

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

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1 Introduction

LiNbO₃ (LN)-type structure have a common framework with perovskite (Pv)-type ones in terms of MO₆ (*M*: metal) octahedra linking all vertices, but a small number of LN-type oxides have been reported compared to Pv-type oxides. On the other hand, 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]. It is anticipated that novel functional LN-type oxides will be synthesized under high-pressure the same as perovskite-type oxides. Recently we have synthesized novel LN-type oxides such as a polar ZnSnO₃ [3], a magnetic semiconductor PbNiO₃ [4] in addition to known LN-type MnMO₃ (*M* = Ti, Sn) showing the dielectric-magnetic coupling [5] by a solid-state reaction under high-pressure at elevated temperature and investigated their structure, and physical properties. Among them, it has been reported that Pv-type 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 clarified.

We have performed synchrotron X-ray diffraction (XRD) measurements to observe the behaviour of LN-type PbNiO₃ under high pressure at room and/or high temperature. It was found that LN-type PbNiO₃ transforms into Pv-type PbNiO₃ under about 8 GPa at room temperature [6]. In this report, the variation of lattice parameters as a function of pressure for LN-type PbNiO₃ is primarily presented.

2 Experimental procedure

Pv-type PbNiO₃ were synthesized at high-pressure and high-temperature using a cubic-anvil-type apparatus NAMO2001 at Gakushuin University. LN-type PbNiO₃ was prepared by a heat treatment of Pv-type PbNiO₃. *In-situ* powder XRD experiments of LN-type PbNiO₃ under high-pressure at room temperature were performed with a diamond-anvil cell (DAC) and imaging plate at BL18C (PF). MeOH – EtOH mixed liquid was used as a pressure-transmitting medium. The reaction at high-pressure and high-temperature was monitored by an *in-situ* energy dispersive XRD experiment using a multianvil-type high

pressure apparatus MAX80 installed in BL NE5C (PF-AR).

3 Results and Discussion

Figure 1 shows the variation of the relative lattice parameters for *a* and *c* for LN-type PbNiO₃ with a pressure at room temperature. As shown in Fig. 1, both of the lattice parameters decrease linearly with a pressure. In addition, the larger variation in *c* parameter than that of *a* parameter was observed. The anisotropic variation is probably attributed to the displacement of Pb ions along *c*-axis with a pressure.

The analysis of *in-situ* XRD results at high-pressure and high-temperature on the formation of LN-type ZnSnO₃ is now in progress, which will be reported in the near future.

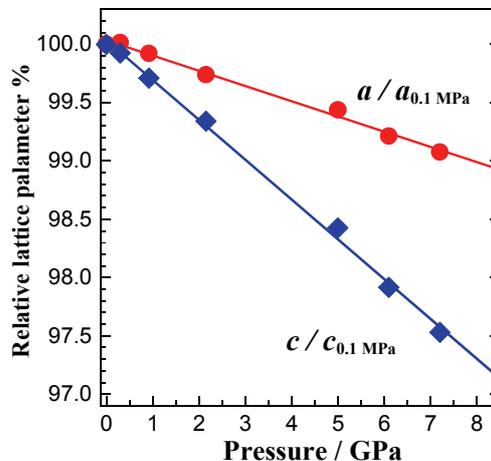


Fig. 1 Variation of relative lattice parameters of *a* and *c* versus a pressure for PbNiO₃ at room temperature.

References

- [1] K. Leinenweber et al., Phys. Chem. Miner. **18**, 244 (1991).
- [2] A. Navrotsky, Chem. Mater. **10**, 2787 (1998).
- [3] Y. Inaguma et al., J. Am. Chem. Soc. **130**, 6704 (2008).
- [4] Y. Inaguma et al., J. Am. Chem. Soc. **133**, 16920 (2011).
- [5] A. Aimi et al., Inorg. Chem., **50**, 6392 (2011).
- [6] K. Tanaka et al., PF Activity Report 2010 #28, Part B p. 240.

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