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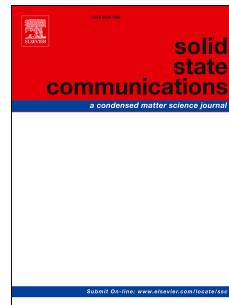
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ACCEPTED MANUSCRIPT

Phase transformations in LiH₂PO₄ (LDP) revealed by Raman spectroscopy

Rawdha Dekhili^{a,b,c,d}, Thomas H. Kauffmann^{a,b}, Hassen Aroui^{c,d} and Marc D. Fontana^{a,b}

^aUniversité de Lorraine, Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423 - 2, rue Edouard Belin, 57070 Metz, France.

^bCentraleSupélec, Laboratoire Matériaux Optiques, Photonique et Systèmes, EA 4423 - 2, rue Edouard Belin, 57070 Metz, France.

^cUniversité de Tunis Elmanar, Faculté des Sciences de Tunis, 2092 El Manar Tunis, Tunisia.

^dUniversité de Tunis, Laboratoire Dynamique Moléculaire et Matériaux Photoniques, Ecole Nationale Supérieure d'Ingénieurs de Tunis – 5 av. Taha Hussein, 1008 Tunis, Tunisia.

Abstract

We investigate Raman scattering measurements on polycrystalline LiH₂PO₄ (LDP) between 30 and 240°C, in order to detect phase transformations. The thermal behavior of main lines in different wavenumber ranges is discussed and analyzed. Raman spectra show two anomalies at 176°C and 210°C, reflecting changes in chemical bonds, and are attributed to progressive polymerization, in agreement with earlier electrical measurements.

Keywords : Raman spectroscopy, vibrational modes, phosphate compounds, phase transformations

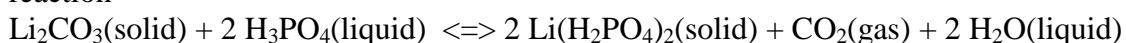
1. Introduction

The family of phosphate compounds with the general formula MX₂PO₄ (M = K, Rb, NH₄, Cs, Tl, Li, X = H, D) is the object of many investigations thanks to several physical and chemical properties interesting for basic research and practical applications [1,2]. Among these compounds, the most widely studied is potassium dihydrogen phosphate (KDP) for ferroelectric, piezoelectric, and electro-optic properties [3,4].

Much less investigated, LiH₂PO₄ (LDP) has a particular interest for its relatively high protonic conductivity [5-7]. The structure of LDP consists into tetrahedral groups PO₄ and LiO₄ which are bonded together by oxygen ions. Lee et al [8] have recorded Raman data on LDP between 70 and 300 K but did not observe any change in spectra at low temperature. They did not investigate high temperature range but by means of electrical conductivity and dielectric constant measurements they found two anomalies at 178°C (Tp₁) and 196°C (Tp₂) [9]. They interpreted them as due to super-protonic phase transformations induced by polymerization at Tp₁ and Tp₂. Therefore we have performed Raman spectroscopy measurements at high temperature with a special attention to the temperature range 170–220°C.

2. Experimental

LDP polycrystals were prepared by employing a slow evaporation method using Li₂CO₃ (purity of 99.99%), phosphoric acid (purity of 95%) and distilled water as starting materials according to the reaction



The resulting solution was stirred at room temperature. A quantity of the obtained homogeneous solution was kept in Petri dishes at ambient temperature during a few days; the final product consists into transparent cm-size samples.

Raman spectra were recorded on a polycrystalline sample using confocal Raman microscope LabRAM HR Evolution (*Horiba*) with an exciting laser line of 532 nm. The system leads to a

spectral resolution of 1 cm^{-1} using a 1800 grooves per millimeter grating and is equipped with an ultra-low frequency module to detect wavenumbers down to 5 cm^{-1} . The laser light was focused through a 50x objective (*Olympus*) at a distance above 1 cm from the sample placed into a temperature stage (*Linkam*). Raman spectra of LDP were recorded in the spectral range of 5–3500 cm^{-1} as a function of temperature from 30°C up to 240°C.

3. Results and analysis

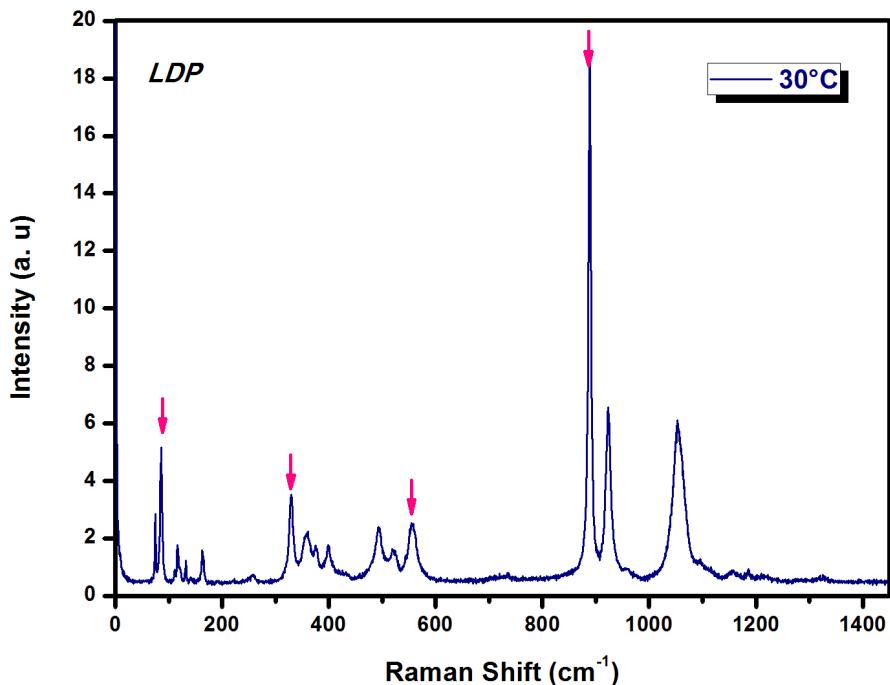


Figure 1. Raman spectrum of LiH_2PO_4 recorded at room temperature in the region from 5 to 1400 cm^{-1} . Arrows indicate the lines which are particularly analyzed.

The Raman spectrum recorded at room temperature is shown in figure 1 and is found to be relatively similar to spectra reported earlier [8,10]. We distinguish different frequency ranges: below 300 cm^{-1} are lying the bands generally associated to external modes; between 300 and 1100 cm^{-1} the lines generally attributed to LiO_4 and PO_4 internal vibrations and above 1100 cm^{-1} very weak structures corresponding to OH vibrations.

We report and discuss the temperature dependence of Raman spectra especially between 170 and 220°C. For this we describe and analyze the temperature behavior of the most intense lines lying in 4 different wavenumber ranges. These peaks are indicated by arrows in figure 1.

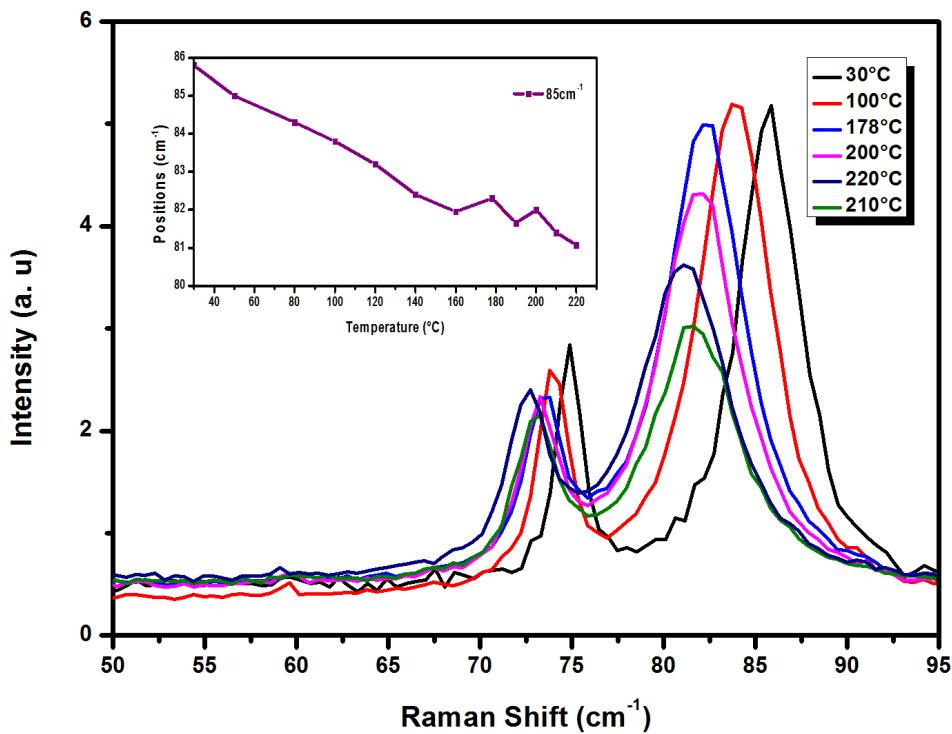


Figure 2. Raman spectra of LiH_2PO_4 recorded at different temperatures in the region from 50 to 95 cm^{-1} . In the insert is reported the temperature dependence of the position of the line lying at 85 cm^{-1} at room temperature.

In figures 2 and 3 are shown the Raman spectra recorded at different temperatures, in the ranges corresponding to external modes and high-frequency internal modes respectively.

We note a continuous change of the profile when heating between 30 and 170°C, with a clear down-shift of the maxima positions, and a decrease of intensity of all considered lines. The diminishing of the maximum position with increasing temperature is expected regarding the thermal dilatation. The chemical bonds are expected to increase on heating, so that the force constant diminishes and subsequently the frequency decreases. Above 170°C the maximum position of main lines displays two breakdowns in its monotonous decrease on heating (see insert of figure 2).

Likewise, regarding the intensity we remark that for larger temperature, all lines (see figures 2 and 3) exhibit a large discontinuity in their behavior, with an abrupt decrease of intensity, between 210 and 220°C. In particular, we can point out the large diminishing of the line at about 85 cm^{-1} which is very intense at room temperature.

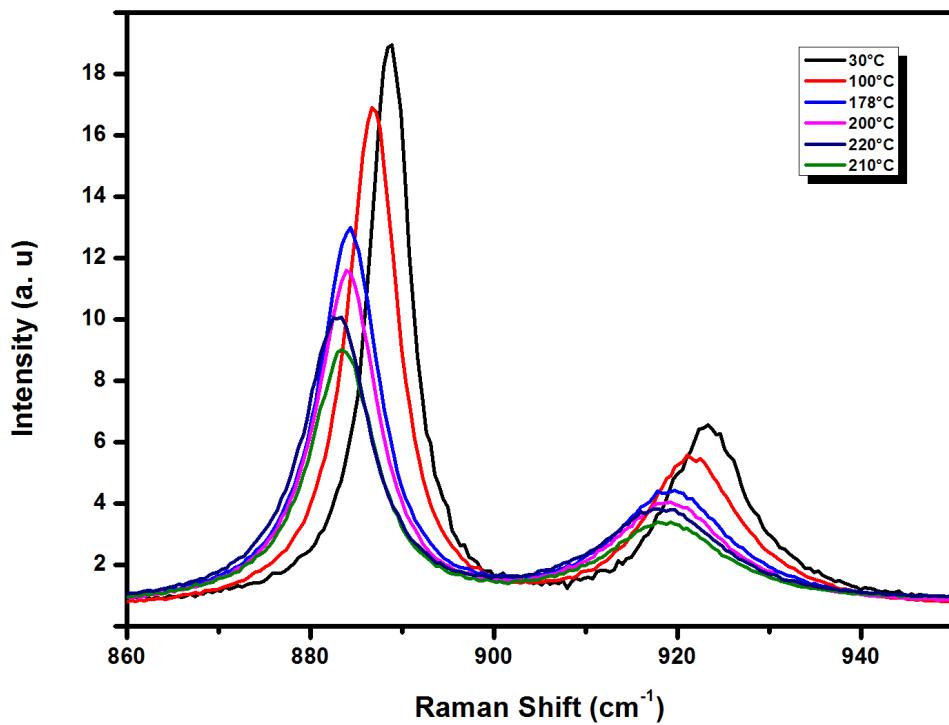


Figure 3. Raman spectra of LiH_2PO_4 recorded at four different temperatures in the region from 860 to 960 cm^{-1} .

To attempt to rely more precisely the Raman data with the phase transformations, we report in figure 4 the temperature dependence of the maximum intensity of the main lines.

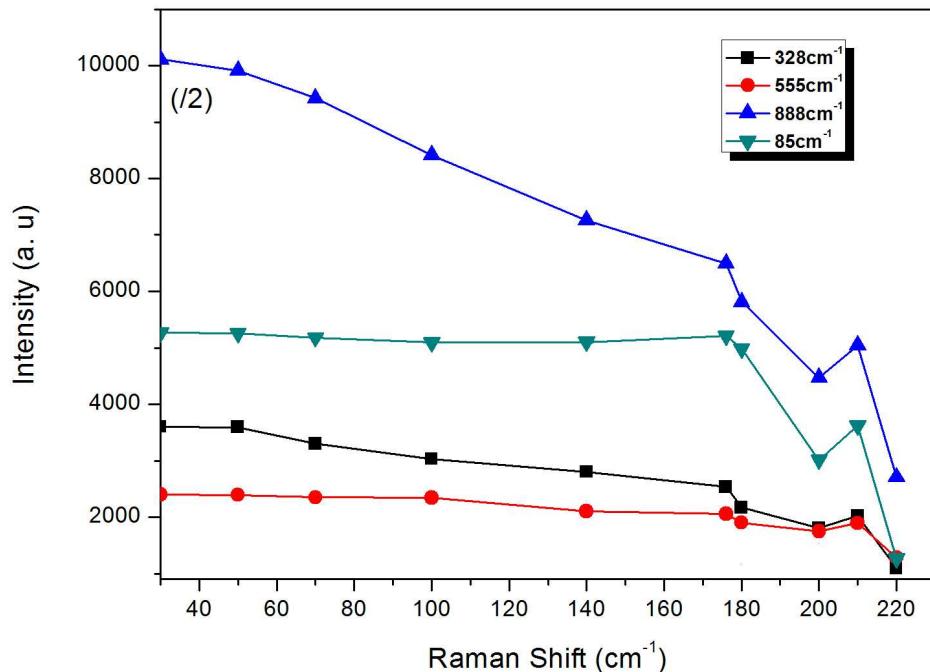


Figure 4. Temperature dependence of the maximum intensity of four different Raman peaks of LiH_2PO_4 (the lines are labeled according to their position at room temperature).

The intensity of all peaks shows firstly a monotonous decrease on heating, but the line at 85 cm^{-1} which is nearly constant, and then two clear breakdowns in their dependence. These two clear anomalies appear around 176°C and 210°C , close – but slightly shifted – to Tp_1 and Tp_2 reported by Lee by means of electrical measurements [9].

It is to be noted that, on the one hand the external modes, and on the other hand the internal modes sensitive to P-O and Li-O bonds, are all affected by a structural rearrangement. These features reflect a change of the whole structure of the material, and constitute therefore an evidence of phase transformations.

An additional remarkable feature is given in figure 5 by the temperature dependence of the quasi-elastic scattering, i.e. the signal beside the Rayleigh and external mode bands (see the insert). In this figure is reported the integrated intensity between 5 and 30 cm^{-1} as function of temperature. This plot shows a large peak around 176°C and a second small maximum around 210°C . The spectral range below 20 cm^{-1} covers (even partly) the collective protonic and relaxational motions of PO_4 and LiO_4 .

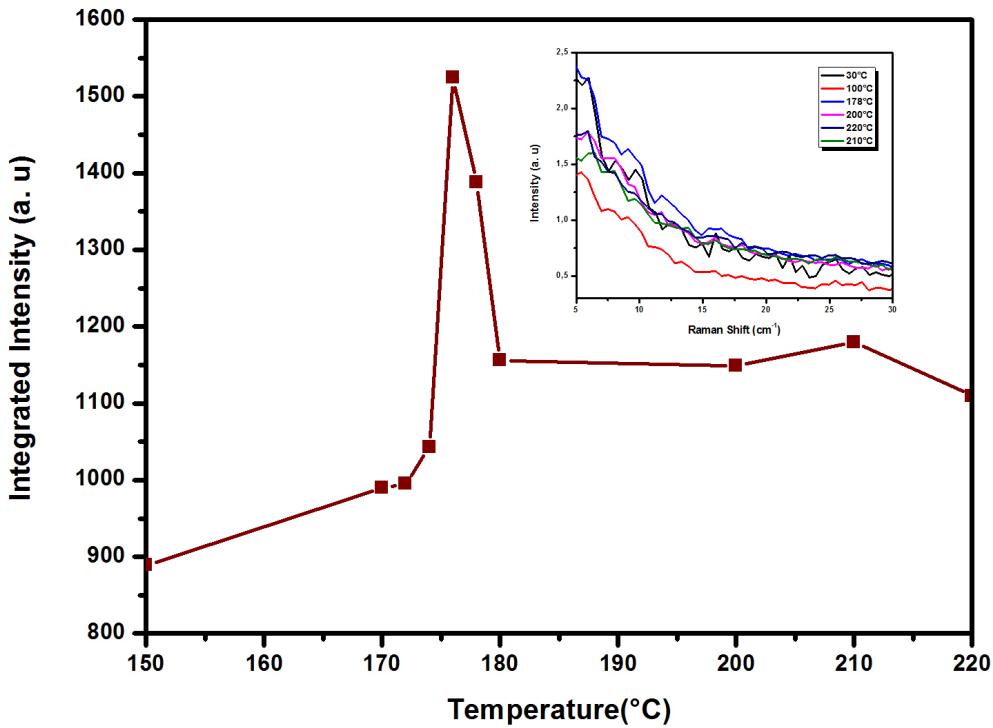


Figure 5. Temperature dependence of the integrated intensity between 5 and 30 cm^{-1} of the quasi-elastic scattering reported in the insert.

The quasi-elastic scattering can be related to the dielectric response in the teraHertz or sub-teraHertz frequency range. Thus, as the Stokes Raman intensity is proportional to the imaginary part of the dielectric susceptibility $\chi''(\omega)$ [11], the integration of the Raman intensity over the frequency range 0 – 30 cm^{-1} provides the real part of the susceptibility $\chi'(\omega)$ at 1 THz . This last feature can be related to dielectric permittivity measurements of Lee et al [9] and thus shows some consistencies with them. This demonstrates that the whole Raman spectrum is found to be affected by structural transformations.

As shown in figure 6 the thermal change affects also the very high wavenumber range, corresponding to the OH bands. At first we note a shift on heating of the whole spectrum, which is

mainly caused by the increase of the background (see level around 1400 cm^{-1} , i.e. far from any Raman band). This can be related to the loss of transparency of the sample which becomes milky above 200°C . The most remarkable change occurs at 240°C . The narrow lines around 1200 cm^{-1} , and the broad stretching bands between 2600 and 3600 cm^{-1} disappear, and are replaced by a very intense and wide signal. This huge profile change occurs simultaneously with the appearance of water on the surface of the sample. In fact the sample is notably damaged by heating process. This is confirmed by the spectrum obtained after cooling which completely differs from this previously recorded on heating (see figure 6). Therefore the transformations invoked above are clearly irreversible. A thermal decomposition does exist at high temperature with water releasing. The progressive let of water is consistent with the chemical reactions proposed by Lee et al. [9]

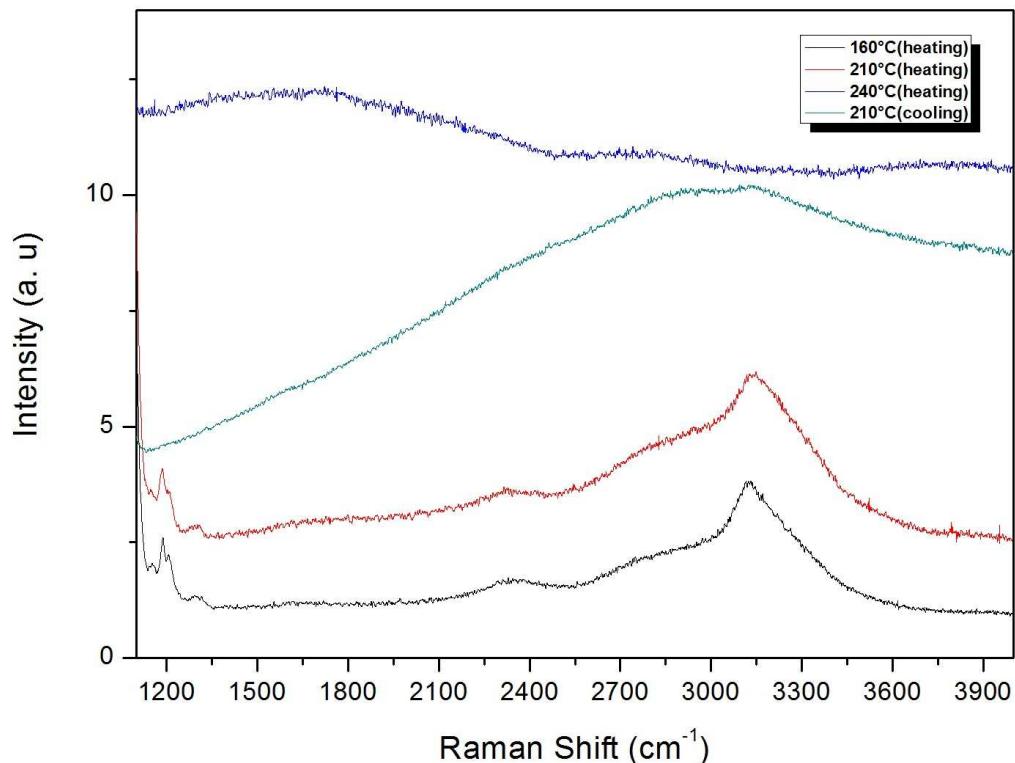


Figure 6. High wavenumber Raman spectra of LiH_2PO_4 recorded during a heating-cooling process. Spectra at 240°C (heating) and 210°C (cooling) are vertically shifted for clearness.

The thermal behavior of the largest peak around 888 cm^{-1} (position at room temperature) reported in figure 4 corroborates this analysis. This line which shows the strongest decrease of intensity on heating, corresponds to the internal vibration $\nu_1(\text{P-OH})$. This bond is therefore affected by the continuous releasing of water, explaining more abrupt changes at Tp_1 and Tp_2 , suggested to be the onset of dimerization and oligomerization respectively.

4. Conclusion

On heating up to 170°C , Raman lines show an expected decrease of their maximum position. At higher temperature their intensity shows a breakdown in their monotonous behavior with temperature. Two anomalies were detected in the temperature dependence around 176°C and 210°C , for all main Raman lines. Consequently these features reflect the large modifications of the chemical bonds at high temperature, and therefore transformations of the whole structure. These

results are consistent with electrical data reported by Lee et al [9] and corroborate their interpretation.

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- Use of Raman spectroscopy to detect phase transformations
- Phase transformations in a new material (LDP) among KDP family compounds
- Link between Raman data and dielectric measurements