Synthesis and characterisation of the high pressure polymorphs of BaRhO₃

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We report the synthesis and characterisation of two phases of BaRhO₃ stabilised under high pressure, high temperature (HPHT) synthesis conditions. Synthesis at pressures of 4 to 7 GPa resulted in stabilisation of the 4H perovskite polymorph. Synthesis at higher pressures of 14 to 22 GPa stabilised a novel 6H phase of BaRhO₃. Structure refinement carried out against X-ray diffraction data collected at SPring-8 confirms the hexagonal $P6_3/mmc$ structure for the 4H polymorph.¹ The 6H polymorph was determined to crystallise in the monoclinic space group C2/c. X-ray data did not indicate any oxygen or rhodium non-stoichiometry. This confirms the uncommonly high oxidation state of Rh⁴⁺ (S = $\frac{1}{2}$) is stabilised through high oxygen pressures achieved via HPHT synthesis.

Magnetisation, heat capacity, and resistivity measurements were carried out for both compounds. The magnetic susceptibilities include large temperature-independent terms. Metallic conductivity is observed for the 4H polymorph, while resistivity measurements indicate the 6H polymorph is a semiconductor due to grain boundary effects. High Wilson ratios of approximately $R_w \approx 2$ indicate both polymorphs are strongly electron correlated systems, consistent with the high spatial diffusivity of the 4*d* orbitals. Magnetic ground state and density of state calculations were carried out for both compounds. These electronic structure calculations give metallic ground states for both structures. All these results indicate Pauli paramagnetic ground states for both polymorphs.



1) B. L. Chamberland and J. B. Anderson, J. Solid State Chem. 1981, 39(1), 114-119.