学位論文要旨

Structural Phase Transition in LiNbO₃-type Ferroelectrics Studied by Synchrotron Radiation X-ray Diffraction
（放射光 X 線回折による LiNbO₃ 型強誘電体の構造相転移の研究）

氏　名　ZHANG ZHIGANG

Lithium niobate ($LiNbO_3$) and the isomorphous lithium tantalite ($LiTaO_3$) undergo the phase transition from the paraelectric phase (space group: $R\bar{3}c$) to the ferroelectric phase (space group: $R3c$) with decreasing temperature. After the discovery of their ferroelectricity in 1949, these $LiNbO_3$ family crystals have attracted great attention to the applications. The Curie temperatures T_C of these two materials are fairly high as ~ 1480 and 960 K, and the spontaneous polarizations P_S at room temperature are reported to be 71 and 55 $\mu C/cm^2$, respectively. Therefore, the $LiNbO_3$ and $LiTaO_3$ crystals are expected to be a base-material for promising lead-free piezoelectric ceramics, especially for the uses at high temperatures.

Although the materials are widely used in many electronic devices, the phase transition mechanism is not clear. Some groups theoretically suggest that the phase transition is of a displacive type, which is supported by the soft modes in the phonon dispersions. However, others have not observed any soft modes near T_C, and hence argue that it should be an order-disorder type phase transition from the observed central peak mode and the results of perturbed angular correlation spectroscopy.

Regarding the order of phase transition, some groups measure the spontaneous polarization and the latent heat through T_C, and claim that the ferroelectric phase transition is of second order, which is supported by the optical properties and the dielectric susceptibilities. However, others report that the bond length changes discontinuously at T_C, which means the first-order phase transition.

The origin of the large difference in T_C and P_S between $LiNbO_3$ and $LiTaO_3$ is not clear as well. The ionic radii of the Nb and Ta ions are the same as 0.64 Å, which results in the similar crystal structure with almost the same lattice parameters a and c. The electronic structures of both materials are reported to be almost identical by the first-principles calculations, with comparable hybridization of Nb4d-O2p and Ta5d-O2p orbitals in the valence bands.

In this study, electron charge density distribution in stoichiometric $LiNbO_3$ and $LiTaO_3$ have been visualized by synchrotron radiation X-ray powder diffraction (SXRD) to adduce the conclusive evidence on the mechanism of structural phase transition and to clarify the structural origin of difference in T_C between $LiNbO_3$ and $LiTaO_3$. It is normally difficult to determine the atomic position of a light element such as Li in a material including a heavy

element such as Nb or Ta by standard X-ray diffraction. The excellent counting statistics and the high angular resolution in synchrotron radiation X-ray diffraction enable us not only to determine the atomic position of the light element but also to visualize the chemical bonding nature in the electron charge density distribution maps of the materials.

The electron charge density distribution maps visualized by the maximum entropy method clearly demonstrate that the disordered Li ion along the polar direction at the two sites in the paraelectric phase is ordered at one site in the ferroelectric phase. The ordering of the disordered Li ion in the polar direction accompanied by the deformation of the oxygen octahedra gives rise to the ferroelectric phase transition. The structural change occurs continuously at the phase transition temperature, which suggests a second-order phase transition.

The clear relationships between the Nb(Ta)-O bond length, the electron charge density on the Nb(Ta)-O bond and the phase transition temperature T_C are revealed for the isomorphic structures. The Nb(Ta)-O bonding plays an important role for the elevation of T_C. The higher T_C in $LiNbO_3$ compared with the T_C in $LiTaO_3$ is attributed to the larger lattice distortion of the Nb-O oxygen octahedron in $LiNbO_3$.

The evaluated spontaneous polarization P_S by the point charge model gradually increases below T_C with decreasing temperature. The P_S evaluated from the crystal structure of $LiNbO_3$ and $LiTaO_3$ are almost the same as the results of electronic measurement, respectively, which suggests that the main contribution to the P_S of $LiNbO_3$ and $LiTaO_3$ is from the ionic polarization. The larger atomic shift of the Nb atom is considered to play an important role in the emergence of larger P_S in $LiNbO_3$.