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

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## Abstract

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We report and analyze Raman spectra recorded on crystals of  $\text{LiH}_2\text{PO}_4$  (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  $\text{PO}_4$  tetrahedra, the modes related to Li–O bonds and those due to the O–H vibrations. In the wavenumber range between 300 and 600  $\text{cm}^{-1}$  the lines associated with O–P–O or Li–O show different temperature dependencies. The bands of  $\text{PO}_4$  are red-shifted with increasing temperature according to thermal dilatation, while the positions related to Li–O are temperature independent.

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

## 1. Introduction

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

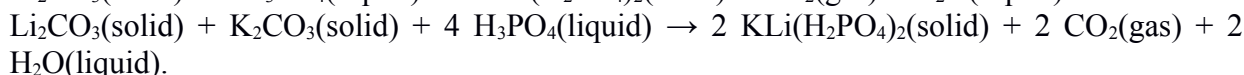
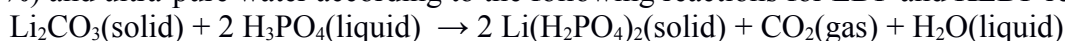
In any phosphate material,  $\text{PO}_4^{3-}$  group shows four fundamental modes: Modes  $\nu_1$  and  $\nu_3$  corresponding to elongations of the P–O bonds and the  $\nu_2$  and  $\nu_4$  modes corresponding to angular deformation (O–P–O). All these modes are Raman active:  $\nu_1$  and  $\nu_3$  are lying in wavenumber range 900–1100  $\text{cm}^{-1}$  and  $\nu_2$  and  $\nu_4$  in the domain 400–600  $\text{cm}^{-1}$ .<sup>7,8</sup> The wavenumbers of internal vibration modes of  $\text{LiO}_4$  groups are expected in the spectral range 390–500  $\text{cm}^{-1}$ .<sup>9</sup> As a consequence, the  $\text{LiO}_4$  vibrational modes may occur within the same wavenumber range as those of  $\nu_2(\text{PO}_4)$  and  $\nu_4(\text{PO}_4)$ . Since  $\text{LiO}_4$  group shares oxygen atoms with two neighbouring  $\text{PO}_4$ , the decoupling between the vibrational modes of the two entities is not so easy. Lee et al.<sup>10</sup> have reported on Raman data in LDP recorded between 70 and 300 K. Within their attribution of the lines between 390 and 500  $\text{cm}^{-1}$ , they did not elucidate if they are due to  $\text{PO}_4$  or  $\text{LiO}_4$ .<sup>10</sup> Furthermore these authors considered the bands between 1053 and 1222  $\text{cm}^{-1}$  as due to  $\text{PO}_4$  bending or OH vibrations. More recently, within a similar Raman investigation, Rhimi et al. attributed all Raman bands in the range 400–470  $\text{cm}^{-1}$  to vibrations of  $\nu_1(\text{LiO}_4)$  from data recorded at room temperature.<sup>5</sup>

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.,<sup>5</sup> reported on X ray diffraction, Raman and IR data. They attributed the vibrational modes to H<sub>2</sub>PO<sub>4</sub>, LiO<sub>4</sub> 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 LiO<sub>4</sub> and PO<sub>4</sub> differ in their behavior as function of temperature. For internal PO<sub>4</sub> modes we use the mode positions of the free H<sub>2</sub>PO<sub>4</sub> and we compare the spectra in both crystals as well. Finally we briefly analyze OH vibrations.

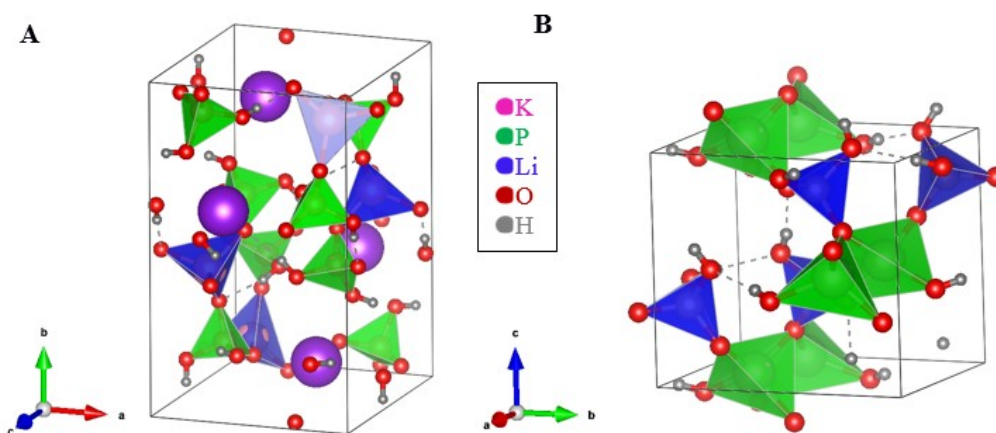
## 2. Preparation and structural properties of LDP and KLDP

The LDP and KLDP crystals were grown by slow evaporation solution growing technique at ambient temperature. The crystals were prepared from highly pure reagents Li<sub>2</sub>CO<sub>3</sub> (purity of 99.99%) and K<sub>2</sub>CO<sub>3</sub> (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 cm<sup>3</sup> and 1.2 x 0.9 x 0.5 cm<sup>3</sup> respectively. LiH<sub>2</sub>PO<sub>4</sub> has the orthorhombic structure at room temperature with the space group Pna2<sub>1</sub>-C<sub>2v</sub> (Z = 4) and lattice parameters a = 6.241 Å, b = 7.643 Å, c = 6.870 Å.<sup>6</sup> It contains two different types of tetrahedra LiO<sub>4</sub> and PO<sub>4</sub> as shown in Fig. 1. The structure presents two different hydrogen bridges O–H<sub>1</sub>---O and O–H<sub>2</sub>---O, with a length of 2.684 Å and 2.564 Å respectively.<sup>4</sup> PO<sub>4</sub> 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<sub>21/c</sub> (C<sub>2h</sub>), and 4 entities inside, each one on site C<sub>1</sub>. 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) Å<sup>3</sup>. Li, P, O and H atoms are located in the 4e Wyckoff positions.

The structure contains PO<sub>4</sub> and LiO<sub>4</sub> 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 PO<sub>4</sub> and LiO<sub>4</sub> tetrahedra. PO<sub>4</sub> ions are linked each to the other by hydrogen bonds. LiO<sub>4</sub> coordination tetrahedra shares two O atoms with PO<sub>4</sub> 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  $1\text{ cm}^{-1}$  using a 1800 grooves per millimeter grating and is equipped with an ultra-low wavenumber module to detect wavenumbers down to  $5\text{ cm}^{-1}$ . A 532 nm diode laser light was focused on the sample with a 50x objective (Olympus).

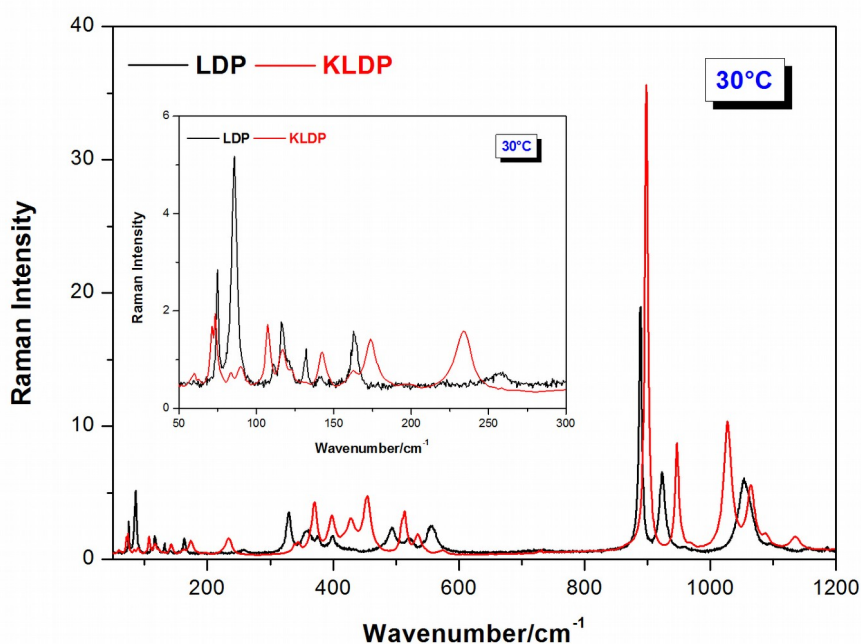
Raman spectra were obtained in a wide spectral range  $5\text{--}3500\text{ cm}^{-1}$  as a function of temperature using a HFS temperature stage (*Linkam*).

Measurements were performed from 30 up to  $176^\circ\text{C}$  on a polycrystalline LDP sample and from 30 up to  $120^\circ\text{C}$  on a KLDP single crystal. These temperature ranges have been chosen below the first structural transformations occurring at about  $176^\circ\text{C}$  in LDP<sup>11</sup> and  $125^\circ\text{C}$  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  $\text{PO}_4$  and  $\text{LiO}_4$  groups, and then we consider the positions of Raman lines of the free tetrahedra hydrogenated phosphate anion  $\text{H}_2\text{PO}_4^-$  for the assignment of internal modes of  $\text{PO}_4$  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  $\text{H}_2\text{PO}_4^-$  has the symmetry  $\text{C}_{2v}$ , and possesses 9 modes of vibration.<sup>12</sup> Likewise in  $\text{PO}_4$ , the main vibrations are labeled  $\nu_1$  for the symmetric stretching mode  $\text{P}(\text{OH})_2$ ,  $\nu_2$  for the in-plane bending vibration  $\text{PO}_2$ ,  $\nu_3$  for the asymmetric stretching vibration  $\text{P}(\text{OH})_2$  and  $\nu_4$  for the out-of-plane bending mode  $\text{PO}_2$ . These modes are shown in Fig. S1 (Supporting Information).

The vibrational modes of  $\text{H}_2\text{PO}_4^-$  in solution are located respectively at  $886\text{ cm}^{-1}$  ( $\nu_1$ ),  $356\text{ cm}^{-1}$  ( $\nu_2$ ),  $1085\text{ cm}^{-1}$  ( $\nu_3$ ) and  $495\text{ cm}^{-1}$  ( $\nu_4$ ).<sup>13</sup>

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  $\text{LiH}_2\text{PO}_4$  recorded at room temperature in the region from 5 to  $1200\text{ cm}^{-1}$ . The spectra within the low wavenumber range are reported in the insert.

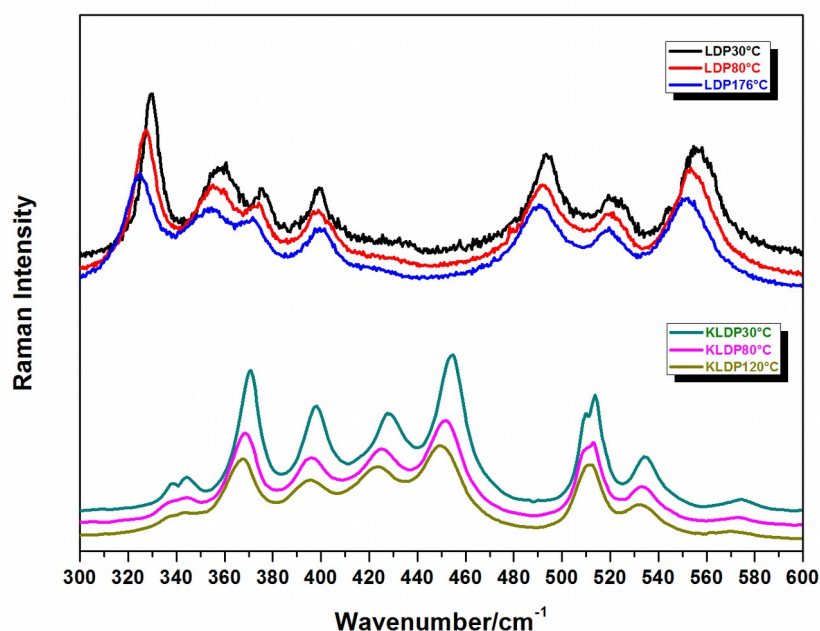
The Raman spectra recorded at room temperature in both crystals are shown in Fig. 2. Both spectra present some similarities according to the wavenumber range, so that they can be compared

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  $300\text{ cm}^{-1}$  are lying the bands generally associated to external modes, between  $300$  and  $600\text{ cm}^{-1}$  two groups of lines, and between  $800$  and  $1100\text{ cm}^{-1}$  intense and narrow peaks. Above  $1200\text{ cm}^{-1}$  (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  $300\text{ cm}^{-1}$  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  $\text{LiO}_4$  and  $\text{PO}_4$ .



**Figure 3.** Raman spectra of LDP and KLDP recorded at three different temperatures in the region from  $300$  to  $600\text{ cm}^{-1}$ . 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  $440\text{ cm}^{-1}$ . The lines lying at  $328\text{ cm}^{-1}$ ,  $358\text{ cm}^{-1}$  and  $375\text{ cm}^{-1}$  (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.

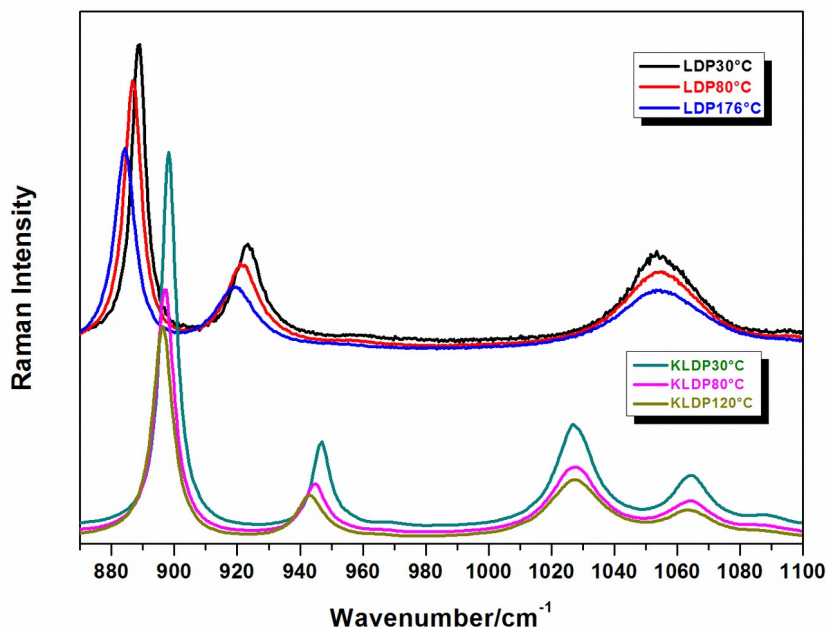
These three lines are assigned to the  $\nu_2$  internal vibrations inside the group  $\text{PO}_4$ . Indeed they are close to the wavenumber of the free molecular group  $\text{H}_2\text{PO}_4$  ( $356\text{ cm}^{-1}$ ) and it is well known that the wavenumber of a vibrational mode can be shifted due to the surrounding of the molecular group. By contrast of these 3 lines  $\nu_2\text{-PO}_4$ , the band located at  $399\text{ cm}^{-1}$  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  $\text{LiO}_4$  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  $491\text{ cm}^{-1}$  and  $556\text{ cm}^{-1}$  (at room temperature) present on heating a down-shift of the

maximum position and consequently are attributed to  $\nu_4$ - $\text{PO}_4$  vibrations (close to the wavenumber  $495\text{ cm}^{-1}$  in the free molecular group  $\text{H}_2\text{PO}_4$ ). On the other hand, the peak at  $520\text{ cm}^{-1}$  is unaffected by the temperature change and is consequently assigned to internal mode of  $\text{LiO}_4$  group. This attribution is supported by the observation of  $\text{Li-O}$  vibrations in other compounds, such as  $\text{Li}_2\text{CO}_3$ , in which Hase et al. assigned 4 vibrational modes between  $375$  and  $500\text{ cm}^{-1}$ .<sup>14</sup>

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  $\text{H}_2\text{PO}_4$  in KLDP. Furthermore the two groups of lines within  $300$ - $600\text{ cm}^{-1}$  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  $454\text{ cm}^{-1}$  in the first group, and  $534$  and  $574\text{ cm}^{-1}$  in the second group, are slightly shifted towards lower wavenumber on heating, and are attributed to  $\text{PO}_4$  ( $\nu_2$ - $\text{PO}_4$  for the first group and  $\nu_4$ - $\text{PO}_4$  for the second group). The lines located at  $398$  and  $513\text{ cm}^{-1}$  have positions unchanged with temperature, and are therefore assumed to derive from  $\text{LiO}_4$  internal vibrations. It is remarkable that these peaks are lying at nearly the same positions as in LDP (at  $399$  and  $520\text{ cm}^{-1}$  respectively). This reinforces our interpretation within the attribution of these lines to  $\text{LiO}_4$  in both crystals.

The thermal independence of the line positions attributed to  $\text{LiO}_4$  can be explained by the relative rigidity of this molecular group since it is linked to other  $\text{LiO}_4$  along chains (see Fig. 1). Moreover the fact that the internal vibrations of  $\text{Li-O}$  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  $\nu_2$ - $\text{PO}_4$  and  $\nu_4$ - $\text{PO}_4$  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  $\text{LiH}_2\text{PO}_4$  and  $\text{KLi}(\text{H}_2\text{PO}_4)_2$  recorded at three different temperatures in the region from  $850$  to  $1100\text{ cm}^{-1}$ . 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  $850$ - $1100\text{ cm}^{-1}$ , 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  $888\text{ cm}^{-1}$  and  $923\text{ cm}^{-1}$  are assigned to  $\nu_1$ - $\text{PO}_4$  vibrations regarding their temperature dependence and the position of  $\nu_1$  vibration in the free molecular group  $\text{H}_2\text{PO}_4$  ( $886\text{ cm}^{-1}$ ). Then we attribute the band at  $1053\text{ cm}^{-1}$  to  $\nu_3$ - $\text{PO}_4$  vibration since its position is

relatively close to this of the free molecular group lying at  $1085\text{ cm}^{-1}$ . However we can point out that the position of this line is unaffected by the temperature change contrary to other peaks attributed to the  $\text{PO}_4$  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  $946\text{ cm}^{-1}$ , which are affected by temperature change, are attributed to  $\nu_1\text{-PO}_4$  vibrations, whereas the bands around  $1026$  and  $1065\text{ cm}^{-1}$  are assumed to be assigned to  $\nu_3\text{-PO}_4$  vibrations.

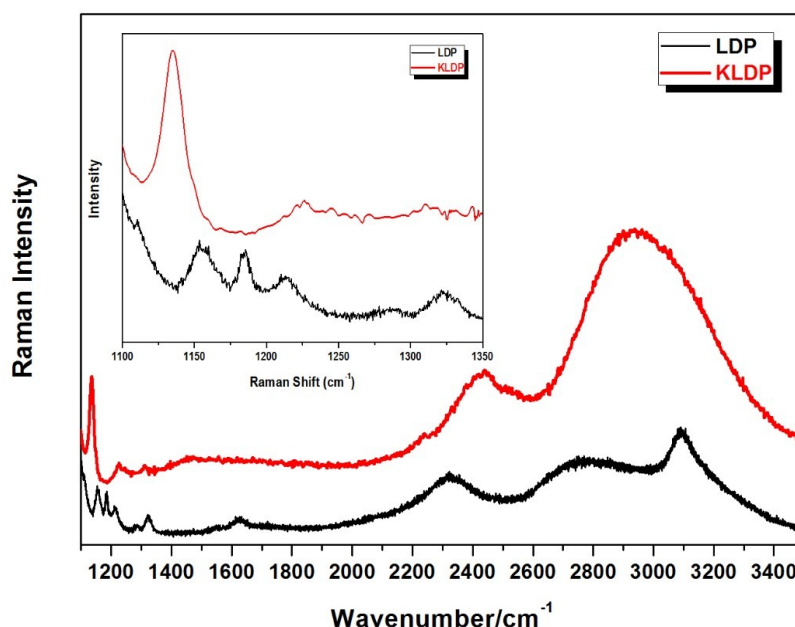
Lines occurring above  $1100\text{ cm}^{-1}$  characterize O–H---O vibrations of the hydroxyl groups of the anion  $\text{H}_2\text{PO}_4^-$  involved in hydrogen bonding and correspond to  $\nu_{\text{O-H}}$  and  $\gamma_{\text{O-H}}$  motions. These lines shown in Fig. 5 for both crystals are generally weaker in intensity and higher in wavenumber than the internal modes of  $\text{PO}_4$ . In LDP, consistently with the attribution given by Lee et al. they are attributed to  $\gamma(\text{O-H})$  at  $1156\text{ cm}^{-1}$  and  $1185\text{ cm}^{-1}$  and  $\delta(\text{O-H})$  around  $1217\text{ cm}^{-1}$  and  $1323\text{ cm}^{-1}$ .<sup>10</sup> In KLDP by analogy, the lines lying at  $1089$  and  $1136\text{ cm}^{-1}$  are assigned to  $\gamma(\text{O-H})$  and the bands around  $1226$  and  $1316\text{ cm}^{-1}$  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<sup>15,16,17</sup> 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.<sup>18</sup> In our case this feature is in agreement with direct measurements in LDP<sup>19</sup> and KLDP<sup>20</sup> and is confirmed by the increase of widening of these bands at higher temperature.

The bands located in LDP around  $1612$ ,  $2332$  and  $2767\text{ cm}^{-1}$  are respectively labeled C, B and A for  $\text{OH}_2$  while the peak at  $3109\text{ cm}^{-1}$  is attributed to the  $\text{OH}_1$  motion.<sup>21</sup> In KLDP we found wide bands around  $2422$  and  $2934\text{ cm}^{-1}$  which are attributed to B and A, by comparison with LDP.

According to Novak<sup>22</sup> the bands may be classified according to hydrogen bond length. Thus the fact that the B band is located around  $2332\text{ cm}^{-1}$  in LDP and around  $2422\text{ cm}^{-1}$  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 <sup>-1</sup> )	Assignment	Wavenumber (cm <sup>-1</sup> )	Assignment
328 m	$\nu_2$ ( $\delta_s$ O-P-O)	338 w	$\nu_2$ ( $\delta_s$ O-P-O)
358 m	$\nu_2$ ( $\delta_s$ O-P-O)	344 w	$\nu_2$ ( $\delta_s$ O-P-O)
375 m	$\nu_2$ ( $\delta_s$ O-P-O)	370 m	$\nu_2$ ( $\delta_s$ O-P-O)
399m	LiO <sub>4</sub> (Li-O)	398 m	LiO <sub>4</sub> (Li-O)
491 m	$\nu_4$ ( $\delta_{as}$ O-P-O)	427 m	$\nu_2$ ( $\delta_s$ O-P-O)
-		454 m	$\nu_2$ ( $\delta_s$ O-P-O)
-		510 m	$\nu_4$ ( $\delta_{as}$ O-P-O)
520 m	LiO <sub>4</sub> (Li-O)	513 m	LiO <sub>4</sub> (Li-O)
556 m	$\nu_4$ ( $\delta_{as}$ O-P-O)	534 m	$\nu_4$ ( $\delta_{as}$ O-P-O)
-		574 w	$\nu_4$ ( $\delta_{as}$ O-P-O)
888 s	$\nu_1 = \nu_s$ (P-O-H)	898 s	$\nu_1$ ( $\nu_s$ (P-O-H) <sub>2</sub> )
923 m	$\nu_1 = \nu_s$ (P-O-H)	946 m	$\nu_1$ ( $\nu_s$ (P-O-H) <sub>2</sub> )
1053 m	$\nu_3$ (P—O-H)	1026 m	$\nu_3$ ( $\nu_{as}$ (P-O-H) <sub>2</sub> )
-		1065 m	$\nu_3$ ( $\nu_{as}$ (P-O-H) <sub>2</sub> )

#### 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.<sup>10,5</sup> The main novelty of our investigations results into the attribution of bands lying at 398 or 399 cm<sup>-1</sup> and around 513 or 520 cm<sup>-1</sup> to LiO<sub>4</sub> vibrations in LDP and KLDP as well.

Regarding specifically LDP, it should be noted that Rhimi et al.<sup>5</sup> assigned a line at 402 cm<sup>-1</sup> to LiO<sub>4</sub> whereas Lee et al. did not choose between PO<sub>4</sub> and LiO<sub>4</sub>.<sup>10</sup> The main discrepancy compared with our investigations concerns the peak at 520 cm<sup>-1</sup> attributed to P—O vibration in earlier descriptions. Furthermore in our study the peak around 1053 cm<sup>-1</sup> in LDP is attributed to PO<sub>4</sub> motion in agreement with Rhimi et al.<sup>5</sup> whereas Lee et al. did not exclude the OH vibration.<sup>10</sup>

Regarding KLDP, our assignment of Raman lines notably differs from the previous one by Rhimi et al.<sup>5</sup> In particular these authors attributed the whole group of bands between 400 and 470 cm<sup>-1</sup> to vibration modes of LiO<sub>4</sub>, in agreement with earlier investigation on LDP by Lee et al.<sup>10</sup> 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<sub>4</sub> tetrahedra are coupled with LiO<sub>4</sub> 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<sub>4</sub> and LiO<sub>4</sub> entities in both crystals. Instead of 4 lines in free molecular group H<sub>2</sub>PO<sub>4</sub>, we detect 7 lines attributed to internal modes of PO<sub>4</sub> 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<sub>4</sub>. The positions of these vibrations around 400 cm<sup>-1</sup> and 520 cm<sup>-1</sup> 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<sup>+</sup> ions are quite immobile and stable in the structure.<sup>4</sup>



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