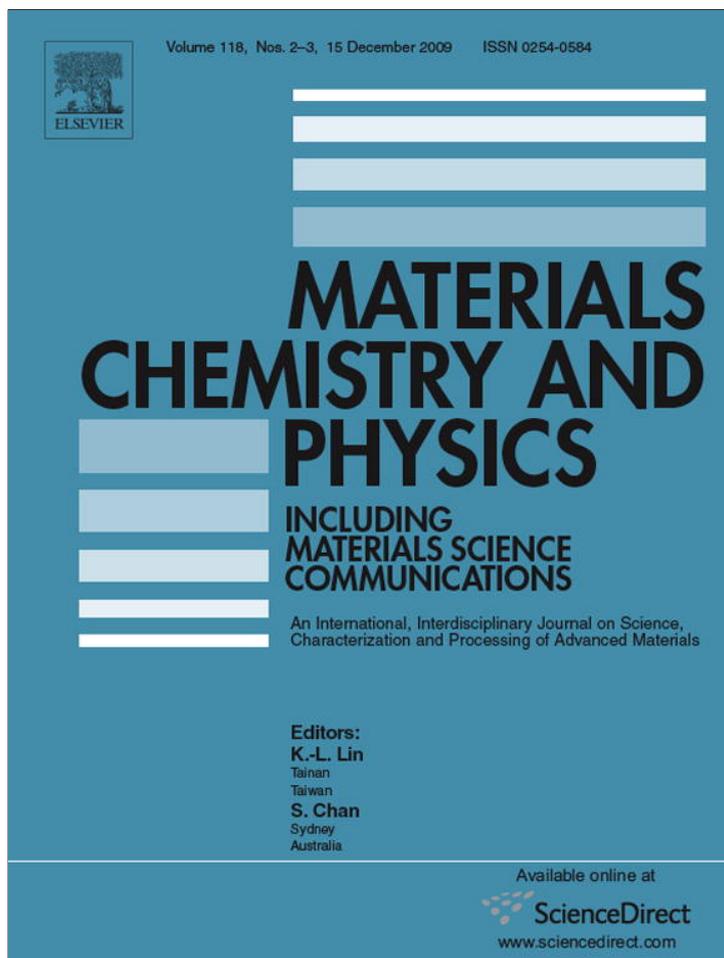


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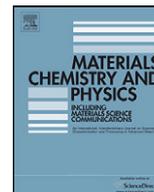
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# Maximum substitution of magnesium for calcium sites in Mg- $\beta$ -TCP structure determined by X-ray powder diffraction with the Rietveld refinement

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## ABSTRACT

The purpose of this study was to determine the maximum substitution of magnesium, Mg<sup>2+</sup>, for calcium, Ca<sup>2+</sup> sites in a beta-tricalcium phosphate (Mg- $\beta$ -TCP) powder using the Rietveld method. Ca-deficient apatite with a theoretical 0.2 Mg/Ca ratio was synthesized and the resultant powder sintered at 1000 °C for 4 h. The maximum Mg<sup>2+</sup> substitution of nearly 15 mol% in  $\beta$ -TCP structure was deduced from the occupancy factors. The analysis indicated that the maximum substitution of Mg<sup>2+</sup> on the M(4) and M(5) sites was, approximately, 4.21 and 10.72 mol%, corresponding to the Ca<sub>2.61</sub>(Mg<sub>1.028</sub>Mg<sub>2.011</sub>)(PO<sub>4</sub>)<sub>2</sub> stoichiometric formula. A small displacement of the Ca atoms position was observed around the Mg1(5)PO<sub>4</sub> octahedral, and their increasing shift to the PO<sub>4</sub> triangles corners.

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## 1. Introduction

Tricalcium phosphates (TCP), Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, are materials of interest for orthopedic and dental applications [1]. TCP can be obtained either by solid-state reaction or by sintering calcium-deficient apatites. Depending on the sintering temperature, the polymorphic  $\beta$ -TCP (below 1120 °C) or  $\alpha$ -TCP (from 1125 °C to 1430 °C) can be obtained [2,3]. Some bone graft commercial products described as biphasic calcium phosphate, BCP, consist of an intimate mixture of hydroxyapatite (HA) and  $\beta$ -TCP [4], and are based on the higher resorbability of the  $\beta$ -TCP compared to the HA component.

Magnesium (Mg) is one of the most abundant trace ions present in the biological hard tissue. Mg<sup>2+</sup> can replace calcium (Ca<sup>2+</sup>) ions in  $\beta$ -TCP, causing structure stability [2,3,5,6]. Mg-substituted beta-tricalcium phosphate (e.g., Mg- $\beta$ -TCP) is present in biologic systems [2,5], and synthetic Mg- $\beta$ -TCP has been proposed for osteoporosis therapy [7] attaining acceptance for biomedical applications due to the extension of  $\beta$ -TCP stability caused by magnesium additions [7]. As reported by Schroeder et al. [6],  $\beta$ -TCP crystallizes in the rhombohedral space group R3c, and the unit cell contains 21 cation sites and 16 PO<sub>4</sub> groups. Enderle et al. [8] exam-

ined  $\beta$ -TCP powders with Mg ranging from 0 to 20 mol% obtained by solid-state reaction using X-ray powder diffraction combined with the Rietveld method [9]. A maximum ~16 mol% of Mg<sup>2+</sup> substitution on Ca(4) and Ca(5) sites in the  $\beta$ -TCP structure was found, corresponding to a solid solution with (Ca<sub>0.86</sub>Mg<sub>0.14</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> composition.

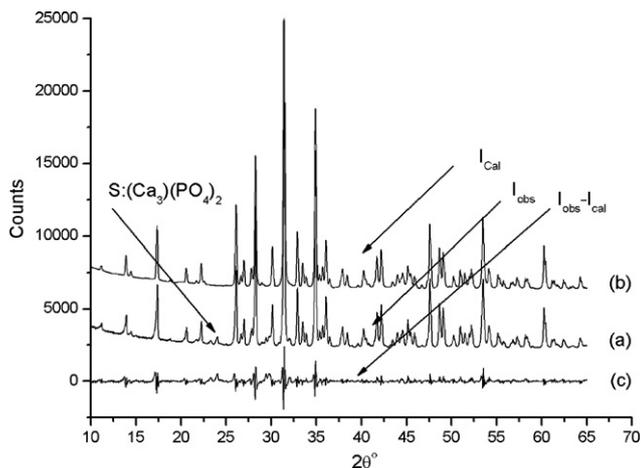
Other method as linear-polarized infrared (IR-LD) spectroscopy [10] can be used for structural and local elucidation of crystalline inorganic compounds with PO<sub>4</sub> units. The IR-band assignment of the typical local structural PO<sub>4</sub> units in  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> can be proposed by a comparison with the IR-characteristics of appropriate crystalline similarity structure as Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> [11].

In our previous work [12], the Mg containing Ca-deficient apatite (Mg-CDA) powder with Mg/Ca molar ratio equal to 0.20 was synthesized by wet precipitation. The goal of these kinds of synthesis is to obtain a (Ca, Mg) solid solution without the presence of a significant amount of second phases such as stanfieldite [7]. Mg-CDA sintering resulted in Mg- $\beta$ -TCP [12]. The sintered powder was analyzed by the Rietveld method, using a pseudo-Voigt profile function and only one isotropic thermal parameter to describe all of the atomic vibration of the structural model. The (Ca<sub>0.90</sub>Mg<sub>0.1</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> formula was obtained, indicating that only ~55% of added Mg could be effectively incorporated into the Mg- $\beta$ -TCP cell structure [12].

In this paper, the same data was reanalyzed using a Thompson-Cox-Hasting profile function [13] in order to determine the maximum Mg content in the  $\beta$ -TCP solid solution. The environment of sites Ca(4) and Ca(5) was evaluated and some additional

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**Fig. 1.** A comparison of the observed [curve (a)] and calculated [curve (b)] obtained by powder diffraction pattern of Mg-β-TCP. Curve (c) is the difference profile and (S) is the diffraction due to the secondary phase, Stanfieldite.

evidences of Mg<sup>2+</sup> replacement in both M(4) and M(5) sites were also reported. No attempt was made to determine, in the structural refinement process, the position of Mg<sup>2+</sup> in the unit cell.

**2. Materials and methods**

Calcium deficient apatite, in which 20 mol% of Ca<sup>2+</sup> was substituted by Mg<sup>2+</sup> (Mg/Ca ratio = 0.2), was synthesized by the precipitation method of an aqueous solution of calcium hydroxide 1.25 M [Ca(OH)<sub>2</sub>], orthophosphoric acid 2.85 M [H<sub>3</sub>PO<sub>4</sub>] and magnesium chloride [MgCl<sub>2</sub>·6H<sub>2</sub>O] at 38 °C, pH 9. The precipitate was aged for 24 h at 25 °C, washed, filtered, dried overnight at 40 °C, ground and sieved to 125 μm, then sintered at 1000 °C for 4 h in the air. The sintered powder was characterized by the use of X-ray diffraction and the Rietveld method [14] (XRD – XPERT PRO – Panalytical) using the FULLPROF software [14]. XRD was performed with Bragg-Brentano geometry, CuKα radiation (40 kV, 40 mA), data collected from 5–65° (2θ) with the step size = 0.02 and set time = 5 s. These data range (2θ°) and step size were adopted previously by Kannan et al. [15] in the analysis of β-tricalcium phosphate mixtures results were compared with data from a pure β-TCP [1] and Mg-β-TCP data from literature [2,6,8]. The Rietveld analysis [9] modeled the background by

**Table 1**  
Refined occupancy factors calculated for the five different Ca-sites.

Site	Number of atoms/site	Ion	Occupancy factor
Ca(1)	18	Ca <sup>2+</sup>	1.05(1)
Ca(2)	18	Ca <sup>2+</sup>	0.95(1)
Ca(3)	18	Ca <sup>2+</sup>	1.00(1)
Ca(4)	6	Mg <sup>2+</sup>	0.377(7)
		Ca <sup>2+</sup>	0.123*
Ca(5)	6	Mg <sup>12+</sup>	1.00(3)

\*The occupancy factor for Ca<sup>2+</sup> in M(4) site is equal to 0.5 min the occupancy factor for Mg<sup>2</sup>

**Table 2**  
Atomic parameters (× 10<sup>4</sup>) for Ca<sub>3-x</sub>Mg<sub>x</sub>(PO<sub>4</sub>)<sub>2</sub>, where x = 0.39 (present work) and x = 0.29 [6].

Site	x value	Fractional coordinates			Anisotropic thermal parameters					
		x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Ca(1)	0.39	-2716(7)	-1454(6)	1678(8)	18.5	18.7	1.0	10.1	-0.2	-0.7
	0.29	-2730(1)	-1420(1)	1665(1)	75(1)	76(1)	70(1)	41(1)	-3(1)	-11(1)
Ca(2)	0.39	-3766(1)	-1775(0)	-345(4)	21.4	16.3	1.1	8.4	-1.4	-0.3
	0.29	-3840(1)	-1769(1)	-348(1)	87(1)	66(1)	75(1)	34(1)	-24(1)	-5(1)
Ca(3)	0.39	-2746(2)	-1469(4)	595(4)	75.6	36.7	2.0	42.9	-6.1	-4.7
	0.29	-2738(1)	-1480(1)	595(1)	307(1)	149(1)	140(1)	174(1)	-103(1)	-79(1)
M(4)	0.39	0	0	-725(1)	31.3	31.3	1.9	15.8	0	0
	0.29	0	0	-780(1)	127(1)	127(1)	134(1)	64(1)	0	0
M(5)	0.39	0	0	-2646(7)	10.3	10.3	0.6	5.2	0.0	0.0
	0.29	0	0	-2652(1)	42(2)	42(2)	44(3)	21(2)	0	0

**Table 3**  
Occupancy of Mg in M(5) and associated structural parameters.

Crystal sample	(x=0) [1]	Mg-β-TCP (x=0.38)	ICSD 1491 (x=0.29)[6]
O <sub>Mg</sub> <sup>+</sup>	0.0	1.000(3)	1.000(7)
d (Å)M(5)-O(4)	2.238(2)	2.05(4)	2.070(1)
d (Å)M(5)-O(7)	2.287(2)	2.01(3)	2.084(1)
<° O(4)-M(5)-O(4)	82.7(1)	88.0(2)	85.4(1)
<° O(7)-M(5)-O(7)	79.1(1)	84.1(4)	84.1(1)

\*Occupancy factor for Mg<sup>2+</sup>.

a fifth order polynomial, and the shape of the peaks by a Thompson-Cox-Hastings function (TCHZ) [12]. A total of 59 parameters were refined.

The Mg-β-TCP structure was refined, starting from the fractional coordinates of the ICSD1491 model data [6]. A constraint was imposed on the sums of the occupancy factors for the atoms in sites M(4) and M(5) that should be equal to the crystallographic values, e.g., 0.5 and 1.0, respectively, following the strategy used firstly by Bigi et al. [16,17]. Only the Ca(1), Ca(2), Ca(3), M(4) and M(5) occupancy factors were refined; this procedure was also adopted by Kannan et al. [15] when using the Rietveld refinement of β-TCP mixtures structural models. At the end of the refinement, the anisotropic thermal factors were fixed since they affected the occupation ones. Moreover, no differentiation between calcium and magnesium positions was considered. The 0° to 5° (2θ) refinement range was excluded to reduce the R<sub>wp</sub> residue, yet this region did not evidence any relevant data.

**3. Results and discussion**

The powder X-ray diffraction (XRD) revealed that the sintered sample was transformed into magnesian whitlockite (Mg-β-TCP – JCPDS 13-0404 card) phase. Also, a non-significant amount of secondary phase (CaMg)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (Stanfieldite) was identified in opposition to its massive presence (13.3 ± 0.2 wt%) in samples with similar Mg/Ca ratio [8]. This difference is the consequence of the used route. During wet synthesis, pH and temperature define the phase in equilibrium, and some reagents may remain in solution without being incorporated into the formed solid [2].

Although a total of 59 parameters was refined by a Thompson-Cox-Hastings function (TCHZ) [9], the diffraction profile can be described using only two TCHZ parameters, namely U = 0.00413(0) and Y = 0.036(1). The average “full width at a half height” (FWHM) was of 0.1346°, which corresponds to a sample with relatively large crystals, compatible with the 1000 °C sintering. The agreement indices of the refinement were R<sub>wp</sub> = 0.0177, R<sub>Bragg</sub> = 0.0399 and R<sub>F</sub> = 0.0260. Consequently, residual Stanfieldite phase identified on XRD patterns seems to have no significant influence on the refinement procedure.

Fig. 1 shows the Rietveld refinement of the model adopted to describe the real crystal structure. The a = b and c lattice parameters calculated values of 1.03236 and 3.72090 nm, respectively, are lower than the β-TCP cell parameters without magnesium [1,8]. This contraction in lattice parameters is well known, and is due to the substitution of Ca<sup>2+</sup> ion (1.00 Å) by Mg<sup>2+</sup> ion, with lower ionic

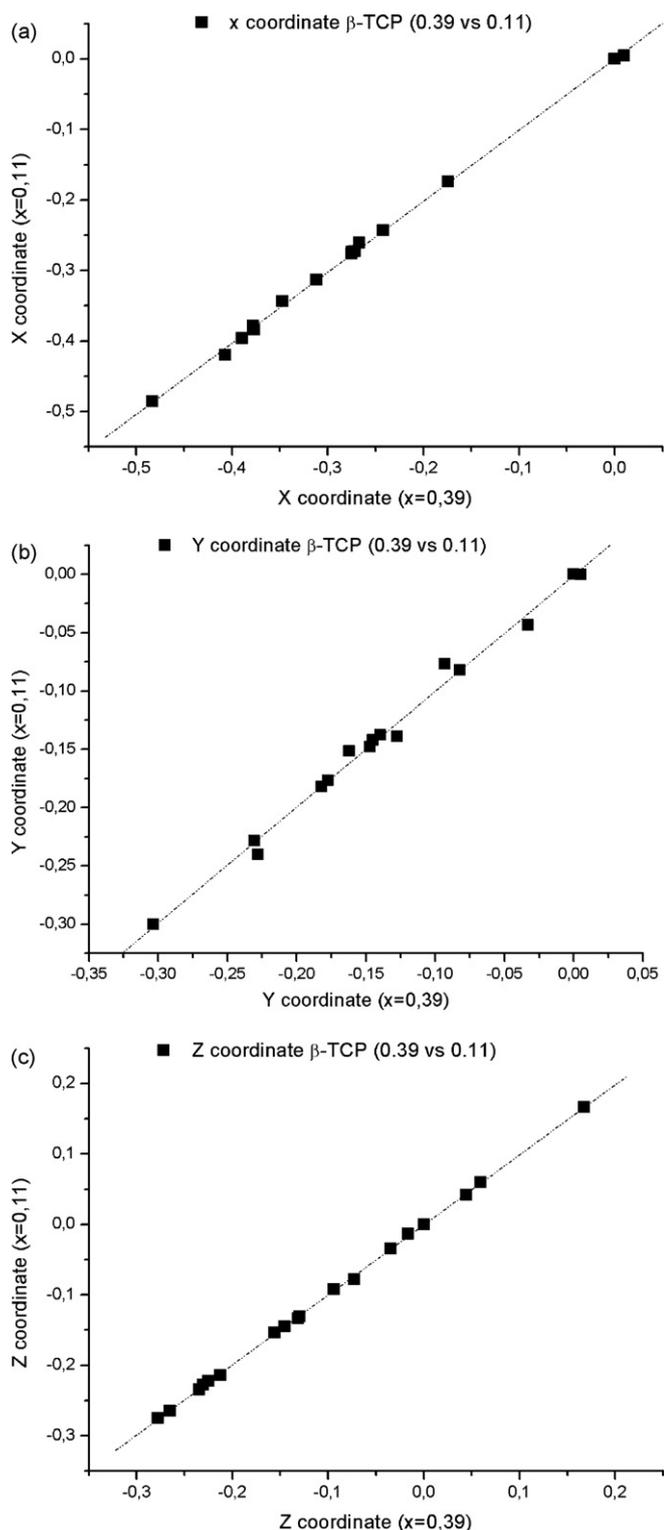


Fig. 2. Plots of the atomic positional parameters from Mg-β-TCP ( $x=0.39$  and  $x=0.29$ ): (a) x-coordinate (b) y-coordinate and (c) z-coordinate.

radius of (0.72 Å). According to Enderle et al. [8], initially Ca(5) site is occupied up to 10 mol% Mg<sup>2+</sup>, followed by the occupation of Ca(4). With the replacement of Ca(4) by Mg<sup>2+</sup>, the *c* parameter starts increasing, yet remains lower than β-TCP. Instead of Ca(4) and Ca(5) sites, the M(4) and M(5) nomenclature, respectively, is frequently used to indicate the presence of a second ion in these calcium sites.

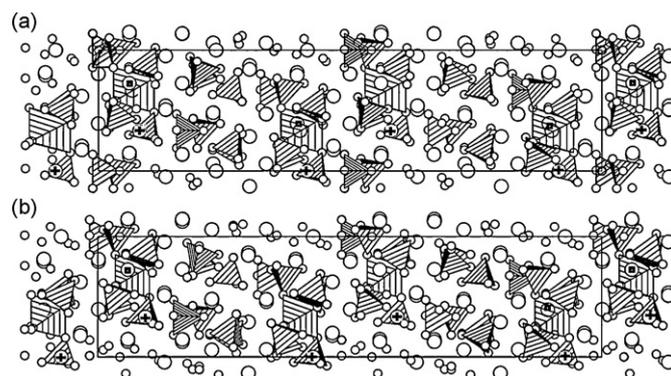


Fig. 3. A view from direction [010] for (a) β-TCP [1], and (b) Mg-β-TCP (~15.00 mol%Mg<sup>2+</sup>). Small circles represent O atoms and Ca atoms are represented by large circles. There is a small displacement toward the Ca atoms position (□) around the Mg1(5)PO<sub>4</sub> octahedral and an increasing shift of the Ca atoms (•) to the corners of the PO<sub>4</sub> triangles. (Plot program: Struplo 1996, 2005 version).

Table 1 shows the atomic occupation site of each calcium atom as well as the respective calculated occupancy factor. The Mg1 and Mg2 calculated occupancy factors, equal to 1.00(3) and 0.377(7), respectively, are in good agreement with the occupancy factors values at the maximum structural replacement by Mg<sup>2+</sup> on the M(4) and M(5) obtained by Enderle et al. using the Mg-β-TCP reference synthesized with 20 mol% Mg by solid-state reaction [8].

The total number of atoms is equal to  $\sum$  (number of atoms  $\times$  occupancy factor), resulting in 54.738 and 8.262 atoms for Ca and Mg sites, respectively. The formula Ca<sub>2.61</sub>(Mg<sub>1.028</sub>Mg<sub>2.011</sub>)(PO<sub>4</sub>)<sub>2</sub> equivalent to Ca<sub>3-x</sub>Mg<sub>x</sub>(PO<sub>4</sub>)<sub>2</sub>, where  $x=0.39$  or (Ca<sub>0.87</sub>Mg<sub>0.13</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was then obtained. This corresponds to a 0.15 Mg/Ca ratio, which means the Ca<sup>2+</sup> sites substitution for around 15.00 mol%Mg<sup>2+</sup> in the TCP structure. Moreover, the maximum substitution of Mg<sup>2+</sup> on M(4) and M(5) sites was of, approximately, 4.21 and 10.72 mol%, respectively. Exceeding 15.00 mol%Mg<sup>2+</sup> will result either in un-reacted magnesium chloride (in solution bath), Mg adsorbed on calcium phosphate surface or even the precipitation of Mg-rich phase, such as Stanfieldite.

Table 2 shows the atomic parameters for the Mg-β-TCP with  $x=39$  (15.00 mol%Mg<sup>2+</sup>) and data from Schroeder et al. [6] for  $x=29$  (11.00 mol%Mg<sup>2+</sup>). Differences in the atomic position parameters from Mg-β-TCP with 15 and 11 mol% Mg structural were lower than 5.3% for x-coordinate, 7.8% for y-coordinate and 3% for z-coordinate, compatible with the structural similarity for both Mg-TCP samples. Therefore, differences in the atomic positional parameters from Mg-β-TCP and literature reference [6] are small, resulting in larger coincidence with the atomic parameters reported by Schroeder et al. [6]. The atomic positional parameters plot was approximately linear, with declivity near the unit, Fig. 2.

Besides, Table 2 also shows that the thermal parameters (or displacement parameters) for Ca atoms were smaller when compared with the reference [6]. Moreover, the larger thermal parameters for M(4) reference [6] seem to indicate an extensive nonexpected thermal vibration, due to the lower occupancy factor  $\approx 0.5$  of this site. The anisotropic displacement parameters can be visualized as ellipsoids where the atoms are located, typically at the 50% probability level; so there is a certain doubt concerning these positions. In this sense, our results indicated that only the Ca(1) of Mg-β-TCP thermal parameters did not present a physical meaning, since it would form a flat thermal ellipsoid. Fortunately, the main items of our investigation are the atomic positions (Table 2), and occupancy factors that are used to estimate the distribution of Mg<sup>2+</sup> ions over the M(4) and M(5) sites (Table 1), in good agreement with the references [6,8]. The significant changes noticed in *a* (=b) and *c* cell parameters are other important evidences of the Mg<sup>2+</sup> ions incorporation into the β-TCP structure.

Table 3 shows that, comparing with the sample without Mg, the cation-oxygen coordination distances  $M(5) \dots O(7)$  and  $M(5) \dots O(4)$  become shorter and closer, and the  $O \dots M(5) \dots O$  angles tendency toward  $90^\circ$  when  $M(5)$  sites are filled with  $Mg^{2+}$ , in good agreement with Schroeder et al. data [6]. Plotting these data (Fig. 3), we can observe a small displacement toward the Ca atoms position (marked in its center with small square) around the  $Mg1(5)PO_4$  octahedral and an increasing shift of the Ca atoms (marked in its center by small cross) to the corners of the  $PO_4$  triangles as a consequence of the Mg incorporation into the  $\beta$ -TCP structure.

#### 4. Conclusion

The new refinement confirms that  $Mg^{2+}$  fills the  $M(5)$  site and partially the  $M(4)$  site of Mg- $\beta$ -TCP obtained by sintering magnesium-containing calcium-deficient apatite with Mg/Ca ratio equal to 0.20. The value of nearly 15.00 mol%Mg<sup>2+</sup> in  $\beta$ -TCP structure could be deduced from the estimated values of the occupancy factors, indicating that the maximum substitution of  $Mg^{2+}$  on  $M(4)$  and  $M(5)$  sites was, approximately, 4.21 and 10.72 mol%, respectively. Other partial evidences that the  $M(5)$ -sites were completely filled with  $Mg^{2+}$  are the short distances of the  $M(5) \dots O(4)$  and  $M(5) \dots O(7)$  and the increase in  $O \dots M(5) \dots O$  angles approaching  $90^\circ$ , compared with Mg-free  $\beta$ -TCP. The approximately stoichiometric formula  $Ca_{2.61}(Mg_{1.028} Mg_{2.011})(PO_4)_2$  was proposed for the Mg- $\beta$ -TCP crystal from the refined occupancy factors. With the maximum substitution of Mg on  $M(4)$  and  $M(5)$ -sites in the  $\beta$ -TCP lattice, a small displacement toward the Ca atoms position, around the  $Mg1(5)PO_4$  octahedral and an increasing shift of the Ca atoms to the corners of the  $PO_4$  triangles was observed.

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