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# A new route to pentavalent post-perovskite

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**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$_4$ and nominally pentavalent KSbO$_3$-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 study of electronic and magnetic responses of 5$d$ compounds is at the centre of a considerable research effort due to their fascinating properties that can be adopted for spintronics and other advanced electronic technologies. In recent years, much of the research has concentrated on osmium-containing systems [1-5].The high-pressure synthetic procedures used to isolate new compounds in the Na-Os oxide system have been further elaborated recently to include the production of hexavalent Na$_2$OsO$_4$ [6,7], of pentavalent perovskite NaOsO$_3$ [8] and the description of the heptavalent compounds Na$_3$OsO$_5$ [9] and Na$_5$OsO$_6$ [10]. Clearly, in the Na-Os-O system, Os can be incorporated in many formal oxidation states; e.g. Os$^{IV}$O$_2$, NaOs$^V$O$_3$, Na$_2$Os$^{VI}$O$_4$, Na$_3$Os$^{VII}$O$_5$. Before these, NaOsO$_3$ had been only briefly described as a stoichiometric KSbO$_3$-type compound (primitive cubic lattice with $a$ = 9.17 Å) as part of a survey of related chemistries produced at 3 GPa and 900 °C [11]. KSbO$_3$ structures are, more generally, a family of tunnel-containing compounds that exhibit a range flexibility in their chemistries and a plethora of attractive physical properties; including ionic conduction, catalytic activity and oxygen sensing. Some of these have been prepared only at high pressure and temperature conditions; *e.g.* Ba$_2$Ir$_3$O$_9$ [12] or NaOsO$_3$ itself [11]. Combining these, osmate KSbO$_3$-family compounds are therefore ideally suited for targeting new synthetic protocols that can exploit changes in oxidation state and bulk chemistry to produce novel 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 [13]. Pentavalent KIrO$_3$ and KBiO$_3$ share the KSbO$_3$-type [14,15] structure, while NaBiO$_3$ is an ilmenite [16] and NaSbO$_3$ is known as both ilmenite and pv [17].

The synthesis of pv, KSbO$_3$-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], 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 [6], 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 [6,8,11], we used two near-identical schemes that incorporate the same nominal mixtures of 1:1 Na$_2$O$_2$:OsO$_2$ with excess peroxide. In the first case, the temperature was kept below 1100 K and the synthesis produced a mixture of KSbO$_3$-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].

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-NaOsO$_3$ was pressurised up to 16.35 GPa and the temperature increased in a manner similar to a previous pv-ppv study [18]. While approaching 1135 K, the diffraction profiles rapidly changed (see SI). No further heating was applied. An inspection demonstrated the formation of CaIrO$_3$-type ppv-NaOsO$_3$. This is generally unexpected as many structural indicators are completely against pv-NaOsO$_3$ 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, $\phi = 10.55°$ [19, 20], than are normally considered sufficient to lead to the crystallisation of ppv at high $P$ [21]. 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 [22]. However, contrary to the expectation from Tateno's observations of limiting tilt, increasing pressure does increase distortion in the pv-NaOsO$_3$, in agreement with Fujino *et al*'s assessment of suitability [23]. 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; V/Z = 50.47 Å$^3$/f.u. and ppv a = 2.769 Å, b = 10.034 Å, c = 7.218 Å; V/Z = 50.14 Å$^3$/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.
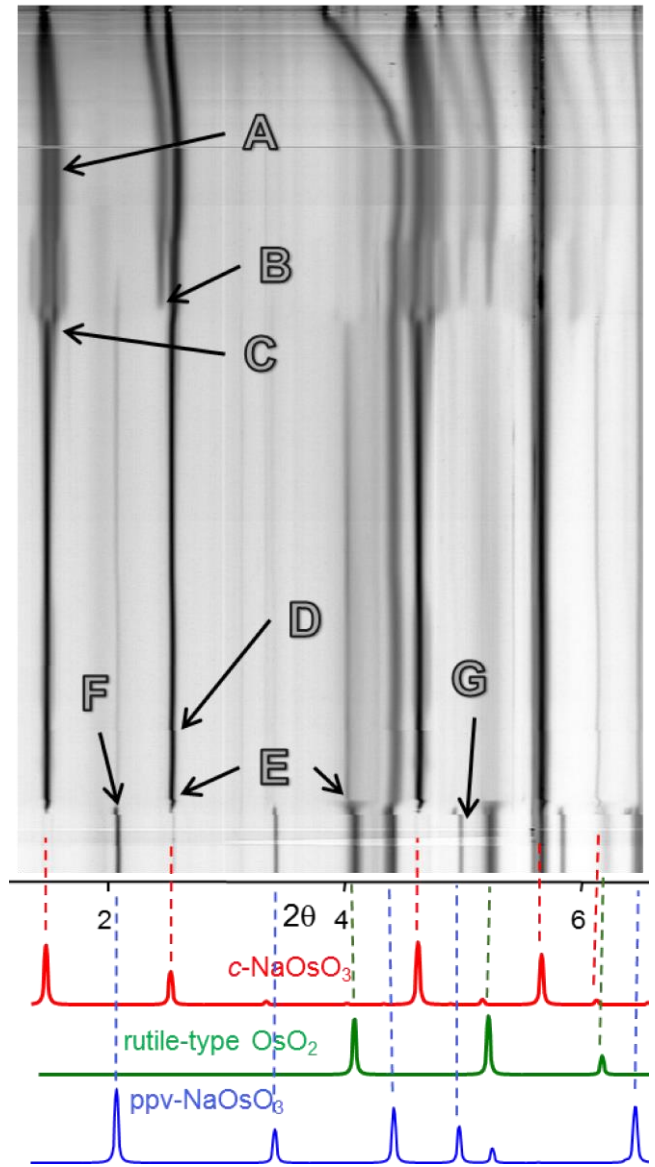


*Figure 1 A series of semi-continuous x-ray diffraction patterns collected upon pressurizing and during two heating-cooling cycles. Shown is the lower angle part only. Of note: A. Increased splitting of the (110/1-10) pair; B. Loss of Na$_2$OsO$_4$ C. rR to c-NaOsO$_3$ transformation. D. Quench, end heating cycle 1. E. 's'-shaped-kink, onset of OsO$_2$ and crystallization of ppv (F). G. Quench end of heating cycle 2, followed by reheat. Simulated diffraction patterns for c-NaOsO$_3$, OsO$_2$ and ppv-NaOsO$_3$ are shown as key. Other peaks are due to h-BN (the fast-moving peak at ~4° is the 002) and the 111 of MgO, at about 5.4°.*

**Table 1.** Atomic positions and bond lengths for ppv-NaOsO$_3$, refined in space group *Cmcm*, from in cell data, upon return to ambient conditions.

| Atom | site | x/a | y/b | z/c |
|------|------|-----|-----|-----|
| Os | 4a | 0 | 0 | 0 |
| Na | 4c | 0 | 0.2435(29) | 0.25 |
| O1 | 4c | 0 | 0.921(3) | 0.25 |
| O2 | 8f | 0 | 0.3973(23) | 0.5569(23) |

| | | | |
|------|------|------|------|
| Os-O | 4 x 1.840(15) | 2 x 2.017(12) Å | |
| Na-O | 2 x 2.37(4) Å | 4 x 2.51(3) Å | 2 x 2.79(3) Å |

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 [21], by at least 10°. Assuming a $dP/dT$ slope of 10-17 MPa/K [19,21,23,24], and that 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 $KSbO_3$-type ($a \approx 9.1415(4)$ Å; $c$-$NaOs^VO_3$, Z = 12, $V/Z$ 63.7 Å$^3$/f.u.) and hexagonal $Na_2Os^{VI}O_4$ ($a = 9.6242(6)$ Å, $c = 3.1619(3)$ Å, $P$-$62m$, following [6,7]). The assumed pseudocubic lattice of $KSbO_3$ is close to that reported by Sleight of 9.17 Å [11], though the diffraction signal of this phase does not appear to be *only* cubic at ambient conditions. Most obviously reflections of type $hk0$ 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 $Na_2OsO_4$ and the remaining peaks were indexed by distorting the $Pn$-3 $KSbO_3$-type model to $R$-3 (same size; *translationengleiche* subgroup) while adjusting $a = 9.146$ Å and $\alpha = 91.5$°; $R$-3R, $f^bdcb$; equivalent to the refined values of $R$-3H $a = 13.1042(7)$, $c = 15.4203(12)$ Å. Various rhombohedral forms of $KSbO_3$-like chemistries are described as ilmenite- and related types, with $a \approx 5.4$ Å, $c \approx 16.0$-18.25 Å; $R$-3H, $fc^2$; e.g. [16,17]. However, these lattices do not account for peak splitting in the same manner as the model proposed here where the $110_c$ forms a doublet $1$-$10/110_{rR}$ rather than to the single basal 003 of the smaller $rR$ lattice of *e.g.* $NbSbO_3$ [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, $Na_2OsO_4$ is consumed into the single phase rhombohedral $KSbO_3$-like phase ($\alpha$ rapidly increases to 92.5°) at 750 K, Figure 1, **B**. As there is no concomitant appearance of $OsO_2$ visible, we assume that the rhombohedral form is flexible in its chemistry (like related $KSbO_3$-types; *e.g.* compare [11, 12]). Immediately after this, a continuous transformation from $rR$ to $c$-$NaOsO_3$ is observed (830 K), Figure 1, **C**. The (111) peak, which is characteristic of $Pn$-3 symmetries of $KSbO_3$-type chemistries is weak but present, as per Sleight's observation [11]. The $c$-$NaOsO_3$ 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 $c$-$NaOsO_3$ peaks (**E**) that occur with the growth of rutile-type $OsO_2$ and, (ii) at 825 K, **F**, the growth of ppv-$NaOsO_3$. The rapid peak-shift to lower $d$-spacing of all cubic peaks and concomitant growth of $OsO_2$ is indicative of a reduction of lattice size, due to loss of Os to its rutile-structured oxide. Ppv-$NaOsO_3$ 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 ($V/Z = 53.66$ Å$^3$/f.u.); with $c$-$NaOsO_3$ at $a = 9.0709(7)$ Å ($V/Z = 61.20$ Å$^3$/f.u.) and their relative volume difference is $\Delta V = -12.3$%. 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 $KSbO_3$-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, $V = 222.12(4)$ Å$^3$; $V/Z = 55.7$ Å$^3$/f.u. and $\rho_{calc} = 7.810$ g·cm$^{-3}$, Table 1. Ppv-$NaOsO_3$ is considerably more distorted than $NaIrO_3$ ($a = 3.03968(3)$ Å, $b = 10.3576(12)$ Å, $c = 7.1766(3)$ Å [8]); 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, foreshort-

ening the $c$-axis. The Os-bridging O-Os angle is 130.8(13)° in $NaOsO_3$ compared to the more corrugated 140° in $NaIrO_3$, with almost identical average Na-O distances (2.53 and 2.57 Å).

From the latter route, it is quite clear that ppv-$NaOsO_3$ can be formed from an assemblage that does not yet contain any pv-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 $KSbO_3$-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 $c$-$NaOsO_3$. Our results also show that ppv $NaOsO_3$ 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.

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interests.

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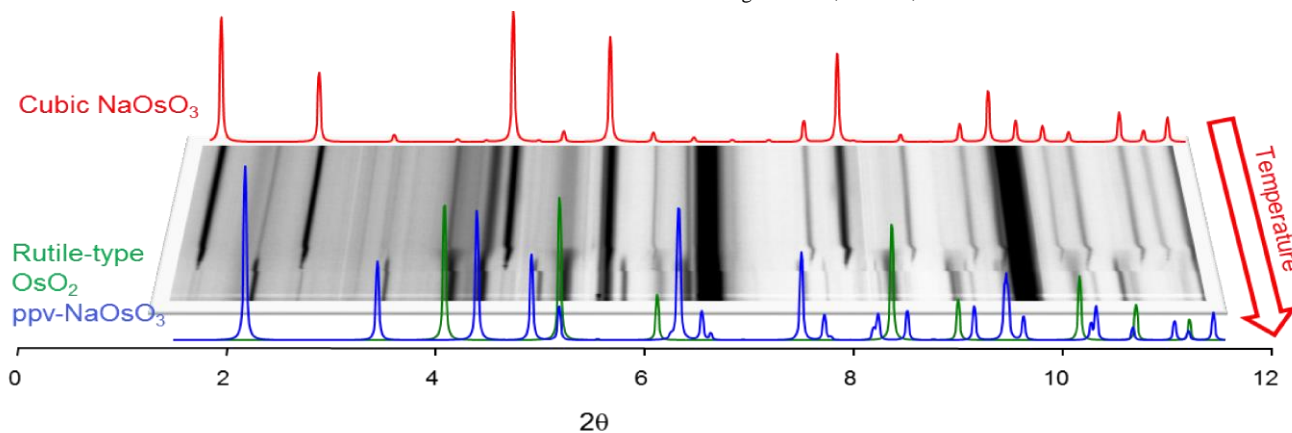
## Synopsis

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 $KSbO_3$-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.