MS2 - O2: Ettringite at high pressure: structure evolution and elastic behaviour

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In order to predict the elastic properties of the complex multi-component Portland cement, database of the thermodynamic parameters of the main constituents is needed. Ettringite (ideally $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot27H_2O$, with $a=b \sim 11.21$ and $c \sim 21.43$ Å, Sp. Gr. $P31c$) is a common crystalline phases in Portland cements. It contains more than 45 wt% of H_2O. In the early hydration stages, the crystallization of ettringite governs the set rate of the highly reactive $Ca_3Al_2O_6$ phase (also known as "C3A"), whereas in aged cements its formation is associated to degradation processes[1]. The crystal structure of ettringite is rather complex and it consists of $[Ca_3[Al(OH)_6]\cdot12H_2O]$-columns (in which $Al(OH)_6$-octahedra are alternated with triplets of $Ca(OH)_4(OH_2)_4$-polyhedra) and sulphate groups connected by a complex H-bonding net[2]. Previous studies on the behavior of ettringite at high pressure reported only the isotropic compressional behavior of ettringite [3,4]. Because of that, the linear bulk moduli (K_a and K_c) and a full description of the deformation mechanisms at the atomic scale are still missing. We compressed a single crystal of ettringite up to 4.2 GPa by means of in-situ synchrotron X-ray diffraction, using a diamond-anvil cell and the mix methanol:ethanol (4:1) as P-transmitting fluid. Ettringite shows a marked anisotropic compressional pattern (K_a 21(1) GPa, K_c 47(1) GPa), which dramatically changes at $P>3$ GPa (Fig. 1). At $P>3$ GPa, the bulk modulus K_V of ettringite drops from 26.6(5) to 10.4(8) GPa. Such a softening is governed by the structural changes which affect mainly the elastic behavior on the ab plane (K_a drops from 21(1) to 7.3(8) GPa whereas K_c decreases only moderately). The structure refinements reveal that the elastic softening reflects the collapse of the H-bonding net, due an average decrease of the $O_{donor}\cdots O_{acceptor}$ distances (up to 0.20 Å in some cases), which mainly affect the interaction between the sulphate groups and the $Ca(OH)_4(OH_2)_4$-polyhedra lying in the ab plane.
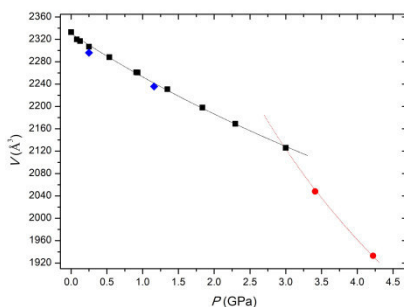

Figure 1. High-pressure evolution on the unit-cell volume of ettringite (*black squares* first compression regime, *red spheres* second compression regime, *blue diamonds* decompression path).

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