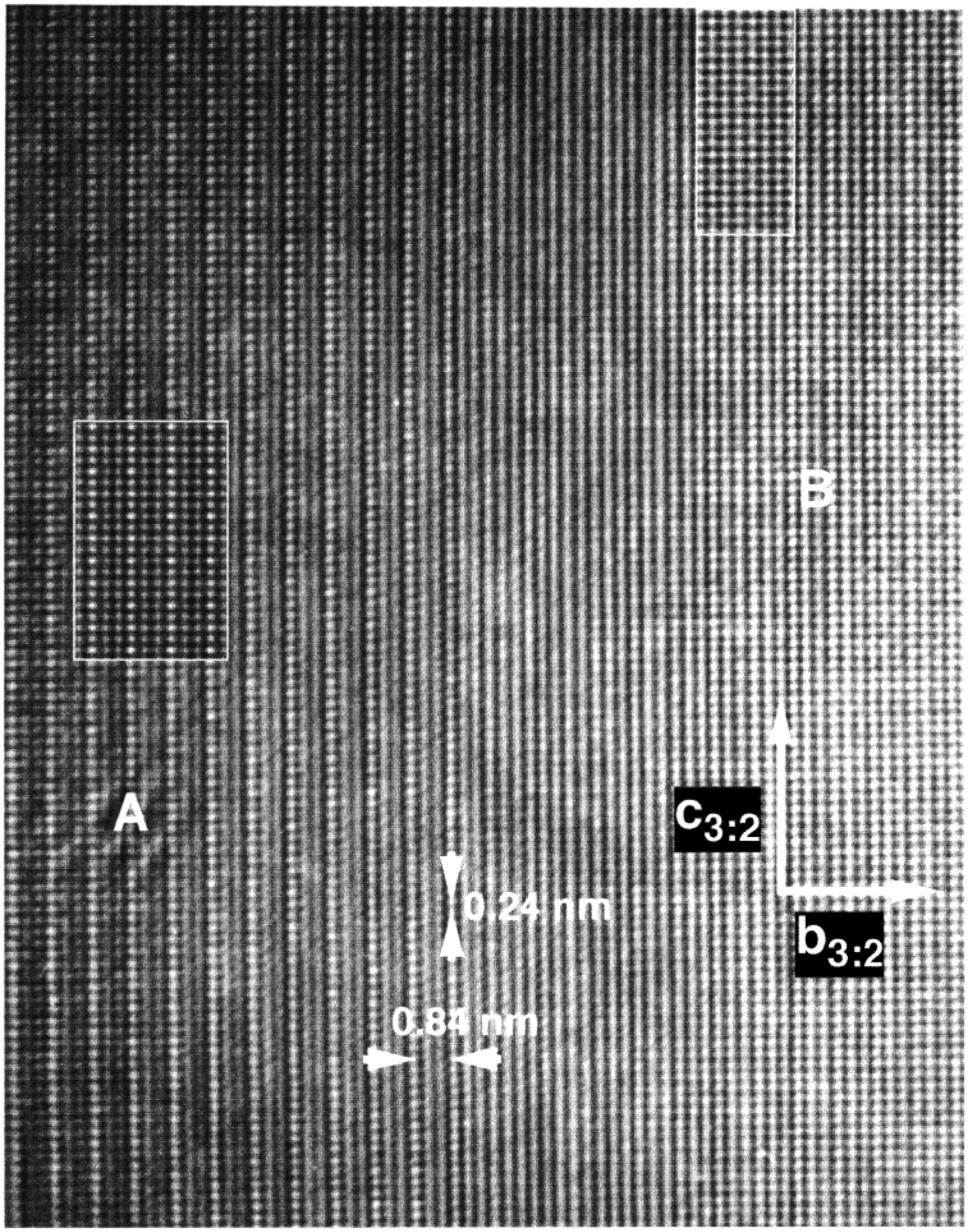

Figure 6. HREM image of $Ba_3Co_2O_6(CO_3)_x$ along the /$[1\bar{1}0]_{2H}$//$[100]_{3:2}$. Calculated images for two zones (A and B) of the crystal are also included.

along the $[1\bar{1}0]_{2H}$//$[100]_{3:2}$ direction, gives some more information about the structure: a 2-fold superstructure along the c^*_{2H}-axis appears, not observed by XRD. A considerable streaking along the b^*_{2H} direction is seen in the SAED pattern along the $[100]_{2H}$//$[210]_{3:2}$ zone axis (Figure 4c).

From the information obtained by SAED, we conclude that the Ba:Co = 3:2 phase shows a hexagonal unit cell with parameters $a = 0.97$ and $c = 0.95$ nm; the actual *c*-axis is double than that determined by XRD. This new unit cell includes four Ba_3O_{9-y} layers stacked along the *c*-axis in a hexagonal sequence and three rows of the 2H-type arranged along the $[010]_{3:2}$//$[110]_{2H}$ direction partially occupied by cobalt. According to the cationic ratio, several models of ordering of unoccupied Co positions can be envisaged to account for the observed periodicity. The two simplest ones are schematically represented in Figure 5. In the first model (Figure 5a), every three rows of octahedral positions, one does not contain cobalt. In the second one (Figure 5b), every three rows of octahedra positions, one is fully occupied, but the other two are only half filled. This second model includes either a random or an ordered distribution of unoccupied octahedra.

The HREM micrograph along $[1\bar{1}0]_{2H}$//$[100]_{3:2}$ shows an apparently well-ordered material (Figure 6). The 3-fold superstructure along $[110]_{2H}$ is reflected in the d_{010} spacing ($\approx$0.84 nm) which is equivalent to three $(110)_{2H}$ planes. Two areas of different contrast can be seen in Figure 6. The contrast variation in the first area, (zone A), corresponds to two rows of dots of identical intensity running parallel to the *c*-axis alternating along the *a*-axis with a row of brighter dots. Such a variation of the contrast can be associated with the alternating arrangement of two chains of CoO_6 octahedra and one Co-free row, where carbonate groups are probably located. The thinnest area of the crystal (zone B) shows a contrast only due to the 2H basic subcell (*hcp* arrangement of Ba atoms). No additional ordering is observed.

It is worth mentioning that Negas et al.[6,7] proposed for the Ba:Ni = 3:2 phase a structural model with $P6_3/mmc$ symmetry; however, this space group is not consistent with the SAED patterns of the Ba:Co = 3:2 phase which show no systematic extinctions. Thus, keeping the hexagonal symmetry, only the space groups $P\bar{6}$, $P6/m$, $P\bar{6}m2$, $P622$, $P6mm$, $P\bar{6}2m$, $P6/mmm$, and $P6$ could be suitable. We have tried to determine the symmetry by convergent beam electron diffraction (CBED); however, experimental problems arise since the material decomposes when exposed under the electron beam. Fortunately, we could obtain the CBED pattern along the $[210]_{3:2}$ direction. Figure 4c shows the SAED pattern taken along $[210]_{3:2}$ on the same crystal used to obtain the CBED pattern shown in Figure 4d. Combining the information on both patterns, we conclude that the symmetry of the structure projected along $[2\bar{1}0]$ is $p11m$. Among the possible space groups, only $P\bar{6}$ and $P\bar{6}2m$ are compatible with this result. Even more, the space group $P\bar{6}$ seems to be the most likely, since one can derive this group through a group−subgroup relationship from that of the 2H structure (SG $P6_3/mmc$). In fact, the $P\bar{6}$ space group is the only subgroup of $P6_3/mmc$ which allows a hexagonal close packing of Ba and O atoms within the new unit cell (a = 0.97 and c = 0.95 nm), being in agreement with the arrangement of Co ions suggested by HREM and depicted in Figure 5b.

Thus, using this space group ($P\bar{6}$) and disregarding the light elements, simulated images have been obtained. The atomic coordinates for Ba atoms are those corresponding to a regular hcp arrangement: Ba1 in $3j$ positions ($x = ^1/_3$, $y = 0$), Ba2 in $3k$ ($x = 0$, $y = ^1/_3$), and Ba3 in $6l$ ($x = y = ^1/_3$, $z = ^1/_4$); the Co atoms being located in the octahedral rows at $x = 0$ and $^1/_3$ according to the structural model proposed in Figure 5b: Co1 and Co2 in $2g$ ($z = ^1/_6$ and $z = ^2/_3$, respectively), Co3 and Co4 in $2i$ positions ($z = ^1/_3$ and $^1/_6$, respectively). The calculated image for $\Delta t = 5$ nm and $\Delta f = -95$ nm, fits with the experimental one (zone A) as shown in Figure 6. Even more, the image calculated with $\Delta t = 2$ nm and $\Delta f = 0$ (also included in Figure 6) agrees with the contrast observed in zone B of the experimental image, indicating that the crystal is ordered and contrast variations are only due to different thickness.

From the HREM results, we can conclude that the cobalt distribution in the Ba:Co = 3:2 structure leads to two chains of CoO_6 octahedral sharing faces along the c-axis, alternating along the $[110]_{2H}//[010]_{3:2}$ direction with one cobalt-free row; this is the model proposed in Figure 5b. However, although this structural model describes correctly the metal arrangement, it does not account for the doubling of the c-axis of the 2H subcell. In fact, the HREM experimental image does not show any variation of the contrast doubling the c-axis, as observed by SAED. Since the contribution to the image formation of light atoms, such as oxygen and carbon, is very small in comparison to the heavy ones (Ba and Co), it can be assumed that this supercell is due to the distribution or to any structural feature related to the carbonate groups. Therefore, to fully determine the structure of the Ba:Co = 3:2 compound a neutron diffraction study was performed.

Table 1: Refined Atomic Parameters for $Ba_3Co_2O_6(CO_3)_{0.60(4)}$ Obtained from Neutron Diffraction Data and Some Agreement Factors[a]

atom	site	x	y	z	B (Å^2)	occupation
Ba1	3j	0.335(1)	0.012(1)	0	0.3(1)	1
Ba2	3k	−0.004(1)	0.310(1)	$^1/_2$	0.3(1)	1
Ba3	6l	0.327(1)	0.335(1)	0.256(1)	0.3(1)	1
Co1	2g	0	0	0.134(1)	0.5(1)	1
Co2	2g	0	0	0.625(1)	0.5(1)	1
Co3	2i	$^2/_3$	$^1/_3$	0.376(1)	0.5(1)	1
Co4	2i	$^2/_3$	$^1/_3$	0.136(1)	0.5(1)	1
C1	1d	$^1/_3$	$^2/_3$	$^1/_2$	0.62(5)	0.78(2)
C2	2h	$^1/_3$	$^2/_3$	0.187(7)	0.62(5)	0.80(2)
O1	6l	0.848(1)	0.847(1)	0.250(1)	0.62(5)	1
O2	3k	0.848(1)	0.001(1)	$^1/_2$	0.62(5)	1
O3	3j	0.001(1)	0.847(1)	0	0.62(5)	1
O4	3k	0.516(1)	0.340(1)	$^1/_2$	0.62(5)	1
O5	6l	0.520(1)	0.184(1)	0.252(1)	0.62(5)	1
O6	3j	0.657(1)	0.173(1)	0	0.62(5)	1
O7	3k	0.322(2)	0.523(3)	$^1/_2$	0.62(5)	0.78(1)
O8	6l	0.203(2)	0.529(2)	0.187(7)	0.62(5)	0.80(1)

[a] $R_p = 0.039$; $R_{wp} = 0.052$; $R_{exp} = 0.010$; $R_B = 0.052$; $R_F = 0.034$; a (nm) = 0.9683(1); c (nm) = 0.951 80(8); S.G. = $P\bar{6}$.

The refinement of the neutron diffraction data was undertaken using as starting model for the metal atoms (Ba and Co) that suggested by SAED and HREM in the SG. $P\bar{6}$ determined by CBED. Oxygen atoms were placed in positions corresponding to a hexagonal close packing: O1 in $6l$ ($x = ^5/_6$, $y = ^5/_6$, $z = ^1/_4$); O2 in 3k ($x = ^5/_6$, $z = 0$); O3 in $3j$ ($x = 0$, $y = ^5/_6$); O4 in $3k$ ($x = ^1/_2$, $z = ^1/_3$); O5 in $6l$ ($x = ^1/_2$, $y = ^1/_6$, $z = ^1/_4$); and O6 in $3j$ ($x = ^2/_3$, $y = ^1/_6$).

On the other hand, several positions and orientations were tried for carbonate groups. There are two independent carbonate groups in the structure; that formed by C1 in $1d$ ($^1/_3$, $^2/_3$, $^1/_2$) and the other one by C2 in $1c$ ($^1/_3$, $^2/_3$, 0). When refined, the former does not move while the latter is split into two symmetry equivalent groups by moving toward a $2h$ site ($^1/_3$, $^2/_3$, z) $z = 0.1877$. Concerning the oxygen atoms of the carbonate groups, we have also tried different possibilities. As the first choice, we considered both CO_3^{2-} groups oriented along the same direction, with the oxygen atoms located in $3k$ ($x = 0.2626$, $y = 0.5263$) and $6l$ ($x = 0.2626$, $y = 0.5263$, $z = 0.1877$) positions; thus, every corner of the carbonate triangle pointed toward the space between two Ba atoms of the same layer. However, when refined, it was clear that both carbonate groups were not oriented in the same direction. One of them is oriented along the a-axis, and the other one is rotated 60°; thus, the oxygen atoms of both carbonate groups are pointed directly toward three Ba atoms of the same layer. It is worth noting that both carbonate positions are partially occupied.

Table 1 summarizes the final structural parameters and some standard agreement factors of the refinement, while Figure 7 shows the experimental and calculated neutron diffraction patterns together with their difference. The final structural parameters obtained from neutron diffraction data confirm that the arrangement of the metal atoms are very close to that corresponding to the 2H-sublattice as suggested by XRD, SAED, and HREM. The *hcp*-Ba subarray is maintained, and the oxygen environment of cobalt is always octahedral.

The neutron diffraction study confirms the presence of C, as carbonate group, into the structure; the final values of the occupancy factor for C1 and C2 (O7 and

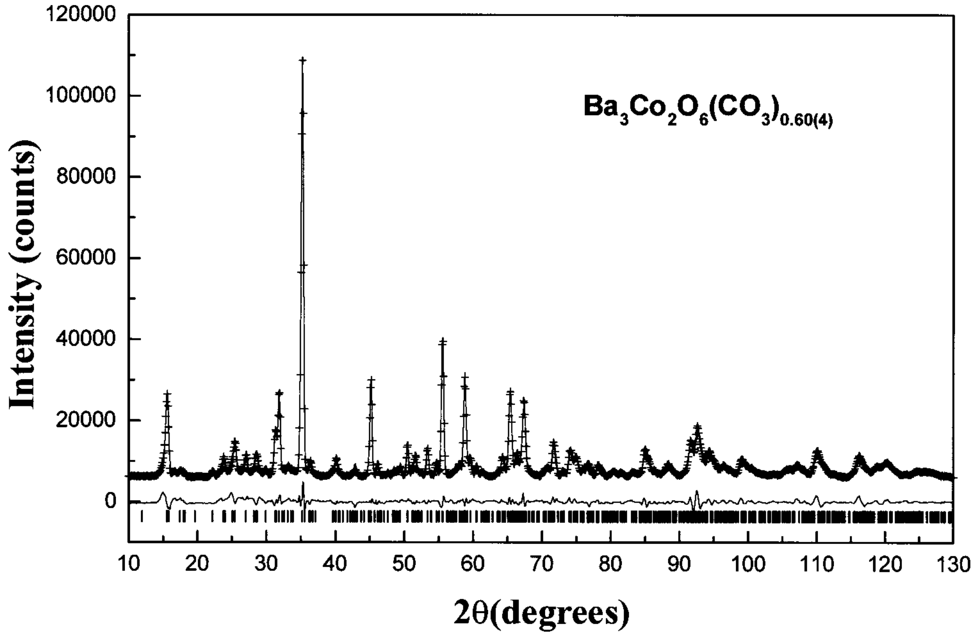

Figure 7. Experimental and calculated neutron diffraction patterns at room temperature for $Ba_3Co_2O_6(CO_3)_{0.6}$ and their difference.

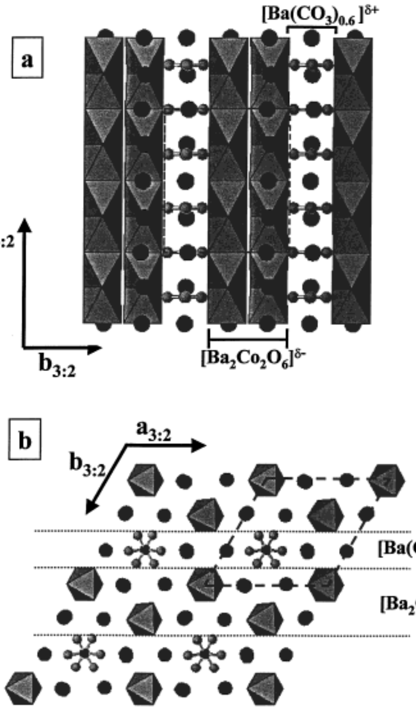

Figure 8. Projections along $[100]_{3:2}$ (a) and $[001]_{3:2}$ (b) of the structure of $Ba_3Co_2O_6(CO_3)_{0.60}$.

O8) atoms lead to a Ba:(CO_3^{2-}) = 12:2.4 ratio per unit cell; thus, the Ba:Co = 3:2 phase should be formulated as $Ba_{12}Co_8O_{24}(CO_3)_{2.40}$, i.e., $Ba_3Co_2O_6(CO_3)_{0.60(4)}$. According to these results, the average oxidation state for Co in the sample results 3.6 indicating that Co(IV) and -(III) must be present in the structure.

As a consequence of the different orientation of both nonequivalent carbonate groups, an ordered sequence of pairs of carbonate groups in alternate and eclipsed disposition occurs along the *c*-axis, as can be observed in Figure 8a. Such a disposition of the carbonates is the result of the 2-fold superstructure along the c_{2H}-axis found by SAED but not observed by HREM. The small contributions of the (CO_3^{2-}) groups to the HREM images justifies the homogeneous contrast along *c*-axis observed in the experimental micrograph shown in Figure 6.

On the other hand, the crystallographic positions for C and O atoms defining both nonequivalent carbonate groups are partially occupied at random, originating a relative disorder in the (*ab*) plane which produces the streaking observed along the b^*_{2H}-axis in the SAED pattern shown in Figure 4c.

Selected interatomic distances are gathered in Table 2. All of them are similar to those of the 2H-type structure (also listed in Table 2). The set of Ba−O distances and O−O distances are different even for atoms within the same layer. Such a deviation of the ideal close packing is also observed in 2H−$BaBO_3$ (B= Co[13] and Ni[1]). The CoO_6 octahedra are quite regular, and the Co−O distances in every coordination polyhedra correspond to an average value close to 0.19 nm, as observed for CoO_6 octahedra in other compounds.[13,15] The distances between Co atoms are quite short (0.23−0.25 nm), similar to those found in other phases such as 2H−$BaCoO_3$ with face-sharing octahedra. The C−O distances are close to 0.13 nm as expected for a carbonate group (0.128 nm).[16]

Projections of the of $Ba_3Co_2O_6(CO_3)_{0.60}$ structure along $[100]_{3:2}$ and $[001]_{3:2}$ are shown in parts a and b of Figure 8, respectively. The structure can be described from a hexagonal stacking sequence of $Ba_3O_{9-y}\square_y$ layers (y = 1.2) where Co atoms occupy, in an ordered way, two-thirds of the octahedral sites defined by the oxygen atoms. The ordered occupation of octahedral sites gives rise to rows of face-sharing octahedra running along the *c*-axis; every three rows two are occupied by cobalt, and the carbonate groups are located at random in the third Co-free row.

An alternative and probably more suitable description of the structure is as formed by two structural blocks

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Table 2: Interatomic Distances (nm) for $Ba_3Co_2O_6(CO_3)_{0.60}$

Co1−O1	0.186(9)	×3	Ba2−O1	0.285(4)	×2	Ba1−O1	0.291(6)	×2	Ba3−O1	0.283(4)	
Co1−O3	0.195(9)	×3	Ba2−O2	0.262(5)		Ba1−O3	0.269(9)		Ba3−O1	0.280(7)	
d_{av} Co1−O = 0.190			Ba2−O2	0.268(7)		Ba1−O3	0.280(9)		Ba3−O2	0.293(4)	
			Ba2−O4	0.281(7)		Ba1−O5	0.296(5)	×2	Ba3−O4	0.290(5)	
Co2−O1	0.197(6)	×3	Ba2−O4	0.285(7)		Ba1−O6	0.272(9)		Ba3−O5	0.284(7)	
Co2−O2	0.182(7)	×3	Ba2−O5	0.298(4)	×2	Ba1−O6	0.279(6)		Ba3−O5	0.277(8)	
d_{av} Co2−O = 0.189			Ba2−O7	0.277(5)		Ba1−O8	0.270(5)	×2	Ba3−O8	0.281(6)	
			d_{av} Ba2−O = 0.282			d_{av} Ba1−O = 0.2814			Ba3−O8	.0290(4)	
Co3−O4	0.194(7)	×3							d_{av} Ba3−O = 0.285		
Co3−O5	0.182(6)	×3									
d_{av} Co3−O = 0.188						O1−O2	0.280(5)		C1−O7	0.132(3)	×3
						O1−O2	0.279(6)		C2−O8	0.129(2)	×3
Co1−Co1	0.25(1)		O1−O1	0.258(6)		O1−O3	0.280(5)		C1−C2	0.298(1)	
Co1−Co2	0.24(1)		O2−O2	0.251(8)		O1−O3	0.281(6)		C2−C2	0.352(1)	
Co2−Co2	0.23(1)		O3−O3	0.259(5)		O4−O5	0.281(5)		O7−O7	0.229(4)	
Co3−Co3	0.24(1)		O4−O4	0.258(8)		O4−O5	0.274(5)		O8−O8	0.223(3)	
Co3−Co4	0.23(1)		O5−O5	0.250(6)		O5−O6	0.276(5)				
Co4−Co4	0.25(1)		O6−O6	0.255(6)		O5−O6	0.285(5)				
			d_{av} O−O = 0.255 (same layer)			d_{av} O−O = 0.2795 (diff layers)					

2H−$BaCoO_3$[13]

d Ba−O = 0.2828	d O−O$_{\text{(same layer)}}$ = 0.2511	d O−O$_{\text{(diff layer)}}$ = 0.2783	d Co−O = 0.187	d Co−Co = 0.238

$[Ba_2Co_2O_6]^{\delta-}[Ba(CO_3)_{0.60}]^{\delta+}$. These blocks intergrow in an ordered manner in a 1:1 sequence along the *a*-axis. This is a useful crystal chemical description since the first framework corresponds to two 2H-like blocks and the second one can be related to the $BaCO_3$ aragonite-type structure.[16]

Figure 8b shows the *ac* projection of the $Ba_3Co_2O_6(CO_3)_{0.60}$ structure, in which the 2H-like and aragonite-like blocks are indicated. In this projection, the analogy between the aragonite structure and the $[Ba(CO_3)_{0.60}]$ blocks of the Ba:Co = 3:2 phase is easily observed if the $c_{3:2}$-axis is placed parallel to the *b*-axis of aragonite. The only significant difference is the relative orientation of neighboring CO_3^{2-} groups along such a direction. In $BaCO_3$, the carbonate groups are arranged in alternate position, the distance between two consecutive groups being 0.32 nm.[16] In the $[Ba(CO_3)_{0.60}]$ blocks, the C1−C2 distance (0.29 nm) is slightly shorter than in $BaCO_3$ forcing an alternate arrangement of these carbonate groups whereas the C2−C2 distance is slightly larger (0.35 nm), allowing the CO_3^{2-} groups to be in an eclipsed position.

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