Structural, Thermal behaviour and Vibrational study of a new Cesium-Ammonium Dihydrogen Phosphate–Arsenate: \( \text{Cs}_{0.55}(\text{NH}_4)_{0.45}\text{H}_2(\text{PO}_4)_{0.39}(\text{AsO}_4)_{0.61} \)

Samia CHAUCHENE, Khaled JAOUADI*, Tahar MHIRI, Nabil ZOUARI

Laboratoire physico-chimie de l’état solide, Faculté des Sciences de Sfax, BP 1171, 3038 Sfax, Tunisie

chouchane.samia@gmail.com
khaledjaouadi@yahoo.fr
taharmhiri@yahoo.fr
bizrirl@yahoo.fr

ABSTRACT

Mixed crystals \( \text{Cs}_{0.55}(\text{NH}_4)_{0.45}\text{H}_2(\text{PO}_4)_{0.39}(\text{AsO}_4)_{0.61} \) (CADPA) of the two antiferroelectric \( \text{NH}_4\text{H}_2\text{PO}_4 \) (ADP) and \( \text{NH}_4\text{H}_2\text{AsO}_4 \) (ADA) and of the two ferroelectric \( \text{CsH}_2\text{PO}_4 \) (CDP) and \( \text{CsH}_2\text{AsO}_4 \) (CDA) have been prepared by slow evaporation from aqueous solution at room temperature. The structural properties of the crystal were characterized by X-ray single analysis (performed at room temperature), which revealed that (CADPA) crystallizes in space group \( I4_2d \) with lattice parameters: \( a = 7.6473(1) \, \text{Å}, \ c = 7.6803(1) \, \text{Å} \) and \( Z = 4 \). The title compound is isostructural with the tetragonal phases of (ADP) and (ADA). This structure is characterized by two kinds of disorder: a statical or dynamical disorder of the acidic proton in the \( \text{O–H…O} \) hydrogen bond and another one which is connected with a reorientational motion of \( \text{NH}_4^+ \) ions. Broader peaks in the IR spectrum confirm a structural disorder in this material. Thermal analysis of the (CADPA) were characterized by differential scanning calorimetry (DSC), showed that the title compound undergo two phase transitions at \( T = 204 \, \text{K} \) and \( T = 407 \, \text{K} \).

Indexing terms/Keywords

Inorganic materials; \( \text{Cs}_{0.55}(\text{NH}_4)_{0.45}\text{H}_2(\text{PO}_4)_{0.39}(\text{AsO}_4)_{0.61} \); X-Ray diffraction; IR spectroscopy; Thermal behavior.
1. INTRODUCTION

The KDP family compounds (MH\textsubscript{2}XO\textsubscript{4} with M = NH\textsubscript{4}, K, Rb, Cs and X = P, As) have been of continuing interest due to their structural and physical properties [1–6]. This series offers an opportunity of examining a structure type with various combinations of the cationic and anionic substitution groups. The appearance of the high proton mobility in these types of compounds on heating above room temperature, is accompanied by a solid–solid phase transition and another one on cooling. Ammonium dihydrogen phosphate and arsenate, NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} (ADP) and NH\textsubscript{4}H\textsubscript{2}AsO\textsubscript{4} (ADA) are very interesting compounds belonging to the above category of materials. At room temperature (ADP) and (ADA) are paraelectric and crystallize in the tetragonal system I\textbar 42d. The structures of these materials are formed of (H\textsubscript{2}PO\textsubscript{4}) or (H\textsubscript{2}AsO\textsubscript{4}) groups linked by short hydrogen bonds parallel to (a, b) plane [5]. Both compounds became antiferroelectric in two phases below room temperature, at 148 K and 216 K and show a further high temperature phase transitions at 433 K and 355 K, respectively [6–8]. The NH\textsubscript{4}H\textsubscript{2}(PO\textsubscript{4})\textsubscript{0.52}(AsO\textsubscript{4})\textsubscript{0.48} (ADPA) has an interesting three dimensional network, composed of two interpenetrating sets of body-centered sublattice of (AsO\textsubscript{4}, PO\textsubscript{4}) tetrahedra, and is also composed of two interpenetrating sets of body-centered sublattice of NH\textsubscript{4}\textsuperscript{+} ions. NH\textsubscript{4}\textsuperscript{+} and structures, P\textsuperscript{5+}(As\textsuperscript{5+}) ions are alternately arranged in different layers. These layers are perpendicular to the c-axis and are spaced from each other by a distance of 1/4 c. Further interaction linkages are provided by strong O–H…O and N–H…O hydrogen bonds. The DSC analyses of (ADPA) show three anomalies at 193, 418 and 475 K corresponding respectively, to paraelectric–antiferroelectric, superprotonic phase transitions and to the melting point [9–10]. The aims of this work were: (i) to examine the influence of a partial anionic and cationic substitutions over crystalline symmetry and physical properties, (ii) to characterise spectroscopically this phase, (iii) to evidence the phase transitions in (CADPA) and (iv) to determine the dynamic of proton in the O–H…O hydrogen bonds.

In the present study, we report and discuss the results of a structural investigation, concerning a new solid solution: Cs\textsubscript{55}(NH\textsubscript{4})\textsubscript{45}H\textsubscript{2}(PO\textsubscript{4})\textsubscript{0.39}(AsO\textsubscript{4})\textsubscript{0.61}. We have performed preliminary X-ray diffraction measurements providing us information about the complete crystal structure at room temperature of the new compound. This structural study is accompanied by infrared and Raman measurements, and we try to evidence the phase transitions in (CADPA) by differential thermal analysis.

2. EXPERIMENTAL

2.1. Crystal growth and characterization

Single crystals of the title compound were grown from an aqueous stoichiometric solution of cesium carbonate Cs\textsubscript{2}CO\textsubscript{3}, Ammonium carbonate (NH\textsubscript{4})\textsubscript{2}CO\textsubscript{3}, orthophosphoric acid H\textsubscript{3}PO\textsubscript{4} and orthoarsenic acid H\textsubscript{3}AsO\textsubscript{4} with the following reaction:

\[
(1-x)(\text{NH}_4)_2\text{CO}_3 + x\text{Cs}_2\text{CO}_3 + 2y\text{H}_3\text{PO}_4 + 2(1-y)\text{H}_\text{AsO}_4 \rightarrow 2(\text{NH}_4)_\text{1.55}\text{Cs}_\text{0.45}(\text{PO}_\text{4.39})(\text{AsO}_\text{4.61}) + \text{H}_2\text{O} + \text{CO}_2
\]

The resulting solution is kept under ambient conditions, which was allowed to evaporate slowly. A few days later, colorless, transparent and lamellar-shaped crystals with a size about (0.22 x 0.25 x 0.28) mm\textsuperscript{3} of (CADPA) were obtained. The formula of this material was determined by chemical analysis and confirmed by structural refinement.

Infrared absorption spectra of suspensions of crystalline powder KBr were recorded on Perkin–Elmer FTIR 420 spectrophotometer in the range 400–4000 cm\textsuperscript{–1}. Raman spectra of polycrystalline samples sealed in glass tubes, were performed employing a RTI Dilor instrument using the 514.5 nm line of a spectra-physics argon ion laser, in the range 50–1300 cm\textsuperscript{–1}. Calorimetric measurements were performed between 173 and 673 K on a Mettler TA 4000 differential scanning calorimeter under the following conditions: heating rate of 3 K min\textsuperscript{–1}, sample weight of 23 mg and sensitivity of 10 µV. mW\textsuperscript{–1}.

2.2. Intensity data collection and refinement

A single-crystal of the title compound was selected from the homogeneous powder using an optical microscope. Intensities of the diffraction data were measured using an Enraf Nonius Kappa CCD diffractometer, using graphite monochromatized MoK\textalpha radiation (\lambda = 0.71069 Å). The unit cell parameters optimized by least-squares refinement, were calculated and refined using indexation of the collected intensities. The raw intensity data were corrected for Lorentz and polarizing effects before proceeding to the refinement of the structure. An absorption correction was performed with the program SADABS [11]. Atomic scattering factors were taken from the International Tables for X-ray crystallography [12]. 2465 reflections were collected in the whole Ewald sphere for 1.23 ≤ θ ≤ 34.24. Classical methods for structure determination were used. X-ray examinations at room temperature indicate that the space group in phase I is I\textbar 42d. We solved the structure by first locating cesium atom position using SHELXS-97 [13], and subsequently the remaining non-hydrogen atoms were deduced from difference Fourier maps during the refinement of the structure with SHELXL-97 program [14]. The H atoms were located through difference maps with the aid of a calculation of bond distances and angles. We started the refinement with the H-atom of the acidic groups, situated on the two-fold axis between two phosphate–arsenate groups, in the middle of the hydrogen bridge. In the first refinement, the H-atoms were found to have a markedly anisotropic thermal motion with the large amplitude directed approximately along the O…O line. So a disorder model for H-atom of the acidic groups was tried, with half occupancy of two general positions symmetrically displaced from a two-fold axis, which is located between two phosphate–arsenate groups (double-well potential model). Full matrix refinement with anisotropy thermal parameters for all atoms converged to a final R value of 0.0272. The details of data collection and refinement for the title compound are summarized in Table 1. The final fractional atomic coordinates...
and the equivalent anisotropic thermal parameters for all (non-H) atoms are given, respectively in Tables 2 and 3. The structure graphics were created by the Diamond program [15].

Table 1: Main crystallographic feature, X-ray diffraction data parameters results of Cs$_{0.55}$(NH$_4$)$_{0.45}$H$_2$(PO$_4$)$_{0.39}$(AsO$_4$)$_{0.61}$

<table>
<thead>
<tr>
<th>Formula</th>
<th>Cs$_{0.55}$(NH$<em>4$)$</em>{0.45}$H$_2$(PO$<em>4$)$</em>{0.39}$(AsO$<em>4$)$</em>{0.61}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>I42d</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.64730(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.68030(10)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>449.153(10)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>F(000)</td>
<td>572</td>
</tr>
<tr>
<td>Formula weight (g mol$^{-1}$)</td>
<td>317.82</td>
</tr>
<tr>
<td>μ (mm$^{-1}$)</td>
<td>21.509</td>
</tr>
<tr>
<td>ρ cal (g cm$^{-3}$)</td>
<td>4.700</td>
</tr>
<tr>
<td>Morphology</td>
<td>prismatic</td>
</tr>
<tr>
<td>Color</td>
<td>colorless</td>
</tr>
<tr>
<td>Maximum crystal dimensions</td>
<td>0.22x 0.29x0.11 mm</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Kappa CCD</td>
</tr>
<tr>
<td>Theta range (°):</td>
<td>1.23 ≤ θ ≤ 34.24</td>
</tr>
<tr>
<td>h</td>
<td>-9 ≤ h ≤ 10</td>
</tr>
<tr>
<td>k</td>
<td>-10 &lt; k &lt; 10</td>
</tr>
<tr>
<td>l</td>
<td>-10 &lt; l &lt; 10</td>
</tr>
<tr>
<td>Refined parameters</td>
<td>17</td>
</tr>
<tr>
<td>Reflections observed with F$_0$ &gt; 4 σ (F$_0$)</td>
<td>463</td>
</tr>
<tr>
<td>Total reflections</td>
<td>2465</td>
</tr>
<tr>
<td>R$_1$ = [F$_2$ &gt; 4σ (F$_2$)]</td>
<td>0.0272</td>
</tr>
<tr>
<td>WR$_2$ (F$_2$)</td>
<td>0.0698</td>
</tr>
<tr>
<td>ρ min (e Å$^{-3}$)</td>
<td>-0.496</td>
</tr>
<tr>
<td>ρ max (e Å$^{-3}$)</td>
<td>0.880</td>
</tr>
</tbody>
</table>

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$WR_2 = \frac{\sum w(F_o^2 + 2F_c^2)^2}{\sum w(F_o^2)^2}^{1/2}$$

$$w^{-1} = [a^2(F_o^2) + (0.0527 P)^2 + 0.3136 P]$$

$$P = (F_o^2 + 2F_c^2)/3.$$
Table 2: Fractional atomic coordinates and temperature factors for CADPA

<table>
<thead>
<tr>
<th>ATOMS</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Ueq</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0194(2)</td>
<td>0.612(15)</td>
</tr>
<tr>
<td>P</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0194(2)</td>
<td>0.388(11)</td>
</tr>
<tr>
<td>Cs</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.0327(7)</td>
<td>0.553(14)</td>
</tr>
<tr>
<td>N</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.0327(7)</td>
<td>0.447(12)</td>
</tr>
<tr>
<td>O</td>
<td>0.1547(3)</td>
<td>0.0870(3)</td>
<td>0.1208(4)</td>
<td>0.0340(7)</td>
<td>1</td>
</tr>
<tr>
<td>H(N)</td>
<td>-0.0285</td>
<td>0.1186</td>
<td>0.4486</td>
<td>0.050</td>
<td>1</td>
</tr>
<tr>
<td>H(O)</td>
<td>0.1483</td>
<td>0.2172</td>
<td>0.1199</td>
<td>0.050</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\[ U_{eq} = \frac{1}{3} \sum_{i<j} U_{ij} a_i^* a_j^* \]

Table 3: Anisotropic displacement parameters of CADPA

<table>
<thead>
<tr>
<th>Atomes</th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{23}</th>
<th>U_{13}</th>
<th>U_{12}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.0167(3)</td>
<td>0.0167(3)</td>
<td>0.0248(3)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>As</td>
<td>0.0167(3)</td>
<td>0.0167(3)</td>
<td>0.0248(3)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Cs</td>
<td>0.0361(10)</td>
<td>0.0361(10)</td>
<td>0.0259(11)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>N</td>
<td>0.0361(10)</td>
<td>0.0361(10)</td>
<td>0.0259(11)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O</td>
<td>0.0321(12)</td>
<td>0.0248(10)</td>
<td>0.0452(13)</td>
<td>-0.0084(10)</td>
<td>-0.0135(11)</td>
<td>0.0070(8)</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. Structural study

Fig. 1 shows a perspective drawing of (CADPA) with atom labeling. The results obtained confirmed that (CADPA) is tetragonal with lattice parameters intermediate between those of (ADP) and (ADA) pure compounds and superior to those of (ADPA). Its structure consists of (P/As)O₄ and Cs/NH₄ groups held together by O-H…O and N-H…O hydrogen bonds. The mean feature of this structure, is the simultaneously coexistence of two different anions (PO₄³⁻ and AsO₄³⁻) and two different cations (Cs⁺ and NH₄⁺) in the same crystal. If we compare this structure to (ADP), (ADA), (ADPA) and (KDP) [5, 9, 16], we conclude that, there is a great similarity between the atomic arrangement in all these compounds. The phosphorus and the arsenic atom as well as the ammonium and cesium ions lie on points with site symmetry S₄, the oxygen atoms lie in general positions about the phosphorus–arsenic atoms, in a tetrahedral arrangement (Fig. 1). The (P/As)O₄ tetrahedra are connected by O-H…O hydrogen bonds laying essentially in the a,b plane (Fig. 2). The distance between two oxygen participating in the formation of O-H…O hydrogen-bonding are equal to 2.506 Å, they are slightly longer than those for (ADP) (2.490 Å) and for (ADPA) (2.500 Å) and slightly shorter than those found in the structure of (ADA) (2.512 Å). The high-resolution neutron diffraction study of (KDP) has resolved two peaks in the proton-density distribution map of the H-bond of 2.495 Å [16, 17], this result indicates that the proton in the crystallographically symmetric H-bond O-H…O in (CADPA) will also certainly be disordered. In the (CADPA) structure, we observe one type of (P/As)O₄ tetrahedra. The main interatomic distances and bond angles for this tetrahedra are given in Table 4. An important point in this structure, that the value of (P/As)-O distances (P/As-O = 1.624 Å) are intermediate between those of As-O distance (As-O = 1.682 Å) in (ADA), and P-O distance (P-O = 1.537 Å) in (ADP) pure compounds and they are slightly longer than those for (ADPA) (1.605 Å). (PO₄³⁻/AsO₄³⁻) tetrahedra are slightly flattened into the (001) plane as can be seen from the values of the angles O-(P/As)-O (Table 4). This seems to be mainly due to the pull exerted by the hydrogen bonds O-H…O which are positioned in the (001) plane, between the different tetrahedra.
It is well known, that A-OH (A = P or As) distances are in general longer than A-O distances, and that A-OH distances increase as the strength of the hydrogen bond O-H...O increases, that is, as O...O decreases [18]. In our investigation of this structure, we can notice the equality of (P/As)-O and (P/As)-OH distances; this can be interpreted as a result of a disorder in (CADPA) compound. Similar effects have been reported in other crystals of the (KDP) family [16]. In many hydrogen-bonded ferroelectrics, it is usual for the protons to be disordered in the paraelectric phase and to become ordered in the ferroelectric phase. In (CADPA), on the basis of the hydrogen bonds network and of all (P/As)-O bonds in each (PO$_4^{3-}$, AsO$_4^{3-}$) tetrahedra, we can conclude that the interphosphate–arsenate hydrogen bonds in the present structure are disordered, and because of the presence of a two-fold axis, they are symmetric. So it is better to describe the H atom in the O-H...O bond as disordered with one half of each of it residing in a general position on both sides of the eight-fold special position. This is obvious from the neutron diffraction results of Tenzer et al. [19] on room temperature (ADP), and of Bacon and Pease [20] on room temperature (KDP), who both preferred the half proton disordered model over a model in which the protons vibrate anisotropically parallel to the O-H...O vector. The distance between two potential wells is 0.494 Å and the O-H...O angle of 176.37° show that it is almost linear (Fig. 2). This disordered hydrogen bond is of particular interest in relation to the structural phase transitions in (CADPA), which leads to fast proton conduction. The coordination sphere of Cs$^+$/NH$_4^+$ cations is determined by eight oxygen atom neighbors forming two interpenetrating tetragonal disphenoids (Fig. 3). One of the disphenoids is flat and the other is steep with respect to the c axis. Four (Cs/N)--O bond distances are equal to 2.938 Å in the flat disphenoids and also four (Cs/N)--O bond distances are equal to 3.273 Å in the steep disphenoids (Table 4). These values are slightly longer than those found in (ADP) and
(ADA) (2.889 and 2.909 Å, respectively, for N–O(f); 3.170 and 3.220 Å, respectively, for N–O(s); where O(f) and O(s) refer to the oxygen atoms of the flat and steep disphenoids, respectively). Like in (ADP) and (ADA), there is a tendency for the NH$_4^+$ groups to engage in four hydrogen bonds with the flat disphenoids. The oxygen atoms of the (PO$_4^{3-}$, AsO$_4^{3-}$) tetrahedra also serve as acceptors of the (Cs/N)–H . . . O bonds from the Cs$^+$/NH$_4^+$ groups, and thus hold the adjacent (PO$_4^{3-}$, AsO$_4^{3-}$) tetrahedra together (Fig. 4). It can be seen that all hydrogen bonded to the nitrogen atoms participate in the formation of (Cs/N)–H . . . O hydrogen bond bending with an averaging distance (H(N) . . . O) = 1.888 (2) Å. The structure of (CADPA) has been described as similar to those of (ADP), (ADA) and (ADPA) and on the basis of the hydrogen bonds network; the hydrogen bonds connect the tetrahedra in such a way as to form a three-dimensional network.

3.2. Vibrational study

At room temperature, Cs$_{0.55}$(NH$_4$)$_{0.45}$H$_2$(PO$_4$)$_{0.39}$(AsO$_4$)$_{0.61}$ exhibits a tetragonal symmetry with space group (I42d, Z = 4). The IR and Raman spectra of this compound (Figs. 5 and 6), have been investigated in the frequency range (4000 – 400) cm$^{-1}$ and (50 – 1300) cm$^{-1}$ respectively, in order to confirm the presence of the two anions (AsO$_4^{3-}$, PO$_4^{3-}$) in the same crystal and to elucidate the hydrogen bonds in their crystal lattice. The frequencies for the corresponding bands are given in Table 5.
Figure 4: Projection view of the title compound in the cb-plane. Hydrogen bonds N–H...O are drawn.

Table 4: Inter atomic bond distances (Å) and angles (°) in CADPA

<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Distance</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Phosphate–arsenate groups</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P/As) – O</td>
<td>1.624(2)</td>
<td></td>
</tr>
<tr>
<td>(P/As) – O'</td>
<td>1.624(2)</td>
<td></td>
</tr>
<tr>
<td>(P/As) – O''</td>
<td>1.624(2)</td>
<td></td>
</tr>
<tr>
<td>(P/As) – O'''</td>
<td>1.624(2)</td>
<td></td>
</tr>
<tr>
<td>O–P/As–O'</td>
<td>108.56(10)</td>
<td></td>
</tr>
<tr>
<td>O–P/As–O''</td>
<td>111.3(2)</td>
<td></td>
</tr>
<tr>
<td>O–P/As–O'''</td>
<td>108.56(10)</td>
<td></td>
</tr>
<tr>
<td>O'–P/As–O''</td>
<td>111.3(2)</td>
<td></td>
</tr>
<tr>
<td>O''–P/As–O'''</td>
<td>108.56(10)</td>
<td></td>
</tr>
</tbody>
</table>

| (b) Hydrogen bonds                      |          |       |
| O–H(O)                                  | 0.997(2) |       |
| H(O)...O'                               | 1.500(2) |       |
| O...O'                                  | 2.506(3) |       |
| H(O)...H(O)'                            | 0.494(1) |       |
| O–H(O)...O'                             | 176.37(16)|     |

| (c) Nitrogen-cesium coordination        |          |       |
| N/Cs–O                                 | 3.273(3) |       |
| N/Cs–O''                               | 3.273(3) |       |
| N/Cs–O'''                              | 3.273(3) |       |
| N/Cs–O''''                             | 3.273(3) |       |

Symmetry code: i'=y,-x,z; ii'=x,y,z; iii'=y,-x,z; iv'=y,0.5-x,0.25+z; v'=y,0.5+x,0.25+z; vi'=0.5-x,y,0.75-z; vii'=0.5+x,-y,0.75-z; viii'=y,-x,1-z; ix'=y,x,1-z; ii'x'=0.5-y,0.25-z.

3.2.1. IR spectroscopy investigation

To make a qualitative assignment of IR peaks to vibrational modes, most of which are tied to XO₄ group vibrations, we examine the modes and frequencies observed for H₃XO₄ anions [21]. The ideal, five atoms PO₄ or AsO₄ tetrahedral group exhibits T₄ symmetry. Thus, there are nine vibrational modes, only four of which are independent: v₁(A¹) = XO₄ symmetric stretch; v₂(E×2) = X-O-X bend; v₃(F₁×3) = XO₄ asymmetric stretch; and v₄(F₂×3) = X-O-X bend. The influence of the addition of protons to the anion can be understood through a two-step process. First, in HXO₄ one of the
oxygen atoms is replaced with a hydroxyl group with point mass. This reduces the symmetry from $T_d$ to $C_{3v}$, and eliminates degeneracies such that there are six rather than four independent vibrational modes. Second, the vibrations associated with the hydroxyl group are considered. There should be three such modes: O-H stretching, X-O-H in-plane bending, and X-O-H out-of-plane bending (or torsion). Similarly, the $H_2XO_4$ (ion or molecule) can be considered a group with $C_{2v}$ symmetry and therefore nine independent internal modes. In addition, there are six modes associated with the hydroxyl groups, as the $X(OH_2)$ stretching and bending modes may now be either symmetric or asymmetric. The case of $H_3XO_4$, which displays $C_{3v}$ symmetry, is similar to that of $H_2XO_4$. However, there are additional O-H modes.

To apply these concepts to the IR spectra of (CADPA) compound, it is necessary to first identify the $H_2XO_4$ groups present in the structure. So, the compound (CADPA) has one $H_2(P/As)O_4$ group (Table 4). The IR peaks obtained in the low-frequency region of the spectra ($< 530$ cm$^{-1}$) most likely correspond to internal bending modes of the $H_2XO_4$ groups. The peaks obtained in the region from 760 to 1030 cm$^{-1}$ most likely correspond to $H_2XO_4$ stretching modes. The IR peak obtained at 1273 cm$^{-1}$ is presumed to result primarily from X-O-H in-plane bending modes, although there may be some contribution from X-O and X-OH stretching modes. The high frequency peaks noted in the IR spectra at 2858, 2355 and 1665 cm$^{-1}$, have also been observed in the spectrum of CsH$_2$PO$_4$ [4] at (2750, 2300 and 1640 cm$^{-1}$) and are interpreted as OH stretching modes in Fermi resonance with combination of OH bending vibrations (three broad bands of the ABC type) [22]. The bands at 3117 cm$^{-1}$ and 3242 cm$^{-1}$ are attributed, respectively, to $\nu_1$ (NH$_4$) and $\nu_3$ (NH$_4$). The frequencies for the corresponding bands are given in Table 5.
3.2.2. Raman spectroscopy investigation

The Raman spectrum of both internal and external modes of polycrystalline samples of Cs$_{0.55}$(NH$_4$)$_{0.45}$H$_2$(PO$_4$)$_{0.39}$(AsO$_4$)$_{0.61}$ were recorded at room temperature (Fig. 6). This study was restricted to the 50 – 1300 cm$^{-1}$ spectral region because it included the lattice vibrations and $\nu$(X-OH) and $\nu$(X-O) stretching modes, which are the most sensitive to phase transition and crystal changes. In the Raman spectrum, the band appears at 61 cm$^{-1}$ is assigned to translational vibration of the NH$_4^+$ and Cs$^+$ ions and the peak at 118 cm$^{-1}$ is attributed to $\delta$ (O–H…O). While the band observed at 157 cm$^{-1}$ is corresponded to $\nu$(O…H…O). The two peaks detected at 276 cm$^{-1}$ and 355 cm$^{-1}$, can be attributed to $\nu_2$(AsO$_4^-$) vibration and the band observed at 446 cm$^{-1}$ is corresponding to $\nu_3$(PO$_4^3-$). The line at 538 cm$^{-1}$ in the Raman spectra is assigned to $\nu_4$(PO$_4^3-$). The peak that appears at 749 cm$^{-1}$, can be attributed to $\nu_1$(AsO$_4^-$). While, the band at 905 cm$^{-1}$ corresponds to $\nu_1$(PO$_4^3-$). The observed Raman bands and their assignments are given in Table 5.

Table 5: Infrared and Raman frequencies for Cs$_{0.55}$(NH$_4$)$_{0.45}$H$_2$(PO$_4$)$_{0.39}$(AsO$_4$)$_{0.61}$ compound.

<table>
<thead>
<tr>
<th>IR (cm$^{-1}$)</th>
<th>Raman (cm$^{-1}$)</th>
<th>Assignement</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>61</td>
<td>Lattice vibrations of Cs$^+$ and (NH$_4^+$)</td>
</tr>
<tr>
<td>-</td>
<td>118</td>
<td>$\delta$(O…O)</td>
</tr>
<tr>
<td>-</td>
<td>157</td>
<td>$\nu$(O…O)</td>
</tr>
<tr>
<td>424</td>
<td>276</td>
<td>$\nu_2$(AsO$_4^-$)</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>496</td>
<td>446</td>
<td>$\nu_4$(AsO$_4^-$)</td>
</tr>
<tr>
<td>547</td>
<td>538</td>
<td>$\nu_4$(PO$_4^3-$)</td>
</tr>
<tr>
<td>762</td>
<td>794</td>
<td>$\nu_1$(AsO$_4^-$)</td>
</tr>
<tr>
<td>-</td>
<td>905</td>
<td>$\nu_3$(AsO$_4^-$)</td>
</tr>
<tr>
<td>1029</td>
<td>-</td>
<td>$\nu_1$(PO$_4^3-$)</td>
</tr>
<tr>
<td>1273</td>
<td>-</td>
<td>$\delta$(OH)</td>
</tr>
<tr>
<td>1413</td>
<td>-</td>
<td>$\nu_4$(NH$_4^+$)</td>
</tr>
<tr>
<td>1665</td>
<td>-</td>
<td>$\nu_1$(PO$_4^3-$)</td>
</tr>
<tr>
<td>2355</td>
<td>-</td>
<td>B $\nu$(OH)</td>
</tr>
<tr>
<td>2858</td>
<td>-</td>
<td>A</td>
</tr>
<tr>
<td>3117</td>
<td>-</td>
<td>$\nu_1$(NH$_4^+$)</td>
</tr>
<tr>
<td>3242</td>
<td>-</td>
<td>$\nu_3$(NH$_4^+$)</td>
</tr>
</tbody>
</table>

3.3. Calorimetric study

A typical result of the calorimetric study is presented in Fig. 7 which shows the diagram obtained on heating from 173 to 673 K recently prepared samples. Three distinct endothermal peaks are detected at $T_1 = 204$ K, $T_2 = 407$ K and $T_3 = 585$ K. The last peak corresponding to the melting of the product. Whereas, the first and the second peaks denote structural phase transitions. It is shown from the DSC result that the first transition is distinctly small in comparison with that associated with the second transition. By comparison with the thermograms of ADP and ADA pure compounds and of the mixed compound ADPA, the thermal accidents at 204 K and 407 K conserve approximately in all these compounds. So that the first DSC peak observed at 204 K for CADPA probably corresponds to a ferroelectric or antiferroelectric–paraelectric phase transition and the strong DSC peak at 407 K, seems to indicate a superprotonic phase transition. These two transitions are confirmed by dielectric permittivity at different frequencies and temperatures for the first transition and by conductivity measurements using impedance spectroscopy for the second [23]. In fact the H-atom of the
NH₄ groups are responsible and more sensible for the antiferroelectric properties of these systems. Similar to the case of ADP, ADA and ADPA crystals, at temperature above Tc (Curie temperature), NH₄ groups rotate about their center of mass at a high speed and are characterized by essentially spherical symmetry. As a result, the crystal in the paraelectric phase (at room temperature) is isostructural to KDP crystals. The ac conductivity and the dielectric relaxation behavior of the new phosphate–arsenate CADPA have been examined also [23]. We point out a break observed in the curve of log(σT) vs. 1000/T accompanied at high temperature (above 407 K) of a decreasing in activation energy (E = 0.32 eV) and increasing in conductivity. This shown that a superprotonic phase transition occurs at 407 K.

**Figure 7:** DSC heating curve of CADPA material

### 4. CONCLUSION

This paper presents the involving synthesis, vibrational and structural determination of a new mixed phosphate–arsenate CADPA. Its structure (performed at room temperature) is determined by single crystal X-ray analysis, shows that this compound crystallizes in a quadratic system I 42d. This structure has been described as similar to those of (ADP), (ADA) and (ADPA) and on the basis of the hydrogen bonds network; the hydrogen bonds connect the tetrahedra in such a way as to form a three-dimensional network. The cesium/ ammonium atoms have eight oxygen atoms neighbours. The main feature of this structure is the coexistence of two different anions (AsO₄³⁻ and PO₄³⁻) in the same crystal. The infrared and Raman spectra of the title compound was acquired at room temperature and is characterized by the apparition of a few bonds which confirm the presence of these two different anions.

In addition to the chemical preparation and crystal structure, the thermal behaviour of this compound was examined by DSC. The first DSC peak observed at 204 K for CADPA probably corresponds to a ferroelectric or antiferroelectric–paraelectric phase transition and the strong DSC peak at 407 K, seems to indicate a superprotonic phase transition. Additional studies with dielectric and impedance measurements can confirm that the breaking of the hydrogen bonding can be responsible for the existence of a high ionic conductivity at high temperature. A complete discussion of the electrical properties has been reported elsewhere [23].

### 5. REFERENCES