Revealing the Short and Long-range Structural Distortions at Nb-doped KTaO3

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Revealing the Short and Long-range Structural Distortions at Nb-doped $KTaO_3$

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Potassium niobate ($KNbO_3$) is a lead-free perovskite ferroelectric structure, while potassium tantalate ($KTaO_3$) is a quantum paraelectric material with a cubic structure. However, due to its high polarizability, a small chemical substitution or stress can drive $KTaO_3$ to a ferroelectric state. $K(Ta,Nb)O_3$ (KTN) is an unlimited solid solution of these compounds where Nb atoms replace Ta atoms. Depending on the Nb concentration, KTN can undergo a ferroelectric phase transition from the temperatures above room temperature to lower temperatures. However, the nature of this transition is debated and there is evidence for both a soft mode freezing (displacive transition) and an order-disorder transition[1,2]. Electron microscopy can solve this puzzle by providing direct evidence of local and subtle lattice distortions and their correlation length with picometer resolution.

This study investigates the nature of ferroelectric phase transition in KTN single crystal and thin film. We use multislice electron ptychography[3] and HAADF-STEM to directly image short- and long-range lattice distortion. We studied 25% Nb-doped $KTaO_3$ thin films grown on $GdScO_3$ substrate[4] and (001) KTN single crystal with similar Nb concentration. Second harmonic generation (SHG) measurement shows while KTN thin films are ferroelectrics at room temperature, the KTN single crystals do not show a SHG signal at room temperature.

Fig. 1(a) shows the multislice ptychography reconstruction of KTN single crystal. The TEM foil thickness is 15nm with added 3nm vacuum layer. Each slice thickness is 0.5nm, and the reconstructed image was obtained by summing each slice along [100] direction. The position of each atomic column was determined by fitting it to a 2D Gaussian function. The enlarged region highlights the position of the Ta/Nb atomic column in red, the K column in green, and the O column in blue, respectively. While the effective ionic radii of Nb^{+5} and Ta^{+5} are the same (0.64Å), Nb ions off-center in <111> direction leading to a unit cell with a net dipole moment[5]. The distortion caused by Nb dopants is evident in this image. The off-centered location of Nb atoms forms a locally tetragonal structure in the cubic host of $KTaO_3$. Fig. 1(b) shows a transition from a cubic to a tetragonal structure. Note that the effective atomic radius of K^{+1} is larger than Nb^{+5} and Ta^{+5}, but they appear dimmer in Z-contrast imaging. Therefore, to provide visual aid, the atomic radii of elements at the schematic structure are not to scale. The local tetragonal lattice at a cubic host can be tracked by a subtle shift of oxygen octahedra marked by the cyan arrows. While four basal oxygen of NbO_6 displaces along [001] direction, the other two displace in the opposite direction. We track this shift by analyzing the intensity line profile along a vertical and horizontal direction. Fig. 1(c) shows the average depth profile along horizontal (pink) and (d) vertical (yellow) directions. The measured intensity of the Nb/Ta column along the horizontal direction is lower on the tetragonal side because of the displacement of oxygen atoms. In comparison, the vertical line profile has a uniform intensity. While these displacements lead to a polar point group of P*4mm*, the structure is not globally ferroelectric at room temperature. This suggests that the off-center displacement is dominated by the short-range interaction between the Nb and its near neighbors and only it is present in the unit-cell scale.

To understand the correlation length of the polar displacements, we looked at cross-section HAADF-STEM images of KTN single crystal (Fig. 2a) and KTN thin film (Fig.2b). We tracked the displacement along [001] direction and marked the difference between the center of four Ta/Nb columns and K columns for (Fig. 2c) single crystal and (Fig. 2d) thin KTN film. An epitaxial in-plane strain of 0.5% is applied to the film, creating an easy polar axis and motivates long-range correlation and room-temperature ferroelectricity. While displacements are short ranged for single crystal samples, they are highly correlated for the KTN film. To have better statistics, we analyzed more than 15000 columns. Polar histograms of KTN single crystal and KTN thin film are shown in Fig. 2 (e) and (f), respectively. Histograms are color-coded based on the 22.5° intervals for displacements. An overall direction of displacement is along [001] direction for the thin film but less well correlated for the KTN single crystal. The results highlight how the competition between short-range interaction caused by the off-center displacements of Nb atoms and long-range coulomb interactions, drives the ferroelectric phase transition in this system [6].

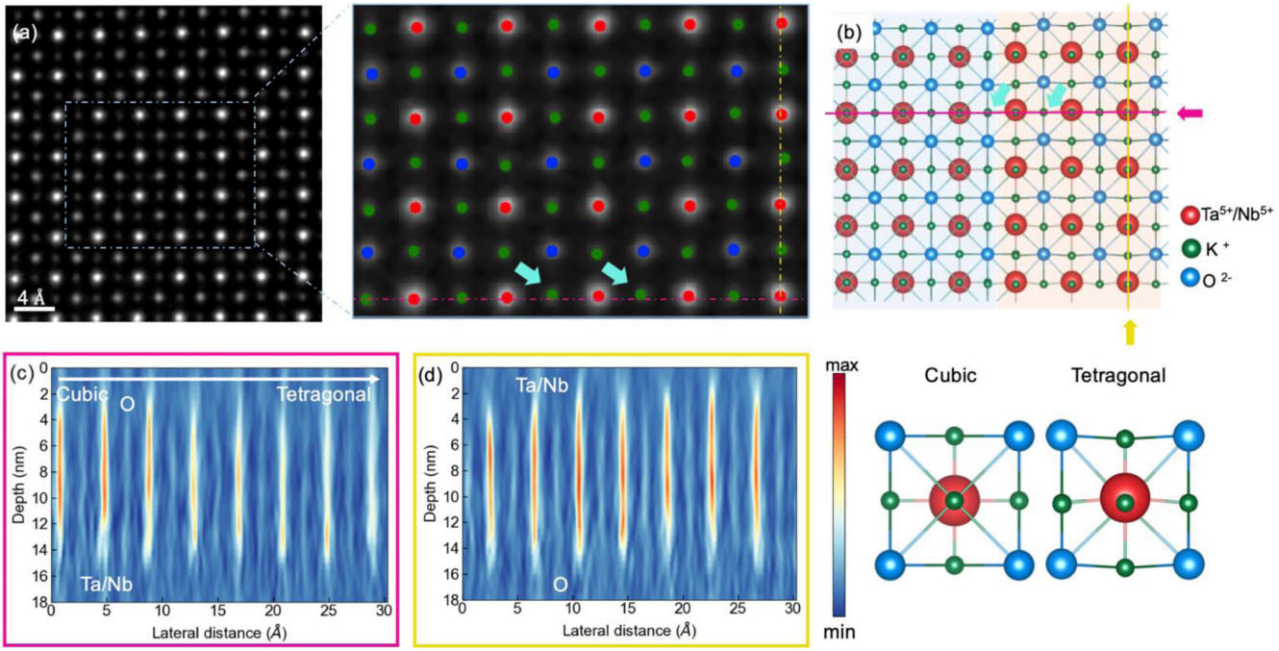

Fig. 1. (a) Cross-sectional multislice ptychography reconstruction of a KTN single crystal. The enlarged region highlights the position of the Ta/Nb atomic column in red, the K column in green, and the O column in blue, respectively, obtained by 2D Gaussian fitting. The transition between the undistorted cubic structure of $KTaO_3$ (right side) and the distorted structure of $KTaO_3$ (left side) caused by the Nb dopant is clear. (b) Schematic cubic to tetragonal lattice transition caused by off-centered Nb dopants. Local tetragonal lattice at a cubic host can be tracked by a subtle shift of oxygen octahedral marked by the cyan arrows. (c) Average depth profile along horizontal (pink) and (d) vertical direction (yellow). While oxygen shift causes lower intensity along the horizontal direction, the vertical line profile has a uniform intensity.

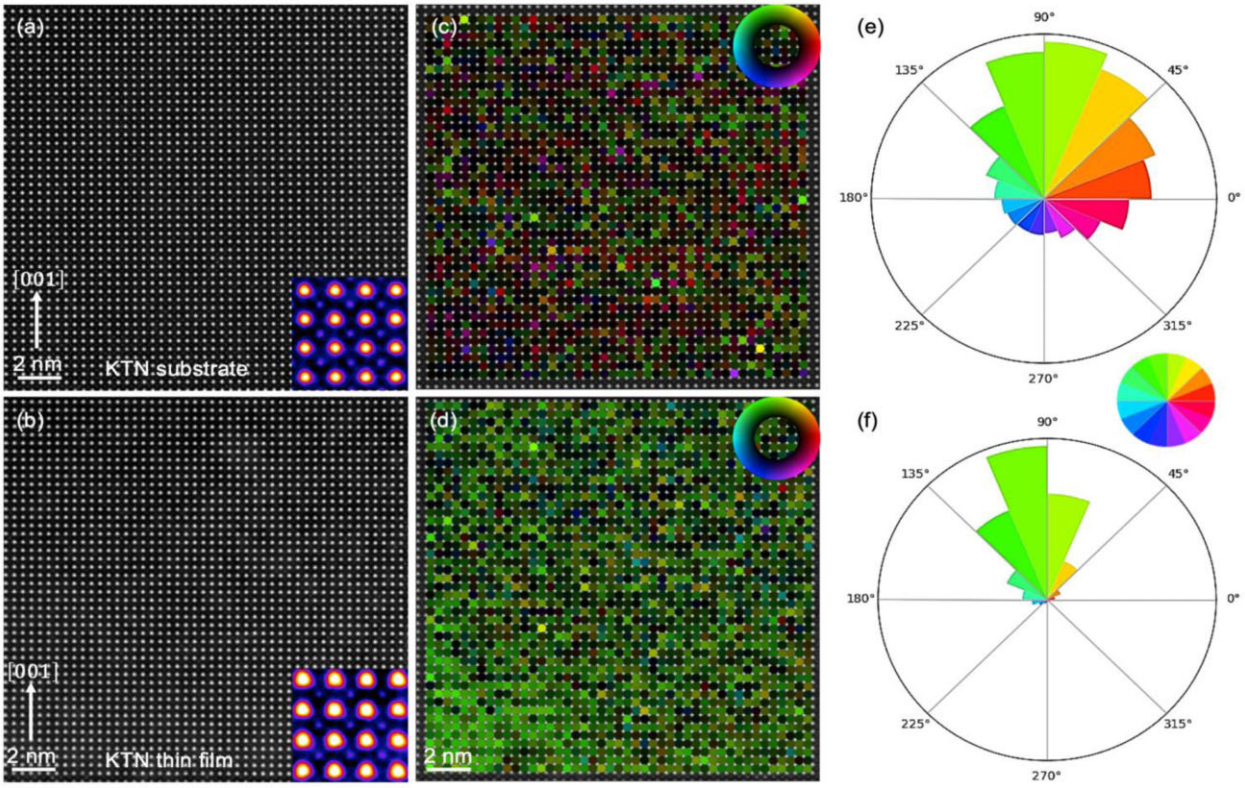

Fig. 2. Cross-section HAADF-STEM images of (a) KTN single crystal and (b) KTN thin film Displacement vector of difference between the center of four Ta/Nb columns and K columns for (c) single crystal and (d) thin KTN film. Displacements are short ranged for single crystal samples and are correlated for the KTN film. Polar histograms, based on more than 15000 analyzed columns, shows the overall direction of displacements for (e) KTN single crystal and (f) KTN thin film.

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