

High-Pressure Transitions of NaZnF₃ and NaMnF₃ Perovskites with Implication to MgSiO₃ Postperovskite Analogues

Masaki Akaogi^{1*}, SHIRAKO, Yuichi¹, NAGAKARI, Takayuki¹, KOJITANI, Hiroshi¹, YUSA, Hitoshi², YAMAURA, Kazunari²

¹Dept. Chem., Gakushuin University, ²Nat. Inst. Mater. Sci.

It is accepted that MgSiO₃-rich perovskite (Pv) transforms to postperovskite (pPv) in the lowermost mantle. Investigations on MgSiO₃ pPv properties are of great interest to clarify the structure and dynamics of the core-mantle boundary region. However, because of high stability pressure and temperature of MgSiO₃ pPv exceeding 120 GPa and 2000 oC and amorphization of the pPv on release of pressure, ABX₃ compounds that undergo the Pv-pPv transition at lower pressure and are quenchable to ambient conditions are important as analogues for MgSiO₃. In recent years, we found that CaRuO₃, CaRhO₃, NaNiF₃ and NaCoF₃ undergo the Pv-pPv transition below about 20 GPa, and determined the phase relations. We also refined the pPv structures and measured some physical properties (Kojitani et al., 2007, Shirako et al., 2009, 2012, Yusa et al., 2012). In this study, we have examined high pressure transitions in NaZnF₃ and NaMnF₃ and determined the phase relations as well as structural refinement of the NaZnF₃ pPv. Combining the previous results on NaNiF₃ and NaCoF₃, we discuss on A+B₂+F₃ fluorides as analogue compounds for the Pv-pPv transition in MgSiO₃.

High pressure experiments on NaZnF₃ and NaMnF₃ were made at 9-24 GPa and 600-1000 oC using a multianvil apparatus. The recovered NaZnF₃ samples were crushed into powder in liquid nitrogen, and examined by powder X-ray diffraction for phase identification. The run products of sintered NaMnF₃ samples were examined by microfocus X-ray diffraction method. The structure of NaZnF₃ pPv was refined by Rietveld analysis.

NaZnF₃ Pv transforms to pPv at 10-15 GPa. The NaZnF₃ pPv partially transforms back to Pv on release of pressure. The transition boundary in NaZnF₃ is expressed as $P(\text{GPa}) = 4.9 + 0.011T(\text{oC})$, and its volume change is -1.9 %. At 8-11 GPa, NaMnF₃ Pv dissociates into two phases of Na₃Mn₂F₇ and MnF₂. Although the MnF₂ phase in the recovered samples has a ?PbO₂-type structure, it is suggested to be an O-I type or cotunnite-type structure at high pressure. The refined structure of NaZnF₃ pPv is close to that of NaNiF₃ pPv. Deformation of octahedra in the two pPv structures is similar to that of MgSiO₃ pPv at 120 GPa (Murakami et al., 2004), but is smaller than those in CaMO₃ pPv (M = platinum group elements and Sn). The Pv-pPv transitions in NaZnF₃, NaNiF₃ and NaCoF₃ occur at pressure below about 20 GPa. The axial compressibilities of Pvs and pPvs of the three fluorides change in the same order as those of MgSiO₃ Pv and pPv. The Pv-pPv transitions in the three fluorides occur at the Pv octahedral tilt-angle of about 26°, at which the transition occurs in MgSiO₃. All of the above results suggest that the fluorides are good quenchable, low-pressure analogues for the Pv-pPv transition in MgSiO₃. In particular, NaNiF₃ is most valuable, because the pPv phase is quenchable as the single-phase material at ambient conditions.

Keywords: perovskite, postperovskite, high-pressure transition, fluoride, lower mantle, analogue material