Article

Non-Invasive Visualization of Ferroelectric Domain Structures on the Non-Polar y -Surface of KTiOPO_4 via Raman Imaging

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Abstract: Potassium titanyl phosphate (KTP) is a nonlinear optical material with applications in high-power frequency conversion or quasi-phase matching in submicron period domain grids. A prerequisite for these applications is a precise control and understanding of the poling mechanisms to enable the fabrication of high-grade domain grids. In contrast to the widely used material lithium niobate, the domain growth in KTP is less studied, because many standard methods, such as selective etching or polarization microscopy, provides less insight or are not applicable on non-polar surfaces, respectively. In this work, we present results of confocal Raman-spectroscopy of the ferroelectric domain structure in KTP. This analytical method allows for the visualization of domain grids of the non-polar KTP y -face and therefore more insight into the domain-growth and -structure in KTP, which can be used for improved domain fabrication.

Keywords: Raman spectroscopy; KTP; periodic poling; ferroelectric domains; Raman imaging

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1. Introduction

Potassium titanyl phosphate (KTiOPO_4 , KTP) is a nonlinear optical material that belongs to the point group $mm2$ and the space group $Pna2_1$ [1], offering a wide transparency window, as well as large electro-optic and nonlinear constants [2,3]. Additional advantages are the low photorefractivity [3] and the high damage threshold.

More recently, it was demonstrated that KTP allows for the fabrication of ultra-short ferroelectric domain grids [4–6], i.e., submicron periods. These find application in efficient frequency conversion interfaces between the UV and mid IR that link photonics and solid-state quantum systems [6], mirrorless optical parametric oscillators [7], or counter-propagating parametric down-conversion (PDC) [8]. The latter provides spectrally decorrelated photons with narrower bandwidths and at higher source brightness than could be achieved with standard forward-propagating PDC and spectral filtering [8]. Efficient frequency conversion processes require phase matching between the interacting waves, which is typically achieved by employing the quasi-phase matching (QPM) technique by fabricating periodically poled ferroelectric domain structures [9,10]. The main advantage of QPM over other phase matching schemes, such as birefringence phase matching or modal phase matching, is that QPM allows for phase matching of the conversion process independent from the material properties (birefringence) or waveguide design, hence allowing for optimizing the different properties for best conversion efficiencies [11]. Furthermore such a design allows for addressing the highest nonlinear coefficient d_{33} [12]. The challenge, however, is to fabricate a homogeneous domain structure. The usual method for this is

electric field poling. Electric field poling of KTP is more challenging than the poling of lithium niobate (LN) [13,14] mainly due to the large ionic conductivity observed along the polar axis of KTP [15]. On the one hand, this conductivity makes it demanding to maintain high electric fields on large poling areas, while on the other hand the ionic current at the same time masks the typical ferroelectric switching current [13], which is used in other materials, such as LN, as a convenient measure for the poling progress. Even more, in some cases this ionic conductivity has often been observed to spatially vary over flux grown wafers [13], which is connected to a spatially dependent potassium deficiency often inevitably introduced during growth. This led to the development of novel poling and monitoring schemes for KTP different from traditional LN approaches [10,16]. To optimize and understand domain fabrication in KTP and any other material, the assessment and analysis of the transferred domain structure is imperative. However, studies of the ferroelectric domain structure, the underlying poling mechanism and domain growth in depth, i.e., domain cross-sections on non-polar x- and y-surfaces, are sparsely studied in KTP [13,17]. The standard method to visualize the domain structures is selective chemical etching; however, our own experiments, as well as previous works by Canalias et al. [17], show that this method cannot be employed to visualize domain structures on the non-polar surfaces. Another standard method to analyze domain structures is Piezo-response force microscopy (PFM) [18]. This method can be conveniently employed to study domain structure on polar and non-polar surfaces on KTP. As an AFM derivative, it offers nanometer scale spatial resolution, which is mostly limited by the tip size. However, it is mostly a surface sensitive method. Most domains can be detected up to 1.7 μm depth [19]. Non-invasive optical microscopy methods, such as Raman imaging [20,21] or second harmonic microscopy [22–25], offer an additional depth discrimination [26–28] and are sensitive to other material properties, such as stoichiometry [29], defects [30] or crystal symmetry changes [31,32]. Therefore, these methods offer a route to study interaction between domain structure and stoichiometry or strain, which potentially plays an important role in Rb-exchanged waveguides in KTP [33]. Recently, we investigated the Raman imaging contrast mechanism of ferroelectric domain walls (DW) [34]. In the present study, we apply this knowledge to investigate and image DWs on the non-polar surfaces of KTP to gain more insight into the domain growth mechanism as well as investigate the reliability of the utilized poling monitoring based on the electro-optic effect.

2. Experimental Design

A commercially obtained flux grown single-crystalline and mono-domain KTP wafer is diced into pieces of dimensions of typically 10 mm by 6 mm by 1 mm (X by Y by Z). The potassium stoichiometry of flux grown KTP has previously been observed to vary over the wafer scale, which influences the local poling behavior. The poling structure is transferred to the sample by a standard optical lithography process (photo resist patterned with 7.6 μm period on the -z face) as schematically shown in Figure 1. Here, the long axis of the periodically domains are oriented parallel to the y-direction. The -z and +z surfaces are then electrically contacted by an electrolyte and a metal back electrode, respectively. The domain inversion is achieved by applying several high voltage pulses generated via a pulse generator with an attached high-voltage amplifier (Trek 20/20C). The same poling process is used to fabricate samples suitable for a Rb-exchange process to obtain periodically poled Rb:KTP waveguides [35]. Typical waveguides have depths of less than 10 μm . It is imperative that the design parameters of the domain structure are met close to the surface intended for the waveguide fabrication. To monitor the poling progress we employ an all optical monitoring method based on the electro-optic effect developed by Karlsson et al. [10,16]. We place a weakly focused laser beam within 100 to 200 μm close to the -z surface. The laser beam is linearly polarized at 45° with respect to the z-axis. As KTP is birefringent, the laser will exit the crystal at an arbitrarily, elliptically polarized state. Via a quarter wave-plate the light polarization is linearized, directed to another linear polarizer and detected by a photo-diode. If the voltage is increased the light field

component polarized parallel to the z-axis will see a voltage-dependent phase shift due to the linear electro-optical effect (Pockel's effect) and the detected signal intensity will oscillate with linearly increasing voltage as discussed in detailed by Karlsson et al. [14]. Depending on the domain orientation, the refractive index will be increased or decreased due to the electro-optic effect. This is because the sign of the electro-optical tensor is reversed in domains of opposing orientation. This means when half of the domains are inverted along the light path, i.e., in an ideal case a 50/50 duty cycle is reached, as shown in Figure 1c, the voltage dependent oscillation will vanish, because there is no net phase shift for the light component parallel to the z-axis. We apply voltage pulses to the sample until this point is reached.

Figure 1. Principle sketch of: (a) Poling and monitoring geometry used in this study. (b) Poling start: With application of the first pulse over the coercive field, inverted domains will nucleate under the electrically contacted area. (c) Poling stop: After application of multiple pulses, the domains will have grown deeper and have merged until an approximately 50/50 duty cycle in the monitored regions is achieved. (d) Geometries for the presented Raman analysis. Figure is not to scale.

Domain reversal is microscopically subdivided into four steps [36,37]: (1) nucleation of new domains on one or two of the polar surfaces, (2) forward growth of the nucleated, switched domains along the z-axis, (3) sideways spreading in the x- and y-plane, and (4) coalescence of neighboring domains. Domain propagation speeds are characterized by a substantial directional dependence. In KTP for forward growth, typical values between 50 and 200 $\mu\text{m/s}$ are observed [13]. However, in the y-direction, the domain propagation speed is between 10 and 30 $\mu\text{m/s}$, while it is only 0.2 to 1.2 $\mu\text{m/s}$ in the x-direction [13]. The two to three orders of magnitude difference between forward and sideways growth is among one of the reasons why KTP is a suitable material for fabrication of ultra-short domain periods [5,7].

When the monitoring indicates that 50% of the electrically contacted area is flipped, poling is stopped. This is sufficient, for example, to achieve homogeneously poled surface-near waveguides [38]. However, we expect only incomplete domain inversion in the deeper regions of the crystals, as schematically indicated in Figure 1c. Raman measurements were performed incident from z-face via light oriented parallel to the crystallographic c-axis and

incident y-face via light perpendicular to the c-axis. As previously established [34], both allow for a domain wall contrast. In each case, the surface-near interaction provides the best resolution possible. Alternatively, the confocal mode allows for imaging the cross-section (y-face) by gradually focusing deeper into the material from the z-face. However, in this case, a refracting (and in this case even a birefringent) medium will lead to a gradual decrease in intensity as well as a gradual decrease in resolution due to the increasing distortion of the focus field. Therefore, such scans may be limited to depths closer to the respective surface, e.g., $<100\ \mu\text{m}$, which is suitable for the analysis of (periodically poled) waveguides. The Raman analysis was performed on a custom built confocal setup, which utilizes excitation light of 532 nm at 50 mW focused via an infinity-corrected objective (NA = 0.7) on the sample. The scattered light is collected by the same objective and directed to the spectrometer (KOSI Holospec, f/1.8i) with attached CCD camera (Andor Newton, BI) for detection. Spectral suppression of the Rayleigh scattered light is provided by a dichroic mirror separating excitation and detection path and an appropriate Notch filter integrated in the spectrometer unit. A pinhole of 10 μm diameter is inserted in the detection path providing in combination with the objective lens a spatial resolution of $<400\ \text{nm}$ in lateral direction and $<2000\ \text{nm}$ in axial direction. With respect to a fixed laser focus, the confocal application demands raster scanning via 3D positioning of the sample to obtain an image. In our setup, the scanning is performed with respect to a fixed focus via a nanopositioning stage with 2 nm resolution and 180 μm by 180 μm by 20 μm scan range (Tritor, Piezosystem Jena). This piezo-stage is mounted on a custom-built long range positioning system with 40 mm by 40 mm in lateral direction and 25 mm in axial direction. This long range stage provides a μm -scale accuracy over the whole range. In particular, the latter stage is important for this study, as it allows us to study the domain structure over a large area in three dimensions and repeatably select areas of interest for high resolution imaging. Further details on the system can be found in previous work [39].

3. Raman Analysis on KTP

As known from previous works, the Raman spectrum is modified by the presence of DWs [34]. This comprises intensity variations, changes in peak position or full-width-at-half-maximum (FWHM) and depends on the specific phonon, as indicated in Figure 2. A spatial mapping of these spectral features allows for the visualization of domain structures.

Figure 2. Raman spectra of a DW compared to bulk spectra for the scattering geometry $z(y,y)\bar{z}$. For better visibility of the changes, a difference spectrum is given.

In Figure 2, the as-measured Raman spectrum of bulk KTP compared to a spectrum taken at a DW measured for z-incident is shown. The scattering geometry can be conveniently described in Porto's notation, here for example $z(y,y)\bar{z}$, where the symbols in the brackets denote the polarization of the incoming and outgoing light in crystal coordinates, while the outer symbols denote the propagation direction of the incident light (z) and detected light ($\bar{z}$). The presented bulk and DW spectra only show minor differences, with intensity changes for certain modes in the order of a few percent and some peak-shifts by a few cm^{-1} . For both scattering geometries the differences between the bulk and DW spectra are small, which can be partly explained by the diffraction-limited optical resolution >400 nm and the size of a DW, which is supposed to be only a few nm down to a unit cell large [40]. To better highlight the changes, the corresponding difference spectrum is shown. In the literature, the changes in the Raman spectra of DWs are explained by two mechanisms. On the one hand, ferroelectric DWs are expected to be accompanied by strain [40,41]. Therefore, inner electric fields are generated via piezo-electricity, which influences the Raman data [42–44]. This is referred to as the elasto- and electro-optic coupling [45]. The second mechanism assumes changes in the Raman selection rules according to Stone and Dierolf [46]. Here, the DW is understood as a planar defect. A planar defect is accompanied by a defect momentum due to the step-wise change in crystal structure. Therefore, in the presence of DWs phonons propagating at angles non-parallel to the incident beam may be present in the measured spectrum. If the spectrum of these phonons propagating at oblique angles differs from the bulk spectrum, a change at the DW spectrum is observed [46,47]. Based on the model by Stone and Dierolf [46], we have recently shown that the DW spectrum of KTP can be explained and predicted by measuring the angular dependency of the spectrum [47]. For example, the dominating peak in Figure 2 is an A_1 -LO type, which shifts to lower wavenumbers at higher phonon propagation angles resulting in a spectral intensity increase in the $69\text{--}700\text{ cm}^{-1}$ range. Due to the diffraction-limited spatial resolution, the spectrum measured at a DW is always a sum of the DW spectrum and a bulk spectrum. In total this explains the decrease in intensity of this mode, the shift to lower wave-numbers, as well the observed slight broadening as bulk and DW spectra are detected simultaneously.

Based on our spectral analysis we performed Raman imaging in terms of the spatial variation of the three parameters: intensity, FWHM and peak frequencies for specific phonons. As an example, the corresponding results for the dominating phonon around 760 cm^{-1} are shown in Figure 3. Here, for z-cut an intensity decrease (Figure 3a), broadening of linewidth (Figure 3b) and a decrease in wave number by more than 1 cm^{-1} is observed (Figure 3c). For all three fitting parameters, the domain structure becomes clearly visible with the targeted domain period ($7.6\text{ }\mu\text{m}$) and duty cycle. A comparison of the three images shows that plotting the peak shift provides the best results for visualization of DWs, because peaks shifts are not susceptible for slight intensity variations, e.g., by surface irregularities.

The focus of this work lies on the visualization of the ferroelectric domain structure on the non-polar y-face of KTP. Therefore, we performed a spectral analysis to reveal fingerprints of phonon modes sensitive to the domain wall. It should be noted, that in y-face KTP only for the crossed polarization configuration a strong DW contrast is expected, as only these spectra show a directional dependency [34]. Therefore, the Raman spectrum of the DW is compared to the bulk spectrum as shown in Figure 4 for the $y(x,z)\bar{y}$ scattering geometry.

Figure 3. Raman images of the -z-surface of a periodically poled KTP sample based on the variation of intensity (a), FWHM (b) and peak wave numbers (c) of the 760 cm^{-1} phonon mode highlighted in Figure 2.

Figure 4. Raman spectra of a DW compared to bulk spectra for the scattering geometry $y(x,z)\bar{y}$. For better visibility of the changes a difference spectrum is given.

Corresponding structure sensitive phonon modes are listed with respect to changes in intensity, FWHM and peak frequency in Table 1 in order to provide a phonon mode assignment. The 287 cm^{-1} mode is assigned to the ν_5 (TiO_6) vibration. The neighboring 313 cm^{-1} mode also belongs to the same crystallographic structure, but is related to the ν_4 (TiO_6) vibration according to literature, whereas the 991 cm^{-1} mode is linked to the ν_1 vibration of the PO_4 tetrahedron.

Table 1. Comparison of the intensity, FWHM and Raman shift of the peak frequency of the measured spectra in $y(x,z)\bar{y}$ scattering geometry of bulk KTP and a KTP DW. Positive change indicates, respectively, a gained intensity, FWHM or shift to higher frequencies, whereas a negative value indicates a lowered intensity, FWHM or a shift to lower frequencies.

Mode $y(x,z)\bar{y}$ (cm^{-1})	Intensity Bulk (a.u.)	Intensity DW (a.u.)	$\Delta_{\text{Int.}}$ (%)	FWHM Bulk (cm^{-1})	FWHM DW (cm^{-1})	Δ_{FWHM} (cm^{-1})	Shift Bulk (cm^{-1})	Shift DW (cm^{-1})	Δ_{Shift} (cm^{-1})
175	5026	5198	3	8.2	8.3	0.1	174.6	174.7	0.1
190	1712	1680	−2	4.7	4.7	−0.1	190.3	190.3	0.0
210	1246	1660	33	5.1	6.3	1.3	209.7	209.8	0.1
265	8015	8172	2	8.4	8.3	−0.1	265.4	265.4	0.0
287	8325	7656	−8	7.4	7.9	0.5	287.2	287.2	0.1
313	11,860	10,815	−9	10.1	9.8	−0.3	313.0	313.2	0.2
360	10,980	11,004	0	14.7	15.6	0.9	359.8	360.2	0.4
400	4235	3636	−14	19.8	18.7	−1.1	400.0	400.1	0.1
423	2571	2521	−2	10.1	10.6	0.6	423.1	423.3	0.1
514	3356	3115	−7	9.1	8.5	−0.6	514.4	514.4	0.0
544	2150	1579	−27	15.0	13.4	−1.7	554.1	554.4	0.3
691	8095	8214	1	17.7	18.1	0.4	691.5	691.6	0.1
737	1117	2488	123	11.6	18.9	7.2	737.7	737.3	−0.4
783	19,738	20,040	2	15.3	16.7	1.3	783.2	784.0	0.9
991	9999	8495	−15	28.8	27.0	−1.7	991.1	990.4	−0.6

One striking feature is that the previously intensity-sensitive modes assigned to the TiO_6 octahedron are almost not responsive for the DW in context of the FWHM with one exception discussed below, while in z -face geometry, the opposite was often observed. Here, a change in FWHM, but not in intensity, is to be found. When a phonon features a directional dependent coupling (e.g., LO-phonons), it can be an indication that those phonons do offer polar parts in those directions.

The 991 cm^{-1} mode is the only vibration that is intensity- as well as FWHM-sensitive for DWs. The ν_1 (PO_4) vibration assigned peak stands out in contrast to the other changing modes for this parameter, since it is becoming narrower at the DW. Therefore, one may eliminate the influence of defects in this area, which would broaden the allowed selection rules and therefore also the peak.

However this broadening, which may be stoichiometric induced, is observable for the 360 cm^{-1} mode and 783 cm^{-1} mode. The first one is linked to the ν_2 (PO_4) vibration, whereas the second one is assigned to the ν_3 (TiO_6) vibration. It is not surprising that these phonons react differently, since the angular dispersion on the xy -surface is different than in the xz - or yz -surface. Therefore, there are also other shifts or changes in the FWHM.

The most sensitive modes are registered for the shift of the center frequency. While the 313 cm^{-1} mode is already striking for the intensity changes, the 360 cm^{-1} and 783 cm^{-1} peaks appear in the FWHM difference. A noticeable change in even both features is visible for the 991 cm^{-1} mode. Just the 738 cm^{-1} vibration is only sensitive for DWs via shifting. This mode is linked to the ν_1 (TiO_6) vibration. It is important to note, that there are two PO_4 related vibrations, and two more certain TiO_6 assigned vibrations. For both crystallographic structures a shift to higher as well as to lower wavenumbers can be observed. Such a shift in this case can often be related to local strain at the domain wall.

With respect to the assessed suitable fitting parameter for this scattering geometry, we present the resulting Raman images for the 783 cm^{-1} B_1 -TO mode on y -cut KTP shown in Figure 5.

To analyze the domain evolution in the entire depth of the crystal (z -direction), a detailed visualization of the domain structure on the y -face was performed in $y(x,z)\bar{y}$ scattering geometry, whereby the the spatial varied peak frequency shift of the B_1 -TO phonon mode at 783 cm^{-1} was utilized. In this specific configuration, the peak frequency at domain walls is shifted to higher frequencies in the range of 0.8 cm^{-1} from the central frequency peak. Corresponding Raman images for three different regions are depicted in

Figure 6: (a) a scan close to the $-z$ surface ($z = 5 - 35 \mu\text{m}$), (b) a scan around $300 \mu\text{m}$ depth ($z = 300 - 330 \mu\text{m}$), where the domain structure becomes inhomogeneous, and (c) a scan close to the $+z$ surface ($z = 970$ to $1000 \mu\text{m}$).

Figure 5. Raman images of the non-polar y -surface of a periodically poled KTP sample based on the variation of intensity (a), FWHM (b) and peak wave numbers (c) of the 783 cm^{-1} phonon mode highlighted in Figure 4.

Figure 6. Detailed images of domain structures on y -cut ($y(x,z)$) measured in three areas of interest, (a) close to the $-z$ surface, (b) in the region, where irregular domain structures appear and (c) close to the back side evaluated from the 783 cm^{-1} mode. A sketch of the measurement geometry is given in (d). A scale for the peak frequency with respect to the acquired Raman images (a–c) is to be found in (e).

In principle over the entire depth, specific domain walls can be found. Additionally, over the complete scan range, not all inverted domains follow a path parallel to the z -direction, but instead show some lateral movement on the order of a few μm . Based on this data, three distinct regions can be subdivided: In the surface-near region (c.f. Figure 6a) the domain structure appears nearly to be homogeneous. This corresponds to the region, where the monitoring was performed resulting in a duty cycle of approximately 50/50 and a transferred domain period of 7.6 μm . A complex domain structure built up by various only partly merged spike-like domains can be found within the depth region from 300 to 330 μm (c.f. Figure 6b). From the opening angle between 0.5° to 1° of this spike domain, it can be estimated that the domain velocity in the z -direction is at least 50 to 100 times faster compared to the domain velocity in the x -direction. This is slightly lower than the previously measured ratio of about 200 to 250 by Canalias et al. [48]. A possible reason may be a different crystal stoichiometry in our crystals, as in particular the potassium stoichiometry is known to influence the material properties [49] and to vary between different crystals and even within the same wafer. This behavior can also be found in regions beyond this area. Close to the z -face (bottom of the sample, $z = 970\text{--}1000\ \mu\text{m}$) the imaged domain structure (c.f. Figure 6c) shows a strongly altered duty cycle. However, the period of 7.6 μm suggests that the inverted domains originally started their growth from a single nucleation side under adjacent electrodes. Note that the scan area for Figure 6c was especially chosen for inverted domains completely transferred to the bottom of the sample; there are also regions without a complete domain structure due to the merging of spike-like domains.

4. Conclusions

In this work, we have analyzed the vibrational properties in terms of the ferroelectric domain structure on the non-polar y -surface KTP. In this context, structure sensitive phonon modes have been assigned and based on this investigation we have demonstrated Raman imaging of the ferroelectric domain structure in y -face of KTP. Our analysis confirms, that our in situ poling monitoring method yields suitable domain structures close to the surface region and provides samples suitable for fabrication of periodically poled Rb-exchanged waveguides in KTP. For deeper regions we found spike-like merging of domains and change of the duty cycle to the bottom of the sample. All in all we demonstrated that the visualization of the domain structure on the non-polar y -face of KTP via Raman spectroscopy is also possible, and therefore enables a more elaborated improvement of the poling process and dynamics.

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Abbreviations

The following abbreviations are used in this manuscript:

AFM	Atomic force microscopy
CCD	Charged-coupled device
DW	Domain wall
FWHM	Full width at half maximum
IR	Infrared
KTP	Potassium titanyl phosphate
LN	Lithium niobate
LO	Longitudinal optical
NA	Numerical aperture
PDC	Parametric down conversion
PFM	Piezoresponse force microscopy
QPM	Quasi phase-matching
TO	Transversal optical
UV	Ultraviolet

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