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Preparation and Structure of a Ternary Oxide of Barium and Rhenium, $Ba_3Re_{2-x}O_9$

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Attempts to synthesize $BaReO_3$ resulted in formation of a slightly nonstoichiometric compound with the ideal formula $Ba_3Re_2O_9$. It was found to have the space group $R\bar{3}m$ with hexagonal unit cell parameters $a = 5.7699$ (5) Å and $c = 20.799$ (2) Å, $Z = 3$. A total of 2816 reflections were measured on an automatic diffractometer, and the structure was refined by full-matrix least squares on 308 unique reflections to a final R value of 0.027 and R_w of 0.036. It consists of a nine-layer repeat sequence of hexagonal and cubic close-packed layers of composition BaO_3. The stacking of these layers along the c axis leads to the formation of two types of octahedral sites, M(1) and M(2), for the Re atoms. An M(2) octahedron shares opposite faces with two M(1) octahedra. Site population analysis has shown that about 8% of the M(2) sites are occupied and that simultaneous occupation of two octahedral sites sharing a face is avoided, resulting in the Re deficient compound $Ba_3Re_{1.96}O_9$. All the Ba atoms are 12-coordinated and both ReO_6 octahedra show a distortion corresponding to an elongation along the trigonal axis.

Introduction

A large number of ternary oxides AMO_3, where A is a large cation and M is a transition-metal cation, crystallize in the perovskite structure or structures related to it. The variation among these structures and the stoichiometry of these compounds and their derivatives have been discussed by Katz and Ward[2] in terms of stacking of close-packed anion layers in which the large cation A orders into the anion sites of the layer. Combinations of cubic (c) and hexagonal (h) packing of these layers result in various structure types characterized by the repeat sequence of these layers. One of the structure types predicted by these authors is the nine-layer structure for compounds of the stoichiometry $A_9B_6O_{27}$ involving vacant octahedral sites. The first ternary oxide found to crystallize in this nine-layer structure is $BaRuO_3$[3] in which all the octahedral sites are filled. This results in face-sharing of RuO_6 octahedra with possible metal–metal bonding between Ru. Our attempts to synthesize $BaReO_3$ resulted in the formation of crystals having the ideal formula $Ba_3Re_2O_9$. The crystals were formed in a tetrahedral anvil at pressures of 60–65 kbar and 1180 °C for 2 h and then quenched to room temperature prior to the release of the applied pressure. A crystal structure determination on this product was undertaken.

Experimental Section

Crystal Data. $Ba_3Re_2O_9$ is hexagonal with $a = 5.7699$ (5) Å, $c = 20.799$ (2) Å, $Z = 3$, $d_x = 7.71$ g/cm^3, and formula weight = 928.4. The equivalent primitive rhombohedral cell has dimensions $a = 7.692$ (2) Å and $\alpha = 44.06$ (3)° and $Z = 1$. The unit cell parameters were obtained from a least-squares refinement of Guinier powder data on 30 indexed reflections (Table I). Precession photographs indicated that the diffraction symbol was $\bar{3}mR$, with systematic absences $-h + k + l \neq 3n$ for reflections hkl referred to the hexagonal cell. The centric space group $R\bar{3}m$ was chosen over the noncentric ones $R32$ and $R3m$, as suggested by the statistical distribution of intensities.

X-Ray Intensity Measurements. A good quality single crystal ground into a sphere of 0.074 mm radius was used for intensity measurements on a Syntex $P\bar{1}$ automatic diffractometer using graphite monochromatized Mo Kα radiation (λ 0.71069 Å). θ–2θ scan was used with a variable scan rate from 8.0 to 24.0°/min in 2θ to minimize counting errors for the weak reflections. The intensity of a reflection was corrected for background which was measured on both sides of the peak. A total of 2816 reflections were collected within a sphere defined by $2\theta < 65°$. Subsequent averaging led to 308 symmetry independent reflections of which 270 had intensities greater than three times their standard errors, based on counting statistics. The data were corrected for Lorentz, polarization, and absorption effects (μ(Mo Kα) = 469.05 cm^{-1}).

Table I. Guinier Powder Diffraction Data for $Ba_3Re_{1.96}O_9$

h	k	l	Relative intensity	d(obsd), g cm^{-3}	d(calcd), g cm^{-3}
0	0	3	20	6.923	6.933
1	0	1	30	4.857	4.859
1	0	4	4	3.605	3.603
0	0	6	5	3.466	3.467
0	1	5	100	3.197	3.197
1	1	0	100	2.887	2.885
1	1	3	10	2.663	2.664
1	0	7	10	2.554	2.554
0	1	8	25	2.307	2.306
0	2	4	5	2.252	2.252
2	0	5	90	2.142	2.142
1	0	10	60	1.921	1.920
0	2	7	10	1.913	1.912
2	1	1	5	1.882	1.881
2	0	8	20	1.802	1.801
0	1	11	2	1.769	1.768
1	2	5	70	1.720	1.720
3	0	0	50	1.666	1.666
0	2	10	40	1.599	1.598
2	1	7	10	1.594	1.594
1	2	8	15	1.528	1.528
1	0	13	15	1.524	1.524
1	1	12	5	1.486	1.486
2	2	0	45	1.443	1.442
2	1	10	40	1.398	1.398
0	0	15	10	1.387	1.387
1	3	1	45	1.382	1.383
0	2	13	15	1.347	1.347
3	1	5	30	1.315	1.315
1	1	15	25	1.249	1.250

Structure Determination. A trial structure was derived based on the ideal nine-layer structure proposed by Katz and Ward.[2] This idealized structure referred to the hexagonal cell in $R\bar{3}m$ would place the Ba atoms at 0, 0, 0 and 0, 0, $^{4}/_{18}$ and the Re atom at 0, 0, $^{7}/_{18}$. The two independent oxygen atoms were placed at $^{1}/_{2}$, 0, 0 and $^{1}/_{6}$, $-^{1}/_{6}$, $^{2}/_{18}$. Scattering curves for Ba^{2+}, Re, and O were taken from Cromer and Waber[4] and an anomalous dispersion correction[5] was made for Ba^{2+} and Re. The full-matrix least-squares program CUDLS written for the CDC6400 computer at McMaster University was used for the refinement, in which the function $\sum w(|F_o| - |kF_c|)^2$ was minimized. The structure refined to a conventional R factor of 0.13 with individual isotropic temperature factors, but the refinement was found to be insensitive to the positions of the oxygen atoms. A difference Fourier synthesis was performed with the oxygen atoms excluded from the model. In additon to peaks corresponding to the oxygen atoms, the difference map revealed a residual peak at 0, 0, $^{1}/_{2}$. This was recognized as due to partial occupancy of this site by Re. The population parameter for this site was estimated to be 0.06 from the height of this peak with respect to those from oxygen atoms. Refinement was resumed with this additional population parameter and the oxygen positional parameters obtained from the difference map. The occupancy of the other Re site was constrained to the ideal stoichiometry at this stage. A weighting function $w = (25.0 + 0.08F_o + 0.00016F_o^2)^{-1}$ was chosen so that $\omega(\Delta F)^2$ would be independent of the local average value of F_o. The structure readily refined to an R_w (= $[\sum w(|F_o| - |kF_c|)^2/\sum wF_o^2]^{1/2}$) of 0.038 with anisotropic temperature factors for all atoms. The site population parameters for both Re sites were allowed to vary independently and this led to a final R value of 0.027 and R_w of 0.036. The significance test of

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Table II. Positional and Thermal Parameters of $Ba_3Re_{1.96}O_9$ (Esd in Parentheses)

Atom	Position type	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	3a	0	0	0	0.0121 (6)	$=U_{11}$	0.0115 (6)	$={}^1/_2U_{11}$	0	0
Ba(2)	6c	0	0	0.21218 (5)	0.0143 (5)	$=U_{11}$	0.0145 (6)	$={}^1/_2U_{11}$	0	0
Re(1)[a]	6c	0	0	0.39166 (3)	0.0069 (4)	$=U_{11}$	0.0114 (4)	$={}^1/_2U_{11}$	0	0
Re(2)[b]	3b	0	0	$^1/_2$	0.006 (6)	$=U_{11}$	0.052 (10)	$={}^1/_2U_{11}$	0	0
O(1)	9e	$^1/_2$	0	0	0.030 (5)	0.065 (10)	0.008 (4)	$={}^1/_2U_{22}$	0.007 (5)	$=2U_{13}$
O(2)	18h	0.175 (1)	$-x$	0.1052 (4)	0.014 (4)	$=U_{11}$	0.022 (3)	0.011 (2)	0.002 (2)	$=-U_{13}$

[a] $p_1 = 0.941$ (7). [b] $p_2 = 0.079$ (5).

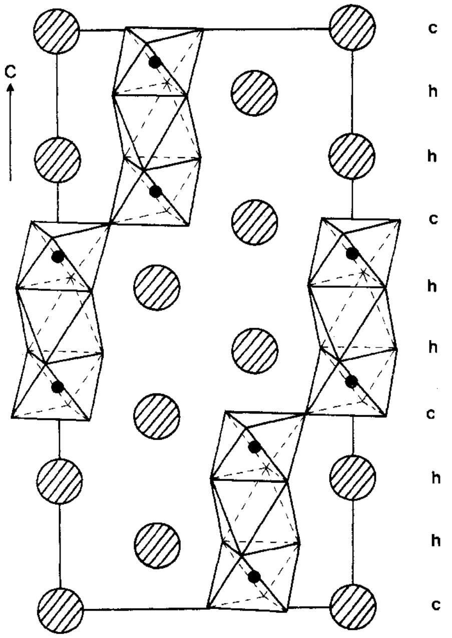

Figure 1. Arrangement of cations on the hexagonal 110 plane of $Ba_3Re_{2-x}O_9$ showing nine-layer sequence. c and h represent "cubic" and "hexagonal" layers, respectively. Large striped circles are Ba. Re atoms largely occupy octahedra with small filled circles.

Table III. Bond Distances and Angles of $Ba_3Re_{1.96}O_9$ (Esd in Parentheses)

Bond	Distance, Å	Bond	Angle, deg
1. Ba(1) Polyhedron			
Ba(1)-O(2)	2.798 (7) × 6	O(2)-Ba(1)-O(2)2[a]	65.4 (3)
-O(1)	2.885 (1) × 6	-O(1)	57.3 (1)
2. Ba(2) Polyhedron			
Ba(2)-O(1)25	3.020 (1) × 3	O(2)28-Ba(2)-O(2)29	62.7 (1)
-O(2)	2.829 (7) × 3	-O(2)30	56.4 (2)
-O(2)28	2.905 (4) × 6	O(2)30-Ba(2)-O(2)29	118.7 (1)
		-O(2)30	166.5 (2)
		O(2)-Ba(2)-O(2)2	64.6 (1)
		-O(1)25	145.7 (1)
		O(1)25-Ba(2)-O(2)2	108.4 (1)
		-O(1)26	57.05 (2)
3. Re(1) Octahedron			
Re(1)-O(1)25	2.061 (1) × 3	O(1)25-Re(1)-O(1)26	88.86 (2)
-O(2)25	1.861 (7) × 3	-O(2)26	95.1 (3)
		O(1)25-Re(1)-O(2)25	87.9 (1)
		-O(2)26	175.5 (2)
4. Re(2) Octahedron			
Re(2)-O(2)25	2.037 (8) × 6	O(2)25-Re(2)-O(2)26	84.8 (2)
		-O(2)17	95.2 (2)
		-O(2)16	180.0

[a] The position of an oxygen atom is denoted by O(*m*)*n*, being related to that of O(*m*) by the *n*th symmetry operation in the order shown in "International Tables for X-Ray Crystallography" for space group No. 166, $R\bar{3}m$.

Hamilton[6] on the R_w factors was performed, which suggested that the model with constrained Re site population parameters could be rejected at the 0.005 significance level. The maximum shift in the parameters was less than 10% of the estimated standard deviation in the last cycle of refinement. The final scaling constant k was 1.462 (6) and the refined secondary extinction parameter[7] was 2.7 (2) × 10^{-7}. The population parameters p_1 and p_2 for sites Re(1) and Re(2) were 0.941 (7) and 0.079 (5), respectively. The final positional and thermal parameters are listed in Table II.

Discussion

The structure of $Ba_3Re_2O_9$ is based on a close-packed arrangement of layers of oxygen and barium atoms. The basic unit of a layer consists of Ba atoms at the corners of the basal plane of the hexagonal cell and oxygen atoms lying on the edges and in the center of the plane; i.e., they occupy the centers of symmetry on the basal plane of the unit cell. Two similar layers, related by the centers of symmetry, are stacked above and below this basal layer with a layer separation of about $^2/_9$ the c axis. These three layers in turn generate six more layers by the rhombohedral centering of the space group. The whole unit cell then consists of nine layers, each of composition BaO_3, stacked along the c axis (Figure 1). These layers are designated, following Katz and Ward, as hexagonal layers if the two neighboring layers are of the same type and cubic layers if the two neighboring layers are of different types. All the Ba atoms are then 12-fold coordinated. Ba(1) is coplanar with six neighboring oxygen atoms at 2.885 Å (Table III), with three other oxygen atoms each from layers above and below at 2.798 Å. The two triangular faces formed by the latter oxygens from the two layers are oppositely oriented since Ba(1) belongs to a c layer. Ba(2) is almost coplanar with six oxygen atoms at 2.905 Å, but the triangular faces formed by the other six oxygens from layers above and below are similarly oriented.

Since one-quarter of the "anion" sites in a layer are actually occupied by the large cations Ba, the number of octahedral sites available for the small cations in this close-packed structure is reduced to one-quarter of its total to avoid cation–cation repulsion. These octahedral sites are again of two types, Re(1) and Re(2). Re(1) octahedra are formed between c and h layers and each has its three corners shared with three other octahedra of the same type. The average Re–O distance is 1.961 Å. Re(2) octahedra are formed between two h layers and each has its opposite faces shared with two Re(1) octahedra above and below so that three adjacent Re octahedra form a string along with the c axis in a unit cell. The six oxygen atoms of the Re(2) octahedron are equidistant at 2.037 Å. Both Re(1) and Re(2) octahedra are distorted. The distortion corresponds to an elongation of a regular octahedron along its trigonal axis so that the O–Re–O angle deviates from 90 by about 5°.

Only the Re(1) sites were expected to be occupied in ideal $Ba_3Re_2O_9$, leaving the Re(2) sites vacant. The results of this study indicated that about 8% of the Re(2) sites were occupied. Such face-sharing octahedral arrangement between highly charged cations should not be stable according to Pauling's third rule.[8] In the present case it results in a Re(1)–Re(2) distance of 2.253 Å, considerably shorter than the interatomic distance of 2.75 Å found in Re metal. Although many ternary oxides of the type $Ba_3M_2O_6$ with BaO_3 layers involve face-sharing of filled octahedra, their small cations have lower formal charges. Therefore the partial occupancy of the Re(2) sites is expected to be accompanied by some vacancies in the Re(1) sites. The refined site population parameters show that about 6% of the Re(1) sites are vacant. It may be concluded that, within the limit of 3σ, for each Re(2) site occupied the occupancy of the two Re(1) sites sharing octahedral faces with it is precluded so as to avoid strong metal–metal repulsion. This results in about 2% deficiency of Re in the structure. It remains speculative whether the required charge balance is achieved by a corresponding deficiency of oxygen or by oxidation of Re(VI) to Re(VII) or both. By way of contrast, it was reported that the compound $Ba_5Ta_4O_{15}$ could be obtained from oxidizing $Ba_5Ta_4O_{13}$ without change in structure,[9,10] which is related to the present one in having a five-layer sequence (cchhc) and vacant octahedra sharing opposite faces with filled octahedra.

The strong metal–metal repulsion between face-sharing octahedra may explain why the compound $BaReO_3$, which could have all the Re(2) sites filled in the 9R structure, fails to form under normal conditions. It is possible, however, that the occupancy of the octahedral sites and consequently the exact stoichiometry of $Ba_3Re_2O_9$ is pressure dependent. The nonstoichiometric $Re_{1+x}O_3$ ($0.14 < x < 0.21$) formed at high pressure was reported to contain hexagonal close-packed oxygen with one type of octahedral site partially filled.[11] Complete filling of these sites would have given the compound R_2O_3 which is hitherto unknown. Another example of cation deficiency in related structures may be found in the mineral senaite with the general formula $AM_{21}O_{38}$, which also features a nine-layer sequence of close-packed anion lattice where the layer composition is AO_{38}.[12] It has been suggested[13] that its structure is derived from natural oxidation and leaching of iron and manganese from an original structure of the formula $AM_{24}O_{28}$, in which the Fe^{2+} and Mn^{2+} occupy the h–M–h octahedral sites that share faces with the h–M–c octahedral sites occupied by Ti.

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Registry No. $Ba_3Re_2O_9$, 65149-61-3.

Supplementary Material Available: A listing of calculated and observed structure amplitudes (1 page). Ordering information is given on any current masthead page.

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Sulfinato Coordination of Triplet-State Cobalt(III) through Sulfur. Crystal and Molecular Structure of Bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}cobalt(III) Perchlorate Dihydrate

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The crystal and molecular structure of bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}cobalt(III) perchlorate dihydrate, $[Co(C_8H_{11}N_2SO_2)_2]ClO_4\cdot 2H_2O$, has been determined by single-crystal x-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional R index of 0.043. The bright orange crystals form as rectangular prisms in the monoclinic space group $C2/c$ with a = 23.171 (4) Å, b = 11.397 (2) Å, c = 9.210 (2) Å, and β = 96.62 (2)° and with four molecules per unit cell. The cobalt(III) ion lies at an inversion center and is coordinated octahedrally by two amine nitrogen atoms at 1.974 (3) Å, two pyridyl nitrogen atoms at 1.945 (2) Å, and two sulfur atoms of the sulfinato groups at 2.233 (1) Å—the oxygen atoms do not coordinate to Co(III). The compound was prepared by the reaction of Co(II) with 2-[(2-pyridylmethyl)amino]ethanethiol in the presence of hydrogen peroxide in basic solution and was recrystallized from water–ethanol–ethyl acetate. In the absence of hydrogen peroxide, a cobalt(II) disulfide complex is obtained. The cobalt(III) sulfinato complex is paramagnetic, with Co(III) in an intermediate spin state (μ = 3.27, as determined by the Evans NMR method); the occurrence of this unusual spin state is attributed to the presence of d_{z^2} and d_{xy} levels of comparable energy as a result of electronic distortion. The preparation of a sulfinate from a thiol in the presence of cobalt has its biological analogue in the formation of cysteinesulfinic acid from cysteine, a reaction most likely catalyzed by a metalloenzyme.

Introduction

Cobalt(III) sulfinato complexes may be prepared by reacting a sulfinate salt with a Co(III) complex,[1-3] by SO_2 insertion into a Co(III)–C bond,[2-5] or by oxidizing a cobalt(III) thiolato complex by hydrogen peroxide.[6-10] This work appears to exemplify the last method and describes the synthesis and structure of bis{2-[(2-pyridylmethyl)amino]ethylsulfinato}cobalt(III) perchlorate dihydrate, obtained from the reaction of cobalt(II) perchlorate with 2-[(2-pyridylmethyl)amino]ethanethiol in the presence of hydrogen peroxide. In the absence of hydrogen peroxide, the reaction product is {2-[(2-pyridylmethyl)amino]ethyl disulfide}cobalt(II) perchlorate.

The preparation of a sulfinate from a thiol in the presence of a metal ion has its biological analogue in the formation of

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