

# Thermal analysis and high-temperature X-ray diffraction of nano-tricalcium phosphate crystallization

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**Abstract** Calcium phosphate biomaterials have long ago attracted the interest of world-wide scientists because they form the main inorganic constituent of the human bones and teeth. Classical approaches to synthesize this ceramic material did not give satisfactory results until present, so new approaches are required. In this article the tricalcium phosphate achievement by a method which is a combination of sol–gel and classic precipitation from solution is presented, starting from  $\text{CaCl}_2$  as calcium precursor and  $\text{H}_3\text{PO}_4$  as phosphorus precursor, without pH adjustment. The reaction mixture was allowed to mature for 2 months, the time influence on the precipitated material being presented in previous articles. Present studies aimed at the influence of temperature on the structural characteristics of precipitated and matured material, by means of thermal analysis, X-ray diffraction, infrared spectroscopy, and high-temperature X-ray diffraction. A complex type thermal decomposition takes place while heating the sample to 1000 °C, with superposed and parallel processes. The sample goes through alternative amorphous and crystalline stages before final crystallization of  $\beta$ -tricalcium phosphate takes place. The high-temperature XRD studies offered the great advantage of being both a synthesis and a

physico-chemical characterization technique, which along with thermal analysis and infrared spectroscopy, gave a lot of useful information in a very short time.

**Keywords** Biomaterials · Crystallization · Heat treatment

## Introduction

The synthesis of calcium phosphate ceramic materials has long ago become a field of interest for researchers, in the attempt to mimic the natural calcium phosphate species present in the human hard tissues (bones, teeth) [1]. The dedicated field is to use this kind of synthetic materials for reconstructive and restorative medicine (natural materials are not easily available and imply a series of health risks). The advantages of calcium phosphates among other synthetic biomaterials are the very good biocompatibility and osteoconductivity, the ability to bond directly to the hard tissue without the need for any other connective tissue, non-toxicity [2]. Wet chemistry methods (sol–gel, wet precipitation) are preferred as the synthesis methods for this group of materials due to a series of advantages like the possibility of controlling the final product morphology and phase composition [3].

The inorganic matrix of the hard tissues is constituted mainly of  $\beta$ -tricalcium phosphate (TCP) and hydroxyapatite (HA). Attention has been focused on TCP because it possesses good properties of dissolution in the physiological environment compared with HA which is relatively insoluble. Some other calcium phosphate family compounds are present in the matrix of the hard tissues, but few investigations are presented.

The TCP has three polymorphic forms:  $\beta$ —stable until 1180 °C,  $\alpha$ —between 1180 and 1400 °C, and  $\alpha'$ —after

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1400 °C. The  $\beta$  form is preferred in biomedical applications because its structure resembles the most to the TCP present in human tissues, it possesses stability and good dissolution behavior. The wet chemistry synthesis, performed to achieve  $\beta$ -TCP, is greatly influenced by water molecules, the type of bonds between them, and other elements of the crystalline structure.

The crystallization behavior of TCP (from amorphous stage, resulted by wet chemistry synthesis) is related to many factors and is very important for its *in vivo* degradation behavior. Knowing the interactions of the reactants and by-products, their stability domains, and compositions at certain values of time or temperature will help in tailoring the physico-chemical and mechanical characteristics of the final reaction product and its degradation behavior *in vitro* and/or *in vivo*.

As physico-chemical characterization techniques, scientists have been using a series of very valuable methods: spectroscopy, microscopy, X-ray techniques and so on. In our previous experience, thermal analysis (TA) is a very useful tool in the study of biomaterials behavior under the influence of thermal treatment [4, 5]. Another technique extensively used in calcium phosphate investigations is fourier-transformed infrared spectroscopy (FTIR), which we have also used in previous articles. The  $\text{XO}_4^{n-}$  form tetrahedral ions will exhibit a wide absorption band typically in the range 800–1200  $\text{cm}^{-1}$ , but the frequency may vary with the type of anion [3]. After identifying the type of bonds, X-ray diffraction technique will help one identify the crystalline phases present and perform deeper studies related to crystallinity degree, ratio of phases present, elemental cell characteristics, etc. Typically, the calcium phosphate family compounds will develop diffraction peaks in the domain 10–40°  $2\theta$ ; hydroxyapatite and  $\beta$ -TCP will have the most intense diffraction peaks in the range of 30–33°  $2\theta$ .

In comparison with the classical method of alternating (a) the heating and weighing of the sample and (b) room temperature XRD (after cooling) [2], the high-temperature X-ray diffraction (HTXRD) presents the advantage of *in situ* analysis of the sample, at the desired temperature, eliminating errors that may appear due to factors like cooling effects, time between the two analyses, or atmosphere impurities (HTXRD equipment is a closed system). Apart from being an *in situ* analysis system, in our case the high-temperature chamber proved itself to give the opportunity of performing the synthesis of the desired material, simultaneously giving real-time information about its evolution with time and temperature. Besides the information provided, the short time needed to perform both synthesis and analysis of the sample is to be appreciated. We have found evidence of similar investigations,

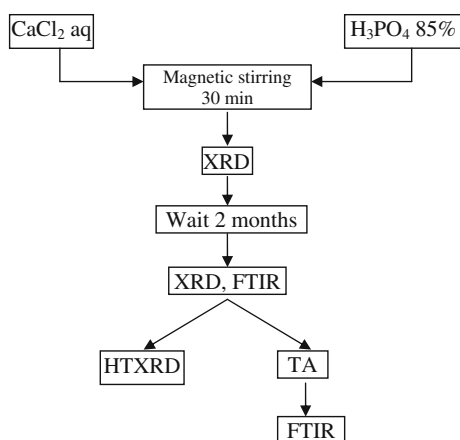
using parallel studies by means of HTXRD and TA [6, 7], to study the thermal stability of hydroxyapatite in terms of *in situ* phases transformations, but there had been no such study (to our knowledge) about  $\beta$ -TCP, or parallel studies of long-time influence and also temperature influence on the very same material.

## Experimental

The purpose of this study was to achieve TCP from solution at room temperature and pressure without pH adjustment, and study the crystallization behavior (in terms of time and temperature influence) of this compound by means of TA and high-temperature X-ray diffraction (HTXRD). Calcium chloride ( $\text{CaCl}_2$  anhydrous, Reactivul Bucuresti) and phosphoric acid ( $\text{H}_3\text{PO}_4$  85%, Merck) were used as calcium and phosphorus precursors. The calcium chloride was dissolved in distilled water, and the phosphorus precursor was used as received, in a molar ratio of 1.5 (Ca:P). The phosphorus precursor was added dropwise onto the calcium precursor under magnetic stirring. The usual pH adjustment step was excluded, and also temperature control; the initial mixture of precursors, with a pH of 0.5, was only magnetically stirred for 30 min at room temperature. The mixture was investigated at room temperature by X-ray diffraction using a PANalytical Xpert PRO MPD diffractometer with Cu  $K\alpha$  incident radiation and PIXcel detector, working conditions 45 kV and 30 mA, and scanning range of 10–40°  $2\theta$ . The software used for data analysis and phase identification was X'Pert High Score Plus and ICDD database version 2009, respectively.

After a period of 2 months at room temperature allowed for aging, the mixture was again subjected to XRD investigation and FTIR using a Perkin-Elmer Spectrum 100 spectrometer by means of U-ATR technique. Thermal analysis of the sample was performed using a Perkin-Elmer Diamond thermal analyzer with a heating rate of 10  $\text{deg} \cdot \text{min}^{-1}$ , from room temperature to 1000 °C in synthetic air flow 100 mL/min. *In situ* HTXRD was performed using the same X'Pert Pro MPD diffractometer equipped with an Anton Paar High-Temperature Chamber with Pt heating strip, heating rate of 10  $\text{deg} \cdot \text{min}^{-1}$ , from room temperature to 1000 °C in air, working conditions same as room temperature for XRD analysis. Patterns were recorded at different temperatures (°C): 110, 150, 200, 250, 300, 350, 450, 550, 600, 650, 670, 690, 800, 900, and 1000, with an isothermal step of 10 min before recording each pattern (for stabilization).

After the thermal treatment, the sample was again subjected to infrared spectroscopy analysis.



**Fig. 1** Working algorithm scheme

The entire working algorithm is presented in Fig. 1:

## Results and discussions

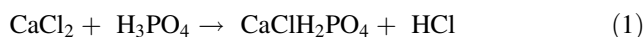
The XRD pattern of the reaction mixture right after the magnetic stirring of the reactants presented the formation of an amorphous compound [8, 9].

Within a few days after the mixing of precursors, the formation of a white sol was observed, which during the 2 months aging time transformed into a white gel, and then into paste, continuing to dry very slowly under room conditions.

Following a 2 months' time period, the sample was analyzed again by means of XRD [8, 10] and FTIR (see Fig. 2). The XRD results showed that the analyzed sample is a mixture of small microcrystalline formations, composed of  $\text{CaClH}_2\text{PO}_4$ ,  $\text{CaHPO}_4$ , and small quantities of

unreacted precursors. Our data interpretation software could not perform a quantitative analysis of the phases present in the mixture because not all the reference patterns contain calculated RIR values [11].

Equation of the chemical reaction for the  $\text{CaClH}_2\text{PO}_4$  formation is as follows:

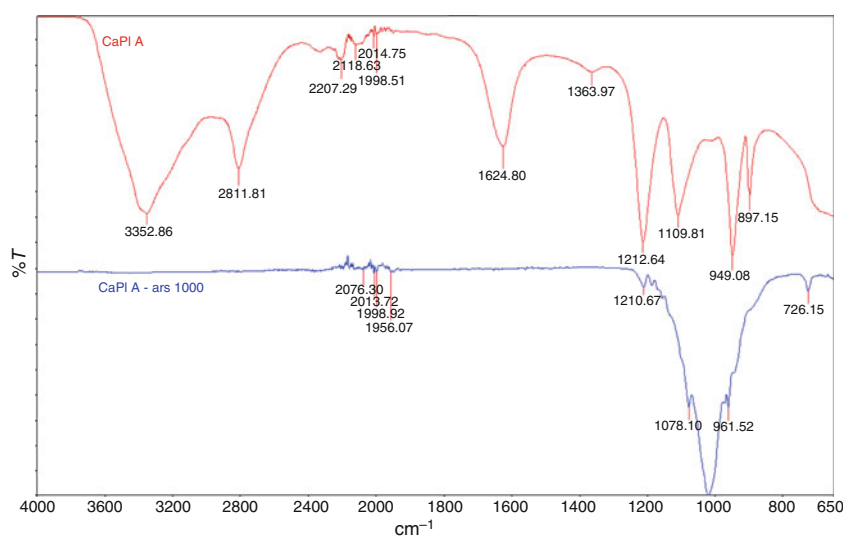


The peaks present in the FTIR pattern are characteristic to the P–O and P=O bond in the  $\text{PO}_4^{3-}$  group ( $1300\text{--}950\text{ cm}^{-1}$ ) [12, 13]. More than that, reference data [10] was found to match the XRD identification of  $\text{CaClH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  formation as a major phase in the analyzed sample (897, 949, 1109, 1212, and  $2207\text{ cm}^{-1}$ ). Hydration water vibrations are also strongly present in the pattern ( $3352, 2811\text{ cm}^{-1}$ ) and crystallization water bands ( $2118\text{--}1998, 1624\text{ cm}^{-1}$ ) [13]. The formation of the hydrated forms of compounds is favored by the synthesis method itself [1]. The small shoulder at  $1363\text{ cm}^{-1}$  was ascribed to the deformation vibration of OH group, and the small absorption bands in the area  $1998\text{--}2118\text{ cm}^{-1}$  represent the first degree overtones of the fundamental absorption band.

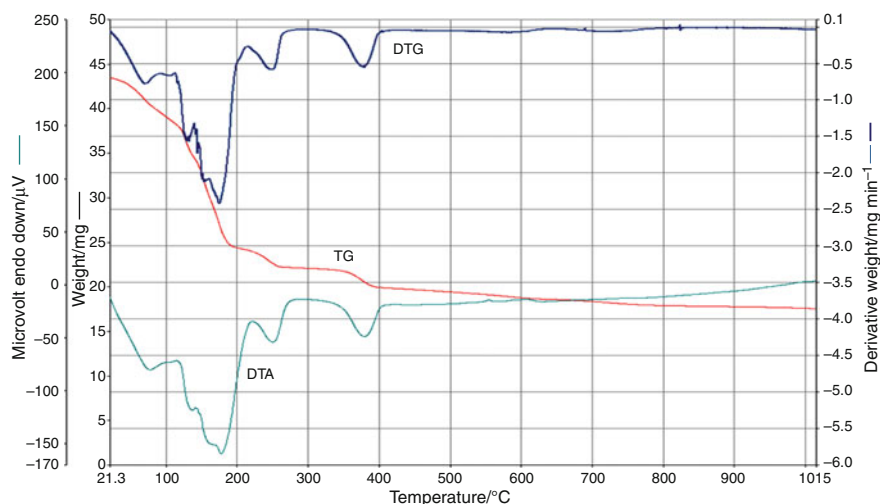
After identification, the sample was subjected to TA from room temperature up to  $1000\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ deg min}^{-1}$  in air, the thermal curve being presented in Fig. 3:

What can be seen is a complex type thermal decomposition, the shape of the curve being similar to previous thermal curves that we have obtained for hydroxyapatite gels [5]. The derivative curve shows five stages of decomposition, all of them being endothermal—according to the heat flow curve, characterized by mass losses presented in Table 1:

**Fig. 2** Comparison of FTIR patterns of the sample before (up) and after (down) the thermal analysis



**Fig. 3** TA curve, DTG curve and DTA curve, in dynamic air flow, 10 deg min<sup>-1</sup> from room temperature to 1000 °C



**Table 1** Details of thermal analysis decomposition processes, with temperature ranges and characteristic mass losses

Process	I	II	III	IV	V	Total
Temperature range/°C	25–114	114–138	138–214	223–268	345–400	
Mass loss/%	12.09	9.44	29.85	7.91	9.23	68.52

The loss of mass continues slowly after 400 °C, so apart from the mass losses given by these clear processes shown in Table 1, we have a supplementary mass loss of 5.32%.

What can be noticed is that all the mentioned processes are endothermic, after 400 °C the system becomes stable and a slow increase of the baseline of the DTA curve can be noticed, presenting an exothermal tendency of the system, due to the slow crystallization of the  $\beta$ -TCP with temperature.

The first decomposition process I actually consists of two stages which were considered together due to the appearance of the DTG curve, which shows a small observable effect for the second stage, probably some successive reactions. This 12.09% mass loss results from the loss of water, and also from the completion of the chemical interaction between precursors (reaction given by Eq. 1)—reaction that was not complete at the starting moment of thermal treatment—small tracks of precursors found in the XRD analysis before thermal treatment.

A very valuable help in data interpretation was given by HTXRD which was performed in the temperature ranging from room temperature to 1000 °C (Fig. 4) on a  $2\theta$  range of 10–38°, in the high-temperature chamber (HTK 2000 MSW) with platinum-heating strip. After heating to a certain temperature, an isothermal step of 10 min was performed before recording the xrd pattern, to stabilize the system.

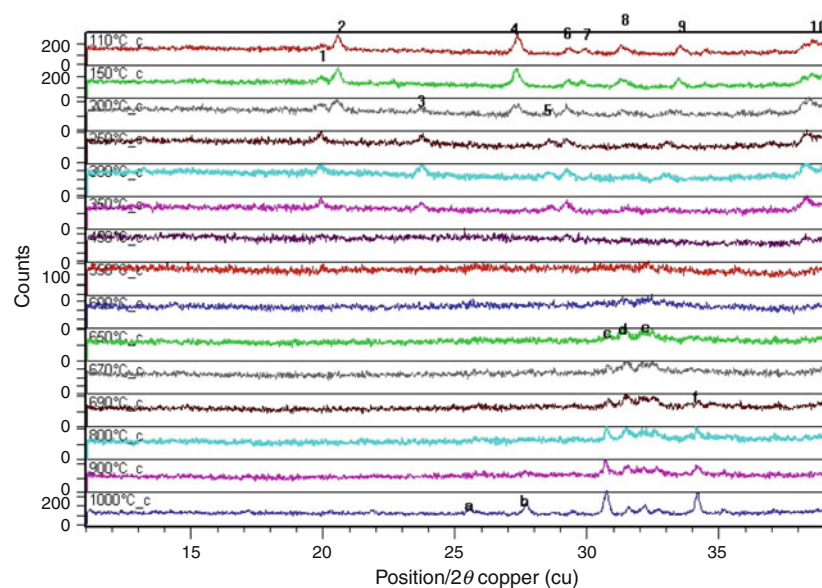
In Fig. 4, the patterns obtained by HTXRD technique are presented. The peaks that appear in the small

temperatures range are identified by numbers, from left to right as a function of  $2\theta$  position. The peaks in the high temperature range are identified by letters, using the same criterion. The identification of the peaks was a very difficult task, due to factors like the small intensity of peaks, and mostly the fact that calcium phosphate class materials give reflexions at approximately the same  $2\theta$  values, and one peak can be identified with quite a number of compounds.

The X-ray diffraction confirmed the hypothesis of the thermal decomposition curve: some complex processes take place during the thermal treatment of the sample. Among the peaks that are present on the 110 °C pattern, some are present up to 200 °C, and some until 350 °C. New peaks appear at 200 °C and some of the peaks (numbers 9 and 10 on the patterns) appear to slightly shift to the left as a function of the temperature increase. In the region 450–600, no peaks are present, which means no crystalline phase can be found (except for a small track of peak number 10). The crystallinity degree increases slowly with temperature, so after 650 °C the peaks can be ascribed. This statement is in agreement with the exothermal tendency observed on the DTA curve (crystallization) and characterized by a very small mass loss (crystallization from amorphous state coincides with the complete removal of water).

All the mentioned results were correlated to investigate the mechanism of sample transformation during the thermal treatment it was subjected to. What is presumed to

**Fig. 4** High-temperature X-ray diffraction from room temperature to 1000 °C, 10 deg min<sup>-1</sup>, in air. Peaks identification is: 2, 4, 7, 8, and 9—CaClH<sub>2</sub>PO<sub>4</sub>; peaks 1, 6, 10—CaHPO<sub>4</sub>; peaks 3 and 5—Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>; a, b, c, d, e, f—Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>



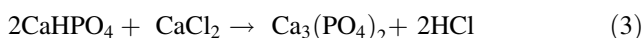
have happened first is a dehydration process, loss of hydration water which is present in the sample, and happening until around 100 °C. The first decomposition stage on the thermal curve represents mostly the loss of water.

The HTXRD pattern recorded at 110 °C shows the presence of CaClH<sub>2</sub>PO<sub>4</sub> (peaks 2, 4, 7, 8 and 9) compound the presence of which is expected until not more than 200 °C. The formation of CaClH<sub>2</sub>PO<sub>4</sub> started before the thermal treatment, its presence is proved by the FTIR analysis (Fig. 2) and XRD, but its characteristic peaks disappear after 200 °C. CaHPO<sub>4</sub> was also found in the HTXRD at 110 °C (peaks 1, 6, 10), as a result of decomposition of calcium chloride phosphate according to Eq. 2), and it is present until around 450 °C.



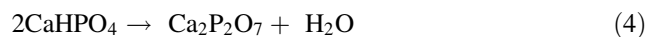
The theoretical mass loss of the decomposition of calcium chloride phosphate is 21.15%. The attempts to ascribe equations of chemical reactions to each decomposition process on the thermal curve have failed, because of the complexity of the data to be interpreted and phenomena taking place. Decompositions take place simultaneously along domains of temperature, like the previously mentioned decomposition (Eq. 2), which we presume to be taking place during the third decomposition step III (correlation with HTXRD).

The fourth decomposition process is related to the reaction by which amorphous calcium phosphate is formed.



the mass loss of which is 19.06%. The process will take place with maximum intensity around 250 °C, and it will stop not straight at 268 °C but around 300 °C.

The last observed decomposition process on the thermal curve is the decomposition of CaHPO<sub>4</sub> to Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, which according to the literature [10] will take place in the range 350–400 °C. The theoretical mass loss of this process is 6.61%. This decomposition is clearly seen on the DTA curve as an endothermal effect and on the HTXRD by the disappearance of the CaHPO<sub>4</sub> peaks.



The sum of the processes 3, 4, and 5 on the thermal curve is 46.99%, while the sum of the theoretical mass losses of calcium chloride phosphate decomposition and transformation of calcium hydrogen phosphate into TCP and calcium pyrophosphate is 46.82%. The meaning of the decomposition processes numbers 1 and 2 on the thermal curve is dehydration and parallel completion of the reaction of calcium chloride and phosphoric acid (practical sum of the processes 1 and 2 is 21.53%, and the practical mass loss for the formation of calcium chloride phosphate is 17.46%).

According to the data presented above, the sum of the theoretical mass loss of the thermally induced decompositions (see Eqs. 2, 3, 4) is in very good agreement with the experimentally determined values for steps III–V, namely 46.82% compared with 46.99%. The differences observed for the individual steps are certainly due to the superposition of the mentioned steps, especially steps IV and V, corresponding to the processes described by Eqs. 3 and 4 (see also TA curve in Fig. 3). Supplementary arguments for the steps described by Eqs. (2–4) have been given by HTXRD and FTIR data.

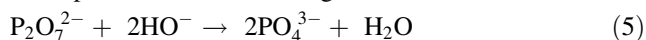
The CaHPO<sub>4</sub> phase did not actually form straight after the completion of the chemical interaction between the

calcium chloride and phosphoric acid, but represents a parallel presence in the system. Also, the peaks of calcium pyrophosphate appear at 200 °C (peak numbers 3 and 5), the explanation being that a small quantity of phosphoric acid has dehydrated to pyrophosphoric acid, the latter reacting with the calcium precursor.

The differences between the theoretical and practical values of mass losses exist because of water evaporation from the hydrated forms of the compounds, taking place at the same time for different intermediates.

After the thermal treatment, the number of peaks on the FTIR pattern is smaller, the wide absorption band in the region 1300–950  $\text{cm}^{-1}$  is characteristic to the  $\text{PO}_4^{3-}$  group, and the water vibrations are no longer present.

Some information seemed a little strange at the beginning: in the pattern recorded at 450, 550, and 600 °C, no peak was observed (except for a shadow of peak number 10). One possible explanation is given by the formation of amorphous TCP, which of course will show no peak on the XRD pattern. References [3] and [14] present the idea of decomposition of CPP-like phases ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) at higher temperatures (500–680 °C), with water evaporation, and the formation of  $\beta$ -TCP. Indeed, this hypothesis is proved here by the fact that peaks numbers 3 and 5 on the XRD at high temperatures—initially ascribed to  $\text{Ca}_2\text{P}_2\text{O}_7$ —appear only until 350 °C. After this temperature, as mentioned, the system contains amorphous phase(s), mainly TCP, the crystallization of which starts at 650 °C. The water loss of 5.32%, taking place after 400 °C, is precisely given by the loss of the water which is the product of the following reaction:



After 650 °C, we can see on the thermal curve that the mass loss continues slowly, and the shape of the DTA curve along this domain has an exothermal tendency, which is related to the increase of the crystallization degree of  $\text{Ca}_3(\text{PO}_4)_2$ , in agreement with other studies [3]. The HTXRD shows the formation of the characteristic peaks for TCP starting with the pattern recorded at 650 °C (peaks denoted with c, d, e). Peaks are growing in intensity when the temperature is raised, and also in number: peak f appears at 690 °C, peaks a and b at 1000 °C.

The differences observed between the theoretical (calculated) values for the mass loss and the practically obtained values are due to the fact that we have to deal with a complex system, which is changing continuously, and it is impossible to say that at a specific time, only one compound exists in the analyzed sample.

The broadening of the peaks of  $\beta$ -TCP XRD pattern lead to the idea that the ceramic material we have achieved is a nanometer-sized one. Calculating the crystallites size by Scherrer equation (applicable only to nanomaterials) for the most intense peak,

$$d = \frac{0.9 \cdot \lambda}{B \cdot \cos \theta} \quad (6)$$

The result shows that the assumption was correct: 2.628 nm at 1000 °C. Of course, there is a series of factors contributing to the peak broadening other than particles size, so errors are involved. With all that, we can still say that the  $\beta$ -TCP achieved is a nanoceramic material.

## Conclusions

Nanosized  $\beta$ -TCP was achieved from solution by a sol–gel approach, maturation for 2 months, and high-temperature crystallization. The full sequence of phase transformations that take place in the ceramic under study when thermally treated up to 1000 °C was constructed. Maturation leads to the formation of crystalline calcium chloride phosphate, which decomposed further, under thermal treatment, to calcium hydrogen phosphate, calcium pyrophosphate, and finally to crystalline  $\beta$ -TCP. The parallel reactions that took place were clearly evidenced on the thermal decomposition curve and X-ray patterns at different temperatures, the latter being a very valuable help in identifying the composition of the analyzed sample at a given temperature. The borders between the chemical reactions cannot be established, due to the fact that they take place simultaneously, along the domains of temperature. HTXRD proved itself to be a good method to perform both synthesis and characterization of materials, with advantages like considerable decrease of time consumption and minimization of influences like cooling, impurities, etc.

Nevertheless, the combination of long time maturation and high temperature treatment led to a nanometer-sized ceramic material ( $\sim 3$  nm), the application of which in the biomedical field depends strongly on the dimensional requirements of the application, among other factors.

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