

High-pressure high-temperature phase transitions in ZnTiO_3

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It is widely accepted that perovskite-type MgSiO_3 is the most abundant mineral in Earth's lower mantle. Ilmenite-type MgSiO_3 transforms to perovskite at 23 GPa and 1600 °C. It was reported that ilmenite-type ZnTiO_3 , an analogue to ilmenite-type MgSiO_3 , decomposes into ZnO and TiO_2 at about 20-25 GPa (Ito and Matsui, 1979). However, phase relations in ZnTiO_3 have not been studied yet in detail. Therefore, we investigated the phase relations in ZnTiO_3 by high-pressure high-temperature experiments.

A starting material of ilmenite-type ZnTiO_3 was synthesized by heating a mixture of ZnO and TiO_2 with 1:1 mol ratio at 800 °C for 32 hours in air. High-pressure phase relation experiments were made by using a Kawai-type 6-8 multi-anvil apparatus in the pressure and temperature ranges of 13-35 GPa and 1000-1400 °C, respectively. After keeping the starting sample at desired conditions for 1-2 hours, the samples were quenched, and then decompressed to ambient pressure. Recovered samples were identified by using the powder X-ray diffraction method.

We found that the recovered samples which were compressed between 15 and 20 GPa at 1000-1400 °C had the LiNbO_3 -type (LNO) structure. The ilmenite-LNO phase boundary was determined as $P(\text{GPa})=19.9-0.0038T(^{\circ}\text{C})$. FeTiO_3 ilmenite which is an analogue to ilmenite-type MgSiO_3 transforms to perovskite above 15 GPa, and the perovskite transforms to the LNO-type structure during decompression (Ming et al., 2006). The ilmenite-perovskite phase boundary in FeTiO_3 has a negative slope which is caused by a positive entropy change for the transition due to increase of coordination number of divalent cation from 6 to 8. If the LNO-type ZnTiO_3 is a stable phase, the slope of the boundary should be positive because of no change in the coordination number of the divalent cation. Therefore, the negative slope of the boundary implies that the recovered LNO-type ZnTiO_3 was originally perovskite-type at 15-20 GPa.

The recovered samples synthesized above 20 GPa were identified to be an assembly of wurtzite-type ZnO and $\alpha\text{-PbO}_2$ -type TiO_2 . The post-perovskite phase boundary in ZnTiO_3 is determined as $P(\text{GPa})=9.5-0.010T(^{\circ}\text{C})$. Wurtzite-type ZnO transforms to NaCl-type at about 6 GPa (Kusaba et al., 1999). Also, $\alpha\text{-PbO}_2$ -type TiO_2 transforms to baddeleyite-type at about 17 GPa (Tang and Endo, 1993). Therefore, we suggest that the phase assembly of NaCl-type ZnO and baddeleyite-type TiO_2 is stable above 20 GPa.

Keywords: ZnTiO_3 , Perovskite, LiNbO_3 , High pressure