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High-pressure synthesis, structure, phase relation of polar LiNbO₃-type ZnTiO₃

Y. Inaguma¹, A. Aimi¹, Y. Shirako², D. Sakurai¹, D. Mori¹, H. Kojitani¹, M. Akaogi¹, T. Katsumata³, M. Nakayama⁴

¹Gakushuin University, Department of Chemistry, Tokyo, Japan, ²Nagoya University, Department of Crystalline Material Science, Nagoya, Japan,

³Tokai University, Department of Chemistry, Hiratsuka, Japan, ⁴Nagoya Institute of Technology, Department of Materials Science and Engineering, Nagoya, Japan

Ferroelectricity, piezoelectricity, pyroelectricity, and second-order nonlinear optical behavior are technologically important. Because these properties are attributable to the noncentrosymmetric (NCS) structure[1], the search for materials exhibiting such characteristics must begin with a search of NCS materials. Among them, LiNbO₃-type (LN-type) compounds with a chemical formula of ABX₃ exhibit NCS structures with hexagonal polar space group R3c whose BX₆ octahedra three-dimensionally share their corners the same as perovskite-type compounds[2]. In LN-type compounds, the A cation - B cation repulsion directs the spontaneous polarization along c-axis(Fig. 1). Therefore, we might find attractive functional properties by the selection of constituent ions based on their having a naturally occurring polar LN-type structure attributable to the cation-cation repulsion. With the ideas mentioned above, we have investigated the high-pressure synthesis and characterization of novel LN-type oxides such as ZnSnO₃, PbNiO₃, CdPbO₃ as well as known MnMO₃ (M = Ti, Sn). Recently, we have successfully synthesized a polar LN-type titanate ZnTiO₃ (LN-ZTO) under high pressure and high temperature [3]. The first principles calculation indicates that LN-ZTO is a meta-stable phase obtained by the transformation in the decompression process from the perovskite-type phase, which is stable at high pressure and high temperature. The Rietveld structural refinement reveals that LN-ZTO exhibits greater intra-distortion of the TiO₆ in LN-ZTO than that of the SnO₆ in LN-type ZnSnO₃ (LN-ZSO). The estimated spontaneous polarization are greater than those of LN-ZSO, which is attributed to the great displacement of Ti along c-axis and the greater Born effective charge of Ti (+6.1) than that of Sn (+4.1). Furthermore, the spontaneous polarization of LN-ZTO is greater than that of LiNbO₃, indicating that LN-ZTO, like LiNbO₃, is a candidate ferroelectric material with high performance. The second harmonic generation (SHG) response of LN-ZTO is 24 times greater than that of LN-ZSO. The findings indicate that the intra-octahedral distortion, spontaneous polarization, and SHG response are caused by the stabilization of the polar LN-type structure and reinforced by the second-order Jahn-Teller effect attributable to the orbital interaction between oxygen ions and d⁰ ions such as Ti⁴⁺. We also discuss the relationship between the intra-distortion of BO₆ and polarity in several LN-type oxides.

[1] P. S. Halasyamani, K. R. Poppelmeier, *Chem. Mater.*, 1998, 10, 2753-2769., [2] A. Navrotsky, *Chem. Mater.*, 1998, 10, 2787-2793., [3] Y. Inaguma, A. Aimi, Y. Shirako, et al., *J. Am. Chem. Soc.*, 2014, 136, in press, doi: 10.1021/ja408931v.

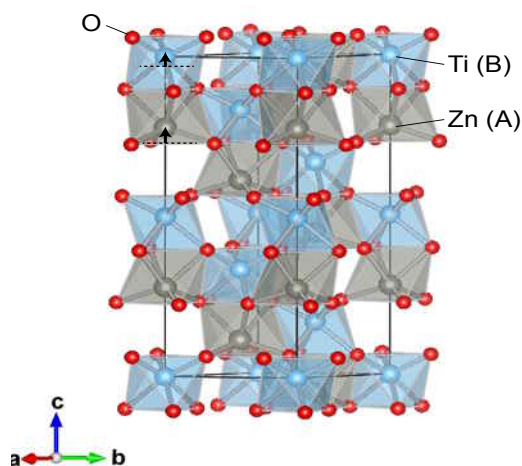


Fig. 1 Lithium niobate-type structure.

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