

## High-pressure behavior of gypsum: A single-crystal X-ray study

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### ABSTRACT

High-pressure X-ray diffraction was carried out on a single crystal of gypsum compressed in a diamond anvil cell. The sample maintained its crystal structure up to  $4.0 \pm 0.1$  GPa. The fit of pressure dependence of the unit-cell volume to the third-order Birch-Murnaghan equation yielded  $K_{T0} = 44(3)$  GPa and  $(\partial K_T/\partial P)_0 = 3.3(3)$ , where  $K_{T0}$  and  $(\partial K_T/\partial P)_0$  are the isothermal bulk modulus and its pressure derivative in ambient conditions. The axial compressibility values, fitting data collected up to 3.94 GPa, were  $\beta_{0a}^{\text{EoS}} = 6.1(1)$  and  $\beta_{0c}^{\text{EoS}} = 5.6(1) \cdot 10^{-3} \text{ GPa}^{-1}$ . The value of  $\beta_{0b}^{\text{EoS}}$  was  $6.2(8) \cdot 10^{-3} \text{ GPa}^{-1}$  fitting the data collected up to 2 GPa, due to non-linearity above this pressure; axial compressibility of gypsum is almost isotropic ( $\beta_{0a}:\beta_{0b}:\beta_{0c} = 1:1:0.9$ ). This behavior is partly unexpected for a layered mineral based on alternate layers of Ca- and S-polyhedral chains separated by interlayers occupied by water molecules. Above 4.0 GPa the compression curve of gypsum shows a discontinuity with a 2.5% contraction in volume. Structural refinements indicate that  $\text{SO}_4$  volume and average S-O bond distances remain almost unchanged from room pressure to 3.9 GPa [range 1.637(4)–1.66(9)  $\text{\AA}^3$ ; 1.4733–1.48  $\text{\AA}$ ]. The  $\text{SO}_4$  tetrahedron undergoes distortion: the smaller distance decreases from 1.4731(9) to 1.45(2)  $\text{\AA}$  and the larger increases from 1.4735(9) to 1.51(2)  $\text{\AA}$ . In contrast, the calcium polyhedra show expected high-pressure behavior, becoming more regular and decreasing in volume from 25.84(8)  $\text{\AA}^3$  at ambient  $P$  to 24.7(1)  $\text{\AA}^3$  at 3.9 GPa. The largest variations were observed in the interlayer region where the water molecules are located. Along the  $b$  axis, the two structural layers have very different compressibilities: the polyhedral layer is almost incompressible in the pressure range studied, whereas water layer compressibility is  $9.7(3) \cdot 10^{-3} \text{ GPa}^{-1}$ , about twice that of the other two lattice parameters. At ambient conditions, water molecules form weak hydrogen bonds with the O atoms of Ca and S polyhedra. With increasing pressure, the weakest hydrogen bond becomes the strongest one: from 0.001 to 4 GPa, the distance changes from 2.806(1) to 2.73(2)  $\text{\AA}$  for OW-H1 $\cdots$ O2, and from 2.883(2) to 2.69(3)  $\text{\AA}$  for OW-H2 $\cdots$ O2. Structure refinements show that water remains in the structure when  $P$  increases. The observed distortion of sulfate tetrahedra explains the splitting of the  $\nu_1$  sulfate stretching mode, and the various measured compressibilities of the two hydrogen bonds and the coalescence of the Raman stretching mode observed at pressures over 5 GPa.

**Keywords:** Gypsum, high pressure, single-crystal X-ray diffraction, phase transition