

## Synthesis and investigation of the 4H and newly discovered 6H perovskite polymorphs of BaRhO<sub>3</sub> between 7 – 22 GPa

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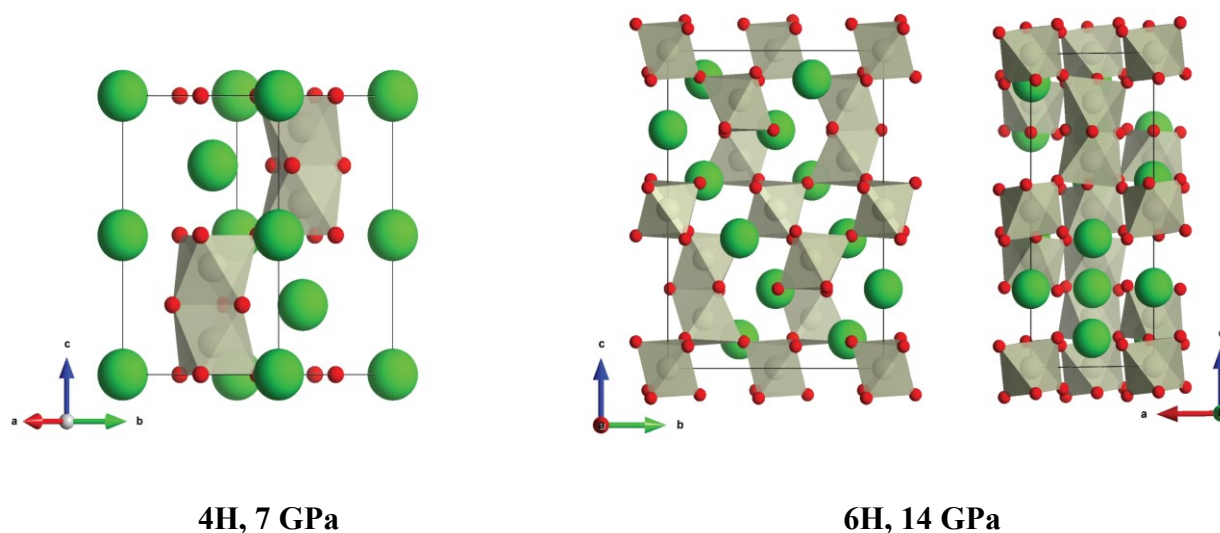
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This study explored the pressure dependent polymorphism of BaRhO<sub>3</sub> within the 7 – 22 GPa pressure range. We report the synthesis of a previously undiscovered 6H perovskite polymorph of BaRhO<sub>3</sub>, which was stabilised between 14 – 22 GPa, below which a previously known 4H polymorph is yielded.[1] From Rietveld analysis of synchrotron X-ray powder diffraction data, the polymorph was found to crystallise in the monoclinic *C2/c* 6H perovskite structure, similar to the analogous BaIrO<sub>3</sub> 6H polymorph which is also synthesised at high pressure.[2] This data analysis also confirms a 4+ oxidation state for Rh which we believe is stabilised by the extremely high oxygen pressures accessible via high pressure synthesis. Physical property measurements and electronic structure calculations were carried out on the 4H and 6H polymorphs. Both polymorphs were found to be Pauli paramagnetic metallic oxides. Resistivity measurements confirm a metallic state for the 4H polymorph, while bulk resistivity indicates semiconductivity for the 6H polymorph. We believe this semiconducting behaviour to arise due to grain boundary effects and not to be intrinsic. High Wilson ratios of approximately 2 for either compound indicate strong electron correlations which is rationalised by strong intermetallic interactions within the Rh<sub>2</sub>O<sub>9</sub> dimers.

Overall this study suggests that like the neighbouring Ru, Rh oxides display physical properties driven by competing localised and itinerant electron behaviour, and that the higher oxidation states of Rh are readily accessible under high pressure, high temperature conditions.



**Figure 1.** Representations of the 4H and 6H polymorphs of BaRhO<sub>3</sub> synthesised under high pressure, high temperature conditions.

[1] Chamberland, B. L. & Anderson, J. B. The preparation and crystal structure of a BaRhO<sub>3</sub> polytype, *J. Solid State Chem.*, 1981, 39(1), 114–119

[2] Cheng, J-G., Alonso, J. A., Suard, E., Zhou, J-S., and Goodenough, J. B. A New Perovskite Polytype in the High-Pressure Sequence of BaIrO<sub>3</sub>, *J. Am. Chem. Soc.* 2009, 131(21), 7461–7469

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