

High-pressure decomposition of FeTiO₃, MgTiO₃ and ZnTiO₃ perovskites

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It is generally accepted that transition of MgSiO₃-rich perovskite (bridgmanite) to CaIrO₃-type postperovskite is responsible for formation of D'' layer in the lowermost mantle. Since discovery of the perovskite-postperovskite transition in MgSiO₃, numerous studies have been made to clarify high-pressure transitions of ABX₃ perovskites. FeTiO₃ and MgTiO₃ are endmembers of natural ilmenite, and ZnTiO₃ is an analogue for these compounds. Previous studies revealed that at 15-20 GPa range FeTiO₃ and MgTiO₃ ilmenites transform to perovskites, which are recovered as LiNbO₃-type phases at ambient conditions. In contrast to many perovskite-type oxides including MgSiO₃ perovskite, FeTiO₃ and MgTiO₃ perovskites do not transform to CaIrO₃-type postperovskite but decompose into two-phase assemblages. However, the transition behaviors of these perovskites are still in controversy, and little has been known on phase assemblage of ZnTiO₃.

We have examined high-pressure transitions in ZnTiO₃ and MgTiO₃ to about 25 GPa and those of FeTiO₃ to about 33 GPa using multianvil apparatus. Pressure was calibrated against press-load using pressure-fixed points at room temperature including GaP and Zr. The pressure was further corrected at high temperature using transition boundaries including dissociation of pyrope into Mg-rich perovskite + corundum. Quenched samples were examined by powder X-ray diffractometers and a scanning electron microscope with an energy-dispersive X-ray spectrometer. Some in-situ X-ray observations on ZnTiO₃ phases have also been made using a diamond anvil cell with synchrotron X-ray diffraction method.

The results by quench and in-situ experiments on ZnTiO₃ indicate that at 1200 °C ZnTiO₃ ilmenite transforms to perovskite at 10 GPa, which dissociates into rocksalt-type ZnO + baddeleyite-type TiO₂ at 22 GPa. On release of pressure, perovskite-type ZnTiO₃, rocksalt-type ZnO and baddeleyite-type TiO₂ are converted into LiNbO₃-type, wurtzite-type and αPbO₂-type phases, respectively. MgTiO₃ perovskite decomposes into MgO + baddeleyite-type TiO₂ at 20 GPa and 1400 °C. FeTiO₃ perovskite dissociates first into CaTi₂O₄-type Fe₂TiO₄ + TiO₂ phase at about 28 GPa. At about 30 GPa, this assemblage further changes into Fe₃Ti₂O₇ phase + TiO₂ phase below about 1100 °C, above which CaTi₂O₄-type Fe₂TiO₄ + FeTi₂O₅ phase were synthesized. These two assemblages have not yet been found in the previous studies. Combination of our results on ZnTiO₃, MgTiO₃ and FeTiO₃ with those of other titanate perovskites suggests that transition pressure of titanate perovskite increases with tolerance factor or ionic radius of divalent cation. It is also indicated that all the titanate perovskites studied dissociate into two-phase assemblages which are denser than hypothetical CaIrO₃-type postperovskites. This is consistent with the previously suggested tendency that ABX₃ perovskites with relatively ionic B-X bonds do not transform to postperovskites.

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