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# Rietveld Refinement of Sintered Magnesium Substituted Calcium Apatite

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**Abstract**. The incorporation of magnesium in the synthetic apatite has been associated with biomineralization process and osteoporosis therapy in human and animals. Magnesium easily replaces calcium in the apatite lattice and influences or controls the hydroxyapatite crystallization processes. In this work, Mg-substituted calcium deficient apatite, with Mg/Ca ratio = 0.1, 0.15 and 0.2 were synthesized by precipitation method. Then, sintered at 1000 $^{o}$C and compared with a commercial product labeled as tricalcium phosphate sintered at the 1000 $^{o}$C. The sintered products showed tricalcium phosphate (β-TCP) structure. The $Mg^{2+}$ substitution in the Ca(4) and Ca(5) sites of β-TCP and the lattice parameter changes were estimated using the Rietveld method. Using this method, the formulas $Ca_{2.73}(Mg_{0.27})(PO_4)_2$, $Ca_{2.71}(Mg_{0.29})(PO_4)_2$ and $Ca_{2.70}(Mg_{0.23}Mg_{0.07})(PO_4)_2$ were calculated for the samples with Mg/Ca ratio = 0.1, 0.15 and 0.2 respectively.

## Introduction

The preparation of modified synthetic apatites mimetizing to natural bone in terms of crystallinity degree and stoichiometry has been of major interest for bone filling materials due to their similarity with the inorganic part of the major normal (bones and teeth) and pathological (dental caries, osteoporosis, arthrosclerosis) calcified tissues of the human being [1]. Properties such as biocompatibility, bioactivity and osteoconductivity allow the use of this material as bone substitutes. Several types of ionic substitutions in the bone apatite lattice change the mineral characteristics modifying the dissolution rate and crystallite size [2].

Magnesium is one of the most abundant trace ions present in biological hard tissue. Its concentration is approximately 0.1-0.4% in dental enamel, higher in dentine (up to 1.1%) and around 0.6% in bone [1]. Magnesium easily replaces calcium in the apatite lattice and influences or controls the hydroxyapatite cristalization process, affecting the stability of the lattice, causing decrease in the unit-cell parameters and consequently in crystallite size and/or increase in crystal strain [3]. The incorporation of magnesium in the synthetic apatite has been associated with biomineralization process and osteoporosis therapy in human beings and animals [4]. In this work three samples of Ca-deficient apatites with different Mg content were prepared, sintered and evaluated by XRD analyses and the molecular formulas obtained from structural Rietveld refinement. The influence of the Mg substitution in the lattice parameters of the unit cell beta-tricalcium phosphate (β-TCP) was evaluated.

## Materials and Methods

Magnesium substituted calcium deficient apatite (Mg-CDA) with Mg/Ca ratio equal to 0.1 (Mg1CaD), 0.15 (Mg1.5CAD) and 0.2 (Mg2CaD) were synthesized by precipitation method from an aqueous solution of calcium hydroxide 1.25M [$Ca(OH)_2$], orthophosphoric acid 2.85M [$H_3PO_4$] and magnesium chloride [$MgCl_2.6H_2O$] at 38°C, pH = 9. The precipitates were aged for 24h at 25°C, washed, filtered, dried overnight at 40°C, sieved at 125µm and sintered at 1000 °C for 4 hours in air (2.8°C/min heating rate). A commercial product labeled as tricalcium phosphate (β-TCP**,** Merck, dried extra pure, Darmstadt, Ge) was also sintered at 1000 °C using the same conditions.

The sintered materials were characterized by X-ray diffraction Rietveld method (XRD - XPERT PRO - Panalytical) performed with Bragg-Brentano geometry, CuKα radiation, (40kV, 40mA) data required from 5 - 65° (2θ) The Rietveld analyses modeled the backgrounds by a linear interpolation function and the shape of the peaks by a pseudovoight function.

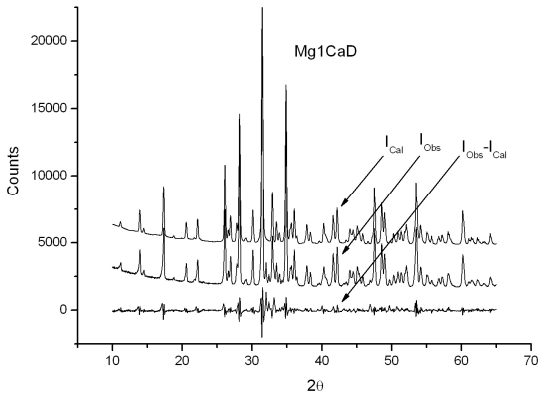
## Results and Discussion

The XRD profiles showed that all the sintered Mg-CDA samples were completely transformed to magnesian whitlockite (β-TCMP-JCPDS 13-0404 card) phase. The crystal structures of Mg-substituted β-TCPs were analyzed by the Rietveld Method [5] using FULLPROF software [6]. Table 1 shows the lower values found for all R-Factor ($R_{wp}$, $R_{Bragg}$ and $R_F$) denoting that the refined structural models were adequate to describe the crystals of the sintered samples. There was a good agreement of the parameters among the three β-TCMP samples and the β-TCP used as the reference sample.

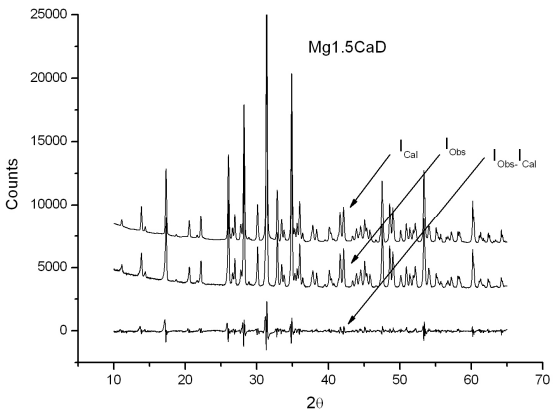
**Table 1:** Agreement factors for sintered Mg-Ca deficient apatite at 1000 °C

| *(%)* | *Mg1CaD* | *Mg1.5CaD* | *Mg2CaD* | *β-TCP Merck* |
|---|---|---|---|---|
| $R_{wp}$ | 18.7 | 15.9 | 16.4 | 11.1 |
| $R_{Bragg}$ | 4.43 | 2.90 | 3.52 | 3.84 |
| $R_F$ | 2.88 | 2.35 | 2.31 | 3.11 |

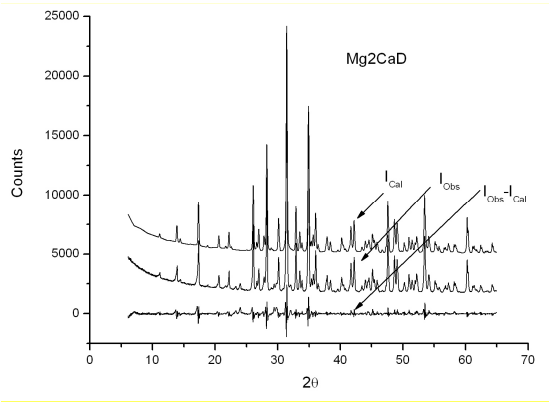
Figure 1 shows the Rietveld refinement of the unit cell of the β-TCMP samples obtained from the sintered Mg-CDAs with Mg/Ca ratio = 0.1, 0.15 and 0.2. The partial Mg-for-Ca substitution in the β-TCP, $Ca_3(PO_4)_2$ was reflected in the XRD peaks shifts indicating contraction in the unit cell dimensions.




Mg1CDA




Mg1.5CDA




Mg2CDA

**Figure 1:** XRD Rietveld refinement of Mg substituted Ca-deficient apatites (Mg-CDAs) with different Mg/Ca ratio before and after sintering at 1000 °C

Table 2 summarizes the crystallographic data obtained for the β-TCMPs after sintering Mg-CDAs compared with other authors. The contraction of the parameters a=b and c, when compared with the Mg-free reference samples (β-TCP) was correlated to the Mg content in the structure (Fig. 2).

**Table 2:** Lattice parameters of **β-TCP and β-TCMP samples**

| *Sample* | ***Mg mol(%)*** | *a =b(nm)* | *c (nm)* |
|---|---|---|---|
| β-TCP Merck | 0 | 1.04208(2) | 3.73711(7) |
| β-TCP[8] | 0 | 1.043520 | 3.740290 |
| Mg1CaD | 9.0 | 1.03415(1) | 3.71543(2) |
| Mg1.5CaD | 9.7 | 1.03153(7) | 3.72117(2) |
| Mg2CaD | 10.0 | 1.03229(0) | 3.72066(0) |
| β-TCMP [7] | 8.0 | 1.03599(4) | 3.7175(3) |
| β-TCMP [7] | 12.0 | 1.03296(6) | 3.7208(5) |

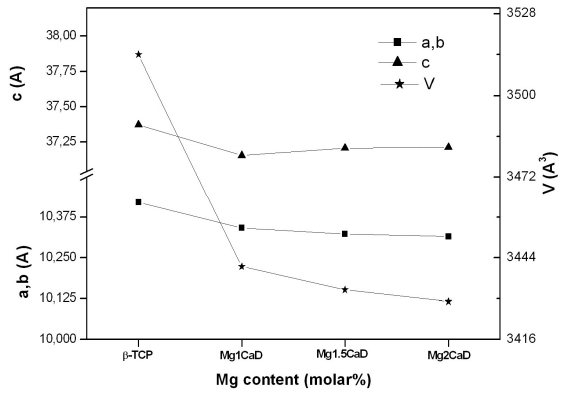



**Fig. 2**: Cell parameters and unit cell volume of sintered Mg-CDAs as function of Mg content in the β-TCMPs.

The occupancy values obtained from the Rietveld refinement were used to estimate quantitatively the inclusion of the $Mg^{2+}$ in the β-TCP lattice.

Rietveld refinement analysis showed that $Mg^{2+}$ incorporated in β-TCMP for the sintered Mg2-CDA sample occupied 24% of the Ca(4) site and 87% of the Ca (5) site with the $Mg^{2+}$molar content around 11.1%, and could be approximately represented by the molecular formula: $Ca_{2.70}(Mg^{V}_{0.23}Mg^{IV}_{0.07})(PO_4)_2$. Similarly, the approximate structural formula for sintered Mg1.5CDA is $Ca_{2.71}(Mg_{0.29})(PO_4)_2$ with Mg occupying 96% of the M(5) site, with $Mg^{2+}$molar concentration of abaut 10.6%. The approximate structural formula for sintered Mg1CDA is $Ca_{2,73}(Mg_{0,27})(PO_4)_2$, with $Mg^{2+}$ occupying 90% of the Ca (5) site, with $Mg^{2+}$molar concentration of about 9.8%. The average crystallite sizes were determined by XRD data and are shown in Table 3. As expected, increasing the amount of Mg in calcium deficient apatite, the apatite crystallite size decreased.

**Table 3:** Average crystallite size of the Mg-substituted calcium deficient apatite (MgCDA) samples

| ***Sample*** | ***Cristallize size* (nm)** | **Mg mol(%)** |
|---|---|---|
| Mg1CDA | 256 | **9.0** |
| Mg1.5CDA | 183 | **9.7** |
| Mg2CDA | 152 | **10.0** |

## Conclusion

The crystallite size of Mg-CDA decreased with increasing $Mg^{2+}$ content. XRD analysis showed that the MgCDA samples sintered at 1000 °C were transformed into Mg-substituted tricalcium phosphate, β-TCMP, $(Ca,Mg)_3(PO_4)_2$. The approximate structural formulas obtained using Rietveld refinement analysis were: $Ca_{2.73}(Mg_{0.27})(PO_4)_2$, $Ca_{2.71}(Mg_{0.29})(PO_4)_2$ and $Ca_{2.70}(Mg_{0.23}Mg_{0.07})(PO_4)_2$ for MgCDA samples with Mg/Ca ratio = 0.1, 0.15 and 0.2 respectively.

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