Exploring polar ordering in lead-free K0.5Na0.5NbO3 ferroelectrics using in situ biasing and 4D STEM techniques

prof. Goran Dražić[1,2,3], Ms. Katarina Žiberna[2,3], Dr. Oana Condurache[2,3], prof. Andreja Benčan Golob[2,3]
[1]Department for materials chemistry, National institute of chemistry, Ljubljana, Slovenia, [2]Electronic ceramics department, Jožef Stefan Institute, Ljubljana, Slovenia, [3]Jožef Stefan international postgraduate school, Ljubljana, Slovenia

The effectiveness of ferroelectric materials is fundamentally dependent on their ability to switch polarization, a process driven by complex dynamics that include the movement of ferroelectric domain walls (DWs), domain growth, and the nucleation of new domains. Traditionally, the behaviour of ferroelectric domains and DWs has been examined using indirect methods, such as nonlinear ferroelectric / piezoelectric measurements or in situ x-ray diffraction techniques. While these methods have significantly enhanced our understanding of the relationship between domain structures and functional properties, they only offer an averaged, collective response that may mask the details of individual events. In contrast, in situ transmission electron microscopy (TEM) provides a direct observation method for ferroelectric switching and domain dynamics. This approach reveals phenomena that are often concealed in macroscopic studies, offering a clearer, more detailed view of the microscale processes that govern the macroscopic properties of ferroelectric materials.
One key aspect of ferroelectric research involves determining the direction and magnitude of polar ordering, typically achieved through precise measurements of atomic displacements from their equilibrium positions in centrosymmetric structures. The adoption of advanced atomic-scale Scanning Transmission Electron Microscopy (STEM) technologies, especially those equipped with 4D STEM pixelated detectors, combined with the insights from STEM image simulations and first-principles calculations, has not only enabled the direct determination of polar directions but has also expanded the research to include analysing various defect types such as oxygen vacancies, strain fields, and charge density distributions around defects. Moreover, the use of in-situ biasing/heating holders for structural examinations under applied external stimuli has enriched our understanding of the dynamic nature of ferroelectrics.

This presentation will focus on a series of structural studies exploring the dynamic properties of potassium sodium niobate. The STEM analyses were conducted using Jeol ARM 200CF and Thermo Fisher Scientific Spectra 300 Cs-corrected microscopes, both equipped with advanced Merlin and EMPAD pixelated detectors, respectively. Our studies of potassium sodium niobate materials focus on directly observing domain growth, coalescence, and interactions among different types of domain walls within the microscope's environment under applied voltage. Through these investigations, we aim to elucidate how the type, quantity, and dynamics of structural defects influence local material properties, offering opportunities for tailored manipulation and optimization.

In the study, we explore the voltage-driven dynamics of mobile, needle-like domains and DWs within a $(K,Na)NbO_3$ single crystal (KNNsc) utilizing in situ Transmission Electron Microscopy (TEM) in a miniaturized capacitor setup [1]. Our findings suggest that the immobile DWs act as random bound pinning centres, capable of pinning larger regions while the edges of the sample facilitate the nucleation of new domains. The process of domain growth and coalescence is not consistently continuous; specific voltages can disrupt it, leading to fine domain splitting and the creation of nanoscale domains. Discontinuities in the functional response also occur when two orthogonal, needle-like domains intersect, resulting in soft-pinning events. These insights deepen our understanding of ferroelectric domain behaviour and may extend to other perovskite-based ferroelectric materials that exhibit similar domain morphologies or coexistence of dynamic and stationary DWs.

Slovenian research and innovation agency (ARIS) is acknowledge for financial support through projects J2-3041, J7-4637, P2-0105 and P2-0421.

Keywords:

KNN, ferroelectrics, 4DSTEM

Reference:

[1]. O. Condurache et al., Applied physics letters, 2023, 20, 202902-1-202902-7