

High-pressure synthesis and phase transformation of LiNbO₃-type oxide

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Introduction

LiNbO₃ (LN)-type structure have a common framework with perovskite (Pv)-type ones in terms of MO₆ (M : metal) octahedra linking all vertices. In the field of earth science, LN-type phase is considered as unquenchable high pressure Pv-type phase, and several LN-phases have been reported as meta-stable quenched phases [1, 2].

We reported that Pv-PbNiO₃ synthesised under high-pressure keeps its structure under ambient pressure and the Pv-phase transforms into the LN-phase by a heat treatment under ambient pressure [3, 4]. However, details of mechanism of phase transformation have not been elucidated. On the other hand, we reported that ZnSnO₃ can be synthesized under high-pressure as LN-phase [3, 5].

In this study, we performed synchrotron X-ray diffraction (XRD) measurements to observe the behaviour of LN-type oxides PbNiO₃ and ZnSnO₃ under high pressure at room and/or high temperature.

Experimental

In-situ powder XRD patterns of LN-type PbNiO₃ and ZnSnO₃ under high-pressure at room temperature were measured with a diamond-anvil cell (DAC) and imaging plate at BL18C (PF). MeOH – EtOH mixed liquid was used as a pressure-transmitting medium. LN-type PbNiO₃ was prepared by a heat treatment of Pv-type PbNiO₃. Pv-type PbNiO₃ and LN-type ZnSnO₃ were synthesized at high-pressure and high-temperature using cubic-anvil-type apparatus.

The reaction between ZnO and SnO₂ to form LN-ZnSnO₃ at high-pressure and high-temperature was monitored by an *in-situ* energy dispersive XRD at BL NE5C (PF-AR). High-pressure was then applied using the cubic-anvil-type apparatus, MAX80. Measurements were performed under the same pressure / temperature conditions as synthesis.

Results and discussion

Fig. 1 shows the variation of the unit cell volume (formula unit) with pressure for PbNiO₃ and ZnSnO₃ at room temperature. PbNiO₃ was transformed from LN-type phase into Pv-type phase under about 8 GPa with a decrease in volume of ~4%. Structure refinement of XRD data at 17 GPa revealed that Pv-type PbNiO₃ possesses an orthorhombic structure with the space group *Pnma* independent of pressure.

On the other hand, ZnSnO₃ showed no structural phase transition. Pv-phase and another polymorph of ZnSnO₃ weren't found in the pressure range up to 24 GPa. This suggests that LN-ZnSnO₃ is stable under high-pressure and high-temperature.

From the *in-situ* XRD studies at high-pressure and high-temperature on the formation of ZnSnO₃, we found that in the low pressure range, spinel-type Zn₂SnO₄ was formed. The formation of LN-ZnSnO₃ requires a sufficiently high pressure.

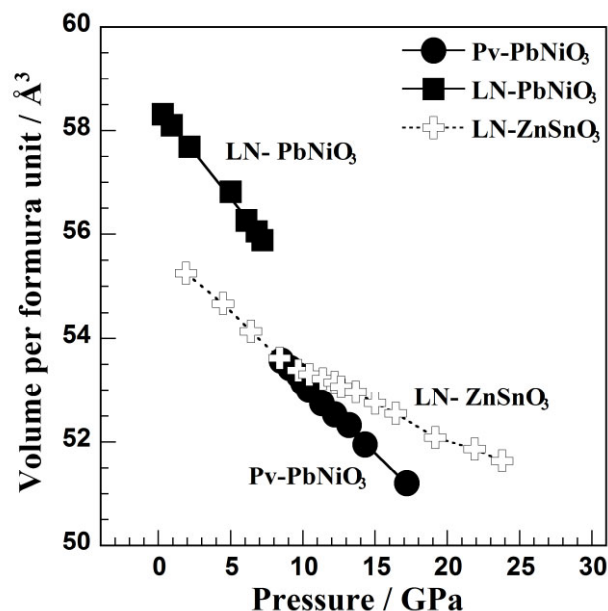


Fig. 1 Relative cell volume per formula unit plotted as a function of pressure for PbNiO₃ and ZnSnO₃ at room temperature.

References

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