

## **Polyhedral Compressibilities drive Structural Phase Transitions in Perovskites**

Ross John Angel, Jing Zhao, Nancy Ross, *Department of Geosciences, Virginia Tech, Blacksburg VA, USA*. E-mail: rangel@vt.edu

Recent advances in laboratory based single-crystal techniques for measuring the intensities of diffraction from crystals held at high pressures in the diamond-anvil cell have been used to determine the role of polyhedral compression in the response of the  $\text{ABO}_3$  perovskite structure type to high pressures. All perovskites studied exhibit compression of the  $\text{BO}_6$  octahedra. We have been able to show that when the  $\text{BO}_6$  octahedra are less compressible than the  $\text{AO}_{12}$  sites the octahedra become more tilted with increasing pressure [1]. In such perovskites there are no structural phase transitions to high-symmetry structures.

When the  $\text{BO}_6$  octahedra are more compressible than the  $\text{AO}_{12}$  sites the structure becomes less tilted and evolves towards a higher-symmetry configuration [2]. Thus  $\text{LaGaO}_3$  undergoes a Pbnm to R-3c transition with first-order character at approximately 2.5 GPa at room temperature. The structural evolution of  $\text{LaAlO}_3$  has been followed in the R-3c phase before its transition to Pm3m at about 14GPa [3].

We have also developed a new model, based on the bond valence concept, that successfully predicts the relative compressibilities of the cation sites in most oxide perovskites [4] and hence their response, including phase transitions, to pressure.

[1] Zhao J., Ross N. L., Angel R. J., *Phys Chem Miner*, 2004, **31**, 299. [2] Ross N. L., Zhao J., Angel R. J., *J. Solid State Chemistry*, 2004, **177**, 1276. [3] Zhao J., Ross N. L., Angel R. J., *J. Phys.: Condens. Matter*, 2004, **16**, 8763. [4] Zhao J., Ross N. L., Angel R. J., *Acta Cryst.*, 2004, **B60**, 263-271.

**Keywords:** perovskites, phase transitions, pressure