

## Synthesis of barium carbonate with calcite structure and rotational disorder of carbonate ions

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Structures of divalent metal carbonate is constrained by the ionic radii of cations. Cations larger than  $\text{Ca}^{2+}$  take the aragonite structure and cations smaller than  $\text{Ca}^{2+}$  take the aragonite structure. Barium carbonate (witherite) takes the aragonite structure and  $\text{Ba}^{2+}$  is incompatible to calcite. We have reported that large incompatible cations can be introduced to calcite through amorphous calcium carbonate (ACC). In this study, we synthesized  $\text{Ba}_{0.7}\text{Ca}_{0.3}\text{CO}_3$  with the calcite structure by heating treatment on ACC containing  $\text{Ba}^{2+}$ . The obtained crystal 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 supersaturated solutions.

X-ray diffraction (XRD) patterns of Ba-doped calcite measured at 300 K shows the extinction of 113 reflection with increasing Ba concentration (see Figure 1). The extinction of the 113 reflection was reported on pure calcite at temperatures higher than 1240 K (Ishizawa et al., 2013). The change was attributed to the rotational disorder of  $\text{CO}_3^{2-}$  ions. In contrast, we have observed the extinction of 113 reflection on the Ba-doped calcite at 300 K.

To investigate the behavior of  $\text{CO}_3^{2-}$  ions at an atomistic level, molecular dynamics (MD) simulation of Ba-doped calcite was conducted using the MD program, MXDTRICL (Kawamura 1997). Intensity ratio of reflections 113 to 104 ( $I_{113}/I_{104}$ ) was measured from XRD patterns obtained from experimental study and MD simulation.  $I_{113}/I_{104}$  from experiment dropped to 0 at  $\text{Ba}/(\text{Ba} + \text{Ca}) = 26.8 \pm 1.6$  mol% while that of MD-simulated Ba-doped calcite gradually weakened and did not fall to zero. MD simulations of 25.5% and 50.9% Ba-doped calcite at high temperature were also conducted. In 25.5% Ba-doped calcite,  $I_{113}/I_{104}$  remarkably dropped at around 1050 K with the structure of rotationally disordered  $\text{CO}_3^{2-}$  ions. The transition temperature to the rotational disorder was at around 850 K for 50.9% Ba-doped calcite. These simulated temperatures are much lower than the transition temperature (1250 K) obtained from MD simulation on pure calcite (Kawano et al., 2009). The simulated results showed that the transition temperature to the rotationally disordered phase dramatically decreased with increasing  $\text{Ba}/(\text{Ba} + \text{Ca})$  in calcite.

Keywords: barium carbonate, molecular dynamics simulation, rotational disorder, calcium carbonate (calcite)

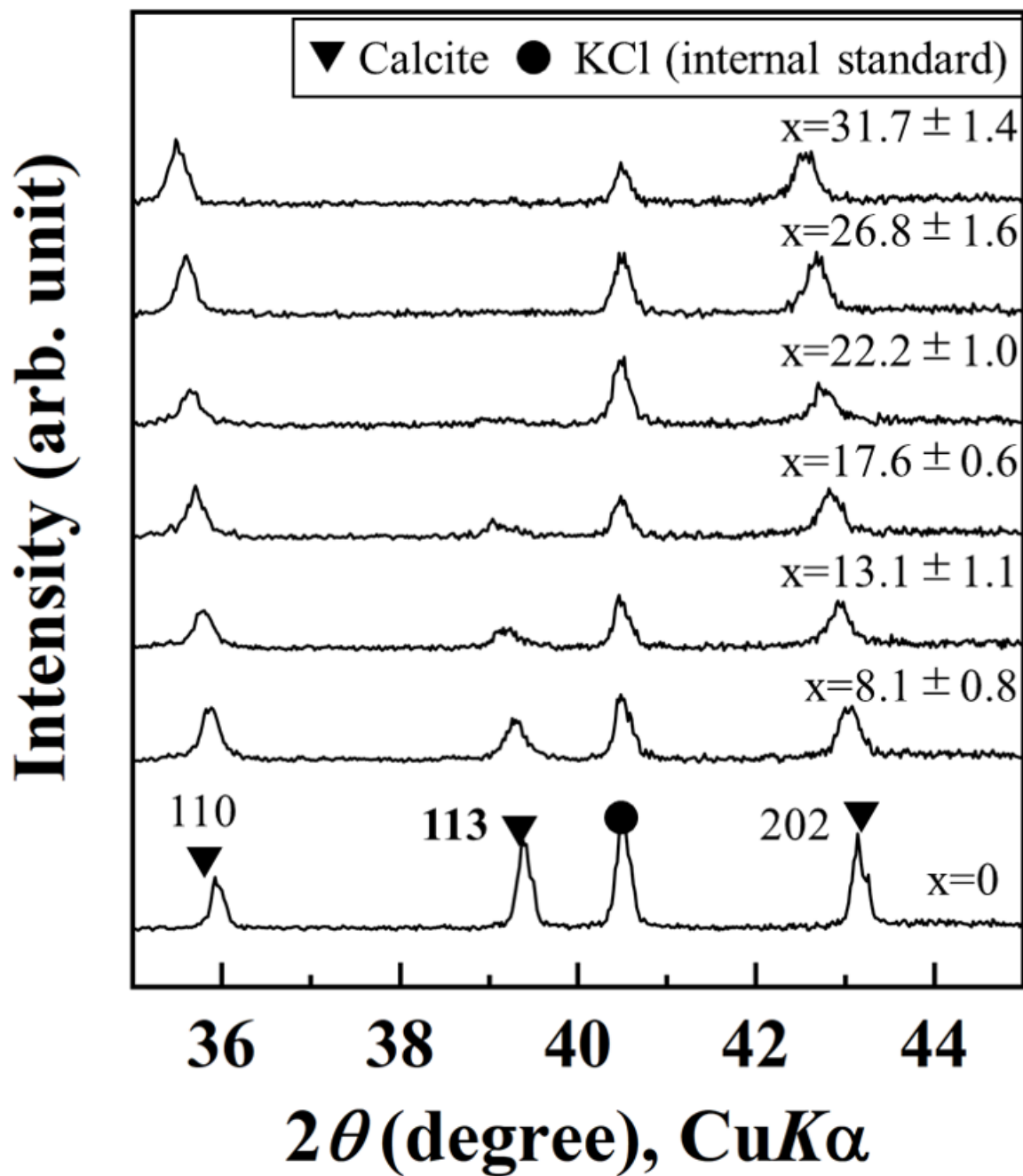


Figure 1. Broadening and disappearance of reflection 113 observed from powder X-ray patterns of Ba-doped calcite samples.  $x$  stands for Ba/(Ba+Ca) mol% in Ba-doped calcite.