Supporting Information for:

<u>Ba4Ru3O10.2(OH)1.8</u>: a New Member of the Layered Hexagonal <u>Perovskite Family Crystallised from Water</u>

Craig I. Hiley, Martin R. Lees, David L. Hammond, Reza J. Kashtiban, Jeremy Sloan,

Ronald I. Smith and Richard I. Walton.

1. Further Experimental Details

Ba₄Ru₃O_{10.2}(OH)_{1.8} was prepared by hydrothermal synthesis. In a typical synthesis approximately 0.2 g (~1 mmol, 1 equivalent) of KRuO₄ (Alfa Aesar, 98%) and 0.34 g (~2 mmol, 2 equivalents) BaO₂ (Sigma, 98%) were added to 10 ml H₂O in a 23 ml Teflon-lined steel autoclave. After 5 minutes stirring, the autoclave was sealed and placed in a preheated fan oven at 200 °C for 24 hours. The liner was then cooled to room temperature, and the resulting silver-grey precipitate was recovered from a pale orange solution (indicative of a small amount of Ru^{6+}) by suction filtration. The solid was then washed with 10 ml 0.1 mol dm⁻³ hydrochloric acid to remove any solid Ba(OH)₂ and BaCO₃ byproducts, the presence of which were observed by powder X-ray diffraction (XRD) in early exploratory syntheses. Adding the stoichiometric ratio (1 KRuO₄:1.33 BaO₂) results in a mixed phase product of the target Ba₄Ru₃O_{10.2}(OH)_{1.8} perovskite and the previously reported Ba₂Ru₃O₉(OH).¹ Longer reactions (up to 1 month) did not yield any other crystalline products and did not noticeably alter the crystallite morphology (examined by scanning electron microscopy (SEM)). Reducing the reaction temperature to 125 °C causes a large proportion of ruthenium to remain in solution as evidenced by the orange colour of the filtrate and the solid product was BaRuO₄·H₂O.

X-ray absorption near edge structure XANES spectra were collected at Beamline B18, Diamond Light Source, U.K. Samples were diluted with polyethylene powder and pressed into pellets approximately 1 mm thick. Absorption data were collected in transmission mode. Spectra were normalised using ATHENA.²

Simultaneous thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectrometry (MS) were performed using a Mettler Toledo TGA/DSC 1-600 instrument with a Hiden HPR-20 QIC R&D specialist gas analysis system, a triple filter mass spectrometer with SEM detection on heating in nitrogen to 1200 °C at 10 °C min⁻¹.

Initial transmission electron microscopy (TEM) and electron diffraction measurements were performed in a JEOL 2100 instrument equipped with LaB₆ filament. The microstructure of the sample was analysed using a JEOL ARM200F TEM with a Schottky emitters. Scanning transmission electron microscopy (STEM) analysis on the ARM200F, with probe and image aberration CEOS correctors, was performed at 200 kV. HAADF STEM images were obtained using a JEOL ADF detector with a fine-imaging probe, at a probe current of approximately 23 pA with a convergence semi-angle of ~25 mrad and an inner angle of 45–50 mrad. The scanning rate of each image was typically 20 μ s per pixel and each image consists of 1024 by 1024 pixels.

2. Structural Solution and Refinement

After confirmation of sample purity and initial indexing from powder X-ray diffraction, timeof-flight powder neutron diffraction data were collected using the GEM diffractometer (ISIS Facility, UK), and structural solution and refinements were carried out using banks 3, 4 and 5 (average 2θ angles 35.0°, 63.3° and 91.4° respectively). An initial structural solution was carried out by a Monte Carlo optimisation in direct space using FOX³ in space group P1 to give a model with composition Ba₄Ru₃O₁₂. After development of this initial model, the ADDSYM algorithm in Platon⁴ was used to find two higher symmetry potential space groups. Following this, Rietveld refinement of each structural model was carried out in the GSAS suite,⁵ implemented using EXPGUI.⁶ Difference Fourier maps of the disordered model (see below) indicated points of negative nuclear density ~1 Å from an otherwise undercoordinated oxygen site, which was attributed to the presence of H. The occupancy of this site was refined to a value of 0.294(6); equivalent to 1.76(4) H per formula unit (3.52(8) H per unit cell). However, in order to create a fully coordinated oxygen site, an H occupancy of 0.5 was required. Since the sensitivity of the refinement to the H occupancy was unclear (due to the proximity of the H site to a partially occupied Ru site), several refinements with fixed H occupancies were carried out (Table S1). These show that the H occupancy is highly correlated to its thermal displacement parameter, U_{iso} and its coordinates. Deviation from the refined value leads to unphysical O-H bond lengths and thermal parameters, in addition to a worse fit to the data. As such, the refined occupancy was retained.

TABLE S1. Details from refinements of $Ba_4Ru_3O_{12}H_x$ ($0 \le x \le 6$) in disordered model ($P6_3/mmc$) against powder neutron diffraction.

H per unit cell (site occupancy)	χ^2	R_p / %	R_{wp} / %	0–H bond length / Å	H U _{iso} / Å ²
0 (0)	2.462	2.27	2.96	-	-
1 (0.0833)	2.158	2.13	2.79	1.22(1)	-0.18(2)
2 (0.1667)	2.042	2.05	2.69	1.21(2)	0.002(4)
3 (0.25)	1.984	2.02	2.65	1.18(1)	0.030(4)
4 (0.3333)	1.987	2.04	2.65	1.11(1)	0.074(5)
5 (0.4167)	2.025	2.10	2.68	1.11(1)	0.124(6)
6 (0.5)	2.066	2.11	2.71	1.05(1)	0.195(7)

Two initial structural models were developed: one in space group $P6_3mc$ with a vacant Ru site and another in space group $P6_3/mmc$ with a half-occupied Ru site with double the multiplicity of the vacant site in the previous model (due to the presence of an additional mirror plane parallel to the *ab* plane). Despite TEM suggesting the ordered model, the disordered fit offers a significantly better fit, with fewer refined parameters (Table S2). Furthermore the refined composition in the ordered model contains considerably (~60%) less H than found in the disordered model. Other analytical techniques (principally TGA) yield H content more consistent with the disordered model, suggesting that whilst ordered domains exist within the material, on average it contains disordered Ru- and H-containing octahedra (though each tetrameric chain contains one of each).

	Ordered (P6 ₃ mc)	Disordered (P6 ₃ /mmc)
χ^2	2.22	1.90
$R_{\rm p}$ (Total, Banks 3, 4 and 5)/%	2.43, 2.25, 2.43, 2.61	2.00, 1.85, 1.92, 2.24
R_{wp} (Total, Banks 3, 4, and 5)/%	2.80, 2.71, 2.62, 3.06	2.60, 2.40, 2.43, 2.90
Variables	77	66
Lattice Parameters / Å	<i>a</i> = 5.79905(8)	a = 5.79905(7)
	c = 18.7547(5)	c = 18.7562(5)
Refined composition	$Ba_4Ru_3O_{12}H_{1.11(3)}$	$Ba_4Ru_3O_{12}H_{1.76(4)}$
Ba1 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	0; 0; 0.010(1);	0; 0; 0;
U _{iso} /Ų; occupancy	0.010(1); 1	0.010(1); 1
Ba2 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	0; 0; 0.2535(4);	0; 0; 0.25;
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.008(1); 1	0.015(1); 1
Ba3 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	¹ ⁄3; ² ⁄3; 0.1308(4);	¹ ⁄ ₃ ; ² ⁄ ₃ ; 0.1280(2);
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.010(1); 1	0.0070(5); 1
Ba4 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	¹ / ₃ ; ² / ₃ ; 0.3802(4);	-
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.0030(8); 1	
Ru1 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	¹ ⁄3; ² ⁄3; 0.5751(3);	¹ ⁄3; ² ⁄3; 0.5584(1);
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.0097(7); 1	0.0159(4); 1
Ru2 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	¹ / ₃ ; ² / ₃ ; 0.8141(2);	¹ / ₃ ; ² / ₃ ; 0.8044(2);
$U_{\rm iso}/{\rm \AA^2}$; occupancy	0.0111(8); 1	0.0080(6); 0.5
Ru3 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	¹ ⁄3; ² ⁄3; 0.9564(3);	-
U _{iso} /Ų; occupancy	0.0123(8); 1	
01 x/a; y/b; z/c;	0.5033(3); 0.0067(7); 0.2596(3);	0.5045(3); 0.0090(6); ¼;
U _{iso} /Ų; occupancy	0.0150(4); 1	0.0151(4); 1
02 x/a; y/b; z/c;	0.5008(7); 0.002(1); 0.0119(3);	¹ ⁄ ₂ ; 0; 0;
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.0049(3); 1	0.0046(2); 1
03 x/a; y/b; z/c;	0.1774(4); 0.3547(8); 0.8896(2);	0.1751(2); 0.3502(4); 0.8778(1);
<i>U</i> _{iso} /Ų; occupancy	0.0162(5); 1	0.0129(2); 1
04 x/a; y/b; z/c;	0.1734(5); 0.347(1); 0.6347(2);	-
U _{iso} /Å ² ; occupancy	0.0075(3); 1	
H1 <i>x/a</i> ; <i>y/b</i> ; <i>z/c</i> ;	0.216(1); 0.432(3); 0.6812(6);	0.2349(8); 0.470(2); 0.294(6);
$U_{\rm iso}/{\rm \AA}^2$; occupancy	0.053(6); 0.37(1)	0.056(5); 0.294(6)

TABLE S2. Refinement details for the two crystallographic models refined against room temperature, time-of-flight powder neutron diffraction data collected on GEM (ISIS, UK) using banks 3, 4 and 5.



FIGURE S1. Comparison of ordered model (left) and disordered model (right), with barium atoms shown in orange, oxygen atoms in yellow, the partially occupied hydrogen site in red, fully occupied RuO_6 octahedra shown in green and O_6 octahedra containing either Ru or H shown in blue.

			Ordered (P6 ₃ mc)	Disordered (P6 ₃ /mmc)
Ba1		03	2.88(2)	2.889(1)
		02	2.900(8)	2.8995(1)
		04	2.92(2)	-
Ba2		04	2.829(7)	-
		01	2.902(2)	2.900(3)
		03	3.111(7)	2.973(2)
Ba3		02	2.793(8)	2.927(3)
		04	2.901(4)	-
		01	2.958(8)	2.862(4)
		03	-	2.903(2)
Ba4		01	2.834(8)	-
		03	2.907(5)	-
		02	2.979(9)	-
Ru1		04	1.958(6)	-
		03	-	1.990(3)
		02	2.045(8)	2.000(1)
Ru2		01	1.933(5)	1.922(3)
		03	2.111(5)	2.103(3)
Ru3		02	1.978(80	-
		03	2.006(5)	-
H1		04	0.97(1)	1.14(1)
TABLE S4.	. O-Ru-O b	ond angles.		
		6	Ordered (P6 ₃ mc)	Disordered (P6 ₃ /mmc)
Ru1	04	04	90.6(2)	-
	04	02	89.8(2)	-

TABLE S3. Bond distances in ordered and disordered models in Å.

			Ordered (P6 ₃ mc)	Disordered (P6 ₃ /mmc)
Ru1	04	04	90.6(2)	-
	04	02	89.8(2)	-
	04	02	179.6(3)	-
	02	02	89.8(2)	92.90(6)
	03	02	-	89.71(8)
	03	02	-	176.2(1)
	03	03	-	87.54(9)
Ru2	01	01	94.6(2)	94.4(1)
	01	03	92.3(2)	91.6(1)
	01	03	169.9(2)	171.2(2)
	03	03	80.0(2)	81.8(1)
Ru3	02	02	94.8(3)	-
	02	03	89.8(2)	-
	02	03	173.1(3)	-
	03	03	85.1(2)	-

The bond valence sum⁷ of an atom *i*, V_i , was calculated according to the equation:

$$V_i = \sum_j v_{ij}$$

where v_{ij} is the valence of a bond between atom *i* and *j*, defined as:

$$v_{ij} = \exp\left[\frac{R_{ij} - d_{ij}}{b}\right]$$
(2)

(1)

where R_{ij} is the 'bond valence parameter', d_{ij} is the length of the atoms' bond and *b* is a constant (0.37 Å). For Ru, the Ru(V) bond valence parameter was taken to be 1.888 Å, after Dussarrat *et al.*⁸



FIGURE S2. Ordered and disordered Rietveld fits to powder neutron diffraction data collected on GEM (Banks 3-5).

3. Elemental Analysis

Elemental analysis was performed by ICP-OES (Table S3), following digestion using HBr. In addition to confirming the Ba:Ru ratio, elemental analysis shows that no K (present in the synthesis from the KRuO₄ precursor) is incorporated into the product.

y 4 5 10.2 1 .8				
Metal	Measured Metal Content / %	Atomic Ratio		
Ru	29.03(3)	1		
Ва	52.3(3)	1.33(1)		
K	< 10 ppm	-		

TABLE S3. Measured metal content by mass in Ba₄Ru₃O_{10.2}(OH)_{1.8} and elemental ratios.

4. In situ Variable Temperature Powder XRD

In situ powder XRD data from $Ba_4Ru_3O_{10.2}(OH)_{1.8}$ were collected using a Bruker D8 Advance X-ray diffractometer operating with Cu K α radiation, equipped with a VÅNTEC-1 solid state detector and fitted with a Anton Parr XRK900 chemical reaction chamber to allow measurements to be made as a function of temperature. The furnace was heated at 10 °C min⁻¹ to the target temperature in increments of 100 °C. After 10 minutes of temperature equilibration a diffraction pattern was collected over the 2 θ range 10° - 70° in scans of ~1 hour.



FIGURE S3. Offset powder XRD patterns of $Ba_4Ru_3O_{10.2}(OH)_{1.8}$ heated in air *in situ*. RT = Room temperature.

XRD patterns from room temperature to 200 °C contain only Bragg peaks which can be indexed to the 8H-hexagonal perovksite (Figure S3). At 300 °C – 400 °C a transition occurs, evidenced by the appearance of peaks belonging to rutile RuO₂ coupled with the loss of some 8H perovskite peaks (e.g. peaks at $2\theta \sim 38^{\circ}$ Figure S3 inset). This temperature coincides with

the loss of water seen by TGA-MS (Figure 3(a)), demonstrating that the mass loss observed is indeed a due to the loss of structural hydroxide and not adsorbed water. Further heating the sample above 600 $^{\circ}$ C leads to the loss of RuO₂ Bragg reflections and the appearance of new peaks which could not be indexed to a single phase.

5. Magnetometry

Field cooled and zero-field cooled magnetic susceptibility data from a 24.674 mg powdered sample of Ba₄Ru₃O_{10.2}(OH)_{1.8} in a gel capsule were collected using a Quantum Design MPMS XL7 SQUID magnetometer in an applied field of 1000 Oe (Figure 4, Figure S4(a)). In the paramagnetic region ($250 \le T \le 400$ K) the reciprocal susceptibility, $1/\chi$, as function of temperature, *T*, could be fitted to a Curie-Weiss law (Figure S4(b)):

$$\chi = \frac{C}{T - \theta} \tag{3}$$

where *C* is the Curie constant, 1.22(2) emu K $\text{mol}_{\text{Ru}}^{-1}$ and θ is the Weiss temperature, -629.2(8) K. The effective moment, μ_{eff} per Ru is related to *C*:

$$C = \frac{N\mu_0\mu_{\rm eff}^2}{3k_B} \tag{4}$$

where N is the Avogadro constant, μ_0 is the permeability of free space, and k_B is the Boltzmann constant. μ_{eff} was found to be 3.13(1) μ_B .



FIGURE S4. (a) Field cooled (FC) and zero-field cooled (ZFC) molar susceptibility of $Ba_4Ru_3O_{10.2}(OH)_{1.8}$ and (b) reciprocal molar susceptibility as a function of temperature with a linear fit (orange) to the paramagnetic region (250 K – 400 K, green points).

The Ru^{4.75+} site was approximated to contain a mixture of Ru(IV) (spin, $S_{,} = 1$; spin only moment, $\mu_{,} = 2.83\mu_{\rm B}$) and Ru(V) (S = 3/2, $\mu_{S} = 3.87\mu_{\rm B}$) ions in a 3:1 ratio. The spin only moment, $\mu_{\rm average}$ of the mixed Ru(IV)/Ru(V) site was thus evaluated:

$$\mu_{average}^{2} = 0.25\mu_{Ru(IV)}^{2} + 0.75\mu_{Ru(V)}^{2}$$
(5)

to give a value of $3.64\mu_{\rm B}$.

6. Comparison With Other Ru-Containing 8H Hexagonal Perovskites

Ba₄Ru₃O_{10.2}(OH)_{1.8} has a unique (*chhh*)₂ stacking sequence resulting in tetrads of facesharing octahedra (Figure S5). However, due to the 50% occupancy of the Ru2 site, each tetrad contains only one Ru-Ru bond (Figure 1), as typified by other 8H perovskites (Figure S6). Ba₄Ru₃NaO₁₂ has the typical 8H hexagonal perovskite stacking sequence (ccch)₂,⁹ Figure S6(a), but like Ba₄Ru₃O_{10.2}(OH)_{1.8} it contains [Ru₂O₉] dimeric units corner-linked at one end to a RuO₆ octahedron (assuming that the Ru2 site occupancies order locally in Ba₄Ru₃O_{10.2}(OH)_{1.8}). In Ba₄Ru₃NaO₁₂, a Na sits on an octahedral site corner linked to six Ru octahedra (Figure S6(a)). This may be compared to the Ba₄Ru₃O_{10.2}(OH)_{1.8}, where an otherwise vacant O₆ octahedron is occupied by 1.8 hydroxide groups. Structurally, Ba₄Ru₃O_{10.2}(OH)_{1.8} can also be compared to Sr₄Ru_{3.05}O₁₂ and Ba₅Ru₂O₁₀. Sr₄Ru_{3.05}O₁₂ also contains partially occupied Ru sites, but the stacking sequence $(ccch)_2$ means that there are no Ru-Ru bonds formed,¹⁰ Figure S6(b). This can be rationalised by the fact that the small distance between SrO₃ layers (~2.1 Å) would lead to an unfavourably short Ru–Ru distance (cf. in Ba₄Ru₃O_{10.2}(OH)_{1.8} the distance between BaO₃ layers is ~2.3 Å). Ba₅Ru₂O₁₀ adopts a pseudo-8H hexagonal perovskite cell with one Ba₂O layer for every 3 [BaO₃] layers, leading to isolated [Ru₂O₉] dimers (Figure S6(c)).¹¹ Like Ba₄Ru₃O_{10.2}(OH)_{1.8}, Ba₅Ru₂O₁₀ has columns consisting solely of Ba ions with coordinates (0, 0, z).



FIGURE S5. Structure of $Ba_4Ru_3O_{10.2}(OH)_{1.8}$ (disordered model) with stacking sequence and RuO_6 octahedra shown on right with Ba and H ions omitted for clarity (fully occupied octahedra shown in green, partially occupied octahedra shown in dark blue).



FIGURE S6. Structures of (a) $Ba_4Ru_3NaO_{12}$,⁹ (b) $Sr_4Ru_{3.05}O_{12}^{10}$ and (c) $Ba_5Ru_2O_{10}^{11}$ Stacking sequences of RuO₆ octahedra shown on right, with counter-ions omitted for clarity. Ba shown in orange, O shown in yellow, Na shown in purple, Sr shown in red, fully occupied Ru sites shown in green and partially occupied Ru sites shown in light blue.

7. <u>References</u>

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