

## Post-perovskite phase transitions in $\text{CaB}_4\text{O}_3$

Yuichi Shirako[1]; # Masaki Akaogi[1]; Hiroshi Kojitani[1]; Sayaka Takamori[2]; Kazunari Yamaura[3]; Eiji Takayama-Muromachi[3]

[1] Dept. of Chem., Gakushuin Univ.; [2] Depart. Chem., Gakushuin Univ.; [3] Nat. Inst. Mater. Sci.

Since high-pressure transition from perovskite to post-perovskite in Mg-silicate has been discovered, a number of experimental studies have been performed to clarify the nature and dynamics of the earth's lowermost mantle. Because the post-perovskite transition occurs at pressure exceeding 100 GPa and the post-perovskite type mantle silicate cannot be quenched to ambient conditions, some physical properties of the post-perovskite phase would be difficult to study at very high pressures. Therefore, studies on quenchable analogue materials that show the same transition would be useful to estimate the properties of post-perovskite type mantle silicate.  $\text{CaIrO}_3$  (McDaniel and Schneider, 1972),  $\text{CaRuO}_3$  (Kojitani et al., 2007a) and  $\text{CaPtO}_3$  (Ohgushi et al., 2008) have been so far found as the quenchable post-perovskite analogues. In this study, we have searched for new analogue materials, and have found that  $\text{CaRhO}_3$  transforms to the post-perovskite phase. We have also measured enthalpy of post-perovskite transition in  $\text{CaRuO}_3$ . Based on these results, we discuss on relationship of structural distortion of perovskite with the post-perovskite transition.

The starting material was  $\text{CaRhO}_3$  perovskite synthesized at 6 GPa and 1600-1900 C. The high-pressure equilibrium experiments were carried out using a multianvil apparatus up to 27 GPa and 1930 C. The quenched samples were examined by micro-focus and powder X-ray diffractometers. Enthalpies of  $\text{CaRuO}_3$  perovskite and post-perovskite were measured using a Calvet type calorimeter.

The experimental results show that  $\text{CaRhO}_3$  perovskite transforms to post-perovskite via an intermediate phase with increasing pressure. Molar volume changes from  $\text{CaRhO}_3$  perovskite to the intermediate phase and from the intermediate phase to post-perovskite are -1.1% and -0.7%, respectively. The b axis length of the monoclinic intermediate phase suggests that the structure has edge-sharing octahedra like post-perovskite. Clapeyron slopes of the transition boundaries are  $29 \pm 2$  and  $62 \pm 6$  MPa/K, respectively, for the perovskite-intermediate phase and the intermediate phase-postperovskite transitions. Enthalpy of the  $\text{CaRuO}_3$  perovskite-postperovskite transition is  $15.2 \pm 3.3$  kJ/mol, and enthalpies of formation of  $\text{CaRuO}_3$  perovskite and post-perovskite from  $\text{CaO} + \text{RuO}_2$  are -55.7 and -40.5 kJ/mol, respectively.

Structural distortion from cubic perovskite to orthorhombic one can be expressed by a tilt angle of octahedral framework,  $\phi = \cos^{-1}(\sqrt{2}a/2bc)$ , where a, b and c are orthorhombic cell parameters. The  $\phi$  increases in the order of  $\text{CaRuO}_3$ ,  $\text{CaRhO}_3$  and  $\text{CaIrO}_3$ . The measured enthalpies indicate that enthalpy of  $\text{CaIrO}_3$  perovskite (Kojitani et al., 2007b) from constituent oxides is much larger than that of  $\text{CaRuO}_3$  perovskite, suggesting that  $\text{CaIrO}_3$  perovskite with a larger  $\phi$  is energetically less stable than  $\text{CaRuO}_3$  perovskite with a smaller  $\phi$ . The fact that transition pressures of  $\text{CaBO}_3$  perovskite (B = Ir, Rh, Ru) to post-perovskite at around 1200 C are approximately proportional to  $\phi$  of the perovskites supports the idea that the transition of perovskite to post-perovskite may be attributed mostly to instability of perovskite structure due to increase of the tilt angle with pressure.