Poster Presentation

MS061.P03

Precursor phenomenon before phase transitions in $PbTiO_3$ and $BaTiO_3$

Akira Yoshiasa[1], Tomotaka Nakatani[1], Akihiko Nakatsuka[2], Maki Okube[3], Hiroshi Arima[3], Kazumasa Sugiyama[3]
[1]*Kumamoto University, Kumamoto, Japan,* [2]*Yamaguch University, Ube, Japan,* [3]*Tohoku University, Sendai, Japan*
E-mail: yoshiasa@sci.kumamoto-u.ac.jp

Single-crystal X-ray diffraction study of synthetic PbTiO3 and BaTiO3 perovskite was carried out in the wide temperature range 298–928 K [1,2]. Transitions from tetragonal to cubic phases have been revealed near 753 and 413 K in PbTiO3 and BaTiO3, respectively. The Pb and Ba ions contribute sufficiently to electric polarization as well as Ti because the positions of all cations shift to the opposite direction of negatively charged O positions in ferroelectric phases. The deviation from the linear changes in Debye-Waller factors and bonding distances in the tetragonal phases can be interpreted as a precursor phenomenon before the phase transition. In PbTiO3, disturbance of temperature factor Ueq for O is observed in the vicinity of transition point while Ueq values for Pb and Ti are continuously changing with increasing temperature. The O site in PbTiO3 and Ti site in BaTiO3 include the clear configurational disorder in the cubic phase. The polar local positional distortions remain in the cubic phase and are regarded as the cause of the para-electricity. The estimated values of Debye temperature ΘD for Pb and Ti are 154 and 467 K in tetragonal PbTiO3 phase and decrease 22% in the high temperature phase. Effective potentials for Pb and Ti in PbTiO3 change significantly and become soft after the phase transition. Ti K-edge X-ray absorption near edge structure (XANES) spectra of PbTiO3 and BaTiO3 were measured in the temperature range from 10K to 900K. Quantitative comparisons for the pre-edge peaks were performed in a wide temperature range and were clarified how intensity of the pre-edge peaks and shoulders changed with temperature. In ferroelectric tetragonal and paraelectric cubic phases, some kinds of peak and shoulder intensity greatly decreases with increasing temperature and the peak top energy shifts to the higher energy side. The decrease of peak intensity in ferroelectric phases is caused by decrease of the distortion in the coordination environment (atomic movement from off-center to center positions). Precursor phenomenon is also observed in the temperature dependence for the pre-edge structure in XANES spectra.

[1] Yoshiasa, A., et al. (2016) Acta Crystallographica B72, 381-388.
[2] Nakatani, T., et al. (2016) Acta Crystallographica B72, 151-159,

Keywords: Single-crystal diffraction, Phase transition, ferroelectric