Complex phase evolution of Brushite-based calcium phosphate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ using in situ high temperature X-ray diffraction and thermal analysis

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Abstract

This study focused on a detailed examination of the thermal behavior of Brushite-based calcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD) to identify and characterize the intermediate phases which have been the subject of previous several controversies. For that, in situ high-temperature X-ray diffraction supported by infrared spectroscopy, thermal analysis, and scanning electron microscopy analysis were used and the results showed that the progressive thermal stress of DCPD in air resulted in a heterogeneous formulation consisting of dibasic calcium phosphate anhydrous (CaHPO_4 , DCPA) and an amorphous phase, which appears at low temperatures ($\sim 160^\circ\text{C}$) and persists up to 375°C . The deep examination of the amorphous phase by infrared spectroscopy revealed that its chemical composition is similar to that of disordered calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$, CPP) with the appearance of a characteristic band $\delta(\text{P-O-P})$, located at 740 cm^{-1} . This IR band is shifted to low frequencies (725 cm^{-1}) as the temperature is increased, indicating the crystallization of the amorphous phase into γ -CPP. The high temperature treatment ($\geq 375^\circ\text{C}$) leads to β -CPP polymorph. According to the present characterization results, obtaining pure DCPA from the thermal dehydration of DCPD is not effective and leads to biphasic materials including an amorphous phase.

1. Introduction

The calcium-phosphate system constitutes an attractive class of materials in many fields of science and technology due to its diversity of compositions and structures, depending on the molar ratio Ca/P which can vary from 0.5 to 2 [1-3]. Several two and three-dimensional structures have been isolated and different synthesis strategies have been proposed. Among them, Dibasic Calcium Phosphate Anhydrous (DCPA) (CaHPO_4 , Monetite) and Dibasic Calcium Phosphate Dihydrate (DCPD) ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Brushite) with molar ratio Ca/P=1 have gained much attention owing to their wide applications such as potential precursors for the synthesis of biomaterials useful for the orthopedic engineering and dental implants [4,5], selective adsorbents of pesticides, organic pollutants and containment matrices of radioactive elements in environmental science [6,7] and supports of active phases in numerous heterogeneous catalytic reactions, among others vapour-gas conversion of alcohols [8], oxidative dehydrogenation of alkanes [9] and hydroxylation of aromatic compounds [10].

Brushite DCPD remains one of the most studied calcium phosphate materials because it has several other technological applications as additives in food or dietary supplement [11] and in the pharmaceutical industry as tablet excipient and toothpaste [12,13]. For these purposes, the thermal degradation of DCPD has been extensively studied for several years using different experimental techniques but controversial results still remain, especially on the intermediate phases that may be formed during the dehydration process to give crystalline Calcium Pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$, CPP) [14-17]. As a result, the mechanism of the dehydration process of DCPD is not yet clear.

Several authors stated that the dehydration of DCPD proceeds through two steps with DCPA and crystalline CPP, respectively as only products formed [18-22]. While others showed that the dehydration

process of DCPD is more complicated and involves the formation of intermediates with indefinite structures [23-26]. For instance, Lin et al. [18] have examined the dehydration of DCPD by thermogravimetry and conventional X-ray diffraction analysis. According to their results when DCPD was heated up to 300 °C, two water molecules were released with the formation of DCPA, which then converted to crystalline CPP at 500 °C. Similarly, Rabatin et al. [19] pointed out that in humid air the loss of hydrates water proceeds rapidly and DCPD decompose to DCPA and CPP at 135 and 430 °C, respectively. Landin et al. [20], studied the dehydration process of DCPD up to 240 °C by means of X-ray diffraction equipped with a high temperature camera and Fourier transform Raman spectroscopy. They found that the process led to the formation of DCPA without the occurrence of intermediate phases. Analogous conclusions were also proposed by Mulley [21] and Joshi [22]. However, Dosen and Giese [23] and Myazaki et al. [24] later suggested that an amorphous intermediate phase was formed concomitantly with DCPA during dehydration of DCPD. Likewise, Gisla et al. [25] reported that in dried air, the dehydration process of DCPD takes place in three steps with the formation of amorphous phases of composition $\text{CaHPO}_4 \cdot 1.5\text{H}_2\text{O}$ and $\text{CaHPO}_4 \cdot 1\text{H}_2\text{O}$, as intermediates between 85 and 240 °C. Rabatin et al. [19] proposed a complex dehydration pathway when the reaction is conducted in the presence of dry air than in humid air. These authors concluded that prolonged heating of the DCPD to 135 °C could lead to a lower hydrate of formula $\text{CaHPO}_4 \cdot x\text{H}_2\text{O}$, with x ranges from 0.9 to 1.2, and which is then converted to amorphous DCPA at 195 °C. The dehydration behavior of DCPD was also examined by Duff [26] who found that two molecules of DCPD combine and eliminate one water molecule at 105 °C and formed an intermediate phase of composition $\text{Ca}_2(\text{HPO}_4)_2 \cdot 3\text{H}_2\text{O}$ which turns into DCPA at 165 °C. Based on this brief literature report, it seems that the thermal dehydration process of DCPD is not yet clearly established especially with regard to the number of stages as well as the intermediate phases which can be occurred during heating. Several suggestions have been found doubtful, in the absence of in situ investigations by appropriate analytical techniques.

For that, we have undertaken in this work the thermal dehydration of commercial Brushite DCPD using in situ high temperature X-ray diffraction (HT-XRD) in order to identify and characterize the nature and composition of the possible intermediate phases encountered. Fourier transform infrared spectroscopy (FTIR), simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and scanning electron microscopy (SEM-EDX) were also utilized to provide complementary information about products that may form during the dehydration process of DCPD material including the eventual presence of the amorphous phase.

2. Materials And Methods

2.1 Material

All the calcium phosphates used in this work are commercial products of analytical grade, Brushite DCPD ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) (Riedel-de Haën, > 98 wt.%) and Monetite DCPA (CaHPO_4) (Fluka, > 98.5 wt.%). Prior

experiments, the samples were first checked by thermogravimetry analysis to ensure the number of hydration molecules.

2.2 Methods

2.2.1 High temperature X-ray diffraction (HT-XRD)

An X-ray powder diffractometer (Shimadzu-6100) equipped with a variable temperature attachment (model HA-1001) was used. A sample of Brushite DCPD was filled in an alumina holder and exposed to CuK α ($\lambda_{\text{CuK}\alpha} = 0.15419 \text{ nm}$) radiation (40 kV $\times$ 30 mA) in a continuous temperature step scan operation mode from 30 to 650 °C at a heating rate of 10 °C min⁻¹. During the experiment, the sample was maintained 30 min at the selected temperature prior to being analyzed over the angular range from 5 to 50 °(2 θ) at scanning speed of 0.03 °s⁻¹. The resulting mineral phases were identified using Joint Committee on Powder Diffraction Standards (JCPDS) database.

In order to determine the composition of the different products including the amorphous phase which are formed during the in situ thermal treatment of the DCPD in air, HT-XRD analysis was carried out using Silicon 640 as internal standard reference. Prior the XRD scans, DCPD and Si powders with a mass ratio 80%:20% were intimately homogenized for 30 min in an agate mortar and then heated at selected temperatures. The HT-XRD patterns were treated using Rietveld method (FullProf program) combined with Quantitative Phase Analysis (QPA) as has been detailed elsewhere [27]. The Rietveld procedure scales all crystalline phases included in the refinement to a total of 100%, if any non-crystalline phase is present, the internal standard content would be overestimated by the Rietveld analysis. The amount of internal standard at each dehydration step must be corrected since the loss of water during heating leads to an increase in the Si content in the initial mixture. The corrected amount of silicon was calculated as follows:

$$W\%_{Si (corrected)} = \frac{W\%_{Si (Known)}}{W\%_{(total)} - W\%_{(water loss)}}$$

Where $W\%_{(total)}$ is the amount of DCPD and Si, and $W\%_{(water loss)}$ is the weight loss of water deduced from the TG analysis of DCPD at the same heating rate as that taken during the HT-XRD analysis ($10\text{ }^{\circ}\text{C min}^{-1}$).

The quantification of amorphous phase is given by the following equations:

$$(wt. \%)_k = (wt. \%)_{k(FullProf)} \times \frac{(wt. \%)_{Si(FullProf)}}{(wt. \%)_{Si(corrected)}}$$

Where $(wt. \%)_{Si(FullProf)}$ is the percentage of silicon calculated by FullProf and $(wt. \%)_{Si(corrected)}$ is the corrected weight percent of silicon, and $(wt. \%)_k$ is the weight percent of phase k.

$$(wt. \%)_{Amorphous} = 1 - \sum_{k=1}^n (wt. \%)_k + (wt. \%)_{Si (Known)}$$

With $(wt. \%)_{Amorphous}$ is the percentage content of amorphous calcium phosphate phase.

2.2.2 Fourier transform infrared spectroscopy (FTIR-ATR)

The FTIR-ATR analysis was carried out at room temperature on the phases obtained after heating the DCPD in a tubular oven at the same temperatures as those used for the in situ HT-XRD experiments. Spectra were recorded on a Jasco FTIR 4600 spectrometer equipped with an attenuated total reflection (ATR) Pro-One module. The samples were scanned at ambient temperature, in the range from $4000\text{--}400\text{ cm}^{-1}$ using a resolution of 4 cm^{-1} .

2.2.3 Thermal analysis (TG-DTA)

Simultaneous TG-DTA analysis of the DCPD sample was performed on a LabsysTM Evo (1F) Setaram apparatus under non-isothermal conditions from $30\text{ to }700\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$. Experiments were conducted on $10.0 \pm 0.1\text{ mg}$ of samples, placed in an alumina pan under air atmosphere of 40 mL min^{-1} . Thermal results were done in duplicate to ensure reproducibility of experiments.

2.2.4 Scanning electron microscopy (SEM-EDX)

SEM micrographs were recorded on a Jeol JSM-IT100 scanning electron microscope equipped with an Energy Dispersive X-ray (EDX) system in order to get information about the morphology of particles and microstructure of the products formed after different heating temperatures. Before examination, the powder sample was deposited on thin films of amorphous carbon and coated with gold (2 nm).

3. Results And Discussions

3.1 In situ high temperature X-ray diffraction (HT-XRD)

To get information on the possible phases formed during the thermal dehydration process of Brushite DCPD, the samples obtained at selected temperatures were subjected to in situ XRD analyzes as described in the method section. The HT-XRD patterns obtained at different thermal treatments are shown in **Fig. 1a**. At room temperature (30 °C), the XRD diagram shows a high crystalline phase and all observed peaks are matched with those of the standard DCPD (JCPDS card No. 9-77). According to the crystallographic data previously obtained by Neutron and X-ray diffractions [28,29], the DCPD crystallizes in the monoclinic unit cell with space group Ia. Its structural framework consists of a linear arrangement of corrugated CaHPO_4 sheets, normal to [010] axis. These sheets are interconnected through two types of water molecules, which are joined together by hydrogen bonds thus forming a tridimensional network.

By increasing the temperature up to 160 °C, the Bragg peak intensities of DCPD relatively decreased and concomitantly a new broad and weak peak emerged at 26.4 °(2 θ) which is attributed to a maximum XRD reflection of Monetite DCPA (CaHPO_4) with JCPDS card No. 9-80. At 160 °C, the DCPD starts to decompose into DCPA with partial loss of water molecules and no other crystalline phases were observed. Indeed, the DCPA crystallizes in the triclinic system (P) and its crystal structure can be described by infinite corrugated sheets of $[\text{HPO}_4^{2-}]_n$ linked by Ca-O polyhedra [28]. More than 210 °C, the dehydration process of the DCPD still persists and the reflection peaks of DCPA visibly appear. The broad reflections of DCPA observed at this temperature are probably linked to the difference in microstructure between the DCPD and DCPA materials, and to the crystallization kinetics of DCPA that is slower under the experimental analysis conditions. It should be noted that at 210 °C, the existence of an amorphous phase cannot be excluded since a broad hump between 23 and 35 °(2 θ) was observed in the XRD patterns (**Fig. 1b**). This amorphous phase is formed parallel to the DCPA even below 210 °C and kept up to 375 °C as previously reported in the literature [23]. The reaction scheme of the dehydration step at 210 °C can be written as follows:

Where *Am* indicates the amorphous phase and *z* is the corresponding number of water molecules losses.

As shown in **Fig. 1a**, the DCPA phase is stable in the range of temperature between 210 and 300 °C. The poorly crystalline DCPA observed is probably related to the concomitant presence of the amorphous phase that arises in wide temperature range (**Fig. 1b**) and to crystals form of DCPA particles issued from DCPD which are different from those of commercial DCPA. For comparison, **Fig. 2** shows the XRD diagrams of DCPA obtained after in situ heating the DCPD at 300 °C (30 min), DCPD heated in an air oven at 300 °C (24 h) and commercial DCPA.

At 375 °C, the intensity of DCPA peaks significantly decreases and a new poorly crystalline phase is observed and attributed to low temperature calcium pyrophosphate (LT-CPP). At this temperature, the presence of the amorphous phase is also observed in XRD pattern. The composition of the phases estimated from the in situ HT-XRD data using the Rietveld method combined with the quantitative phase analysis for all explored dehydration temperatures (**Table 1**) shows that the percentage of the amorphous phase increases with the increase of DCPD dehydration temperature and reaches a maximum of about 21 wt. % in the temperature range between 300 and 375 °C and then it tends to disappear in favor of the crystallization of high temperature calcium pyrophosphate (HT-CPP) when the temperature exceeds 450 °C.

Table 1 Quantification of the phases from HT-XRD experiments

T (°C)	wt. % DCPD	wt. % DCPA	wt. % CPP	wt. % Am
30	100	0	0	0
160	83.9	16.1	0	0
210	11.3	69.8	0	18.9
300	0	78.9	0	21.1
375	0	59.3	20.1	20.6
450	0	0	95.2	4.8
650	0	0	100	0

The comparison of our results with those reported by Dosen and Giese [23] who evaluated amorphous calcium phosphate by using conventional XRD at ambient temperature shows great consistency. Indeed, these authors indicated that the maximum of the amorphous phase composition was observed of about 43 wt.% at 240 °C and when the dehydration process of the DCPD was conducted on a heating rate of 1 °C min⁻¹. This excessive value (43 wt.%), by comparison with our results (21.1 wt.% at 300 °C), seems to be due to the kinetics of the amorphous phase formation and to the differences in the operating conditions used. On the other hands, the more heating rate increases, the more the formation temperature moves towards higher temperatures and the more the amorphous phase content decreases [30].

Further heating the DCPD to 450 °C results in the total disappearance of DCPA and substantial formation of LT-CPP (γ -Ca₂P₂O₇, γ -CPP) (JCPDS card No.17-499). Finally, the XRD pattern obtained at 650 °C showed the crystallization of HT-CPP polymorph (β -CPP) with JCPDS card No. 9-346. From the HT-XRD results, it is clear that dehydration of DCPD is complex and occurs in two distinct stages. The first one consists of the formation of DCPA and an amorphous calcium phosphate phase at temperature below

300 °C. The second stage, occurred at high temperature, leads to CPP materials by condensation process of DCPA and crystallization of the amorphous phase.

From the foregoing, it should be noted that obtaining pure DCPA from thermal dehydration of DCPD is not completely effective, contrary to what is suggested in some earlier studies [31,32]. However, pure DCPA can be directly prepared from stoichiometric mixture of soluble calcium reagents and phosphoric acid at 80 °C as reported in several reports [33,34].

3.2 FTIR-ATR spectroscopy

FTIR-ATR analysis allowed the identification of the possible phases obtained after heating the DCPD material, in particular the amorphous phase previously observed in the XRD experiments. The spectra obtained at different temperatures are presented in Fig. 3.

At ambient temperature, the IR spectrum shows a similar signature to that of the standard DCPD [35,36]. In the region $3700\text{--}3000\text{ cm}^{-1}$, two distinct doublets are visible, the first one with components located at 3531 and 3475 cm^{-1} and the other with components at 3263 and 3158 cm^{-1} . These bands are assigned to the O-H stretching modes belonging to two kinds of crystallization water molecules, in agreement with the crystal structure data [37]. The water molecule also shows another band at about 1645 cm^{-1} due to O-H bending mode [38]. The main characteristics of internal modes of tetrahedral $[\text{PO}_4]$ groups are observed between $1150\text{--}900\text{ cm}^{-1}$ and $650\text{--}520\text{ cm}^{-1}$ [39]. The bands at frequencies 1215 , 875 and 780 cm^{-1} are due to vibration modes of P-O-H and P-OH of $[\text{HPO}_4^{2-}]$ species, respectively [39,40]. For IR spectra of heated materials, there is a strong evidence for the dehydration process. Indeed, the crystallization band intensities of water molecules decrease gradually until their almost total disappearance at 210 °C and three new weaker vibrations give rise at 2923 , 2851 and 2320 cm^{-1} which are inferred to different kinds of hydrogen bonds belonging to DCPA structure [28,37]. It should be noted that above 160 °C a weak flared band was shown around 740 cm^{-1} and becomes clearly visible with increasing temperature up to 375 °C (**Fig. 3b**). At $T \geq 375\text{ °C}$, an additional IR band appeared at 725 cm^{-1} . As the process temperature increases over 300 °C , the band located at 740 cm^{-1} gradually disappears while the intensity band at 725 cm^{-1} increases and becomes narrower. These two bands are assigned to $\delta(\text{P-O-P})$ of pyrophosphate groups $[\text{P}_2\text{O}_7^{4-}]$, as reported for many pyrophosphate materials [41,42]. The first was attributed to the amorphous CPP and the second to crystalline CPP. As can be seen, the possible pyrophosphate that is formed during the dehydration process of DCPD is the CPP compound and no other reported composition of calcium phosphates. This CPP phase was previously reported by Duff [26] as a result of the direct product of DCPD when heated over 270 °C . The same author suggested that the calcium pyrophosphate formed during heating could have a composition similar to that of $\gamma\text{-CPP}$ but without giving any evidence. Alike, the calcium pyrophosphate (CPP) was also observed in the IR spectra obtained by Dosen and Giese [23], although its associated band was not signaled and nor discussed. According to our HT-XRD results (**Fig. 1b**), the large hump observed between 23 and $35\text{ °}(2\theta)$ and which is previously assigned to disordered phase of calcium phosphate is responsible for the occurrence of the band at 740 cm^{-1} in the IR

spectra. As can be seen in **Fig. 3b**, the broad shape of this band and its relatively high frequency value confirm the presence of a disordered CPP material (Amorphous CPP). Further heating, the IR profiles change and a new phase appeared which is assigned to crystalline γ -CPP. Concomitantly, the band which observed at 740 cm^{-1} disappears at beyond $375\text{ }^{\circ}\text{C}$ to the profit of single sharp one at 725 cm^{-1} indicating the total transformation of the amorphous CPP into an ordered LT-CPP with γ polymorph structure (**Fig. 3b**). At $650\text{ }^{\circ}\text{C}$, γ -CPP converts to HT-CPP polymorph (β -CPP) as previously reported in the literature [43].

According to HT-XRD and FTIR-ATR experiments, the amorphous CPP results from the partial dehydration of DCPD and reaches a maximum between $300\text{-}375\text{ }^{\circ}\text{C}$. The crystalline CPP phase firstly appears at $T \geq 375\text{ }^{\circ}\text{C}$ and essentially comes from DCPA material. When the temperature increases further, all the resulting products (amorphous CPP and DCPA) convert to LT-CPP (γ -CPP) and then to HT-CPP (β -CPP). **Fig. 4** shows the distribution of the crystalline and amorphous CPP during thermal treatment of the DCPD.

3.3 Simultaneous TG-DTA analysis

A study of the thermal dehydration of DCPD was also carried out using the TG-DTA technique, in order to confirm our previous interpretations made in the HT-XRD and FTIR analyzes. **Fig. 5** shows the thermal profiles of DCPD performed at $10\text{ }^{\circ}\text{C min}^{-1}$ under air flow (40 mL min^{-1}) from ambient temperature up to $700\text{ }^{\circ}\text{C}$. The thermograms obtained are similar to those reported by several authors [44,45] and show a complex thermal behavior characterized by a progressive dehydration of the DCPD. Five mass loss steps (Pi) accompanied with endothermic effects can be distinguished in thermal curves. **Table 2** shows the thermal characteristics of DCPD observed as a function of temperature. All degradation steps correspond to elimination of water molecules at different degrees, in similarity with results previously obtained by Frost et al. [17] when studying the thermal degradation of mineral Brushite (DCPD) using TG combined with MS spectroscopy.

Table 2 Thermal dehydration characteristics of DCPD

Steps	P1	P2	P3	P4	P5	Total mass loss	
Temperature (°C)	90-170	170-210	210-300	300-375	375-450	Experimental	Theoretical
Mass loss (%)	4.11	15.89	2.10	1.02	2.99	26.11	26.17
Mass loss (mol)	0.393	1.519	0.201	0.098	0.286	2.497	2.50

Based on the results obtained by HT-XRD and FTIR analyzes, the possible phases corresponding to each thermal degradation step are presented in **Table 3** and the comparison of the weight percentage of CPP from HT-XRD and Thermal analysis are illustrated in **Table 4**.

Table 3 Correlation of TG-DTA data with HT-XRD and FTIR analyzes

Steps	T (°C)	XRD and IR identification	TG-DTA analysis
P1	90-170	DCPD, DCPA	0.804DCPD, 0.196DCPA
P2	170-210	DCPD, DCPA, Amorphous CPP	0.094DCPD, 0.706DCPA, 0.1CPP
P3	210-300	DCPA, Amorphous CPP	0.774DCPA, 0.113CPP
P4	300-375	DCPA, Amorphous and crystalline CPP	0.578DCPA, 0.213CPP
P5	375-450	LT-CPP (γ -form)	0.5CPP

Table 4 Comparison of CPP content obtained from HT-XRD and TG analysis

Steps	T (°C)	wt.% CPP (HT-XRD)		wt.% CPP (TG analysis)
		crystalline CPP	Amorphous CPP	
P1	90-170	0	0	0
P2	170-210	0	18.9	18.5
P3	210-300	0	21.1	21.4
P4	300-375	20.1	20.6	40.8
P5	375-450	95.2	4.8	100

Thermal results of the DCPD show a great concordance with those obtained by HT-XRD and FTIR analyzes (**Table 3**). Indeed, the disordered phase which has been controversial in the literature was therefore identified in this study as amorphous calcium pyrophosphate (Am-CPP). This amorphous phase appears increasingly dependent on heating and is transformed into crystalline γ -CPP when the temperature increases (**Table 4**). Further heating up to 650 °C, an exothermic effect in DTA curve was observed at 535 °C without mass loss and attributed to the transformation of γ -CPP (LT-CPP) into high temperature allotropic form β -CPP (HT-CPP). From the above results, the combination of both techniques HT-XRD and TG-DTA allowed to remove completely the ambiguity of the phases produced during the

thermal dehydration of DCPD, in particular the amorphous phase object of controversies in the literature. This combination of the techniques also revealed that obtaining pure DCPA from the thermal dehydration of DCPD is not entirely effective because of the presence of the amorphous phase which occurs at low temperature ($T < 210\text{ }^{\circ}\text{C}$) and which then directly transforms into LT-CPP (**Fig. 6**). The maximum of the DCPA obtaining from commercial DCPD is observed at $300\text{ }^{\circ}\text{C}$ with mole percentage of 87.3 %, as shown in **Fig. 6**.

3.4 SEM-EDX analysis

The phases obtained after in situ HT-XRD analysis of the DCPD at different temperatures were further subject to SEM-EDX examination to explore the microstructure and texture of the resulted products. **Fig. 7** displays the micrographs of SEM analysis. As can be seen from **Fig. 7a**, the morphology of commercial DCPD particles is dominated by plate-shaped crystals superimposed showing the sheet structure of DCPD as reported for other sources of DCPD [46,47]. This microstructure persists even for DCPA crystals (**Fig. 7b**), when DCPD is heated up to $210\text{ }^{\circ}\text{C}$. At $375\text{ }^{\circ}\text{C}$ (**Fig. 7c**), the flat plate morphology of DCPD disappears completely in favor of large particles of different sizes asserting the presence of CPP phase, as shown generally in CPP materials [48,49]. The texture of the particles becomes well organized when the heating temperature reaches $450\text{ }^{\circ}\text{C}$ indicating the appearance of the LT-CPP phase (γ -CPP) (**Fig. 7d**). By heating up to $650\text{ }^{\circ}\text{C}$ (**Fig. 7e**), the γ -CPP microstructure changes and appears to be dominated by small particles of the HT-CPP allotropic form (β -CPP). The SEM results are found in good agreement with those obtained by HT-XRD, FTIR spectroscopy and thermal analyzes.

4. Conclusions

Calcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, DCPD) is an important material used in medical industry and modern technologies. The thermal dehydration of DCPD was subject of numerous previous studies due to the complexity of its mechanism process especially, the intermediate phases that can occur during heating. However, some controversies still remain about the nature and composition of the amorphous phase encountered during the thermal process. In this report, we have undertaken the thermal dehydration of DCPD using in situ HT-XRD experiments. The XRD results showed the presence of an amorphous intermediate product, which appeared at low dehydration temperature ($T < 210\text{ }^{\circ}\text{C}$) and becomes clearly visible at the temperature of $375\text{ }^{\circ}\text{C}$. The characterization of the resulted products at different dehydration steps by FTIR spectroscopy indicated that the amorphous phase exhibited a vibration band at 740 cm^{-1} which attributed to $\delta(\text{P-O-P})$ of pyrophosphate species. This IR band disappeared at the temperature more than $375\text{ }^{\circ}\text{C}$ and a new vibration band emerged at 725 cm^{-1} due to the formation of crystalline calcium pyrophosphate, in good agreement with XRD results. The thermal process of DCPD using TG-DTA showed the complex nature of the degradation reaction. Indeed, five processes are involved and all are attributed to elimination of water molecules at different degrees. The thermal reaction equations corresponding to each degradation step were proposed according to the results of HT-XRD, FTIR, TG-DTA

analyzes and SEM-EDX observations. An exothermic effect appeared at 535 °C was assigned to γ -CPP- β -CPP allotropic forms. The results obtained in the present work made it possible to remove the ambiguity regarding the identification of the amorphous phase formed during thermal degradation of DCPD and showed that the pure DCPA could not be obtained from DCPD material.

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Figures

Figure 1

Figure 2

XRD patterns of DCPD heated at 300 °C for 30 min (a), for 24 h (b) and commercial DCPA (c)

Figure 3

FTIR-ATR profiles of DCPD and its thermal dehydration products

Figure 4

Distribution of crystalline and amorphous CPP phases during the thermal dehydration of the DCPD

Figure 5

Thermal dehydration profiles of DCPD material

Figure 6

Mole percentage of products formed from commercial DCPD versus temperature

Figure 7

SEM-EDX analysis of the DCPD samples heated up to different temperatures