Raman and structural studies on the high-temperature regime of the
KH$_2$PO$_4$-NH$_4$H$_2$PO$_4$ system

J.F. Jurado$^{a,*}$, C. Vargas-Hernández$^{a}$, and R.A. Vargas$^{b}$

$^{a}$Laboratorio de Propiedades Ópticas de Materiales (POM), Departamento de Física y Química, Universidad Nacional de Colombia, A.A. 127, Manizales, Colombia.

$^{b}$Departamento de Física, Universidad del Valle, A.A. 25360, Cali, Colombia.

We have studied the high-temperature phase transition (HTPT) of crystalline potassium and ammonium dehydrogen phosphates and solid solutions of them with composition (1-$x$)KH$_2$PO$_4$ + $x$NH$_4$H$_2$PO$_4$ (KADPx, for $x$ = 0.0, 0.1, 0.2, 0.3, 0.4, 0.6 and 1.0), by means of X-ray diffraction analysis at room temperature and in situ Raman spectroscopy as function of temperature. Analysis of the Raman spectra made it possible to monitor the temperature dependence of vibrational bands associated to structural changes taking place during a proposed partial dehydration reaction that starts to take place at a characteristic temperature $T_p$ and tends to increase above it. This assignment is supported using characteristic vibrational bands of phosphates and polyphosphates (produced as a consequence of the partial dehydration reaction of the crystals above $T_p$). The presence of the polyphosphate vibrational bands assigned to the stretch vibration of its PO$_2$ species (at about 1120 cm$^{-1}$ for pure KDP) accompanied by a broad band assigned to P-O-P backbone vibrations (at about 713 cm$^{-1}$ for pure KDP) [14] become evident at temperature higher than $T_p$ depending on the composition of KADPx.

Keywords: X-ray diffraction; ionic crystals; vibrational states in crystals.

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1. Introduction

Potassium dehydrogenate phosphate, KH$_2$PO$_4$ (KDP) and ammonium dehydrogenate phosphate, NH$_4$H$_2$PO$_4$ (ADP) are well known ferroelectric (Curie temperature, $T_c$ = 150°C) and antiferroelectric (Néel temperature, $T_N$ = -125°C) crystals, respectively, belonging to the KDP-family compounds. They are widely used as electro-optic modulator, Q-switch, and high power laser frequency conversion material due to his magnificent performance as an active element in such devices: piezoelectric, ferroelectric, electro-optics and nonlinear optical responses [1,2]. At higher temperatures, different experiments performed on these compounds indicate a high degree of structural disorder, the origins of which are still controversial. However, they are considered the most promising compounds for a membrane in a medium temperature fuel cells [3,4]. The properties of the KDP salts at high temperatures are studied carefully nowadays and are modified and optimized for practical use as a proton intermediate temperature membrane. Most of the hydrogen-bonded materials undergo phase transition in the high temperature region. In the high temperature phases, the materials exhibit high electric conductivities which have been considered to be due to the proton transfer [5]. Recently, these H-bonded oxycacid salts or solid acids have attracted much more attention not only in its fundamental aspects but also in the potential application to various conversion systems such as fuel cells, capacitors, sensors or electrochromic displays. See, for example Ref. [6]. The transport properties of protons in such compounds may be treated in terms of high-proton mobility in open high-temperature solid phases, and in order to explain the electrical conductivity, various proton transport models have been proposed [7]. However, other investigators have claimed that mechanism in H-bonded crystals must considerer thermal decomposition as well as ionic transport because it is known that many H-bonded crystals reveal thermal dehydration at high temperature ($>150^\circ$C), such as that proposed by Lee [8]:

$$n\text{KH}_2\text{PO}_4(s) \rightarrow K_n\text{H}_2\text{PnO}_{3n+1}(s) + (n - 1)\text{H}_2\text{O}(g)$$ (1)

where $n$ is the number of molecules involved in the process, the letters $s$ and $g$ correspond to liquid and gaseous phases, respectively. Most investigators have considered the high-temperature phase transition, (HTPT) of KDP and ADP near 180 and 150°C, respectively, as a structural phase transition from a tetragonal to a monoclinic phase [9-11]. Others have claimed [12] that a dehydration process occurred gradually over the crystal surface at temperatures above 150°C and then on increasing temperature it occurs in the interior of the sample. Using Raman scattering Choi [13,14] and more recently, Jager, Prinsloo [15] and Daniel et al., [16] at higher temperatures, have monitored the dehydration of potassium, sodium dihydrgene phosphates and KDP doped with nickel respectively. Using characteristic vibrational bands of phosphates they were able to monitor structural changes taking place during reaction. Raman spectroscopy is an excellent method for studying PO$_4$ units in different environments as the number of positions of P-O bands in the spectra depend on crystal structure and resultant bond strength. For the particular case of KDP, the relevant optical modes to considerer at room temperature [17] are those associated with vibrations in the plane of PO$_4$ bonds ($\nu_2$ modes), the collective movements of the H$^+$ proton along the c-axis which are very sensitive to the existence of other bonds ($\nu_4$ modes) and the P-O stretch vi-
brations ($\nu_1$ modes). The $\nu_3$ modes correspond to antisymmetric and not well-defined vibrations. For ADP, there are additional modes associated with N-H-O bonds.

In the present work, we have decided to study the binary system $(1-x)KH_2PO_4+xNH_4H_2PO_4$ (KADP$_x$, for $x=0.0$, 0.1, 0.2, 0.3, 0.4, 0.6 and 1.0) by Raman spectroscopy to follow the evolution of the vibrational modes and to distinguish between the phases at different temperatures. X-ray diffraction at room temperature was done on the samples with the concentration prepared.

2. Experimental Details

KDP and ADP powders commercially available (Panreac Química SAU) were used as starting materials. Crystals of $(1-x)KH_2PO_4+xNH_4H_2PO_4$ (KADP$_x$, for $x=0.0$, 0.1, 0.2, 0.3, 0.4, 0.6 and 1.0) were grown from aqueous solutions at room temperature by low evaporation of the solvent. Transparent crystals with pyramidal geometry, average crystallite size of $3 \times 2 \times 2$ mm$^3$ and preferential direction of growth along $\{100\}$ were obtained. X-ray diffraction at room temperature was performed with an Advance A8 Boker AXS diffractometer, with monochromatic radiation source CuK$_\alpha$ (1.5406 Å). Raman scattering measurements were carried out with a LabRAM HR800 Jobin Yvon Horiba high-resolution spectrometer, excited with the 473 nm line, exposure of 2 $\mu$m diameter, in the spectral range from 150 to 4000 cm$^{-1}$.

The crystalline sample was located in a home-made microfurnace coupled to the micro-Raman instrument for in situ Raman spectroscopy measurements as a function of temperature. The temperature was recorded with a type-K thermocouple located very close to the sample, the Raman spectra were recorded at various isotherms in the temperature range from 25 to 288°C. The experimental temperature was maintained within ±0.5°C by the temperature-controlled microfurnace.

3. Results and Discussion

3.1. X-ray diffraction

The dependence of the lattice parameters on partial cation substitution in the double salts KADP$_x$ (all of them with the KDP tetragonal $I\bar{4}2d$ structure) is shown in Fig. 1. The results are consistent with literature reports [19]. The cell parameters of the double salts (Table I) are comparable to those of KDP, probably because the effective size of the substituting cations is comparable in the crystalline phase. This is so because the effect of ammonium substitution by potassium ions on changing the $a$ and $b$ parameters is negligible since the crystals are primarily formed by phosphate units (PO$_4$) linked together via strong hydrogen bonds. On other hand, the parameter $c$ is dependent on the radii of the both the constituent anions and cations. Table I also gives the stress values as calculated for the $c$ parameters for ADP according to the expression [20]

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction at room temperature of KADP$_x$-system for: $x=0.0$, 0.1, 0.2, 0.3, 0.4 and 0.6. For $x>0$, only the most intense peak (200) are shown for data analysis (see text). The inset shows the dependence of the peak position and strain with concentration. The dashed line is a guide to the eye.

![Figure 2](image2.png)

**Figure 2.** Raman spectra at room temperature of KDP and ADP crystalline compounds. The arrows indicate the location of the modes in correspondence with Ref. [14] and [17].
\[ e = \left( \frac{c_{\text{exp}} - c_{\text{ADP}}}{c_{\text{ADP}}} \right) \times 100\% \]

where \( c_{\text{exp}} \) is the experimental value of the lattice parameter at a given concentration and \( c_{\text{ADP}} \) the lattice parameter of ADP without effort. When the bigger ammonium ions (1.42 Å) substitute the smaller potassium ions (1.33 Å), both the H-bond length and strength around the central PO\(_4\) unit are consequently changed.

### 3.2. Raman spectra

The room temperature Raman spectra of KDP and ADP crystals with the laser beam incident on the \( \{100\} \) face are shown in Fig. 2. In correspondence with the experimental geometric arrangement of the crystals (i.e., \( x(zz)y \)) and the Raman data, the various observed active modes of KDP and ADP were assigned in accordance with Ref. [21]. Figure 3i shows the

![Figure 3i](image)

**Figure 3.** (i) Raman spectra of KADPx-crystals, for \( x=0.0, 0.1, 0.2, 0.3, 0.4, 0.6 \) and 1.0, at room temperature. The arrows indicate two selected peaks \( I_1 \) and \( I_2 \) of the ADP spectrum for analysis of the \( \text{K}^+/\text{NH}_4^+ \) substitution in KADPx (see text). (ii) Variation of peak positions of \( I_1 \) and \( I_2 \) and their intensities relationship \( I_1/I_2 \) as a function of the content of ADP at room temperature. The dashed lines are guide for the eye.

The room temperature Raman spectra of KADPx as the ADP concentration increases. All spectra display one band at approximately 915 cm\(^{-1}\) (\( \nu_1 \)) associated with the total symmetric breathing vibration of PO\(_4\). The cationic substitution of \( \text{K}^+ \) by \( \text{NH}_4^+ \) is evident by following the evolution of a localized mode at 1660 cm\(^{-1}\) which is characteristic of the ADP tetragonal phase, as well as the displacement of the peaks denoted as \( I_1 \) and \( I_2 \), respectively. The relative shift position of the peaks \( I_1 \) and \( I_2 \), is consistent with earlier reports by Choi et al. [14,17]. From these two peaks intensity ratio \( I_1/I_2 \) it was estimated the \( \text{K}^+/\text{NH}_4^+ \) substitution in the KADPx solid solution (see Fig. 3ii). This behavior is consistent with X-ray analysis (shown in the inset of Fig. 1). Figure 4 shows the Raman results when the KDP crystal is heated gradually from room temperature up to 285°C at atmospheric pressure, and the Raman spectra are recorded in situ at different isotherms. The spectra show clear changes in the vibrational modes of the KDP crystal as a function of temperature, related to complete disappearance or presence of various bands, the shifts to different wave numbers or broadening of others. In particular, we want to emphasize the following changes: (a) Comparing the spectrum recorded at 151°C to that at 177°C it is observed: (i) the almost complete extinction of the band located at 189 cm\(^{-1}\) (ii) a shift in the band from 474 to 518 cm\(^{-1}\) and 915 to 901 cm\(^{-1}\) respectively, (iii) the presence of a new band located at 1176 cm\(^{-1}\). (b) Comparing the spectra at 204°C and 235°C it is evident: (i) the almost complete extinction of the bands 518 cm\(^{-1}\) and 1176 cm\(^{-1}\) (ii), the presence of a new band at 713 cm\(^{-1}\), and (iii) a shift of the band from 901 to 926 cm\(^{-1}\). This latest displacement is reversible, as long as the crystal is cycled about 235°C for less than 10°C and during less than 5 minutes of temperature cycling. When the temperature is increased from 243 to 285°C the spectra show: (i) The almost disappearance of the band located at 365 cm\(^{-1}\), (ii) the presence of the band located at 519 cm\(^{-1}\), (iii) band shift to lower wave number from 926 to 900 cm\(^{-1}\), (iv) band broadening is evident at around 1120 cm\(^{-1}\).
The shift to higher wave number, the broadening and final disappearance of the 189 cm\(^{-1}\) band as well as the overlapping the bands around 300 and 600 cm\(^{-1}\), show that the KDP crystal continuously adopts a new structural configuration as the temperature increases, that is to say that the hydrogen bonds or the P(OH)\(_4\) (in KDP, each PO\(_4\) tetrahedron is hydrogen bonded to four others) adopting new configuration due to their thermal softening. In other words, the thermal softening of the H-bonds leads to a variation in the number and position of the P-O bands in the spectra, depending of the crystal structure and resultant bond strength at a given temperature.

The change environment of the PO\(_4\) on increasing temperature is also evident by the shift and broadening of the \(\nu_1\) band (located at 915 cm\(^{-1}\) at room temperature). The appearance of a new phase at the high temperatures is justified by the presence at 285\(^\circ\)C of the \(\nu_5\)(P-O-P) and \(\nu_5\)(O-P-O) modes, located at 713 and 1120 cm\(^{-1}\), assigned to the stretch vibrations of the PO\(_2\) species and the P-O-P backbone vibration of the polyphosphate formed during the dehydration reaction suggested by Lee [8]. The gradual change observed in the Raman spectra of KDP crystal as the temperature is increased from room temperature support the idea that the high temperature phenomena in this compound are effects of partial thermal decomposition set in around 180\(^\circ\)C as it is evident from other studies [22]. The results are consistent with a coexistence of phases above this temperature (KDP and partial dimers K\(_2\)H\(_2\)P\(_2\)O\(_7\)) or polymers K\(_n\)H\(_2\)P\(_n\)O\(_{3n+1}\) (\(n > 2\), according to equation), whose mass ratio depends on temperature and the thermal treatment and the water vapor pressure of the surrounding atmosphere. Figure 5i shows the Raman results when the ADP crystal with the same size as the KDP is heated gradually from room temperature up to 162\(^\circ\)C at atmospheric pressure, and the Raman spectra were recorded in situ at different isotherms. Raman active modes are located at: 183, 341, 475, 570, 922, 1122, 1303, 1436, 1660, 2370, 2884, 3157 cm\(^{-1}\). As the temperature is increased there is no appreciable variation in the number and positions of the bands. These results indicate that the vibrations associated with the crystal structure and the molecular modes of vibrations of the ADP crystal, remains identical up to 153\(^\circ\)C. Figure 5ii shows a qualitative analysis of the temperature dependence of peak width (as measured by its FWHM) of the three main peaks (see Fig. 5i), located at 922(a), 1660(b) and 3157(c) cm\(^{-1}\) which are assigned to the symmetric stretching vibrations of PO\(_4\), N-H-O and O-H-O bonds, respectively. The results indicate that there is a distortional effect in the crystal with increasing temperature. The first (a) and second (b) peaks evolution indicates a decreasing distortion, while the third one (c) shows instead an increasing distortion. These tendency are maintained up to about 145\(^\circ\)C, but above this temperature there is an abrupt downwards change. This
This change is more pronounced for the \((b)\) peak showing that the vibrations associated with the \(N-H-O\) bond strength are more sensible with increasing temperature than those of the \(PO_4\) and the \(O-H-O\) bonds. The steep variation of the peak width assigned to the \(N-H-O\) stretch vibrations observed above \(145^\circ C\) is probably responsible for the high conductivity that \(ADP\) shows above \(154^\circ C\). [23].

Figure 6 shows Raman spectra of the \(KADP_x\) \((x=0.1)\) recorded in situ at different isotherms between room temperature and \(258^\circ C\). The spectra show clear changes in the vibrational patterns of the crystal as a function of temperature. (a) The spectra recorded below \(155^\circ C\) show no significant changes and are similar to those observed in the \(KDP\) spectra in the same temperature range (Fig. 4). (b) In going from the spectrum recorded at \(155^\circ C\) to that at \(193^\circ C\), more evident the presence of the bands at \(522\ \text{cm}^{-1}\) and \(665\ \text{cm}^{-1}\), the appearance of a new band located at \(713\ \text{cm}^{-1}\), and a shift of the peak position from \(915\ \text{cm}^{-1}\) to \(910\ \text{cm}^{-1}\). (c) From \(206\ to \(243^\circ C\), the spectra show the almost complete extinction of the band located at \(183\ \text{cm}^{-1}\), the overlap of the bands at about \(473\) and \(550\ \text{cm}^{-1}\) and it is more evident a shift position and broadening of the band at about \(901\ \text{cm}^{-1}\). (d) From \(243\ to \(258^\circ C\), the presence of new bands at about \(966\) and \(1097\ \text{cm}^{-1}\) are evident. From the \(KADP_x\) \((x=0.1)\) Raman results as a function of temperature, we can conclude that the vibrational modes of \(KADP_{0.1}\) are the same as those of the \(KDP\) crystal, such that the effects of this dilute substitution of \(K^+\) by \(NH_4^+\) ions on the \(KDP\) characteristic bands are not transcendental. The Raman data for concentrations \(x > 0.1\) showed similar patterns with increasing temperature to those reported for \(x=0.1\), except that the temperatures at which vibrational bands change decrease as the concentration increases.

4. Conclusions

The appearance of high proton conductivity in both \(KDP\) and \(ADP\) near \(180^\circ C\) and \(150^\circ C\) respectively, have been considered by most of the investigators as a structural phase transition from a tetragonal to a monoclinic phase. On the basis of our study in \(KADP_x\) double salts, using in situ Raman spectroscopy, we suggest that the high conductivity in the high temperature phase is a consequence chemical dehydration process in the crystals. X-ray diffraction data analysis at room temperature verified the substitution of the \(K^+\) by \(NH_4^+\) ions in the \(KADP_x\) combinations for all concentrations \(x\) with a common crystallographic tetragonal phase. The composition of the \(KADP_x\) solid solution is also verified by analysis of the Raman spectra. Contrary to those cases for dihydrophosphate salts in which the effective size of the introduced cations is significant different, as for sodium, rubidium and cesium [24] the substitution of ammonium by potassium does not alter the cell parameters appreciably. However, when a \(KADP_x\) crystal is heated stepwise in a continuous and progressive thermalization time of 10 min. in each isotherm,
Raman data verified that the compound adopts new vibrational patterns similar to those presented by KDP-crystal. Bands changes such as complete disappearance or presence of various bands, the shifts to different wave numbers or broadening of others are observed at temperature higher than about 180°C, depending on the concentration. The thermal softening of the H-bonds leads to a variation in the number and position of the P-O bands in the spectra, depending of the crystal structure and resultant bond strength at a given temperature. The change environment of the PO₄ group is also evident by the shift and broadening of the ν₁ band (located at about 900 cm⁻¹ at room temperature for all concentration). The appearance of a new phase at high temperatures is justified by the presence at higher temperatures of new modes assigned to the stretch vibration of the PO₂ species and the P-O-P backbone vibration of the polyphosphate formed during the dehydration reaction suggested by Lee [8]. Thus, the results are consistent with a coexistence of phases at temperatures above 180°C temperature, a dominant low-temperature tetragonal phase and a partial polyphosphate phase, whose mass ratio depends on temperature and the thermal treatment time and the water vapor pressure of the surrounding atmosphere. In summary, our findings support the view of those investigators that claim that the high conductivity shown by the KADPₓ double salts above 180°C is a consequence of dehydration of the crystals instead of being related to polymorphic transitions as suggested by others.

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* Author to whom correspondence should be addressed: jfjurado@unal.edu.co

2. Ferroelectrics, special issue on KH₂PO₄-type ferro- and antiferroelectrics 71-72 (1987)