Raman studies of ferroelectric domain walls in lithium tantalate and niobate

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Using confocal Raman spectroscopy at low temperature we investigated the perturbation of the phonon modes across a domain wall region as a function of sample stoichiometry in lithium tantalate and niobate. For all samples, we found that the Raman spectra were changed. The intensity of the A(LO) phonon modes and most of the E(TO) phonon modes were shifted and changed in their relative intensity over a 20 µm length scale. Our measurements suggest that the intensity of the A(LO)phonon modes change due to local charges induced by pyroelectric effect and/or photionization, while the observed shifts are due to strains that are not relaxed in the domain wall region.

1 Introduction

The local structure of ferroelectric domain walls and its dependence on intrinsic defects and dopants is of great interest both from a basic science and an application point of view. For instance, in the ferroelectrics lithium niobate (LiNbO3) and lithium tantalate (LiTaO3) that are widely used in nonlinear and electro-optical devices (for example [1]), the stability, shape, switching fields and smallest achievable domain size are determined by the defect concentration. The domain wall region and its thickness were studied theoretically [2] and practically [3–6] by different methods. In this paper we present the results of an experimental study of the domain wall region using Raman spectroscopy as a diagnostic tool. The sensitivity of Raman spectroscopy to structural changes has been demonstrated in studies probing variations in the crystal composition induced by in-diffusion and out-diffusion of ions [7–9] as well as identifying different phases in HxLi1−xNbO3 [10]. However, the technique has not been applied to local domain wall studies thus far.

2 Experimental techniques

Samples. Commercially available optically polished z-cut stoichiometric and congruent LiNbO3 and congruent LiTaO3 samples (7 mm x 7 mm x 0.5 mm) were partially poled under external high voltage. To invert the direction of spontaneous polarization, a coercive field was used of magnitude ≈ 22 kV/mm and ≈ 102 V/mm for congruent and stoichiometric samples, respectively.

Raman confocal microscopy. Raman confocal spectroscopy was used to achieve diffraction limited resolution. In our set-up the samples were mounted in a He-cooled cryostat that allows for temperatures down to 4 K for low temperature measurement. We used the 488 nm and 514 nm lines of an argon laser for excitation. The input and output pinholes usually required in a confocal microscope were replaced by optical fibers. The resulting Raman signal was detected in the reverse direction through the same microscope, separated from the excitation light by a beam splitter, and coupled into the output fiber. To avoid an additional Raman signal from the input and output fiber, 488 nm (514 nm) laser line and edge
filters were placed in front of the respective collimation lenses. Finally, the emission spectra were measured in a 0.5m-spectrometer equipped with a liquid nitrogen cooled CCD array, allowing the measurement of 20 spectra per second. For imaging purposes, the microscope is mounted on a nanocube, which allows for movement of the microscope by 100 µm in the x, y and z directions. The optical resolution for our microscope is 0.5 µm and the used step size was 250 nm. While the domain wall width is only of few lattice constants, the perturbations are felt in larger regions (1-100 µm) that can be resolved with our microscope.

3 Experimental results and discussion The Raman intensities of the lithium tantalate and lithium niobate are depicted in Fig. 1. The spectra were taken in backscattering geometry under parallel polarization $z(xy)\hat{z}$ and crossed polarization $z(xy)\hat{z}$. From group theory, 26 phonon modes are allowed in lithium niobate and tantalate [11, 12]. However, the number of observed peaks depend on scattering geometry, resolution and sensitivity of the spectrometer. Due to high numerical aperture of the microscope objective the polarization selection rules are not strictly valid in our experiments such that we detect $A_\text{LO}$ modes even for crossed polarization. The low energy phonon modes were not detected due to the Raman edge filter used in the experiment. The observed $E(TO)$ Raman peaks are numbered from $E_3$ to $E_9$ and $A_1$($LO$) Raman peaks are numbered from $A_1$ to $A_4$. The Raman spectra were obtained across the domain wall in a range of 20-80 µm with a step size 250 nm. The differential Raman spectra, calculated by subtracting a Raman spectrum far away from the domain wall from the Raman spectrum inside the domain wall, is shown in Fig. 1 (b). For all samples and for all variations of pump and probe light polarization $z(xy)\hat{z}$, $z(xy)\hat{z}$, $z(xy)\hat{z}$, $z(yy)\hat{z}$, $z(yy)\hat{z}$ three different changes across domain wall region were observed:

1. the intensity of the $A(LO)$ phonon modes are changed,
2. the $E(TO)$ and $A(LO)$ phonon modes are shifted, and,
3. the Raman intensity is enhanced around 610 cm$^{-1}$ for LiNbO$_3$ and around 596 cm$^{-1}$ in LiTaO$_3$.

We will concentrate here on the first two effects which are the most pronounced.

Change in intensity ratios. The scanning confocal microscope enables us to evaluate these changes over an 80 µm region around the domain wall. The intensity of the $A_1$($LO$4) phonon mode is depicted in Fig. 2(a) for stoichiometric lithium niobate for a parallel scattering geometry. To further elucidate the origin of the effect, we used two modes of observation geometries as shown in in the Fig. 2(b). We find that the effect is not related to the fact that one side has been newly domain inverted but it depends on which surface (+c or −c) we are looking at. We find that coming from the +c surface the intensity is decreasing rapidly in the domain wall region and increases much more slowly to the initial value within a range of 30 µm. We suspect that the effect might be caused by uneven charging across domain wall due to pyroelectric effects and/or photoionization. Such fields will lead to birefringence due to the electro-optic effect in the $xy$ plane, which leads to depolarization of pump and probe light in the Raman measurement. This interpretation was confirmed by line scans across the domain wall region for different depths (from 10 µm to 60 µm) in which we found that with increasing depth, the intensity of the $A(LO)$ phonon modes on −c side close to the domain wall are decreasing for parallel polarization while increasing for the cross polarization.

Spectral shifts. We observe in the domain wall region both shifts to higher ($E(TO3)$, $E(TO4)$, $A_1$($LO1$), $A_1$($LO3$), and $E(TO8$) and lower ($E(TO5)$, $A_1$($LO2$), $E(TO7$), and $A_1$($LO4$)) frequencies. The $E(TO6)$ phonon mode was not shifted at all. These shifts are not correlated with the shifts that are caused by the directional dispersion of the polar Raman modes [13] which we have measured under crystal rotation. This excludes a tilt of the ferroelectric axis in the domain wall vicinity as the origin of the effect.

On the other hand, our observed shifts are of the same magnitude and direction as the shift in congruent lithium niobate that are observed within 260 min. after an electric-field repoling step [14]. The latter shifts were interpreted as strains that are caused by the domain inversion which relax with time. Our shifts, however, persist for a long time after the domain inversion and are most pronounced on the +c surface in
Fig. 1 (a) Raman spectra of congruent lithium niobate at low temperature $T = 4\, \text{K}$ for the $z(\text{xx})z$ and $z(\text{xy})z$ scattering geometry. The $E_3...E_9$ peaks correspond to $E(\text{TO})$ phonon modes and $A_{11...A_{14}}$ correspond to $A(\text{LO})$ phonon modes; (b) The differential Raman spectra for the $z(\text{xx})z$ and $z(\text{xy})z$ scattering geometry show the differences between the spectra taken from the domain wall region and the spectra taken outside the domain wall region; (c) Raman spectra and differential spectra of congruent lithium tantalate at low temperature $T = 4\, \text{K}$ for the $z(\text{xx})z$ and $z(\text{xy})z$ scattering geometry.

the vicinity of the domain wall. This is depicted for the $E(\text{TO3})$ and $E(\text{TO8})$ phonon modes in Fig. 2. One may speculate that the relaxation of the strain (observed in the bulk) is hindered in the domain wall region at the $+c$ surface leading to the observed behavior.

It is interesting to note that in comparison to the change of the intensity of the $A_1(\text{LO4})$ phonon mode, the spatial behavior extend over a similar spatial region but is just reversed: Abrupt change coming from the $-c$ surface geometry, and slow changes on the $+c$ side of the domain wall. The question, if this anti-correlation has any significance, is currently under investigation.

4 Conclusion We have presented our confocal Raman studies of the domain wall region in lithium niobate and tantalate and have shown that three types of changes occur that are most likely not directly related. Our measurements suggest that the intensity of the $A(\text{LO})$ phonon modes change due to local charges induced by pyroelectric effect and/or photoionization, while the observed shifts are due to strains that are not relaxed in the domain wall region. Confirmation of this interpretation will require further
studies such as Raman studies under application of electric field and uniaxial stress. The third effect of enhanced Raman modes around 600 cm$^{-1}$ is currently under further investigation as well.

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**References**