

## High-pressure high-temperature phase transitions in $\text{ZnTiO}_3$

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It is widely accepted that perovskite-type  $\text{MgSiO}_3$  is the most abundant mineral in Earth's lower mantle. Ilmenite-type  $\text{MgSiO}_3$  transforms to perovskite at 23 GPa and 1600 °C. It was reported that ilmenite-type  $\text{ZnTiO}_3$ , an analogue to ilmenite-type  $\text{MgSiO}_3$ , decomposes into ZnO and  $\text{TiO}_2$  at about 20-25 GPa (Ito and Matsui, 1979). However, phase relations in  $\text{ZnTiO}_3$  have not been studied yet in detail. Therefore, we investigated the phase relations in  $\text{ZnTiO}_3$  by high-pressure high-temperature experiments.

A starting material of ilmenite-type  $\text{ZnTiO}_3$  was synthesized by heating a mixture of ZnO and  $\text{TiO}_2$  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  $\text{LiNbO}_3$ -type (LNO) structure. The ilmenite-LNO phase boundary was determined as  $P(\text{GPa})=19.9-0.0038T(^{\circ}\text{C})$ .  $\text{FeTiO}_3$  ilmenite which is an analogue to ilmenite-type  $\text{MgSiO}_3$  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  $\text{FeTiO}_3$  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  $\text{ZnTiO}_3$  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  $\text{ZnTiO}_3$  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  $\text{TiO}_2$ . The post-perovskite phase boundary in  $\text{ZnTiO}_3$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  is stable above 20 GPa.

Keywords:  $\text{ZnTiO}_3$ , Perovskite,  $\text{LiNbO}_3$ , High pressure