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The study of Mg^{2+} /Ca^{2+} substitution of β-tricalcium phosphate

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This study aimed to investigate the formation and properties of magnesium substituted tricalcium phosphate containing various amounts of Mg^{2+} and Ca^{2+} ions (β-TCMP), isostructural with β- Mg^{2+} ions (β-Ca_3 $(PO_4)_2$. Beta-TCP and β-TCMP were prepared by a solid-state reaction, then calcination at 900ºC for 2hr, and finally sintered at 1100ºC for 2hr. The incorporation of Mg was reflected in the shift in the x-ray diffraction peaks due to partial Mg-for-Ca substitution in tricalcium phosphate, causing a contraction in the unit cell dimension. Unit cell parameters a_o and c_o, and molar volume V_o decrease linearly for atomic ratios Mg^{2+}/ Mg^{2+}+Ca^{2+} varying from 0 to 10 mol%. The morphology and chemical composition were analyzed semiquantitatively using X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM) and infrared spectroscopy (IR). The dissolution behaviour of Mg-substituted samples was tested in distilled water, at pH=6.1. Results demonstrated that Mg^{2+} ions can easily substitute for Ca^{2+} ions in the TCP lattice. Increasing the Mg content from 0 to 10%m reduces the dissolution rate of Mg-TCP samples.

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1. Introduction

Pure beta-tricalcium phosphate (β-TCP) is obtained by sintering calcium-deficient apatite (Ca/P < 1.67) above 700 ºC or by solid-state reaction and cannot be obtained from solutions [1]. The most important bioceramics phosphate materials are based on hydroxyapatite (HAP), tricalcium phosphate (β-TCP) and other combinations of them. [2-4]. The idea to use ceramic materials for the treatment or replacement of parts from diseased bone, had been revealed by the bone composition which, in its inorganic part, the majority is formed by hydroxyapatite, salts of calcium (phosphate and carbonate). Nowadays, one of the greatest challenging concerning the science and technology of materials is represented by the development of a new generation of biomaterials used in the "repairmen" of several parts of the human body. This materials must be designed to have a long life, but also to help at the tissues regeneration instead of replacement them.

Recently, Pramatarova et al. [5] developed a procedure for pattering the surfaces by laser irradiation, for in vitro hydroxyapatite growth.

The phosphate tricalcium [β-$Ca_3(PO_4)_2$] is the most important ceramic material biodegradable (dense or porous state) because it contains the property of osteosynthesis. The resorption and biodegradability of the bioceramic materials are characterized by factors such as physical-chemical dissolution, physical decay in small particles, but also by a biological factors such as fagocitosis. Taking into consideration this facts, the material may be projected so that the degradability step by step control of the rate dissolution and thus it could be adapted for each case. The biological performance of synthetic materials depends on fundamental parameters: chemical composition, morphology and biodegradability.

All calcium phosphates are biodegradable, but with different degree. On the basis of solubility data, it is expected that the resorption of this phosphates as implants to occur in this order: FAP < Mg-TCP < HAP< β –TCP< α – TCP. The reduction of biodegradation rate is caused by Mg in β-TCP substitution or β-TCP/HAP ratio abatement, in biphasic calcium phosphates.

Magnesium is known to reduce the degradation rate of tricalcium phosphate ceramics and to influence the crystallization of mineral substance. Moreover, it is always associated with the mineralization of calcified tissues, mainly in bones and teeth. The selection of the additive used in this research is not only based on their role in dissolution behaviour but also on the ability to enhance bone formation, which are desirable for a chirurgical implant. In particular, magnesium for calcium substitution in tricalcium phosphate, in limited amounts have been considered. Tricalcium phosphate containing various amounts of Ca^{2+} and Mg^{2+} is isostructural with β –TCP. Unit cell parameters a_o and c_o, and molar volume V_o decrease linearly for atomic ratios Mg^{2+}/ Mg^{2+}+Ca^{2+} varying from 0 to 14 mol.%. These variations indicated that Mg^{2+} ions can easily substituted for Ca^{2+} ions in the TCP lattice to that value [6,7]. A wide range of analytical methods (TGA, DTA, XRD, FTIR) was used to investigated these properties. As each of these methods has its limitation, it is necessary to combine all results to obtain a comprehensive view. The purpose of this work was to study the effect of partial Mg^{2+} substitution for Ca^{2+} on the structure and properties of beta-tricalcium phosphate.

2. Experimental methods

For experiments there have been used prime materials of high-purity such as $CaCO_3$, $NH_4H_2PO_4$ and MgO, all made by Merck and used as received. The elaboration of tricalcium phosphate was realized by the ceramic classical technology, as the reactions described below:

$$2NH_4 \bullet H_2 \bullet PO_4 + 3CaCO_3 \rightarrow Ca_3(PO_4)_2 + 2NH_3 + +3CO_2 + 3H_2O \quad (1)$$

All magnesium-substituted samples were prepared by reacting the appropriate chemical mixture, by solid-state reaction, at 1100 °C for 2 hours, in air. Before sintering, the mixture was milled in ethanol for 6 hours using alumina media, the slurry was dried and calcined at 900 °C for 2 h – when starts the formation of the compound tricalcium phosphate (TCP). Samples containing various levels of Mg were prepared with the aim to investigate the role of additive on the crystal structure and stability characteristics of Mg-TCP. The molar ratios of (Mg_x,Ca_{3-x}) / (PO_4) were kept constant at 1.5, as in stoichiometric tricalcium phosphate, and the maximum Mg^{2+} substitutions were limited to 10 mol.%. The substitution samples were noted as follows: M2-for x = 2.5 mol.%, M3-for x = 5 mol.% and M4-for x = 10 mol.%.

Thermogravimetric analysis are used to determinate the main elements of the formation of the tricalcium phosphate. The curves TG and DTG indicate the total weight loss for a temperature range 20÷1100 °C. The curves DTA by the endothermic and exothermic peaks delimitate all the phenomena which take place in the temperature range, for the loss weight (by the elimination of the water and the gas), till the stages of the formation of the compound. An X-ray powder diffractometer , Bruker-AXS, D8 ADVANCE with CuK_α radiation was used for crystal structure analysis, mineralogical composition and lattice parameter determinations. The recorded peaks were compared with those from ASTM files. By analysing the diffractogrames were calculated the parameter of the unit cell. Infrared spectroscopy was used in order to study the influence of the dopant on the formation of compound and also over the properties, in correlation behaviour as biomaterial. The stability of the samples (effect of the magnesium additive on the resorption characteristics of β-TCMP) was evaluated by pH-measurements, in distilled water, at a concentration of 1mg/mL, with a slow stirring. The measurements were made with Mettler-Toledo, at a temperatures of 23.5 °C, at different time ranges.

3. Experimental results

Firstly, it was determined the optimal calcination temperature and on the other hand the kinetics the process of the tricalcium phosphate. From the curves DTA combined with the X-ray diffraction results that the 900 °C is the optimal temperature of calcination. The main precursors in a qualitative and semiquantitative measurement are shown in the table 1. Difractograms for the substitution compounds are shown in Fig. 1.

The patterns show an excellent agreement with the published JCPDS files for β-TCP. As the level of doping increases, magnesium dominates the structural changes. The changes in lattice parameters and unit cell volume clearly demonstrate that Mg^{2+} ion are structurally incorporated into TCP and stabilizes the structure. The incorporation of Mg^{2+} ions takes place with the contraction of the cell dimension (Fig. 2). The stabilizing effect of Mg is attributable to the markedly smaller ionic radius of Mg^{2+} (0.65 Å) comparised to Ca^{2+} (0.99 Å): substitution of the smaller size ion gives rise to lattice strain, which favors the contraction.

Table 1. The kinetics of the formation of the compound tricalcium phosphate, β-TCP.

Temperature of calcination	β-TCP	C2P	C4P	CaO	$CaCO_3$
700 °C	-	+++	+	++	+++
850 °C	+++	+	+	++	u
900 °C	++++	+	u	-	-

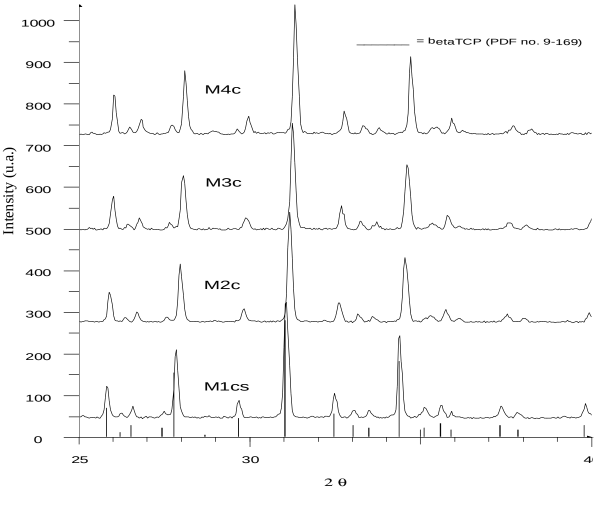

Fig. 1. The X-ray diffraction for β-TCP, with and without the Mg^{2+} substitution.

The unit cell parameters and the volume of the unit cell as function of composition are plotted in Fig. 2. The unit cell parameters a_o and c_o, and molar volume V_o decrease linearly for atomic ratios Mg^{2+}/ Mg^{2+}+Ca^{2+} varying from 0 to 10 mol.%.

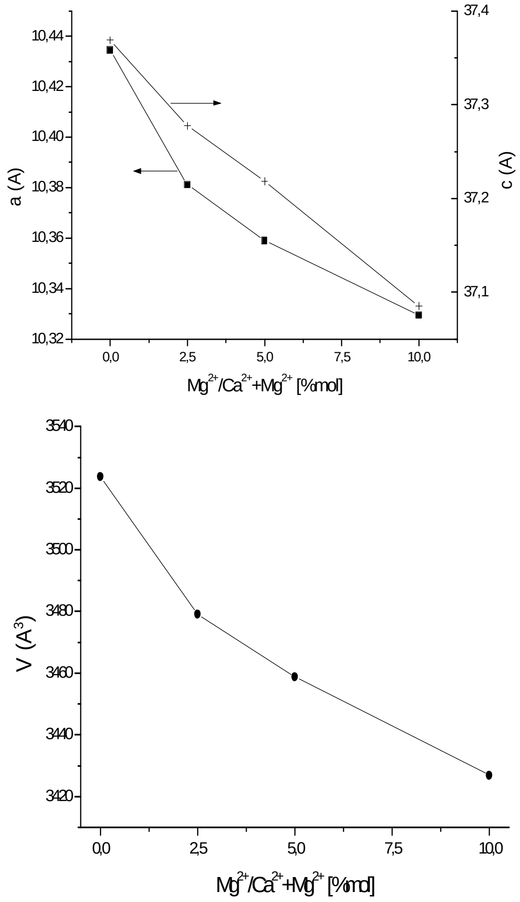

Fig. 2. The variation of lattice parameters and volume of unit cell for Mg-substituted compound.

The thermogram of TCP (Fig. 3) shows a continuously endothermic evolution and four distinct thermal events during the reaction of $CaCO_3$ and $NH_4H_2PO_4$., from room temperature to 950 ºC. The solid state reaction between $CaCO_3$ and $NH_4H_2PO_4$, mixed in a Ca/P molar ratio of 3/2 to form TCP, may suffer a complex procedure. The first endothermic peak over 180 to 220 ºC is due to the ammonia and water loss, in proportion of ~ 16.5wt. %. The theoretical total weight loss due to the escape of all gaseous species calculated from the reaction is 40.8 %. The total observed weight loss is 40.5 % upon heating to 950 ºC; this compares very well to the calculated value. The second endothermic event took place between 450 and 500 ºC, as shown in the DTA curve of Fig. 3, due to the residual water losses. At about 552 ºC took place an exothermic event due to the reaction of P_2O_5 and $CaCO_3$ to form the intermediary compound $Ca_2P_2O_7$ (reaction 3), by the elimination of the CO_2 in proportion of ~ 6,5wt. % The process continues during until at 800 ºC when starts the decay of the carbonate (reaction 4), with the CO_2 released in proportion of ~ 15wt. %.

$$ {}_2NH_4 \cdot H_2 \cdot PO_4 + CaCO_3 \rightarrow P_2O_5 + {}_2NH_3 + {}_3H_2O + CaCO_3 \quad (2)$$

$$P_2O_5 + {}_4CaCO_3 \rightarrow Ca_2P_2O_7 + {}_2CaCO_3 + {}_4CO_2 \quad (3)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (4)$$

$$Ca_2P_2O_7 + CaO \rightarrow Ca_3\,(PO_4)_2 \quad (5)$$

The formation of the tricalcium phosphate starts at 900 ºC, through the reaction between $Ca_2P_2O_7$ and spare calce (reaction 5), subsequently.

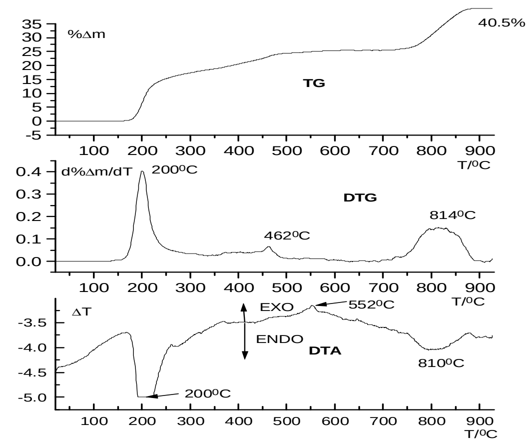

Fig. 3. The curves of TG/DTG/DTA for formation of the β-TCP compound.

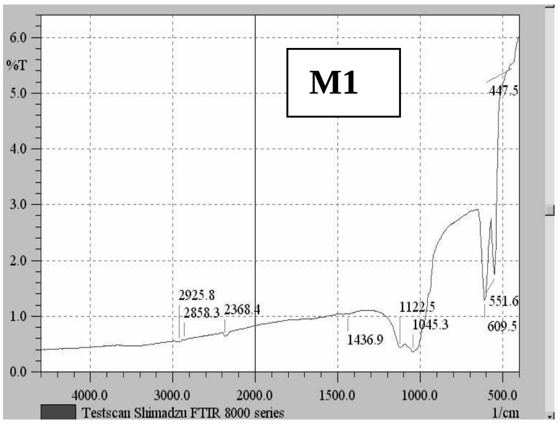

Fig. 4.The IR spectra of beta-tricalcium phosphate compound prepared by solid state reaction.

The IR spectra of tricalcium phosphate compounds exhibits two wide adsorption bands, at 1045-1122.5cm^{-1}, representatively for β-TCP compound; in the same case as the X-ray diffraction the peaks are slowly displaced, because the network parameters are changed. Both IR and XRD show that all the powders has apatite structure. The sintered materials has beta-whitlockite mineralogical composition.

The hydrolytical stability for all the tricalcium phosphate compounds was evaluated by pH-measurements. The measurement of the pH, was carried out in distilled water at concentration of 1mg/1mL, using an Ph-meter, Mettler-Toledo. The main results are shown in Table 2.

Table 2. The pH value for the substitution compound Mg-TCP.

TIME	M1CS	M2S	M3S	M4S
0 (distilled water)	6.1	6.1	6.1	6.1
30”	6.15	6.26	6.59	6.33
1’	6.47	6.46	6.70	6.45
2’	7.06	6.95	6.85	6.60
4’		7.32		
5’	8.15	7.42	7.22	6.81
6’	8.31			6.87
8’	8.44		7.41	6.94
10’	8.47	7.57	7.48	7.00
12’			7.52	7.09
18’	8.31		7.54	
20’	8.24	7.54	7.56	7.10
24’		7.48	7.56	
30’	8.10	7.48	7.56	7.02
1 hour	7.8	7.30	7.35	7.00

Regarding the pH measurements, the results show a better stability of the substitution compound, in the same time as the growth of the isomorphic substitution rapport. The final pH values, only for the substitution masses reach the maximum values between 7.59 and 7.10, after 10 min, and 20 min. Of the same importance, the pH value are correlated very well with those for the network parameters, showing once again that the substitution of the Mg^{+2} ions is between the isomorphism limit whit a good influence over the formation and the stability of the β-$Ca_3(PO_4)_2$, compound as a unique phase.

4. Conclusions

By a classical ceramic technology we synthesized stoichiometric beta-tricalcium phosphate as well as magnesium-substituted beta-tricalcium phosphate (in good agreement with XRD and IR measurements), doped with 2 wt.%, 5 wt.% and 10 wt.%, respectively. The incorporation of Mg^{2+} ions into the structure do not influence formation of the compound, the changes are just at a unit cell level, stabilizes the tricalcium phosphate phase and makes all the substitution compounds less soluble than β-TCP. This order is consistent with data from this material now available in literature. Of the same importance, the pH values are correlated very well with those for the lattice parameters, showing once again that the substitution of the Mg^{2+} ions is between the isomorphism limit, whit a good influence over the formation and the stability of the β-$Ca_3(PO_4)_2$, compound as a unique phase. Regarding the pH measurements, the results show a better stability of the substitution compounds, the final pH values being near the physiological medium, suggesting a typical comportment of a biomaterial.

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