High-pressure studies of hydrogen bonding in gypsum via Quantum Crystallography methods

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Abstract

Gypsum, $CaSO_4 \cdot 2H_2O$, is a model hydrous mineral in which pressure-induced structural transformations are governed not only by the compression of the crystal lattice, but also by the response of molecular water and hydrogen bonding. The ambient-pressure hydrogen geometry was established by neutron diffraction, showing two significantly different O–H distances of 0.942(3) and 0.959(3) Å and two non-equivalent hydrogen bonds to sulfate oxygen atoms, with H···O distances of 1.856(2) and 1.941(2) Å (Pedersen and Semmingsen, 1981). High-pressure single-crystal X-ray diffraction later showed that gypsum-I preserves its C2/c structure up to ca. 4.0 GPa, where the compression curve displays a discontinuity accompanied by a 2.5% volume contraction (Comodi et al., 2008). In that pressure range, the [CaO_8–SO_4] polyhedral layer remains comparatively incompressible, whereas the water-bearing interlayer is much more compressible, highlighting the central role of hydrogen bonding in the compression mechanism (Comodi et al., 2008). The structure of gypsum-II was subsequently solved from synchrotron single-crystal XRD with monoclinic $P2_1/n$ symmetry, with enhanced SO_4 tetrahedral distortion and a strong change in the bonding style of water molecules (Nazzareni et al., 2010). Spectroscopic studies also suggested that the transition is reversible and related primarily to the hydrogen-bonding network and water-molecule symmetry rather than to sulfate distortion (Knittle et al., 2001; Nazzareni et al., 2010).

Here we present a high-pressure quantum-crystallographic study of synthetic gypsum single crystals compressed in a diamond anvil cell. Synchrotron single-crystal X-ray diffraction data were collected over a dense pressure series from ambient pressure to 14.1 GPa, covering gypsum-I, the transition region, gypsum-II, and further structural transformations above 9 GPa with triclinic crystal symmetry. Despite the low monoclinic symmetry and the severe reciprocal-space restrictions imposed by the diamond anvil cell, high-pressure datasets reached up to ca. 90% completeness by merging measurements from several crystals collected at the same pressure point. This multi-crystal strategy is crucial for quantum crystallography, because multipole refinement, Hirshfeld Atom Refinement, and experimental electron-density analysis require not only accurate intensities, but also high completeness and reliable weak high-resolution reflections.

As an ambient-pressure reference, an in-house Mo Kα dataset was collected and refined using Hirshfeld Atom Refinement with anisotropic hydrogen atoms. The HAR-refined O–H distances, 0.965(10) and 0.929(11) Å, agree within uncertainty with the neutron-derived values of Pedersen and Semmingsen and confirm the intrinsic asymmetry of the water molecule in gypsum. Structures were solved and refined within the independent atom model for each observed phase, and compressibilities and bulk moduli were determined separately for the corresponding stability fields. Selected datasets were further treated using Hirshfeld Atom Refinement, multipole-model refinement, and topological analysis of the electron density within Bader's Quantum Theory of Atoms in Molecules and Crystals.

This combined structural and topological approach allows us to follow the evolution of O–H bonds, O–H···O hydrogen bonds, water-layer compression, and electron-density descriptors at bond critical points across the pressure-induced phase transformation. In contrast to previous studies, which established the ambient neutron reference structure, the pre-transition equation of state, or the structural model of gypsum-II, the present work provides a pressure-resolved experimental description of hydrogen-bond evolution at the level of electron density. The results show how hydrogen bonding accommodates compression, contributes to symmetry lowering, and evolves towards structural degradation, demonstrating the potential of high-pressure quantum crystallography for studying hydrated minerals and weak interactions under extreme conditions.

References

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