

Raman spectra of KTP crystal in an in situ electric field

M.J. Bushiri^a, V.P. Mahadevan Pillai^b, R. Ratheesh^b, V.U. Nayar^{b,*}

^aDepartment of Physics, University of Kerala, Kariavattom, Thiruvananthapuram 695581, Kerala, India

^bDepartment of Optoelectronics, University of Kerala, Kariavattom, Thiruvananthapuram 695581, Kerala, India

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Abstract

Raman spectra of the KTP single crystal are recorded in electric fields (dc and ac) applied along the polar axis c . Spectra with the laser beam focused near the cathode end, anode end and the centre of the crystal are recorded. The cathode end of the crystal develops a spot 'grey track' where the laser beam is focused after a lapse of 5 h from the application of a dc electric field of 38 V/cm. The spectra recorded at the cathode end after the application of field show variations in intensity of bands. A new band appears at 177 cm^{-1} . Changes in band intensities are explained on the basis of changes in polarizability of the crystal due to the movement of K^+ ions along the polar axis. K^+ ions accumulate at the cathode end, where the 'Grey track' formation occurs. The intensity enhancement observed for almost all bands in the ac field is attributed to the improvement of crystalline quality. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Potassium Titanyl Phosphate, KTiOPO_4 (KTP), is an excellent non-linear optical material in the field of Photonics [1]. It is an electric polar crystal in the non-centrosymmetric space group $\text{Pna}2_1$ with $a = 12.814$, $b = 6.404$, and $c = 10.616\text{ \AA}$. The crystal framework is constructed by three-dimensional chains which are made from corner linked TiO_6 octahedra and PO_4 tetrahedra. Four oxygen ions of the TiO_6 octahedra belong to the PO_4 groups and the two remaining oxygen ions that do not belong to the PO_4 tetrahedral groups are linked to TiO_6 groups. The TiO_6 octahedra are highly distorted as Ti atoms are displaced from the centre of the octahedra. Structural channels exist along the c -axis and K^+ ions are located at structural voids [2]. It is a quasi-one-dimensional ionic conductor available in the single crystal [3]. The ionic dc conductivity of KTP along its polar z -axis is about four orders magnitude higher than that normal to it [4]. This is attributed to the hopping motion of K^+ ions in this direction. This makes the crystal susceptible to electrical damage if fields of quiet small magnitude (e.g. 20 V/mm) are applied along the z -axis [5]. Many technical devices using KTP require the application of an electric

field. Changes of crystal structure and electron redistribution induced by an externally applied electric field play a fundamental role in electronic and optical properties [6]. The application of an electric field leads to damage by electrolysis, and is detrimental to device function [7]. The damage in KTP is attributed to Ti^{3+} formation [8], and the damage susceptibility of KTP has been shown to increase with increasing ionic conductivity of the crystal [9,10]. Several studies on the Raman spectra of KTP have been reported [11–14]. Temperature dependent Raman spectra of KTP and KTA, micro-Raman spectra of as-grown and high temperature annealed KTP and Raman spectra of 'grey tracked' KTP produced by applying a dc field have also been investigated [15–17]. In this paper, the effect of dc and ac electric fields on the Raman spectra of KTP single crystal is investigated.

2. Experimental

Crystals for the present investigation were grown from the phosphate flux [7]. The crystal was cut with its faces perpendicular to the crystallographic a , b , and c axes, identified by a polarizing microscope. A rhomb shaped crystal, shaped like 'V' at the ends with thickness 0.55 mm (b),

* Corresponding author.

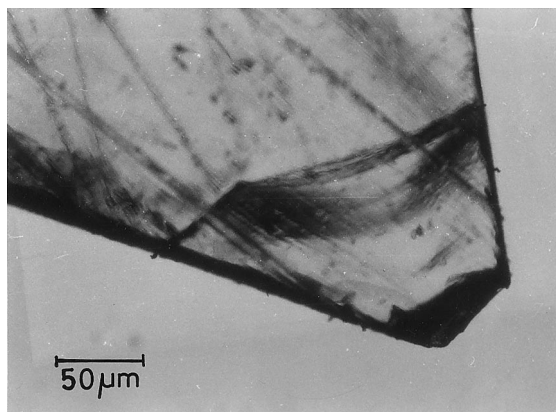


Fig. 1. Optical microphotograph of the 'grey tracked region' in the ac plane on the side where the laser beam is focussed. The 'grey track' region is to the right of the crystal (front view).

breadth 2.6 mm (a), and length 7.83 mm (c) was used. The microphotograph of the crystal was taken using an Olympus BH-2 microscope (Figs. 1–3). Good electrical contacts were ensured using silver paste between the copper electrodes and the crystal. A Spex 1401 double monochromator equipped with a Spectra Physics Model 165 Argon ion laser (514.5 nm) was used to record the Raman spectra in the Stokes region at a resolution better than 3 cm^{-1} . The virgin state spectrum (Fig. 4(a)) of the crystal in the b(cc)a and b(cb)a orientations were recorded with a laser power of 60 mW. A dc potential of 26 V/cm and a current of 1 A was then applied along the polar axis *c*. Immediately the bands at 221, 271 and 698 cm^{-1} alone were recorded under the field near the cathode end of the crystal without recording the whole spectrum. It took about 6 min to record these bands. After a lapse of 30 min the spectrum in the whole region was recorded. It took about 60 min to record the whole spectrum. The crystal is then kept in this electric field with the laser beam focused near the cathode end for

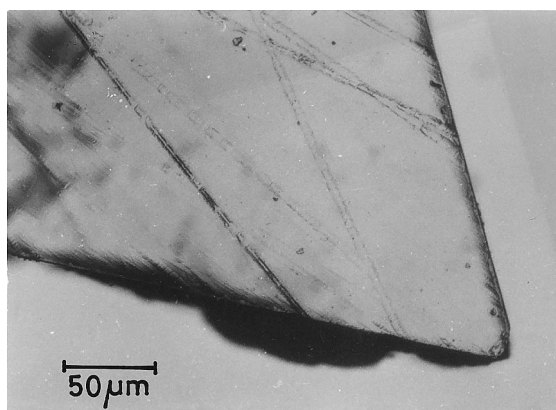


Fig. 2. Optical microphotograph of the 'grey tracked region' in the ac plane (rear view).

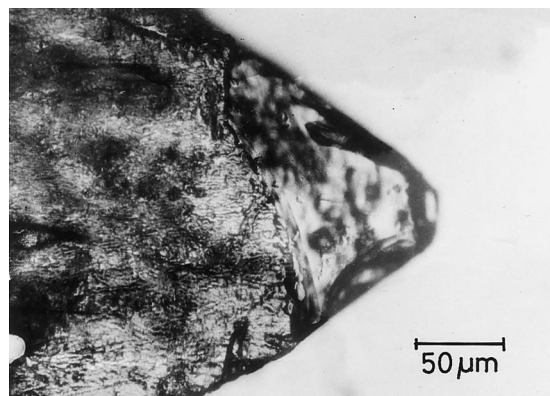


Fig. 3. Optical microphotograph of the 'grey tracked region' in the ac plane after etching with a 1:1 mixture of HF and H_2SO_4 solution on the side where the laser beam is focused. The 'grey track' region is to the right of the crystal (front view).

about 5 h. A small 'grey spot' develops around the point where the laser beam is focused.

3. Results and discussion

The analysis of the spectra is carried out on the basis of vibrations of TiO_6 octahedra and PO_4 tetrahedra. The TiO_6 octahedra with O_h symmetry has six internal modes of vibration. In KTP, all the six modes are found to be activated in the Raman spectra (Table 1) due to the lowering of symmetry from O_h to C_1 [13]. The PO_4 tetrahedra with T_d symmetry has four internal modes [18]. The bands corresponding to PO_4 tetrahedra are comparatively weak as compared to those of the TiO_6 octahedra (Table 1). The assignments of the bands in the Raman spectra have been reported earlier [1] and they agree generally with the one given by Kugel et al. [13]. The TiO_6 bands corresponding to the inactive mode ν_6 around 221 cm^{-1} , the asymmetric bending mode ν_5 around 271 cm^{-1} and the symmetric stretching mode ν_1 around 698 cm^{-1} exhibit extraordinary higher cross-section (Fig. 4 (a)) as observed by them. Particular attention is paid to these bands, owing to its relation to the non-linear optical properties of the crystal [13].

The intensity of the bands at 221, 271 and 698 cm^{-1} are observed without any change in the spectrum recorded at the instant of application of the field in the b(cc)a orientation. In the spectrum recorded after 30 min (Fig. 4(b)) all these bands are observed but with a reduction in intensity. The 221 cm^{-1} band undergoes a reduction of 45% of its intensity without field, the 271 cm^{-1} band a reduction of 14% and the 698 cm^{-1} band a reduction of 52%. The ν_5 mode at 271 cm^{-1} is shifted to 275 cm^{-1} . The band at 126 cm^{-1} splits into two components and they appear at 120 and 128 cm^{-1} . A few weak bands also appear at 830, 1029 and 1071 cm^{-1} and a shoulder at 308 cm^{-1} near the broad

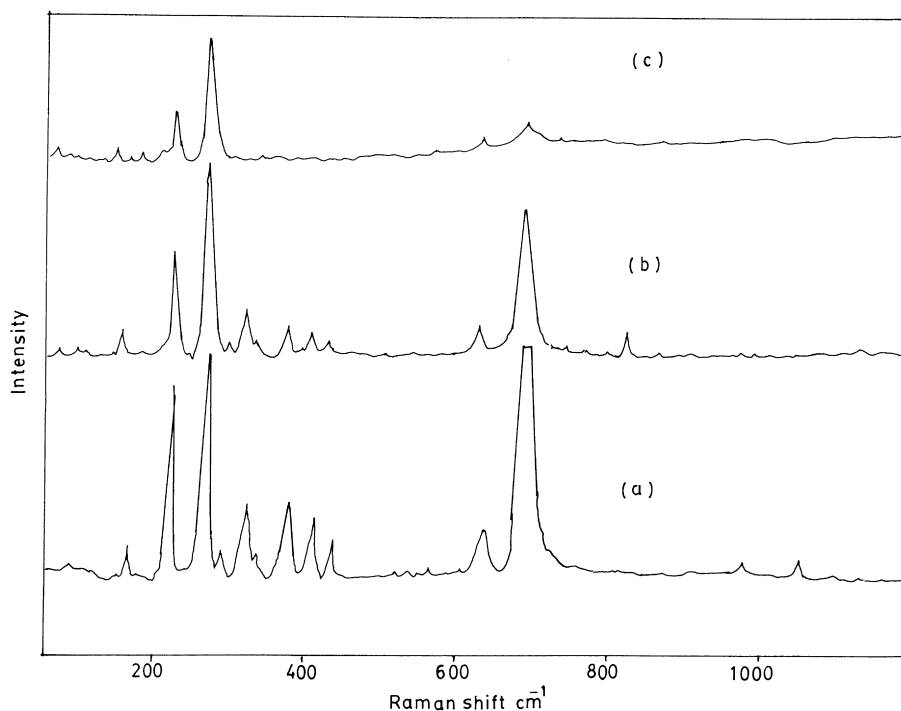


Fig. 4. Raman spectra of KTP crystal at the cathode end in the 50–1200 cm^{-1} region: (a) without electric field; (b) with an electric field of 26 V/cm after 30 min from the application of the field; (c) with an electric field of 38 V/cm after 30 min from the application of the field.

band at 315 cm^{-1} . When the electric field is increased to 38 V/cm and the spectra are recorded as explained in the experimental section, the intensity of the bands at 221, 271 and 698 cm^{-1} are not affected at the instant of application of the field. In the whole spectrum (Fig. 4(c)) recorded after 30 min from the application of this field, the weak bands at 54, 64 and 126 cm^{-1} are not observed. A new weak band appears around 177 cm^{-1} . The shoulder observed at 308 cm^{-1} in the electric field at 26 V/cm is not observed in the 38 V/cm field. A large reduction in intensity occurs for all the bands. The 221 cm^{-1} band undergoes a reduction of 73% of its intensity without the field and the 271 cm^{-1} band a reduction of 61%. The intensity of the 698 cm^{-1} band is only 1% of its intensity in the virgin state. After a lapse of 5 h from the application of the electric field, the cathode end of the crystal develops a 'spot' around the point where the laser beam is focused. This 'spot' can be seen at the face where the laser beam falls on the crystal (Fig. 1), and it is not circular in shape but similar to the 'grey track' observed earlier [7,8,17]. This is not clearly visible in the microphotograph taken from the other side of the crystal (Fig. 2). The other parts of the crystal remain without any noticeable change as can be seen clearly in the microphotograph taken after etching the crystal in the 1:1 mixture of HF and H_2SO_4 solution at 333 K (Fig. 3). In the spectrum recorded at the 'grey spot' all the characteristic bands of the TiO_6 group appear, but with a very small intensity.

Even these bands disappear after about 7 h. The spectra of the crystal are recorded near the anode end by applying a field of strength 38 V/cm. All the bands are observed at the same wavenumbers as in the spectrum of the virgin state. The previously observed band at 177 cm^{-1} is also present. The intensity of the bands are found to be at the same level as observed in the virgin state. A new weak band appears at 342 cm^{-1} .

The laser beam is focussed at the centre of the crystal and the spectrum is recorded in the b(cc)a orientation with a field strength of 63 V/cm along the polar axis *c*. The band at 342 cm^{-1} observed in the spectrum recorded at the anode end becomes more prominent. The intensity of the bands does not change with time as observed at the cathode end. The laser beam is focused at another point near the previously damaged spot and the spectrum is recorded in the b(cb)a orientation without electric field. All the previously observed bands in this orientation in the virgin state appear. The weak bands at 177 and 342 cm^{-1} also appears in the spectrum. Raman spectra are again recorded in the b(cc)a orientation with the field strengths 76, 102, 127, 191, 255, 319 and 382 V/cm. The bands at 208, 221 ($\nu_6\text{TiO}_6$), 271, 295 ($\nu_5\text{TiO}_6$), 315, 322 ($\nu_4\text{TiO}_6$) and 698 ($\nu_1\text{TiO}_6$) cm^{-1} are examined. They exhibit no change in intensity or wavenumber values as observed in the spectrum recorded at the cathode end (damaged region).

The crystal is then subjected to an ac field of strengths 38

Table 1

Raman bands (cm^{-1}) of KTP crystal at the cathode end in the dc electric field (vww, very very weak; vw, very weak; w, weak; vs, very strong; vvs, very very strong; s, strong; m, medium; ms, moderately strong; sh, shoulder)

0 V/cm b(cc)a 1	26 V/cm b(cc)a 2	38 V/cm b(cc)a 3	Assignments 4
56vw	54vw		
60vw			
65vw	64vw		
		96vw	K–O
110vw	108vw	108vw	Lattice mode
	120w		K–O
126w	128w		
162m	159w	159w	
		177w	Ti translational
213sh	209sh	211sh	
221ms	218ms	218m	$\nu_6\text{TiO}_6$
271vvs	275vs	275s	$\nu_5\text{TiO}_6$
295w	293w		
	308sh		
317ms	315m	316w	
325sh	324sh		$\nu_4\text{TiO}_6$
378ms	374ms	375w	
409m	406m	406vw	
438w	436vw	439vw	$\nu_2\text{PO}_4$
527vw	527vw	528vw	
555vww	552vww	552vww	$\nu_4\text{PO}_4$
638m	633m	636vw	$\nu_2\text{TiO}_6$
698vs	698s	698m	$\nu_1\text{TiO}_6$
	830vww		Ti–O–P
981vww	979vww		
1001vww	997vww		$\nu_1\text{PO}_4$
		1029w	
1051w	1056w		$\nu_3\text{PO}_4$
	1071w		

and 102 V/cm (rms values) at a frequency of 50 Hz and a current of 5 A along the polar axis and the spectrum is recorded in the b(cc)a orientation. The bands of interest to non-linear optical properties at 221, 271, and 698 cm^{-1} are recorded. When the ac field is applied the intensity of the bands at 698 cm^{-1} is first enhanced. Then the intensity decreases and attains a steady value which is marginally higher (by 11%) than the initial intensity. In the case of the band around 275 cm^{-1} the intensity of this band first increases with time. Later the intensity decreases and attains the initial value. The intensity of the band at 221 cm^{-1} increases marginally and remains steady. Increase in the electric field strength does not have much effect on the intensity of the bands.

To examine the effect of an ac field on a crystal not subjected to any other studies, another crystal grown under the identical conditions is selected. The new crystal has the dimension of length 4 mm (c), breadth 1.5 mm (b) and thickness of 0.5 mm (a). An ac field of strength 20 V/cm and frequency of 1 KHz is applied along the polar axis and the spectrum is recorded in the b(cc)a orientation. After the crystal is kept in the ac electric field for about 2 h the spec-

trum is again recorded. All the bands show slight enhancement (around 15%) in intensity.

In KTP, the K^+ ions are highly coordinated by eight or nine O atoms. There are structural channels parallel to the polar axis through which K^+ ions can move easily under the influence of an electric field by a vacancy mechanism [19]. Two crystallographically distinct ion sites K_1 and K_2 and two distinct hole sites h_1 and h_2 are available along the *c*-axis. Therefore the ionic dc conductivity parallel to polar *c*-axis is four orders of magnitude higher than that normal to it [5]. Kugel et al. [13] have attributed the bands near 90, 120, and 331 cm^{-1} to vibrations involving K^+ ions and the surrounding oxygen atoms. Close to the 331 cm^{-1} band $\nu_4\text{TiO}_6$ also appears. The splitting of the band at 126 cm^{-1} and the appearance of the shoulder 308 cm^{-1} near the broad band 315 cm^{-1} at the cathode end when the dc electric field is applied, is in agreement with the motion of K^+ ions to the cathode end. Therefore this effect is observed only in the spectrum recorded there. In $\alpha\text{-LiO}_3$, Li^+ ions and Li^+ vacancies collect at the cathode and anode respectively under the driving force, and a number of them are not able to discharge [20]. For KTP, K^+ ions accumulate near the

cathode end. Sebastian et al. [7] have reported large quantities of potassium at cathode end from an analysis of the decomposition product there, in agreement with the present result. When the crystal is subjected to the electric field of 38 V/cm and the laser beam is focused near the cathode end, a spot referred to as ‘grey track’ is obtained after about 5 h around the point where the laser beam falls on the crystal. Appearance of all bands except those of a few lattice modes obtained in the virgin state of the crystal, in the Raman spectra recorded with the laser beam focused at this ‘spot’ indicates that no major structural change has taken place in the crystal due to the formation of the ‘grey spot’. Raman spectra of the high temperature annealed KTP has shown that KTP decomposes at the temperature of 1000°C and an intense band appears at 143 cm⁻¹ indicating the formation of the antase form of TiO₂ [16]. But such a band is not observed in the present study confirming no such decomposition.

Rejmankova et al. [21] have observed that the potassium atoms in the polarised channels are displaced with respect to their regular sites by 1.42 Å along the *c*-axis. The displacement of the positive charges implies a displacement of negative charges and introduces a deformation in the crystal lattice. Heavier atoms like titanium are also displaced in the polarized channel. In the present study a weak band appears at 177 cm⁻¹ after the appearance of the ‘grey spot’. Translational modes of Ti atom appear around 185 cm⁻¹ [22]. Therefore the 177 cm⁻¹ band can be due to the Ti translational mode. The intensity of this mode increases due to the distortion produced by the motion of K⁺ ions. The changes that occur in the intensity of Raman lines can be due to the modification of electronic levels associated with the movement of ions under the electric field as suggested by the Satyanarayan et al. [17].

In the b(cb)a scattering geometry the non-degenerate symmetric stretching mode ν_1 shows two bands of equal intensity at 698 and 722 cm⁻¹ when the spectrum is recorded with the laser beam focused near the cathode end before the application of the electric field. The spectrum of this mode recorded without the electric field in the same scattering geometry at a point near to the ‘damaged spot’ (grey track) after crystal is subjected to different dc fields discussed earlier, shows intensity redistribution. The intensity of the band at 698 cm⁻¹ is found to be decreased when compared to that of the band at 722 cm⁻¹. This redistribution of intensity along with the appearance of a few weak bands (Table 1) in the ν_3 region of the PO₄ tetrahedra also suggest that the polarizability in the crystal is changed due to the prolonged application of the dc fields of different strengths. The application of the field leads to the formation of individual dipoles in the structure. These individual dipoles interact through the electrostatics and elastic deformation fields that they create in the surrounding lattice [21]. The formation of these individual dipoles leads to the change of polarizabilities.

The bands of TiO₆ octahedra at 698 (ν_1), 271 (ν_5) and

221 cm⁻¹ (ν_6) are present until the complete disappearance of the scattering intensity. This clearly indicates that the TiO₆ octahedra is retained in the ‘grey spot’ region with increased distortion as compared to the virgin state condition till the bands disappear. The presence of characteristic bands of the KTP in other parts of crystal except the ‘damaged spot’ shows that, the observed effect near the cathode end is a local phenomenon. The attempts to produce the ‘damaged spot’ (grey track) again in the same crystal, by reversing the polarity, increasing field strength and irradiating laser at different points have not succeeded. The ‘grey track’ formation is not reproducible in the same crystal indicating an irreversible change of crystal perfection in those regions as observed by Sebastian et al. [7]. The intensity enhancement observed in the ac field for both the crystals used in the present study are due to the improvement of crystalline quality by favouring the setting of the potassium ions in to their regular crystallographic sites [21].

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