Anisotropic Behavior of Permittivity of Tetragonal-phase BaTiO₃ :A First-Principles Study

Hiroki Moriwake[1], Tsukasa Hirayama[1], Tamotsu Hashimoto[2], Kiyoyuki Terakura[2,3]

[1]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
[2]Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan
[3]Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan

Perovskite structure $BaTiO_3$, its tetragonal-phase has been widely used as a dielectric materials for Multi-layer ceramics capacitor(MLCC) due to its exceptionally large permittivity. $BaTiO_3$ shows series of ferroelectric phase transition, form non-ferroelectric cubic ($Pm\bar{3}m$) through tetragonal ($P4mm$) and orthorhombic($Amm2$) to the ground state phase rhombohedral ($R3m$) as a function of temperature. This ferroelectric phase transition mechanism can be understood by successive freezing of the triply degenerated polar soft-mode phonon at Γ point in high symmetry $Pm\bar{3}m$ structure.[1] As a pretransitional phenomenon of ferroelectric phase transitions, permittivity divergences are found at the phase transition temperatures. These permittivity divergences can be described by Curie-Weiss law. However, the tetragonal phase $BaTiO_3$ exhibits huge anisotropic behavior of their permittivity. i.e., along c-axis, its permittivity shows around a few hundreds. Although, along a-axis it shows around 4000.[1] The mechanism of this anisotropy can not be understood by phenomenological theories (e.g., Slater's theory, Lyddane-Sachs-Teller law, Curie-Weiss law etc.) Therefore, in this study, to reveal the microscopic mechanism of the anisotropic behavior of permittivity of tetragonal phase $BaTiO_3$, first-principles calculations have been made. All calculations in this study were performed within the local density approximation (LDA) of the density functional theory (DFT), using a plane-wave pseudo-potential method[2,3] in comparison with tetragonal $PbTiO_3$. The Vanderbilt type ultra-soft pseudo-potentials were used. The semi-core electrons of Ti ion (i.e., Ti-3p) were explicitly treated as valence electrons. Internal atomic positions were fully optimized until residual Hellmann-Feynman force on the atoms became below $1\times10^{-4}eV/Å$. Optimized lattice parameters by LDA-DFT underestimated experimental values by 1-2%, which is within typical errors of LDA calculations. However, the ferroelectric properties are quite sensitive to the small amount of lattice strain. Thus, experimental lattice parameters were used in this study. The ionic part of the permittivity was determined by constrained force approach. The ionic positions under the finite electric field were determined by optimization until forces on each atoms (Hellmann-Feynman force by DFT calculations) equal to the forces from applied electric field (product of the Born effective charge and the applied electric field). The lattice deformation under the finite electric field due to the piezoelectricity was taken into account by the method proposed by Fu et al.[4] The polarization were estimated by the Berry-phase calculations. The results are summarized in Table.1. By our theoretical calculations, the permittivity of tetragonal $PbTiO_3$ is well reproduced. And the permittivity along c-axis of tetragonal $BaTiO_3$ which has the spontaneous polarization by one of the frozen soft-modes is well reproduced, too. On the other hand, experimentally non-polar a-axis of tetragonal $BaTiO_3$ has non-frozen polar soft-mode. In the theoretical DFT calculation at the zero-temperature, reflecting the presence of this polar soft-mode, the structure with the spontaneous polarization along a-axis shows lower energy than that of the non-polar structure. The permittivity calculation using this theoretical a-axis polar structure, large permittivity along a-axis of tetragonal $BaTiO_3$ can not be reproduced. Theoretical permittivity is under estimated by about one order of magnitude for the experimental value. Experimentally, this tetragonal phase is found at around room the temperature not at low temperatures. In this temperature range, thermal vibrations effect can not be ignored. In this case, the polarization along a-axis can be fluctuated between four polar structures along two of a-axes of the tetragonal structure by the thermal effect. Therefore, no spontaneous polarization can be observed in experiment. When electric field along the polarization fluctuating structure is applied, the large polarization can be generated. Thus, the large permittivity must be found in this direction. To confirm this mechanism, first-principles molecular dynamics calculations

under the finite electric field should provide useful information.

References
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TABLE 1 Calculation results of permittivity for tetragonal $BaTiO_3$ and $PbTiO_3$ in comparison with experimental results (shown in parentheses).

	BaTiO$_3$		PbTiO$_3$	
	a-axis	*c*-axis	*a*-axis	*c*-axis
$\varepsilon_{(ionic)}$	120	40	120	10
$\varepsilon_{(piezo)}$	40	38	0	71
$\varepsilon_{(total)}$	160 (4000)[*]	78 (100-200)[*]	120 (100-200)[**]	81 (70-150)[**]

*ref.1, **ref.5

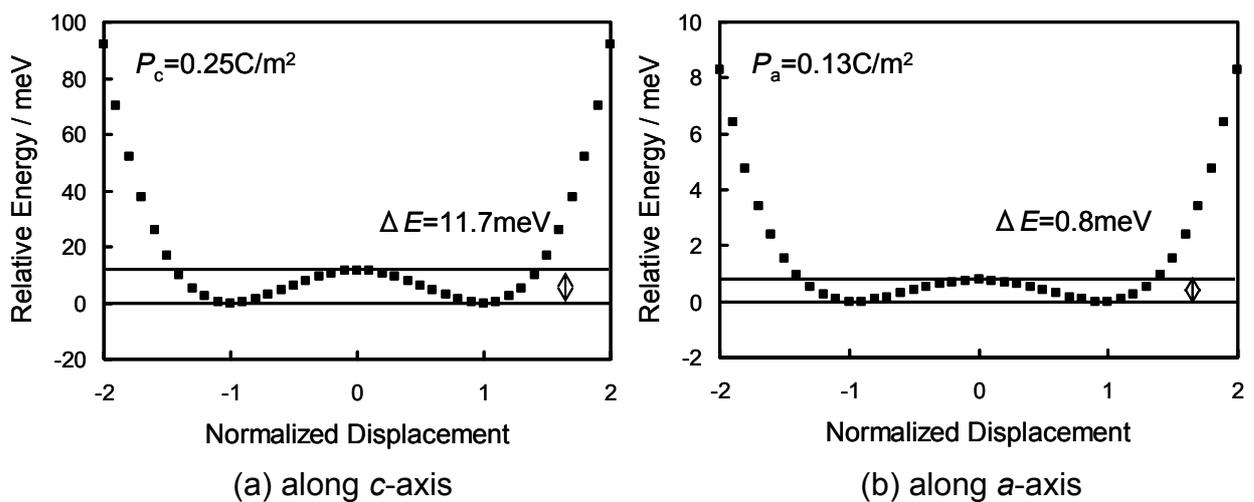(a) along *c*-axis   (b) along *a*-axis

FIG.1 Theoretical potential surface of tetragonal (*P4mm*) BaTiO$_3$. In both panels, the horizontal axis is the displacement normalized by atomic positions of the polar structure. Along *c*-axis, deep double-well potential (ΔE=11.7meV) is found, which is natural. However, it is noteworthy that even in the experimental non-polar *a*-axis, a shallow double-well potential (ΔE=0.8meV) is found.