Raman Study of Neutral and Charged Domain Walls in Lithium Niobate

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In this work, we demonstrate the application of micro-Raman spectroscopy for the investigation of the neutral and charged domain walls in the congruent and MgO-doped lithium niobate single crystals. We present local changes of the intensity and frequency of three Raman lines in the vicinity of the domain walls and discuss the influence of the bulk screening of depolarization field on these parameters.

Keywords Lithium niobate; periodic domain structures; atomic-force microscopy; charged domain walls

I. Introduction

Lithium niobate LiNbO$_3$ (LN) is an attractive material for a great number of various photonic and optoelectronic applications thanks to its electro-optical and nonlinear-optical properties. It is known that these properties can be improved by tailored periodical micro- and nanodomain patterns (domain engineering) [1, 2].

The formation of the stable domain structures in LN crystals as well as in any other ferroelectrics is a result of bulk screening of the depolarization field [3]. Moreover, the crucial role of the competition between the depolarization and screening fields must be considered while explaining the domain kinetics [4]. Screening ineffectiveness caused by retardation of the bulk screening effect is an important parameter, which defines the shape of growing isolated domains [3, 5]. It has been shown both experimentally and by computer simulation that the shape of growing isolated domain in LN can change from regular hexagon for complete screening to three-rayed star—for ineffective screening [6]. Effective bulk screening allows us to stabilize even the blind domain structures with charged domain walls [7]. Thus, investigation of the domain structure formation at various experimental conditions taking into account the influence of screening process is an important challenge for basic research and for domain engineering as well.

The screening mechanisms used for compensation of the depolarization field can be divided in external and bulk screening [3]. The fast external screening caused by current...
in the external circuit can never compensate the depolarization field due to the existence of
the intrinsic or artificial dielectric layer on the crystal surface. That is why the slow bulk
screening is the only way for compensation of the residual depolarization field. Two bulk
screening mechanisms are considered usually in LN crystals: (1) redistribution of the
bulk charges, and (2) reorientation of the defect dipoles [8]. The wide spectrum of the time
constants of the bulk screening effects ranged from milliseconds to weeks and even months.
It is clear that the screening rate depends on the bulk conductivity.

Neutral domain walls are formed in LN after growth of the domains through the
sample. Directions of the spontaneous polarization on the opposite sides of the domain
wall are antiparallel, and there are no bonding charges in the vicinity of the wall. An
incomplete screening of the depolarization field near the surface due to the existence of
inherent dielectric layer leads to appearance of strong electric field in the vicinity of the
wall. This field has components oriented both in the surface plane perpendicular to the wall
and in polar direction.

Charged domain walls have bound charges over the whole wall surface both near the
surface and in a bulk of the sample. Electric field occurring in this case contains a horizontal
as well as a polar component.

In 2004 Dierolf and Sandmann [9] carrying out Raman measurements at high temper-
atures (above 120°C), detected the spectral variations in the vicinity of the domain walls in
Er-doped periodically poled LN (PPLN) around 600 cm\(^{-1}\) only. These variations were very
small, and authors concluded the inefficiency of this method. At the same time, Kong et al.
report the observation of the frequency shift about 1.5 cm\(^{-1}\) for the 580 cm\(^{-1}\) spectral line
[10]. In works of Hammoum [11–13], author mainly showed intensity changes of several
Raman lines in congruent PPLN.

In this paper, we applied micro-Raman spectroscopy for investigation of the neutral
and charged domain walls in LN. The investigated neutral domain walls were produced by
electrical poling in congruent and MgO-doped PPLN, whereas the charged domain walls
appeared as a result of pulse IR and UV laser irradiation of congruent LN.

II. Experiment

Raman scattering (RS) measurements were made at room temperature in the backscattering
Z(xx)Z configuration using exciting 633 nm He-Ne laser line with power 30 mW focused
by objective x100 (NA = 0.90). The size of the light spot at the sample surface was
about 0.6 \(\mu m\). Spectra were recorded along a line with 0.1 \(\mu m\) step, providing a relative
spatial resolution of the method 0.1 \(\mu m\). Reflected light has been split into the spectrum by
diffraction grating with spectral resolution 0.027 nm and detected by CCD camera.

Among the thirteen Raman lines expected in LN in the Z(xx)Z configuration, nine ones
correspond to transversal vibrations of E(TO) type and four ones correspond to longitudinal
vibrations of A\(_1\)(LO) type. In Ref. [11] it has been shown that the intensity of low-frequency
E(TO\(_1\)) and two high-frequency E(TO\(_5\)) and A\(_1\)(LO\(_4\)) lines with intensity maxima at 152,
580, and 870 cm\(^{-1}\), respectively [14], changes in the vicinity of the domain walls in PPLN.
These lines are well resolved and have high intensity that allows us to calculate the integrated
intensity and phonon frequency without any spectrum deconvolution and ambiguity. It is
known that the E(TO\(_1\)) vibration mode corresponds to out-of phase displacement of Nb and
O ions in XY plane perpendicular to the ferroelectric Z axis, whereas E(TO\(_5\)) and A\(_1\)(LO\(_4\))
modes are associated with stretching of oxygen octahedra in the XY plane and along the Z
axis, respectively [15, 16].
III. Neutral Domain Walls in PPLN

Earlier, the essential changes of integrated intensity of E(TO$_8$) and A$_1$(LO$_4$) Raman lines in the vicinity of neutral domain walls were reported [11]. The relative changes of the integrated intensity of these lines during scanning through domain walls in congruent PPLN are shown in Fig. 1. The obtained spatial distribution of the integrated intensity for E(TO$_1$) line is similar to E(TO$_8$), but the relative change is essentially weaker.

The opposite sign of the variations of the relative integrated intensity for E(TO$_8$) and A$_1$(LO$_4$) lines is worth noting. This effect can be attributed to the difference of the sign of elasto-optic coefficient involved into the opto-mechanical coupling [13].

The changes of the integrated intensity of E(TO$_1$) and E(TO$_8$) lines at the domain walls are accompanied with frequency shift (Fig. 2). Since these shifts happen at each domain wall and at different places of various samples, they can be attributed to the effect of walls, regardless rather small absolute value. In contrast to the noted modes, the frequency shift of all other spectral lines including A$_1$(LO$_4$) line is completely absent (Fig. 2).

The observed frequency shift can be attributed to the consequence of internal mechanical stresses existing in the vicinity of the domain walls. It is in contradiction to the classical statement about absence of the essential stresses at 180° domain walls [17]. Though, the strong electric field exists near the domain wall. For the neutral walls, the field is caused by the incomplete screening of the depolarization field near the surface. For the charged domain walls, the field created by bound charges can be essentially stronger. The field can be compensated by the above discussed slow bulk screening effect only.

![Figure 1. Relative change of the integrated Raman line intensity in the vicinity of the neutral domain walls between reversed (R) and virgin (V) domains in congruent PPLN. (See Color Plate II)](image-url)
It is possible to suppose that the strong electric field in the vicinity of the domain wall induces the mechanical stresses by piezoelectric effect which in turn can change the vibration modes in the crystal which can be detected as the frequency shift of the appropriate Raman lines. The screening effect exhibits in slow relaxation of the field induced changes of the Raman spectrum. The relaxation of the Raman spectrum has been observed after electric field switching in CLN by Scott et al. [18]. It is clear that the bulk screening can be essentially accelerated by the increasing of the bulk conductivity in LN using MgO doping or irradiation by UV light.

Raman mapping of the neutral domain walls in MgO-doped PPLN (with 5% of MgO) represents the changes in intensities and frequency shifts of appropriate Raman lines, which are essentially lower (about ten times) than in congruent PPLN. Such behavior can be attributed to higher conductivity in MgO-doped PPLN as compared with CLN. The effective screening of the residual depolarization field in the vicinity of the domain walls leads to diminishing of the Raman lines changes.

It is worth noting also that the surface modification by selective chemical etching usually used for revealing the domain structure can influence the Raman mapping and leads to appearance of some artifacts, which can be considered *ex facto* as an inherent effect. An appearance of the domain contrast on the etched surface of the crystal is one of such effects. The variations of the integrated intensity of E(TO₈) and A₁(LO₄) Raman lines during mapping of the etched surface of congruent PPLN have been measured (Fig. 3). A different level of the intensity is clearly seen for the neighboring domains.

The possible reason of the domain contrast on the etched crystal surface is a different roughness of domain surfaces. Measurements of the surface relief using scanning probe microscope (SPM) allow us to demonstrate that the average roughness of the neighboring domain surfaces in congruent PPLN can differ more than ten times and essentially depends
on the etching conditions. It is clear that the intensity of the reflected light also depends on the surface roughness.

IV. Nanodomain Rays with Charged Domain Walls

The influence of the screening effectiveness on the Raman spectra is more pronounced in the case of charged domain walls, created as a result of laser irradiation without application of external electric fields to the crystal [19]. The studied domain structures were produced in congruent LN by pulse IR laser irradiation using CO$_2$ pulse laser (\(\lambda = 10.6 \mu m\)) and UV laser irradiation using eximer laser (\(\lambda = 308 \text{ nm}\)). The size of irradiated zone (about 1 mm) is much larger than the domain width (below 1 \(\mu m\)). For both lasers the created domain patterns consist of a number of very thin domains (“domain rays”) (Fig. 4) with a typical width about 300–500 nm measured by SPM [20].

The scanning across the ray in IR-irradiated LN allows to reveal that E(TO$_1$), E(TO$_8$), and A$_1$(LO$_4$) lines show essential change of the relative integrated intensity in the vicinity of a domain ray (Fig. 5). It is clear that the spatial resolution of the micro-Raman technique (about 300 nm) is insufficient for separate visualization of the domain walls of the nanodomain ray. That is why only one peak was observed. The frequency shift is observed only for E(TO$_1$) and E(TO$_8$). Thus, the general behavior of the appropriate Raman lines is similar to the neutral walls in congruent PPLN, but the value of the relative intensity changes and frequency shifts are essentially larger.

It was important to study nanodomain rays produced as a result of pulse UV laser irradiation. It has been shown that, although the nanodomain structure appeared after UV irradiation is almost the same in sizes, no changes of the Raman lines can be observed during
Figure 4. SPM image of a nanodomain ray formed as a result of IR pulse laser irradiation. (See Color Plate V)

The mapping across the domain rays. The obtain behavior can be attributed to the effective screening of the depolarization field in the vicinity of the domain walls by UV-induced free charges. Therefore, this effect confirms the proposed mechanism of the Raman spectrum change near the domain walls by electric field.

Figure 5. (a) Relative change of the integrated intensity and (b) frequency shift of Raman lines in the vicinity of the nanodomain ray with charged domain walls created by IR laser irradiation of congruent LN.
V. Conclusion

We have demonstrated that the micro-Raman spectroscopy can be effectively applied for the investigation of the neutral and charged domain walls in lithium niobate single crystals. The local changes of intensity and frequency shift of three Raman lines were observed in the vicinity of the domain walls. The influence of the bulk screening of depolarization field on these parameters has been observed in congruent and MgO-doped LN.

It has been supposed that the strong electric field in the vicinity of the domain wall induces the mechanical stresses which in turn change the vibration modes in the crystal, which has been detected as the frequency shift of appropriate Raman lines. The field induced changes of the Raman spectrum can be compensated by bulk screening effect. The acceleration of bulk screening in LN has been realized by increasing of bulk conductivity by MgO doping and UV laser irradiation. The obtained disappearance of Raman lines changes confirms the supposed role of electric field in changes of the Raman spectrum.

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