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Raman spectra in LiH_2PO_4 and $\text{KLi}(\text{H}_2\text{PO}_4)_2$: Mode assignment

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Abstract

We report and analyze Raman spectra recorded on crystals of LiH_2PO_4 (LDP) and $\text{KLi}(\text{H}_2\text{PO}_4)_2$ (KLDP). We provide a new and complete assignment of Raman lines in both crystals from their behavior as function of temperature. Among internal vibrations we discern the modes within PO_4 tetrahedra, the modes related to Li–O bonds and those due to the O–H vibrations. In the wavenumber range between 300 and 600 cm^{-1} the lines associated with O–P–O or Li–O show different temperature dependencies. The bands of PO_4 are red-shifted with increasing temperature according to thermal dilatation, while the positions related to Li–O are temperature independent.

Keywords : crystal, vibrational modes, mode assignment, phosphate compounds, thermal behavior.

1. Introduction

Phosphate materials MH_2PO_4 ($\text{M} = \text{K}, \text{Li}, \text{Rb}, \text{NH}_4, \text{Cs}$) have a current interest for both basic science and applied research. Among this family, potassium dihydrogen phosphate (KH_2PO_4 KDP), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$ ADP) and potassium titanium phosphate (KTiOPO_4 KTP) are widely investigated for their interest in piezoelectricity, ferroelectricity and nonlinear optics.^{1,2,3} LiH_2PO_4 (LDP) and $\text{KLi}(\text{H}_2\text{PO}_4)_2$ (KLDP) were studied only recently.^{4,5} The peculiarity in the structure of both materials is the presence of tetrahedra LiO_4 when compared to other crystals of MH_2PO_4 family. In LDP and KLDP the structure constitutes on PO_4 and LiO_4 tetrahedra which are bonded together by the oxygen atoms to form a tridimensional network.⁶ LDP has an orthorhombic structure while KLDP crystallizes in the $\text{P2}_1/\text{c}$ (C_{2h}) space group of the monoclinic system.

It is therefore of particular interest to investigate the vibrational modes in LDP and KLDP in relation with the peculiarities of their structure.

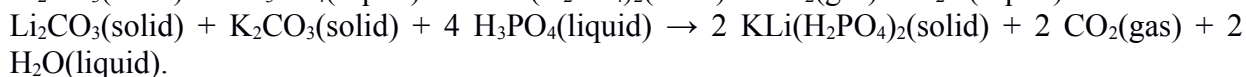
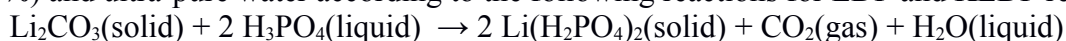
In any phosphate material, PO_4^{3-} group shows four fundamental modes: Modes ν_1 and ν_3 corresponding to elongations of the P–O bonds and the ν_2 and ν_4 modes corresponding to angular deformation (O–P–O). All these modes are Raman active: ν_1 and ν_3 are lying in wavenumber range 900–1100 cm^{-1} and ν_2 and ν_4 in the domain 400–600 cm^{-1} .^{7,8} The wavenumbers of internal vibration modes of LiO_4 groups are expected in the spectral range 390–500 cm^{-1} .⁹ As a consequence, the LiO_4 vibrational modes may occur within the same wavenumber range as those of $\nu_2(\text{PO}_4)$ and $\nu_4(\text{PO}_4)$. Since LiO_4 group shares oxygen atoms with two neighbouring PO_4 , the decoupling between the vibrational modes of the two entities is not so easy. Lee et al.¹⁰ have reported on Raman data in LDP recorded between 70 and 300 K. Within their attribution of the lines between 390 and 500 cm^{-1} , they did not elucidate if they are due to PO_4 or LiO_4 .¹⁰ Furthermore these authors considered the bands between 1053 and 1222 cm^{-1} as due to PO_4 bending or OH vibrations. More recently, within a similar Raman investigation, Rhimi et al. attributed all Raman bands in the range 400–470 cm^{-1} to vibrations of $\nu_1(\text{LiO}_4)$ from data recorded at room temperature.⁵

Regarding LDP the aim of our study is to attempt to solve these ambiguities in the Raman line assignment from new studies as function of temperature from 30 to 176°C. The second crystal, KLDP was still less investigated than LDP and only recently Rhimi et al.,⁵ reported on X ray diffraction, Raman and IR data. They attributed the vibrational modes to H₂PO₄, LiO₄ entities, or O–H bond, according to different wavenumber regions, from the comparison with spectra in LDP and KDP.

We propose here a new and complete assignment of the main Raman lines of LDP and KLDP. For this we show that the groups LiO₄ and PO₄ differ in their behavior as function of temperature. For internal PO₄ modes we use the mode positions of the free H₂PO₄ and we compare the spectra in both crystals as well. Finally we briefly analyze OH vibrations.

2. Preparation and structural properties of LDP and KLDP

The LDP and KLDP crystals were grown by slow evaporation solution growing technique at ambient temperature. The crystals were prepared from highly pure reagents Li₂CO₃ (purity of 99.99%) and K₂CO₃ (purity 99.99 %). These salts were dissolved in phosphoric acid (purity of 95%) and ultra-pure water according to the following reactions for LDP and KLDP respectively:



The resulting solutions were stirred for 12 hours. After they have been deposited in Petri dishes. Transparent and good quality crystals of KLDP and LDP were collected after a few days. The LDP and KLDP samples have the following dimensions 1.5 x 1.2 x 0.5 cm³ and 1.2 x 0.9 x 0.5 cm³ respectively. LiH₂PO₄ has the orthorhombic structure at room temperature with the space group Pna2₁-C_{2v} (Z = 4) and lattice parameters a = 6.241 Å, b = 7.643 Å, c = 6.870 Å.⁶ It contains two different types of tetrahedra LiO₄ and PO₄ as shown in Fig. 1. The structure presents two different hydrogen bridges O–H₁---O and O–H₂---O, with a length of 2.684 Å and 2.564 Å respectively.⁴ PO₄ groups are linked together with the hydrogen bridges and develop a three dimensional framework along zig-zag [100] and [001] chains. The cell parameters of our KLDP crystal have been achieved from X ray diffraction using 4 circle apparatus Bruker SMART CCD with a graphite monochromator using MoKα radiation (λ = 0.71073 Å). The unit cell is monoclinic with the space group P_{21/c} (C_{2h}), and 4 entities inside, each one on site C_i. The cell parameters are a = 7,5010(5) Å ; b = 12,8842(7) Å and c = 7,3876(4) Å ; β = 98,412(2)° and V = 706,29(7) Å³. Li, P, O and H atoms are located in the 4e Wyckoff positions.

The structure contains PO₄ and LiO₄ tetrahedra interconnected by oxygen atoms, to form a tridimensional network (see Fig. 1). Moreover four hydrogen bonds consolidate the structure.

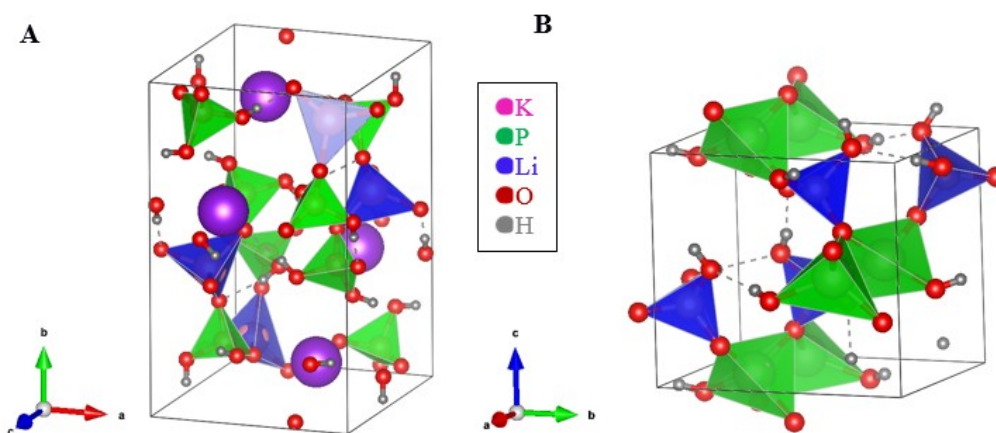


Figure 1. The crystal structure of KLDP (A) and LDP (B). P and Li atoms are coordinated with four O atoms, building PO₄ and LiO₄ tetrahedra. PO₄ ions are linked each to the other by hydrogen bonds. LiO₄ coordination tetrahedra shares two O atoms with PO₄ tetrahedra.

3. Raman data and lines assignment

Raman spectra have been recorded in the back-scattering geometry with LabRAM HR Evolution (*Horiba*) under confocal Raman microscope. The system has a spectral resolution of 1 cm^{-1} using a 1800 grooves per millimeter grating and is equipped with an ultra-low wavenumber module to detect wavenumbers down to 5 cm^{-1} . A 532 nm diode laser light was focused on the sample with a 50x objective (Olympus).

Raman spectra were obtained in a wide spectral range $5\text{--}3500\text{ cm}^{-1}$ as a function of temperature using a HFS temperature stage (*Linkam*).

Measurements were performed from 30 up to 176°C on a polycrystalline LDP sample and from 30 up to 120°C on a KLDP single crystal. These temperature ranges have been chosen below the first structural transformations occurring at about 176°C in LDP¹¹ and 125°C in KLDP. Thus non-monotonous changes in Raman lines caused by structural transitions were not considered here.

For aiming to attribute Raman lines to various vibrational modes in both crystals, at first we look at the thermal behavior of the spectra in LDP, in order to discern between PO_4 and LiO_4 groups, and then we consider the positions of Raman lines of the free tetrahedra hydrogenated phosphate anion H_2PO_4^- for the assignment of internal modes of PO_4 entities. At last the assignment of peaks in KLDP is deduced from both the analysis of their own temperature dependence and the comparison with LDP. It is reminded that the free anion H_2PO_4^- has the symmetry C_{2v} , and possesses 9 modes of vibration.¹² Likewise in PO_4 , the main vibrations are labeled ν_1 for the symmetric stretching mode $\text{P}(\text{OH})_2$, ν_2 for the in-plane bending vibration PO_2 , ν_3 for the asymmetric stretching vibration $\text{P}(\text{OH})_2$ and ν_4 for the out-of-plane bending mode PO_2 . These modes are shown in Fig. S1 (Supporting Information).

The vibrational modes of H_2PO_4^- in solution are located respectively at 886 cm^{-1} (ν_1), 356 cm^{-1} (ν_2), 1085 cm^{-1} (ν_3) and 495 cm^{-1} (ν_4).¹³

The peak positions of the modes are influenced by the environment of the molecular groups and therefore they may shift.

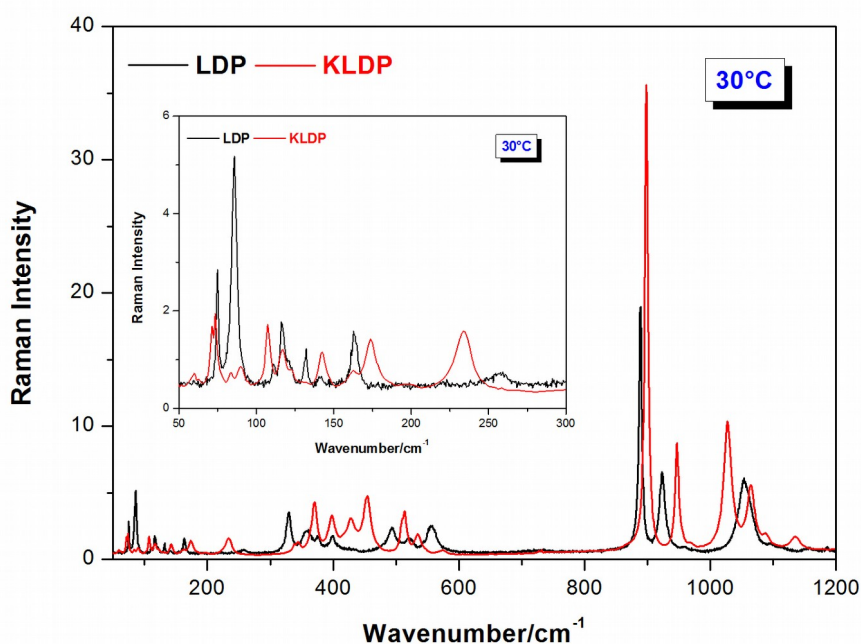


Figure 2. Raman spectrum of $\text{KLi}(\text{H}_2\text{PO}_4)_2$ and LiH_2PO_4 recorded at room temperature in the region from 5 to 1200 cm^{-1} . The spectra within the low wavenumber range are reported in the insert.

The Raman spectra recorded at room temperature in both crystals are shown in Fig. 2. Both spectra present some similarities according to the wavenumber range, so that they can be compared

each to the other. Furthermore we can note that, in this range, the number of lines in KLDP is much larger than in LDP. This can reflect the lower symmetry in KLDP.

We can therefore distinguish different wavenumber ranges: below 300 cm^{-1} are lying the bands generally associated to external modes, between 300 and 600 cm^{-1} two groups of lines, and between 800 and 1100 cm^{-1} intense and narrow peaks. Above 1200 cm^{-1} (not shown in Fig. 2) are located very weak bands corresponding to OH vibrations.

Below we describe and analyze the results according to these successive wavenumber ranges.

The bands below 300 cm^{-1} in the vibrational spectra are generally attributed to external modes or lattice modes and correspond to freedom degrees of translations and rotations of the isolated entities. Here the external modes (reported in the insert of Fig. 2) result from the relative translations and librations of the two groups LiO_4 and PO_4 .

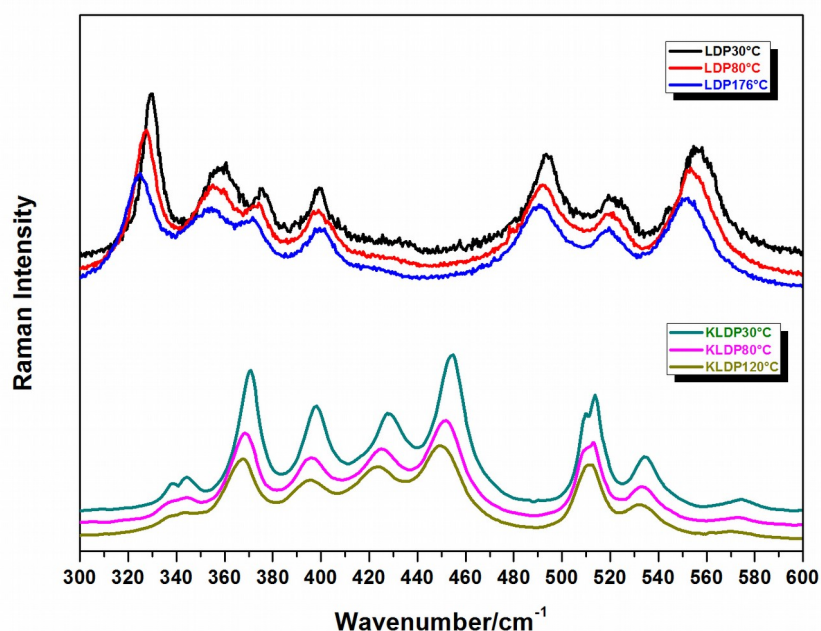


Figure 3. Raman spectra of LDP and KLDP recorded at three different temperatures in the region from 300 to 600 cm^{-1} . The spectra are shifted with respect to each other, in order to show their relative changes with temperature.

As shown in Fig. 3 the Raman spectrum of LDP displays 4 relatively distinct bands between 300 and 440 cm^{-1} . The lines lying at 328 cm^{-1} , 358 cm^{-1} and 375 cm^{-1} (positions of the intensity maximum at room temperature) exhibit a clear down-shift on heating, while their intensity continuously decreases and their linewidth slightly increases. This behavior is expected regarding the thermal dilatation and increasing anharmonicity. The chemical bonds are expected to increase on heating so that the force constant diminishes and consequently the wavenumber of the vibration decreases.

These three lines are assigned to the ν_2 internal vibrations inside the group PO_4 . Indeed they are close to the wavenumber of the free molecular group H_2PO_4 (356 cm^{-1}) and it is well known that the wavenumber of a vibrational mode can be shifted due to the surrounding of the molecular group. By contrast of these 3 lines $\nu_2\text{-PO}_4$, the band located at 399 cm^{-1} shows a remarkably different behavior since its position does not shift and its profile is nearly unchanged with temperature. Due to these differences this line is assumed to arise from internal vibration of LiO_4 group.

When analyzing the three bands of LDP in the range $450\text{--}600\text{ cm}^{-1}$ (Fig. 3) we observe in their temperature behaviors some analogies with the lower wavenumber range, described above. Therefore we propose a similar and consistent assignment of the peaks. On the one hand, the lines located at 491 cm^{-1} and 556 cm^{-1} (at room temperature) present on heating a down-shift of the

maximum position and consequently are attributed to ν_4 - PO_4 vibrations (close to the wavenumber 495 cm^{-1} in the free molecular group H_2PO_4). On the other hand, the peak at 520 cm^{-1} is unaffected by the temperature change and is consequently assigned to internal mode of LiO_4 group. This attribution is supported by the observation of Li-O vibrations in other compounds, such as Li_2CO_3 , in which Hase et al. assigned 4 vibrational modes between 375 and 500 cm^{-1} .¹⁴

We now turn to the analysis of the Raman spectra recorded in KLDP, also shown in Fig. 3. At first, if we compare these data with spectrum on LDP at room temperature, we can note that the number of lines is larger in KLDP. This can be due to the presence of two different H_2PO_4 in KLDP. Furthermore the two groups of lines within 300 - 600 cm^{-1} are shifted with respect of LDP. For the assignment of Raman lines in KLDP, we can use the same approach as above in LDP. The bands lying around 338 , 344 , 370 , 427 and 454 cm^{-1} in the first group, and 534 and 574 cm^{-1} in the second group, are slightly shifted towards lower wavenumber on heating, and are attributed to PO_4 (ν_2 - PO_4 for the first group and ν_4 - PO_4 for the second group). The lines located at 398 and 513 cm^{-1} have positions unchanged with temperature, and are therefore assumed to derive from LiO_4 internal vibrations. It is remarkable that these peaks are lying at nearly the same positions as in LDP (at 399 and 520 cm^{-1} respectively). This reinforces our interpretation within the attribution of these lines to LiO_4 in both crystals.

The thermal independence of the line positions attributed to LiO_4 can be explained by the relative rigidity of this molecular group since it is linked to other LiO_4 along chains (see Fig. 1). Moreover the fact that the internal vibrations of Li-O appear at nearly the same positions in LDP and KLDP as well shows that these vibrations are relatively unaffected by the environment. On contrary the positions of the vibrations ν_2 - PO_4 and ν_4 - PO_4 are changed from one crystal to the other, and are therefore sensitive to the environment and the temperature as well.

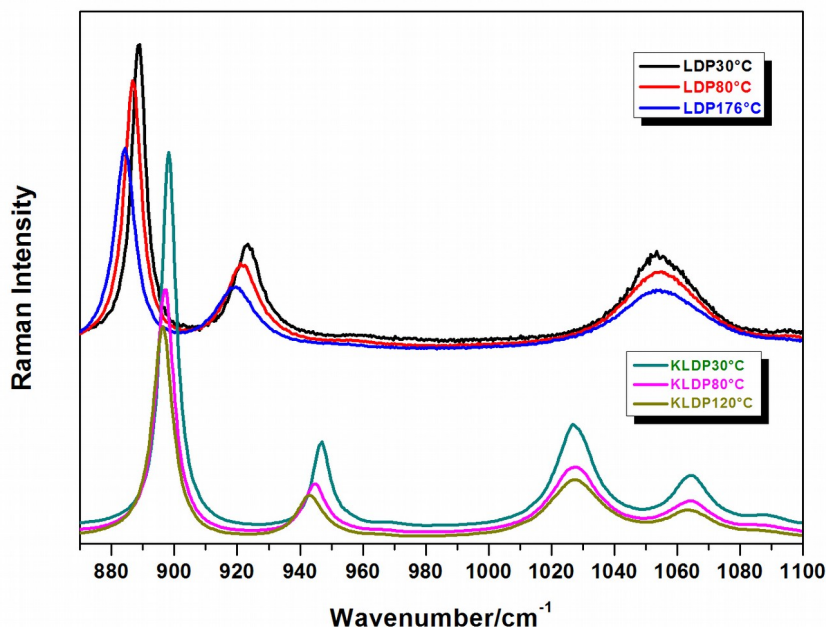


Figure 4. Raman spectra of LiH_2PO_4 and $\text{KLi}(\text{H}_2\text{PO}_4)_2$ recorded at three different temperatures in the region from 850 to 1100 cm^{-1} . The spectra are shifted with respect to each other, in order to show their relative changes with temperature.

Now we look at the spectra in the range 850 – 1100 cm^{-1} , for both crystals as reported in Fig. 4. We use a similar approach as above for the lower wavenumber range. Regarding the LDP spectra, the first and narrow peaks lying at 888 cm^{-1} and 923 cm^{-1} are assigned to ν_1 - PO_4 vibrations regarding their temperature dependence and the position of ν_1 vibration in the free molecular group H_2PO_4 (886 cm^{-1}). Then we attribute the band at 1053 cm^{-1} to ν_3 - PO_4 vibration since its position is

relatively close to this of the free molecular group lying at 1085 cm^{-1} . However we can point out that the position of this line is unaffected by the temperature change contrary to other peaks attributed to the PO_4 vibrations. This difference may be due to the antisymmetric character of this vibration, rendering it insensitive to temperature.

If we turn on the spectra of KLDP within the same wavenumber range (Fig. 4) we note a strong similarity with LDP, which is useful to deduce the assignment of the different lines. Thus the peaks observed at room temperature around 898 and 946 cm^{-1} , which are affected by temperature change, are attributed to $\nu_1\text{-PO}_4$ vibrations, whereas the bands around 1026 and 1065 cm^{-1} are assumed to be assigned to $\nu_3\text{-PO}_4$ vibrations.

Lines occurring above 1100 cm^{-1} characterize O-H---O vibrations of the hydroxyl groups of the anion H_2PO_4^- involved in hydrogen bonding and correspond to $\nu_{\text{O-H}}$ and $\gamma_{\text{O-H}}$ motions. These lines shown in Fig. 5 for both crystals are generally weaker in intensity and higher in wavenumber than the internal modes of PO_4 . In LDP, consistently with the attribution given by Lee et al. they are attributed to $\gamma(\text{O-H})$ at 1156 cm^{-1} and 1185 cm^{-1} and $\delta(\text{O-H})$ around 1217 cm^{-1} and 1323 cm^{-1} .¹⁰ In KLDP by analogy, the lines lying at 1089 and 1136 cm^{-1} are assigned to $\gamma(\text{O-H})$ and the bands around 1226 and 1316 cm^{-1} to $\delta(\text{O-H})$.

Broad bands were detected at higher wavenumber. Similar bands called as A,B,C bands were observed in a large variety of solids^{15,16,17} and have been interpreted as OH vibrations with strong O-H-O bonds. Furthermore, the broadening of these OH features reflects the high conductivity of materials.¹⁸ In our case this feature is in agreement with direct measurements in LDP¹⁹ and KLDP²⁰ and is confirmed by the increase of widening of these bands at higher temperature.

The bands located in LDP around 1612 , 2332 and 2767 cm^{-1} are respectively labeled C, B and A for OH_2 while the peak at 3109 cm^{-1} is attributed to the OH_1 motion.²¹ In KLDP we found wide bands around 2422 and 2934 cm^{-1} which are attributed to B and A, by comparison with LDP.

According to Novak²² the bands may be classified according to hydrogen bond length. Thus the fact that the B band is located around 2332 cm^{-1} in LDP and around 2422 cm^{-1} in KLDP, can be related to the hydrogen bond longer in KLDP and therefore a higher wavenumber. The same observation can be made for the band A.

Finally we summarize the proposed assignment of the lines on LDP and KLDP in Table 1.

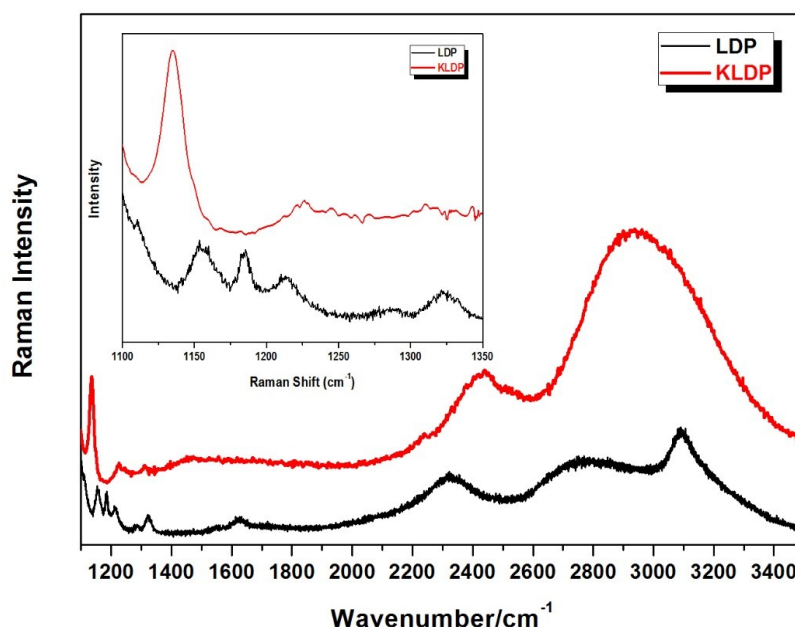


Figure 5. Raman spectra of LDP and KLDP recorded at room temperature for high wavenumbers. Insert is a zoom of the range $1100\text{--}1350\text{ cm}^{-1}$.

Table 1. Observed Raman modes of LDP and KLDP and tentative modes assignment. s: strong, m: medium, and w: weak refer to the relative intensity of the Raman lines.

LDP		KLDP	
Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment
328 m	$\nu_2 (\delta_s \text{ O-P-O})$	338 w	$\nu_2 (\delta_s \text{ O-P-O})$
358 m	$\nu_2 (\delta_s \text{ O-P-O})$	344 w	$\nu_2 (\delta_s \text{ O-P-O})$
375 m	$\nu_2 (\delta_s \text{ O-P-O})$	370 m	$\nu_2 (\delta_s \text{ O-P-O})$
399m	$\text{LiO}_4 (\text{Li-O})$	398 m	$\text{LiO}_4 (\text{Li-O})$
491 m	$\nu_4 (\delta_{as} \text{ O-P-O})$	427 m	$\nu_2 (\delta_s \text{ O-P-O})$
-		454 m	$\nu_2 (\delta_s \text{ O-P-O})$
-		510 m	$\nu_4 (\delta_{as} \text{ O-P-O})$
520 m	$\text{LiO}_4 (\text{Li-O})$	513 m	$\text{LiO}_4 (\text{Li-O})$
556 m	$\nu_4 (\delta_{as} \text{ O-P-O})$	534 m	$\nu_4 (\delta_{as} \text{ O-P-O})$
-		574 w	$\nu_4 (\delta_{as} \text{ O-P-O})$
888 s	$\nu_1 = \nu_s (\text{P-O-H})$	898 s	$\nu_1 (\nu_s (\text{P-O-H})_2)$
923 m	$\nu_1 = \nu_s (\text{P-O-H})$	946 m	$\nu_1 (\nu_s (\text{P-O-H})_2)$
1053 m	$\nu_3 (\text{P—O-H})$	1026 m	$\nu_3 (\nu_{as} (\text{P-O-H})_2)$
-		1065 m	$\nu_3 (\nu_{as} (\text{P-O-H})_2)$

4. Discussion and conclusion

Our assignment of the various Raman peaks to the different internal vibrational modes can be compared with the previous attributions proposed by Lee et al. and Rhimi et al.^{10,5} The main novelty of our investigations results into the attribution of bands lying at 398 or 399 cm⁻¹ and around 513 or 520 cm⁻¹ to LiO_4 vibrations in LDP and KLDP as well.

Regarding specifically LDP, it should be noted that Rhimi et al.⁵ assigned a line at 402 cm⁻¹ to LiO_4 whereas Lee et al. did not choose between PO_4 and LiO_4 .¹⁰ The main discrepancy compared with our investigations concerns the peak at 520 cm⁻¹ attributed to P–O vibration in earlier descriptions. Furthermore in our study the peak around 1053 cm⁻¹ in LDP is attributed to PO_4 motion in agreement with Rhimi et al.⁵ whereas Lee et al. did not exclude the OH vibration.¹⁰

Regarding KLDP, our assignment of Raman lines notably differs from the previous one by Rhimi et al.⁵ In particular these authors attributed the whole group of bands between 400 and 470 cm⁻¹ to vibration modes of LiO_4 , in agreement with earlier investigation on LDP by Lee et al.¹⁰ They invoked the fact that these lines are absent in KDP. In fact, to our opinion, this does not exclude the presence of P–O vibration modes in the same range, like in our attribution above. Indeed in LDP and KLDP, PO_4 tetrahedra are coupled with LiO_4 tetrahedra so that it is not inconsistent to find both internal vibration modes of these entities within the same region.

The analysis of the behavior of Raman spectrum spectra of LDP and KLDP crystals as function of temperature has been used to propose a new assignment of Raman lines to PO_4 and LiO_4 entities in both crystals. Instead of 4 lines in free molecular group H_2PO_4 , we detect 7 lines attributed to internal modes of PO_4 in LDP, and 12 lines in KLDP, due to symmetry lowering of the structure.

These peaks in both crystals display a down-shift of the position and broadening on heating. The lines, the positions of which are independent of temperature, were by contrast attributed to internal modes of LiO_4 . The positions of these vibrations around 400 cm⁻¹ and 520 cm⁻¹ are close in LDP and KLDP. This last result is consistent with neutron-diffraction data reported by Hwan Oh et al. who observed that Li^+ ions are quite immobile and stable in the structure.⁴

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