

## **Incorporation of Ba<sup>2+</sup> into calcite and impurity-induced rotational disorder at room temperature**

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Calcium carbonate, a ubiquitous mineral in nature, has three polymorphs; calcite, aragonite and vaterite. Crystal structures of carbonates are constrained by ionic radii of the cations. Large cations such as Sr<sup>2+</sup> and Ba<sup>2+</sup> are incompatible to calcite. Actually, partitioning coefficients of Sr and Ba into calcite are much smaller than those of Mg into calcite. Recently, we have found that incompatible cations can be structurally incorporated into calcite through crystallization from amorphous calcium carbonate (ACC) [1].

In this study, we synthesized Ba-doped calcite with Ba/(Ba+Ca) up to 68.6±1.8 mol% with the unit-cell volume of 426.42(6) Å<sup>3</sup>. The obtained Ba-doped calcite can be interpreted as Ca-containing barium carbonate with the calcite structure, which cannot be found in nature or synthesized from a direct precipitation from the super saturated solutions.

XRD patterns of the Ba-doped calcite samples obtained at room temperature showed that reflection 113 gradually weakened with increasing Ba/(Ba+Ca) and disappeared at Ba/(Ba+Ca) higher than 26.8±1.6 mol%. Extinction of reflection 113 was reported for pure calcite at temperatures higher than 1240 K, which was attributed to the rotational disorder of CO<sub>3</sub><sup>2-</sup> in calcite [2]. It is note worthy that the disappearance of 113 reflection suggesting the “rotational disorder of CO<sub>3</sub><sup>2-</sup>” was observed at room temperature.

To test the possibility of rotational disorder at room temperature, MD simulation of Ba-doped calcite was conducted to investigate behavior of CO<sub>3</sub><sup>2-</sup>. The details of the obtained results will be presented in the conference.

[1] Matsunuma S., Kagi H., Komatsu K., Maruyama K. and Yoshino T. (2014) Doping incompatible elements into calcite through amorphous calcium carbonate. *Crystal Growth & Design*, **14**, 5344-5348.

[2] Ishizawa N., Setoguchi H. and Yanagisawa K. (2013) Structural evolution of calcite at high temperatures: phase V unveiled. *Scientific Reports*, **3**, 2832.