



Revista Mexicana de Física

ISSN: 0035-001X

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Sociedad Mexicana de Física A.C.

México

Jurado, J.F.; Vargas-Hernández, C.; Vargas, R.A.
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Revista Mexicana de Física, vol. 58, núm. 5, octubre, 2012, pp. 411-416
Sociedad Mexicana de Física A.C.
Distrito Federal, México

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Raman and structural studies on the high-temperature regime of the $\text{KH}_2\text{PO}_4\text{-NH}_4\text{H}_2\text{PO}_4$ 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.*

Recibido el 18 de abril de 2012; aceptado el 24 de julio de 2012

We have studied the high-temperature phase transition (HTPT) of crystalline potassium and ammonium dehydrogen phosphates and solid solutions of them with composition $(1-x)\text{KH}_2\text{PO}_4 + x\text{NH}_4\text{H}_2\text{PO}_4$ (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.

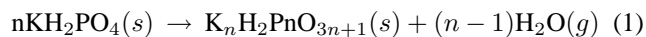
Keywords: X-ray diffraction; ionic crystals; vibrational states in crystals.

PACS: 61.05.cp; 64.70.kp; 63.20.-e

1. Introduction

Potassium dehydrogenate phosphate, KH_2PO_4 (KDP) and ammonium dehydrogenate phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) are well known ferroelectric (Curie temperature, $T_c = -150^\circ\text{C}$) and antiferroelectric (Néel temperature, $T_N = -125^\circ\text{C}$) 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 oxyacid 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 consider thermal decomposition as well as ionic transport because it is known that many H-bonded crystals reveal thermal dehydration at high temperature ($> 150^\circ\text{C}$), such as that proposed by Lee [8]:



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 dihydrogen 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 consider at room temperature [17] are those associated with vibrations in the plane of PO_4 bonds (ν_2 modes), the collective movements of the H^+ proton along the c -axis which are very sensitive to the existence of other bonds (ν_4 modes) and the P-O stretch vi-

brations (ν_1 modes). The ν_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 $(1-x)\text{KH}_2\text{PO}_4 + x\text{NH}_4\text{H}_2\text{PO}_4$ (KADPx, 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 $(1-x)\text{KH}_2\text{PO}_4 + x\text{NH}_4\text{H}_2\text{PO}_4$ (KADPx, 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 $3 \times 2 \times 2 \text{ mm}^3$ and preferential direction of growth along $\{100\}$ were obtained. X-ray diffraction at room temperature was performed with an Advance A8 Buker AXS diffractometer, with monochromatic radiation source CuK_α (1.5406 \AA). Raman scattering measurements were carried out with a LabRAM HR800 JobinYvon Horiba high-resolution spectrometer, excited with the 473 nm line, exposure of $2 \text{ }\mu\text{m}$ diameter, in the spectral range from 150 to 4000 cm^{-1} . The crystalline sample was located in a home-made micro-furnace 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

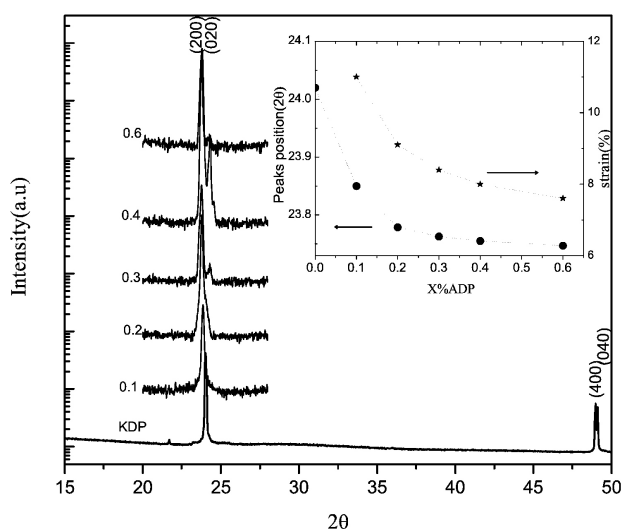


FIGURE 1. X-ray diffraction at room temperature of KADPx-system for: $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.6 . For $x > 0$, only the most intense peak (200) are shown for data analysis (see text). The inset shows the dependence of the peak position and strain with concentration. The dashed line is a guide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

TABLE I. Variations of the lattice parameters and stress with concentration

KADPx	a (Å)	b (Å)	c (Å)	e (%)
$x=0.0$	7.4382 ± 0.0051	7.4382 ± 0.0051	6.9450 ± 0.0313	
$x=0.1$	7.4357 ± 0.0003	7.4165 ± 0.0051	6.7163 ± 0.0285	11
$x=0.2$	7.4285 ± 0.0003	7.4072 ± 0.0017	6.8578 ± 0.0107	9.1
$x=0.3$	7.4208 ± 0.0004	7.4004 ± 0.0006	6.9127 ± 0.0167	8.4
$x=0.4$	7.4356 ± 0.0005	7.4356 ± 0.0005	6.9435 ± 0.0383	8.0
$x=0.6$	7.4341 ± 0.0004	7.4341 ± 0.0004	6.9758 ± 0.0650	7.6

from 25 to 288°C . The experimental temperature was maintained within $\pm 0.5^\circ\text{C}$ by the temperature-controlled micro-furnace.

3. Results and Discussion

3.1. X-ray diffraction

The dependence of the lattice parameters on partial cation substitution in the double salts KADPx (all of them with the KDP tetragonal $\bar{I}42d$ 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]

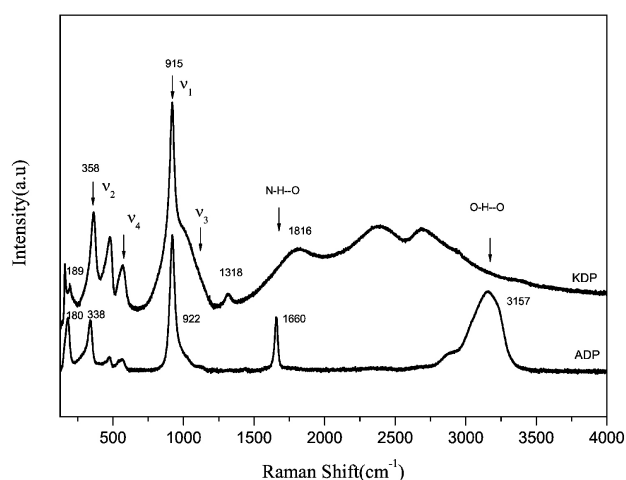


FIGURE 2. Raman spectra at room temperature of KDP and ADP crystalline compounds. The arrows indicate the location of the modes in correspondence with Ref. [14] and [17].

$$e = \frac{(c_{\text{exp}} - c_{\text{ADP}})}{c_{\text{ADP}}} \times 100\%$$

where c_{exp} is the experimental value of the lattice parameter at a given concentration and c_{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.*, $x(\text{zz})y$) and the Raman data, the various observed active modes of KDP and ADP were assigned in accordance with Ref. [21]. Figure 3i shows the

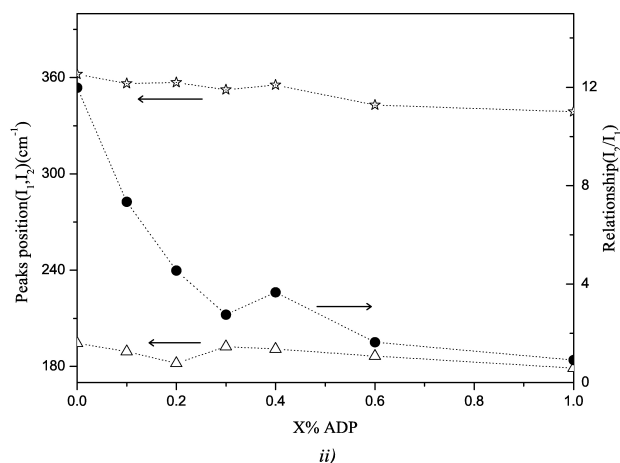
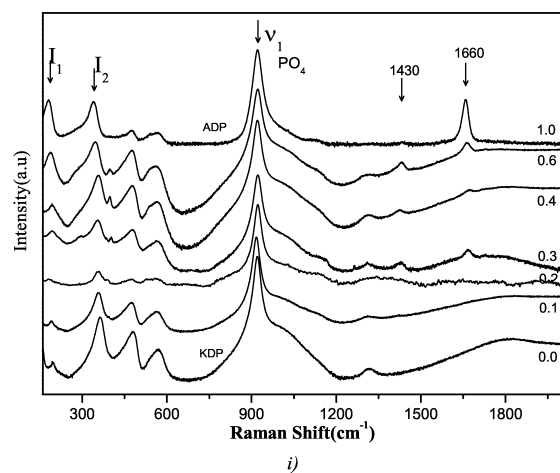


FIGURE 3. (i) Raman spectra of KADPx-crystals, for $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.6$ and 1.0 , at room temperature. The arrows indicate two selected peaks I_1 and I_2 of the ADP spectrum for analysis of the K^+/NH_4^+ substitution in KADPx (see text). (ii) Variation of peak positions of I_1 and I_2 and 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.

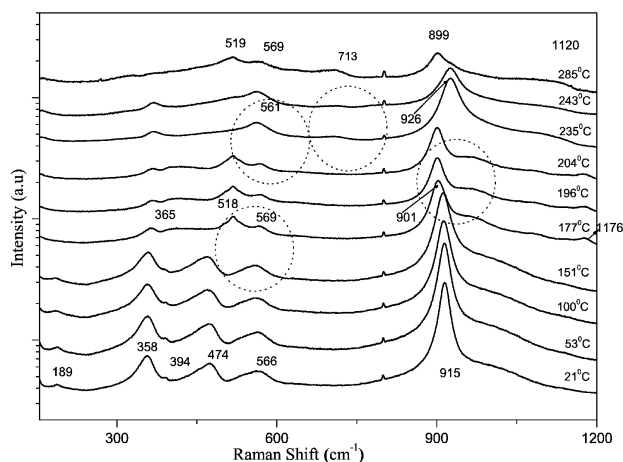


FIGURE 4. Raman spectra of KDP crystal at different temperatures. The dashed circles mark the shifting of the bands with temperature, and are associated with possible changes in the vibrational modes of the compound.

the room temperature Raman spectra of KADPx as the ADP concentration increases. All spectra display one band at approximately 915 cm^{-1} (ν_1) associated with the total symmetric breathing vibration of PO_4 . The cationic substitution of K^+ by 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 K^+/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} .

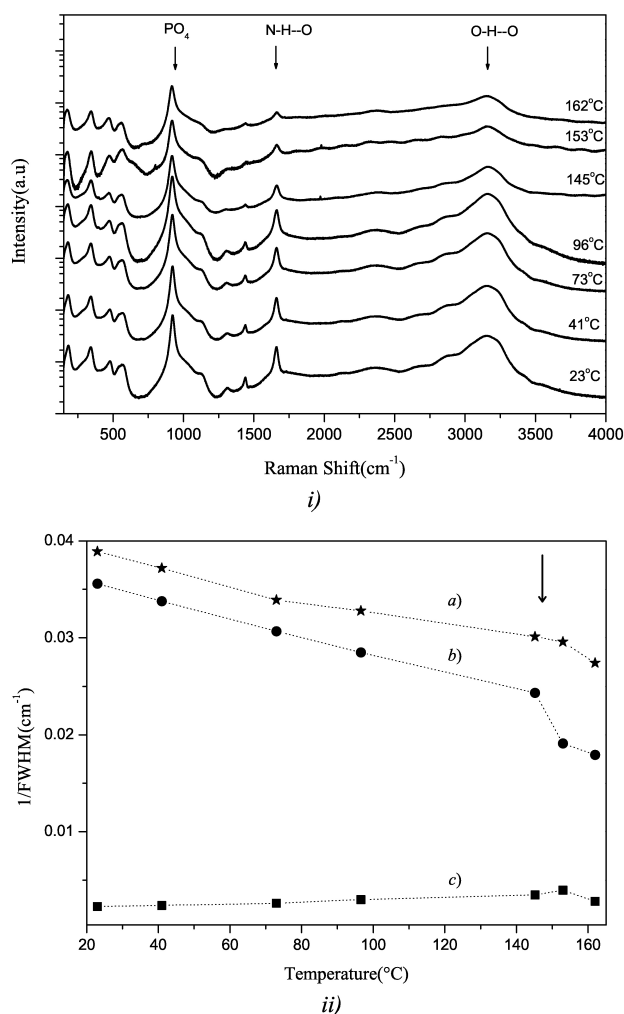


FIGURE 5. i) Raman spectra of ADP-crystal at different temperatures. The arrows indicate the modes associated with stretch vibrations of PO_4 and N-H-O and O-H-O species, respectively. ii) Temperature dependence of FWHM for the peaks located at: a) 922 cm^{-1} , b) 1660 cm^{-1} and c) 3157 cm^{-1} of the ADP crystal. The arrow indicates the transition region that shows an abrupt change of FWHM. The dashed lines are a guide to the eye.

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 $\text{P}(\text{OH})_4$ (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 ν_1 band (located at 915 cm^{-1} at room temperature). The appearance of a new phase at high temperatures is justified by the presence at 285°C of the $\nu_s(\text{P-O-P})$ and $\nu_s(\text{O-P-O-})$ modes,

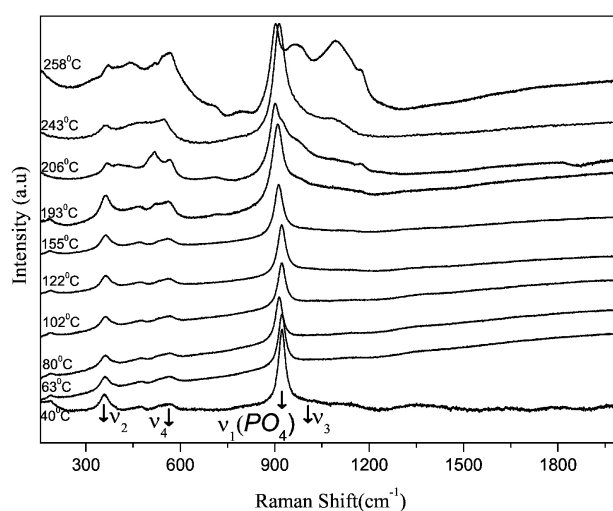


FIGURE 6. Raman spectra of the $\text{KADP}_{0.1}$ crystal at different temperatures. The arrows indicate the evolution of the selected modes with temperature. The modes are assigned in correspondence with Ref. [14] and [17].

located at 713 and 1120 cm^{-1} , assigned to the stretch vibration 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°C as it is evident from other studies [22]. The results are consistent with a coexistence of phases above this temperature (KDP and partial dimmers $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$ or polymers $\text{K}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ($n > 2$, 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°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°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°C, but above this temperature there is an abrupt downwards change. This

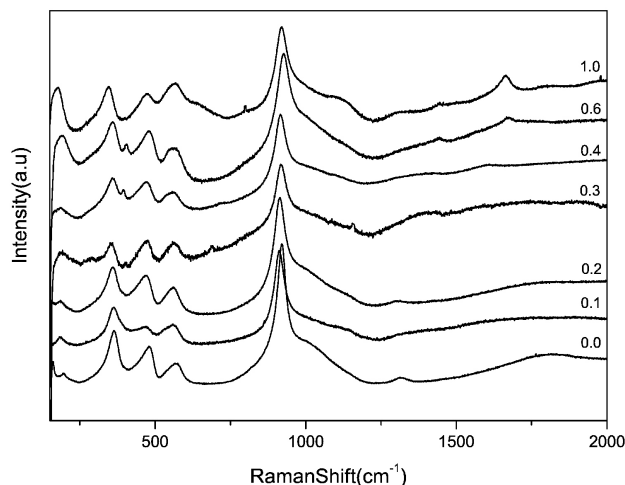


FIGURE 7. Raman spectra of KADPx crystals with $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.6$, and 1.0 , at temperature of 151°C . The compounds retain the vibrational bands that are present in the low temperature region.

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°C is probably responsible for the high conductivity that ADP shows above 154°C [23].

Figure 6 shows Raman spectra of the KADPx ($x=0.1$) recorded in situ at different isotherms between room temperature and 258°C . The spectra show clear changes in the vibrational patterns of the crystal as a function of temperature. (a) The spectra recorded below 155°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°C to that at 193°C , is more evident the presence of the bands at 522 cm^{-1} and 665 cm^{-1} , the appearance of a new band located at 713 cm^{-1} , and a shift of the peak position from 915 cm^{-1} to 910 cm^{-1} . (c) From 206 to 243°C , the spectra show the almost complete extinction of the band located at 183 cm^{-1} , the overlap of the bands at about 473 and 550 cm^{-1} and it is more evident a shift position and broadening of the band at about 901 cm^{-1} , (d) from 243 to 258°C , the presence of new bands at about 966 and 1097 cm^{-1} are evident. From the KADPx ($x=0.1$) 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.

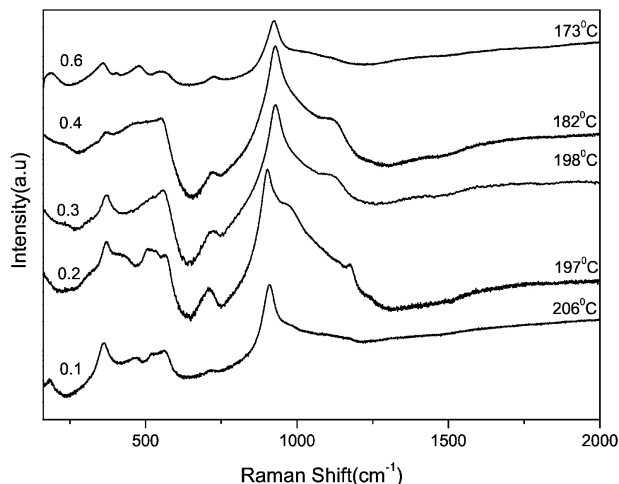


FIGURE 8. Raman spectra of KADPx crystals with $x=0.1, 0.2, 0.3, 0.4$ and 0.6 above 170°C . The isotherm chosen for each concentration depend on the onset temperature where the partial dehydration reaction [8] starts to occur (see text).

The Fig. 7 shows Raman scattering data of the KADPx compounds for temperatures close to 151°C , clearly indicating that each compound maintains the vibrational arrangement adopted in the low temperature region (see Fig. 3i).

The Fig. 8 shows the Raman data for the KADPx at a fixed temperatures above 170°C , depending on the concentration x and it is associated with a characteristic temperature where the corresponding spectrum pattern recorded is quite different from that observed at low temperatures. Comparing this characteristic temperatures for each concentration x , we conclude that it decreases as the concentration increases. This temperature is 173°C for $x=0.6$, close to that of pure ADP, while that for the concentration $x=0.1$ is about 206°C , close to that of pure KDP.

4. Conclusions

The appearance of high proton conductivity in both KDP and ADP near 180°C and 150°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 KADPx 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 KADPx combinations for all concentration x with a common crystallographic tetragonal phase. The composition of the KADPx 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 KADPx 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 x 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 on increasing temperature is also evident by the shift and broadening of the ν_1 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 sug-

gested 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.

Acknowledgements

The authors wish to acknowledge the support of DIMA (Dirección de investigación, Universidad Nacional de Colombia, Sede Manizales) to research project.

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- *. Author to whom correspondence should be addressed: jfjurado@unal.edu.co
1. P. Kumaresan, S. Moorthy Babu, and P.M Anbarasan, *J. Crystal Growth* **310** (2008) 1999-2004.
 2. *Ferroelectrics, special issue on KH₂PO₄-type ferro- and anti-ferroelectrics* **71-72** (1987)
 3. D.A. Boysen, T. Uda, C.R.I. Chisholm, and S.M. Haile, *Science* **303** (2004) 68-70.
 4. T. Uda and S.M. Haile, *Electrochem. Solid State Lett.* **8** (2005) A245-A246.
 5. M. Royle, J. Chao, and S.W. Martin, *J. Non-Crys. Solids* **279** (2001) 97-109
 6. Zikun Li, and Tongbor Tang, *Solid State Ionics* **211** (2012) 34-41
 7. Y. Imry, I. Pelah and E.J. Wiener, *J. Chem Phys.* **43** (1965) 2332-2340, A.I. Baranov, V.P. Khiznichenko and Na. A. Shuvalov, *ferroelectrics* **100** (1989) 135-141
 8. K.E. Lee, *J. Phys. Chem. Solids* **57** (1996) 333-342
 9. R. Blinc, V. Dimic, G. Lahaynar, J. Stepisnik, S. Zumer, and N. Vene, *J. Chem. Phys.* **49** (1968) 4996-5000.
 10. J.Y. Nicholson and J.F. Soest, *J. Chem. Phys.* **60** (1974) 715-716.
 11. R. S. Viswanath, and P. J. Miller, *Solid State Commun.* **29** (1979) 163-166.
 12. R.H. Chen, Chen-Chieh Yen, C.S. Shern, and T. Fukami, *Solid State Ionics* **177** (2006) 2857-2864
 13. B.-K. Choi, *J. Phys. Chem. Solids* **56** (1995) 1023-1030
 14. B.-K. Choi, and J. Korean, *Phys. Soci.* **32** (1998) s515-s517
 15. H.-J. de Jager, and L.C. Prinsloo, *Thermochimica Acta* **376** (2001) 187-196.
 16. D.P. Pereira *et al.*, *Solid State Commun.* **152** (2012) 1023-1026
 17. Y. Kawahata, and Y. Tomina, *Solid State Commun.* **145** (2008) 218-222
 18. D. Xu, and Dongfeng Xue, *J. Crys. Growth* **286** (2006) 108-113
 19. J. A. Subramony, S. Lovell, and B. Kahr, *Chem. Mater.* **10** (1998) 2053-2057, J. A. Subramony, B. J. Marquart, J. W. Macklin, and Bart Kahr, *Chem. Matter.* **11** (1999) 1312-1316.
 20. W.H. Baur, *Acta Crystallographic B* **29** (1973) 2726-2731
 21. G. W. Lu, X. Sun, *Crys. Res. Technol.* **37** (2002) 93-99, G. Lu, C. Li, W. Wang, Z. Wang, J. Guan, H. Xia, *Mater. Science and Eng. B* **116** (2005) 47-53
 22. E. Ortiz, R.A. Vargas and B.-E. Mellander, *J. Phys Chem. Solids* **59** (1998) 305-310
 23. E. Torijano, R.A Vargas, J.E. Diosa, R. Cataño and B.-E. Mellander, *Solid State Ionics* **136-137** (2000) 979-984
 24. V.V. Martsinkevich, and V.G. Ponomareva, *Solid State Ioncs.* (2012), doi:10.1016/j.ssi.2012.04.016(In press)