

# Effect of heat-treatment on grain growth of nanocrystalline tricalcium phosphate powder synthesized via the precipitation method

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Nanocrystalline tricalcium phosphate powder was synthesized via the solution-precipitation method followed by heat treatment in order to achieve phase evolution, which was then studied by XRD and TEM techniques. The crystallites sizes were estimated by the Scherrer method and results were confirmed by TEM micrographs. The experimental observations showed that nanocrystalline tricalcium phosphate can be successfully prepared from raw materials by the precipitation technique. This technique is a competitive method for nanocrystalline tricalcium phosphate synthesis compared to other techniques. Moreover, a simple kinetic growth investigation was performed on the nanocrystalline growth process during heat treatment. Results have shown growth rate to increase exponentially with temperature and the growth rate constants to increase with time. The average activation energies of tricalcium phosphate grain growth obtained by this method were 84.78 and 134.38 KJ/mol.

Keywords: *tricalcium phosphate, nanostructures, crystal growth, electron microscopy, X-ray diffraction*

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## 1. Introduction

Calcium phosphate ceramics (CPCs) have received a great deal of attention as a potentially very useful material in a number of biomedical applications such as orthopedics, dentistry and drug delivery, because they exhibit considerably improved biological affinity and activity, compared to currently existing synthetic materials, to surrounding host tissues when implanted. Among these CPCs, particular attention has been placed to hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAp) and tricalcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$  (TCP) due to their outstanding biological responses to physiological environments [1].

TCP has been proved to be resorbable in vivo with new bone growth replacing the implanted TCP [2-4]. This property makes the TCP more advantageous compared to other biomedical materials, which are not resorbed and replaced by a natural bone. Therefore, TCP bioceramics are widely used as bone replacements in the field of oral and plastic

surgery [2, 5-7]. Most of the TCP is implanted in the forms of granules and rods. It is well known that the poor mechanical behaviour of TCP bioceramics is the main limitation in load-bearing applications in clinic [8, 9]. Thus, despite their favorable biological properties, the poor mechanical strength of TCP bioceramics has severely hindered their clinical applications [8, 9]. It is known that nano-size ceramic powders have high surface area and high sintering activity, which may result in the high mechanical strength of fully dense matrix with fine grain size at low sintering temperature [10].

Solid state reaction and wet chemical routes are two main methods of preparing TCP powders. Depending upon the preparation method, materials with different morphology, stoichiometry (Ca/P atomic ratio) and crystallinity can be obtained. Solid state reactions usually give rise to a stoichiometric and well-crystallized product at the expense of relatively high processing temperatures and long heat-treatment period. Wet methods can be divided into three categories: solution-precipitation method, hydrothermal technique, and finally hydrolysis of other calcium phosphates [11, 12]. In the solution-

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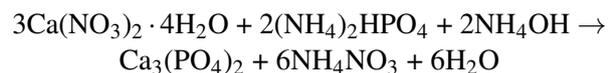
precipitation method, the temperature does not exceed 100 °C and nano-size crystals in the shapes of platelets, needles, rods, or equiaxed particles are obtained. The crystallinity and Ca/P atomic ratio of these products depend strongly upon the preparation conditions and is in many cases far from well-crystallized stoichiometric tricalcium phosphate. The hydrothermal technique usually results in TCP materials with a high degree of crystallization, a Ca/P molar ratio close to the stoichiometric value, and crystallite size in the range of several nanometers to millimeters [13, 14].

Properties of TCP bioceramics may be significantly improved by controlling important parameters of powder precursors such as particle size, shape, particle size distribution, and heat treatment. TCP nanocrystalline powders provide large surface areas, which improves sintering ability and densification of their corresponding ceramics [9].

In this study, the effect of heat-treatment on nano crystallization, phase transformation, and grain growth of tricalcium phosphate particles was investigated. Powder characterizations including phase composition, morphology and distribution of grain size have been performed. Moreover, simple discussion on the grain size growth rate and its activation energy is presented using classical and new grain growth approaches.

## 2. Material and Methods

Tricalcium phosphate powders were prepared by the solution-precipitation method using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Analar No. 10305) and  $(\text{NH}_4)_2\text{HPO}_4$  (Merck No. 1205) as starting materials and ammonia solution as an agent for pH adjustment. A 250 ml of 0.06 M  $(\text{NH}_4)_2\text{HPO}_4$  solution was slowly added dropwise to the 250 ml of 0.09 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  solution while being vigorously stirred at about 25 °C. In all experiments the pH of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  stock solutions was adjusted by ammonia at pH = 11. Under this condition, a stoichiometry composition can be easily achieved through the following reaction:



Once the precipitation reaction was complete, the suspensions were centrifuged at 3000 rpm for 60 seconds to remove the precipitates. The resulting powders were next dried in an oven at 80 °C for 1 hour and then calcined continually at 800, 1000, 1200, 1300 and 1400 °C in a tube furnace under controlled atmosphere. The heating rate was 10 °C/min and air was used as the purging gas. Total time for heat treatment was 2 hour and 20 min.

The phase transformation during the heat-treatment and crystallite size evolution were evaluated by X-ray diffraction using a Siemens diffractometer (30 KV and 25 mA) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and the Scherrer method from the line broadening of the diffraction lines, respectively

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

where  $t$  is the average grain size (nm),  $\lambda$  is the  $\text{CuK}\alpha$  wave length (nm),  $B$  is the diffraction peak with a half maximum intensity (radian), and  $\theta$  is the Bragg diffraction angle.

Transmission electron microscopy was also used for characterizing the size and shapes of particles. For this purpose, the particles were deposited onto Cu grids, which supported a “holey” carbon film. The particles were deposited onto the support grids by deposition from a dilute suspension in acetone or ethanol. The grain shapes and sizes were characterized by diffraction (amplitude) contrast.

## 3. Results and Discussion

### 3.1. Synthesis and Heat-treatment

Fig. 1 depicts the X-ray diffraction (XRD) patterns of tricalcium phosphate powders heat treated at various temperatures. The XRD pattern of TCP powder heated at 800 °C reveals wide peaks with low intensities without the presence of any second phase. The broadened (221), (-110) and (131) peaks indicate that the crystallites are very fine in nature with high atomic oscillations. All XRD patterns of the powders heat treated at different temperatures show similar profiles. However, the intensities of tricalcium phosphate peaks gradually increase

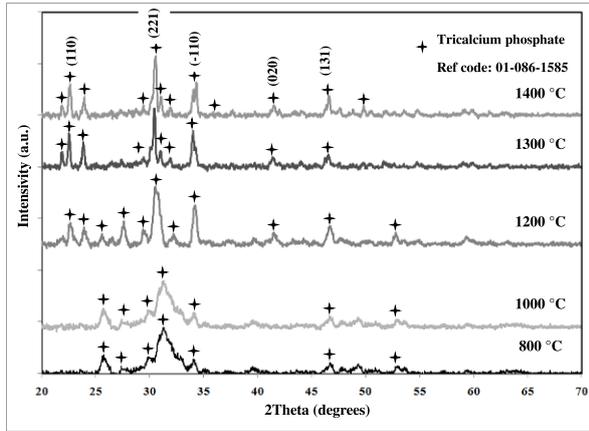


Fig. 1. XRD Patterns of heat treated tricalcium phosphate powders at different temperatures.

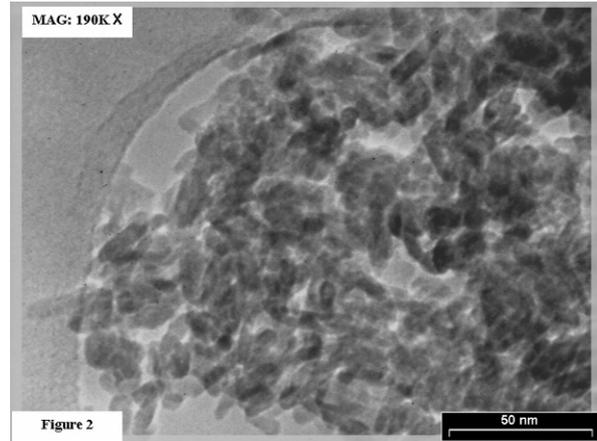


Fig. 2. TEM micrograph of tricalcium phosphate powder heated at 800 °C.

Table 1. Grain size of TCP crystalline as a function of heat treatment temperature and time.

Heat treatment time [s]	Grain size [nm]	Temperature [°C]
4800	17.60	800
6000	21.10	1000
7200	26.40	1200
7800	35.40	1300
8400	52.80	1400

by rising the heat treatment temperature. This suggests further nucleation/growth of the Rhombohedral R-3m nano crystals. This figure also confirms that the Rhombohedral R-3m phase, which is the stable phase of tricalcium phosphate at room temperature, does not transform to the other phases by heating up to 1400 °C.

The XRD pattern of the heat treated tricalcium phosphate at 800 °C is almost similar to that of 1000 °C. Heat treatment at 1200 °C, 1300 °C and 1400 °C results in the enhancement of peak intensities, formation of new crystallographic planes such as (343), (110), (112), (222), (230) and (-211), peak splitting between 20 °C to 60 °C, and contraction of peak widths. This is attributed to the reduction of amorphous phase quantities, enrichment of crystallinity, and arrangement in tricalcium phosphate structure.

Table 1 represents the calculated crystallite sizes at different heat treatment temperatures using XRD

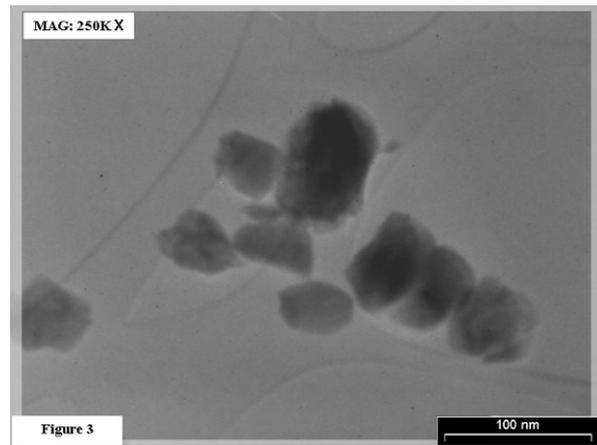


Fig. 3. TEM micrograph of tricalcium phosphate powder heated at 1400 °C.

profile analysis and Scherrer method [15–17]. In this method, the broadening contributions due to the crystallite size are taken into account. Transmission electron microscopy (TEM) micrographs of the tricalcium phosphate powders after heating at 800 and 1400 °C are shown in Fig. 2 and Fig. 3, respectively. The TEM observations are in good agreement with XRD results. The microstructure of tricalcium phosphate particles after heat treatment at 800 °C is observed to be almost like irregular needle, with particle size in the range of 15–20 nm. By increasing temperature to 1400 °C, the particle size of tricalcium phosphate is found to be 50–60 nm with irregular circular plates shape morphology.

### 3.2. Grain Growth Investigation

As mentioned above, heating powders from 800 °C to 1400 °C is accompanied by enhanced nucleation/growth of the nano crystals inside the powder. Although the exact particle nucleation and growth mechanisms are not clear, nucleation occurs probably by either hydrolytic reactions or a salting-out phenomenon. The growth could be progressing by molecular diffusion/deposition or the aggregation of primary particles with increasing temperature.

The results in Table 1 show that during the heat treatment, nano scale grain growth has occurred. In general, grain growth occurs in polycrystalline materials to decrease the system free energy by reducing the total grain boundary energy. The earliest consideration of the kinetics of normal grain growth assumes a linear relation between the growth rate and the inverse of grain size [18]:

$$\frac{dD}{dt} = \frac{k}{D} \quad (2)$$

where  $D$ ,  $t$ , and  $k$  are the mean grain diameter; heating time; and growth rate constant, respectively. The integration form of this equation is:

$$D^2 - D_0^2 = kt \quad (3)$$

and

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

where  $R$ ,  $Q$ ,  $T$ , and  $k_0$  are the universal gas constant, activation energy, absolute temperature and a constant, respectively.

Here, the Eqs. (3) and (4) are used for a simple investigation of the growth rate and activation energy of TCP crystallites. Approximately, a single growth process can be separated as several domains where  $k$  is a constant for each domain [19]:

$$\begin{aligned} \int_{D_0}^{D_n} DdD &= \int_{D_0}^{D_1} + \dots + \int_{D_{n-1}}^{D_n} DdD \\ &= \int_{t_{n-1}}^{t_n} k_1 dt + \dots + \int_{t_{n-1}}^{t_n} k_n dt \end{aligned} \quad (5)$$

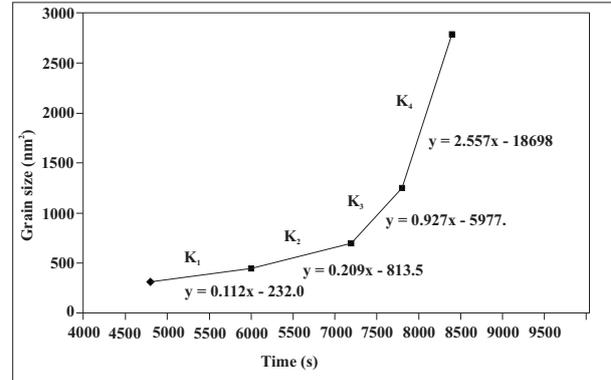


Fig. 4. Growth profile of TCP for  $n = 4$  in Eq. (6).

or

$$D^2 - D_0^2 = \begin{cases} k_1 t & t \leq t_1 \\ \dots & \dots \\ k_1 t + \dots + k_n (t_n - t_{n-1}) & t_n > t > t_{n-1} \end{cases} \quad (6)$$

$k_1, k_2, \dots, k_n$  are the growth rate constants in each domain.  $k_1, k_2, k_3$  and  $k_4$  values for a  $n = 4$  have been calculated in this study. The results are presented in Table 2 and Fig. 4. As shown, the growth rate constants increase with time:  $k_1 < k_2 < k_3 < k_4$ . The activation energy can be obtained from Eq. (4) as the slope of a plot of  $(\ln k)$  against  $(1/T)$ . This plot is shown in Fig. 5 for a minor and a major temperature of every domain. The average activation energies obtained are 84.78 and 134.38 KJ/mol for lower and higher temperatures, respectively.

Table 2. Constant growth rate in each domain.

Time range [s]	Rate constant [ $\text{nm}^2/\text{s}$ ]
4800–6000	0.112
6000–7200	0.209
7200–7800	0.927
7800–8400	2.557

It has been mentioned that for nano-scale materials, grain growth is accompanied by a reduction in diffusion rate and increase in activation energy of diffusion [20]. It is unclear what happens in the growth process of TCP during heat treatment. F. Liu

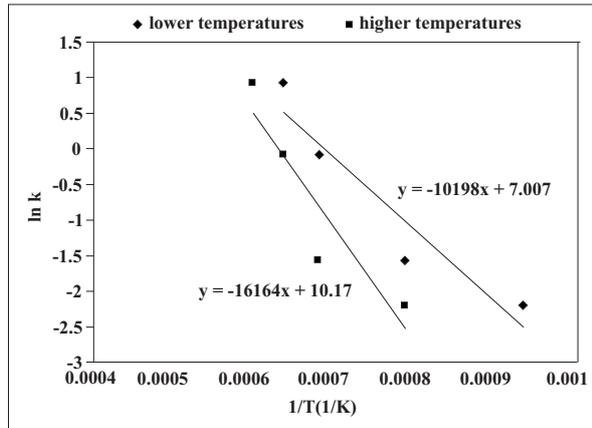


Fig. 5. Arrhenius plot of logarithm of the rate constants against reciprocal heat treatment temperature.

and R. Kirchheim [21] introduced a new empirical relationship using Gibbs adsorption equation and McLean’s grain boundary segregation model. This approach states that in systems with high segregation energy, decreasing grain boundary energy to zero is possible. In addition, the decrease of activation energy can be described with this equation. The grain size is proportional to the inverse exponential part of temperature according to the relation:

$$D = \frac{A}{B - \exp\left(-\frac{C}{T}\right)} \quad (7)$$

where  $A$ ,  $B$ ,  $C$ , are constant coefficients and  $T$  is temperature, respectively.

Therefore this relationship can present a better fitting for the TCP growth profile. It is well known that at high temperatures (about 1400 °C) the P and O atoms leave TCP crystalline lattice giving rise to the formation of calcium oxide, CaO. According to F. Liu and R. Kirchheim, the mobility of P and O atoms may increase at high temperature which causes that the crystallites gain enough energy to pass through the grain boundaries. This can be assigned as a “semi-segregation” phenomenon during heat treatment and explain corresponding changes in rate constants and activation energies at high temperatures. It must be mentioned that the constants in F. Liu and R. Kirchheim relation are not known for TCP.

## 4. Conclusions

Tricalcium phosphate powder of nano particles was successfully prepared via the solution-precipitation technique from  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  solutions as starting materials. The heat treatment was carried out on the tricalcium phosphate samples at different temperatures. The tricalcium phosphate grain sizes gradually increased when the sample was heated from 800 °C to 1400 °C. According to the observed growth investigation, the growth rate constants increased with increasing heat treatment period. Average activation energy obtained was in the range of 84.78–134.38 KJ/mol. Considering the new relationship proposed by F. Liu and R. Kirchheim, the mobility of P and O atoms may increase at higher temperatures leading to semi-segregation which may also explain the behaviors of growth rate constant and activation energy.

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