

Supporting information

Study of polycrystalline bulk Sr₃OsO₆ double-perovskite insulator: comparison with 1000 K ferromagnetic epitaxial films

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Table S1 **Selected bond lengths in a monoclinic Sr₃OsO₆ synthesized under high-pressure**

Bond	Bond length (Å)	Bond	Bond length (Å)
Sr1–O1	2.813(13) ×1, 2.898(6) ×1 2.937(6) ×1, 3.186(13) ×1	Sr2–O3	2.265(1) ×2
Sr1–O2	2.419(6) ×1, 2.692(13) ×1 3.194(13) ×1, 3.424(7) ×1	Os–O1	1.887(1) ×2
Sr1–O3	2.607(10) ×1, 2.795(8) ×1 3.143(8) ×1, 3.259(9) ×1	Os–O2	1.895(1) ×2
Sr2–O1	2.297(1) ×2	Os–O3	1.885(1) ×2
Sr2–O2	2.248(1) ×2		

Based on the bond lengths above, the bond valence sums (BVS)^{S1} of Sr and Os are calculated from the parameters of $R_0 = 1.958 \text{ Å}$ and $B = 0.479 \text{ Å}$ for Sr²⁺ and $R_0 = 1.904$ and $B = 0.375 \text{ Å}$ for Os⁶⁺;^{S2} BVS(Sr1) = 1.82, BVS(Sr2) = 3.13, and BVS(Os1) = 6.25. The averaged Sr2–O (2.27 Å) is significantly shorter, resulting in the typically high BVS; this suggest that the bond is highly compressed. The compressed Sr–O bond seems to be common for a specific class of perovskite oxides, in which the Sr atom locates at the perovskite-B site such as Ba₃SrRu₂O₉ (2.360 Å),^{S3} Sr₂Sr_{0.67}U_{1.33}O₆ (2.3297 Å),^{S4} Ba₂SrTeO₆ (2.328 Å),^{S5} and Ba₂SrWO₆ (2.410 Å).^{S5}

Table S2 Atomic coordinates and equivalent isotropic displacement parameters (U_{eq} , $10^{-3} \text{ \AA}^2$) for a tetragonal Sr_3OsO_6 as measured by the synchrotron X-ray diffraction at room temperature

Site	WP	Occp.	x	y	z	U_{eq}
Sr1	16i	0.25	0.0438(13)	0.5381(14)	0.2810(9)	14.6(6)
Os	2b	1	0	0	0.5	14.6
Sr2	16i	0.125	0.0695(8)	0	0.0521(9)	14.6
O1	4e	1	0	0	0.2766(16)	12.7
O2	8h	1	0.3657(16)	0.1956(14)	0.0	12.7

WP: Wyckoff position. Space group: $I4/m$ (Tetragonal; No.87); lattice constants $a = 5.8595(1) \text{ \AA}$, $b = 8.2380(1) \text{ \AA}$; cell volume = $282.84(1) \text{ \AA}^3$; $d_{\text{cal}} = 6.447 \text{ g cm}^{-3}$; Chemical formula sum: Sr_3OsO_6 ($Z = 2$); and the final R indices are 1.904% (R_{wp}), 1.313% (R_{p}), 1.845% (R_{B}), and 0.769% (R_{F}). The mass fraction of the tetragonal phase is 45.54 wt%.

Table S3 Atomic coordinates and equivalent isotropic displacement parameters (U_{eq} , $10^{-3} \text{ \AA}^2$) for a cubic Sr_3OsO_6 as measured by the synchrotron X-ray diffraction at room temperature

Site	WP	Occp.	x	y	z	U_{eq}
Sr1	32f	0.25	0.2736(4)	0.2736	0.2736	17.6(15)
Os	4b	1	0.5	0.5	0.5	6.9(4)
Sr2	32f	0.125	0.0330(3)	0.0330	0.0330	17.6
O1	24e	1	0.2734(6)	0.0	0.0	12.7

WP: Wyckoff position. Space group: $Fm-3m$ (Cubic; No.225); lattice constants $a = 8.2521(1) \text{ \AA}$; cell volume = $561.94(1) \text{ \AA}^3$; $d_{\text{cal}} = 6.490 \text{ g cm}^{-3}$; Chemical formula sum: Sr_3OsO_6 ($Z = 4$); and the final R indices are 1.904% (R_{wp}), 1.313% (R_{p}), 1.648% (R_{B}), and 0.738% (R_{F}). The mass fraction of the cubic phase is 53.26 wt%.

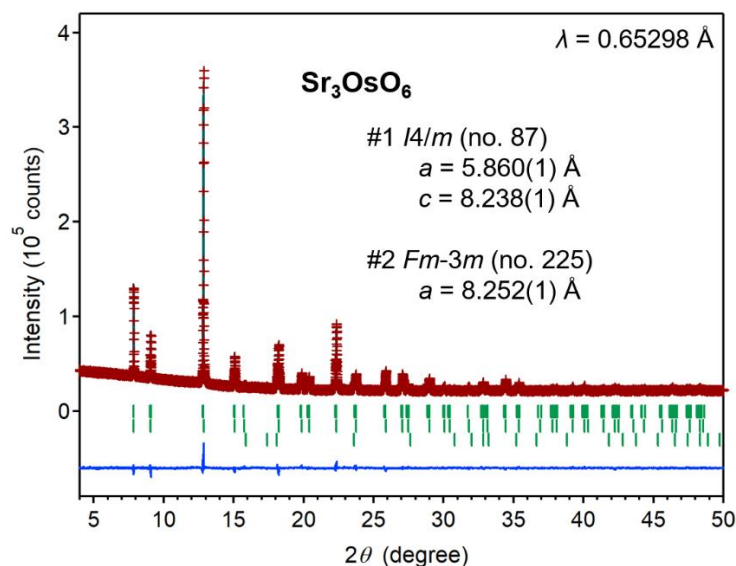


Fig. S1 Rietveld refinement of the synchrotron XRD profile ($\lambda = 0.65298 \text{ \AA}$) collected at room temperature for a high-pressure synthesized Sr_3OsO_6 . Coexisting tetragonal ($I4/m$) and cubic ($Fm-3m$) structures and an Os impurity were considered in the analysis. The crosses and solid lines show the observed and calculated patterns, respectively, with their differences shown at the bottom. The expected Bragg reflections are marked by ticks for the $I4/m$ (top; 53.26 wt.%) and $Fm-3m$ (middle; 45.54 wt.%) structures and Os (bottom; 1.19 wt.%).

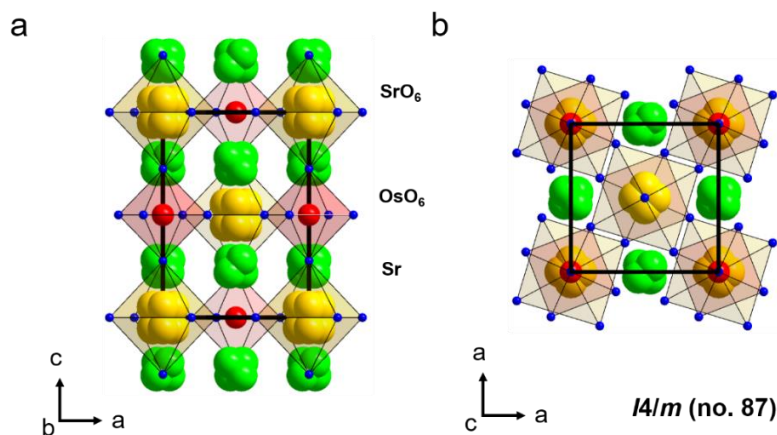


Fig. S2 (a) A crystal structure image of the tetragonal Sr_3OsO_6 ($I4/m$) viewed from the b -axis, in which SrO_6 and OsO_6 octahedra are drawn in orange and red, respectively. The Sr atom position at the perovskite A-site is drawn as a green sphere. (b) Alternative image viewed from the c -axis.

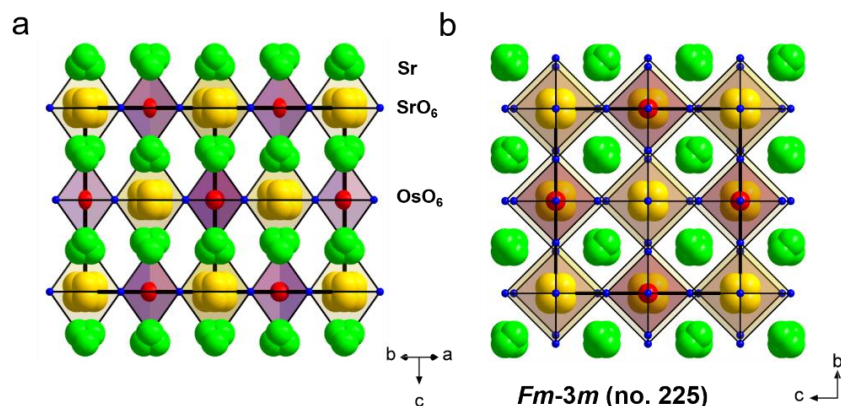


Fig. S3 (a) A crystal structure image of the cubic Sr_3OsO_6 ($Fm-3m$) viewed from the $[110]$ direction, in which SrO_6 and OsO_6 octahedra are drawn in orange and red, respectively. The Sr atom position at the perovskite A-site is drawn as a green sphere. (b) Alternative image viewed from the a-axis.

References

- S1. Brown, I. D., Recent Developments in the Methods and Applications of the Bond Valence Model. *Chem. Rev.* **2009**, *109* (12), 6858-6919.
- S2. Gagne, O. C.; Hawthorne, F. C., Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallogr. Sect. B-Struct. Sci. Cryst. Eng. Mat.* **2015**, *71*, 562-578.
- S3. Zandbergen, H.; Ijdo, D., Tribarium strontium diruthenate (V), $\text{Ba}_3\text{SrRu}_2\text{O}_9$, a Rietveld refinement of neutron powder diffraction data. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1984**, *40* (6), 919-922.
- S4. Cordfunke, E. H. P.; Ijdo, D., $\text{Sr}_2\text{UO}_{4.5}$: a new perovskite-type strontium uranate. *J. Solid State Chem.* **1994**, *109* (2), 272-276.
- S5. Fu, W.; Au, Y.; Akerboom, S.; Ijdo, D., Crystal structures and chemistry of double perovskites $\text{Ba}_2\text{M(II)M'(VI)O}_6$ ($\text{M} = \text{Ca, Sr, M}' = \text{Te, W, U}$). *J. Solid State Chem.* **2008**, *181* (9), 2523-2529.