

Impact of ion exchange on vibrational modes in Rb-doped KTiOPO₄: A Raman spectroscopy study on the interplay between ion exchange and polarization switching

Cherrie S. J. Lee  and Carlota Canalias

Department of Applied Physics, *KTH Royal Institute of Technology*, Roslagstullsbacken 21, 114 21 Stockholm, Sweden

Robin Buschbeck, Boris Koppitz, Franz Hempel, Zeeshan Amber, and Lukas M. Eng 

Institute of Applied Physics, *TU Dresden*, Nöthnitzer Strasse 61, 01187 Dresden, Germany
and Dresden-Würzburg Cluster of Excellence—EXC 2147, *TU Dresden*, 01062 Dresden, Germany

Michael Rüsing

Integrated Quantum Optics, Institute for Photonic Quantum Systems (PhoQS),
Paderborn University, Warburger Strasse 100, 33098 Paderborn, Germany



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Recently, ion exchange (IE) has been used to periodically modify the coercive field (E_c) of the crystal prior to periodic poling, to fabricate fine-pitch domain structures in Rb-doped KTiOPO₄ (RKTP). Here, we use micro-Raman spectroscopy to understand the impact of IE on the vibrational modes related to the Rb/K lattice sites, TiO₆ octahedra, and PO₄ tetrahedra, which all form the basis of the RKTP crystal structure. We analyze the Raman spectra of three different RKTP samples: (1) a RKTP sample that shows a poled domain grating only, (2) a RKTP sample that has an E_c grating only, and (3) a RKTP sample that has both an E_c and a domain grating of the nominally same spacing. This allows us to determine the impact of IE on the vibrational modes of RKTP. We characterize the changes in the lower Raman peaks related to the alkali-metal ions, as well as observe lattice modifications induced by the incorporation of Rb⁺ that extend further into the crystal bulk than the expected IE depth. Moreover, the influence of IE on the domain walls is also manifested in their Raman peak shift. We discuss our results in terms of the deformation of the PO₄ and TiO₆ groups. Our results highlight the intricate impact of IE on the crystal structure and how it facilitates periodic poling, paving the way for further development of the E_c -engineering technique.

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I. INTRODUCTION

KTiOPO₄ (KTP) and its isomorphs are ferroelectrics commonly used in nonlinear optics, with a generic formula of $MTiOXO_4$ where M is K, Rb, Tl, NH₄, or Cs while X can be P or As [1]. The main three-dimensional (3D) framework of KTP is composed of two primary components: the octahedral TiO₆ and the tetrahedral PO₄ [2]. The octahedrons form a continuous chain along the $\langle 011 \rangle$ and $\langle 0\bar{1}1 \rangle$ crystallographic directions, which are linked by the tetrahedrons. The octahedron is not symmetric with the titanium ions in the Ti(1) and Ti(2) positions but are displaced from their centers, resulting in alternating long (2.00–2.10 Å) and short (1.72–1.74 Å) Ti–O bonds within the chains. The alternating long and short Ti–O bonds that occur along this chain contribute to the polarization in the z direction [3]. The remaining four bonds that are not involved in the chain have intermediate lengths of 1.95–2.07 Å [4]. The cation, K⁺, resides in the cavities between the octahedrons and tetrahedrons along the z axis. The

cations occupy two distinct crystallographic sites, $K(1)$ and $K(2)$, which are surrounded by nine and eight oxygen atoms, respectively. The ionic conductivity of KTP is due to the K⁺ cations that are loosely bound to their sites. The diffusion pathways for K⁺ within the crystal are not confined to simple one-dimensional channels along the axis $\langle 001 \rangle$. Instead, they traverse a more intricate network involving the $K(1)$ and $K(2)$ sites and their corresponding hole sites $h(1)$ and $h(2)$, creating a net movement of K⁺ along this direction [5]. Their mobility is governed by a vacancy hopping energy barrier [3,6], which overall, is the smallest along its z axis. This gives the ionic conductivity along the z axis several orders of magnitude larger than along its x and y axes [7]. When an electric field is applied, the K⁺ will migrate towards the negative electrode, confirmed by observation of K⁺ accumulation at the cathode [8]. The K⁺ ions in the nine-oxygen coordinated site shifts to the eight-oxygen coordinated site, similarly, the K⁺ in the eight-oxygen coordinated site shifts to the nine-oxygen coordinated site during poling [9]. The shifts of the K⁺ ions create a slight relaxation in the surrounding oxygen atoms. The heavier Ti⁴⁺ are also displaced in the octahedron. To accommodate this change, the octahedron and the tetrahedron rotate slightly [10].

The isomorphs of KTP are widely utilized in quasiphasematching (QPM) in nonlinear optics ranging from

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spontaneous parametric down conversion to optical parametric oscillators and amplifiers, due to their high optical nonlinearity, wide transparency range, and high damage threshold [4]. The QPM approach utilizes periodic poling to flip the ferroelectric domains periodically. Recently, the isomorph $\text{Rb}_x\text{K}_{1-x}\text{TiOPO}_4$ (RKTP) with $x = 0.003$ demonstrated a decrease of the ionic conductivity, enabling substantial improvement in electric field poling [11]. The conventional method of periodic poling involves the use of patterned metal electrodes deposited onto one of the crystal's polar faces to achieve the desired QPM period. An external electric field is then applied between the polar faces to induce polarization switching, hence creating a domain grating into the crystal. However, a notable drawback of this method manifests in the form of fringing fields along the periphery of the metal electrodes, leading to domain broadening and merging, particularly under the influence of high electric fields [12]. This poses considerable challenges, especially when aiming at fabricating very narrow periods of domains and over a large aperture bulk crystal. However, the significant breakthrough in periodic poling that enabled the realization of bulk domain structures with sub- μm periodicity is the coercive field (E_c) grating technique [13], which eliminates the use of metal electrodes during the electric field poling process. The E_c -grating method involves the local engineering of the crystal's E_c using ion exchange (IE) with Rb^+ , thus bypassing the use of the metal electrode and its associated drawbacks. Coupled with RKTP's anisotropic nature, the diffusion of ions will preferentially occur along the crystal's polar axis [5], allowing precise control on the lateral dimension of the inverted ferroelectric domains. The IE region creates a higher E_c at depths down to a few microns below the polar surface, preventing domain nucleation in this region, whereas domain nucleation is less costly in regions without IE (NoIE) since they have a lower E_c . Moreover, the structurally embedded E_c grating at a few microns below the crystal's surface allows for multiple cycles of polarization switching until an optimal duty cycle is achieved [14], a process that is not possible with metal electrodes, since they degrade after a couple of poling cycles. Despite the technique's success and notable advantages, the comprehensive impact of IE on domain reversal remains poorly understood.

To further refine the E_c -engineering technique, understanding the effect of IE on the crystal lattice structure is essential. Raman spectroscopy, utilizing inelastic scattering of photons with phonons, is sensitive to material properties such as stoichiometry and the presence of defects, strain, and even domain walls (DWs) [15–19], making it an effective tool for identifying the impact of IE on E_c -engineered periodically poled RKTP (PPRKTP). Assigning Raman modes to the vibrational modes of the octahedral TiO_6 , the tetrahedral PO_4 and the K^+ in bulk KTP has been done extensively [19–23]. Raman signatures due to the influence of DWs in periodically poled KTP (PPKTP) have been previously studied [16–18]. Incorporation of the larger Rb^+ ion into the RKTP structural framework during IE will modify its lattice structure and hence induce changes in the internal vibrational modes related to the TiO_6 and PO_4 groups and external vibrational modes related to Rb/K groups to accommodate these structural modifications. It is important to understand how the

combination of structural changes in these groups at the polar surface of RKTP prevents domain nucleation to occur at IE regions. Additionally, the effects of IE are likely to be reflected in the Raman features linked to the DW that separates the two domains ($P\downarrow$ and $P\uparrow$), as it coincides with the boundary of the ion-exchanged regions. Unfortunately, there are no studies addressing these questions so far. Nevertheless, understanding them would be invaluable for fully leveraging the E_c -engineering technique, and thus being able to fabricate domain structures with full control over their optical properties.

Here, we use Raman spectroscopy to study the interplay of IE, DW, and the crystal structure of RKTP by comparing selected Raman peaks of three distinctive samples: (i) E_c -engineered PPRKTP, which has both IE and periodic domains (IE-PD), (ii) single domain RKTP with IE (IE-SD), and (iii) PPRKTP that has been poled using the conventional metal electrode method, i.e., without IE (NoIE-PD). The comparison aims to discern whether the observed differences in these specific Raman peaks arise from either the presence of IE, the nature of the domain structures, or a combination of both. Analyzing the changes in their Raman spectra provides key insights into the influence of IE and its intrinsic Rb/K sites alongside their neighboring octahedral TiO_6 and tetrahedral PO_4 groups at two distinct domains: $P\uparrow$ and $P\downarrow$.

II. EXPERIMENTAL DETAILS

The ion-exchanged PPRKTP crystals used in this work were fabricated via E_c engineering by ion exchanging the RKTP crystal in a mixed Rb -rich melt [13]. First, a periodic grating with a period of $9.36\ \mu\text{m}$ was photolithographically patterned onto the virgin RKTP z face. A duty cycle of 0.4 was deliberately chosen such that IE region (0.4) can unambiguously be distinguished from the non-IE region (0.6) in our later experiments. An IE stop layer was then created on the photoresist openings as well as on the opposite polar face via oxygen plasma ashing. After removing the photoresist, the crystal was immersed in a melt with a composition of 73 mol % RbNO_3 , 7 mol % $\text{Ba}(\text{NO}_3)_2$, and 20 mol % KNO_3 for 4 h at 330°C . The Rb^+ from the IE melt then diffuses into the crystal along its polar axis [6], in exchange for K^+ near the crystal's IE z face. Adding the divalent Ba^{2+} creates more vacancies, facilitating the diffusion of the larger Rb^+ and increasing the depth of diffusion [24]. The K^+ acts as a buffer, preventing excessive in-diffusion of Rb^+ and thus reducing the overall stress in the crystal. This creates a grating of high and low E_c on the z face; notably an area that is exposed to IE will observe an increase of E_c while an area that was blocked from IE maintains its original E_c . Once the periodic E_c grating is defined, a 5-ms triangular electrical pulse of $3.5\ \text{kV}/\text{mm}$ was applied to switch the polarization of the RKTP on the NoIE regions, whereas the IE regions maintained its original polarization.

To visualize the quality of the periodic domains, the sample was characterized using second harmonic generation (SHG) confocal microscopy. SHG microscopy is a common technique to visualize domain structures in ferroelectrics. When the focus is in the bulk, the DWs can appear as bright lines in this type of SHG microscopy due to the dominance of

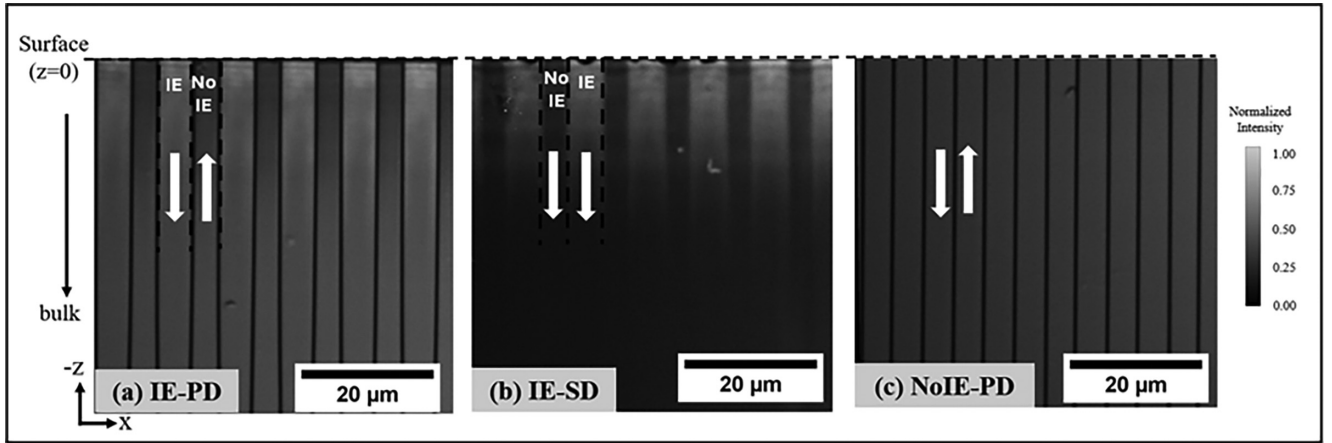


FIG. 1. The SHG microscope image of y -cut RKTp crystal (a) with IE and periodic domain (IE-PD); (b) with IE and single domain (IE-SD); and (c) with periodic domains and NoIE (NoIE-PD).

the Cerenkov-type contrast [25–27] or as dark lines due to destructive interference from opposite domain polarizations [25–28] when the focus is near the surface. Furthermore, the technique offers contrast between regions with different linear (refractive index) and nonlinear (nonlinear susceptibility) properties, which will both change upon IE. Figure 1(a) shows the image of the PPRKTp (IE-PD) taken using SHG confocal microscopy on its polished y face (side view of the exchanged area). The DW (dark lines) separates the $P \uparrow$ and $P \downarrow$ domains, and the periodic domain structures are uniform along the z axis. As the images were taken close to the surface, as well as due to the magnitude of the nonlinear susceptibility tensor elements in the experimental orientation, here the interference contrast is the dominating contrast mechanism. A gradient in contrast along the z direction into the depth of the crystal is observed on the upper side of the image due to the change in material properties induced by IE.

For comparison, we also prepared a sample with only E_c grating on virgin RKTp, without any periodic domains, i.e., the sample with IE before periodic poling (IE-SD). We also prepared a second sample that has periodic domains and NoIE (NoIE-PD). NoIE-PD was poled using the conventional metal electrodes method. After the lithography, aluminum electrodes were deposited on the crystal $-z$ face. Then, the sample was electrically poled using the same parameters as described earlier. Figure 1 shows the SHG micrographs of the three different samples.

The experimental Raman spectroscopy setup used in this work consists of a LabRAM HR Evolution Raman microscope (HORIBA Jobin Yvon GmbH, Oberus, Germany) operating in backscattering geometry. All experiments were conducted with a 632.8-nm monochromatic, linear-polarized continuous wave laser (17 mW, Melles Griot) and a Nikon TU Plan Fluor EPI P 100 $\times$ microscope objective (NA = 0.9). The polarization direction of the incident light was controlled by a rotatable half-wave plate, while the detected signal was analyzed by a rotatable linear polarization filter. The detection system consists of a 600-l/mm grating and a Sincerity charge coupled device (HORIBA Jobin Yvon GmbH, Oberus, Germany). Depth resolution was provided by a confocal pinhole, which suppresses signals generated outside the focal plane.

The sample was mounted on an XYZ translation stage, which enables raster scanning along all three dimensions.

The aim of this Raman spectroscopy experiment is to investigate the influence of IE on ferroelectric domain switching. To do so, we compare specific Raman features of RKTp across three distinct samples: IE-SD, NoIE-PD, and IE-PD as described in the previous section. The scattering geometry used in this experiment is given in the form of the Porto notation, $y(xz)\bar{y}$ whereby the vectors at the outer brackets denote the direction of propagation of the incident (here y) and scattered light (here $\bar{y}$) respectively. The vectors in the inner brackets denote the direction of electric field polarization of the incident and scattered light, respectively, with respect to the crystal's axis. The geometry of $y(xz)\bar{y}$ was chosen because a strong contrast to distinguish the DW is expected in this geometry on the y face of the PPRKTp crystal [18]. Figure 2 illustrates the Raman scan performed on the y face of the PPRKTp (IE-PD) crystal tracing along the crystal's x direction across regions with NoIE ($P \uparrow$) and with IE ($P \downarrow$), with lateral increments of 0.3–0.5 μm . The laser focus was placed 1 μm below the scanned surface (y face) to eliminate surface effects. The scan line was repeated at a few depths: 1, 5, 10, 20, and 80 μm below the $-z$ face, as shown in Fig. 2(b). The expected diffusion depth of Rb^+ is 20 μm , affecting regions between 1 and 20 μm . An 80- μm depth, which is considerably farther away, will be considered as the bulk region. For comparison, similar scans were performed on PPRKTp that is periodically poled using the conventional metal electrode method (NoIE-PD) and RKTp with IE but without any periodic poling (IE-SD).

III. ANALYSIS AND RESULTS

For reference, a Raman spectrum of virgin RKTp without IE and without periodic poling was taken over the spectral range of 70–1150 cm^{-1} in the $y(xz)\bar{y}$ scattering geometry as shown in Fig. 3. When compared to the Raman spectrum of RKTp with IE, specific Raman peaks related to Rb/K , TiO_6 , and PO_4 groups show some distinct changes in their features, as illustrated by the cutouts in Figs. 3(b)–3(e).

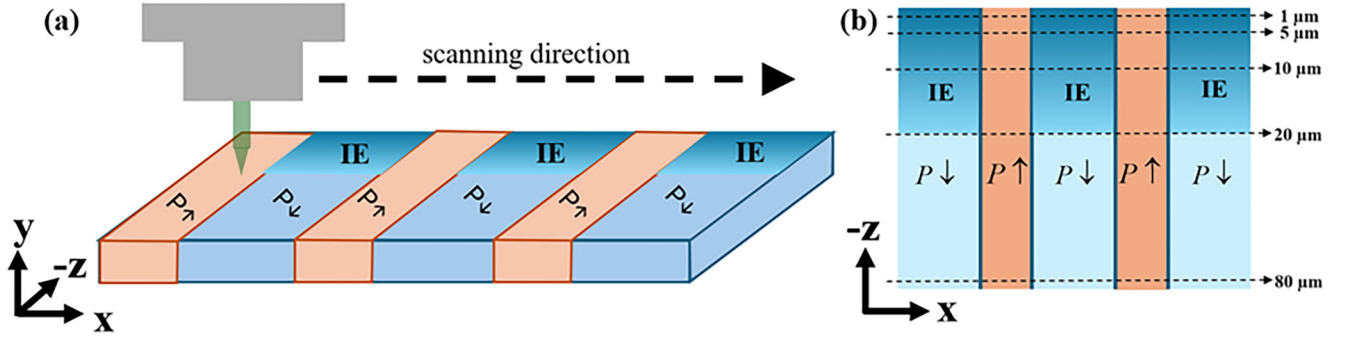


FIG. 2. (a) The Raman scan direction on the y face of the IE-PPRKTP sample with IE-PD; (b) the scan line was performed on the sample y face at several z depths: 1, 5, 10, 20, and 80 μm below the $-z$ face.

First, we examine the most obvious effect of IE, which appears on the lower phonon peaks that are attributed to the Rb/K ions. Figure 4 shows the lower Raman peaks obtained from the Raman scan, as described in Fig. 2, at different distances from the IE surface. There are four distinct low-phonon peaks that are sufficiently large to be resolved by Raman. In the IE regions (highlighted in blue in Fig. 2), two of them (80 and 139 cm^{-1}) show a redshift, while in the NoIE regions, they remain largely unchanged. Meanwhile, the other two low-phonon peaks (102 and 177 cm^{-1}) show a blueshift within the IE regions and remain unchanged in the NoIE regions.

These four low-frequency phonon peak variations can be interpreted by two different phenomena: first, we have the exchanged Rb^+ replacing the intrinsic K^+ , which has a larger

mass and size, redshifting two Raman bands in the IE region. Second, by removing the assumption that the lower phonon peaks are exclusive to the external vibrations of Rb/K ions, there is another possibility to interpret the observed 102- and 177- cm^{-1} bands cases, which is the complex mixture of vibrational modes of the TiO_6 tetrahedrons or the PO_4 octahedron with respect to the lattice [20]. In this case, the observed increase in frequency in the IE region may be due to the shortening of bond lengths in the octahedrons or tetrahedrons, caused by compressive strain from the IE.

There is another plausible explanation if we assume that the lower Raman frequencies are solely related to the external vibrations of Rb/K and their neighboring atoms. It is plausible that these lower Raman peaks at 80, 102, 139, and 177 cm^{-1}

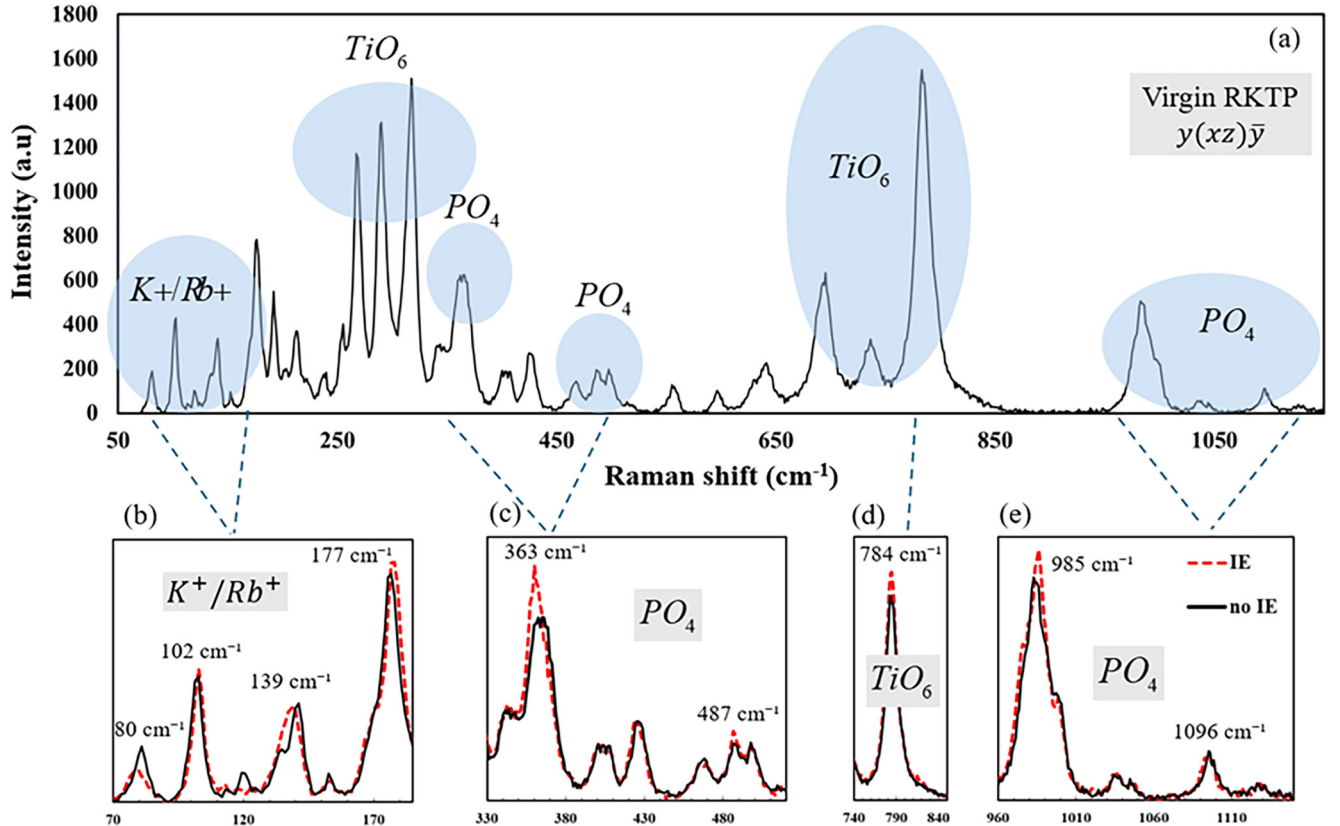


FIG. 3. (a) Typical Raman spectrum of RKTP without IE in $y(xz)\bar{y}$. The insets show specific Raman peaks related to the (b) Rb/K; (c),(e) the TiO_6 groups; (d) the PO_4 groups, in comparison to the IE and NoIE RKTP samples.

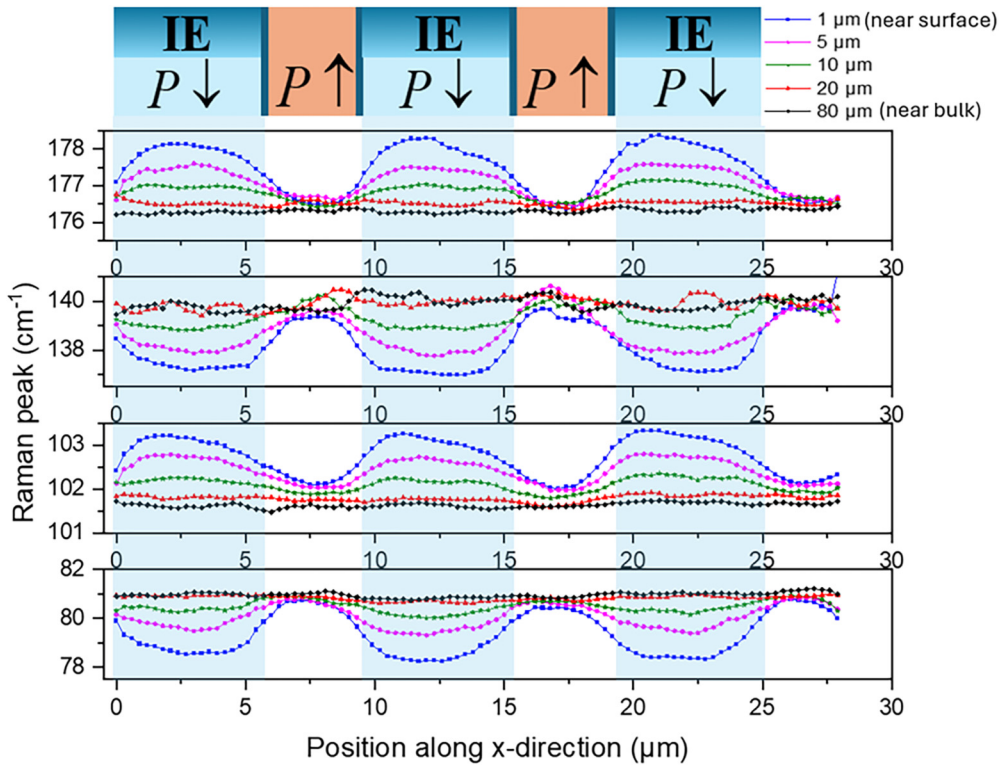


FIG. 4. The Raman peaks of 80, 102, 139, and 177 cm^{-1} at depths of 1, 5, 10, 20, and 80 μm below the $-z$ face (IE face).

are related to their respective $K(1)$, $K(2)$, $h(1)$, and $h(2)$ sites. It has been suggested that the low Raman phonons may be used to study the occupancy of these lattice sites [19]. The $K(2)$ and the normally vacant $h(1)$ sites in KTP are preferred sites for Rb^+ diffusing into KTP, rather than the smaller $K(1)$ and $h(2)$ sites to accommodate the larger Rb^+ atomic size [5,29,30]. Thus the redshifts and blueshifts and the changing intensity ratios might be attributed to the occupation of $K(2)$ and $h(1)$ sites while the K^+ is forced to move to $K(1)$ and $h(2)$ sites, giving rise to expansion and compression of the lattice along different directions, i.e., resulting in the compression and expansion that we mentioned above. However, due to the rather complex Raman spectrum of the KTP family, the accurate attribution of phonons to specific displacement patterns remains still elusive due to both the close overlaps of phonons and the limits in theoretical modeling [14].

Note that in all cases, the largest shift occurs nearer to the z surface (1 μm) and is gradually reduced at IE depths of 5–20 μm . These shifts started to even out beyond depths of 20 μm . This is to be expected since the IE is a diffusion process, resulting in more exchange at the surface than further into the bulk. Moreover, this depth is in good agreement with EDX measurements for IE in RKTP under the same conditions [14]. There is no apparent contrast between regions of $P\downarrow$ and $P\uparrow$ beyond the depth of IE (beyond z depth of 20 μm), and no contrast can be observed in the NoIE-PD sample. This shows that these low-frequency phonon peaks are strongly influenced by IE.

One of the most intense Raman peaks in $y(xz)\bar{y}$ scattering geometry is located at 784 cm^{-1} , assigned to the combination of stretching and bending mode of the octahedral, TiO_6 [20]. Alternatively, given that the Ti^{4+} reside inside the TiO_6

octahedra, where five of the oxygen ions are already involved in the neighboring $(\text{PO}_4)^{3-}$ groups, it has been proposed to group the Ti^{4+} as part of a linear cluster $(\text{Ti}_2\text{O}_2)^{4+}$ [31].

This Raman mode is also sensitive to the presence of DWs [16,18]. To understand the influence of IE on DWs, it is helpful to first examine a periodically poled crystal without IE (NoIE-PD). Figure 5(a) shows the peak shift scan at two different z depths at 5 and 40 μm . The DWs in the sample create a sharp shift to higher frequencies, attributed to the change of selection rules and/or the local strain present at the DWs [16,18]. The width of the observed shifts does not correspond to the actual DW thickness, which is only a couple of unit cells thick. Instead, it is a convolution of the excitation focus with the much narrower DWs region, as well as influenced by the strain region that can expand beyond the typical spatial resolution limit [16,18]. Note that no significant changes along the z direction were observed for this sample.

No contrast on peak shift in the 784- cm^{-1} phonon can be observed for the sample that has IE but without any periodic poling (IE-SD), although a small response is seen in the peak amplitude in the first 10 μm in depth (see Supplemental Material [32] Fig. S1). However, when the crystal experienced both IE and periodic poling (IE-PD), the Raman peak contrast becomes large but does not appear as sharp or spatially localized, indicating that the strains are less constrained to the DW regions but appear more laterally distributed, as seen in Fig. 5(b). Moreover, in the IE region, the redshifted peak suggests an overall expansion of the TiO_6 group due to ion exchange. Considering that the Ti-O chains are known to contribute to the net polarization along the z axis [4,33] and that the TiO_6 and PO_4 groups undergo readjustments upon polarization reversal [10], the introduction of Rb^+ during ion

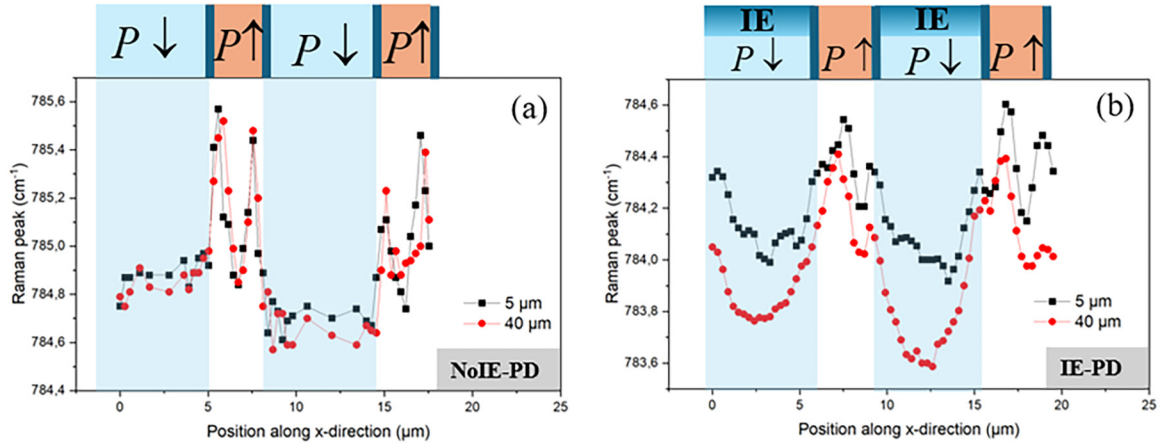


FIG. 5. The Raman peak at 784 cm^{-1} at depths of 5 and $40\text{ }\mu\text{m}$ below the $-z$ face for (a) NoIE-PD and (b) IE-PD.

exchange influences both the net polarizations and these structural readjustments during domain switching. Consequently, remnants of IE at the vicinity of DW are manifested in this DW signature peak.

Figure 6 presents the same Raman peak (784 cm^{-1}) at different depths for all the three samples studied. It compares the inverted domain ($P\uparrow$) versus the original domain ($P\downarrow$) for both IE and NoIE samples, as well as IE versus NoIE for a single domain sample. For the crystal that has undergone periodic poling without IE (NoIE-PD), the domains $P\uparrow$ and $P\downarrow$ show a small difference in peak values (0.15 cm^{-1}) and, as expected, no depth dependence. Depth dependence was only observed in IE samples both in IE-SD and IE-PD. The Raman peak shifts with depth for both the IE and non-IE regions, resembling the characteristic complementary error function of Rb diffusion in KTP [34]. In the single domain sample, there is a small difference in peak shifts between the IE and non-IE regions that becomes minimal at a depth of $15\text{ }\mu\text{m}$, almost close to the depth of the Rb layer observed through energy-dispersive x-ray spectroscopy (EDX) measurements [14]. However, for the IE-PD sample, the difference in peak positions between the IE and non-IE regions starts at 0.2 cm^{-1} and increases to

0.4 cm^{-1} beyond the IE layer. Thus, the phonon at 784 cm^{-1} , associated with the presence of ferroelectric DWs, is influenced by IE in regions with periodic domains. The influence extends not only to the regions directly affected by IE but also to adjacent regions. Furthermore, the local strain at the DW is enhanced by IE and extends laterally to adjacent regions without IE but with opposite domain polarization. The impact of IE on this phonon peak highlights a significant interaction between the IE process and the structural dynamics of the DW. Notably the difference between $P\uparrow$ and $P\downarrow$ domains is larger in IE-PD than in NoIE-PD even at depths beyond IE, implying that the stress or the charges induced propagate into the crystal far beyond the IE layer.

IE also affects the four PO_4 -related modes (363 , 487 , 985 , and 1096 cm^{-1}). For two of these modes (487 and 1096 cm^{-1}), the influence of IE is noticeable only near the surface and no signature of DWs is observed for these peaks (see [32] Figs. S2 and S3). However, the interplay of IE and domain reversal can be seen in the other two peaks (363 and 985 cm^{-1}). Figure 7 shows the 363-cm^{-1} peak at various depths for (a) NoIE-PD, (b) IE-SD, and (c) IE-PD sample, respectively. Figures 8(a)–8(c) display the data for the 986-cm^{-1} peak

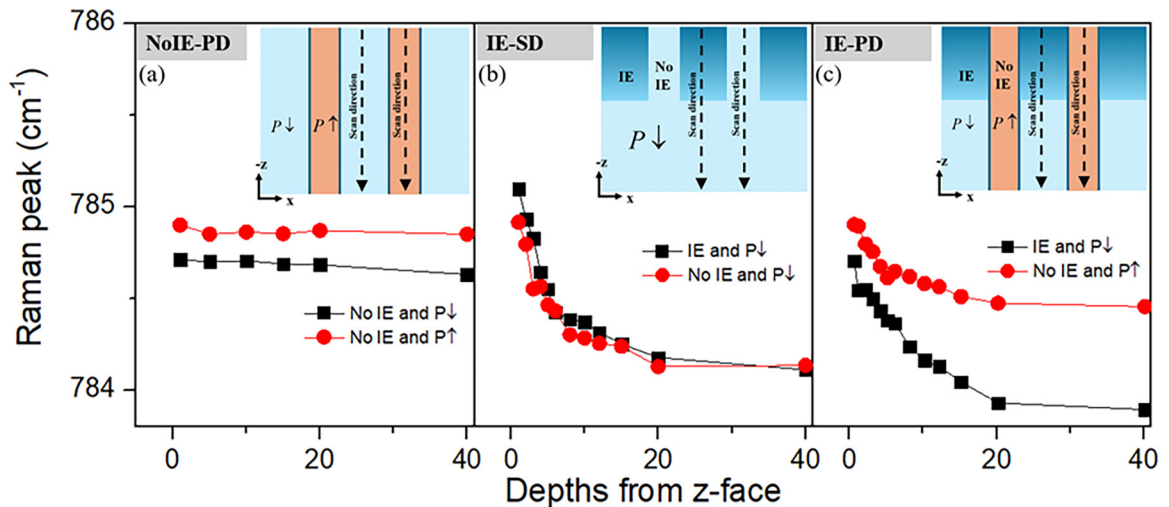


FIG. 6. Tracking the Raman peak 784 cm^{-1} along the z direction of three different samples: (a) NoIE-PD, (b) IE-SD, and (c) IE-PD.

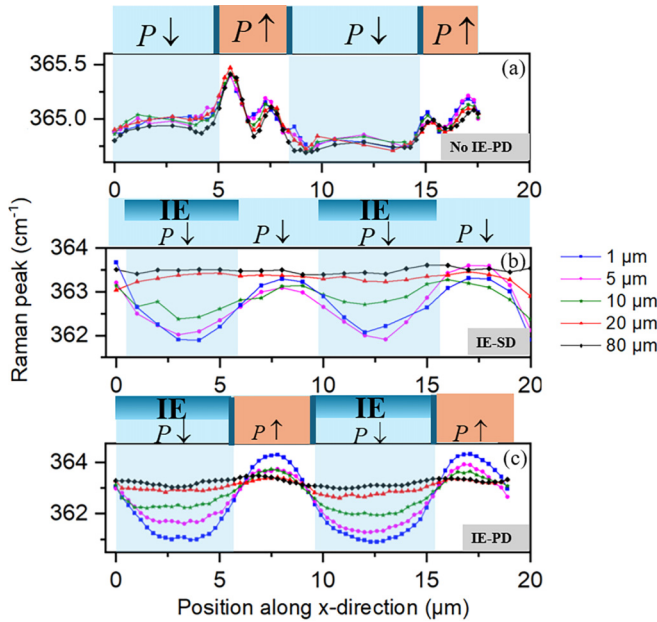


FIG. 7. The Raman peak 363 cm^{-1} at depths of 1, 5, 10, 20, and $80\text{ }\mu\text{m}$ below the patterned z face for (a) NoIE-PD, (b) IE-SD, and (c) IE-PD.

for the same samples. The 363-cm^{-1} Raman mode in the IE-SD crystal is redshifted in the IE regions, while in NoIE regions, it is blueshifted. These shifts flatten out at a depth of the IE layer. This suggests that the expansion in the PO_4 tetrahedral structure in the IE region is compensated by its compression in the adjacent NoIE region. For samples that are periodically poled with NoIE (NoIE-PD), the 363-cm^{-1} peak shows distinct shifts at the vicinity of the DW and no contrast between regions with different domain orientations.

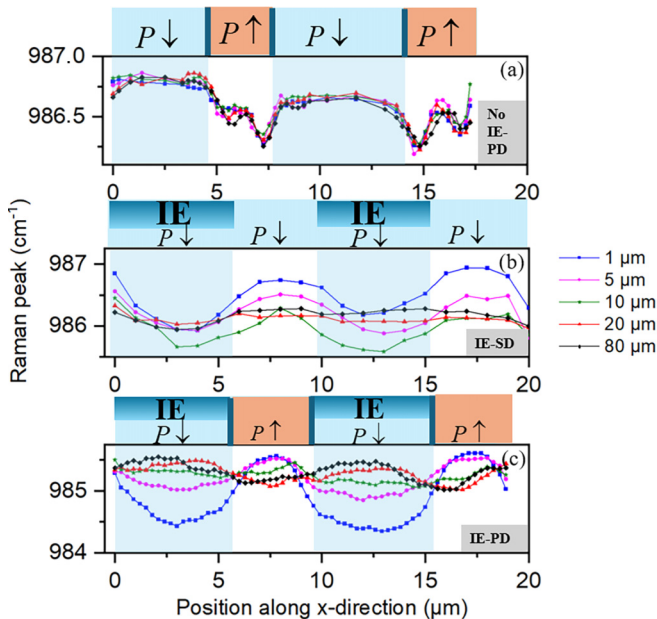


FIG. 8. The Raman peak 985 cm^{-1} at depths of 1, 5, 10, 20, and $80\text{ }\mu\text{m}$ below the patterned z face for (a) NoIE-PD, (b) IE-SD, and (c) IE-PD.

In the case of IE-PD, the Raman peak shift shows the same behavior as for the IE-SD crystal. A notable feature is that no distinct signature of the DW can be seen. This implies that the strain created by IE is larger than that of the DWs, smearing out the DW strain and masking its contrast.

The other PO_4 mode, 986 cm^{-1} , exhibits a similar response to the 363 cm^{-1} for the case of NoIE-PD and IE-SD. In the IE-PD sample, at depths near the patterned face, the response is also similar to that of IE-SD. Specifically, the peak softens in regions with IE, with the redshift gradually fading out at greater depths. However, beyond $20\text{ }\mu\text{m}$, the trend reverses: in IE regions, the peak stiffens (blueshifted), while in NoIE regions, it shows a redshift. This indicates that in IE regions, bond expansion occurs at depths of $0\text{--}20\text{ }\mu\text{m}$, and beyond that ($20\text{--}80\text{ }\mu\text{m}$), bond contraction occurs. These trends are absent in IE-SD and NoIE-PD samples. Notably, even at a depth of $80\text{ }\mu\text{m}$, the DW signature is still not visible but the evidence of strain still persists. A plausible explanation is that the reverse trend observed in this mode at both IE and NoIE regions in IE-PD is due to a combination of strain from IE and DW. This combination of strains persisted even at depths beyond IE. At IE depths ($0\text{--}20\text{ }\mu\text{m}$), strain due to IE is the leading main contributor while at depths beyond $20\text{ }\mu\text{m}$, strain due to DW starts to overtake the effect of IE.

Both the 363- and 985-cm^{-1} peaks are related to lattice substructures associated with the ferroelectricity and the DW. During the process of domain inversion, the PO_4 groups rotate in order to accommodate to the changing of sites of the alkali-metal ions [9]. The addition of Rb^+ during IE will affect the adjustment process of the PO_4 group since Rb^+ is much larger than K^+ . Moreover, the mobility of the intrinsic alkali-metal ions is dependent on the vacancy channel formed by the PO_4 and TiO_6 framework. The energy barrier to hop from a vacancy site to another vacancy site becomes intrinsically more costly when this framework is distorted by IE. This lowers the ionic conductivity at regions with IE whereby the mobile ions are now less able to transport from one coordinate site to another, making domain reversal more difficult. This, in turn, creates a higher E_c at the region with IE and increases the domain nucleation threshold, thus preventing domain formation at IE regions.

The comparison of all the Raman peaks corresponding to Rb/K , TiO_6 , and PO_4 is summarized in Table I.

The influence of IE affects the Raman peaks of TiO_6 and PO_4 groups at regions that have IE, its adjacent NoIE regions, and DWs. The observed influence of IE in Raman is corroborated by SHG microscope imaging of IE-PD [see Fig. 1(a)]. A contrast in intensity between IE and NoIE regions can be observed along the z direction of the sample. Figure 9 shows the intensity line profile of IE-PD samples at z depths of 1, 5, 20, and $40\text{ }\mu\text{m}$. Tracing along one of these line profiles (1 or $5\text{ }\mu\text{m}$ depths), the intensity is the lowest (darkest) at the DW, whereas IE regions appear brighter while NoIE regions appear darker. At a depth of $40\text{ }\mu\text{m}$, the intensity contrast between IE and NoIE disappears, getting at a level between the IE and NoIE regions intensity values. Both these SHG microscopy data and our Raman observations confirm that IE affects not only the IE region, but the influence extends to neighboring NoIE domains. Here it is worth noting that the reversed domains are well contained in the NoIE region for the first

TABLE I. Summary of the Raman peak shifts Δ of the three different samples (IE-PD, IE-SD, and NoIE-PD) at the center of different regions (IE, No IE, $P\downarrow$, and $P\uparrow$) at different z depths.

	Raman peak (cm^{-1})	IE-PD			IE-SD			NoIE-PD		
		Depth (μm)	IE ($P\downarrow$) Δ (cm^{-1})	No IE ($P\uparrow$) Δ (cm^{-1})	Depth (μm)	IE Δ (cm^{-1})	No IE Δ (cm^{-1})	Depth (μm)	($P\downarrow$) Δ (cm^{-1})	($P\uparrow$) ^a Δ (cm^{-1})
Rb/K	80	5	-0.6 ± 0.4	$+0.8 \pm 0.4$	5	0.0 ± 0.5	1.0 ± 0.5	5		
		20	$+0.9 \pm 0.2$	$+0.9 \pm 0.2$	20	1.0 ± 0.5	1.0 ± 0.5	40		
	102	5	$+0.8 \pm 0.3$	$+0.4 \pm 0.3$	5			5		
		20	-0.1 ± 0.3	-0.3 ± 0.3	20			40		
	139	5	-1.1 ± 0.6	$+1.1 \pm 0.6$	5			5		
		20	$+1.1 \pm 1.0$	$+1.1 \pm 1.0$	20			40		
TiO ₆	177	5	$+0.5 \pm 0.3$	-0.5 ± 0.3	5	$+0.7 \pm 0.5$	$+0.1 \pm 0.5$	5		
		20	-0.5 ± 0.3	-0.5 ± 0.3	20	0.0 ± 0.2	0.0 ± 0.2	40		
	784	5	0.0 ± 0.2	$+0.5 \pm 0.2^a$	5	$+0.5 \pm 0.2$	$+0.5 \pm 0.2$	5	$+0.8 \pm 0.2$	$+1.4 \pm 0.2$
		20	-0.3 ± 0.2	$+0.2 \pm 0.2^a$	20	$+0.2 \pm 0.2$	$+0.2 \pm 0.2$	40	$+0.7 \pm 0.2$	$+1.4 \pm 0.2$
	PO ₄	5	$+1.5 \pm 0.3$	$+0.8 \pm 0.3$	5	-1.0 ± 0.2	$+0.3 \pm 0.2$	5	$+1.0 \pm 0.2$	$+2.2 \pm 0.2$
		20	-0.2 ± 0.4	$+0.4 \pm 0.4$	20	$+0.5 \pm 0.2$	$+0.4 \pm 0.2$	40	$+1.8 \pm 0.2$	$+2.2 \pm 0.2$
PO ₄	985	5	-0.1 ± 0.1	$+0.5 \pm 0.1$	5	$+0.9 \pm 0.2$	$+1.5 \pm 0.2$	5	$+1.7 \pm 0.2$	$+1.4 \pm 0.2$
		20	$+0.4 \pm 0.1$	$+0.1 \pm 0.1$	20	$+1.1 \pm 0.2$	$+1.1 \pm 0.2$	40	$+1.7 \pm 0.2$	$+1.4 \pm 0.2$

^aAt the DW “feature”.

20 μm of depth and the DWs do not cross over the IE-NoIE border. Beyond this depth, the inversed domains broaden and the DWs traverse the IE regions. This behavior aligns with our earlier Raman observations. The corresponding variation of SHG intensity for IE-SD and NoIE-PD samples are shown in [32] as Figs. S4(a) and S4(b) respectively. For the IE-SD sample, variation in SHG intensity is evident within the ion-exchanged region, gradually diminishing with depth into the bulk. In contrast, for the NoIE-PD sample, sharp changes in SHG intensity are confined to the vicinity of the domain walls.

IV. CONCLUSIONS

In summary, the distorted Raman signatures of TiO₆ and PO₄ groups in IE-PD samples suggest lattice modifications

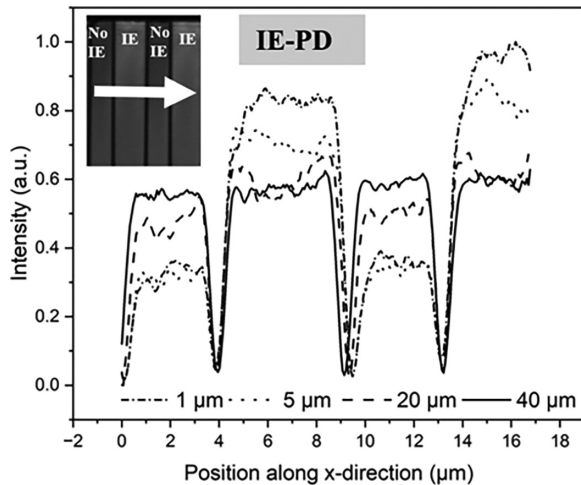


FIG. 9. SHG microscopy line profiles at different z depths of IE. The inset shows the SHG microscope image of the IE-PD sample while the white arrow line indicates the start and end x position of the scanned line profile.

induced by the incorporation of Rb⁺ during the IE process, that extend further into the crystal bulk than the depths of IE regions. This form of disorder was not observed in the case of NoIE-PD that was periodically poled without IE. Particularly, the PO₄ modes (363 and 985 cm^{-1}) and TiO₆ mode (784 cm^{-1}) that are related to the DW signature exhibit strains due to IE and DW. The effect of IE was also observed in the NoIE region adjacent to IE region. The influence of DW was not captured in the lower Raman modes. Only the influence of IE was observed in Raman peaks of 80, 102, 139, and 177 cm^{-1} . There are two possible contributions to their change in Raman peaks: First is the combination of compression of the PO₄ and TiO₆ groups, while second is the possibility that these Raman peaks are related to the $h(1)$, $h(2)$, $K(1)$, and $K(2)$ sites of the RKTP structure. The relatively shallow IE depth of 20 μm in comparison to the crystal's bulk thickness of 1 mm highlights the significant influence of IE in E_c engineering.

The combinational effects due to IE lead to a reduced mobility of intrinsic alkali-metal ions in the crystal to switch sites during domain reversal. This phenomenon contributes to higher E_c in the IE region as compared to regions with NoIE. A region with IE would require a much larger external field to overcome the higher domain nucleation threshold for domain formation. The two distinct zones allow precise selection of domain inversion: under regions of lower E_c , domain inversion occurs, while regions with higher E_c domain inversion are inhibited when appropriate external electric fields are applied. As a result, when the high and low E_c are arranged in a periodic fashion, this process leads to the fabrication of periodically poled RKTP.

The findings here suggest the possibility of temperature dependence effect, particularly on the diffusion channels, which would be interesting to explore in future studies. The insight from this will greatly contribute to the continued development of the E_c -engineering technique, particularly in designing new IE melt compositions and for integrating the technique with

other material functionalities, for instance, refractive index engineering. This study helps to predict the effects of IE and serves as guidance on managing them.

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