High pressure phase transition of calcite and the crystal structure of calcite III

Ayako Yokoyama[1], Masanori Matsui[2], Kenji Hagiya[3], Yuichi Akahama[4]

[1] Material Sci.,Himeji Inst. of Tech., [2] Fac. of Sci., Himeji Inst. of Tech., [3] Life Sci., Himeji Inst. of Tech., [4] Material Sci. Himeji Inst. Tech.

Calcite is observed to transform to calcite II near 1.5 GPa, and further to calcite III near 2 GPa(Bridgman, 1939; Singh and Kennedy, 1974).   The two transitions, calcite to calcite II and calcite II to III, are reversible but first order in character, with discontinous volume changes at the transitions.   The structure of calcite II was determined by Merrill and Bassett(1975) using high-pressure single-crystal X-ray analysis.   However, the structure of calcite III is much controversial. Using high-pressure powder X-ray measurements, Davis(1964) proposed that calcite III is isostructural with KNO_3 IV and is orthorhombic with Z = 10.   Merrill and Bassett(1972) suggested calcite III is monoclinic with Z = 8.   Furthermore, Smyth and Ahrens(1997) proposed another structure for calcite III, which has space group C2 with Z = 6.   Based on energy-dispersive X-ray diffraction experiments, both Fiquet et al.(1994) and Suito et al.(2001) supported the orthorhombic cell of calcite III as proposed by Davis(1964).

In this study, we determined the structure of calcite III, by combining use of computational modeling and high-pressure X-ray powder diffraction analysis.   The energy minimization method is used to obtain a stable structure of calcite III at high pressure.   Interatomic potentials used for simulation were taken from Pavese et al.(1992) who approximated the potential as the sum of two-body interactions and covalent terms in carbonate ions.   High-pressure X-ray diffraction experiments were made using diamond-anvil-cell at the pressures 3.1 and 3.6 GPa and room temperature.

Starting from the calcite II structure, we simulated the structural change with pressure, and found a dense monoclinic phase with space group P21/m and Z = 4 at pressures greater than 4 GPa.   To test this energy-minimized structure of calcite III, we refined the cell parameters using the measured X-ray data at 3.1 and 3.6 GPa, and calculated X-ray diffraction intensities, resulted in a good agreement between the observed and calculated X-ray powder patterns.   We found a volume change at the calcite II to III transition to be 1.95 cm3/mol at 3.5 GPa, which is compared with the reported value of 1.29 cm3/mol at 1.74 GPa measured using a piston-cylinder apparatus by Singh and Kennedy(1974).