

Gowerite, Ca[B₅O₈(OH)][B(OH)₃].3H₂O: Revisiting the crystal structure and exploring its formation context

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ABSTRACT

Investigations into the crystal structure of gowerite are limited, and a comprehensive understanding of the H positions is lacking. Hence, in this study, we synthesized single crystals of gowerite under hydrothermal conditions and obtained reliable single-crystal X-ray diffraction data to determine the H positions, thereby facilitating elucidation of the structural characteristics and formation environment of gowerite. The crystal structure of synthetic gowerite, Ca[B₅O₈(OH)][B(OH)₃].3H₂O, is monoclinic with unit-cell parameters: $a = 12.872(4)$, $b = 16.326(4)$, $c = 6.5634(18)$ Å, and $\beta = 121.319(3)^\circ$, and volume $V = 1178.3(6)$ Å³. The crystal symmetry corresponds to the space group $P2_1/a$; the unit cell contains four formula units ($Z = 4$). The structure is refined via full-matrix least-squares on F^2 to a final $R1$ index of 4.13% for 1730 unique observed [$F_o \geq 4\sigma(F_o)$] reflections, measured with MoK α radiation. The locations of the H atoms are identified on the difference Fourier maps and refined considering constraints on O-H distances together with interatomic distances between the H atoms. The crystal structure is characterized by a curved, corrugated, two-dimensional sheet in the a - c plane, composed of double three-membered borate rings and Ca atoms coordinated to six O atoms from the double three-membered rings. The Ca atom is further coordinated to a H₂O molecule, and an isolated B(OH)₃ triangle is oriented approximately perpendicular to the sheets. Hydrogen-bonding interactions solely govern the linkages between the sheets. Consequently, three H₂O groups are accommodated in the spaces between the sheets. An important feature of gowerite is that within the triangle geometry, the B-O bond length between the B atom and the hydroxyl group cannot be clearly distinguished from that between the B and O atoms. Ab initio quantum chemical calculations reveal that the molecular orbitals are spatially well spread over the three-membered borate ring, indicating that the B atoms are connected to the O atoms through covalent bonding. During the secondary mineralization process, the structural units of the fundamental building blocks (FBBs) are released from parent borate minerals, such as colemanite, priceite, and hydroboracite, by mineral weathering and inherited by the FBBs in gowerite. In addressing gaps in the existing literature, this study provides further information on the crystal structure and structural characteristics of gowerite, shedding light on its possible formation environment and growth conditions.

Keywords: Gowerite, borate minerals, hydrogen bonding, single-crystal X-ray diffraction, ab initio quantum chemical calculation