Crystal Structure of New 10-Layer Perovskite-Related Oxyhalide, $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$

Seung-Tae Hong and Arthur W. Sleight[1]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Crystals of $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ were prepared in a $BaCl_2$ flux and investigated by X-ray diffraction methods. The structure of this new compound was solved and refined in the hexagonal symmetry space group $P6_3/mmc$ with $a = 5.817(2)$ Å, $c = 24.839(2)$ Å, and $Z = 2$ to a final R of 0.0383. The structure of $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ displays a 10-layer stacking sequence of mixed $[BaO_3]$ and $[BaCl]$ layers containing isolated $(Ru/W)_2O_9$ units as face-shared octahedra. Isolated face-shared Ru_2O_9 units are also found in $Ba_5Ru_2Cl_2O_9$ which otherwise has a very different structure. $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ appears to be the first example of Ru and W sharing the same crystallographic site. © 1997 Academic Press

INTRODUCTION

Many structures may be considered as perovskite related with variations on the stacking of different types of layers (1). One series belonging to this large family of compounds results from the stacking of BaO_3 and BaX ($X =$ Cl, Br) layers as shown in Figs. 1a and 1c, respectively. There are several examples with different stacking sequences of these two types of layers, resulting in various layered structures: 6-layer $Ba_6Ru_2PtCl_2O_{12}$ (2) and $Ba_6Ru_{2.5}Mn_{0.5}Cl_2O_{12}$ (3), $Ba_6Nb_2IrCl_2O_{12}$ (4), 10-layer $Ba_5RuTaCl_2O_9$ (5), 21-layer $Ba_7Ru_4Cl_2O_{15}$ (6) and $Ba_7Ru_4Br_2O_{15}$ (7), and 24-layer $Ba_8Ru_3Ta_2Cl_2O_{18}$ (8) and $Ba_8Ru_{3.33}Ta_{1.67}Cl_2O_{18}$ (9). A common structural characteristic of these phases is the consecutive stacking of two BaX ($X =$ Cl, Br) layers. The transition metal cations occupy the octahedral sites formed by the BaO_3 layers. These oxyhalides can be generally formulated as $(Ba_2X_2)(Ba_{n+1}M_nO_{3n+3})$, $n \geq 1$. In the present paper, we describe the crystal structure of the new hexagonal 10-layer oxyhalide $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$, $n = 2$ member of this series. A comparison is made with other 10-layer compounds and with $Ba_5Ru_2Cl_2O_9$.

[1] To whom correspondence should be addressed.

EXPERIMENTAL

Reactants were high purity $BaCO_3$, RuO_2, and WO_3. These reactants were mixed in a $7:2:2$ Ba:Ru:W ratio, pressed into a pellet, heated at 900°C for 12 h, heated again at 1000°C for 12 h, and finally at 1100°C for 12 h with intermediate grindings and pressings. This product was then mixed with a 40-fold excess of $BaCl_2$, heated to 1100°C for 1 h, and cooled slowly to room temperature at a rate of 6°C/h. After dissolving the $BaCl_2$ with water, black hexagonal-plate or hexagonal-prism crystals were found. Laue and precession photographs showed that the plate and prism crystals were in fact the same material. Several crystals were analyzed by electron microprobe, revealing that the crystals are a barium ruthenium oxychloride containing a small amount of tungsten.

Laue and precession photographs on hexagonal prism crystals were used to select a crystal suitable for intensity data collection. These photographs showed the Laue symmetry to be $6/mmm$. Intensity data for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ were collected at room temperature using a Rigaku AFC6R diffractometer with graphite-monochromated $MoK\alpha$ radiation. The diffraction data were corrected for Lorentz and polarization effects. Cell constants ($a = 5.817(2)$; $c = 24.839(2)$ Å) and the orientation matrix for data collection were obtained from a least-squares refinement with 20 automatically centered reflections in the range $30° \leq 2\theta \leq 35°$. Details of the data collection and refinement are given in Table 1. Examination of the data collected confirmed the $6/mmm$ Laue class. The condition for the observed reflections is: $hh2\bar{h}l$, $l = 2n$. Thus, the possible space groups are $P6_3/mmc$, $P6_3mc$, and $P\bar{6}2c$. These space groups gave rise to the same metal arrangement by the interpretation of Patterson maps using SHELXS-86 (10). The positions of the chlorine and oxygen atoms were progressively located from Fourier difference maps during the course of the refinement using SHELXL93 (11). The Ru/W ratio was refined with the constraint that the site be fully occupied, the refined value was consistent with the microprobe analysis on this crystal.
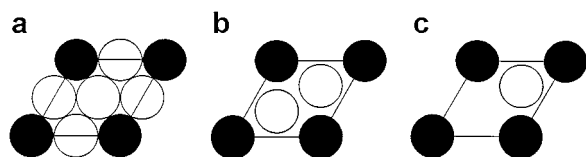
FIG. 1. Representation of hexagonal layers: (a) $[AX_3]$, (b) $[AX_2]$, and (c) $[AX]$. A and X are cations and anions, represented by filled and open circles, respectively.

After a full-matrix least-squares refinement of the model with isotropic thermal parameters on each atom, an absorption correction was applied using the program DIFABS (12) in the TEXSAN software package (13). The best refinement (stable convergence, lowest residuals) was obtained in space group $P6_3/mmc$ (No. 194). The data were averaged ($R_{int} = 0.056$), and the model was refined with anisotropic thermal parameters on each atom.

RESULTS AND DISCUSSION

The positional parameters and thermal parameters for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ are given in Table 2, and the main

TABLE 1
Crystallographic Parameters for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$

Formula	$Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$
Formula weight	2273.7
Crystal size (mm)	$0.05 \times 0.08 \times 0.06$
Color	black
a, Å	5.817(2)
c, Å	24.839(2)
V, Å^3	727.9(4)
μ (Mo$K\alpha$), mm^{-1}	18.454
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$ Å)
	Graphite monochromated
ρ_{calc}, g/cm^3	5.875
Transmittance coefficient range	0.891–1.134
Space group	$P6_3/mmc$, No.194
Z	2
Diffractometer	Rigaku AFC6R
T, K	296(2)
Octants measured	$h, k, \pm l$
Scan mode	$\omega - 2\theta$
$2\theta_{min}, 2\theta_{max}$	4.9, 60
No. of reflections measured	1692
No. of unique data	465
No. of observed refined $[F_o > 4\sigma(F_o)]$	331
No. of parameters refined	27
Refined method	Full-matrix least squares on $|F|^2$
$R[I > 2\sigma(I)]^a$	3.83
$wR[I > 2\sigma(I)]^a$	10.23
Goodness of fit $[I > 2\sigma(I)]$	1.203
Extinction coefficient	$2.1(4) \times 10^{-3}$

$^a R = ||F_o| - |F_c||/\sum|F_o|$ and $wR = \sqrt{(w(F_o^2 - F_c^2)^2/\sum wF_o^4)}$, $w = 1/\sigma^2(F_o^2) + (0.0405P)^2 + 21.9866P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

TABLE 2
Atomic Coordinates and Thermal Parameters (Å$^2 \times 10^2$) for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$

Atom	Site	x	y	z	Occup.	U_{eq}^a
Ba(1)	$4f$	1/3	2/3	0.07456(5)	1	2.73(5)
Ba(2)	$4f$	2/3	1/3	0.16964(5)	1	1.84(4)
Ba(3)	$2c$	1/3	2/3	1/4	1	1.22(4)
Ru	$4e$	0	0	0.19219(6)	0.80(1)	1.34(5)
W	$4e$	0	0	0.19219(6)	0.20(1)	1.34(5)
Cl	$4f$	2/3	1/3	0.0497(3)	1	5.6(3)
O(1)	$12k$	0.160(1)	0.320(2)	0.1563(3)	1	1.6(2)
O(2)	$6h$	0.302(3)	0.151(1)	1/4	1	1.5(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	3.3(1)	U_{11}	1.6(1)	0	0	$0.5U_{11}$
Ba(2)	1.6(1)	U_{11}	2.3(1)	0	0	$0.5U_{11}$
Ba(3)	1.2(6)	U_{11}	1.4(1)	0	0	$0.5U_{11}$
Ru/W	1.1(1)	U_{11}	1.7(1)	0	0	$0.5U_{11}$
Cl	7.2(5)	U_{11}	2.4(3)	0	0	$0.5U_{11}$
O(1)	1.8(4)	0.9(4)	1.7(3)	0.3(4)	$0.5U_{23}$	$0.5U_{22}$
O(2)	0.9(7)	1.7(5)	1.7(5)	0	0	$0.5U_{11}$

^{a} Equivalent U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

interatomic distances and angles appear in Table 3. The structure (Fig. 2) may be described using 10 layers of BaO_3 and $BaCl$ (Fig. 1). As Fig. 1a shows, Ba(3) is coordinated by 12 oxygen atoms as in the perovskite structure. Ba(2) is coordinated by 9 oxygen atoms and 1 chlorine atom. This coordination polyhedron can be derived from the BaO_{12} polyhedron by replacing 3 oxygen atoms with 1 chlorine atom. In this way, hexagonal perovskite-like blocks, three oxygen layers thick, are formed from Ba(3), Ba(2) and all of the oxygen atoms. The ruthenium and tungsten atoms are located in octahedral holes of this oxygen framework. The three oxygen layers forming the blocks of the M_2O_9

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$

Ba(1)–O(1) $\times$ 3	2.677(9)	Ru/W–O(1) $\times$ 3	1.84(1)
Ba(2)–O(1) $\times$ 6	2.928(1)	Ru/W–O(2) $\times$ 3	2.09(1)
Ba(2)–O(2) $\times$ 3	2.71(1)		
Ba(3)–O(1) $\times$ 6	2.908(9)	Ru/W–Ru/W	2.872(3)
Ba(3)–O(2) $\times$ 6	2.913(1)	Ru/W–Ba(2) $\times$ 3	3.405(1)
		Ru–Ba(2) $\times$ 3	3.4816(6)
Ba(1)–Cl $\times$ 1	3.086(7)	Ru–Ba(3) $\times$ 3	3.653(1)
Ba(1)–Cl $\times$ 3	3.415(2)		
Ba(2)–Cl $\times$ 1	2.980(7)	O(1)–Ru–O(1)	98.6(3) $\times$ 3
		O(1)–Ru–O(2)	90.7(3) $\times$ 6
O1–O1 $\times$ 2	2.80(2)	O(1)–Ru–O(2)	165.6(4) $\times$ 3
O1–O2 $\times$ 3	2.808(7)	O(2)–Ru–O(2)	78.1(4) $\times$ 3
O2–O2 $\times$ 2	2.64(2)	Ru–O(2)–Ru	86.6(5)

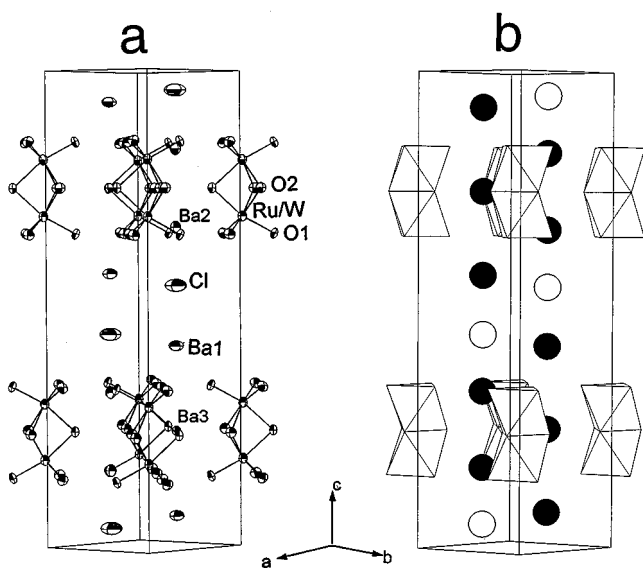**FIG. 2.** Representation of the structure of $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$. Thermal ellipsoids are drawn at the 50% probability level in (a). Ba and Cl are represented as shaded and open circles, respectively, in (b).

another. Thus, the Ba : M metal stoichiometry becomes 5 : 2. Figures 3b and 3c shows two corner-sharing tetrahedra that result from the replacement of BaO_3 by BaOCl or BaO layer, respectively. For comparison, other types of 10-layer compounds are also represented in Figs. 3d, 3e, and 3f for $(hchch)_2$, $(cccch)_2$, and $(cchhh)_2$ stacking sequences of $[AX_3]$ layers, respectively.

The structure of $Ba_5Ru_2Cl_2O_9$, is shown in Fig. 4. The relatively small substitution of W for Ru results in a big change in structure, but the isolated M_2O_9 (M = Ru or Ru/W) dimeric units are common to both structures. While $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ is easily described as a layered structure, no layers are apparent in the structure of $Ba_5Ru_2 Cl_2 O_9$. The volumes per formula unit are 364 and 324 Å^3 for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ and $Ba_5Ru_2Cl_2O_9$, respectively. The larger volume for $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ can be at least partly attributed to the larger sizes of W^{6+} and Ru^{4+} present in $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ but not in $Ba_5Ru_2Cl_2O_9$. The (Ru/W)–(Ru/W) distance (2.872 Å) in $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ being longer than the Ru–Ru distance (2.726 Å) in

(M = Ru or W) octahedra are connected by double layers of Ba_2Cl_2 with Ba(1) as shown in Fig. 1c. The coordination polyhedron BaO_3Cl_4 around Ba(1) may be described as a distorted monocapped octahedron formed by three close O atoms, three more distant Cl atoms in planes parallel to (001), and a fourth Cl atom which caps one of the octahedron's faces.

Some of the 10-layer hexagonal perovskite-related compounds reported are $Ba_5RuTaCl_2O_9$ (5), $Ba_{10}Fe_8Pt_2Cl_2O_{25}$ (14), $Ba_5In_2Al_2ZrO_{13}$ (15), $Ba_5IrIn_2Al_2ClO_{13}$ (16), $10H–BaMnO_{3-x}$ (17), $Ba_5Fe_4NiO_{13.5}$ (18), $BaIr_{0.3}Co_{0.7}O_{2.83}$ (19), $Ba_5W_3Li_2O_{15}$ (20), $SrMn_{0.7}Fe_{0.3}O_{3-x}$ (21), $Ba_{10}Ta_{7.04}Ti_{1.2}O_{30}$ (22), and $Cs_4Ni_3CdF_{12}$ (23). The structures of these compounds are represented on (110) plane in Fig. 3, showing various mixed stacking sequences of AX_3, AX_2, and AX layers (Fig. 1) along the c axis. In Fig. 3, h and c are hexagonal and cubic AO_3 (A = Ba, Sr) or CsF_3 layers, respectively; h' is a hexagonal BaOCl, BaCl, or BaO layer, still termed as hexagonal because of its Ba position. $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ and $Ba_5RuTaCl_2O_9$ have the same stacking sequence $(h'hhhh')_2$ which consists of six BaO_3 and four BaCl layers as shown in Fig. 3a. These two compounds might be considered as isostructural with each other though they have different space groups, $P6_322$ and $P6_3/mmc$, respectively. This structure can be regarded as a 40% replacement of BaO_3 layers by BaCl layers in the 2H $BaNiO_3$ structure which has only hexagonal layers. Every adjacent two BaO_3 layers in five layers are replaced by double BaCl layers, leaving only two oxygen octahedral sites so that the M_2O_9 (M = Ru, Ta, or W) units are isolated from one
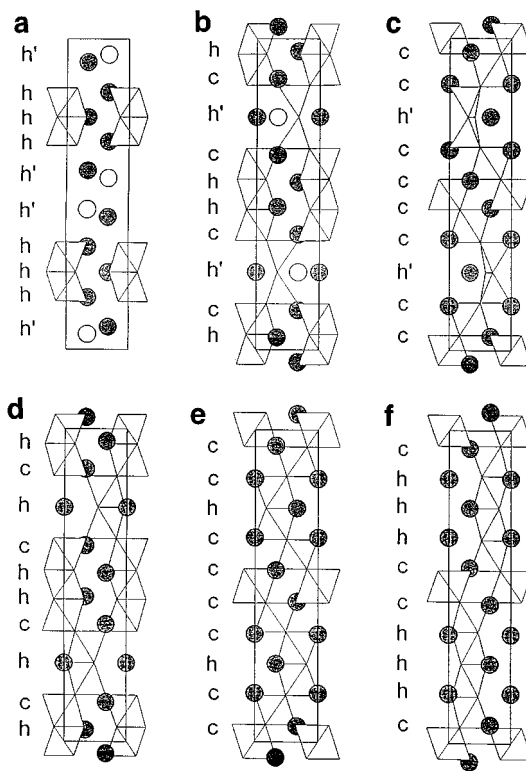

FIG. 3. Structural arrangements in the hexagonal (110) plane for various 10L perovskite-related structures: (a) $Ba_5Ru_{1.6}W_{0.4}Cl_2O_9$ and $Ba_5RuTaCl_2O_9$, (b) $Ba_{10}Fe_8Pt_2Cl_2O_{25}$, (c) $Ba_5In_2Al_2ZrO_{13}$, (d) 10H–$BaMnO_{3-x}$, $Ba_5Fe_4NiO_{13.5}$ and $BaIr_{0.3}Co_{0.7}O_{2.83}$, (e) $Ba_5W_3Li_2O_{15}$, $SrMn_{0.7}Fe_{0.3}O_{3-x}$, and $Ba_{10}Ta_{7.04}Ti_{1.2}O_{30}$, and (f) $Cs_4Ni_3CdF_{12}$. Shaded circles are Ba atoms and open circles are chlorine. Corners of the polyhedra are oxygen or fluorine, with each polyhedra occupied by small cations.
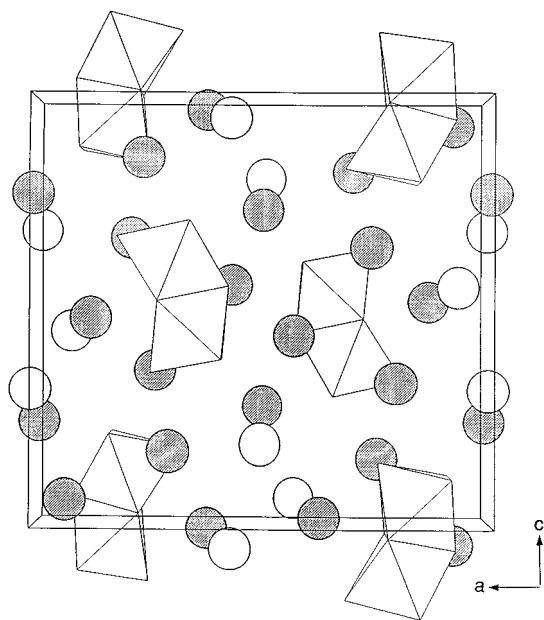
FIG. 4. Representation of the structure of $Ba_5Ru_2Cl_2O_9$ (5). Ru_2O_9 polyhedra are shown. Ba and Cl are represented as shaded and open circles, respectively.

$Ba_5Ru_2Cl_2O_9$ may also be a factor in the volume difference between the two compounds.

ACKNOWLEDGMENT

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