New approaches to understand conductive and polar domain walls by Raman spectroscopy and low energy electron microscopy

There is a growing interest for structural and electric properties of ferroelectric and ferroelastic domain walls. The emerging field of domain boundary engineering\textsuperscript{1,2} holds the promise of using the distinct functional properties of domain walls in and as devices. The key point is the observation that domain walls may have physical properties very different from the bulk crystal matrix, the two cases most commonly studied being (i) conducting walls in insulating crystals and (ii) polar walls in non-polar crystals.

Here, we investigate the structural and electric properties of domain walls to achieve a better understanding of the conduction mechanisms in domain walls of lithium niobate and the polarity of domain walls in calcium titanate.

In a first part, we discuss the interaction between defects and domain walls in lithium niobate. We report the evolution of Raman modes with increasing amount of magnesium doping concentrations and identify specific frequency shifts of the modes at the domain walls. The domains walls appear then as spaces where polar defects are stabilized\textsuperscript{3–5}.

In a second part, we investigate the polarity of domain walls in calcium titanate. We report that single crystals of calcium titanate with domains show a clear response in resonant piezoelectric spectroscopy, \textit{i.e.} mechanical resonances upon excitation by an electric field, which we attribute to the polar nature of the walls. We then obtain a direct image of the domain walls by low energy electron microscopy (LEEM). Figure 1 shows images acquired in the MEM and LEEM regimes, and MEM-LEEM transition curves in domains and at domain walls. As expected, adjacent domains present the same surface potential because the material is non-polar. However, the domain walls show clear surface potential contrast with respect to the domains. This contrast is observed to change reversibly upon electron irradiation due to the screening of polarization charges at domain walls, giving perspectives toward functionalization of polar domain walls.

![Figure 1:](image-url)

\textbf{Figure 1:} (a) MEM and (b) LEEM images of a CaTiO\textsubscript{3} single crystal showing contrasts attributed to the polarity of the domain walls. (c) MEM-LEEM transition curves revealing the difference in surface potential in the domains and at domain walls.