Anisotropic compressional behavior of ettringite

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A Portland cement is a complex multi-component system and, to predict its elastic properties, an exhaustive database of the thermodynamic parameters of the main constituents is needed. Ettringite (ideally $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 27H_2O$, with a=b ~ 11.21 and c ~ 21.43 Å, Sp. Gr. $P31c$) is one of the most important crystalline phases in Portland cements: its crystallization, in the early hydration stages, governs the set rate of the highly reactive "C3A" phase ($Ca_3Al_2O_6$), whereas in aged cements the formation of ettringite is commonly associated with degradation processes (Taylor et al. 2001). The crystal structure of ettringite is significantly complex with a H-bonding net which connects $[Ca_3[Al(OH)_6]\cdot 12H_2O]$-columns (in which $Al(OH)_6$-octahedra are alternated with triplets of $Ca(OH)_4(OH_2)_4$-polyhedra) to sulphate groups (Gatta et al. 2019). Despite the previous studies at high pressure on this material (*e.g.*, Cuesta et al. 2017, Clark et al. 2008), the linear bulk moduli (K_a and K_c) and a description of the deformation mechanisms at the atomic scale are still missing. In this light, we have investigated the compressional behavior of ettringite up to 4.2 GPa by means of *in-situ* single-crystal synchrotron X-ray diffraction, using a diamond-anvil cell (DAC) 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). This anisotropic elastic scheme dramatically changes at P>3 GPa; K_{V0} drops from 26.6(5) to 10.4(8) GPa), which mainly affects the structure on the ab plane (K_a drops from 21(1) to 7.3(8) GPa whereas K_c decreases only moderately). Structure refinements reveal that the elastic softening reflects the collapse of the H-bonding network, 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.

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