

# Disorder of carbonate ions at room temperature and high-pressure behavior of Ba-doped calcite

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## **Introduction**

Calcite, one of the main polymorphs of  $\text{CaCO}_3$ , is a ubiquitous mineral in nature. It is known that ions with larger ionic radius than  $\text{Ca}^{2+}$  (1.00 Å) is incompatible to the structure of calcite. However, Matsunuma et al. (2014) [1] reported that incompatible  $\text{Sr}^{2+}$  (1.18 Å) can be incorporated into calcite through crystallization of amorphous calcium carbonate (ACC). In this study, more incompatible  $\text{Ba}^{2+}$  (1.35 Å) was incorporated into calcite and changes in properties of Ba-doped calcite was investigated. Behavior of Ba-doped calcite at high pressure was also examined.

## **Experimental procedures**

Barium-doped ACC samples were synthesized based on Matsunuma et al. (2014). Obtained Barium-doped ACC samples were heated for 2 hours at 400 °C for crystallization of calcite. Powder X-ray diffraction (XRD) patterns of the obtained samples were measured at room temperature using a silicon zero background plate and an X-ray diffractometer (Miniflex II, Rigaku Corp.). High pressure experiments were conducted using diamond anvil cells (DACs). A stainless steel gasket with thickness of 260 μm was pre-intended to about 140 μm. Synthesized Ba-doped calcite samples were loaded into the gasket hole and 4:1 methanol-ethanol was used as a pressure medium. XRD patterns were obtained at pressure points up to 5.0 GPa. Pressures were determined using ruby fluorescence method.

## **Results and discussion**

Unit-cell parameters of calcite samples obtained from heating treatment of Ba-doped ACC were refined using Rietveld analysis on the XRD patterns. Unit-cell volume of calcite crystallized from Ba-doped ACC monotonically increased with increasing Ba concentration in the starting solutions, which indicates the incorporation of  $\text{Ba}^{2+}$  into calcite. XRD patterns of Ba-doped calcite showed that reflection 113 gradually broadened and finally disappeared at  $\text{Ba}/(\text{Ba}+\text{Ca}) = 26.8 \pm 1.6$  mol% (Fig. 1). Ishizawa et al. (2013) reported the rotational disorder of carbonate ions at 1240 K under  $\text{CO}_2$  atmosphere of 0.4 MPa [2]. When carbonate ions are in rotational disorder, the symmetry of crystal changes and leads to the disappearance of reflection 113. The disappearance of reflection 113 observed in our study indicates that incorporation of  $\text{Ba}^{2+}$  into calcite induced rotational disorder of carbonate ions at room temperature.

Pure calcite undergoes phase transition into calcite II at around 1.5 GPa and transition of calcite II to calcite III occurs at around 2.0 GPa. However, no phase transitions were observed from XRD patterns of Ba-doped calcite obtained in this study.

This study clarified that incorporation of incompatible  $\text{Ba}^{2+}$  into calcite induced substantial changes in properties of calcite.

## **References**

[1] Matsunuma, S.; Kagi, H.; Komatsu, K.; Maruyama, K.; Yoshino, T. *Cryst. Growth Des.* **2014**, *14* (11), 5344–5348.

[2] Ishizawa, N.; Setoguchi, H.; Yanagisawa, K. *Sci. Rep.* **2013**, *3* (1), 2832.

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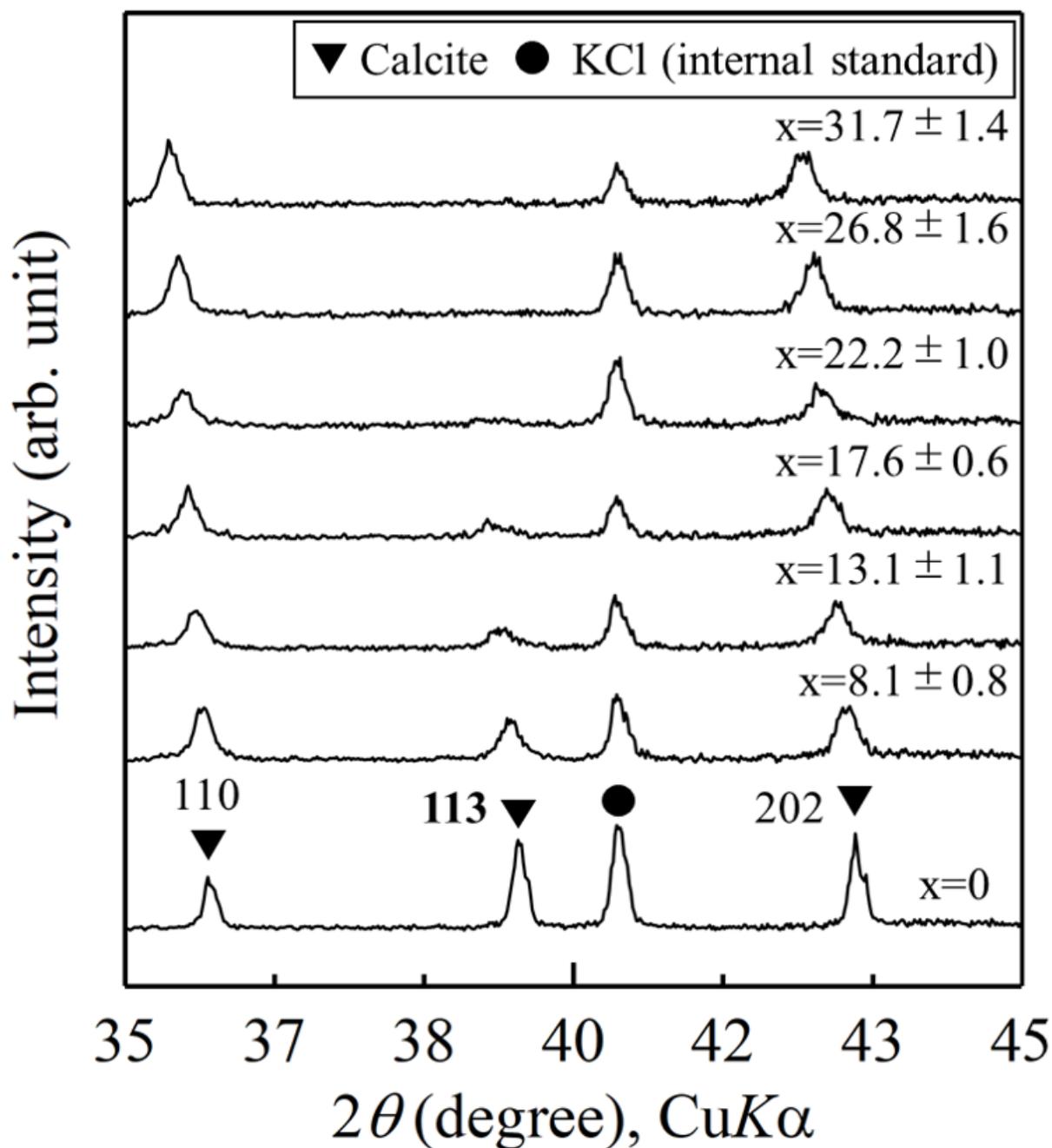


Figure 1. Broadening and disappearance of reflection 113 observed from powder X-ray patterns of Ba-doped calcite samples.  $x$  stands for Ba/(Ba+Ca) mol% in Ba-doped calcite.