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 ± 0.1 GPa. The fit of pressure dependence of the unit-cell volume to the third-order Birch-Murnaghan equation yielded \( K_{0} = 44(3) \) GPa and \( \partial K_{0}/\partial P \) = 3.3(3), where \( K_{0} \) and \( \partial K_{0}/\partial P \) are the isothermal bulk modulus and its pressure derivative in ambient conditions. The axial compressibilities, fitting data collected up to 3.94 GPa, were \( \beta_{0a}^{ab} = 6.1(1) \) and \( \beta_{0b}^{ab} = 5.6(1) \times 10^{-3} \) GPa\(^{-1}\). The value of \( \beta_{0c}^{ab} \) was 6.2(8) \times 10^{-3} \) GPa\(^{-1}\). The 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 \( S_{0} \) volume and average S-O bond distances remain almost unchanged from room pressure to 3.9 GPa [range 1.637(4)–1.669(9) Å; 1.4733–1.48 Å]. The SO\(_4\) tetrahedron undergoes distortion: the smaller distance decreases from 1.4731(9) to 1.45(2) Å and the larger increases from 1.4735(9) to 1.51(2) Å. In contrast, the calcium polyhedra show expected high-pressure behavior, becoming more regular and decreasing in volume from 25.84(8) Å\(^3\) at ambient \( P \) to 24.7(1) Å\(^3\) 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) \times 10^{-3} \) 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) Å for OW-H1···O2, and from 2.883(2) to 2.69(3) Å for OW-H2···O2. Structure refinements show that water remains in the structure when \( P \) increases. The observed distortion of sulfate tetrahedra explains the splitting of the \( v_{1} \) 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

INTRODUCTION

Many of the hundreds of minerals existing on Earth and other planetary bodies are hydrous minerals containing molecular water, OH groups, or both in their crystal structures. Gypsum is the most common sulfate mineral containing molecular water that can easily be removed from the structure at temperatures above about 60 °C (Putnis et al. 1990). Gypsum plays an important role in regulating the hydration reaction rate during the early stages of setting and hardening of Portland cement. There is strong evidence of the presence of gypsum in planetary bodies (e.g., in Martian soil; Langevin et al. 2005). Together with anhydrite, halite, and Ca-Mg-carbonates, gypsum is one of the main minerals forming evaporitic sequences, where it plays an important role in localizing deformation, especially in thrust tectonics. Recent rheology experiments by Barberini et al. (2005) have shown that gypsum can flow plastically even below its dehydration temperature, due to strain weakening related to dynamic recrystallization.

The development of excess pore fluid pressures by dehydration may cause a decrease in strength, favoring brittle failure (Heard and Rubey 1966) with hydrofracturing and faulting taking place due to fluid overpressure (Cartwright 1994). De Paola et al. (2007) recently proposed a conceptual and mechanical model to explain the observed fault patterns and the complexity of the deformation processes occurring during the dehydration of Triassic evaporites.

Gypsum contains both molecular water and sulfate groups ionically bonded to calcium polyhedra. Hydrogen bonding in gypsum has been extensively studied by X-ray and neutron diffraction (Schofield et al. 1996) and by vibrational spectroscopy (Chio et al. 2004). Water molecules in gypsum are asymmetric, with interatomic OH bond lengths of 0.962(1) and 0.944(1) Å and two non-equivalent hydrogen bonds of 2.816 and 2.896 Å.

Since the dehydration mechanism can affect pore pressure