

Poster Presentation

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Valence Electron Distributions in Ferroelectric Barium Titanate Nanopowders

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Barium titanate BaTiO₃ is one of the most important perovskite-type electroceramics, which undergoes the phase transition at 130 °C from cubic to tetragonal, and exhibits ferroelectricity at room temperature. The phase transition depends on the particle size. BaTiO₃ powders with the particle sizes less than several tens of nanometers are known to show no phase transition and hence no ferroelectricity at room temperature. The size effect of BaTiO₃ is the most important issue in designing small ceramic capacitors with high capacitance. Our group has been devoted to visualizing the electron density distributions of perovskite-type oxides by analyzing the synchrotron-radiation x-ray powder diffraction (SXRD) data measured at SPring-8 using the maximum entropy method (MEM)/Rietveld method [1, 2]. In this study, the distributions of valence electrons in the outer shells of atoms are derived accurately from the SXRD data of BaTiO₃ nanopowders to prove the characteristic chemical bondings which govern the ferroelectric phase transition. The powder samples used were 500 and 35 nm in particle sizes. The former showed the phase transition whereas the latter showed no phase transition. The MEM valence electron density studies at 200 °C in the cubic structure revealed the clear structural variations that the Ti-O covalent bonding is found in the 500 nm sample, while all the valence electrons are localized at the O sites in the 35 nm sample exactly like an ionic crystal. Ferroelectricity originates from the balance between the long-range Coulomb force and the short-range repulsion force. The obtained results provide direct experimental evidence that the electron orbitals hybridization on the Ti-O bonds weakens the short-range repulsion force, and causes the second-order Jahn-Teller distortion on the TiO₆ octahedron in the 500 nm sample. We consider that the Ti-O bonding in the prototype structure governs the ferroelectric phase transition temperature in BaTiO₃.

[1] Y. Kuroiwa, S. Aoyagi, A. Sawada, et al, *Phys. Rev. Lett.* 2001, 87, 217601/1-4., [2] H. Tanaka, Y. Kuroiwa, M. Takata, *Phys. Rev. B*, 2006, 74, 172105/1-4.

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