Confocal micro-Raman imaging on 180°-domain structure in periodically poled stoichiometric LiNbO₃

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A domain structure in periodically poled stoichiometric LiNbO₃ was observed by confocal micro-Raman scanning spectroscopy. The 180°-domain, which is nominally invisible by Raman scattering due to equivalency of Raman selection rule for adjacent domains, was clearly visualized with a spatial resolution of 460 nm. At domain walls, an enhancement of Raman intensity was observed in optical modes that are closely related to the Nb–O bond, while there was no significant change in Li-ion related modes. Nb–O covalent bonds would be deformed by opposite ferroelectric displacements of ions across domain walls, to modify an electric polarizability of the Nb-ion related modes.

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1. Introduction

Ferroic materials usually have domain structures, where electric dipole moments align uniformly within each domain and orient along a different crystallographic direction in the neighboring one. A number of functional electronic, mechanical and optic devices have been developed based on the ferroelectric domain, for instance, ferroelectric-based non-volatile memories (FE-RAM) that use the domains as binary-units,¹⁾ a giant electro-mechanical response has been achieved by microscopically textured domains.²⁾ Especially, quasi-phase matching (QPM) elements with periodically poled 180°-domains have made a breakthrough in non-linear optical devices.³⁾ From an academic viewpoint, furthermore, physical properties around the domain wall are intriguing issue, because many exotic phenomena, which differ from bulk properties due to a boundary effect, is expected to be hidden there. Concomitantly with the technological development of the ferroelectric domain engineering, there has been increasing demand on investigation techniques for the domain structure and physical properties around the domain boundary. Many methods heretofore have been employed for the domain observation, for instance, carbon decoration, chemical etching, scanning probe microscopy (SPM), and so on.^{4)–8)} These methods, however, require to contact the probe onto the sample and are sometimes destructive. Recently, a second harmonic generation interference microscope (SHGIM) has been developed as a new optical domain imaging technique.^{9),10)} By using this SHGIM, 180°-domain structure can be clearly visualized with a non-destructive way, though it is generally invisible by a conventional polarized optical microscope due to an equivalency in indicatrices of neighboring domains. A Raman scattering spectroscopy gives further advantages for the optical domain imaging.

With this technique, we can detect not only domain morphology but also fundamental properties of the material for instance defects, strain, and chemical composition distribution.¹¹⁾ This point is quite important for the investigation of domains because such inhomogeneity often play a crucial role on the domain formation. However, it has been generally believed that Raman scattering cannot be applicable for the 180°-domains. The reason is that 180°-domains are mutually identical in terms of the Raman selection rule, therefore they do not exhibit any difference in the Raman spectra. Recently, Tikhomirov et al. reported that 180°-domain structure in the periodically poled LiNbO₃ (PPLN) can be visualized with the Raman scattering by applying an in-plane ac electric field.¹²⁾ However, this method requires attaching electrodes for the observation.

In the present study, we report a complete non-contact and non-destructive observation of 180°-domain structure in PPLN by a precision confocal micro-Raman scattering technique, which has been achieved by a sensitive detection of spectral changes at domain walls. The present precise optical setup has attained a spatial resolution of 460 nm that corresponds to a diffraction limit. The observed spectral change at domain walls is explained by the modification of the electronic polarizability around Nb-related modes at the domain boundary.

2. Experimental

A stoichiometric LiNbO₃¹³⁾ was periodically poled with 28 μm interval between each domain by a periodic electrode technique (Fuji Electric Advanced Technology Co., Ltd.). Surfaces of the sample were polished into optical quality after preliminary checking of the domain structure by the chemical etching method. (Fig. 1). The precision confocal micro-Raman system was constructed by a combination of a specially designed stable confocal microscope (Photon Design Co.) with an objective lens of N. A. = 0.7, the Jovin-Yvon single monochromator HR-320, and a liq. N₂ cooled charge-coupled-device camera. The present frequency resolution is around 1.5 cm^{–1}. A 532 nm diode-pumped solid-state (DPSS) laser was used for the excitation

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Fig. 1. Pictures for the z -surface of the periodically poled LiNbO₃ (PPLN) used in the present study. The panel (a) shows the 180°-domain structure of the sample, which was preliminarily observed by the chemical etching technique. The panel (b) presents the surface of optical quality after the polishing.

beam with a power of 20 mW on sample. The theoretical spatial resolution of the present setup is thus about 464 nm for a lateral direction. For a depth direction, on the other hand, the present confocal optical system attains a penetration depth of around 1 micron when the incident laser is focused just on the surface. The polarization direction of the incident laser was parallel to the crystallographic y -axis. The scattered light was analyzed by a polarizer after the collection with a back scattering geometry. The present Raman scattering configurations were $z(yy)$ - z and $z(yx)$ - z . The 3-dimensional position of the sample was controlled by precision stepping motors with the resolution of 100 nm. The stability of the position attains below ± 100 nm for all directions during whole measurements.

3. Results

Figures 2(a) and 2(b) show typical Raman spectra at single domain regions observed in $z(yy)$ - z and $z(yx)$ - z scattering geometries, respectively. According to C_{3v} point symmetry of LiNbO₃, transverse $A_1(z)$ and $E(y)$ modes are expected to be observed in the $z(yy)$ - z scattering configuration. In the $z(yx)$ - z scattering configuration, on the other hand, only $E(-x)$ mode is allowed by Raman selection rule.¹⁴⁾ Confocal micro-Raman scanning measurements were performed over 50 μm along the x -axis across the periodically inverted 180°-domains. Figure 3 shows the result of the scanning measurement with the selected spectral area from 500 to 700 cm^{-1} [the square bracket in Fig. 2(a)]. As seen in the figure, a distinct spectral change was detected at the high-frequency side of the peak around 580 cm^{-1} [that is also pointed by the solid arrow in Fig. 2(a)]. This high-frequency shoulder periodically appears with the interval of 14 μm , which agrees with that of the domain wall. As mentioned before, 180°-domains, which have opposite polarization direction with each other, cannot be distinguished by the Raman scattering technique due to the equivalency in Raman tensor. Nevertheless, in the present case, the clear observation of the domain wall enables the confocal micro-Raman mapping to visualize the domain structure of PPLN with a high-accuracy. The reason why the domain wall can be detected is discussed in the following section. It should be noted here that, as shown in the inset of Fig. 3, the spatial range of the spectral change around domain wall extends over several hundred nanometers. In the previous theoretical study, however, the size of the ferroelectric domain wall was suggested to be atomically narrow,¹⁵⁾ which is smaller than the present spatial resolution by several orders. A numerical estimation of the peak width in the inset indicates 460 nm as a full width at half maximum (FWHM), which corresponds to the diffraction limit of the present optical setup. Therefore, it seems reasonable that the spectral change around the domain wall is due to the spatial

Fig. 2. Typical Raman spectra at single domain regions observed in (a) $z(yy)$ - z and (b) $z(yx)$ - z scattering geometries, respectively. See text for the arrows and the bracket.

Fig. 3. The result of the confocal micro-Raman scanning over 50 μm across the periodically inverted 180°-domains along the x -axis. The figure shows the selected spectral region, which is denoted by the square bracket in Fig. 2(a). The inset indicates the position dependence of the Raman intensity at 610 cm^{-1} .

resolution of the present system, rather than the width of the ferroelectric domain wall.

4. Discussion

In the present study, several spectral anomalies were observed around the domain boundary. All anomalies are picked up in Figs. 4(a)–4(c), with differences between the spectra of the domain boundary (red lines) and that of single domain region (black lines). Figures 4(d)–4(f) show corresponding line scanning profiles across the domain structures with respect to the spectra shown in Figs. 4(a)–4(c), respectively. As seen in the figures, all anomalies were periodically observed with the interval of 14 μm . This result confirms that all of them stem from domain boundaries of PPLN. It should be noted here that the mismatch in the absolute positions of anomalies between $z(yy)$ - z [Figs. 4(d) and 4(e)] and $z(yx)$ - z [Fig. 4(f)] scattering geometries are due to the deviation of mechanical origins of the positioning system in different runs. The most prominent anomaly is, as presented in Fig. 4(a) and also in Fig. 3, the appearance of the broad shoulder at the side of sharp peak around 580 cm^{-1} . A spectral calculation clarified that this shoulder is caused by the growth of a peak at 619 cm^{-1} (Fig. 5). According to the previous studies by Ridah et al., this peak position coincides with that of $E(\text{TO9})$ mode,

Fig. 4. Comparison between the spectra in the single domain region (black lines) and around the domain boundary (red lines), where spectra in the panels (a) and (b) were observed in the $z(yy)$ - z scattering geometry, on the other hand, the spectra in the panel (c) is for $z(yx)$ - z scattering geometry. The closed circles in the panel (a), (b), and (c) denote the differences between the spectra indicated by the black and red lines, respectively. The panel (d), (e), and (f) present the position dependences of the spectral intensity at 610, 164, and 427 cm^{-1} , which correspond to the spectra in panels (a), (b), and (c), respectively. These spectral positions are also indicated by the solid and broken arrows in Fig. 1(a) and the broken arrow in Fig. 1(b), respectively.

Fig. 5. Peak fittings for the $z(yy)$ - z spectra ranging from 500 to 700 cm^{-1} observed (a) in the single domain region and (b) around the domain boundary.

which is usually smeared by the intense peak around 580 cm^{-1} .¹⁶⁾ They also reported that $E(\text{TO}9)$ mode become enhanced in the near-stoichiometric LiNbO_3 . If we apply this interpretation for the present case, the growth of $E(\text{TO}9)$ mode is explained by the improvement of stoichiometry at the domain boundaries. However, this can be ruled out by following reasons: (1) our samples are originally stoichiometric ones, (2) no change in the peak intensity was observed at domain boundaries except for the peaks that are picked up in Figs. 4(a)–4(c), in marked contrast to the previous result, which indicated that all peaks are enhanced in the stoichiometric sample. The possible interpretation would be the modification of the electronic polarizability of Nb–O bond around the domain boundary. Spontaneous polarization of

LiNbO_3 originates from the relative displacements of Li and Nb cations along c -axis, from oxygen sublattice.¹⁷⁾ At the 180°-domain boundary, their displacements are inverted, and the chemical bondings are distorted due to the opposite shifts of cations about the oxygen sublattice. The charge-density distribution is, thus, deformed due to the distorted bond, and this situation causes the change of electric polarizability, inducing the variation of Raman scattering intensity. The previous first-principle calculation for the charge-density distribution of LiNbO_3 have indicated the significant covalent bonding character between Nb and O, differently from the ionic feature of Li-ion.¹⁸⁾ Therefore, it would be reasonable that, Raman intensity of Nb-related modes are influenced by the domain boundary more than Li-related modes, because the charge-density distribution would be modified more in Nb–O bonding than Li-related bonds due to the stronger covalency of Nb. When we re-examined the present results by taking this speculation in mind, it can be found that all anomalies were indeed detected in Nb-related modes. According to the force field calculation by Reperin et al.,¹⁹⁾ $E(\text{TO}9)$ mode is composed of two Nb–O stretching modes. The appearance of the weak shoulder at the high-frequency side of the peak around 155 cm^{-1} [Fig. 4(b) and the broken arrow in Fig. 2(a)] can be attributed to the intensity enhancement of the $E(\text{TO}2)$ mode, which is mainly due to the Nb–O–Nb bending mode. Furthermore, the slight broadening of the peak around 435 cm^{-1} [Fig. 4(c) and the broken arrow in Fig. 2(b)] is probably caused by the distortion of geometrical configuration of O–Nb–O bond, since this mode includes two Nb–O stretching modes and one O–Nb–O bending mode. It should be mentioned finally that, the previous studies observed a domain boundary effect extended over several hundred nanometers (or sometimes micrometer scale) with X-ray topography, defect luminescence microscopy, and so on, in spite the fact that no corresponding spectral changes were detected in the present study. This controversy can be explained with the frequency resolution of the present optical setup. The previous results are explained with a long-range lattice strain induced by the 180°-domain boundary. Generally, the lattice strain is detected by the Raman scattering as a very slight frequency shift ($<1 \text{ cm}^{-1}$). This is beyond the present frequency resolution with the single monochromator ($\sim 1.5 \text{ cm}^{-1}$). If we employ the high-frequency resolution spectrometer, the long-range strain effect can be detected in addition to the Raman intensity modification at domain boundary, which was observed in the present study.

5. Conclusion

In conclusion, the precision confocal micro-Raman scattering has clearly visualized the periodic domain structure in PPLN with the spatial resolution of 460 nm, contrarily to the general understanding that 180°-domain structures cannot be observed by Raman scattering due to the equivalency in the Raman selection rule for neighboring domains. The present observation has been achieved by the accurate detection of the 180°-domain walls as the modification of Raman spectra. The spectral change around the domain boundary probably stems from the modification of the electronic polarizability in Nb-related strongly covalent chemical bonds due to the opposite ferroelectric displacements between adjacent domains. The present result opens a new door for the non-contact, non-destructive, and non-invasive simultaneous investigation of 180°-domain structure and physical properties with high accuracy.

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