Ba₄Ru₃O₁₀.₂(OH)₁.₈: a new member of the layered hexagonal perovskite family crystallised from water†

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A new barium ruthenium oxyhydroxide Ba₄Ru₃O₁₀.₂(OH)₁.₈ crystallises under hydrothermal conditions at 200 °C: powder neutron diffraction data show it adopts an 8H hexagonal perovskite structure with a new stacking sequence, while high resolution electron microscopy reveals regions of ordered layers of vacant Ru sites, and magnetometry shows antiferromagnetism with $T_N = 200(5)$ K.

When preparing new complex ruthenates, highly oxidising environments are often required to access oxidation states of Ru higher than +4, and, indeed, to prevent reduction to Ru metal, however high oxygen pressure at elevated temperatures can lead to formation and volatilisation of considerable quantities of RuVIIIO₄ making control of composition challenging.17 Low temperature synthesis techniques that can stabilise highly oxidised Ru, such as molten salt flux crystal growth18 and hydrothermal crystallisation,19 are therefore attractive propositions for the isolation of complex ruthenium oxides. Recently we reported the unique structure of Ba₂Ru₃O₉(OH), an oxyhydroxide prepared by a hydrothermal reaction.20 We demonstrate herein that by simply altering the ratio of the two reagents, this synthetic procedure yields a structurally unrelated, 8H-hexagonal perovskite phase Ba₄Ru₃O₁₀.₂(OH)₁.₈, which contains a new stacking sequence, and regions of vacancy ordering.

Phase-pure Ba₄Ru₃O₁₀.₂(OH)₁.₈ was prepared by the hydrothermal reaction of Ba₂O₃ and KRuO₄ at 200 °C for 24 hours in a 2:1 ratio (i.e. an excess of Ba). A silver-grey powder was recovered by suction filtration and washed with 0.1 M HCl to remove any Ba(OH)₂ or BaCO₃ byproducts, as we found necessary in earlier work on other oxides.20 The powder X-ray diffraction pattern of the new phase was indexed to a hexagonal unit cell with lattice parameters $a = 5.79905(7)$ Å, $c = 18.7562(5)$ Å, similar to those of the barium ruthenate 8H-perovskites Ba₄Ru₃NaO₁₂15 and Ba₄Ru₃O₁₉21 ICP measurements give a Ba:Ru 1.33(1):1 ratio, and no K was detected (detection limit 10 ppm). A structural solution was initially found by a Monte Carlo optimisation in direct space using the software FOX,22 and a Rietveld refinement of this structure against time-of-flight powder neutron diffraction data (PND, GEM, ISIS; Fig. 1(a)) was carried out in GSAS implemented using EXPGUIL.24 The best fit was obtained in the space group $P6_3/mmc$.

The structure of Ba₄Ru₃O₁₀.₂(OH)₁.₈ consists of an eight-layer stacking sequence, (chhh)₁₂ (Fig. 2(a)), with chains of four face-sharing octahedral sites (Table 1 and Fig. 1(b)). However, the Ru₂ site, which lies within the two central octahedral sites of the quasitetrameric chains (Fig. 1(c)), is only half-occupied. Examination of high angle annular dark field images obtained in scanning
transmission electron microscopy (HAADF STEM) shows that regions of the sample show extensive vacancy ordering (Fig. 2(b)). A refinement to the powder neutron diffraction using a model in the lower symmetry space group $P6_3/mmc$ with ordered vacant sites yields a poorer fit to the data (see ESI†), suggesting that although vacancies may order in domains on the nanoscale, on average the Ru2 site is randomly occupied. Whilst the Ru1 site sits on the highly symmetrical octahedral site (Ru–O bond distances in the range 1.990(2)–2.000(1) Å), the Ru2 sits off-centre in an octahedral site, generating three long (2.103(3) Å) and three short (1.922(4) Å) Ru–O distances (Fig. 1(c)). This gives a Ru1–Ru2 bond distance of 2.574(5) Å, a value consistent with an average Ru oxidation state of +4.5–4.75 in barium ruthenates, using the correlation established by Kimber et al. in their study of 6H perovskites Ba$_3$ARu$_2$O$_9$. A second consequence of the Ru2 site asymmetry is the unphysically short distance between neighbouring Ru2 sites of 2.041(6) Å, indicating that whilst there is no preferential ordering within the quasi-tetrameric chains, there must be exactly one octahedral vacancy per chain. The structure can be compared to the structure adopted in another ruthenate 8H-perovskite, Sr$_4$Ru$_3.05$O$_{12}$, which also contains partially occupied face-sharing Ru octahedra and, due to the $(ccch)_2$ stacking sequence, also has no Ru–Ru bonding (see ESI†).

| Atom | $x/a$ | $y/b$ | $z/c$ | Occupancy | ADP/Å$^2$ | BVS |
|------|-------|-------|-------|-----------|----------|-----|
| Ba1  | 0     | 0     | 0     | 1         | 0.010(1) | 2.34|
| Ba2  | 0     | 0     | 1/4   | 1         | 0.015(1) | 2.10|
| Ba3  | 1/3   | 2/3   | 0.1280(2) | 1       | 0.0070(5) | 2.32 |
| Ru1  | 1/3   | 2/3   | 0.5584(1) | 1       | 0.0159(4) | 4.39 |
| Ru2  | 1/3   | 2/3   | 0.8044(2) | 0.5     | 0.0080(6) | 4.41 |
| O1   | 0.5045(3) | 0.0090(6) | 1/4   | 1         | 0.0151(4) | 1.72 |
| O2   | 1/2   | 0     | 0     | 1         | 0.0046(2) | 2.22 |
| O3   | 0.1751(2) | 0.3502(4) | 0.8778(1) | 1       | 0.0129(2) | 1.50/2.06/2.09* |

H1 $0.2349(8)$ $0.470(2)$ $0.6741(6)$ $0.294(6)$ $0.056(5)$ $0.59$

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**Fig. 1** (a) Rietveld fit to powder neutron diffraction (GEM Bank 4) with scanning electron micrograph inset. (b) Representation of the unit cell of Ba$_4$Ru$_3$O$_{10.24}$OH$_{1.76}$ with Ba atoms in orange, oxygen atoms in yellow, fully occupied octahedral sites in green and half-occupied octahedral sites in blue. (c) One chain of four octahedral Ru sites with refined bond lengths labelled. H sites in red.

**Table 1** Final refined atomic parameters for Ba$_4$Ru$_3$O$_{10.24}$OH$_{1.76}$. Space group $P6_3/mmc$: $a = 5.79905(7)$ Å, $c = 18.7562(5)$ Å. Refined from PND, $\chi^2 = 1.92$, $R_p = 2.01\%$, $R_{wp} = 2.61\%$. BVS: bond valence sum *O3 BVS dependent on local environment. See text and ESI for further details.

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**Fig. 2** (a) HAADF STEM image of Ba$_4$Ru$_3$O$_{10.24}$OH$_{1.76}$ with inset electron diffraction pattern. (b) Comparison of simulated HAADF images from disordered and ordered Ru vacancies to an experimental HAADF image obtained from a [110] projection. In the disordered simulation partially occupied Ru positions (Ru2') are indicated by a loop in the simulated image. The diffuse red arrows in the experimental HAADF indicate that these are absent observable by comparison with the ‘ordered’ simulation.
Examination of difference Fourier maps revealed a site containing negative scattering density within these partially occupied octahedra, approximately 1 Å from the O3 site (which is otherwise under-coordinated due to Ru vacancies, Table 1), strongly suggesting the presence of H. This 12-fold site has a refined occupancy of 0.294(6), equivalent to 1.76(4) H per formula unit, giving the refined empirical formula Ba$_4$Ru$_3$O$_{10.24(4)}$(OH)$_{1.76(4)}$ and an O–H bond length of 1.14(1) Å (Fig. 1(c)). The O3 bond valence sum has a range of values, depending on its local environment. When it is bonded to either a Ru$_2$ or H atom the value is close to the expected value of 2 (2.06 and 2.09 respectively). However, in the refined model approximately one in six oxygen atoms is under-coordinated, giving a bond valence sum of 1.50. The high correlation of the H1 and Ru2 atomic parameters led us to consider the possibility that the H1 occupancy is truly 0.5, which would result in O3 BVS much closer to 2. However, refinements of fixed H1 occupancies show a poorer fit to the data, with unphysical refined values for Ru2 and H1 atomic displacement parameters (see ESI†).

Thermogravimetric analysis (TGA) under a N$_2$ gas flow combined with mass spectrometry (MS) of the evolved gas confirms the presence of structural hydroxide: after a small initial loss of surface adsorbed water from the ~10 μm crystallites (Fig. 1(a)), a mass loss of 1.55% occurs at ~300 °C (Fig. 1(a)), with MS allowing this to be attributed to the loss of H$_2$O due to the loss of the 1.80 hydroxide groups per formula unit, consistent with the structural model refined from powder neutron diffraction. This also correlates with in situ X-ray thermodiffraction data, which show a structural transition at around 300 °C, which must be brought about by dehydroxylation (see ESI†).

Structural hydroxide has been previously observed in metal-deficient perovskites, although previously reported examples are typically ReO$_3$-type structures where the H atoms project into the voids left by unoccupied A-sites. These are significantly larger than the B-site voids observed in Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$, explaining the partial occupancy of the H-site (1.8 H per vacant octahedron, compared with 3 in ReO$_3$-type hydroxides). Hydroxylation may be driven by both the highly basic, oxidising synthesis conditions and the unique packing sequence observed in this hexagonal perovskite which necessitates Ru deficiency for steric reasons, leading to dehydroxylation of otherwise under-coordinated oxide.

From the refined chemical formula, an average Ru oxidation state of +4.75 is deduced. Ru bond valence sums suggest a similar oxidation state of +4.40, with little difference between the two crystallographically distinct sites despite the large asymmetry seen in Ru2 (Table 1). X-ray absorption near edge structure (XANES) spectroscopy experiments were undertaken for further evaluation of the Ru oxidation state, with the Ru K-edge XANES spectrum of the Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$ compared to spectra of oxides of known oxidation state, Fig. 3(b) (see ESI† for full spectra). Although Ru K-edge XANES has previously been shown to be sensitive to the Ru average oxidation state, significant core-hole broadening at the Ru K-edge introduces large uncertainty in the measured edge position, and differences in local environment are also known to affect edge position. Despite this, the Ru K-edge position of the standards was found to have a linear relationship with oxidation state, with the Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$ Ru K-edge position consistent with Ru oxidation state between 4.70 and 5 (Fig. 3(b)).

A Curie–Weiss law fit to the magnetic susceptibility versus temperature data in the paramagnetic region (250 < T < 400 K), yields an effective Ru moment, μ$_{\text{eff}}$, of 3.13 μ$_{\text{B}}$ and a Weiss temperature, θ, of −629.2(8) K, indicative of significant antiferromagnetic correlations, Fig. 4. The Ru average valence state of +4.75 suggests a mixture of Ru$^{4+}$ (t$_{2g}^6$) and Ru$^{5+}$ (t$_{2g}^3$) ions with spin-only moments of 2.83 μ$_{\text{B}}$ and 3.87 μ$_{\text{B}}$ respectively, which would give an average spin-only moment of 3.64 μ$_{\text{B}}$ in Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$. The difference between the spin-only value and μ$_{\text{eff}}$ can be explained by a combination of crystalline field and spin–orbit coupling effects, commonly observed in Ru(IV) oxides.

![Fig. 3](image-url)  

(a) TGA-DSC under N$_2$ flow (heating rate 10 °C min$^{-1}$) with in situ MS signals associated with H$_2$O (m/z = 18) and O$_2$ (m/z = 32, multiplied by 5 for clarity). (b) Normalised Ru K-edge XANES spectrum of Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$ compared to reference spectra of Ru$^{4+}$O$_2$, La$_{0.86}$Ru$_{4.70}$O$_{12}$ and SrRu$_{10.2}$O$_{6}$. Inset shows a plot of Ru average oxidation state vs. edge position (measured where normalised absorption = 0.5). Black points correspond to reference samples, with a linear fit (blue, 0.5 eV wide, see text) which was then used to infer an average oxidation state from the Ba$_4$Ru$_3$O$_{10.2}$ (OH)$_{1.6}$ (red point). Error bars were estimated from the core-hole broadening.
The system orders magnetically at $T_N = 200(5)$ K. A clear change in $d\chi_p/dT$ that coincides with the minimum in the zero-field-cooled-warming $\chi(T)$ data may indicate a spin reorientation. At 5 K, the magnetisation increases almost linearly with applied field curve, with a moment of just 0.082(1) $\mu_B$ per Ru atom at 70 kOe indicating that the moments are principally aligned antiferromagnetically. A hysteresis in the $\chi(T)$ and $M(H)$ curves only seen below $T_N$ reflects a small net magnetic moment and suggests that there may be a slight canting or a ferrimagnetic component to the spin arrangement at low temperature. A $|\theta|/T_N$ ratio of over 3, although still smaller than for some other Ru oxides, reveals that in Ba$_4$Ru$_3$O$_{10.2}$(OH)$_{1.8}$ there is not a simple relationship between $\theta$ and $T_N$. Similar behaviour in other Ru oxides has been rationalised by considering the variation in the strength of the transfer energy and a crossover from localised to itinerant electrons.

In summary, we have reported the hydrothermal preparation of a complex barium ruthenium oxyhydroxide using just two reagents and avoiding the presence of a second, competing phase. This illustrates how solution chemistry can be utilised to exert a high degree of control of both crystal structure and oxidation state in the solid state for 4d elements that are easily reduced to the elemental state under other synthesis conditions typically used. The use of a metal peroxide as a reagent provides a reactive metal source, and has potential in the discovery of other new phases under mild reaction conditions. Ba$_4$Ru$_3$O$_{10.2}$(OH)$_{1.8}$ is shown to be thermally stable, with a structural transition and loss of hydroxide occurring at temperatures as low as 300°C, suggesting it would be impossible to prepare by conventional solid-state synthesis. The hexagonal perovskite-type structure with hydroxide ions found close to vacant octahedral B-sites is a highly unusual (if not unique) H-environment in oxide chemistry. It may be noted that another hexagonal perovskite, Sr$_3$Ru$_2$O$_9$, previously reported to be synthesised under hydrothermal conditions (at 500°C), contains partially occupied B-site octahedral sites but was characterised only by X-ray diffraction; the presence of H would be undetectable by this method, and that phase could potentially be another example of a ruthenium oxyhydroxide. Our work suggests that the oxyhydroxide chemistry of 4d transition metal could be a fruitful place to discover materials with new structures and interesting magnetic and electronic properties, especially when mild solution synthesis allows access to phases not accessible at high temperatures.

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