論　文　の　要　旨

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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In this study, the valence electron density distribution of $BaTiO_3$, $KNbO_3$, $BaZrO_3$ and $KTaO_3$ in cubic phase were visualized in local space by SXRD with help of first-principles calculations. And the effects of ferroelectric phase transition on SGRs in BT-KN core-shell particle was investigated by SXRD.

The valence electron density distribution reveals evident orbital hybridization between *B*-site atoms and O atoms in materials undergoing ferroelectric phase transitions for $BaTiO_3$ and $KNbO_3$ while for $BaZrO_3$ and $KTaO_3$, which has always maintained a cubic structure, their *B*-site atoms are completely ionized. The valence state of Ti, Nb are +2.89 and +2.75, calculated by grid-based Bader analysis of valence electron density distribution. And the valence state of Ti, Nb much smaller than theortical value. It determined that the Ti-O bonds in $BaTiO_3$ and the Nb-O bonds in $KNbO_3$ are covalent bonds. The t_{2g} orbital of the B-site atom undergoes a head-on collision with the O-2*p* orbital. The involvement of the t_{2g} orbitals of Ti and Nb in orbital hybridization contributes to the attenuation of short-range repulsion between *B*-site atoms and O, as evidenced by the partial density of states PDOS. As the temperature decreasing, the reduction in interatomic distance, the overlap of electric cloud between *B*-site and O atoms will increase, which will enhance orbital hybridization. It will exacerbate the weakening effect of repulsion. When the short-range repulsive force is weakened to the same long-range Coulomb force. The freezing of the soft mode frequency leads to the occurrence of the ferroelectric phase transition.

The temperature-dependent core-shell structure of BT−KN nanocomposite particles was disclosed, revealing that BT and KN are consistently bonded in a pseudo-cubic crystal structure at the heteroepitaxial interface. Stress, arising from lattice mismatch between BT and KN, leads to the generation of SGRs. Phase transitions induced by temperature variations affect both the BT core and KN shell, altering their crystal symmetries. As temperature decreases, crystal symmetry diminishes, resulting in a larger lattice mismatch at the epitaxial interface and larger SGRs. The largest SGRs for the BT−KN core-shell particles were observed at 300 K. Epitaxial growth between the core and shell necessitates matching lattice constants. However, the introduction of a mismatch in crystallographic symmetry between the core and shell occurs due to phase transitions after the creation of core-shell particles. This approach, demonstrated for BT−KN core-shell particles in this study, enables the control of SGR size influenced by lattice mismatch. Such controlled SGRs offer vital insights for designing core-shell structures, with potential applications for enhancing dielectric and piezoelectric responses.