Disorder of Pb Atom in Cubic Phase of Perovskite-Type Solid Solutions PZT and PZN-PT

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Ferroelectric properties of perovskite-type oxides with the chemical formula ABO_3 are enormously influenced by substituting the other atoms for the *A* and/or *B* atoms. A lot of promising materials have been discovered by taking advantages of this substitution effects. Among them, Pb-based perovskite-type solid solutions $PbZr_{1-x}Ti_xO_3$ (PZT) are well known as piezoelectric ceramics for the industrial applications due to their high electromechanical coupling constant and piezoelectric constant. All PZT do not show the high piezoelectric performance. A PZT with a morphotropic phase boundary (MPB) composition possesses the high piezoelectric properties. In $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PZN–PT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN–PT) systems, the prominent properties are also reported around their MPB compositions. Hence, it is essential to understand the formation mechanism of MPB for designing new piezoelectric ceramics nowadays.

The aim of the present study is to investigate the relationship between the crystal structure of the Pb-based perovskite-type solid solutions in the cubic phase and the appearance of MPB that separates the ferroelectric phase by the vertical phase boundary. High-energy synchrotron-radiation powder-diffraction experiments for PZT ($0 \leq x \leq 1$, MPB at $x \sim 0.5$) and PZN–PT ($0 \leq x \leq 0.3$, MPB at $x \sim 0.1$) in the cubic phase were performed at BL02B2 in SPring-8.

Thus far, every crystal structure of the paraelectric phase has generally been considered to be isomorphous to the classical perovskite with a cubic symmetry, where Pb and *B*-site atoms are settled at the cubic corner and body center, respectively, and O atoms at the face centers. Our precise Rietveld analyses for PZT and PZN-PT with various compositions have showed clear evidence that the Pb atom is disordered around the cubic corner site and the thermal motions significantly change near the MPB composition, while no anomaly on the thermal parameter is revealed for the *B*-site atoms. Hence, we considered that the appearance of MPB is strongly related to the changes in local environment around the Pb atom caused by the *B*-site substitution.