

## SYNTHESIS OF HYDROXYAPATITE BY MECHANOCHEMICAL TRANSFORMATION

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### Abstract

The mechanochemical transformation of  $\text{Ca}(\text{OH})_2-(\text{NH}_4)_2\text{HPO}_4$  was carried out for different periods of time from 30 min to 24 h in a horizontal vibration mill using steel vial and ball. The phase transformations obtained at each milling stage were characterized by X-ray diffraction, infrared spectroscopy and transmission electron microscopy. Complete transformation to hydroxyapatite took place during the first 5 h of milling. The contamination was not significant in the periods of milling studied.

**Keywords:** Mechanochemical transformations, Hydroxyapatite, Milling.

### Resumen

La transformación mecanoquímica de  $\text{Ca}(\text{OH})_2-(\text{NH}_4)_2\text{HPO}_4$  fue llevada a cabo durante diferentes tiempos desde 30 min hasta 24 h, en un molino vibratorio horizontal con un vial y una bola de acero. Las transformaciones de fase que tuvieron lugar en cada etapa de molienda fueron seguidas por difracción de rayos X, espectroscopia Infrarroja y microscopia electrónica de transmisión. La transformación completa a hidroxiapatita fue observada a las 5 h de molienda. No se obtuvo ninguna contaminación significativa durante el tiempo de molienda estudiado.

**Palabras Clave:** Transformación mecanoquímica, Hidroxiapatita, Molienda.

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### 1. INTRODUCTION

Mechanochemical processes consist in the application of mechanical methods for the activation of chemical processes and it is currently used for the synthesis of various compounds. The idea to perform the reactions directly in solid state, excluding the dissolution stage is very attractive. In wet chemical methods the dissolved substances, compared to the same substances in solid state substantially change their nature. For instance if hydrolysis occurs in the presence of water, this may result in substantial changes in the state of ions [12].

Solid State reactions usually are carried out at high temperature. However, mechanochemical processes are carried out at room temperature with a great simplicity, although high temperatures can be reached locally in the colliding region of balls, powders and vial walls. These characteristics have increased the attention of the community in this method due to the growing energetic and ecological requirements.

During mechanochemical processes the powder particles are periodically trapped between colliding balls causing fracturing, cold welding and the generation of a great density of defects. Surface chemical interaction between solids is created. For each collision clean new interfaces at the atomic scale are generated and with further milling the number of interfaces increases and the particle size decreases from millimeter to manometer lengths.

New economic and versatile methods of synthesis of Hydroxyapatite (HAp) are of interest due to the importance of this material for biomedical applications. Hydroxyapatite is the main natural inorganic constituent of bones. Therefore the applications of this material as bone substitute or bone graft is very attractive due to excellent biocompatibility.

Several methods have been used for preparation of HAp powders with wet methods [2-9] where the properties of the final product are largely influenced

by various processing parameters related to properties of starting substances such as morphology, composition and proportions. Also, these materials have been prepared by solid-state reactions [10]. Several papers, regarding mechanochemical and mechanochemical-hydrothermal synthesis of HAp powders have been reported in the literature [11-18]. The product obtained by the different authors depended of the method employed, the type of vial and the energy of the mill.

Therefore, by mechanochemical processes products with different morphology, stoichiometry, and level of crystallinity can be obtained depending upon the technique and the materials used.

In the present work the synthesis of Hydroxyapatite has been studied by mechanochemistry transformation for different milling periods using one ball and a steel vial in a horizontal vibrating mill.

## 2. EXPERIMENTAL

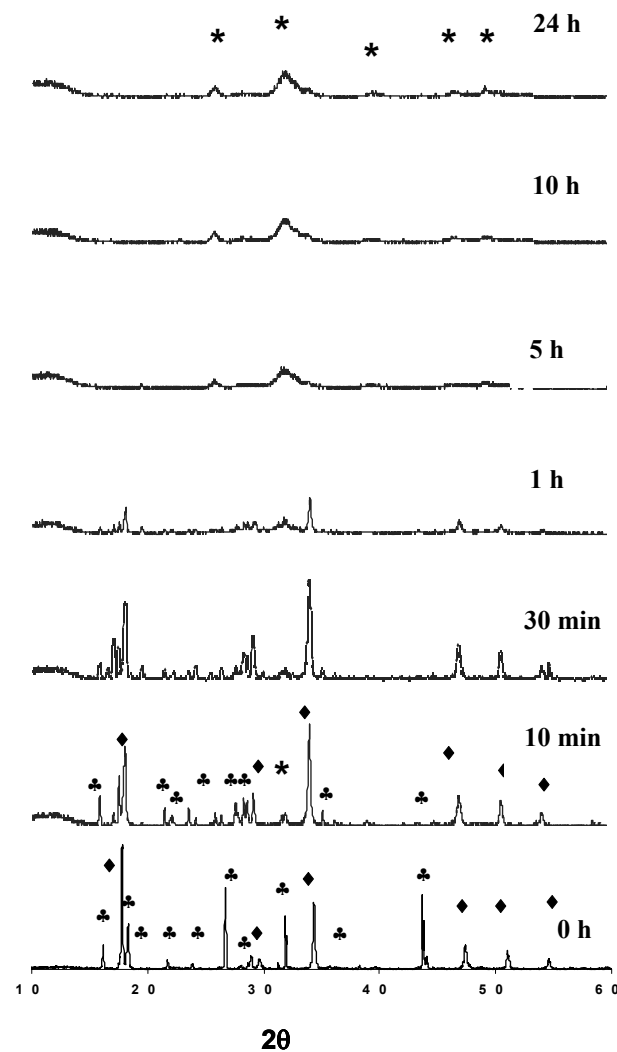
The solid reactants used were calcium hydroxide  $\text{Ca}(\text{OH})_2$ , (96%, Riedel De Haen), ammonium biphosphate  $(\text{NH}_4)_2\text{HPO}_4$  (98% Hopkin-& William). Each of the starting materials was kept in a sealed box to avoid moisture contamination before experiment. The starting materials were weighed to produce 1 gr. of product of stoichiometric Hydroxyapatite (Ca/P: 1.67). These mixtures were mixed and ground using stainless steel mortars with balls of the same material. A Retsch vibratory Mill, Type MM-2, working was used.

The mixture was put in the mill pot and ground at 1800 rpm in a three-dimensional motion for micro grinding and homogeneous mixing. The duration of grinding was varied from 10 min to 24 hours.

X-ray diffraction (XRD) analysis was employed using a Siemens D-5000 with  $\text{Cu-K}_\alpha$  radiation to investigate the evolution of phases formed and the crystallinity of the ground mixtures after different periods of grinding. Infrared absorption spectra of the mixtures at the different stages of grinding were measured employing Fourier-transform infrared spectroscopy (FT-IR, Nicolet 560). The different mixtures were also analysed for trace metal content by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer, Optima 3000).

## 3. RESULTS AND DISCUSSION

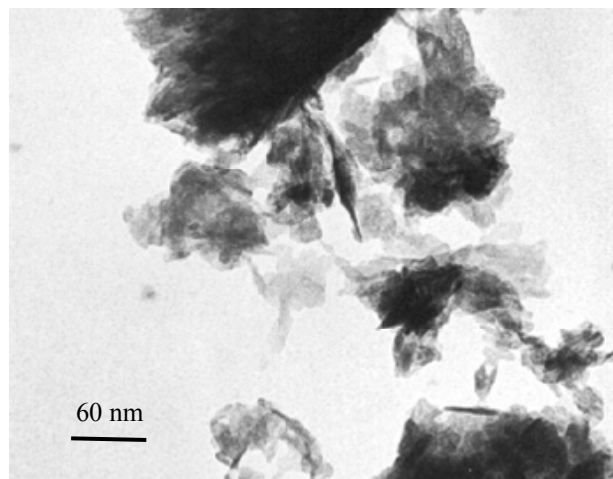
The transformation of  $\text{Ca}(\text{OH})_2$  and  $(\text{NH}_4)_2\text{HPO}_4$  for different milling times was followed by XRD and FTIR. Fig. 1 shows the XRD patterns for the different milling periods. After only 30 min the formation of some amount of HAp is observed but also the presence of some other reflections corresponding to the original reactants and intermediate phases are present.



**Figure 1.** XDR of  $\text{Ca}(\text{OH})_2 + (\text{NH}_4)_2\text{HPO}_4$  mixture milled during different periods. \* HAp  $\blacklozenge$   $\text{Ca}(\text{OH})_2$ ,  $\clubsuit$   $(\text{NH}_4)_2\text{HPO}_4$

The formation of HAp increases as milling time proceeds and only after 5h of milling the reaction is completed by the total consumption of both reagents. Formation of nanocrystalline HAp is obtained, the crystal size measured from the XRD patterns applying the Scherrer equation was 20 nm

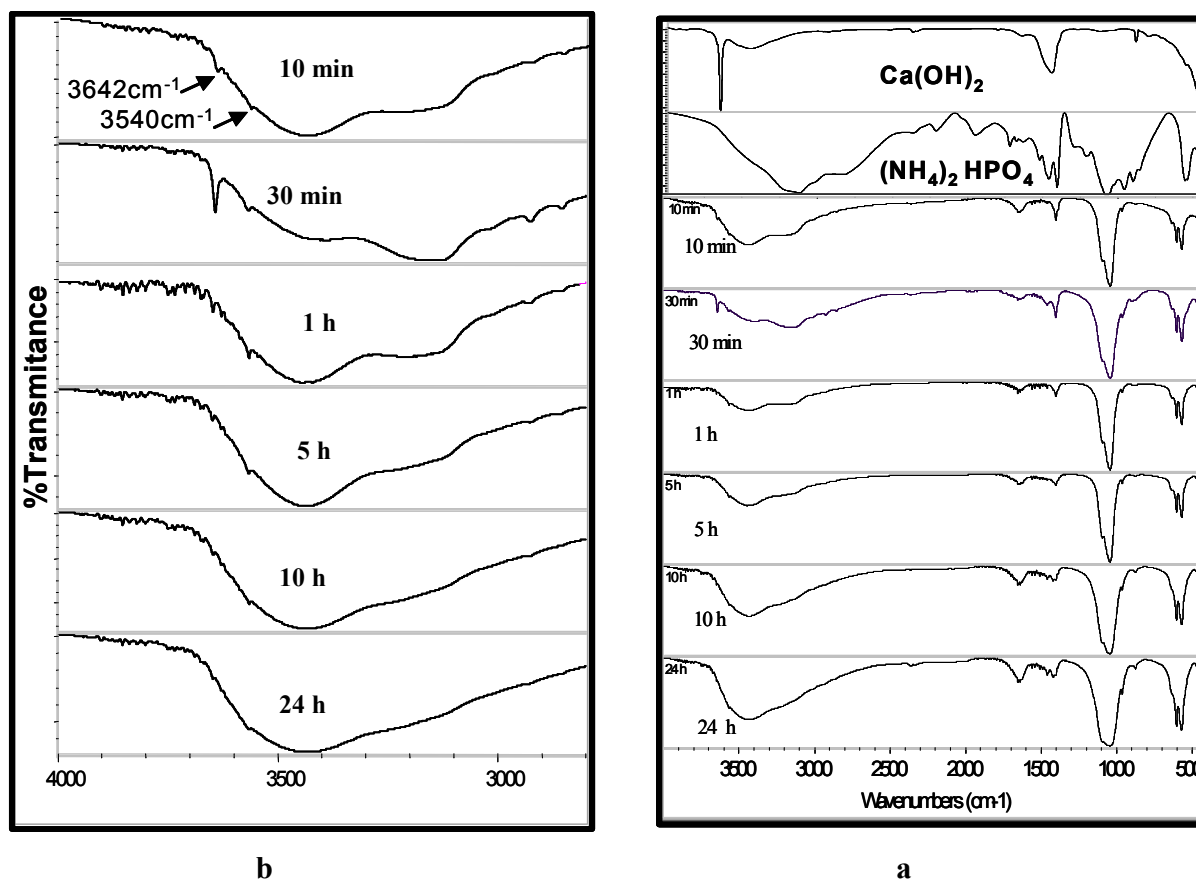
in very good agreement with the observation by transmission electron microscopy (Fig. 2) which shows long narrow needle-shape crystals of average crystals size of 20 nm wide and 80 nm length.



**Figure 2.** Transmission electron microscopy bright field image showing Hydroxyapatite crystals formed after 5 h of milling.

The FT-IR absorption spectra for these experiments (Fig. 3) show that the intensity of O–H bands from the  $\text{Ca(OH)}_2$  at  $3642\text{ cm}^{-1}$  and the N–H bands from  $(\text{NH}_4)_2\text{HPO}_4$  at  $3122\text{ cm}^{-1}$  decrease as the grinding times increase and after 5h the presence of the characteristic HAp bands are observed.

The vibration band at  $3642\text{ cm}^{-1}$  is attributed to the hydroxyl group of calcium hydroxide and the band at  $3540\text{ cm}^{-1}$  to the OH from hydroxyapatite. It has been reported [16] that hydroxyl stretch is observed at  $3569\text{ cm}^{-1}$  in the spectra of synthetic commercial hydroxyapatite and carbonated apatite powders. The bands between  $3600$  and  $2500\text{ cm}^{-1}$  are assigned to N–H vibrating mode of  $(\text{NH}_4)_2\text{HPO}_4$ . The bands detected at  $1050$ ,  $995$ ,  $660$  and  $520\text{ cm}^{-1}$  correspond to the  $\text{PO}_4^{3-}$  vibrating group of HAp. Theoretically, there are four vibrational modes present for phosphate ions,  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  and have been observed in hydroxyapatite powders [16]. The  $\nu_3$  band has three different sites present at  $1096$ ,  $1085$  and  $1056\text{ cm}^{-1}$ . The phosphate  $\nu_1$  band is present at

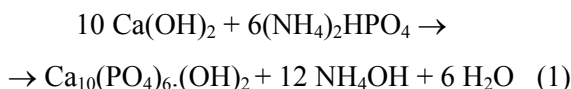


**Figure 3.** a). FT-IR spectra of  $\text{Ca(OH)}_2 + (\text{NH}_4)_2\text{HPO}_4$  mixture milled during different periods  
b). OH region magnified ( $4000 - 3000\text{ cm}^{-1}$ )

961  $\text{cm}^{-1}$  and the phosphate  $\nu_4$  band is present in the region of 660 and 520  $\text{cm}^{-1}$  as a well-defined sharp band in HAp and has also three sites observed at 633, 602 and 566  $\text{cm}^{-1}$ .

Further milling up to 24 h does not cause major changes in the product obtained, though a slight increment in the peaks intensity of HAp is observed.

The equilibrium reaction expected for these mixtures is the following:



It is known that milling produces dehydration and further reactions that can generate intermediate metastable products different from those expected in equilibrium. However, in this case although intermediate phases were formed for short milling periods, after 5 h of milling the phases obtained were those expected from the equilibrium reaction.

Yeong *et al.* [12] obtained HAp by mechanochemical synthesis of calcium oxide and Brushite after 30 h of milling. Gonzalez *et al.* [14] using dried grinding in an open mortar grinder from  $\text{Ca(OH)}_2$  and  $(\text{NH}_4)_2\text{HPO}_4$  initial reagents obtained very small formation of some HAp after 1.5 h of grinding with the presence of some intermediate compounds and further grinding produced amorphization of these products. In the present work a close vial was used and it seems that the energy transferred by the impact of the balls to the powder is higher than in a mortar open one and therefore the transformation more effective.

The mechanochemical reactions are based in the high reactivity of surface functional groups, notably OH groups originating acid-base reactions. Therefore, the combination of mechanical activation with the interaction according to the acid-base mechanism provides an increase of the efficiency of these reactions.

ICP measurements to detect the amount of possible contamination due to milling were carried out. The concentration of 14 elements analyzed was below the detection limit (50  $\mu\text{g/g}$ ), except for Fe in the samples with 10 and 24 hours of milling, whose concentration was 122 and 387  $\mu\text{g/g}$  respectively. According to the results of milling the synthesis of HAp was completed within the first 5 hours therefore after this time Fe contamination is not a potential problem.

#### 4. CONCLUSIONS

The synthesis of nanometric hydroxyapatite was obtained after only 5 h of milling.

No relevant traces of contamination were observed with milling.

Mechanochemical transformation with a low ball powder ratio is a suitable method for the synthesis of nanometric powders of hydroxyapatite due to its simplicity and efficiency.

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