Thermoelastic behavior and temperature induced structural evolution of grossite; experimental and *ab-initio* calculation data

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The thermal expansion of grossite ($CaAl_4O_7$) has been investigated by single crystal X-ray diffraction at the XRD1 beamline in Elettra, using a Cryostat and a gas blower, in the 100-1080 K temperature range, collecting every 20 K. A 100 K *T*-range of overlap was collected to scale low-*T* cryostat data collections with high-*T* gas blower data collections. This resulted in 55 datasets from which full structure refinement was obtained. No change in symmetry was observed in the whole *T*-range. Instead, a negative thermal expansion has been observed for the *c*-lattice parameter up to 400 K. At $T > 400$ K, this lattice parameter increases with a rate that increases with temperature. Overall, the change is within 0.012 Å. A change of 1.2% in volume is observed in the whole *T*-range. These results agree with the previous experimental evidence of very limited thermal expansion ($\alpha_V = 4.1\times10^{-6}$/K at 1173 K), following Jonas et al. (1998) and Fukuda & Yamauchi (2002), with had much more limited and low precision data. We have also observed negative volume thermal expansion, but only at $T < 160$K, a temperature value coincident with the start of *b*-lattice expansion. Therefore, it appears that the *c*-lattice contraction is responsible for the observed cell-volume contraction below 160 K. A Detailed study of bond geometries and bond-valence variations extracted from the structure refinement sheds light on this particular behaviour.

The thermal expansion was also studied by *ab-initio* calculations using density functional theory and the quasiharmonic approximation (DFT-QHA) and WC1LYP functional. The data obtained for the phonons volume dependence yields α_V that is negative < 130K and a very low value ($\alpha_{V,300} = 6.31\times10^{-6}$/K) in agreement with experimental data.

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