



## Dehydration and decomposition behavior of the $\text{NaH}_2(\text{PO}_4)_{0,48}\text{AsO}_4)_{0,52} \cdot \text{H}_2\text{O}$ compound in the temperature range from 253 K to 333 K.

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### Abstract

The mixed compound  $\text{NaH}_2(\text{PO}_4)_{0,48}(\text{AsO}_4)_{0,52} \cdot \text{H}_2\text{O}$ , which has been examined by Raman spectroscopy, XRD powder and dielectric, exhibits solid–solid phase transitions and one reversible solid–liquid phase transition. Besides, the investigation of dehydration behavior of sodium dihydrogenate phosphate-arsenate monohydrate was undertaken in a temperature range from 253 K to 333 K. The onset temperature of dehydration was determined from changes in ionic conductivity and X-ray powder on heating. It was confirmed by the Raman study not only in the disappearance of the vibrations assigned to the  $\text{PO}_4$ ,  $\text{AsO}_4$  but also in the appearance of the new vibrations attributed to the  $(\text{PO}_3)_x$ , which constitutes the P-O-P chain, giving a polymer with the formula:  $\text{NaH}_2(\text{P}_2\text{O}_7)_x(\text{As}_2\text{O}_7)_{(1-x)}$ . The important variation was observed in all studies at 313 K, which could correspond to the transformation of the NDAP compounds of a solid crystal into a liquid form.

**Keywords:** Phase transition; Raman Spectroscopy; XRD powder; Ion conductivity; Dehydration-Decomposition.

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## 1. INTRODUCTION

The mixed compound  $\text{NaH}_2(\text{PO}_4)_{0.48}(\text{AsO}_4)_{0.52}\cdot\text{H}_2\text{O}$  (denoted by NDAP) [1], which is crystallized in the orthorhombic system with a space group of  $\text{P2}_1\text{2}_1\text{2}_1$  has revealed three reversible solid–solid phase transitions and one reversible solid–liquid phase transition below the decomposition point at  $T_d = 391$  K. This material belongs to a group of compounds that have intermediate properties between those of a normal salt and an acid, and undergoes a transition from a paraelectric to a superprotonic phase at room temperature [2] This is an important discovery for the compounds derived from the KDP family ( $\text{KH}_2\text{PO}_4$ ) of the general formula  $\text{MH}_2\text{XO}_4$  (where M is a monovalent cation: K, Rb, Cs and X is P or As), whose use is possible in technological applications (fuel cells ...). The superprotonic phase of NDAP exhibits greater proton conductivity than  $1.07 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  to 296 K [3], and stability at room temperature. In fact, the compounds of the formula  $\text{MH}_2\text{XO}_4$  have all been studied excluding those in which M is sodium because the latter is not stable at room temperature except in the hydrated state. In this process, the structural phase transitions in similar compounds KDP, RDP and CDP are located at high temperature 453, 359 and 503.8 K, respectively. Besides, the room temperature crystal structures are maintained up to the decomposition of a tetragonal structure for KDP and RDP and a monoclinic symmetry for CDP. The thermal dehydration takes place at the surface of the salts [4] which can be described by the formation of  $\text{K}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ,  $\text{RbH}_2\text{PO}_4 + \text{Rb}_2\text{H}_2\text{P}_2\text{O}_7$  and  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$  [5-7], respectively .

This work is an attempt to figure out and explain the mechanisms of the transition and dehydration of the title compound above room temperature, building on the studies of Raman, XRD powder and ac-conductivity. Thus, it is important to study this transition which consists in the passage of a solid state to an intermediate state described by liquid crystals that are present just before the start of decomposition.

## 2. EXPERIMENTAL

Raman spectra were measured with a powder sample between 253 K and 333 K by a HR800 micro-Raman spectrometer (Jobin Yvon Horiba, Longjumeau, France), equipped with a He–Ne laser emitting at 633 nm with a power of 20 mW in the range of  $50\text{--}4000 \text{ cm}^{-1}$ . The instrument was directly controlled by a PC equipped with the software “LabSpec” (Jobin Yvon Horiba, Longjumeau, France). The measurements, whose objective has a magnifying power of 100x in an open furnace (Under the air, at an ambient pressure) on a heating from 253 to 333 K, were carried out under BX40 microscope and had a focal gradation of  $1\mu\text{m}$ . It is worth noting that only the temperature range (303-333 K) would be discussed here because, with the exception of a classical narrowing and weak shift of the bands, a non spectral change occurred between 253 and 303 K. The heating rate was 5 K/min, waiting for 5 min after temperature stabilization and collecting time for each spectrum was 10 min. The measurements of the complex dielectric permittivity ( $\epsilon^* = \epsilon' - j\epsilon''$ ), were performed over a frequency interval of  $10^1\text{--}10^6$  Hz and in a temperature range of 233 to 323 K. To cover the above frequency range, a NOVOCONTROL spectrometer integrating an ALPHA dielectric interface was employed with a precision in  $\tan\delta = \epsilon''/\epsilon' = 10^{-5}$ . In these experiments, the temperature was controlled by a nitrogen jet (QUATRO from Novocontrol) with a  $\pm 0.1$  K temperature error, during every single sweep in frequency. Conductivity is usually associated with the generation and transport of polarization-induced charges through the compound under the action of an electric field. The X-ray powder diffraction patterns were collected from samples at various levels of dehydration. Diffraction patterns were measured between 283 and 333 K using a Philips X’Pert Pro (Cu-K $\alpha$ , 40 kV, 40 mA) at a scan rate of  $0.6^\circ 2\theta \text{ min}^{-1}$  with an angular resolution of  $0.02^\circ$ .

## 3. RESULTS AND DISCUSSION

All the results achieved by Raman spectroscopy at different temperatures are gathered in (Fig.1).

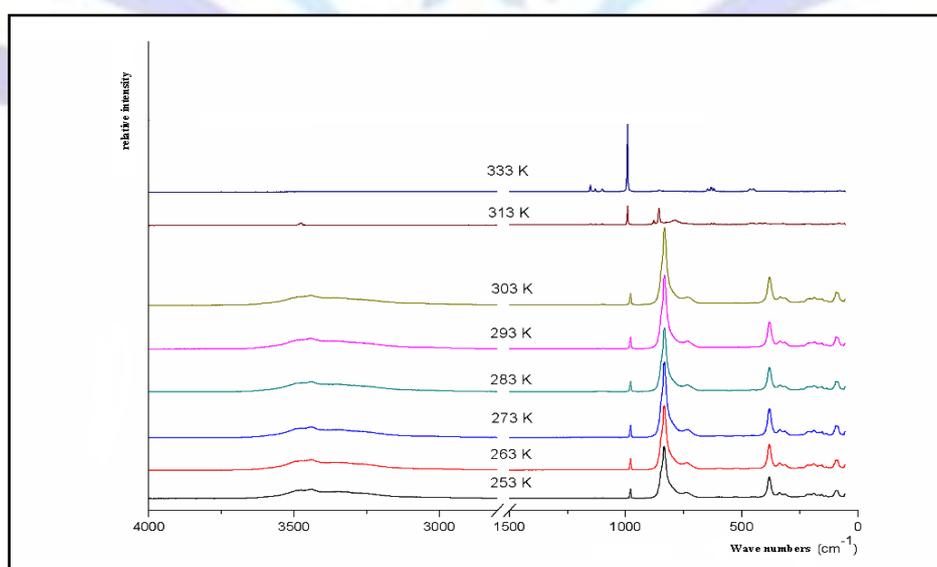


Fig.1. Raman spectra of crystalline  $\text{NaH}_2(\text{PO}_4)_{0.48}(\text{AsO}_4)_{0.52}\cdot\text{H}_2\text{O}$  between 253 and 333 K



### 3.1. Before 313 K: state solid form of NDAP

The internal vibrations in Raman spectra of the PO<sub>4</sub> tetrahedra are presented in Table 1. The symmetric stretching ν<sub>1</sub> at 985 cm<sup>-1</sup> is active with an intense peak, which is a characteristic of this group. ν<sub>2</sub>(PO<sub>4</sub>) appears at 382 cm<sup>-1</sup> with a strong peak. In the same vein, an intense peak appears at 848 cm<sup>-1</sup>, which corresponds to a typical vibration of (P-OH). A broad stretching vibration at 745 cm<sup>-1</sup> corresponding to ν<sub>1</sub>(AsO<sub>4</sub>) and a vibration at 824 cm<sup>-1</sup> assigned to ν<sub>3</sub>(AsO<sub>4</sub>) are also detected. However, ν<sub>3</sub>(PO<sub>4</sub>) that appeared at 838 cm<sup>-1</sup> is invisible because it is embedded in the strong peak measured at 848 cm<sup>-1</sup>. Furthermore, two weak peaks at 324 and 338 cm<sup>-1</sup> associated with ν<sub>2</sub> of AsO<sub>4</sub> can be observed. The presence of the broad peaks detected at 3354, 3459 and 3491 cm<sup>-1</sup> corresponds to ν<sub>1</sub> and ν<sub>3</sub> of water, respectively. What should be noted from the irrational spectra is that the strength

**Table 1.** Wave numbers (cm<sup>-1</sup>) and relative intensities of the bands in the Raman spectra of NaH<sub>2</sub>(PO<sub>4</sub>)<sub>0.48</sub>(AsO<sub>4</sub>)<sub>0.52</sub>.H<sub>2</sub>O : (before, at and after 313 K).

Before 313	At 313	After 313	Assignments
56 w	56 vw	56 vw	<b>Lattice vibrations</b>
95 s 135 m 156 vw 195 w		-	δ O...O
209 vw 220 w		-	O...H-O vibrations □
324 w 338 w	324 w	-	ν <sub>2</sub> (AsO <sub>4</sub> )
382 vs	382 vw		ν <sub>2</sub> (PO <sub>4</sub> )
-	-	455 w 469 w 629 m 640 m 658 m	δ(PO <sub>3</sub> ) et ρ (PO <sub>3</sub> )
745 mb	-		ν <sub>1</sub> (AsO <sub>4</sub> )
824 vs	794 s		ν <sub>3</sub> (AsO <sub>4</sub> )
848 vs	862 s		ν (P-OH)
		862 w	ν (As <sub>2</sub> O <sub>7</sub> ) <sup>4-</sup>
985 s	985 s		ν <sub>1</sub> (PO <sub>4</sub> )
-		991 s	ν <sub>1</sub> (PO <sub>3</sub> )
-	-	1116 w 1145 w 1167 w	ν <sub>3</sub> (PO <sub>3</sub> ) & (P-O-P)
1637 wb 3354 vb 3459 vb 3491 vb	1637 wb 3459 m	-	ν <sub>1</sub> (H <sub>2</sub> O) ν <sub>3</sub> (H <sub>2</sub> O)

δ: bending ; ρ: rocking ; ν: stretching  
s: strong ; m: medium ; w : weak ; b: epaulement



and the type of O–H...O hydrogen bonds remain practically the same in the strong hydrogen bonded crystals such as  $\text{KH}_2\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{CsHSO}_4$  and  $\text{CsH}_2\text{PO}_4$  [8-11]. The corresponding OH stretching vibration gives rise to broad bands characteristics at  $3467$  and  $1637\text{ cm}^{-1}$ , associated with strong hydrogen bonded systems [12, 13]. The diffraction diagram of X-ray powder corresponds to that of the monohydrate compound NDAP performed at  $293\text{ K}$  and will be used as a reference (Fig.2).

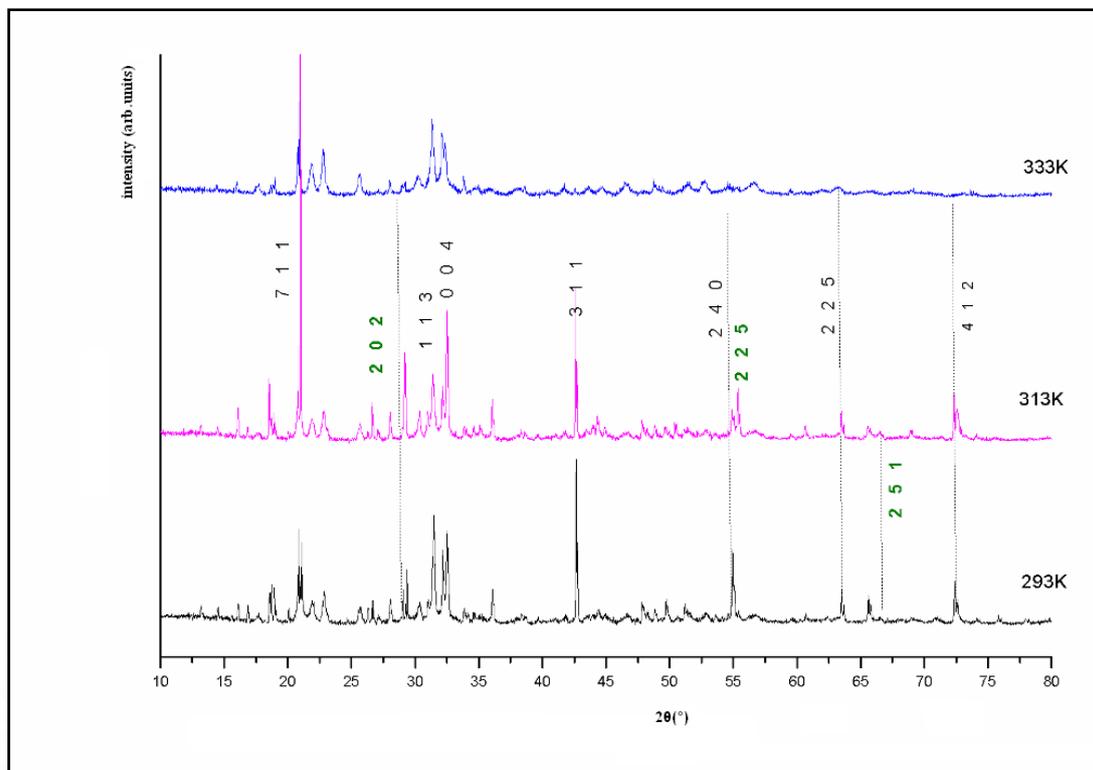
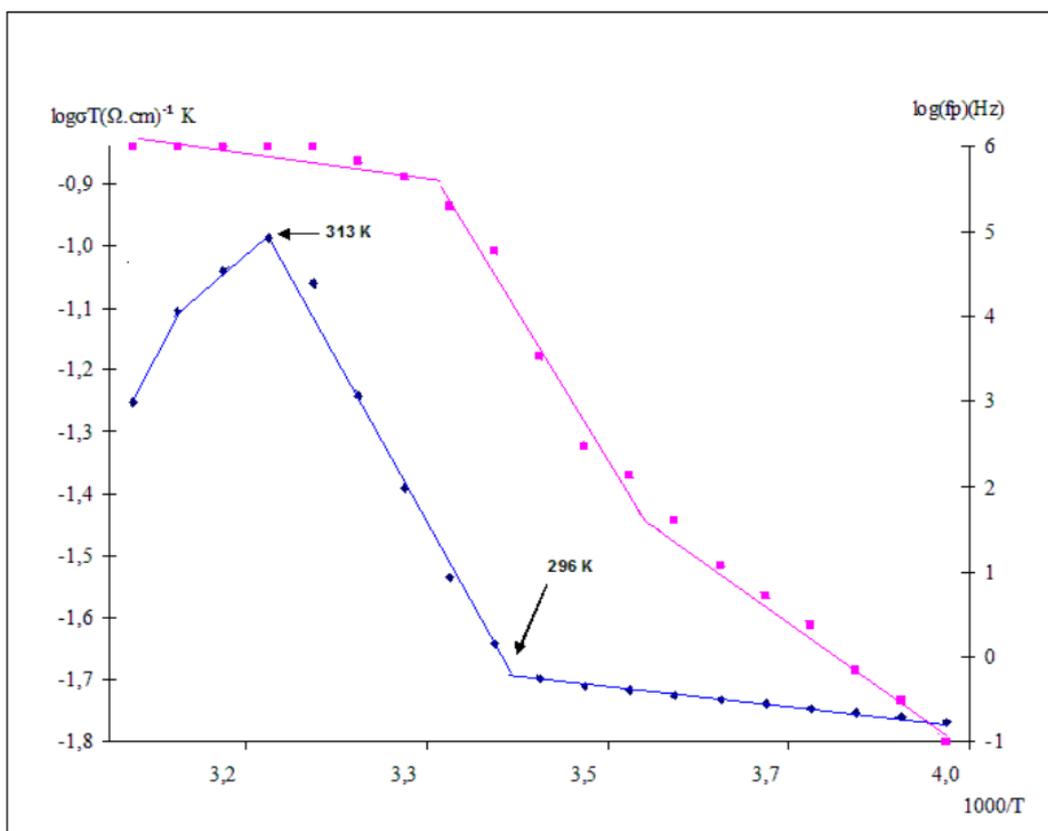


Fig.2. X-ray powder diffraction for NDAP material at 293; 313 and 333 K

### 3.2. At 313 K: liquid crystal form of NDAP

As can be seen from (Fig.1), the rise of temperature to  $313\text{ K}$  shows modifications in the Raman spectra of this compound, these changes are detected firstly by the decrease-increase in some peaks intensity and secondly by the translation of others. In fact, the decrease of the intensity of the peaks at  $382\text{ cm}^{-1}$  assigned to  $\nu_2(\text{PO}_4)$  and the increase of the intensity of the peaks at  $985\text{ cm}^{-1}$  are assigned to  $\nu_1(\text{PO}_4)$  [14]. Besides, the translation and decrease of the intensity of the peaks at  $862$  and  $794\text{ cm}^{-1}$  are attributed to  $\nu(\text{P-OH})$  and  $\nu_3(\text{AsO}_4)$ , respectively. Moreover, the peaks characteristics to the  $\nu_2(\text{AsO}_4)$  at  $324\text{ cm}^{-1}$  are shown to keep the same place. The appearance of a one-medium peak at  $3459\text{ cm}^{-1}$  instead of three broad peaks at ( $3354$ ,  $3459$  and  $3491\text{ cm}^{-1}$ ) is related to the symmetric stretching  $\nu_1$  and  $\nu_3(\text{H}_2\text{O})$ . The disappearance of the lines at  $209$  and  $220\text{ cm}^{-1}$  characterizes the change of the O...H–O vibrations. On the other hand, a change in the X-ray diagram carried out at  $313\text{ K}$  can be noted. Indeed, the appearance of new peaks represented by hkl [202] and [225] and the disappearance of the peak represented by [251] are detected (Fig.2). These modifications in the two analyses (Raman & DRX) confirm the presence of the phase transition in this temperature [15].

Indeed, this family of compounds is characterized by large proton conduction due to the presence of hydrogen located between the tetrahedra and voids in the unit cell to facilitate the migration of the proton so as to assure the high conduction near the temperature of decomposition [2, 16]. This transformation is shown by the breaking of hydrogen bonding. What leads us to confirm this conclusion is the decrease of proton conductivity with temperature higher than that of the processing and the analysis of the variation of conductivity as a function of temperature. (Fig.3) displays the evolution of the conductivity versus inverse temperature  $\log_{10}(\sigma T) = f(1000/T)$  for NDAP compound in the temperature range of  $233$ - $333\text{ K}$ . An Arrhenius-type  $\sigma T = \sigma_0 \exp(-\Delta E_0/kT)$  characterizes the low and high temperature domain until  $313\text{ K}$ . After this temperature, fast conductivity decreases from  $13.6 \times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$  to  $7.5 \times 10^{-5}\ \Omega^{-1}\text{cm}^{-1}$  at  $323\text{ K}$ . This rapid change in conductivity may be due to a shift in the atomic arrangement of the compound. Indeed, this family is characterized by high protonic conductivity owing to the presence of hydrogen located between the tetrahedra and the interstitial voids facilitate the migration of its protons to ensure a high conductivity near the decomposition temperature [16]. This transformation may be accredited to changes in hydrogen bonds. This hypothesis is confirmed by the analysis of the spectra of X-ray diffraction powder that shows a change in the number and the location of some diffraction peaks [15, 17].



**Fig.3. Temperature dependencies of  $\log(\sigma T)$  and  $\log fp = f(1000/T)$ , where  $fp$  is the M<sup>max</sup> peak frequency for NDAP**

Based on a previous thermal study made by DSC and DTA analysis [2], no mass loss is associated with the solid – liquid phase transition at this temperature. This phase transition is also reversible of a second order type and an order-disorder character, with a gap of temperature of 0.5 K and  $\Delta H = 2.02 \text{ kJmol}^{-1}$ .

Furthermore, from the studies of Raman, XRD powder and ac-conductivity, we can come to the conclusion that the NDAP compounds were transformed from a solid crystal, before 313 K, to an intermediate state described by a liquid crystal form at 313 K. This may be due to the dynamic disorder, by elevating the temperature of the acidic protons on the hydrogen bond network linking  $\text{P(As)O}_4$  groups and to the order or disorder type of the  $\text{P(As)O}_4$  tetrahedra. The latter affects the motion of hydrogen atoms and increases the reorientational movement of the anions  $\text{H}_2\text{P(As)O}_4^-$  tetrahedra as well as the increased thermal agitation.

### 3.3 At 333 K: dehydration-decomposition

The evolution of the line in (Fig.1) is an important modification pertaining to the hydrogen bonds; the loss of water is very face observed with the disappearance of the vibrations near  $3400 \text{ cm}^{-1}$ . At the same time, there are significant changes of positions and intensity of some bonds corresponding to the internal vibrations of  $\nu(\text{PO}_4)$  and  $\nu(\text{AsO}_4)$ . It is worthy to note that there is a disappearance of the peak at  $985 \text{ cm}^{-1}$  attributed to  $\nu_1(\text{PO}_4)$  and substituting new strong peak at  $991 \text{ cm}^{-1}$  assigned to the stretching vibrations of  $\nu_1(\text{PO}_3)$ . There are also other three weak peaks that appear at 1116, 1145 and  $1167 \text{ cm}^{-1}$  respectively, which are attributed to  $\nu_3(\text{PO}_3)$  and (P-O-P) vibrations. The appearance of the weak lines at  $455, 469 \text{ cm}^{-1}$  and medium triobonds at  $629, 640$  and  $658 \text{ cm}^{-1}$  correspond to  $\delta(\text{PO}_3)$  and  $\rho(\text{PO}_3)$ , respectively.

The important spectral alterations observed at 333 K correspond to the chemical transformation in  $\text{P(As)O}_4^{3-}$  to  $\text{P}_2\text{O}_7^{4-}$  and  $\text{As}_2\text{O}_7^{4-}$  ions, as in the similar compounds  $\text{CsH}_2\text{PO}_4$  [18]. Thus, when  $\text{NaH}_2(\text{PO}_4)_{0.48}(\text{AsO}_4)_{0.52} \cdot \text{H}_2\text{O}$  is heated, it tends to quickly lose its water, leading to a dehydration starting from 333 K. Indeed the compound is transformed into an infinite chain of polyphosphate-arsenate connected by P(As)-O-P(As) bridge. Therefore, it loses two molecule of water of its components, and constitutes a condensed phosphate-arsenate including polymer with the formula:  $\text{NaH}_2(\text{P}_2\text{O}_7)_x(\text{As}_2\text{O}_7)_{(1-x)}$  according to the decomposition reaction such as that proposed by Lee [5]. The diffraction X-ray powder NDAP compound carried out at 333 K given in (Fig.2) shows the changes in the positions and intensities of several diffraction peaks from the diffractogram conducted at  $T = 313 \text{ K}$ .

X ray powder at 333 K corresponds to the dehydration-decomposition of NDAP hydrate. The latter can be shown by the DSC and ATD for previous studies [2], in which the total weight loss of this sample was 11 % corresponding well to

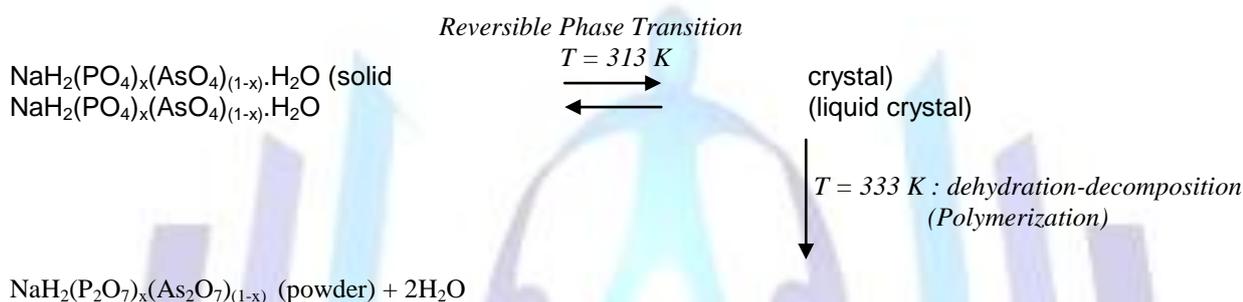


the formation of  $\text{Na(P/As)O}_3$ . The transformation to  $\text{Na(P/As)O}_3$  requires the coordinated rearrangement of all the phosphate-arsenate anions to form the metaphosphate-arsenate chain  $[\text{P(As)O}_3]_\infty$ .

#### 4. CONCLUSION

The present study has shown that the transformation of the NDAP compounds of a solid crystalline form before 313 K to a liquid crystal at 313 K is relevant. This hypothesis opens the horizon for another study on this compound at this temperature. Another significant change was observed at 333 K corresponding to the chemical transformation in  $\text{P(As)O}_4^{3-}$  to  $\text{P(As)}_2\text{O}_7^{4-}$  ions. These findings have proven that the compound is transformed into an infinite chain of polyphosphate-arsenate connected by (P/As)-O-(P/As) bridge losing water of constituents.

It can be concluded that the dehydration-decomposition of  $\text{NaH}_2(\text{PO}_4)_{0.48}(\text{AsO}_4)_{0.52} \cdot \text{H}_2\text{O}$  begins at 333 K giving a polymer of the formula  $\text{NaH}_2(\text{P}_2\text{O}_7)_x(\text{As}_2\text{O}_7)_{(1-x)}$ . The following reaction can be suggested:



Finally, what differentiates NDAP from other similar compounds (RDP, CDP and KDP) is not only its low decomposition temperature but also its passage through an intermediate state "liquid crystal" just before its polymerization and not by the formation of liquid superficial detected in all other similar compounds. This is strongly linked to its structural properties:

- Presence of alkaline sodium
- Structural disorder by partial substitution of phosphorus by arsenic.
- Presence of a structural water molecule.

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## FIGURE CAPTIONS

Figure 1 Raman spectra of crystalline  $\text{NaH}_2(\text{PO}_4)_{0.48}(\text{AsO}_4)_{0.52}\cdot\text{H}_2\text{O}$  between 253 and 333 K

Figure 2 X-ray powder diffraction for NDAP material at 293; 313 and 333 K

Figure 3 Temperature dependencies of  $\log(\sigma T)$  and  $\log f_p = f(1000/T)$  where  $f_p$  is the  $M^{\text{th}}$ max peak frequency for NDAP

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