

Pressure-induced crystallization of amorphous calcium carbonate

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Amorphous calcium carbonate (hereafter ACC, $\text{CaCO}_3 \cdot n\text{H}_2\text{O}$), a metastable phase of calcium carbonate, contains variable amounts of water molecules and is a precursor of crystalline calcium carbonate, such as calcite, aragonite and vaterite. ACC immediately crystallizes in an aqueous solution or a humid condition. In nature, ACC stably exists only in biominerals, produced by living organisms. Crystals with complicated shapes are formed via ACC in biomineralization. Understanding crystallization of ACC will contribute to well understandings of the fundamental properties of ACC such as stability, structure, and mechanism of biomineralization. It is already known that ACC crystallizes by heating (e.g. Koga et al., 1998). On the other hand, stability of ACC at high pressure is unknown. In general, it is known that some amorphous materials show structural changes and pressure-induced crystallization by pressure. This study newly investigated pressure response of ACC at room temperature.

ACC was synthesized by the following procedure; aqueous solutions of 0.1 M CaCl_2 and 0.1 M Na_2CO_3 at 0 degree C were mixed, and the obtained suspension was filtered and dried in vacuum condition at room temperature. Vacuum drying was conducted using a diaphragm pump (about 10^2 Pa) for one day. The water content of ACC was estimated from water loss in TG-DTA. The compression experiment on ACC was conducted using a piston-cylinder and a hydraulic press. The applied pressure was kept in the range of 0.08-0.8 GPa for 10 min in the each run. The appearance of crystalline phases of calcium carbonate was characterized by power XRD patterns of as-grown ACC and the samples recovered from high pressure.

Chemical formula of the obtained ACC was $\text{CaCO}_3 \cdot 1.5\text{H}_2\text{O}$, which is consistent with previous studies. XRD patterns of the ACC ($n = 1.5$) and its pressured samples demonstrated that ACC transforms to crystalline calcium carbonate (calcite and vaterite) at pressures greater than 0.2 GPa at room temperature. The crystallization pressure of ACC is the lowest in amorphous materials reported before: for instance, amorphous alloys, silicon, and so on.

It is expected that the properties, including pressure response, of ACC depend on its water content. For comparing pressure response between ACCs with different water contents, ACC with less water content was necessary to be synthesized. We tested the possibility that the water content of ACC can be controlled by changing vacuum condition. For this purpose, additional evacuation for another day was applied to the ACC ($\text{CaCO}_3 \cdot 1.5\text{H}_2\text{O}$) using a turbo-molecular pump (about 10^{-3} Pa). As a result, water content of the obtained ACC was substantially decreased ($\text{CaCO}_3 \cdot 0.6\text{H}_2\text{O}$). XRD patterns of the ACC ($n = 0.6$) and its pressured samples indicated that ACC ($n = 0.6$) crystallized at pressure over 0.6 GPa, which is notably higher than the transition pressure of ACC ($n = 1.5$). These results suggest that the water contained in ACC plays an important role in pressure-induced crystallization of ACC.

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