A new route to pentavalent post-perovskite

Wilson A. Crichton*†, Kirill V. Yusenko‡, Sephira Riva‡, Francesco Mazzali‡ and Serena Margadonna*‡

†ESRF – The European Synchrotron, 71 avenue des Martyrs, Grenoble 38000, France.
‡College of Engineering, Swansea University, Bay Campus, SA1 8EN, Swansea, UK.

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Supporting Information Placeholder

ABSTRACT: Two different high pressure and temperature synthetic routes have been used to produce the second-only known pentavalent CaIrO$_3$-type structure. Post-perovskite NaOsO$_3$ has been prepared from GdFeO$_3$-type perovskite NaOsO$_3$ at 16 GPa and 1135 K it has also been synthesized at the considerably lower pressure of 6 GPa and 1100 K from a precursor of hexavalent Na$_2$OsO$_6$, and nominally pentavalent K$_3$BiO$_2$-like phases. The latter synthetic pathway offers a new lower pressure route to the post-perovskite form – one which completely foregoes any perovskite precursor or intermediate. This work suggests that post-perovskite can be obtained in other compounds and chemistries where generalized rules based on the perovskite structure may not apply, or where no perovskite is known. One more obvious consequence of our second route is that perovskite formation may even mask and hinder other less extreme chemical pathways to post-perovskite phases.

The recent identification of a perovskite (pv) phase in NaOsO$_3$ has generated quite some interest as it displays a continuous metal insulator transition driven by 3D antiferromagnetic order. 1-5,8 Similarly, a very significant body of work now exists for the synthesis of CaIrO$_3$-type post-perovskite (ppv) phases in fluorides and oxides, the most pertinent to this work is NaIrO$_3$, which is not known as a perovskite, or any other pentavalent form, but it is the sole pentavalent ppv reported to date. 3,7 Pentavalent KIrO$_3$ and KBiO$_3$ share the K$_3$BiO$_2$-type structure, while NaBiO$_3$ is an ilmenite 10 and NaSbO$_3$ is known as both ilmenite and pv 17.

The synthesis of pv, K$_3$BiO$_2$-type NaOsO$_3$ or related phases is rather complex and traditional ceramic routes fail to produce such phases. The synthetic pathway should cope with the requirement of increasing the oxidation state from tetravalent Os to pentavalent 2-12, 14 avoiding production of toxic OsO$_4$ and while being held in a generally reducing high pressure assembly. Sodium peroxide, Na$_2$O$_2$, is used to promote high oxygen fugacities during the reaction that is presumed to proceed between component oxides inside noble metal capsules. It has been suggested that the capsules themselves (typically Au or Pt) promote crystallization of pv 5, though the Pt is apparently incompatible with the pv produced. Indeed, we observe significant recrystallization in the interior of Pt capsules used for pv syntheses. This combination of reaction conditions hampers in situ experimentation by x-rays, as the sample and capsule absorb all but a small percentage of even high energy x-rays, rendering any investigation a considerable challenge.

We have sought to overcome these by first pre-synthesising two precursors offline, in Pt capsules, at 6 GPa. Following previously reported conditions 5,8,11, we used two near-identical schemes that incorporate the same nominal mixtures of 1:1 Na$_2$O:Os$_2$O$_2$ with excess peroxide. In the first case, the temperature was kept below 1100 K and the synthesis produced a mixture of K$_3$BiO$_2$-type NaOsO$_3$ and hexavalent Na$_2$OsO$_4$, where excess Na$_2$O$_2$ has reacted to enrich the mixture towards Na$_2$OsO$_4$.

The scenario was quite different when the reaction temperature was increased above 1100 K (at 6 GPa). In this case the final product contained perovskite-type (i.e. pentavalent) pv-NaOsO$_3$ that, under higher temperature capsuleless samples, eventually reduces to Os metal, with loss of Na from the assembly. Shi et al. reports similar results. 6,8,9.

In using these products for in situ investigation we have effectively fixed the Os oxidation state at, or on average, higher than that required for the production of Os$^{V}$ ppv. In this way some
reduction of the sample could be entertained, and the use of metal capsules could be avoided during our in situ exploration of pressure-temperature space.

A single phase sample of pv-NaOsO₃ was pressurised up to 16.35 GPa and the temperature increased in a manner similar to a previous pv-ppv study. While approaching 1135 K, the diffraction profiles rapidly changed (see SI). No further heating was applied. An inspection demonstrated the formation of CaIrO₃-type ppv-NaOsO₃. This is generally unexpected as many structural indicators are completely against pv-NaOsO₃ forming ppv. For example, its lattice parameters at ambient conditions (Pnma; Z = 4, a = 5.3830(3), b = 7.5763(4), c = 5.3245(3) Å) are closer to cubic, $\phi = 10.55^\circ$, than are normally considered sufficient to lead to the crystallisation of ppv at high $P$. The tolerance factor is also higher than $t = 0.9$ (at $t = 0.924$). Furthermore, the ratio of polyhedral volumes, $V_A/V_B = 4.82$, is well above the normal cut-offs for pv to ppv transitions, at 4.036. However, contrary to the expectation from Tateno’s observations of limiting tilt, increasing pressure does increase distortion in the pv-NaOsO₃, in agreement with Fujino et al’s assessment of suitability. Although the sample was left at 1135 K for 2.5 hours, the pv component did not completely disappear, but the initial signs of transition did not suggest a sluggish transformation, suggestive of evolution of the pressure and temperature conditions towards equilibrium. After one hour of heating, the lattice of pv was approximately $a = 5.28$ Å, $b = 7.428$ Å, $c = 5.1480$ Å; $\Phi = 50.47$ Å/f.u., and ppv $a = 2.769$ Å, $b = 10.034$ Å, $c = 7.218$ Å; $\Phi = 50.14$ Å/f.u. Therefore, there is less than 1% volume change upon transition. The gold lattice parameter was $a/a_0 = 0.9807$ and the pressure after return to ambient temperature (after heating for 2.5 hours) was 13.26 GPa.

**Figure 1** A series of semi-continuous x-ray diffraction patterns collected upon pressurizing and during two heating-cooling cycles. Shown is the lower angle part only. Of note: A. Increased splitting of the (110/1-10) pair; B. Loss of Na₂OsO₄; C. IrR to c-NaOsO₃ transformation. D. Quench, end heating cycle 1. E. ‘s’-shaped-kink, onset of OsO₂ and crystallization of ppv (F). G. Quench end of heating cycle 2, followed by reheat. Simulated diffraction patterns for c-NaOsO₃, OsO₂ and ppv-NaOsO₃ are shown as key. Other peaks are due to h-BN (the fast-moving peak at ~4º is the 002) and the 111 of MgO, at about 5.4º.

**Table 1.** Atomic positions and bond lengths for ppv-NaOsO₃, refined in space group Cmcm, from in cell data, upon return to ambient conditions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
</tr>
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<tbody>
<tr>
<td>Os</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Na</td>
<td>4c</td>
<td>0</td>
<td>0.2435(29)</td>
<td>0.25</td>
</tr>
<tr>
<td>O1</td>
<td>4c</td>
<td>0</td>
<td>0.921(3)</td>
<td>0.25</td>
</tr>
<tr>
<td>O2</td>
<td>8f</td>
<td>0</td>
<td>0.3973(23)</td>
<td>0.5569(23)</td>
</tr>
<tr>
<td>Os-O</td>
<td>4 x 1.840(15)</td>
<td>2 x 2.017(12) Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-O</td>
<td>2 x 2.37(4) Å</td>
<td>4 x 2.51(3) Å</td>
<td>2 x 2.79(3) Å</td>
<td></td>
</tr>
</tbody>
</table>
This initial pv sample appears to behave as expected and, following the same reasoning as other pv-ppv transformations, can be interpreted as growth of stable ppv from metastable pv due to the positive Clapeyron slope for the equilibrium transition. Nonetheless, the pseudocubic tilt of the pv phase continues to be distinctly different from that which we expect in the region of a pv-ppv transformation, by at least 10°. Assuming a dP/dT slope of 10-17 MPa/K, the synthesis is representative of an equilibrium transformation, this would place the room temperature transition at near ambient pressure.

The lower temperature synthetic product was used to elaborate an alternate route. It resembles a close to 1:1 mixture of KSB0-type (a ≈ 9.1415(4) Å; c-NaOsO₃, Z = 12, V₁/₂ ≈ 63.7 Å³/f.u.) and hexagonal Na₂Os₄O₁₁ (a = 9.6242(6) Å, c = 3.1619(3) Å, P-6m, following 6). The assumed pseudocubic lattice of KSB0 is close to that reported by Sleight of 9.17(1) Å, though the diffraction signal of this phase does not appear to be only cubic at ambient conditions. Most obviously reflections of type hkl are doubled and the cubic 312-equivalent is at least a triplet, while the 200, 400, etc are not indicative of a rhombohedral distortion. The cubic phase was introduced along with the hexagonal Na₂OsO₄ and the remaining peaks were indexed by distorting the Pn-3 KSB0-type model to R-3 (same size; translationengleiche subgroup) while adjusting a = 9.146 Å and α = 91.5°; R-3R, fdc; equivalent to the refined values of R-3H α = 13.1042(7), c = 15.4203(12) Å. Various rhombohedral forms of KSB0-like chemistries are described as ilmenite-related types, with a ≈ 5.4 Å, c ≈ 16.0-18.25 Å; R-3H, fcc; e.g. 16,17. However, these lattices do not account for peak splitting in the same manner as the model proposed here where the 110 forms a doublet 1-10/110s rather than to the single base 003 of the smaller R lattice of e.g. NbSbO₃ 17. Upon pressurization, the proposed Rr form is evidently preferred as peak-splitting becomes more prominent with load, Figure 1. A (and SI). During heating, at 6.05 GPa, Na₂OsO₄ is consumed into the single phase rhombohedral KSB0-like phase (α rapidly increases to 92.5°) at 750 K, Figure 1. B. As there is no concomitant appearance of OsO₂ visible, we assume that the rhombohedral form is flexible in its chemistry (like related KSB0-types; e.g. compare 11, 12). Immediately after this, a continuous transformation from Rr to c-NaOsO₃ is observed (830 K), Figure 1. C. The (111) peak, which is characteristic of Pn-3 symmetries of KSB0-type chemistries is weak but present, as per Sleight’s observation 11. The c-NaOsO₃ sample was cooled, (D), without change and reheated (now at 5.75 GPa), whereupon two almost coincident events were observed: (i) at 750 K, the sharp ‘s’ shaped kink in the c-NaOsO₃ peaks (E) that occur with the growth of rutile-type OsO₃ and, (ii) at 825 K, F, the growth of ppv-NaOsO₃. The rapid peak-shift to lower d-spacing of all cubic peaks and concomitant growth of OsO₃ is indicative of a reduction of lattice size, due to loss of Os to its rutile-structured oxide. Ppv-NaOsO₃ crystallises immediately after, at conversion, the lattice of the ppv-phase is a = 2.8192(17) Å, b = 10.4047(21), c = 7.3179(18) Å (V₁/₂ = 53.66 Å³/f.u.); with c-NaOsO₃ at a = 9.0709(7) Å (V₁/₂ = 61.20 Å³/f.u.) and their relative volume difference is AV = -12.3%. The pressure after this second heating cycle was 4.96 GPa.

A recovered sample from a further near-identical run, see SI, shows fine-grained texture for ppv, while a minor KSB0-like component is spotty and has reverted to rhombohedral. The ppv lattice has dimensions a = 2.8323(3) Å, b = 10.6927(14) Å, c = 7.3345(7) Å, V = 222.12(4) Å³, V₁/₂ = 55.7 Å³/f.u. and g (scale) = 7.810 g cm⁻³. Table 1. Ppv-NaOsO₃ is considerably more distorted than NaIrO₃ (a = 3.03968(3) Å, b = 10.3576(12) Å, c = 7.1766(3) Å), with slightly shorter a and c lengths and a longer b length. This is a consequence of the similar edge-sharing distances (1.893 Å) and the shorter apical distances, 1.907 Å, foreshortening the c-axis. The Os-bridging O-Os angle is 130.8(13)° in NaOsO₃ compared to the more corrugated 140° in NaIrO₃, with almost identical average Na-O distances (2.53 and 2.57 Å).

From the latter route, it is quite clear that ppv-NaOsO₃ can be formed from an assemblage that does not yet contain any pvi-structured compound. This illustrates that ppv can be formed from phases other than pv (even in systems where pv occurs) and that the growth of pv as a precursor or indicator to ppv is counterproductive, requiring almost three times higher pressure to initiate the transformation. The difference in volumes of >10% between KSB0-type and ppv compared to just 1-2% for pv-ppv at transformation, especially with ppv being less dense than pv at ambient, plays a crucial role in the lower pressure stabilization of ppv, via c-NaOsO₃. Our results also show that ppv NaOsO₃ can be produced even though all structural criteria commonly used to predict such transitions are not fulfilled. It appears then that tilt, polyhedral volume ratio, etc should be reassessed to include more pentavalent chemistries, for which ppv can be obtained - even in the absence of pv. This may be through incorporating adjustments for the effects of electronegativity 13,17,24.

ASSOCIATED CONTENT
Supporting Information
Experimental details, illustrated diffraction data and structure descriptions are supplied as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION
Corresponding Author
* crichton@esrf.fr (WAC)
* s.margadonna@swansea.ac.uk (SM)

Author Contributions
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**Synopsis**

The second-known pentavalent NaOsO$_3$ post-perovskite has been transformed by a new synthetic route illuminated by in situ synchrotron data. This synthesis, from a KSB$_3$-like assemblage occurs without any perovskite intermediate, at almost one third of the pressure required by the direct perovskite route. This work indicates that post-perovskites can be more common than specified from perovskite-based indicators and could even occur in systems where no perovskite is yet known. It appears that post-perovskite could be more efficiently obtained if prior perovskite synthesis is avoided.