Incorporation of Incompatible Strontium and Barium Ions into Calcite (CaCO$_3$) through Amorphous Calcium Carbonate

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Ba Concentrations in ACC

Ba/(Ca + Ba) ratio in ACC samples was determined by measuring the Ca and Ba concentrations using ICP-MS (iCAP Qc, Thermo Fisher Scientific). Sample solutions were prepared by dissolving 10 mg of ACC sample in 10 mL of 1.5 M HCl. As an internal standard, a solution containing 1 ppm of Y was used. Ba and Ca concentrations in the solutions were determined by monitoring ^{130}Ba and ^{43}Ca ions.

Figure S1 shows obtained Ba concentrations of starting solutions versus those of ACC samples precipitated from the solutions. No obvious difference was observed between Ba concentrations of a starting solution and ACC precipitated from the solution.
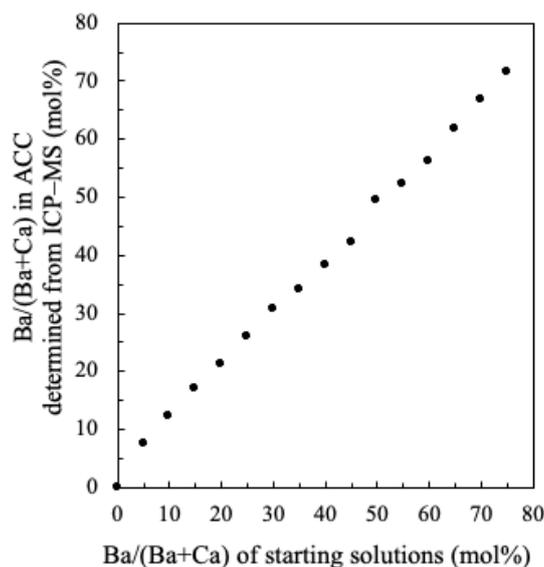
Figure S1. Ba/(Ba + Ca) molar ratios of starting solutions versus those of ACC samples precipitated from the solutions.

Derivation of Interatomic Potentials of Ba

Interatomic potentials of Ba for MD simulation of Ba-doped calcite were derived by conducting MD simulations of witherite ($BaCO_3$ with aragonite structure). The unit cell adopted in this MD simulation was composed of 96 crystallographic unit cells of $BaCO_3$ ($a_{MD} = 4b$, $b_{MD} = 4c$, $c_{MD} = 6a$, in the orthorhombic setting), containing 1820 atoms. Experimentally obtained structure of Wyckoff (1963) was used as the initial structure. After preliminary annealing of initial structure at 300 K and 1 atm, (1) temperature was increased from 300 K at 1 atm, and (2) pressure was increased from 1 atm at 300 K. Crystallographic properties were obtained from time average taken over a sufficiently long time (at least 5 ps) after annealing at each condition for 5 ps.

Newly derived potential parameters listed in Table 2 were validated by comparing density, thermal expansivity (Figure S2a), and compressibility (Figure S2b) of $BaCO_3$ between experimental data and MD simulation. Phase transition of orthorhombic low temperature phase (α-$BaCO_3$) to trigonal high temperature phase (β-$BaCO_3$) at 1093 K was also reproduced successfully, although calculated transition temperature was lower than the experimental value Furthermore, cell parameters of Ba-doped calcite obtained from MD simulation with this parameter set are consistent with the experimental results (Figure S3), which certified that newly derived parameters should be reliable enough to analyze the atomic behavior of Ba-doped calcite.

(a)   (b)
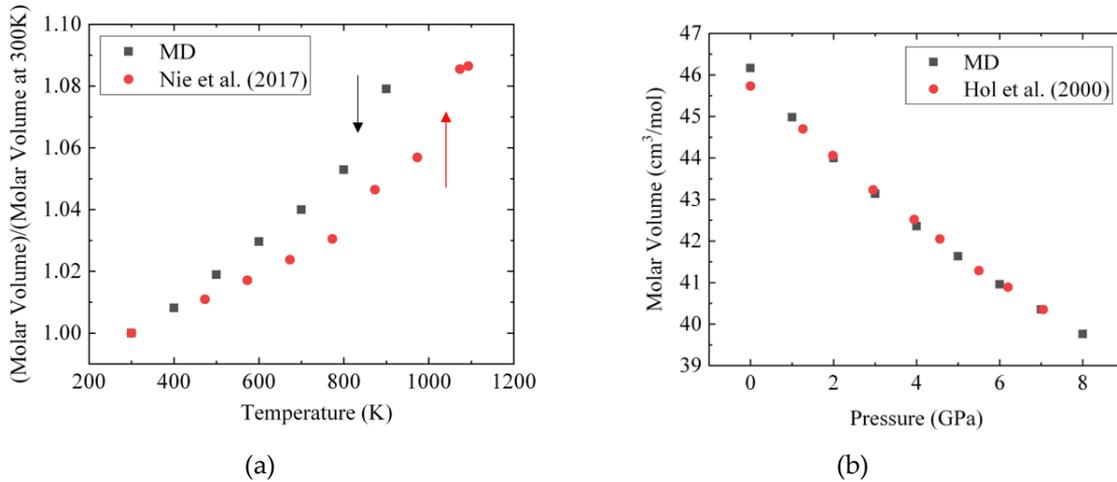
Figure S2. (**a**) Temperature and (**b**) pressure dependence of the molar volume of MD-simulated and experimentally obtained $BaCO_3$. Black and red arrows in Figure S2(a) shows that phase transitions occurred at that temperature.
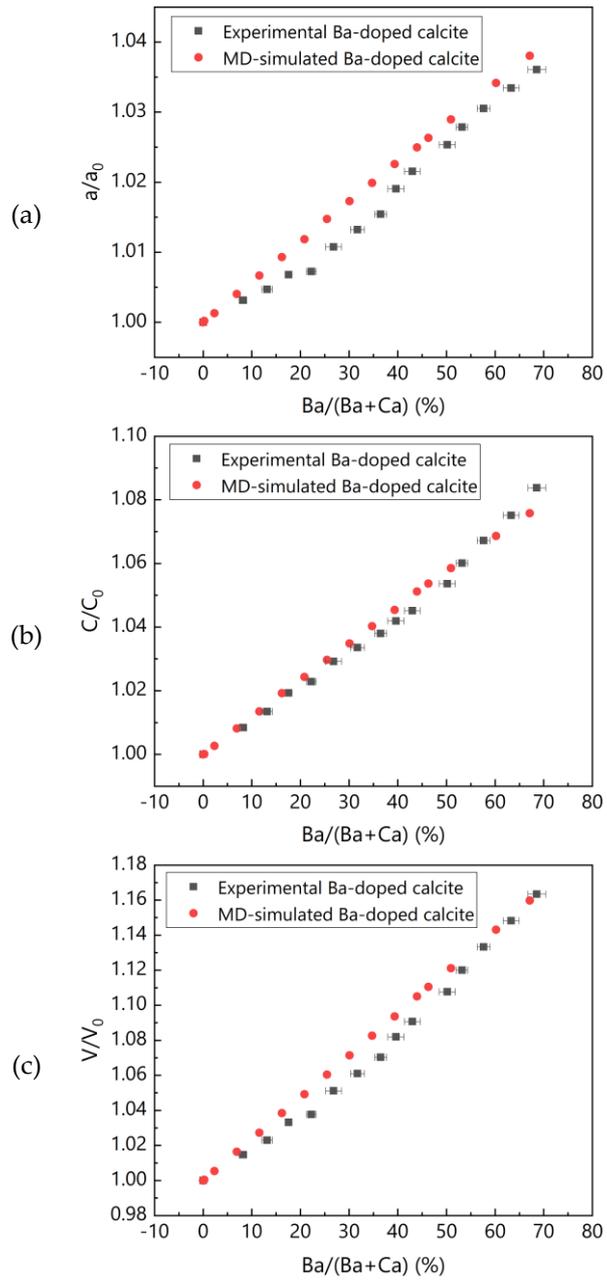
Figure S3. Cell parameters of MD-simulated and the present experimental results of Ba-doped calcite.