学 位 論 文 要 約

題　目　　　Ferroelectric phase transitions in perovskite-type oxides and their composites studied by synchrotron radiation X-ray diffraction

（放射光 X 線回折を用いたペロブスカイト型酸化物とその複合体における強誘電相転移の研究）

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As we entered the information age, ferroelectric materials, recognized as pivotal foundational materials, have come into the spotlight as essential contributors supporting a diverse range of industries in our daily lives. Their significance spans various applications, including non-volatile memory technologies, sensors, actuators, piezoelectric devices, capacitors for energy storage. However, to optimally harness ferroelectric materials across these diverse fields, there are still some challenges that need to be addressed and overcome. These challenges include understanding the microscopic mechanisms of ferroelectric phase transitions and the development of environmentally friendly, lead-free ferroelectric materials, and so on.

In general, the physics of ferroelectrics is lattice-based rather than electronic. Therefore, when ferroelectricity is manifested, it is accompanied by changes in crystal structure. Studying the crystal structure of ferroelectric materials not only helps to understand the mechanism of ferroelectric phase transition but also provides new material design guidelines for various ferroelectric materials. With the emergence of advanced synchrotron radiation light sources, the level of crystal structure analysis has been extended from atomic position levels to visualizing electron density levels using synchrotron radiation X-ray diffraction (SXRD). This enables precise structural analysis of the crystal structures of several composite materials.

In this study, first, the spatial distributions of valence electrons are selectively visualized in cubic phases of perovskite-type oxides $BaTiO_3$, $BaZrO_3$, $KNbO_3$ and $KTaO_3$, represented by the chemical formula ABO_3. Experiments were carried out using SXRD to identify lattice instabilities in the cubic phase associated with the ferroelectric phase transitions. It is revealed that B-O hybrid atomic orbitals play a significant role in the ferroelectric phase transition. For $BaTiO_3$ and $KNbO_3$, which undergo ferroelectric phase transitions as the temperature decreases, there was observed overlap in the valence electron density distribution between B-site atoms and O atoms. This overlap is attributed to the presence of orbital hybridization, specifically Ti-$3d$ and O-$2p$ orbitals for $BaTiO_3$, and Nb-$4d$ and O-$2p$ orbitals for $KNbO_3$. The evaluated valence states of Ti and Nb ions, calculated through grid-based Bader analysis from the valence electron density distribution, were +2.89 and +2.75, respectively. These values are significantly smaller than the formal ionic valence of +4 and +5, respectively, confirming the unique characteristics of these materials with the formation of B-O covalent bonding. For $BaZrO_3$, and $KTaO_3$, on the other hand, where there is no overlap of valence electrons between the B-site atom and O atoms, the B-O bonds are ionic. Ferroelectric phase transitions are suggested to emerge from a delicate balance between long-range Coulomb forces (favoring the ferroelectric state) and short-range repulsions (favoring the nonpolar cubic structure). If there were orbital hybridizations on the B-O bond, it would play a role in weakening short-range

repulsion due to the overlap of atomic orbitals, even as the interatomic distance decreases with decreasing temperature. In ferroelectric phase transitions, the weakening of short-range repulsion, harmonizing effectively with long-range Coulomb forces, leads to the freezing of the soft mode and allow the phase transition. This concept has been demonstrated by the present study.

Second, this study revealed the potential of three-dimensional artificial superlattices with strain gradient regions (SGRs) to enhance the dielectric properties of materials. To investigate the effect of ferroelectric phase transition on SGRs in $BaTiO_3$-$KNbO_3$ (BT-KN) nanocomposite particle. The temperature-dependent crystal structure of a BT-KN nanocomposite core-shell particle, in which the KN shell epitaxially covers the BT core, was examined using SXRD. The experiments were conducted over a temperature range from 300 to 800 K. The temperature-dependent lattice constants of each component with different crystal structures constituting the particles were revealed by applying multi-component refinement to diffraction patterns. At the boundary between the BT core and KN shell, they were found to be bonded in a pseudo-cubic crystal structure with similar lattice constants across all temperatures. As the temperature decreased, SGRs near the interface, caused by lattice mismatch, enlarged significantly owing to phase transitions. The largest SGRs, characterized by a tetragonal BT core and an orthorhombic KN shell were observed at 300 K. At 800 K, where both BT and KN possessed cubic crystal structures, SGRs were minimized. Therefore, it is suggested to consider combining materials with different crystal symmetries but similar unit cell volumes to create composite materials as a strategy for improving dielectric properties.