

Raman and FTIR spectroscopic studies of potassium titanyl phosphate (KTiOPO₄) doped with lanthanum and praseodymium

M J Bushiri

Department of Physics, University of Kerala, Kariavattom, Thiruvananthapuram, Kerala-695 581, India
and

V U Nayar*

Department of Optoelectronics, University of Kerala, Kariavattom, Thiruvananthapuram, Kerala-695 581, India
E-mail : vunagar@rediffmail.com

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Abstract KTP crystals doped with rare-earth (La, Pr) are grown from the tungstate flux. The crystals are characterized using X-ray diffraction and FTIR and Raman spectroscopic techniques. The vibrational bands are assigned in terms of the vibrations of TiO₆ octahedra and PO₄ tetrahedra on the basis of the polarisation of the bands. The TiO₆ octahedra and PO₄ tetrahedra are considerably distorted in undoped KTP as well as in doped KTP crystals. The dopants La and Pr do not affect significantly the wavenumber values of the TiO₆ and PO₄ vibrations. Raman bands of KTP, LKTP and PKTP in the same polarization geometries show intensity variations. The presence of La and Pr atoms affect the polarizability in the crystal leading to changes in intensities. The slight variations in the unit cell parameters of crystals indicate that the dopant incorporation is inhomogeneous.

Keywords Raman spectra, Infrared spectra, KTP.

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Introduction

Potassium titanyl phosphate KTiOPO₄ (KTP) is a promising material in the field of photonics, with excellent non-linear optical properties [1]. KTP exhibits high ionic conductivity along the crystallographic z-axis and this is attributed to the movement of K⁺ ions along the structural channels parallel to the z-axis [1,2]. The laser damage susceptibility of KTP has been shown to increase with increasing ionic conductivity of the crystal [1]. The effect of dopants on the various properties of KTP has been of considerable interest for technological applications. The bulk damage threshold of KTP can be further enhanced by reducing the ionic conductivity parallel to the z-axis. This can be achieved by doping KTP with ions of lower valence, for example, trivalent cations like Al³⁺, Ga³⁺, Cr³⁺ and Sc³⁺ [3,4]. The divalent rare-earth ions can also be used as dopants for modifying the non-linear optical (NLO) properties of the crystal [5]. Raman spectra of KTP have been investigated

by several authors to understand its structure and dynamics and to probe its nonlinear optical properties [6–10]. In this paper, the effects of Lanthanum and Praseodymium dopants on the vibrational spectra of tungstate flux grown KTP single crystals are investigated and an attempt is made to clear certain ambiguities regarding the assignments of vibrational modes of KTP crystal.

2. Experimental

Single crystals for the present investigation were grown from the tungstate flux [11]. To dope with La and Pr, 1 wt% lanthanide oxides were added to the mixture separately to grow Lanthanum and Praseodymium doped crystals. Lanthanum and Praseodymium incorporated in the crystal were estimated by dissolving a portion of the crystal in a 1 : 1 mixture of H₂SO₄ and HF and using an ARL 3410 ICP Atomic Emission Spectrometer. A Spex 1401 double monochromator equipped with a Spectra Physics model 165 argon ion laser was used to record the Raman spectra in the

*Corresponding Author

Stokes region at a resolution better than 3 cm^{-1} . The spectra were recorded in the $a(bb)c$, $a(ba)c$, $a(ch)c$, $a(ca)c$, $a(cc)b$ and $b(aa)c$ orientations. The FTIR spectra were obtained from a Bruker IFS 66v spectrometer using KBr pellet method in the 400 to 1400 cm^{-1} region and using polyethylene pellet method in the 50 to 400 cm^{-1} region. The X-ray diffraction patterns of the crystals were obtained from a X-ray diffractometer (Model-XDS 2000 Scintag) using CuK_α radiation.

3. Factor group analysis

KTP belongs to the non-centrosymmetric space group $Pna2_1$ (C_{2v}) with eight molecules in the unit cell [12]. The factor group analysis [7,8] gives 189 modes excluding acoustic modes and the irreducible representation is

$$\Gamma_{189} = 47A_1(\text{R,IR}) + 48A_2(\text{R}) + 47B_1(\text{R,IR}) + 47B_2(\text{R,IR})$$

4. Results and discussion

The morphology of the as grown crystals is in agreement with that reported by Bolt [5]. The ICPAES data show that 0.0189 wt% of La and 0.398 wt% of Pr are incorporated in the crystal and is comparatively less than the dopants (1 wt%) added to the flux. The powder X-ray diffraction patterns of KTP, LKTP and PKTP correspond to an orthorhombic system. The unit cell parameters of the doped crystals along with undoped KTP are shown in Table 1. The unit cell parameters of doped crystals are only marginally

Table 1. Unit cell parameters in Å units

Unit cell parameters	KTP	LKTP	PKTP
<i>a</i>	12 8101	12 8411	12 8203
<i>b</i>	6 4135	6 4214	6 3768
<i>c</i>	10 5921	10 6228	10 9138

altered from those of undoped KTP crystal. These changes indicate that the KTP structure accommodates a large number of pentavalent and trivalent cations that are stable in octahedral oxygen coordination at the Ti^{IV} site [13]. Therefore, solid solutions exist among the various members of this family with slight changes in the lattice parameters

4.1. Vibrational analysis

The lattice of the crystal is made up of three dimensional chains of weakly distorted TiO_6 octahedra linked at two corners. The chains are separated by PO_4 tetrahedra. There are two chains per unit cell and the chain direction alternates between (011) and $(0\bar{1}1)$. The structural voids are filled with K^+ ions. The Ti^{IV} ions are displaced from the centre of the octahedra leading to different Ti–O bonds of lengths, four Ti–O bonds of lengths 1.95–2.07 Å, one of longer length 2.10 to 2.15 Å and one of shorter length 1.72 Å [12].

4.1.1. Vibrations of TiO_6 octahedra :

The TiO_6 octahedra with O_h symmetry has six fundamental vibrations, symmetric stretching mode ν_1 (A_{1g}), asymmetric stretching modes ν_2 (E_g) and ν_3 (F_{1u}), asymmetric bending mode ν_4 (F_{1u}), symmetric bending mode ν_5 (F_{2g}) and the Raman and IR inactive mode ν_6 (F_{2u}) [14–16]. The ν_1 , ν_2 and ν_5 modes are Raman active and ν_3 and ν_4 are IR active. In the TiO_2 crystal, the TiO_6 octahedral vibrational modes are assigned as $\nu_1 = 639$, $\nu_2 = 519$, $\nu_3 = 513$, $\nu_4 = 399$, $\nu_5 = 197$ and $\nu_6 = 144\text{ cm}^{-1}$ [6]. The symmetric stretching mode of TiO_6 octahedra is observed above 900 cm^{-1} in NaLnTiO_4 . This is interpreted as due to the strong nature of the Ti–O bond [17]. KTP has Ti–O–Ti–O chains as a result of which strong bands can be expected around 700 cm^{-1} as observed in $\text{Na}(\text{TiO})\text{PO}_4$ and $(\text{TiO})_2\text{P}_2\text{O}_7$ [18]. Also, in rare-earth titanates prominent Raman bands are below 720 cm^{-1} [19]. The internal modes of TiO_6 octahedra of KTP have been assigned differently by various authors [6–8,10]. Kugel *et al* [7] and Watson [8] have assigned the symmetric stretching mode (ν_1) around 700 cm^{-1} while Vivekanandan *et al* [6] have assigned it around 625 and Tu *et al* at 770 cm^{-1} [10]. As this mode is a polarized one, in the present investigation, the band around 700 cm^{-1} is assigned as the ν_1 mode of TiO_6 octahedra. This band appears with different intensities in all polarization geometries, the largest intensity being in $b(aa)$ orientation. In the IR spectra, this mode is observed around 706 cm^{-1} as a moderately intense band (Figures 4(a–c)).

In Raman spectra, two more bands, a shoulder around 730 and a weak band around 790 cm^{-1} , are obtained in this region. Vivekanandan *et al* [6] and Watson [8] have assigned the 730 cm^{-1} band to the ν_2 mode of TiO_6 . But in MO_6 octahedra ν_2 mode is observed at a lower wavenumber than that of ν_1 [14,20,21]. Therefore, the 730 cm^{-1} mode can be due to the short Ti–O bond of length 1.72 Å. The ν_1 mode positions are not much affected by the incorporation of dopants La and Pr (Tables 2–4). But intensities of this mode in most of the polarization orientations are significantly affected in LKTP and PKTP (Figures 1–3).

A very weak band near 830 cm^{-1} in Raman spectra is assigned as Raman inactive ν_3 mode of TiO_6 by Watson [8] and Vivekanandan *et al* [6]. But in MO_6 octahedra, ν_3 mode is assigned below ν_1 vibrations [14]. In systems like SbOPO_4 and $\text{Ba}_2\text{Mo}(\text{PO}_4)_2$, bands around 872 cm^{-1} [21] and 750 cm^{-1} [14] are assigned to M–O–P or M–O–M vibrations (M = Sb or Mo). The band obtained in the present study is therefore assigned to Ti(1)–O–Ti(2) or Ti–O–P vibrations. The very weak Raman band around 600 cm^{-1} is assigned to the ν_3 mode of TiO_6 as in $\text{La}_2\text{MgTiO}_6$ [22].

The asymmetric stretching mode ν_2 of TiO_6 is also expected at a lower wavenumber than that of the ν_1 mode [14]. Therefore, the moderately intense Raman band near

630 cm^{-1} in all polarization orientations and the moderately intense band near 639 cm^{-1} (IR) are assigned to the ν_2 mode in agreement with that of Kugel *et al* [7]. As KTP has corner-shared TiO_6 octahedra, this band is observed at slightly lower wavenumbers than the 647 cm^{-1} band assigned to this mode in TiNb_2O_7 having edge-shared octahedra [23].

The IR active ν_4 mode is assigned to the intense IR band around 320 cm^{-1} . This mode is observed as moderately intense bands in all polarization geometries of the Raman spectra. The Raman active ν_5 mode gives intense bands around 270 cm^{-1} in all polarizations of the Raman spectra in KTP, PKTP and LKTP. A weak band around 290 cm^{-1}

$a(bb)c$ 1	$a(ba)c$ 2	$a(cb)c$ 3	$a(ca)c$ 4	$a(cc)b$ 5	$b(aa)c$ 6	FTIR 7	Assignments 8
					59 vvw		Lattice modes
	70 vvw				72 vvw		
100 w	91 vvw	97 vw			99 w	87 w	K-O
			104 wbr	100 vw			
120 w			125 w	126 vw	121 w	115 w	K-O
	155 vvw			159 vw	159 w	132 w	
178 w	174 m		176 m	181 w		156 w	Ti tr
		208 sh	208 sh			168 w	
218 s	218 msbr	218 s	216 s	218 m	218 ms	212 w	$\nu_6 \text{TiO}_6$
						220 w	
274 vs	272 s	273 vs	275 vs	275 ms	275 s	268 w	$\nu_5 \text{TiO}_6$
						279 w	
	292 vvw	292 sh				289 w	
320 mbr	324 ms	321 mbr	323 s	321 mbr	325 mbr	320 s	$\nu_4 \text{TiO}_6$
				347 w	341 vvw		
376 m	378 m	378 m	380 m	375 m	375 m	385 vs	$\nu_2 \text{PO}_4^{3-}$
405 w	405 w	404 w		407 w	409 w		
429 vw		426 vw	431 vw		429 vw	432 m	
465 vw						467 m	
				478 w	475 vw	489 m	
						502 m	
525 w	525 w	520 w	521 vvw	521 w	521 w		$\nu_4 \text{PO}_4^{3-}$
555 w	560 w	555 wbr	559 w	555 vw	559 vw	557 ms	
600 w	600 vw				600 vw	597 ms	$\nu_3 \text{TiO}_6$
635 m	631 m	635 mbr	640 mbr	638 m	639 mbr	640 m	$\nu_2 \text{TiO}_6$
701 vsbr	702 vsbr	701 sbr	702 vsbr	702 msbr	700 vs	706 s	$\nu_1 \text{TiO}_6$
750 sh	739 sh	735 sh	732 sh	733 sh	731 sh		
790 vvw	796 w	791 vvw		795 vvw		784 w	
				832 vvw		819 w	Ti-O-P
990 wbr		980 wbr	945 wbr	975 w	997 w	975 s	$\nu_1 \text{PO}_4^{3-}$
						1000 wbr	
1046 w			1040 vw		1049 w	1025 s	$\nu_3 \text{PO}_4^{3-}$
						1048 s	
						1100 s	
						1125 w	

vwv - very very weak, v - very weak, w - weak, m - medium, wbr - weak and broad, sh - shoulder, sbr - strong and broad; vs - very strong, s - strong, vvs - very very strong; ms - moderately strong, msbr - moderately strong and broad; tr - translational, vsbr - very strong and broad

Table 3. Spectral data (cm⁻¹) and band assignments of La doped KTP

Raman						FTIR 7	Assignments 8
<i>a(bb)c</i> 1	<i>a(ba)c</i> 2	<i>a(cb)c</i> 3	<i>a(ca)c</i> 4	<i>a(cc)b</i> 5	<i>b(aa)c</i> 6		
58 vw					58 vw	62 w	Lattice modes
78 vvw	71 vvw					88 m	
	95 vw			92 vvw			K-O
100 w	105 vw	103 vw	103 vvw	104 vw	101 vvw		
120 w	122 vw	120 vvw	120 w	121 vw	119 vw	117 m	K-O
	140 w		140 vvw			131 w	
158 w	155 vvw	154 vvw	155 w	156 w	155 w	157 w	
176 w	174 vw	176 w	178 w	176 w	172 w	169 m	Ti tr
208 sh	205 sh	205 sh	205 sh	205 sh	206 sh	211 m	ν_6 TiO ₆
215 sh	215 m	216 m	215 ms	215 ms	214 m		
	225 sh	222 sh		226 sh		220 m	
						231 w	
271 ¹ s	270 s	270 ms	271 s	272 s	270 ms	269 m	ν_5 TiO ₆
						279 s	
						290 m	
292 w	290 w	291 w	290 vw	292 w	291 m		
311 ms							
320 s	319 w	318 wbr	318 m	318 m	328 mbr	321 s	ν_4 TiO ₆
343 w	345 w	344 w	345 vw	342 w	345 w		
					378 m	386 vs	
376 ms	373 w	371 m	372 w	372 m			
404 w	401 w	402 vw	401 w	401 w	402 w		
431 w	430 w		431 w	430 vvw	421 vw	432 m	ν_2 PO ₄ ³⁻
462 vvw	462 vvw				475 vvw	467 s	
						489 m	
525 vvw	520 vw	520 w	519 vw	520 w	520 w	502 m	ν_4 PO ₄ ³⁻
555 w	549 vw	565 vvw	550 vw		548 vvw	557 m	
601 w	598 vvw	589 vw	599 vvw	599 vvw	600 vw	597 ms	ν_3 TiO ₆
633 ms	633 w	632 w	631 m	632 m	636 w	640 s	ν_2 TiO ₆
				650 sh			
695 vs	696 msbr	698 ms	695 m	701 s	700 vs	707 vs	ν_1 TiO ₆
		732 sh	732 sh	730 sh			
790 wbr	795 w			790 w	795 w	784 m	
				834 vvw	831 vw	819 w	Ti-O-P
980 w	979 w	940 w	965 w	982 wbr	974 vvw	975 s	ν_1 PO ₄ ³⁻
996 vw						1006 wbr	
1049 w			1045 w	1045 w	1045 vw	1026 s	ν_3 PO ₄ ³⁻
					1095 vw	1048 s	
						1100 s	
						1122 m	

vw – very very weak, vw – very weak, w – weak, m – medium; wbr – weak and broad, sh – shoulder; sbr – strong and broad; vs – very strong; s – strong; vvs – very very strong; ms – moderately strong; msbr – moderately strong and broad, tr – translational; vsbr – very strong and broad.

Table 4. Spectral data (cm⁻¹) and band assignments of Pr doped KTP.

Raman						FTIR	Assignments
<i>a(bb)c</i>	<i>a(ba)c</i>	<i>a(cb)c</i>	<i>a(ca)c</i>	<i>a(cc)b</i>	<i>b(aa)c</i>		
1	2	3	4	5	6	7	8
					57 vvw	56 vw	Lattice modes
						68 w	
					79 vw	87 ms	
						116 m	
				94 w	94 wbr		K-O
101 vvw		104 vw			105 vw		
125 w				121 vw	120 w	131 w	K-O
158 m	158 vvw	158 w		156 w	158 vw	156 w	
178 w	172 vvw	174 w		175 w	176 vw	168 m	Ti tr
218 wbr	218 mbr	218 ms	218 ms	219 m	218 s	211 m	v ₆ TiO ₆
						220 m	
						230 w	
						248 vw	
269 m	271 ms	275 s	273 s	271 m	274 vvs	268 m	v ₅ TiO ₆
						279 m	
						289 m	
		295 vw	295 w				
321 wbr	320 m	325 mbr	325 w	321 mbr	315 w	320 ms	v ₄ TiO ₆
	345 m			345 w	325 sh		
378 m		376 m	375 w	375 m	378 s	386 ms	
406 w	404 w	405 w	406 w	402 w	409 ms		v ₂ PO ₄ ³⁻
			430 w		434 w	431 m	v ₂ PO ₄ ³⁻
				496 vvw	475 wbr	467 m	
						488 m	
						502 m	
	521 vvw	522 vvw		521 w	524 w		v ₄ PO ₄ ³⁻
	552 w					556 ms	
600 w			599 vvw	595 vw	606 w	596 m	v ₃ TiO ₆
636 m	635 w	638 mbr	635 w	636 mbr	636 m	639 m	v ₂ TiO ₆
702 vvs	699 wbr	701 ms	700 sbr	699 sbr	701 vvs	706 vs	v ₁ TiO ₆
750 sh	739 sh		731 sh	745 sh			
794 w	790 vvw	795 w	792 vw		794 w	784 m	
831 w	830 vvw			835 vvw	835 w	819 m	Ti-O-P
990 vvw		978 vvw				975 s	v ₁ PO ₄ ³⁻
				990 w	981 w	1005 wbr	
					996 wbr		
					1050 w	1025 m	v ₃ PO ₄ ³⁻
						1048 w	
						1099 w	
						1125 s	

vw – very very weak; w – very weak; w – weak; m – medium, wbr – weak and broad; sh – shoulder; sbr – strong and broad; vs – very strong; s – strong; vvs – very very strong; ms – moderately strong; msbr – moderately strong and broad; tr – translational, vsbr – very strong and broad.

is also observed in a few polarization geometries (Tables 2-4). The inactive ν_6 mode is observed as an intense band around 216 cm^{-1} in the Raman spectra. In the IR spectra, these bands are observed as weak bands. A shoulder also

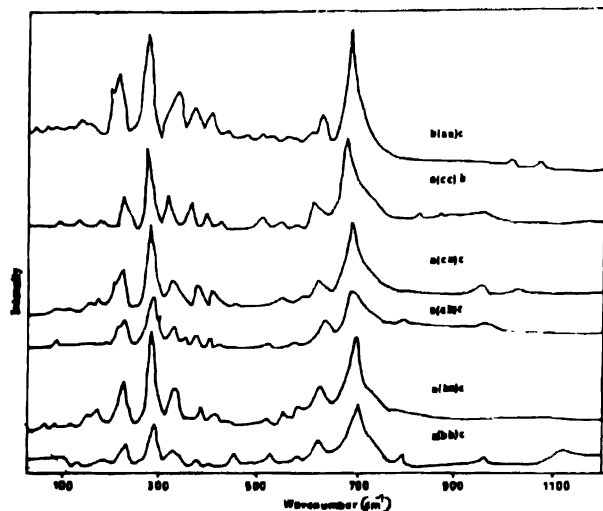


Figure 1. Raman spectra of KTP crystal in the region $50\text{--}1200\text{ cm}^{-1}$ for $a(bb)c$, $a(ba)c$, $a(cb)c$, $a(ca)c$, $a(cc)b$ and $b(aa)c$ orientations.

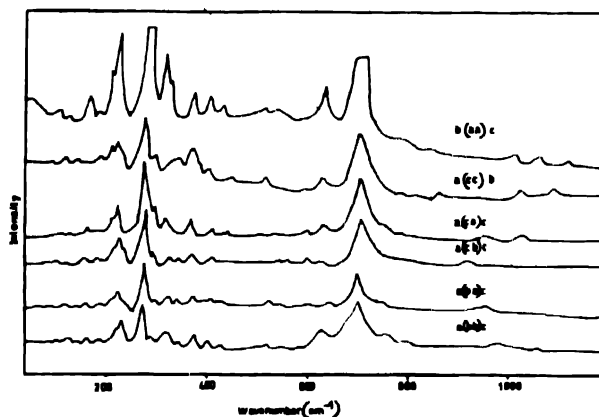


Figure 2. Raman spectra of LKTP crystal in the region $50\text{--}1200\text{ cm}^{-1}$ for $a(bb)c$, $a(ba)c$, $a(cb)c$, $a(ca)c$, $a(cc)b$ and $b(aa)c$ orientations.

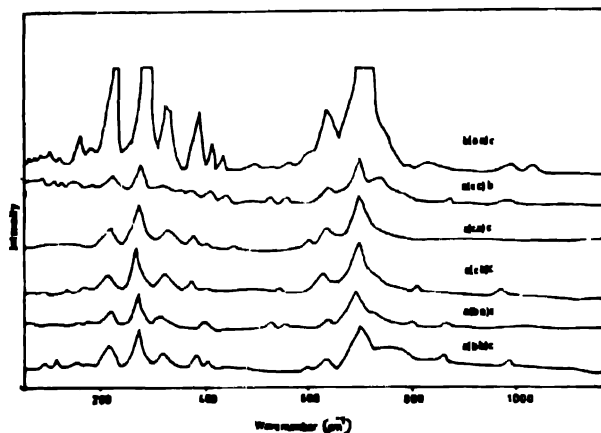


Figure 3. Raman spectra of PKTP crystal in the region $50\text{--}1200\text{ cm}^{-1}$ for $a(bb)c$, $a(ba)c$, $a(cb)c$, $a(ca)c$, $a(cc)b$ and $b(aa)c$ orientations.

appears in the Raman spectra in $a(ca)c$, $b(aa)c$ and $a(cb)c$ orientations of KTP. In LKTP, shoulders are observed around 205 and 226 cm^{-1} on both sides of this intense band in most of the orientations while in PKTP a single broad band is obtained. These assignments are in agreement with those of Kugel *et al* [7] while they disagree with those given by Vivekanandan *et al* [6].

According to Hardcastle and Wachs [24], the lower the stretching frequency of the shortest metal-oxygen bond, the more regular is the structure of the MO_6 octahedra. In the present study, in the crystals of KTP, LKTP and PKTP, the M-O stretching frequencies ν_1 , ν_2 and ν_3 are shifted considerably to higher wavenumber side, confirming the distortion of TiO_6 octahedra. Moreover, the existence of chains of octahedra allows the coupling of Ti-O vibrations in these chains leading to a higher value of this frequency [14].

4.1.2. Vibrations of PO_4 tetrahedra :

Four oxygen atoms of TiO_6 octahedra are shared by PO_4 tetrahedra leading to different Ti-O bond lengths and P-O bond lengths [12]. A free PO_4 tetrahedra with T_d symmetry has four internal modes of vibration, ν_1 (A_1) 938 , ν_2 (E) 420 , ν_3 (F_2) 1017 and ν_4 (F_2) 567 cm^{-1} . All the above modes are Raman active while ν_3 and ν_4 alone are IR active [15].

The intensity of PO_4 modes in KTP can be seen to be relatively weak when compared to those of TiO_6 modes. The symmetric stretching mode ν_1 is observed as weak bands around 998 cm^{-1} in the Raman spectra in all polarization geometries except $a(ba)c$ orientation of KTP. This mode is found to be slightly shifted towards lower wavenumbers in PKTP and LKTP (Tables 3 and 4), while it is absent in the $a(ba)c$ and $a(ca)c$ orientations of PKTP and it is split into two, in $b(aa)c$ orientation of PKTP and in $a(bb)c$ orientation of LKTP. In the IR spectra, this band is observed around 975 cm^{-1} with a very weak broad band at 1000 cm^{-1} . In the asymmetric stretching mode (ν_3) region, four bands are present in the IR at 1025 , 1048 , 1100 and 1125 cm^{-1} [Figure 4(a-c)]. The triply degenerate bending vibration ν_4 gives two bands in the IR and in most of the polarization of the Raman spectra of KTP, LKTP and PKTP.

The symmetric bending mode (ν_2) which is Raman active is present in both Raman and IR spectra of the KTP and the doped systems in the region 370 to 480 cm^{-1} . In the IR spectra, a highly intense band is obtained for this IR inactive mode at 385 cm^{-1} and a weak band at 432 cm^{-1} . The assignment of this band is consistent with those of crystals with KTP related structure *viz* NbOPO_4 , MoOPO_4 and SbOPO_4 [14,16,21]. The ν_2 bands are found to be shifted by 3 to 5 cm^{-1} in the same polarization orientation in LKTP and PKTP (Tables 2-3).

In the KTP structure, two distinct types of PO_4 tetrahedra are present with a mean P-O distance (1.5425 \AA) and a

minimum (1.5234 Å) [12]. This is confirmed by the appearance of two bands for the P–O symmetric stretching modes in the IR spectra of all the three crystals. In compounds

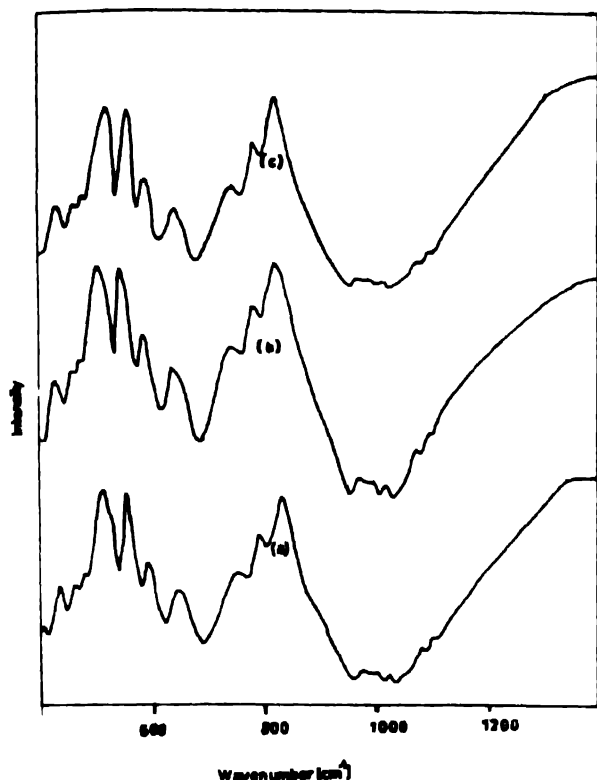


Figure 4. FTIR spectra of (a) KTP, (b) LKTP, (c) PKTP in the region 400–1300 cm^{-1}

with Ti–O–Ti–O chains, the stretching modes of PO_4 tetrahedra are relatively weak [18]. Hence, this splitting is not observed in the Raman spectra of KTP. But this band is shifted by a few wavenumbers from one polarization geometry to another. The degeneracy of the asymmetric stretching vibration ν_3 (F_2) is lifted and an additional band is also observed in the IR spectra in all the three crystals. But the degeneracy of the bending mode ν_4 (F_2) is only partially lifted. These facts and the appearance of the symmetric stretching modes ν_1 at higher wavenumber values than in a regular tetrahedra indicate linear distortion of the PO_4 tetrahedra [14].

4.1.3 Bands below 200 cm^{-1} :

Bands below 200 cm^{-1} are lattice vibrations consisting of rotational and translational modes. The exact assignment of these bands is difficult. Barj *et al* [25] have assigned the band near 185 cm^{-1} as due to Ti translational modes. This appears around 175 cm^{-1} in all the three crystals in the present study. The bands due to K–O bonds are expected to appear below 150 cm^{-1} in agreement with their strong ionic character and bond length. Hence, the bands in the 90–120 cm^{-1} region are assigned as vibrations of polar type involving K^+ ions and the surrounding eight or nine oxygen atoms [7]. The

band around 120 cm^{-1} is present in almost all orientations of the Raman spectra of KTP and LKTP. But this band is present only in the $b(aa)c$, $a(cc)b$ and $a(bb)c$ orientations of PKTP. Kugel *et al* [7] have observed a band near 90 cm^{-1} in the phosphate flux grown KTP. In the present study, this band is obtained in the $a(cc)b$ orientation in all the crystals. It also appears in LKTP and PKTP in a few other polarization orientations. A very weak band is observed at 140 cm^{-1} in the $a(ba)c$ and $a(ca)c$ orientations of the Raman spectra of LKTP alone.

5. Conclusions

The TiO_6 octahedra and PO_4 tetrahedra are considerably distorted in all the crystals and most of the assignments confirm the assignment given by Kugel *et al*. While disagreeing with those given by Vivekanandan and Tu *et al*. The dopants La and Pr do not affect significantly the wavenumber values of the TiO_6 and PO_4 vibrations. But Raman bands of KTP, LKTP and PKTP in the same polarization geometries show intensity variations. The presence of La and Pr atoms affect the polarizability leading to changes in intensities. The dopant incorporation is not homogenous as can be seen from the changes in the unit cell parameters of the doped crystals.

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