

## Structural stability of CsCaCl<sub>3</sub> perovskite under pressure

M.T. Candela<sup>1</sup>, J.A. Barreda- Argüeso<sup>2</sup>, J.A. Gonzalez<sup>2</sup>, F. Rodriguez<sup>2</sup>, A.C. Perdigón<sup>3</sup>, S.A.T. Redfern<sup>4</sup> and F. Aguado<sup>2\*</sup>

<sup>1</sup> Applied Physics Department. University of Cantabria. Avda. Los Castros, s/n. 39005- Santander. Spain

<sup>2</sup> CITIMAC Department. University of Cantabria. Avda. Los Castros, s/n. 39005- Santander. Spain

<sup>3</sup> QUIPRE Department. University of Cantabria. Avda. Los Castros, s/n. 39005- Santander. Spain

<sup>4</sup> Department of Earth Sciences. University of Cambridge. Cambridge CB2 3EQ. UK

Keywords: Perovskite, structural distortion, tilting

\*e-mail: aguadof@unican.es

Perovskite-structure systems have been widely studied under extreme conditions because of their geophysical importance as well as for their multiple applications in materials science [1]. The most studied compounds are oxides with stoichiometry ABO<sub>3</sub>, although more and more attention has been paid to oxide analogues, such as halide perovskites ABX<sub>3</sub> (X: F, Cl, Br, I). In addition to their recent technological applications, halides are more compressible than oxides, so are advantageous to observe similar structural response at narrower pressure ranges.

CsCaCl<sub>3</sub> is a compound that crystallizes in the perovskite-type structure and has promising scintillation properties [2]. At ambient conditions, it is one of the few ABCl<sub>3</sub> perovskites that preserves the cubic symmetry (space group *Pm-3m*, *a* = 5.396 Å) and at low temperatures, T<sub>c</sub> = 95 K, it undergoes a cubic-to-tetragonal phase transition (space group *I4/mcm*) that results in an alternate rotation of CaCl<sub>6</sub> octahedra (see Figure 1) [3].

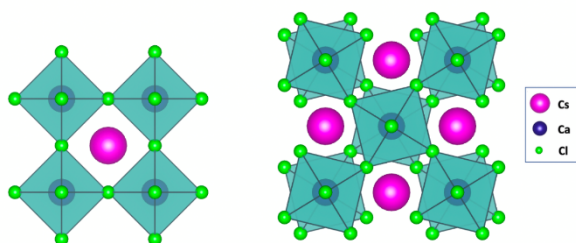


Figure 1. Structure of the cubic CsCaCl<sub>3</sub> perovskite (left) and the tetragonal phase, distorted by tilting of octahedra (right).

A low symmetry structure has been already observed in similar ABCl<sub>3</sub> cubic perovskites under hydrostatic pressure [4]. Larger distortion related to higher pressures and eventually a destabilization of the perovskite structure at higher compression rates have been observed in other halides [5]. CsCaCl<sub>3</sub> is therefore a good soft candidate to explore the stability of the perovskite structure under high-pressure conditions.

In this work we study the structure of CsCaCl<sub>3</sub> perovskite under pressure at ambient temperature.

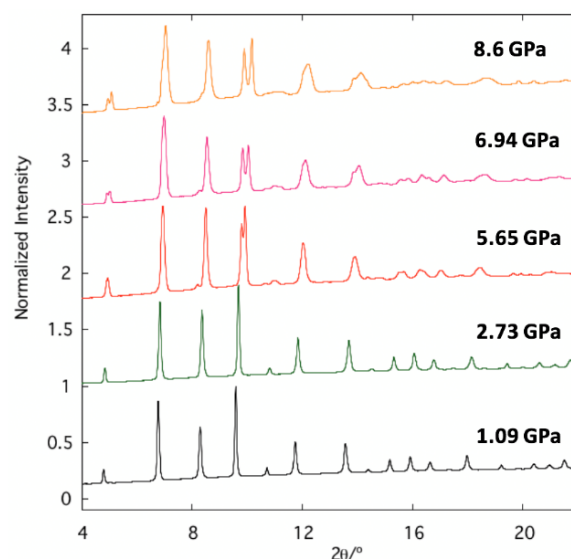


Figure 2. ADXRD patterns of CsCaCl<sub>3</sub> at selected pressures ( $\lambda = 0.444 \text{ \AA}$ ).

Pressure evolution has been determined by ADXRD experiments and Raman spectroscopy up to 20 GPa. Special attention has been paid to possible pressure-induced phase transitions involving symmetry reduction. Thus, we show that CsCaCl<sub>3</sub> retains its cubic structure up to 5 GPa and, above that pressure, it undergoes a second-order phase transition associated with tilting of CaCl<sub>6</sub> octahedra. Structural analysis of the high pressure phases and compressibility response based on different existing models has been carried out. The stability limit has also been evaluated. The high pressure behaviour of this compound is compared with that from other ABX<sub>3</sub> (X: Cl, F) perovskites showing different structural distortion.

- [1] R.J.D. Tilley, *Perovskites: Structure-Property Relationships* 2016 (Wiley).
- [2] M. Koshimizu *et al.*, *Opt. Mater.* 2014, **36**, 1930.
- [3] Y. Vailis *et al.*, *Solid State Commun.* 1986, **60**, 139.
- [4] F. Aguado *et al.*, *J. Phys.: Conf. Ser.* 2010, **215**, 012009.
- [5] C.D. Martin *et al.*, *Geophys. Res. Lett.* 2006, **33**, L11305.