Ruthenium(V) Oxides from Low-Temperature Hydrothermal Synthesis**

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Abstract: Low-temperature (200°C) hydrothermal synthesis of the ruthenium oxides Ca\textsubscript{2}Ru\textsubscript{3}O\textsubscript{9}(OH), SrRu\textsubscript{2}O\textsubscript{7}, and Ba\textsubscript{2}Ru\textsubscript{3}O\textsubscript{9}(OH) is reported. Ca\textsubscript{1.5}Ru\textsubscript{2}O\textsubscript{7} is a defective pyrochlore containing Ru\textsuperscript{IV}O\textsubscript{6} units; SrRu\textsubscript{2}O\textsubscript{7} is a layered Ru\textsuperscript{V} oxide with a PbSb\textsubscript{2}O\textsubscript{6} structure, whilst Ba\textsubscript{2}Ru\textsubscript{3}O\textsubscript{9}(OH) has a previously unreported structure type with orthorhombic symmetry solved from synchrotron X-ray and neutron powder diffraction. SrRu\textsubscript{2}O\textsubscript{7} exhibits unusually high-temperature magnetic order, with antiferromagnetism persisting to at least 500 K, and refinement using room temperature neutron powder diffraction data provides the magnetic structure. All three ruthenates are metastable and readily collapse to mixtures of other oxides upon heating in air at temperatures around 300–500°C, suggesting they would be difficult, if not impossible, to isolate under conventional high-temperature solid-state synthesis conditions.

Oxides of ruthenium find use in topical areas of electrocatalysis for water oxidation and reduction,[1–3] in heterogeneous catalysis,[4] and the magnetic properties of 4d and 5d metal oxides are more generally the focus of much current attention because of their distinct phenomena arising from strong spin–orbit coupling not seen in 3d metal oxides.[5] The majority of oxides of ruthenium contain Ru\textsuperscript{V}, and isolation of the relatively unstable oxidation states +5 or higher typically requires highly oxidizing synthesis conditions, such as oxygen pressure.[6–9] As with many multi-element oxides, synthesis is dominated by the use of high temperature (>1200°C), and this means that usually only the most thermodynamically stable compounds are isolated.[10] Thus potentially large numbers of metastable oxide phases remain undiscovered, particularly for the 4d and 5d transition elements whose chemistry is less explored than the first-row elements, and for which the use of mild reaction conditions may allow access to new phases.[11,12] A range of complex ruthenium oxides containing Ca, Sr, or Ba have been reported and are of interest for their diverse and unusual magnetic and electronic properties. For example, SrRuO\textsubscript{3} is a notable example of a Cu-free high temperature superconductor.[13] whilst SrRuO\textsubscript{4} is both a metallic conductor and ferromagnetic.[14,15] Munenaka and Sato previously reported the high temperature (600°C) hydrothermal synthesis of the Ru\textsuperscript{V} pyrochlore Ca\textsubscript{2}Ru\textsubscript{3}O\textsubscript{7} which exhibits magnetic properties of a spin-glass.[16] Compared to traditional, solid-state techniques, hydrothermal synthesis generally utilizes much lower temperatures, to allow metastable compounds, potentially containing unusual oxidation states of metals, to be prepared.[17] In previous work we considered the formation of iridium oxides by direct crystallization from aqueous solution at temperatures less than 250°C.[19,20] Herein we report details of the synthesis and characterization of three previously unreported Ru\textsuperscript{V} containing oxides. They are prepared under highly oxidizing aqueous conditions by the hydrothermal reaction of K\textsubscript{2}Ru\textsubscript{4}O\textsubscript{7} and an alkaline earth metal peroxide, MO\textsubscript{2} (M = Ca, Sr, Ba) at 200°C (see the Experimental Section). The novelty of our approach lies in its simplicity: only two inorganic precursors are used, in stoichiometric proportions, with no additional mineralizers or pH modifiers (unlike many other hydrothermal crystallizations), and this allows reproducible formation of highly crystalline phases. Furthermore the temperatures used are significantly lower than those used in other “soft chemical” synthesis of ruthenates; in molten hydroxide or carbonate fluxes, for example, temperatures above 600°C are reported to bring about crystallization.[21,22]

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The hydrothermal reaction between CaO₂ and KRuO₄ forms a pyrochlore,[23] space group Fd3m, a = 10.1997(1) Å (Figure 1), with a composition of Ca₁₋₅Ru₂O₇ derived from Rietveld refinements using neutron time-of-flight powder diffraction data (Supporting Information, Figure S2). Elemental analysis using ICP-OES confirms a Ca to Ru ratio of 0.75:1. Such a defective pyrochlore structure is not without precedent: for example several A(BB₃)O₆ pyrochlores with half occupied A-site and a mixed-metal B-site have been reported.[24] The absence of A-site water or hydroxide for the calcium ruthenate was confirmed by IR spectroscopy and thermogravimetric analysis (TGA; Supporting Information, Figures S1 and S7). Furthermore, there is no indication of any oxide vacancies in the structure from the refinement using powder neutron diffraction, and therefore to achieve charge balance we assign a mixed (V,VI) oxidation state of Ru. Ru K-edge X-ray absorption near-edge spectroscopy, XANES, (Figure 2) confirms an average oxidation state of close to 5.5. Bond valence calculations[25] using a bond valence parameter for Ru⁵⁺ derived by Dussarrat et al.[10] yield a Ru oxidation state of 5.19. Addition of excess CaO₂ to the hydrothermal synthesis does not alter the composition of the pyrochlore and instead forms Ca(OH)₂ as a by-product. Upon heating in air, in situ powder X-ray diffraction (XRD) and TGA reveals that at temperatures as low as 300 °C, phase separation begins to occur with the appearance of RuO₂ leading to a mixture of RuO₂ and the stoichiometric rutile RuO₂ with complete reduction of the ruthenium(V) to Ru⁴⁺.

The hydrothermal reaction of SrO₂ and two equivalents of KRuO₄ yields phase-pure, hexagonal plates of Sr₂Ru₂O₆ (Figure 3c). Sr₂Ru₂O₆ adopts the hexagonal lead antimonate structure (PbSb₂O₆, P31m, a = 5.20573(3), c = 5.23454(7) Å), consisting of alternating layers of edge-sharing RuO₆ octahedra and interlayered Sr⁴⁺ ions that are also octahedrally coordinated (Figure 3a,b). Sr₂Ru₂O₆ is a rare example of a PbSb₂O₆ structure type that contains a magnetic transition-metal ion, the only other known examples being UM₄O₁₂ (M = Cr, V)[26] and PdAs₂O₆.[27] Ru K-edge XANES proves the average oxidation state of 5 (Figure 2), which is also confirmed by its bond valence sum (5.17). Room-temperature neutron diffraction data (Figure 4) reveals several Bragg peaks not seen in the powder XRD pattern, which can be explained by magnetic scattering of an antiferromagnetic array of Ru⁵⁺ centers. The magnetic scattering can be indexed to a hexagonal unit cell with lattice parameters a = 5.20573(3), c = 10.46908(14) Å in the space group, P31c (that is, doubled along c) with the Ru atoms antiferromagnetically coupled both in the ab plane (intra-layer) and parallel to the c-axis (inter-layer; Figure 4, inset). The magnetic moment is along the c direction and has a refined magnitude of 2.29 μB. This value is very close to the value previously reported for Ru⁵⁺, 2.43–2.54 μB in a doped double perovskite[28] and is comparable to the moment reported for the isoelectronic, octahedral Tc⁴⁺ in the perovskite SrTcO₃ (1.87 μB at room temperature).[29] These moments are both smaller than the spin-only value, which may be due to a large degree of covalency in M–O bonds for 4d metals.[30] Both Sr₂Ru₂O₆ and Sr₀₅Ru₀₄ exhibit magnetic order above room temperature and for Sr₀₅Ru₀₄ electronic structure calculations revealed this is due to the proximity of the half-filled t₂g shells to an itinerant-to-localized transition.[31] In situ powder XRD upon heating in air shows that at around 400 °C Sr₀₅Ru₀₄ decomposes to Sr₂Ru₂O₆ and RuO₂ (Supporting Information, Figure S8).

A 2:3 molar ratio of BaO₂ and KRuO₄ reacts under hydrothermal conditions at 200 °C to give a phase-pure sample of the new phase Ba₄Ru₃O₁₂(OH) as plate-like crystallites. This was indexed to the orthorhombic space group P2₁2₁2₁, a = 12.19451(1), b = 9.87825(1), and c = 7.05847(1) Å (Figure 5a) from synchrotron radiation powder XRD. Figure 6 shows the refined crystal structure,
solved initially by direct methods and refined against both powder XRD and powder neutron diffraction data (Figure 5b). It can be viewed as corrugated layers of edge- and corner-sharing RuO$_6$ octahedra with Ba$^{2+}$ and H$^+$ ions projecting into the space between the layers. Its structure can be compared to Ba$_4$Ru$_3$O$_{10}$,$^{[32]}$ an orthorhombic barium ruthenate that also consists of layers of RuO$_6$ quasi trimeric units interconnected in a corner-sharing manner. Whilst in Ba$_4$Ru$_3$O$_{10}$ these trimers are face-sharing and link to each other at one vertex to form a checkered structure, in Ba$_2$Ru$_3$O$_9$(OH) the octahedra are part of edge-sharing trimers, and one octahedron from a trimer corner-shares with two octahedra in its neighboring trimer. Ru K-edge XANES spectroscopy confirms an average oxidation state of close to $+5$, Figure 2, while bond valence sums give Ru oxidation states of 4.85, 5.18, and 5.10 for each of the three crystallographic Ru sites. The thermal decomposition of Ba$_2$Ru$_3$O$_9$(OH) to BaRuO$_3$ and RuO$_2$ occurs at around 500°C, as seen by in situ powder XRD (Supporting Information, Figure S10).

The magnetic properties of the new ruthenates were studied. The temperature dependence of the magnetic

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![Figure 3](image3.png)

**Figure 3.** a) The structure of SrRu$_2$O$_6$, as viewed in the $ab$ plane; b) a representation showing the layered structure with green RuO$_6$ octahedra and red Sr$^{2+}$ ions; c) a scanning electron micrograph of SrRu$_2$O$_6$ crystals.

![Figure 4](image4.png)

**Figure 4.** Rietveld refinement of the nuclear and magnetic structure from room temperature neutron diffraction data (GEM, Bank 3, mean scattering angle $2\theta = 34.96^\circ$) of SrRu$_2$O$_6$ with the magnetic contribution offset below. Tick marks denote positions of nuclear ($P\bar{3}1m$, red) and magnetic ($P\bar{3}1c$, green) Bragg reflections. Inset: the antiferromagnetic ordering of Ru atoms.

![Figure 5](image5.png)

**Figure 5.** Rietveld refinements of Ba$_2$Ru$_3$O$_9$(OH) using room temperature a) synchrotron XRD ($\lambda = 0.827154$ Å) and b) neutron diffraction data (GEM, Bank 3, mean scattering angle $2\theta = 34.96^\circ$). Tick marks denote positions of expected reflections for space group $P2_12_12_1$, $a = 12.19451(1)$, $b = 9.87825(1)$, and $c = 7.05847(1)$ Å. Inset: a scanning electron micrograph of rhombohedral Ba$_2$Ru$_3$O$_9$(OH) crystals.

![Figure 6](image6.png)

**Figure 6.** a) Structure of Ba$_2$Ru$_3$O$_9$(OH) viewed along the $c$-direction, with Ba atoms in orange, green RuO$_6$ octahedra, and H atoms in red. b) One layer of RuO$_6$ octahedra viewed along the $a$-direction.
susceptibility $\chi$ of Ca$_{1.5}$Ru$_2$O$_7$ (Figure 7a) is indicative of magnetic frustration at 25 K, similar to that previously reported for Ca$_2$Ru$_2$O$_7$.[16] An additional anomaly at about 53 K corresponds to the onset of hysteresis, indicative of possible spin glass-like behavior; this is supported by heat capacity measurements that show no phase transitions over these temperatures (Supporting Information, Figure S14). At temperatures above this transition the field-cooled (FC) susceptibility can be modeled using the Curie–Weiss law with an added temperature independent term, $\chi_0$ and a Weiss temperature, $\theta$, of $-13(2)$ K, indicative of antiferromagnetic correlations. The observed moment $\mu$ per Ru is 0.36 $\mu_B$ which is identical to the reported Ru moment for Ca$_2$Ru$_2$O$_7$,[16] but an order of magnitude smaller than the spin-only value for $d^3$ or $d^4$ metal ions, 3.87 and 2.83 $\mu_B$, respectively. SrRu$_2$O$_4$ shows no clear transition temperature up to 500 K (Figure 7b; the sample decomposition makes susceptibility measurements at higher temperatures problematic), indicating that antiferromagnetic order persists well above room temperature. Furthermore, the susceptibility does not appear to exhibit a paramagnetic temperature dependence and there is a slight upturn at elevated temperatures, further indicating that it is antiferromagnetically ordered. The small upturn in susceptibility upon cooling to low temperature, beginning at 70 K, may be assigned to uncompensated spins, or due to impurity.

**Experimental Section**

In a typical synthesis, KRuO$_4$ (1 mmol, Alfa Aesar, 98 %) and the appropriate amount of MO$_2$ (M = Ca, Sr, Ba; Sigma; 75%, 98%, 95 % respectively) were added to distilled water (10 mL). The mixtures were sealed in 23 mL Teflon-lined steel autoclaves and then cooled and the resulting precipitates were recovered by suction filtration and washed with dilute HCl, distilled water, and acetone to facilitate drying. Synchrotron powder XRD data were collected using beamline I11,[33] at Diamond Light Source, U.K, using an X-ray wavelength of 0.827154 Å. Time-of-flight neutron powder diffraction experiments were carried out on the GEM instrument,[34] at ISIS, U.K, from powdered samples in a 6 mm diameter cylindrical can made of vanadium. Structural refinement from powder diffraction data was performed using the GSAS suite of software.[35] The initial structural model for Ba$_2$Ru$_2$O$_6$(OH) was obtained using direct methods in the program FOX.[36] Fullprof[37] was used to fit the magnetic Bragg reflections of SrRu$_2$O$_4$. Ru K-edge X-ray absorption spectra were collected on beamline B18,[38] at Diamond Light Source, U.K. Samples were diluted with polyethylene powder and pressed into pellets approximately 1 mm thick. Data were collected in transmission mode and spectra were normalized using ATHENA.[39] DC