

# Influence of cation substitution on the compressibility of Ca-perovskites

T. Boffa Ballaran<sup>1</sup>, K. Kularatne<sup>2</sup>, R.G. Trønnes<sup>2</sup>

<sup>1</sup>*Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany,* <sup>2</sup>*Université de Pau et des Pays de l'Adour, Pau, France* <sup>3</sup>*Natural History Museum, and Centre for Planetary Habitability, University of Oslo, Norway*

*tiziana.boffa-ballaran@uni-bayreuth.de*

Structural refinements of single-crystal X-ray diffraction data collected for the orthorhombic *Pbnm* CaIrO<sub>3</sub> perovskite-type phase at ambient conditions and at several pressures up to 10 GPa have been used to characterise the distortion of this perovskite structure. The octahedral tilting of CaIrO<sub>3</sub> perovskite, as well as that of several other Ca perovskite structures, has been evaluated using both the unit-cell lattice parameters (assuming rigid polyhedra) and the displacements of oxygen and calcium atoms from their ideal positions in the cubic aristotype perovskite structure. The two types of calculations differ significantly, indicating that polyhedral distortions cannot be neglected for these perovskites.

Most of the Ca-oxide perovskites follow linear trends in terms of polyhedral volumes and tilting as a function of their respective molar volume. However, those containing a Pt-group element (i.e., Ir, Ru, and Rh) at the octahedral site clearly deviate from these trends. The larger octahedral tilting observed in CaIrO<sub>3</sub> perovskite is likely responsible for its higher stiffness, as inferred from the analysis of bulk modulus variations among other Ca perovskites. Additionally, unlike other Ca perovskites in which the Ca polyhedron is more compressible than the octahedral site, the compressibilities of the IrO<sub>6</sub> octahedra and the CaO<sub>12</sub> polyhedra in CaIrO<sub>3</sub> are very similar, resulting in octahedral tilting that remains essentially pressure-independent up to at least 10 GPa.

Ca perovskites with a Pt-group element at the octahedral site have been found to undergo a phase transformation to an orthorhombic *Cmcm* post-perovskite phase (CaIrO<sub>3</sub>-type structure), which is either stable or recoverable at ambient pressure. This suggests that a large octahedral tilting, a stiffer structure, and likely similar compressibility of the two cation sites may be prerequisites for stabilising the orthorhombic post-perovskite phase.