Structure Determination of Two New Incommensurate Compounds, $Ba_{1+x}[(Cu_xRh_{1-x})O_3]$ with $x = 0.1605$ and $x = 0.1695$, Using a General Method Based on the Superspace Group Approach

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Abstract: The single-crystal structures of two incommensurate compounds, $Ba_{1+x}[(Cu_xRh_{1-x})O_3]$ with $x = 0.1605$ and $x = 0.1695$, were solved by a general method using the superspace group approach. A saw-tooth function was used to model both the occupational and displacive modulations. This approach requires very few refineable parameters and leads to low residuals, $R = 0.0370$ and $R = 0.0330$ for $x = 0.1605$ and $x = 0.1695$, respectively. The idealized structures of these two compounds consist of $[(Cu_xRh_{1-x})O_3]_\infty$ chains containing groups of five face-shared (RhO_6) octahedra separated by (CuO_6) trigonal prisms. These chains in turn are separated from each other by $[Ba]_\infty$ chains. The idealized composition of both phases is $Ba_7CuRh_5O_{18}$. Their modulated structures, described in the text, deviate from the ideal composition and structure. The approach used for the structure determinations of these compounds is completely general and can be applied to other modulated composite structures of this series.

Introduction

Since the first realization that there exist materials whose structures cannot be satisfactorily explained by the standard 3D crystallographic models, researchers have worked on the development of approaches that could be used to solve the structures of such materials using 4-, 5-, and 6-dimensional space. Numerous materials are found in such incommensurate (higher dimensional) structures, including common compounds such as sodium carbonate, many of the high-temperature superconductors, and the intermetallic quasicrystals.[1−3] Among the oxides, in particular, there has been great interest recently in the investigation of the structures and physical properties of a family of compounds, $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$, that are structurally closely related to the 2-H hexagonal perovskites and whose members often form in incommensurate composite structures. A general classification of the structures of these materials was developed by Darriet and Subramanian and is based on the stacking of $[A_3O_9]$ and $[A_3A'O_6]$ layers and the filling of the thus generated octahedral and prismatic sites by the B and A′ cations.[4] Using this approach the structural composition of all of the commensurate members of this family of structures can be easily described. Moreover, this layer description can also be used to describe the members that form in an incommensurate structure type.

The main structural features of these oxides are $[A]_\infty$ chains that separate $[(A',B)O_3]_\infty$ columns made up of distinct ratios of face-sharing octahedra and trigonal prisms. In a number of cases, the ratio of the repeat distances of the two chains, c_1/c_2, is not a rational number and, consequently, the structure is incommensurately modulated along the c-direction. This type of a structure is referred to as a composite structure, as it can be thought of as resulting from the combination of two independent crystallographic substructures, in this case, one consisting of the $[A]_\infty$ and one of the $[(A',B)O_3]_\infty$ chains. The composition of such composite structures are better formulated as $A_{1+x}(A'_xB_{1-x})O_3$, where $x = n/(3m + 2n)$ and ranges continuously between 0 and 1/2, corresponding to chains containing all face-shared octahedra and alternating octahedra and trigonal prisms, respectively. Obviously, for the simplest fractional values of x, such as 1/5, 2/7, or 1/3, the structure is commensurate and the end-members, the 2H perovskite and the K_4CdCl_6 structure type, are well-known.

There have been several approaches to determining the structures of these modulated materials, including solving each of the substructures separately, which typically does not result in a very accurate structure solution,[5,6] and solving the modulated structure as a conventional 3D structure with a very long c-parameter.[7] In the latter case, the data-to-parameter ratio is typically exceedingly poor, and the refinements are, conse-

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Table 1. Crystallographic Data and Refinements

Crystal **1**		Crystal **2**	
Formula	$Ba_{1.1605}(Cu_{0.1605}Rh_{0.8395})O_3$	Formula	$Ba_{1.1695}(Cu_{0.1695}Rh_{0.8305})O_3$
Parameters	$a = 10.081(1)$ Å $c_1 = 2.6206(1)$ Å $q = 0.58027(1)c_1^*$ $V = 230.64(1)$ Å^3	Parameters	$a = 10.081(1)$ Å $c_1 = 2.6245(1)$ Å $q = 0.58475(1)c_1^*$ $V = 230.98(1)$ Å^3
Superspace group	$R\bar{3}m(00\gamma)0s$	Superspace group	$R\bar{3}m(00\gamma)0s$
θ_{max}	35°	θ_{max}	40°
Observed reflections	2346 with $I>3\sigma(I)$	Observed reflections	2094 with $I>3\sigma(I)$
Independent reflections	864 (Rint = 2.65%)	Independent reflections	1176 (Rint = 2.08%)
Twin matrix (45/55%)	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}$	Twin matrix (41/59%)	$\begin{vmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{vmatrix}$
Absorption correction	Gaussian-type analytical absorption correction : Vol = 585×10^{-7} mm^3 Tmin /Tmax = 0.64/0.87	Absorption correction	Psi-Scan
Final R values	R = 0.0370 (Rw = 0.0487) for all reflections R = 0.0330 (Rw = 0.0410) for 354 main reflections R = 0.0398 (Rw = 0.0568) for 401 satellites of order 1 R = 0.0637 (Rw = 0.0743) for 109 satellites of order 2	Final R values	R = 0.0330 (Rw = 0.0502) for all reflections R = 0.0245 (Rw = 0.0325) for 480 main reflections R = 0.0396 (Rw = 0.0528) for 547 satellites of order 1 R = 0.0741 (Rw = 0.1067) for 149 satellites of order 2
Goodness of fit	2.91	Goodness of fit	2.67

quently, rather inadequate. The more successful methods use a superspace group approach, which was introduced in the 1970s to solve the structures of incommensurately modulated structures and quasicrystals. Recently, Evain et al. published a paper[8] on the structure solution of $Sr_{1.2872}NiO_3$ using a superspace group approach employing a Fourier series as the atomic modulation function (AMF) for this material. Recently, Perez-Mato et al.[9] presented a general superspace group description using a saw-tooth function as the AMF. The model considers that the modulation wave vector is directly related to the x composition ($2\gamma = 1 + x$). Furthermore it has been demonstrated that the upper limit ($x = 1/2$) corresponds to a commensurate composite phase. In this paper we apply this general method and the saw-tooth function to the structure determination of two new incommensurate oxides and illustrate the advantages of this approach which, compared to other methods, leads to higher accuracy and a greatly reduced number of refineable parameters.

Experimental Section

Synthesis and Crystal Growth. Single crystals of these materials were grown by flux synthesis.[10] A total of 1 g of $BaCO_3$ (Alfa, 99.99%), CuO (Johnson Matthey, 99.99%), and Rh (Engelhard, 99.95%) were placed into the bottom of an alumina crucible, and about 20 g of K_2CO_3 (Fisher 99.5%) was packed into the crucible on top of the reagents. The crucibles were covered with an alumina lid to limit the evaporation of the flux. The samples were heated in air from room temperature to the reaction temperature, typically 1050−1150 °C, at 60 °C per hour. The crucibles were held at the reaction temperature for 3 days and were cooled at 6 °C per hour to 880 °C. The furnace was turned off, and the system was allowed to cool to room temperature. Upon cooling, the crucibles were placed in a beaker of water for several hours to dissolve the carbonate flux. The remaining contents of the crucible were washed with water on a glass frit to remove all soluble materials. The crystals were separated from any remaining flux matrix and cleaned by sonication in a saturated ammonium chloride solution. The crystals were washed repeatedly with water and dried with acetone on a glass frit.

Data Collection. Prior to data collection, crystals were carefully checked for quality using Weissenberg and precession cameras. In both cases, it was determined that the crystals are twinned with a transformation matrix ($\bar{1}00/0\bar{1}0/001$). These film studies confirmed that the single crystals are in fact misfit composite crystals with two trigonal/hexagonal subsystems with a common a axis but different c-axes: $a \approx 10.08$ Å, $c_1 \approx 2.62$ Å, $c_2 \approx 4.52$ Å for crystal **1** and $a \approx 10.08$ Å, $c_1 \approx 2.63$ Å, $c_2 \approx 4.49$ Å for crystal **2**. For both $q^* = \gamma c_1^*$, with $\gamma = c_1/c_2 = (1 + x)/2$.[8,9] The two subsystems, $[(Cu,Rh)O_3]_\infty$ and $[Ba]_\infty$, are modulated with respect to each other, and the subsystem $[(Cu,Rh)O_3]_\infty$ ($c \approx 2.6$ Å) was chosen as the reference against which the modulation was determined. The first and second subsystem reflections sets are obtained from the (3+1)D superspace reflection indices by the application of the W^1 and W^2 transformation matrixes, respectively:[11]

$$W^1 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix} \text{ and } W^2 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix}$$

The two possible superspace groups that are compatible with the observed extinction conditions of $-h + k + l \neq 3n$ for $hklm$ and $m \neq 2n$ for $h0lm$ are $R3m(00\gamma)0s$ and the corresponding centrosymmetric superspace group $R\bar{3}m(00\gamma)0s$. $R\bar{3}m(00\gamma)0s$ was chosen initially and confirmed by the successful solution of the structure.

Data collection was performed on a CAD4 diffractometer. Indexing of 25 centered reflections showed that the average 3D unit cell is hexagonal in both cases. A precise centering of reflections of each subsystem led to the following lattice parameters: $a = 10.081(1)$ Å, $c_1 = 2.6206(1)$ Å, $c_2 = 4.5162(1)$ Å for crystal **1** and $a = 10.081(1)$ Å, $c_1 = 2.6245(1)$ Å, $c_2 = 4.4882(1)$ Å for crystal **2**. Crystal **1** corresponds to $x = 0.1605$ ($\gamma = 0.58027$), and crystal **2** corresponds to $x = 0.1695$ ($\gamma = 0.58475$). The data were collected, in both cases, in the 3D option using the closest supercell (crystal **1**, $c \approx 31.522(3)$ Å and crystal **2**, $c \approx 31.428(3)$ Å).

Measured intensities were corrected for decay on the basis of three standard reflections, as well as for Lorentz and polarization effects. Absorption corrections were applied using a Gaussian-type analytical absorption correction for crystal **1** and using the ψ-scan technique for crystal **2**. Further crystallographic data and collection information are summarized in Table 1. The transformation of the 3D indices to (3+1)D $hklm$ values was performed using the Jana 98 program package.[12]

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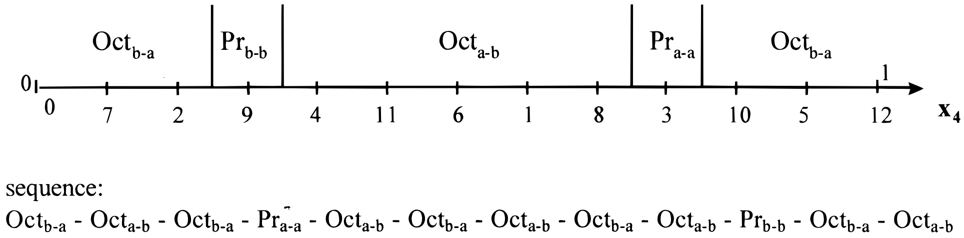

Figure 1. Scheme of the O_6 configurations along the internal coordinate x_4 for a column $[A',B]O_3$ resulting from the model for $x = 1/6$ ($\gamma = 7/12$). The numbered discrete points correspond to the x_4 values $\gamma{\cdot}n + \phi$ associated to consecutive average cells along z. The resulting sequence of octahedra and prisms can be immediately derived.

Results and Discussion

The unit cell of each of the two crystal structures contains three formula units of $Ba_{1+x}[Cu_xRh_{1-x}]O_3$. Using the symmetry operations of the space groups, we can illustrate where the atoms are located in the structure and what gives rise to the modulation. To generate the correct oxygen positions in the structure and the associated polyhedra, octahedra, and trigonal prisms, the centrosymmetric space group was used for the structure determination in line with the proposed general approach.[9]

In the superspace group $R\bar{3}m(00\gamma)0s$, the average position of the oxygen atoms is $(x, \bar{x}, 1/2)$ ($x \approx 1/6$)[8,9] where the symmetry operations of $R\bar{3}m(00\gamma)0s$ generate six oxygen positions that surround the axis of the $[(Cu,Rh)O_3]$ chains. Since it is not possible that all six positions are simultaneously occupied, this effectively generates two types of oxygen positions, O_a and O_b, which are each half occupied. Each set of three oxygens forms an equilateral triangle which corresponds to the vertexes of a triangular face O_3 of the face-sharing polyhedra in the $[(Cu,Rh)O_3]$ chain. To model the occupational modulation of these two types of oxygen atoms, O_a and O_b, a Crenel function (a type of Boolean function)[8,13] is used. The Crenel function, which runs along the x_4-axis (the axis corresponding to the fourth dimension) contains two parameters; the crenel width, $\Delta = 1/2$, and the Crenel midpoint, $\hat{x}_4 = 1/4$. Depending on the value of the Crenel function along x_4, either set O_a or set O_b is fully occupied along the real z-axis. Since two adjacent $O_a{-}O_a$ or $O_b{-}O_b$ triangles create a trigonal prism, while a sequence of $O_a{-}O_b$ or $O_b{-}O_a$ corresponds to an octahedron, the Crenel function and the modulation wavevector, therefore, determine the sequence of octahedra and trigonal prisms along the $[(Cu,Rh)O_3]$ chains (z-direction).

The copper atoms occupy the trigonal prisms, and the rhodium atoms occupy the octahedra in the (0, 0, 0) position. The occupancy of the (0, 0, 0) position by either copper or rhodium along z is also determined by the Crenel functions along x_4. Since we have $(1 - x)$ B atoms (Rh) and x A′ atoms (Cu) to fill two types of polyhedra each, octahedra $O_a{-}O_b$ and $O_b{-}O_a$ and trigonal prisms $O_a{-}O_a$ and $O_b{-}O_b$, there are $(1 - x)/2$ B atoms (Rh) inside each type of octahedra with a midpoint ($\hat{x}_4 = 0$) and $x/2$ A′ atoms (Cu) inside each trigonal prism with a midpoint ($\hat{x}_4 = 1/4$). Consequently, knowing the value of x in $A_{1+x}(A'_xB_{1-x})O_3$, or alternatively, the modulation value γ ($\gamma = (1 + x)/2$), it is possible to predict the sequence of octahedra and trigonal prisms along the $[(Cu,Rh)O_3]$ column.[9]

For the two crystals investigated, the values of $x = 0.1605$ and 0.1695 are not simple numbers; however, we can initially approximate them with the closest simple numeric value, namely, the fraction $x = 1/6$ or equivalently $\gamma = 7/12$. The values of the occupational AMF for the atoms [Cu, Rh] present in the structure correspond to $x_4 = 7/12m + \phi$ with $m = 1, 2, \ldots, 12$, where ϕ represents an initial phase. To complete one full translation we carry out 12 translations of 7/12 along x_4. It is therefore possible to derive the sequence of (5 octahedra−1 prism) from the scheme of O_6 configurations along the internal coordinate x_4 for the column $[(Cu,Rh)O_3]$ (Figure 1). The usefulness of the superspace group approach is illustrated by the fact that the discrete points along x_4 can be associated with consecutive average cells along z. A schematic representation of the sequence is shown in Figure 2. The ideal composition shown ($x = 1/6$) corresponds to $Ba_7CuRh_5O_{18}$ with a supercell of $c = 12c_1$ (space group $P\bar{3}c1$). In the proposed rigid model of mixed n $[A_3A'O_6]$ and m $[A_3O_9]$ layers, the sequence (5 oct−1 prism) corresponds to $n = 3$ and $m = 4$, where the relationship between γ, n, and m is $\gamma = 3(n + m)/2(2n + 3m)$.[9]

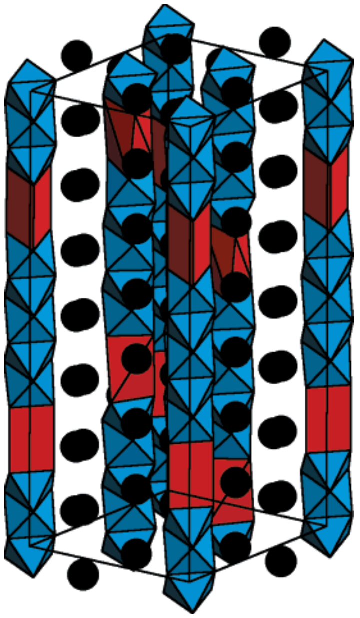

Figure 2. Structure of $Ba_7CuRh_5O_{18}$ ($n = 3$ and $m = 4$). The sequence along the columns (c-direction) is five octahedra and one prism.

The second subsystem, $[Ba]_\infty$, consists of two types of barium atoms. The first one is Ba_1, which is in the $[A_3O_9]$ layers (Ba_3O_9 layers) and Ba_2, which is in the $[A_3A'O_6]$ layers (Ba_3CuO_6 layers). The average positions are x 0 1/4 ($x \approx 1/3$) and the two parameters of the Crenel function for Ba_1 are the width, $\Delta = x/(1 + x)$ and the midpoint $\hat{x}_4 = 0$ and for Ba_2, $\Delta = (1 - 2x)/3(1 + x)$ and $\hat{x}_4 = 1/2$.

The atomic positions are not only modulated with respect to their occupation but also must have some x_4 displacement that will distinguish the prismatic and the octahedral sites. If we assume that all prisms and octahedra are equal, one of the simplest ways to describe the displacive AMF is to use a saw-tooth modulation.[9]

The two structures were refined using the Jana98[12] software package adapted to the saw-tooth function. The crystallographic

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Table 2. Fractional Atomic Average Coordinates, Equivalent Isotropic Displacement Factors, and Atomic Positional and DWF Modulation Coefficients

Crystal **1**

Subsystem $[(Cu,Rh)O_3]$: $R\bar{3}m(00\gamma)0s$

Atoms	x_0	y_0	z_0	Ueq (Å^2)x10^3
Rh1	0	0	0	9.2(1)
Cu1	0	0	0	40(2)
O	0.1517(2)	0.1517(2)	1/2	25(1)

Subsystem [Ba] : $P\bar{3}c1(001/\gamma)$

Atoms	x_0	y_0	z_0	Ueq (Å^2)x10^3
Ba1	0.32666(6)	0	1/4	17.9(2)
Ba2	0.35205(9)	0	1/4	6.7(2)

Rh1 :

$U^{Rh1}_{z,1} = 0.0061(3)$ $U^{Rh1}_{z,3} = -0.0160(4)$

Amplitude = -0.0910 $\hat{x}_4 = 0$ $\Delta = 0.4197$

$U^{Rh1}_{U11,2} = U^{Rh1}_{U22,2} = 2\,U^{Rh1}_{U12,2} = -0.00006(17)$ $U^{Rh1}_{U33,2} = -0.0059(3)$

Cu1 :

Amplitude = -0.0968 $\hat{x}_4 = 1/4$ $\Delta = 0.0802$

O :

$U^{O}_{x,1} = U^{O}_{y,1} = 0.0089(4)$ $U^{O}_{x,2} = -U^{O}_{y,2} = 0.00003(24)$

$U^{O}_{z,2} = -0.0229(15)$

$U^{O}_{x,3} = -U^{O}_{y,3} = -0.0014(2)$ $U^{O}_{z,3} = 0.0128(15)$

$U^{O}_{x,4} = U^{O}_{y,4} = 0.0046(5)$

Amplitude = -0.1497 $\hat{x}_4 = 1/4$ $\Delta = 1/2$

$U^{O}_{U11,1} = U^{O}_{U22,1} = -0.0128(14)$ $U^{O}_{U33,1} = -0.0145(19)$

$U^{O}_{U12,1} = -0.0015(15)$ $U^{O}_{U13,1} = -U^{O}_{U23,1} = 0.0019(10)$

$U^{O}_{U11,2} = -U^{O}_{U22,2} = -0.0025(11)$ $U^{O}_{U13,2} = U^{O}_{U23,2} = 0.0090(10)$

Ba1 :

Amplitude = -0.0301 $\hat{x}_4 = 1/2$ $\Delta = 0.1950$

Ba2 :

Amplitude = -0.0367 $\hat{x}_4 = 0$ $\Delta = 0.1383$

Crystal **2**

Subsystem $[(Cu,Rh)O_3]$: $R\bar{3}m(00\gamma)0s$

Atoms	x_0	y_0	z_0	Ueq (Å^2)x10^3	τ
Rh1	0	0	0	7.9(7)	
Cu1	0	0	0	15(8)	0.57(6)
Cu2	0.0490(6)	0.0490(6)	0	15(8)	0.43(4)
O	0.1534(2)	0.1534(2)	1/2	26.2(8)	

Subsystem [Ba] : $P\bar{3}c1(001/\gamma)$

Atoms	x_0	y_0	z_0	Ueq (Å^2)x10^3	τ
Ba1	0.32717(5)	0	1/4	17.5(1)	
Ba2	0.35305(6)	0	1/4	8(1)	

Rh1 :

$U^{Rh1}_{z,1} = 0.0059(2)$ $U^{Rh1}_{z,3} = -0.0170(2)$

Amplitude = -0.0910 $\hat{x}_4 = 0$ $\Delta = 0.4152$

$U^{Rh1}_{U11,2} = U^{Rh1}_{U22,2} = 2U^{Rh1}_{U12,2} = -0.0011(1)$ $U^{Rh1}_{U33,2} = -0.0032(2)$

Cu1 :

Amplitude = -0.0681 $\hat{x}_4 = 1/4$ $\Delta = 0.0847$

Cu2 :

Amplitude = -0.0681 $\hat{x}_4 = 1/4$ $\Delta = 0.0847$

O :

$U^{O}_{x,1} = U^{O}_{y,1} = 0.0051(4)$ $U^{O}_{x,2} = -U^{O}_{y,2} = -0.0008(2)$

$U^{O}_{z,2} = -0.0100(15)$

$U^{O}_{x,3} = -U^{O}_{y,3} = -0.0008(2)$ $U^{O}_{z,3} = 0.0098(13)$

$U^{O}_{x,4} = U^{O}_{y,4} = 0.0010(4)$

Amplitude = -0.1346 $\hat{x}_4 = 1/4$ $\Delta = 1/2$

$U^{O}_{U11,1} = U^{O}_{U22,1} = -0.0154(9)$ $U^{O}_{U33,1} = -0.0167(16)$

$U^{O}_{U12,1} = -0.0041(11)$ $U^{O}_{U13,1} = -U^{O}_{U23,1} = 0.0025(8)$

$U^{O}_{U11,2} = -U^{O}_{U22,2} = -0.0023(8)$ $U^{O}_{U13,2} = U^{O}_{U23,2} = 0.0092(7)$

Ba1 :

Amplitude = -0.0260 $\hat{x}_4 = 1/2$ $\Delta = 0.1883$

Ba2 :

Amplitude = -0.0206 $\hat{x}_4 = 0$ $\Delta = 0.1449$

Modulation functions for a parameter λ of an atom ν defined in a restricted interval (case of Rh1 and O) are given by :

$$U^{\nu}_{\lambda}(\bar{x}_4) = \sum_{n=1}^{k} U^{\nu}_{\lambda,n}\,\mathrm{Ortho}^{\nu}_{n}(\bar{x}_4)$$

where the orthogonalized functions, obtained through a Schmidt orthogonalization routine, are given by :

$$\mathrm{Ortho}^{\nu}_{i}(\bar{x}_4) = B^{\nu}_{0} + \sum_{n=1}^{k} A^{\nu}_{n}\sin(2\pi n\bar{x}_4) + \sum_{n=1}^{k} B^{\nu}_{n}\cos(2\pi n\bar{x}_4)$$

Crystal **1**

Ortho^{O}_{i}	B^{O}_{0}	A^{O}_{1}	B^{O}_{1}	A^{O}_{2}	A^{O}_{3}
Ortho^{O}_{0}	1				
Ortho^{O}_{1}	-2.069	3.249			
Ortho^{O}_{2}	0	0	1.414		
Ortho^{O}_{3}	0	0	-2.271	2.675	
Ortho^{O}_{4}	-2.187	2.785	0	0	1.953

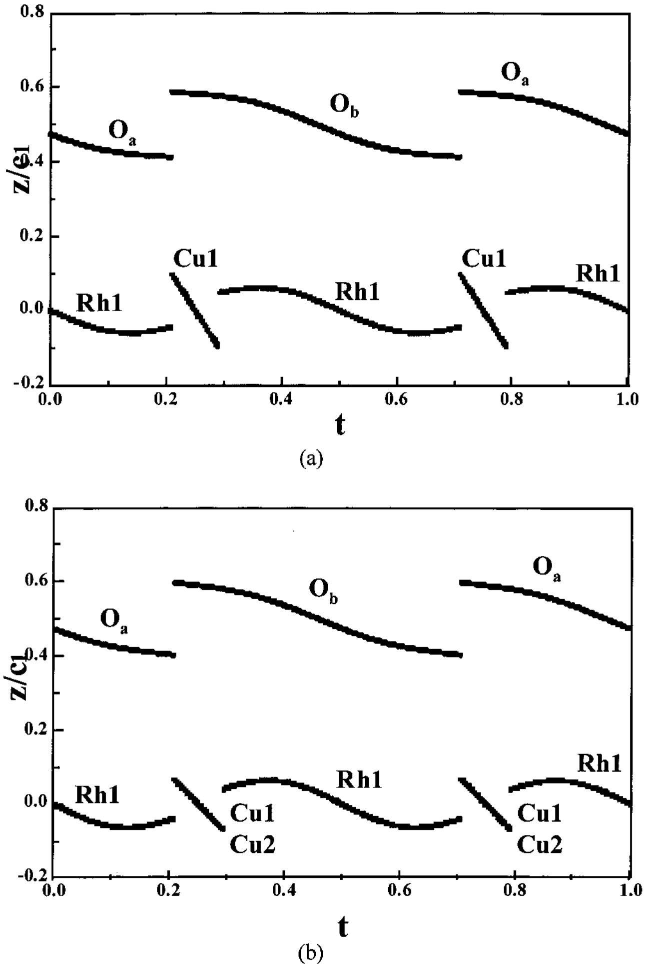
Ortho^{Rh1}_{i}	B^{Rh1}_{0}	A^{Rh1}_{1}	B^{Rh1}_{1}	A^{Rh1}_{2}	B^{Rh1}_{3}
Ortho^{Rh1}_{0}	1				
Ortho^{Rh1}_{1}	0	1.565			
Ortho^{Rh1}_{2}	-3.211	0	4.372		
Ortho^{Rh1}_{3}	0	-4.44	0	3.950	
Ortho^{Rh1}_{4}	6.479	0	-8.099	0	2.893

Crystal **2**

Ortho^{O}_{i}	B^{O}_{0}	A^{O}_{1}	B^{O}_{1}	A^{O}_{2}	A^{O}_{3}
Ortho^{O}_{0}	1				
Ortho^{O}_{1}	-2.069	3.249			
Ortho^{O}_{2}	0	0	1.414		
Ortho^{O}_{3}	0	0	-2.271	2.675	
Ortho^{O}_{4}	-2.187	2.785	0	0	1.953

Ortho^{Rh1}_{i}	B^{Rh1}_{0}	A^{Rh1}_{1}	B^{Rh1}_{1}	A^{Rh1}_{2}	B^{Rh1}_{3}
Ortho^{Rh1}_{0}	1				
Ortho^{Rh1}_{1}	0	1.576			
Ortho^{Rh1}_{2}	-3.295	0	4.456		
Ortho^{Rh1}_{3}	0	-4.618	0	4.052	
Ortho^{Rh1}_{4}	6.877	0	-8.581	0	2.975

data and refinements are given in Table 1. The usefulness of this type of modulation function (saw-tooth) is that (in our case) as a first approximation it describes the occupational and *z*-component displacive AMF at the same time using only one parameter, namely the maximum *z*-amplitude. The model[9] considers that the *x* and *y* components of the displacive AMF



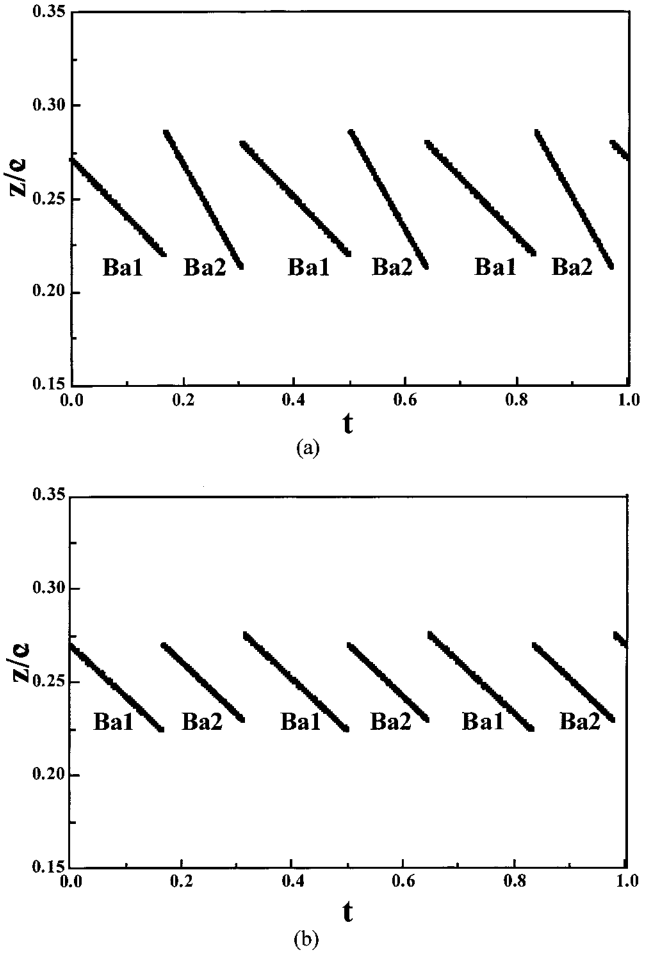
(a)

(b)

Figure 3. Graphical representation of the internal z coordinate of O_a, O_b, Rh1, Cu1, and Cu2 versus the internal coordinate t ($t = x_4 - q{\cdot}r$): (a) crystal **1**, (b) crystal **2**.

are zero. The z-component is correlated to the difference in height between the octahedron and the trigonal prism. Using only the maximum z-amplitude in the refinement, the residual values are near 8.5% for both structures. However, the Fourier difference maps show clearly electron density near the Cu position which can be interpreted as a split position in $x\ x\ 0$ with $x \approx 0.05$ (crystal **2**) or as a nonharmonic atomic displacement factor of the Cu atom (crystal **1**). In subsequent refinement cycles, the maximum z-amplitude of the saw-tooth function was fixed. To account for the remaining electron density in the Fourier difference map, third-order displacive Fourier amplitudes for the rhodium and oxygen atoms and a first-order Fourier amplitude for the thermal parameters were added to the saw-tooth modulation. To avoid correlations, these amplitudes refer to a basis of harmonic functions of period 1 along the internal coordinate x_4, but orthogonalized with respect to the x_4-interval associated with the corresponding occupational Crenel function[13] (Table 2). This caused the refinement to converge quickly, reducing the residual R factors to $R = 0.0370$ (crystal **1**) and $R = 0.0330$ (crystal **2**). The fractional atomic coordinates are given in Table 2. It is important to point out that in this refinement only 39 parameters were used. Using this model we decrease significantly the number of parameters compared to the finite Fourier expansion, where it is necessary to expand the series to very high orders with a concomitant increase in the number of refineable parameters.

The graphical representation of the functions used, as well as z/c_1 versus t (shifted internal coordinate, $t = x_4 - q{\cdot}r_{av}$) of the subsystem $[(Cu,Rh)O_3]$ for both structures, are shown in Figure 3. The same plot is shown for the $[Ba]_\infty$ subsystem in Figure 4. In Figures 3 and 4 it can be seen that the saw-tooth function effectively models the modulation of barium and copper, confirming that the amplitude of the AMFs are mainly along the z axis as proposed in the model.[9] Only the modulation of rhodium and oxygen deviates slightly from the ideal saw-tooth function and, consequently, as described above, an additional modulation was added to the saw-tooth function to accurately model the rhodium positions.



(a)

(b)

Figure 4. Graphical representation of the fractional z coordinate of Ba1 and Ba2 versus the internal coordinate t ($t = x_4 - q{\cdot}r$): (a) crystal **1**, (b) crystal **2**.

Unlike in a conventional structure, where there are discrete metal–metal distances, in a modulated structure it is possible to have a virtually continuous range of metal–metal distances bracketed by a minimum and maximum distance. Consequently, metal–metal and metal–oxygen distances are given as ranges. The measured values for all the metal–metal bond distances, which are all reasonable and consistent with published bond lengths, are listed in Table 3.

The ideal structure, consisting of (5 octahedra–1 trigonal prism), is the same for both crystals of $Ba_{1+x}[(Cu_xRh_{1-x})O_3]$ ($x = 0.1605$ and $x = 0.1695$). However, the real structures differ in the modulation present in the $[(Cu,Rh)O_3]_\infty$ chains. The values of x, which we approximate in the ideal structure by $x = 1/6$ are, of course, much better represented by fractions that more closely match the numeric value of x. Consequently, for crystal **1** ($x = 0.1605$) corresponds to the fractional value $p/q = 13/81$ in which p is the number of prisms and $(q - p)$ is the number of octahedra in the sequence, as can be obtained by using a

Table 3. Bond Distances

crystal 1

	Rh-Rh	Rh-Cu	Rh-O	Cu-O	Ba1-O	Ba2-O
d_{min}	2.474(1)Å	2.494(1)Å	1.763(1)Å	1.789(1)Å	2.601(1)Å	2.535(1)Å
d_{max}	2.654(1)Å	3.031(1)Å	2.088(1)Å	2.340(1)Å	3.141(1)Å	3.412(1)Å

crystal 2

	Rh-Rh	Rh-Cu	Rh-O	Cu-O	Ba1-O	Ba2-O
d_{min}	2.465(1)Å	2.562(1)Å	1.850(1)Å	1.870(1)Å	2.606(1)Å	2.588(1)Å
d_{max}	2.673(1)Å	3.002(1)Å	2.086(1)Å	2.291(1)Å	3.094(1)Å	3.425(1)Å

Farey tree.[9] The unit cell, consequently, contains a chain made up of 81 polyhedra containing 10 × (5 octahedra−1 prism) plus 3 × (6 octahedra−1 prism) in a certain sequence: [4 × (5 oct−1 prism) + 1 × (6 oct−1 prism) + 3 × (5 oct−1 prism) + 1 × (6 oct−1 prism) + 3 × (5 oct−1 prism) + 1 × (6 oct−1 prism)]. Similarly, for crystal **2** ($x = 0.1695$), the fraction $p/q = 10/59$ corresponds to a unit cell that contains a chain made up of 59 polyhedra with a repeat sequence of 9 × (5 octahedra−1 prism) plus 1 × (4 octahedra−1 prism). However, the practical limit is forced upon us by our inability to determine the value of x in $A_{1+x}(A'_xB_{1-x})O_3$ with an accuracy that exceeds four decimal places.

It should be pointed out that the length of the periodic sequence along the c-axis for $x = 13/81$ and $x = 10/59$ corresponds to a length of $c \approx 424$ Å and $c \approx 309$ Å for crystals **1** and **2**, respectively. Clearly, any attempt to refine the data for a unit cell with such a large c parameter would, because of the many unobserved reflections and the large number of metal and oxygen positions that would have to be refined, lead to a very unsatisfactory structure solution. Using the method described in this paper, however, only five metal and oxygen positions, in addition to the modulation function, have to be refined, making it possible to obtain good residuals and an accurate structure solution.

The structure determinations of $Ba_{1+x}[(Cu_xRh_{1-x})O_3]$ ($x = 0.1605$ and $x = 0.1695$) illustrate that these phases, just like the known Vernier phases, can form with an infinite number of unique structures for an infinite number of chemical compositions. As the method described in this article is a completely general approach for both commensurate and incommensurate composite structures, we expect it to be used for the structure determination of many more members of this family of compounds. The continuous variation in structures that can be obtained synthetically and now completely structurally characterized should make this family of materials an excellent choice for the investigation of the effect of structural and compositional changes on electronic and magnetic properties.

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Supporting Information Available: An X-ray crystallographic file is available in CIF format: tables of crystal data and refinement information as well as of fractional atomic coordinates and displacement factors of the atoms and the modulation coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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