

Minerals in cement chemistry: A single-crystal neutron diffraction and Raman spectroscopic study of thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$

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ABSTRACT

Thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$, is recognized as a secondary-alteration mineral and indicator of sulfate attack in Portland cement in contact with sulfate-rich groundwater, especially in cold regions. The hydrogen positions in thaumasite have been determined from single-crystal neutron diffraction structure refinements at 300 and 22 K. No phase transitions occur within the temperature range investigated. The structure of thaumasite is largely held together by hydrogen bonding. The major structural units [CO_3 groups, SO_4 tetrahedra, $\text{Si}(\text{OH})_6$ octahedra, and $\text{Ca}(\text{OH})_4(\text{H}_2\text{O})_4$ polyhedra] are interconnected via 10 distinct hydrogen bonds. Analysis of the difference-Fourier maps of the nuclear density reveals the positions of all 10 hydrogen atoms in the structure, and the hydrogen bonding becomes shorter (stronger) upon decreasing temperature to 22 K. The SO_4 tetrahedron expands upon decreasing temperature (i.e., negative thermal expansion at the molecular level), driven by shortening of the hydrogen bonding between $[\text{Ca}_3\text{Si}(\text{OH})_6(\text{H}_2\text{O})_{12}]^{4+}$ columns. Polarized Raman spectra of thaumasite show that the ν_1 symmetric stretching modes of $\text{Si}(\text{OH})_6$, SO_4 , and CO_3 occur at 658, 983, and 1066 cm^{-1} , respectively. In addition, the out-of-plane bending mode (ν_2) and asymmetric stretching mode (ν_3) of the carbonate group are tentatively assigned to bands at 887 and 1400 cm^{-1} , respectively. Bands at 418 and 455 cm^{-1} (and possibly at 477 cm^{-1}) are attributed to the symmetric bending modes (ν_2) of the sulfate group, and we observe a possible asymmetric stretching mode (ν_3) of SO_4 at 1090–1100 cm^{-1} . Splitting of some sulfate and carbonate vibrational modes may occur due to hydrogen bonding on all the oxygen sites. At 1685–1710 cm^{-1} we observe the H_2O bending modes (H-O-H), and from 2900–3600 cm^{-1} there are 13 distinct bands associated with bending overtones and the O-H stretching vibrations corresponding to H-positions determined in the neutron diffraction study. The effect of the low-temperature stability of thaumasite on the pronounced “thaumasite sulfate attack” of Portland cements observed in cold regions is discussed.

Keywords: Thaumasite, Portland cements, crystal chemistry, single-crystal neutron diffraction, Raman spectroscopy, hydrogen bonding