

Structural change in ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) near the freezing point temperature of water

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Ikaite, one of the calcium carbonate minerals, is thermodynamically stable only at near-freezing temperature and transformed rapidly into calcite and vaterite at ambient temperature. During the phase transformation with dehydration, its crystal shape is preserved as pseudomorphs, termed glendonite, thinolite, and gennoishi. This study aims to clarify the structure change and dehydration mechanisms by using low-temperature single-crystal X-ray diffraction study. At -50 °C, the crystal structure of ikaite is monoclinic, space group $C2/c$ with the unit cell parameter $a = 8.8134$ (1), $b = 8.3108$ (1), $c = 11.0183$ (1) Å, $\beta = 110.418$ (1) °. It is composed of four $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecules in the cell. With increasing temperature, the unit cell volume is increased monotonously from 756.3 to 758.0 Å³ between -50 and -20 °C, and then jumped to 771.0 Å³ at -10 °C. The unit cell lattice anisotropically expands mainly along the c -axis, followed by the a -axis. The intramolecular Ca-O(5) bond distance is drastically elongated at -10 °C, which is associated with elongations of the intermolecular O(2)-O(3), O(2)-O(5), O(4)-O(5) distances. The a unit cell expansion is directly due to the elongation of the O(2)-O(5) aligned parallel to the a -axis. The drastic elongation of the Ca-O(5) bond distance gives rise to an initial dehydration of the $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecule. The intermolecular Ca-O(3)-O(2) angle is constantly increased with temperature, leading to rotational motion of the $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ molecule along b -axis. This is responsible for the highest expansion coefficient of the c lattice parameter.

Keywords: ikaite, vaterite, calcium carbonate, pseudomorph, low-temperature X-ray diffraction study