High-Pressure Transitions of NaZnF3 and NaMnF3 Perovskites with Implication to Mg-SiO3 Postperovskite Analogues

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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(GPa) = 4.9 + 0.011T(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 26o, 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