

## **High-pressure structure and bonding in $\text{CaIrO}_3$ : The structure model of $\text{MgSiO}_3$ post-perovskite investigated with time-of-flight neutron powder diffraction**

**C. DAVID MARTIN,<sup>1,\*</sup> RONALD I. SMITH,<sup>2</sup> WILLIAM G. MARSHALL,<sup>2</sup> AND JOHN B. PARISE<sup>1,3</sup>**

<sup>1</sup>Geosciences Department, 255 Earth and Space Sciences Building, Stony Brook University, Stony Brook, New York 11794-2100, U.S.A.

<sup>2</sup>ISIS Neutron Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

<sup>3</sup>Chemistry Department, Stony Brook University, Stony Brook, New York 11794-3400, U.S.A.

### **ABSTRACT**

The structure of  $\text{CaIrO}_3$  (*Cmcm*) has been refined at high pressure and at low temperature using time-of-flight neutron powder diffraction data. Evidence supporting deviation from space group *Cmcm* to *Cmc2<sub>1</sub>* is inconclusive. As  $\text{CaIrO}_3$  (*Cmcm*) unit-cell volume changes, refinements indicate deformation of cation-centered coordination polyhedra, rather than tilting. Structure models demonstrate  $\text{Ca}^{2+}$ -centered polyhedra are an order of magnitude more compressible than  $\text{Ir}^{4+}$ -centered octahedra. Bond valence sums show significant chemical strain (over-bonding) of calcium and oxygen at ambient conditions. Implications for structure change in  $\text{MgSiO}_3$  post-perovskite are discussed and a method for predicting the Clapeyron slope between perovskite and post-perovskite phases is proposed based on extrapolation of the volume-ratio between cation-centered polyhedra.

**Keywords:** Post-perovskite, high pressure, structure, neutron diffraction, Rietveld refinement, bond valence, D" layer,  $\text{CaIrO}_3$