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Structure Determination of $\text{Ba}_8\text{CoRh}_6\text{O}_{21}$, a New Member of the 2H-Perovskite Related Oxides

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ABSTRACT

Single crystals of $\text{Ba}_8\text{CoRh}_6\text{O}_{21}$ were grown out of a potassium carbonate flux. The structure was solved by a general method using the superspace group approach. The superspace group employed was $R\bar{3}m(00\gamma)0s$ with $a = 10.0431(1) \text{ \AA}$, $c_1 = 2.5946(1) \text{ \AA}$ and $c_2 = 4.5405(1) \text{ \AA}$, $V = 226.60(1) \text{ \AA}^3$. $\text{Ba}_8\text{CoRh}_6\text{O}_{21}$ represents the first example of an $m = 5$, $n = 3$ member of the $\text{A}_{3n+3m}\text{A}'_n\text{B}_{3m+n}\text{O}_{9m+6n}$ family of 2H hexagonal perovskite related oxides and contains chains consisting of six consecutive RhO_6 octahedra followed by one distorted CoO_6 trigonal prism. These chains in turn are separated from each other by $[\text{Ba}]_\infty$ chains.

INTRODUCTION

Low-dimensional magnetic systems have attracted much interest historically due to the presence of magnetic behavior unique to structurally highly anisotropic systems. [1-3] Insights into such behavior can be gained from structural families where it is possible to systematically vary either the structure or the composition independently. For this reason, perovskite and perovskite-related oxides in particular have long provided excellent candidates for structural and physical property studies, due to the compositional and structural flexibility of this huge extended oxide family. Recently, much interest has been focussed on a large and varied group of oxides closely akin to the pseudo-one-dimensional 2H hexagonal perovskites, with the general formula $\text{A}_{3n+3m}\text{A}'_n\text{B}_{3m+n}\text{O}_{9m+6n}$ ($n, m = \text{integers}$, A = alkaline earth; A', B = large assortment of metals including alkali, alkaline earth, transition, main group and rare earth metals). [4-25] An early general structural classification of these materials based on the filling of interstitial sites generated by the stacking of $[\text{A}_3\text{O}_9]$ and $[\text{A}_3\text{A}'\text{O}_6]$ layers was developed by Darriet and Subramanian. [26-27] This approach easily describes the structural composition of all the commensurate members of this family of structures and can be extended to encompass members that form incommensurately modulated (aperiodic) structures.

An alternate, complementary description that highlights the low-dimensional nature of these compounds is the composite structure approach. In this structural description, these oxides consist of two crystallographically independent sub-structures, $[\text{A}]_\infty$ chains and $[(\text{A}',\text{B})\text{O}_3]_\infty$ columns made up of distinct ratios of face-sharing octahedra and trigonal prisms. In many cases, the ratio of the repeat distances of the two chains is not a rational number and, consequently, the structure is incommensurately modulated along the chain direction. As shown previously, a better structural formulation of such composites is $\text{A}_{1+x}(\text{A}'_xB_{1-x})\text{O}_3$, where $x = n/(3m+2n)$ and

ranges continuously between 0 and 1/2, corresponding to chains containing all face-shared octahedra and alternating face-sharing octahedra and trigonal prisms, respectively. [27-29] For simple fractional values of x such as 1/5, 2/7, or 1/3, the structure is commensurate and the end-members, the 2H perovskite (BaNiO_3 , $x = 0$) and the K_4CdCl_6 ($x = 1/2$) structure type, are well known.

Most structural and physical property measurements of these compounds (and oxides in general) have been carried out on polycrystalline samples, as oxide single-crystal growth is often unsuccessful. Recently, however, the application of single-crystal flux-growth techniques has enabled the growth of large, high-quality single crystals of this family of oxides, [30-32] which has made possible precise structural determination of both commensurate and incommensurate compounds, and promises to offer a deeper insight into these materials. We have discussed a 4-dimensional superspace group approach in recent papers, and further detailed explanations of the composite structure approach and its description using the superspace formalism can be found in several papers and references therein. [33-37]

EXPERIMENTAL

Synthesis and Crystal Growth. Black hexagonal rod-like single crystals of $\text{Ba}_8\text{CoRh}_6\text{O}_{21}$ ranging in size from sub-millimeter to ~ 7 mm in length were grown from a molten potassium carbonate flux. Rh powder (0.20 g, 1.94 mmol; Engelhard, 99.5%), Co_3O_4 (0.24 g, 1.00 mmol; Johnson-Matthey, 99.99%), BaCO_3 (1.16 g, 5.88 mmol; Alfa, 99.99%) and K_2CO_3 (15.8 g, 114 mmol; Fisher, reagent grade) were mixed thoroughly and placed in an alumina crucible. The filled crucible was covered and heated in air from room temperature to the reaction temperature of 1050°C at 600°h^{-1} , held at 1050°C for 12 h and cooled at 12°C h^{-1} to 875°C , at which point the furnace was turned off and the system allowed to cool to room temperature. The flux was removed with water and the crystals isolated manually. Figure 1 is an image of several crystals obtained from the flux, showing the variability in size and aspect. For all crystals, the presence of Ba, Co, and Rh was verified by SEM.

Data Collection. For the structure determination, a small crystal was carefully chosen. Data collection was performed on an Enraf-Nonius CAD4 diffractometer (Mo- $\text{K}\alpha$) in the supercell approach. The unit cell parameters of both subsystems were determined precisely and refinements led to the following values : $a = 10.0431(1) \text{ \AA}$, $c_1 = 2.5946(1) \text{ \AA}$ for the $[(\text{Co}, \text{Rh})\text{O}_3]$ subsystem and $a = 10.0431(1) \text{ \AA}$, $c_2 = 4.5405(1) \text{ \AA}$ for $[\text{Ba}]$ subsystem. With the $[(\text{Co}, \text{Rh})\text{O}_3]$ subsystem as the reference system, the modulation wave vector is defined by $\mathbf{q} = \gamma \mathbf{c}_1^*$ where $\gamma = c_2^*/c_1^* = c_1/c_2 = 0.57143(1)$. The γ value of 0.57143(1) is a rational fraction (4/7) and corresponds to a commensurate chain sequence of 1 trigonal prism and 6 octahedra.

The X-ray intensity data were collected in the supercell approach. Data reduction, absorption corrections (Psi - scan) and transformation of the indices were carried out using the JANA 2000 program package. [38] The atomic coordinates for the two subsystems are given in Table I. The first and second subsystems are related to the (3+1)D superspace group by the application of the W_1 and W_2 transformation matrices respectively:

$$W_1 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix} \quad W_2 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{vmatrix}$$

The two possible superspace groups that are compatible with the observed extinction conditions of $-h + k + l \neq 3n$ for (h, k, l, m) and $m \neq 2n$ for $(h, 0, l, m)$ 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. Final R values: $R = 0.0537$ ($R_w = 0.0598$) for all reflections; $R = 0.0417$ ($R_w = 0.0463$) for 501 main reflections; $R = 0.0735$ ($R_w = 0.0718$) for 934 satellites of order 1; $R = 0.0652$ ($R_w = 0.0894$) for 174 satellites of order 2.

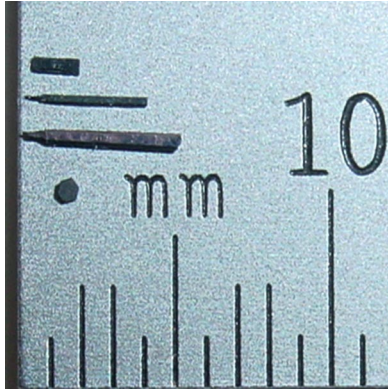


Figure 1: Flux-grown single crystals of $Ba_8CoRh_6O_{21}$. The specimens indicate the range in aspect ratio that is achievable, where the small crystal shown is of a typical size used for the structure determination.

RESULTS AND DISCUSSION

For $Ba_8CoRh_6O_{21}$, the subsystem $[(Co, Rh)O_3]$ was chosen as the reference system with the superspace group $R\bar{3}m(00\gamma)0s$. The fractional atomic average coordinates and thermal parameters are given in Table I. The symmetry of the superspace group generates six equivalent oxygen atoms surrounding the axis of the $[(Co, Rh)O_3]$ chains. Since all six positions cannot be simultaneously occupied, two types of oxygen positions, O_a and O_b , are generated that are each half occupied. Each set of three oxygens forms an equilateral triangle corresponding to the shared face of the polyhedra in the transition metal chain. A Crenel function, which runs along the x_4 axis and is characterized by the Crenel width, Δ , and the Crenel midpoint, \hat{x} , is used to model this occupational modulation. Thus two adjacent O_a or O_b triangles create a trigonal prism, O_a-O_a or O_b-O_b , while a sequence of O_a-O_b or O_b-O_a creates an octahedra, thus determining the polyhedral chain sequence for the transition metal chain. [22,27]

From the value of $\gamma = 0.57143(1)$ (or $4/7$), the value of x can be calculated according to the following relationship $\gamma = (1+x)/2$, thereby $x = 1/7$. For this compound, x is a rational fraction indicating a commensurate structure. From the value of x and γ , it is now possible to predict the polyhedra sequence for the $[(Co, Rh)O_3]$ column. [27] Figure 2 illustrates the ability to predict the sequence of polyhedra by carrying out 7 translations of $4/7$ along x_4 that produces a

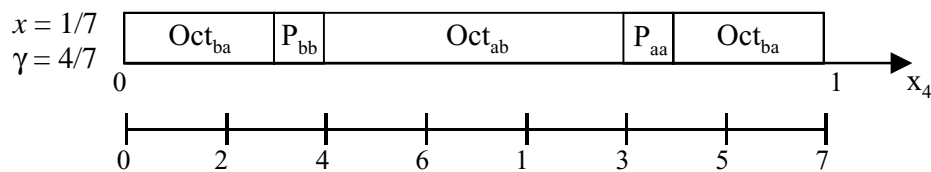


Figure 2: Schematic of the sequence of octahedra and prisms for $x = 1/7$ visualized along the internal coordinate x_4 for a column of $[(A', B)O_3]$.

Table I: Fractional atomic average coordinates and equivalent isotropic displacement factors, and atomic positional and DWF modulation coefficients.

Subsystem [(Co, Rh)O₃]: $R\bar{3}m(00\gamma)0s$

atom	x_0	y_0	z_0	$U_{eq}(\text{\AA}^2)$
Co	0	0	0	0.0312(7)
Rh	0	0	0	0.0078(1)
O	0.148(1)	0.148(1)	1/2	0.049(2)

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

atom	x_0	y_0	z_0	$U_{eq}(\text{\AA}^2)$
Ba1	0.32593(5)	0	1/4	0.0118(2)
Ba2	0.34939(9)	0	1/4	0.0069(3)

Co: Amplitude = -0.0135 $\hat{x} = 1/4$ $\Delta = 0.0714$

Rh: $U_{z,1}^{Rh} = -0.0058(2)$ $U_{z,3}^{Rh} = -0.0050(2)$
Amplitude = -0.0805 $\hat{x} = 0$ $\Delta = 0.4286$
 $U_{U1,2}^{Rh} = U_{U2,2}^{Rh} = 2U_{U12,2}^{Rh} = -0.0032(1)$ $U_{U3,2}^{Rh} = -0.0114(2)$

O: $U_{x,1}^O = U_{y,1}^O = 0.0079(6)$ $U_{x,2}^O = -U_{y,2}^O = 0.0003(2)$
 $U_{z,2}^O = 0.0101(6)$ $U_{z,3}^O = 0.0030(5)$
 $U_{x,3}^O = -U_{y,3}^O = 0.0009(1)$
 $U_{x,1}^O = U_{y,1}^O = -0.00001(7)$
Amplitude = -0.0939 $\hat{x} = 1/4$ $\Delta = 1/2$
 $U_{U11,1}^O = U_{U22,1}^O = -0.032(2)$ $U_{U33,1}^O = -0.024(2)$
 $U_{U12,1}^O = -0.007(2)$ $U_{U13,1}^O = -U_{U23,1}^O = -0.006(1)$
 $U_{U11,2}^O = -U_{U22,2}^O = -0.0011(3)$ $U_{U13,2}^O = U_{U23,2}^O = 0.0025(3)$

Ba1: $2U_{x,1}^{Ba1} = U_{y,1}^{Ba1} = -0.0063(2)$ $U_{z,1}^{Ba1} = -0.0021(1)$
 $U_{x,2}^{Ba1} = -0.0011(2)$
Amplitude = -0.0029 $\hat{x} = 1/2$ $\Delta = 0.2083$
 $U_{U11,1}^{Ba1} = U_{U12,1}^{Ba1} = 0.0013(4)$ $U_{U13,1}^{Ba1} = -0.0034(3)$
 $U_{U11,2}^{Ba1} = -0.0018(4)$ $U_{U22,2}^{Ba1} = 2U_{U12,2}^{Ba1} = 0.0087(7)$
 $U_{U33,2}^{Ba1} = 0.00002(24)$ $2U_{U13,2}^{Ba1} = U_{U23,2}^{Ba1} = 0.0057(4)$

Ba2: $2U_{x,1}^{Ba2} = U_{y,1}^{Ba2} = -0.0019(2)$ $U_{z,1}^{Ba2} = 0.0021(2)$
 $U_{x,2}^{Ba2} = -0.0029(1)$
Amplitude = -0.0032 $\hat{x} = 0$ $\Delta = 0.1250$
 $U_{U11,1}^{Ba2} = U_{U12,1}^{Ba2} = -0.0004(5)$ $U_{U13,1}^{Ba2} = -0.0095(4)$
 $U_{U11,2}^{Ba2} = -0.0092(5)$ $U_{U22,2}^{Ba2} = 2U_{U12,2}^{Ba2} = 0.0033(8)$
 $U_{U33,2}^{Ba2} = 0.0082(4)$ $2U_{U13,2}^{Ba2} = U_{U23,2}^{Ba2} = 0.0026(4)$

sequence of Oct_{ab}-Oct_{ba}-Oct_{ab}-P_{bb}-Oct_{ba}-Oct_{ab}-Oct_{ba} or six octahedra followed by one trigonal prism.

To distinguish the trigonal prismatic sites from the octahedral sites, a saw-tooth function was employed to account for the displacive modulation along x_4 of the atoms. [22] A graphical representation of the functions utilized is shown in Figure 3. Note how well the saw-tooth function effectively models the modulation of cobalt. The modulation of oxygen, rhodium, and barium deviate slightly from the ideal saw-tooth function, and so, consequently, an additional modulation was added to the saw-tooth function; a second order modulation for barium and a third order modulation for both rhodium and oxygen.

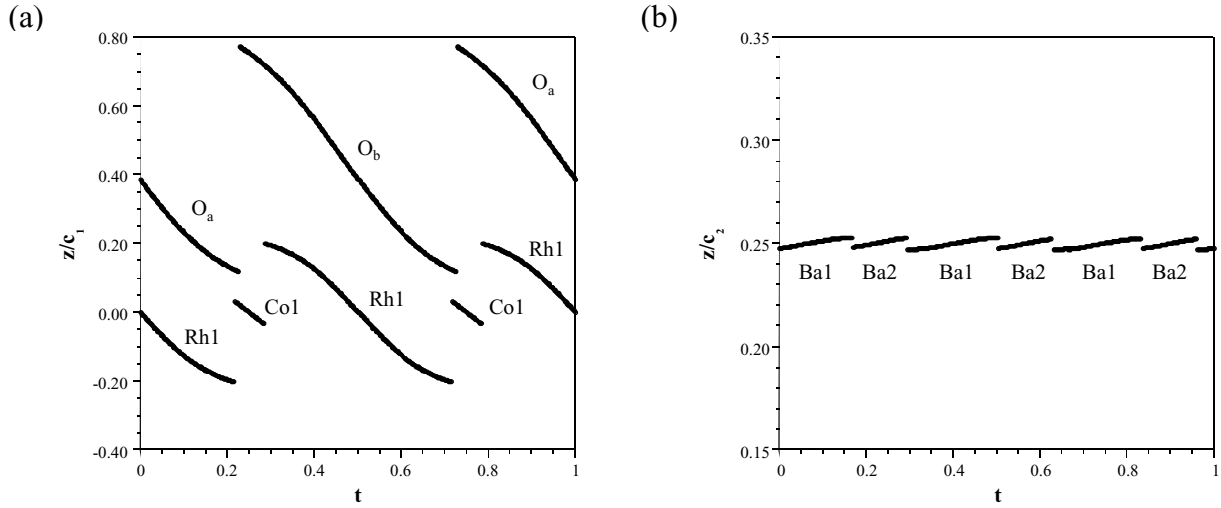


Figure 3: Graphical representation of the internal z coordinate of (a) O_a , O_b , $Rh1$, and $Co1$ and (b) $Ba1$ and $Ba2$ versus the internal coordinate t ($t = x_4 - q \cdot r$).

An approximate [110] view of the composite structure of $Ba_8CoRh_6O_{21}$ is shown in Figure 4. The repeat sequence in the face-shared polyhedral $[(A',B)O_3]_\infty$ subsystem consists of six consecutive RhO_6 octahedra followed by one distorted CoO_6 trigonal prism. The metal-

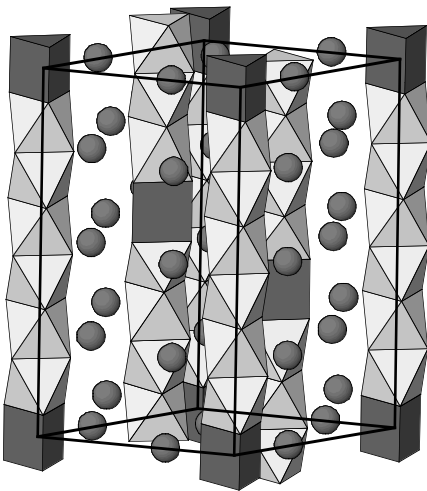


Figure 4: Approximate [110] view of the structure of $Ba_8CoRh_6O_{21}$. Light gray: RhO_6 octahedra; Dark gray: CoO_6 trigonal prisms; Gray spheres: Ba atoms.

oxygen bond distances (Co-O = 2.161(1) Å - 2.241(1) Å; Rh-O = 1.896(1) Å - 2.092(1) Å) are typical for oxides of this type. Intrachain Co-Rh (2.780(1) Å) and Rh-Rh (2.496(1) Å - 2.543(1) Å) distances are essentially non-bonding.

CONCLUSION

Successful structure solution of Ba₈CoRh₆O₂₁ using the superspace formalism indicates the efficiency of the method for commensurate as well as incommensurate structures. This compound represents the first example of an $m = 5$, $n = 3$ member of the $A_{3n+3m}A'_nB_{3m+n}O_{9m+6n}$ family and one of only a few compositions other than $n = 1$ and $m = 0$ that crystallize in a commensurate form. In addition, this compound displays some very interesting and highly anisotropic magnetic behavior that will be reported elsewhere. [39]

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