Mg- and Zn-modified calcium phosphate fine powders examined by Rietveld refinement

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Fine powders, consisting of single phase Mg- or Zn-modified β-tricalcium phosphate (Mg/Zn-β-TCP) or biphase mixture of Mg/Zn-β-TCP and hydroxyapatite (HA) with a (Ca+Mg+Zn)/P ratio of 1.3–1.4 and Me/(Me+Ca) (Me = Mg, Zn) molar ratios from 0 to 0.10 were prepared by a two-step method: (i) continuous precipitation in biomimetic electrolyte systems of simulated body fluids, keeping pH=8; and (ii) step-wise calcination to 1000 °C. Rietveld refinement of the XRD data was performed. The refinement confirms that both Mg^{2+} and Zn^{2+} ions substitute the Ca^{2+} ions in the octahedral Ca(5) sites of Mg/Zn-β-TCP, which results in a decreasing trend of Ca(5)-O average distances and *a* and *c* cell parameters. The contraction of the crystal lattice is more pronounced for the Zn-substituted samples due to differences in the preferred coordination polyhedrons of Zn and Mg. The results also show that in the case of Mg substitution, as well as for the low levels of Zn substitutions, Ca(1), Ca(2) and Ca(3) positions remain fully occupied by Ca^{2+} ions. For high levels of Zn substitution Ca(1) and Ca(2) are partially occupied by Ca^{2+} ions, thus calcium vacancies appear. The latter affects the values of Ca(2)-O and Ca(4)-O mean distances by increasing them.

Keywords: Mg-β-TCP, Zn-β-TCP, biomimetic synthesis, Rietveld refinement.

INTRODUCTION

The studies on the preparation of various nano-sized calcium phosphate apatites having predetermined structure and properties [1], applicable to bone reconstruction and remodeling, have gained increasing interest in the development of new biocompatible materials. Of particular interest are ion-modified calcium phosphates that have a concentration of ionic substituent higher than that in the bone, since they may have additional antimicrobial properties, may increase the solubility of the ceramic material, or be a depot for the release of biogenic elements. In this sense, there is a scientific interest in obtaining ion-substituted calcium phosphates and studying the impact of additives on their chemical and structural parameters. Among the substitutents, Mg and Zn are the preferable ones due to their significance for the living organisms. Magnesium is widely studied, being the fourth most abundant cation in the human body [2]. Enamel, dentin and bone contain 0.44, 1.23, and 0.72 wt% of Mg, respectively [3]. This element plays an important role in the formation and initial growth of the bone tissue, stimulating osteoblast proliferation [4]. Zn content ranges from 0.0126 to 0.0217 wt% in human bones [5] and this element is important for the normal growth and development of the skeletal system, so its deficiency is associated with a decrease in bone density [6]. Mg^{2+} and Zn^{2+} ions participate by modifying morphology and crystallinity (inhibit it) of biological apatite [7–8]. Thus, they are used as additives in calcium phosphate materials that favor bone self-recovery rather than entirely replacing it [9].

The synthesis of Mg- and Zn-containing calcium phosphates could be performed through both solid-state reaction and wet chemical synthesis. Studies in the literature are mainly directed to the preparation of Mg- and Zn-substituted hydroxyapatite and a series of solid solutions with varying content of substituting ions are produced and characterized [10–13]. In recent years, ionic substituents in β-TCP (β-$Ca_3(PO_4)_2$) are of great interest due to their favorable features like higher solubility than hydroxyapatite and thus active participation in the process of bone regeneration [15–17].

In our previous works [18, 19] we have studied the metastable and stable equilibria during the precipitation of Mg- and Zn-substituted calcium phos-

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phates in biomimetic conditions and the influence of type and concentration of substituent ions on the phase composition by low- and high-temperature transformations.

The aims of this work were to enlarge our studies on biomimetically prepared Mg- and Zn-modified fine powders, consisting of single phase Mg- or Zn-modified β-tricalcium phosphate (Mg/Zn-β-TCP) or biphase mixture of Mg/Zn-β-TCP and HA by Rietveld refinement of the XRD data and to compare their structural characteristics.

MATERIALS AND METHODS

Preparation of samples

The detailed description of the precipitation conditions is given elsewhere [18, 19]. Briefly, Mg- and Zn-modified calcium phosphate precursors were biomimetically synthesized in an electrolyte medium of simulated body fluids (SBFs). Modified simulated body fluids (Table 1) were prepared on the base of the well-known conventional SBF [20]. Modified calcium-free conventional simulated body fluid (SBFc-mCa) was used as a solvent for K_2HPO_4. Modified phosphorus-free conventional simulated body fluids (SBFc-mP1 and SBFc-mP2) were used as solvents for $CaCl_2$ and $MgCl_2$ or $ZnCl_2$, respectively (Table 1), thus, preliminary precipitation and seed formation were avoided. The pH of the solutions SBFc-mP1 and SBFc-mCa was adjusted to 8 using 0.1 M HCl or 0.05 M Tris (hydroxymethyl) aminomethane, while the pH of SBFc-mP2 was adjusted to 6 owing to the formation of Zn hydroxy salts at higher pH. Analytical grade (A.R.) reagents were used.

The method of continuous precipitation was applied and all three reagents (SBFc-mP1, SBFc-mP2

and SBFc-mCa) were dropwise added to a glycine buffer medium with a rate of 3 ml/min, keeping pH = 8 by 1M KOH at room temperature.

The precipitates were matured in the mother liquid for 24 h at room temperature, washed and lyophilized.

The dry precursors were stepwise calcined at 200, 400, 600, 800 and 1000 °C at atmospheric pressure in a high-temperature furnace, type VP 04/17 of LAC Ltd Company. The working regime was: heating with a rate of 3 °C/min until the desired temperature was reached and keeping it constant for 3 h.

Characterization

Chemical analysis. The sum of Ca^{2+}, Mg^{2+} and Zn^{2+} ions in the solid samples was determined complexometrically with EDTA at pH 10. The concentrations of Zn^{2+}, Mg^{2+}, K^+ and Na^+ ions were determined by ICP-OES (PRODIGY 7, Teledyne Leeman Labs, USA) and the concentrations of PO_4^{3-} and Cl^- ions were determined spectrophotometrically by NOVA 60 equipment using Merck and Spectroquant® test kits.

X-ray diffraction analysis. The phase transformations of the amorphous precursor to crystalline products in high-temperature treated calcium phosphates were studied by a Bruker D8 advance XRD equipment operating at 40 kV and 40 mA with CuKa radiation and LynxEye detector within the 2θ range of 5.4–120° 2θ with a step of 0.02° 2θ and overall counting time of 175 s/step. The phase analysis was performed with the Eva program using ICDD-PDF2 (2014) database. The main calcium phosphate phases in the studied samples corresponded to β-TCP (β-$Ca_3(PO_4)_2$ – PDF # 09-0169) and HA, ($Ca_5(PO_4)_3(OH)$ – PDF # 09-0432).

Table 1. Ion content (mmol/l) of the initial solutions

Ion content	SBFc [20]	SBFc-mCa	SBFc-mP1	SBFc-mP2
Na^+	142.0	141.9	141.9	141.9
K^+	5.0	506.4	3.0	3.0
Mg^{2+}	1.5	1.5	x	1.5
Ca^{2+}	2.5	–	418.9 - x	418.9 – x
Zn^{2+}	–	–	–	x
Cl^-	147.8	142.8	975.6	975.6
SO_4^{2-}	0.5	0.5	0.5	0.5
HCO_3^-	4.2	4.2	4.2	4.2
HPO_4^{2-}	1.0	251.7	–	–

x = 0–83.9 mmol/l

Rietveld refinement

The Rietveld refinement procedure was performed with the Topas 4.2 program. As a starting model for the crystal structure refinement, data from the paper of Yashima et al. [21] was taken. The set of parameters to be varied included: zero shift, coefficients (7) of the background polynomial, absorption correction coefficient, scale factor, unit cell parameters, positional parameters, occupancies and thermal displacement parameters of the ions present in the structure. The peak shape was described according to the fundamental parameters approach by taking into account the effect of geometry of the diffractometer and of the optical devices on the beam path.

RESULTS AND DISCUSSION

Mixed crystals are non-stoichiometric compounds, where part of the ions building the crystal unit cell are substituted by other ions. The inclusion of another ion in the crystal structure of the main phase is determined by its ability to adopt the coordinating environment characteristic of the basic component, although it is not the most energy-efficient one.

In this study, we discuss magnesium- and zinc-modified fine powders, consisting of single phase Mg- or Zn-modified β-tricalcium phosphate (Mg/Zn-β-TCP) or biphase mixture of Mg/Zn-β-TCP and HA. A two-step method was used for preparation of the samples: (i) precipitation of the precursors with a variable molar Me/(Me+Ca) ratio (Me = Mg, Zn) and (ii) high-temperature treatment. The biomimetic approach for precipitation of the precursors was applied. It included precipitation in an electrolyte medium of a simulated body fluid (SBF)

that has become a modern way for preparation of bioactive materials [22, 23] with composition and properties close to those of biological hard tissues.

As we previously showed [18, 19] all precursors are amorphous calcium phosphates with $(Ca+Mg+Zn+Na+K)/P$ ratio in the range of 1.31–1.4 (Table 2).

The simulated body fluid medium used in the precipitation (Table 1) ensured ion modification of all calcium phosphate precursors with Na^+ (0.02–0.08 mmol/g), K^+ (0.01–0.02 mmol/g and Cl^- (below 0.05 mmol/g) ions (Table 2). Even the precursor S0 (Table 2), without further enrichment of the starting solutions with Mg^{2+} ions, contains 0.04 mmol/g Mg^{2+} ions due to the presence of the latter in the simulated body fluids.

During calcination, the amorphous precursors were transformed into mixtures of HA and β-TCP or single-phase β-TCP depending on the concentration of Zn^{2+} and Mg^{2+} ions incorporated in the structure (Figure 1).

Registered shifting of the peaks of β-TCP in the X-ray patterns of the samples under study is an indication of magnesium and zinc ion substitution in its crystal structure due to their smaller ionic radii (0.72 Å and 0.74 Å, respectively) than calcium ion (1.00 Å).

The Rietveld refinement method was performed for determining the crystal structure of the substituted phases since it is a suitable method for obtaining valuable results for cation distribution in the structure, as well as for quantification of the phases present in the samples.

In Figure 2, the Rietveld plots for samples S0 and Mg5 (Table 2) with different phase compositions are shown as examples.

Rietveld quantification results show that for a low content of substituting ion (samples S0, Mg2 and Zn1) a mixture of HA and β-TCP with a variable

Table 2. Chemical composition of the samples under study

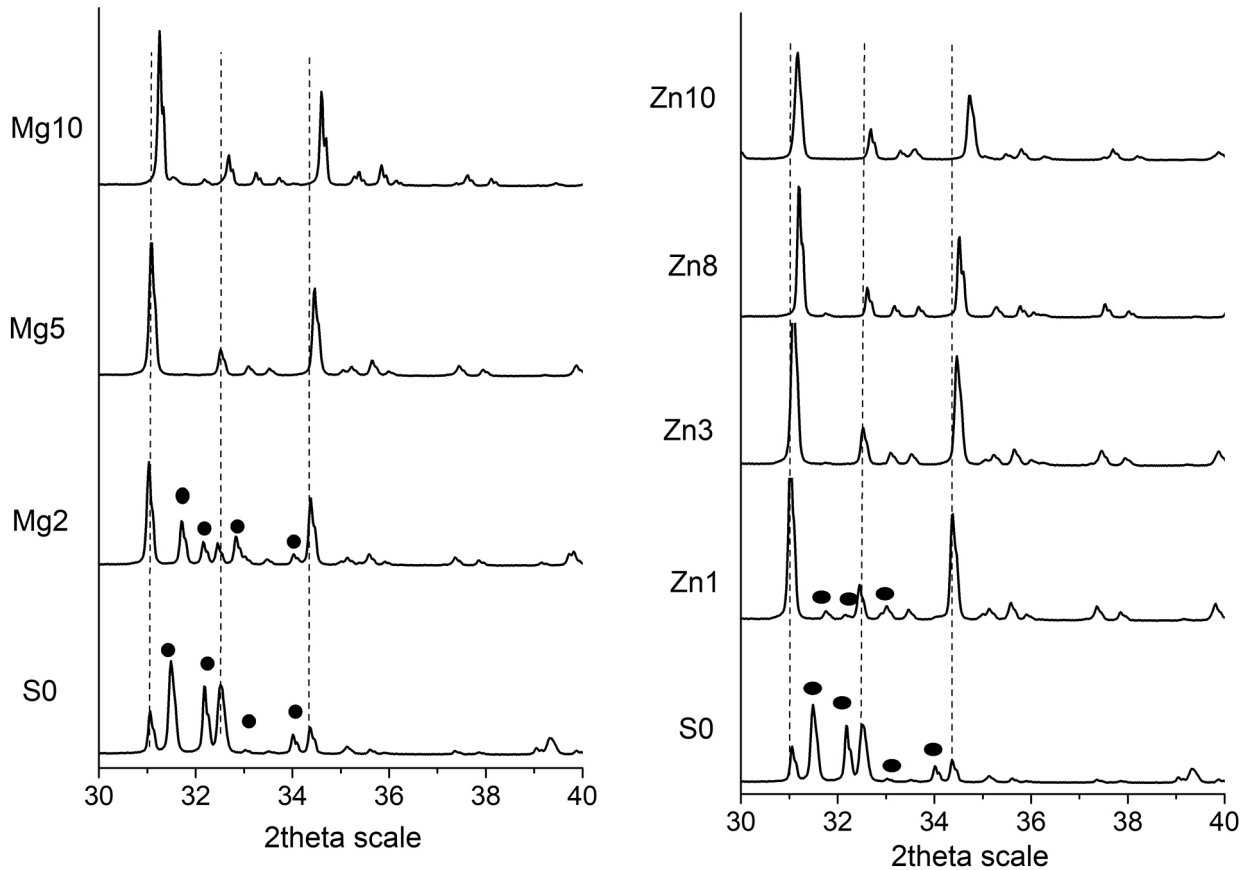| Sample	Me/(Me + Ca)	(Ca + Mg + Zn + Na + K)/P	Zn, mmol/g	Mg, mmol/g	Na+ mmol/g	K, mmol/g	Cl-, mmol/g
S0	0.005	1.33	–	0.04	0.05	0.01	<0.05
Zn1	0.01	1.31	0.09	0.03	0.03	0.01	<0.05
Zn3	0.03	1.35	0.29	0.05	0.04	0.02	<0.05
Zn8	0.08	1.40	0.70	0.04	0.05	0.02	<0.05
Zn10	0.10	1.31	0.90	0.06	0.02	0.01	<0.05
Mg2	0.02	1.36	–	0.21	0.05	0.02	<0.05
Mg5	0.05	1.35	–	0.45	0.08	0.01	<0.05
Mg10	0.10	1.33	–	0.85	0.06	0.02	<0.05

Fig. 1. XRD patterns of Mg-substituted (***a***) and Zn-substituted (***b***) calcium phosphates calcined up to1000 °C (• – HA, unmarked – β-TCP).

ratio is obtained (Table 3). The amount of HA decreases on increasing the concentration of Mg^{2+} and Zn^{2+} ions (Table 3). These changes in phase composition are more pronounced for Zn-substituted compounds. In the Zn1 sample the amount of HA is 4.1%, while in the Mg2 sample it is 27.0%. This fact proves our [18] and reference [22] data that Zn^{2+} ions more effectively stabilize the β-TCP structure than Mg^{2+} ions.

At higher magnesium or zinc concentrations (Mg10, Zn8, Table 3), MeO (Me = Mg, Zn) also was identified as a result of the decomposition of co-crystallized $Me(OH)_2$ during the precipitation. The presence of small quantities of tetracalcium

Table 3. Rietveld quantification results of solid phases presented in the samples under study

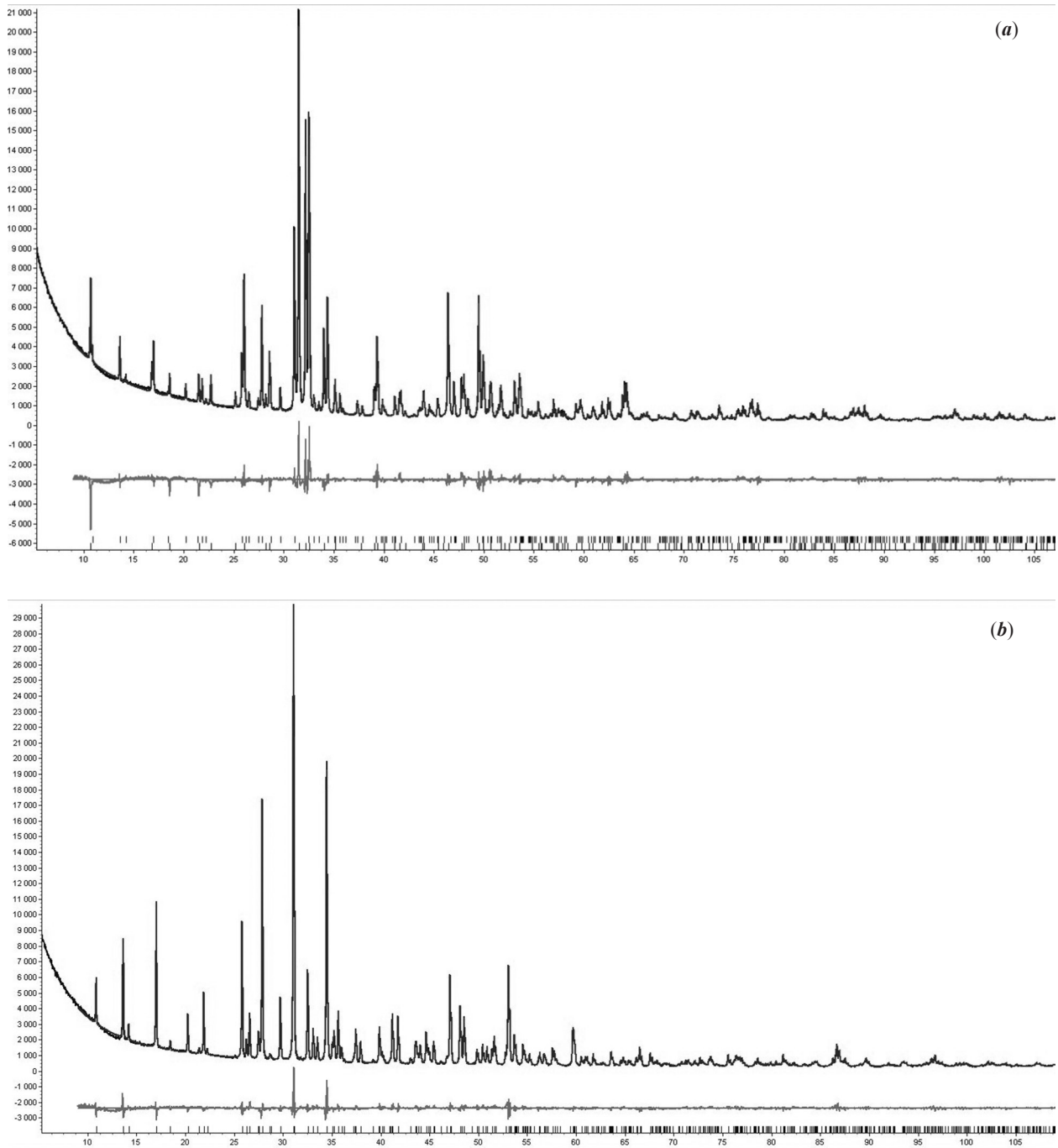| Sample/Solid phase	β–TCP	HA	TTCP	MgO	ZnO
S0	32.3(3)	67.7(3)	–	–	–
Mg2	73.0(2)	27.0(2)	–	–	–
Mg5	100.0	–	–	–	–
Mg10	95.8(8)		1.5(5)	2.7(7)	
Zn1	95.9(1)	4.1(1)	–	–	–
Zn3	100	–	–	–	–
Zn8	99.4(4)				0.6(4)
Zn10	100.0				

Fig. 2. Comparison of the observed and calculated powder diffraction patterns and the different profiles: (*a*) sample S0; (*b*) sample Mg5.

phosphate (TTCP) is a result of thermal decomposition of calcium-deficient apatite [16].

The main phase in the obtained by us Mg- and Zn modified calcium phosphate powders is β-TCP. It crystallizes into a rhombohedral crystalline system, a space group R3c, with crystal lattice parameters: a = b = 10.439(1), c = 37.375(6) Å; γ = 120° [24]. The structure consists of isolated PO_4 tetrahedrons forming disrupted layers perpendicular to c-axis.

Five crystallographically different Ca sites – Ca(1), Ca(2), Ca(3), Ca(4) and Ca(5) can be found in this structure. Each calcium ion is coordinated with different number oxygen atoms from PO_4 groups. The position Ca(4) is threefold coordinated with oxygen atoms and has a partial occupancy factor of 0.5. Each of the Ca(1), Ca(2), Ca(3), and Ca(5) is fully occupied by Ca ions and these positions are coordinated with seven, eight, eight, and six oxygen

atoms, respectively. The six-coordinated position Ca(5) is the most favorable for substitution by cations smaller than Ca^{2+}.

Our refined structural data indicated that Ca(1)-O, Ca(2)-O and Ca(3)-O average distances (Fig. 3a, b) change very little with the increase of the Me substitution level, while a decreasing trend is found for Ca(5)-O average distances with the increasing Me (Me = Mg, Zn) concentration in the solid phases. This leads to the decrease of the *a* and *c* cell parameter values (Fig. 4) and hence to the compression of the cell volume on substitution.

The calculated unit cell parameters *a* and *c* of the sample S0 (without substitution with Mg^{2+} or Zn^{2+} ions) showed significant differences with respect to the unit cell parameters of the β-TCP phase described in the literature [21] (Fig. 3). This is due to the presence of a significant amount of HA and to the biomimetic method of samples preparation that ensures the incorporation in the structure of some Mg^{2+}, Na^+, K^+ and Cl^- ions (Table 2) present in the simulated body fluids. Our results are in accordance with the calculations of Kannan et al. [23] who report a significant decrease of β-TCP unit cell parameters in triple-substituted (with Na^+, K^+ and Mg^{2+} ions) biphasic (HA and β-TCP) mixtures.

The contraction of lattice parameters is known [15, 16, 22, 23] and it is due to the substitution of Ca^{2+} ion (1.00 Å ionic radius) by Mg^{2+} or Zn^{2+} ions with a less ionic radius (0.72 Å and 0.74 Å, respectively) at the Ca(5) crystallographic sites. Our results also show that Mg^{2+} and Zn^{2+} ions prefer to occupy Ca(5) sites with octahedral oxygen coordination in the β-TCP structure rather than the other four crystallographic sites of calcium, forming CaO_3 (Ca(4) sites), CaO_7 (Ca(1) sites) and CaO_8 (Ca(3) and Ca(2) sites) polyhedrons [21, 24]. The R-Bragg factors obtained by us on the assumption of substi-

tution of Mg and Zn at the Ca(5) position are the lowest ones and are within the range 1.92–3.16.

Our results (Fig. 4) reveal that contraction of the crystal lattice is more pronounced for the Zn-substituted samples. We believe that this difference can be explained with the preferred coordination polyhedrons of Zn and Mg in their phosphate salts. MgO_6 octahedrons build the structures of simple magnesium phosphate salts ($Mg_3(PO_4)_2$, $Mg_3(PO_4)_2 \cdot nH_2O$, n = 4, 8, 22) [25] similar to the $Ca(5)O_6$ octahedrons in the β-TCP structure. MgOx (x = 6, 5) polyhedrons build the structures of some double ($NaMgPO_4$, $Na_2Mg_5(PO_4)_4$) or triple ($Na_3RbMg_7(PO_4)_6$) salts [26]. ZnO_4 tetrahedrons are the major structural entities in the structures of zinc phosphate salts [25]. ZnO_4 tetrahedrons and Zn- deficient ZnO_6 octahedrons build the structure of $Zn_3(PO_4)_2 \cdot 4H_2O$ [27]. ZnO_4 tetrahedrons and distorted ZnO_6 octahedrons build the structure of $Zn_4(PO_4)_2(OH)_2 \cdot 3H_2O$ [28].

The chemical analysis of the compounds under study shows the cationic deficiency (Table 2). (Ca+Me)/P (Me = Na, K, Mg, Zn) ratios are by 1.31–1.4 lower than in pure β-TCP (Ca/P = 1.5). This gave us reason to vary the occupancy of calcium ions in all crystallographic positions. The results show that for all levels of Mg substitution, as well as for the low levels of Zn substitution Ca(1), Ca(2) and Ca(3) remain fully occupied by Ca^{2+} ions while for high levels of Zn substitution (Zn/(Zn+Ca) = 0.08 and 0.10) Ca(1) and Ca(2) are partially occupied by Ca^{2+} ions. Partial occupancy affects the values of Ca-O mean distances by increasing them in the case of Ca(2)-O distances (Fig. 3, Zn10) and especially in the case of Ca(4)–O distances (Fig. 3, Zn10). The $Ca(4)O_3$ polyhedrons are not only the smallest polyhedrons in the β-TCP structure but they are half-occupied as well [21], which defines

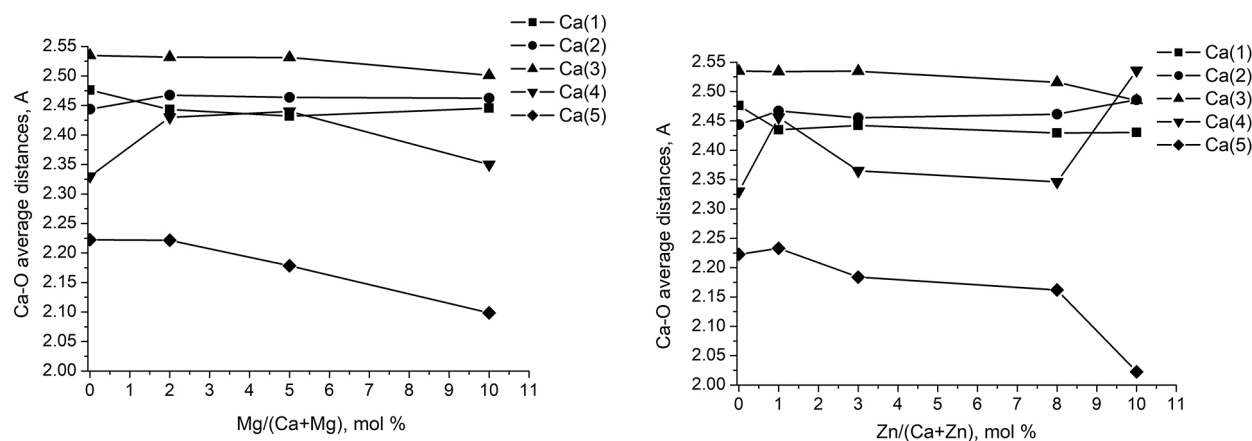**Fig. 3.** Influence of the substitution of Ca^{2+} by Mg^{2+} or Zn^{2+} ions on the Ca-O average distances: (*a*) Mg-β-TCP; (*b*) Zn-β-TCP.
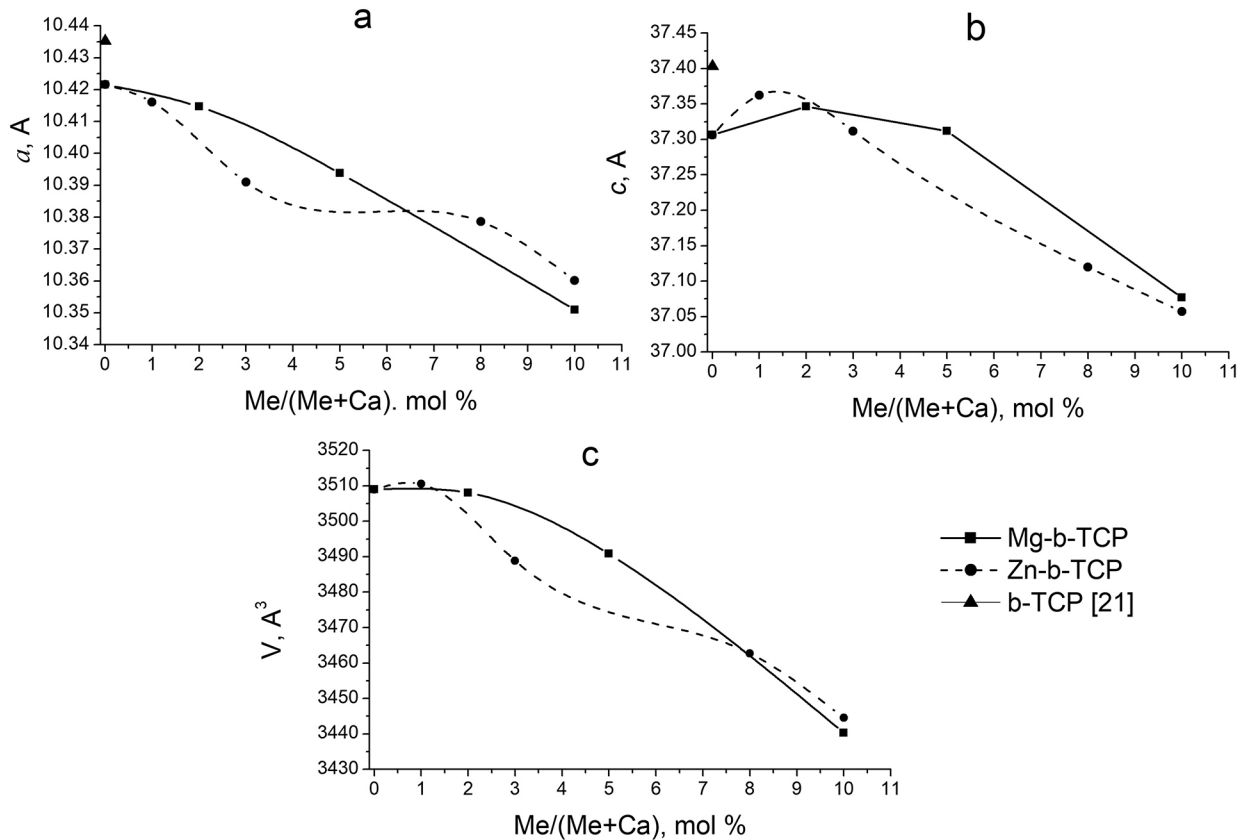
Fig. 4. Influence of the substitution of Ca^{2+} by Mg^{2+} or Zn^{2+} ions on the unit cell parameters a (**a**) and c (**b**) and the cell volume (**c**) of the Me-β-TCP structure.

Table 4. Chemical formulas of β-TCP phases according Rietveld analysis

Sample	Formula	Me/(Ca+Me)
Mg2	$Ca_{2.94}Mg_{0.06}P_2O_8$	0.02
Mg5	$Ca_{2.905}Mg_{0.095}P_2O_8$	0.032
Mg10	$Ca_{2.758}Mg_{0.242}P_2O_8$	0.08
Zn1	$Ca_{2.99}Zn_{0.01}P_2O_8$	0.003
Zn3	$Ca_{2.915}Zn_{0.085}P_2O_8$	0.028
Zn8	$Ca_{2.820}Zn_{0.146}\square_{0.034}P_2O_8$	0.049
Zn10	$Ca_{2.805}Zn_{0.195}\square_{0.065}P_2O_8$	0.065

their stronger dependence on other structural defects like additional calcium deficiency. Hence, the chemical formula of the β-TCP phases in our cases may be written as shown in Table 4.

The differences in Me/(Ca+Me) ratio (Me=Mg, Zn) obtained by chemical (Table 2) and Rietveld (Table 4) analysis revealed that not the entire amount of Mg^{2+} and Zn^{2+} ions present in the solid phases is included in the β-TCP crystal structure. The Ritveld analysis applied by us in this study confirmed our previous assumptions [18, 19] that pre-

cipitation, co-precipitation, ion substitution and ion inclusion reactions take place simultaneously in the complicated electrolyte system of SBFs in particular, and in the natural body fluids in general.

CONCLUSIONS

Zn or Mg modified, cation deficient amorphous phosphates ((Ca+Mg+Zn+Na+K)/P = 1.3–1.4) were prepared by biomimetic approach, that ensures

ion modification of all calcium phosphates with Na^+ (0.02–0.08 mmol/g), K^+ (0.01–0.02 mmol/g and Cl^- (below 0.05 mmol/g) ions. During the calcination till 1000 °C, mixtures of HA and β-TCP or single-phase β-TCP depending on the concentration of Zn^{2+} and Mg^{2+} ions incorporated in the structure were obtained. At high Mg concentration other phases as MgO and TTCP were identified in negligible amount.

The Rietweld refinement have confirmed both Mg^{2+} and Zn^{2+} ions substitute the Ca^{2+} ions on the octahedral Ca(5) sites of Mg/Zn- β-TCP. Lower ionic radii of Mg and Zn ions leads to decreasing trend in *a* and *c* axis parameter values and Ca(5) – O distances with the increasing Me (Me = Mg, Zn) concentration in the solid phases. Decreasing in cell parameter values is more pronounced at Zn substituted samples due to differences in the preferred coordination polyhedrons of Zn and Mg. Contrary, appearing of calcium vacancies in Ca(1) and Ca(2) sites at high levels of Zn substitution increase Ca(2) – O and Ca(4)–O mean distances.

REFERENCES

1. K. L. Lin, C. T. Wu, J. Chang, *Acta Biomater.*, **10,** 4071 (2014).
2. I. Cacciotti, A. Bianco, M. Lombardi, L. Montanaro, *J. Eur. Ceram. Soc.*, **29**, 2969 (2009).
3. R. Z. LeGeros, Calcium Phosphates in Oral Biology and Medicine. Monographs in Oral Sciences, KargerBasel, Switzerland, Basel, 1991.
4. K. Lilley, U. Gbureck, J. Knowles, D. Farrar, J. Barralet, *J. Mater. Sci.: Mater. Med.,* **16**, 455 (2005).
5. W. J. Bettger, B. L. O'dell, *J. Nutr. Biochem.*, **4**, 194 (1993).
6. A. M. Pietak, J. W. Reid, M. Sayer, *Biomater.,* **26,** 3819 (2005)
7. B. R. Constantz, I. C.Ison, M. T. Fulmer, R. D. Poser, S. T. Smith, M. VanWagoner, J. Ross, S. A. Goldstein, J. B. Jupiter, D. I. Rosenthal, *Science,* **267**, 1796 (1995).
8. A. K. Lynn, W. Bonfield, *Acc. Chem. Res.*, **38,** 202 (2005).
9. X. Luo, D. Barbieri, N. Davison, Y. Yan, J. D. de Bruijnac, H. Yuan, *Acta Biomater.*, **10,** 477 (2014).
10. S. J. Kalita, H. A. Bhatt, *Mater. Sci. Eng. C*, **27**, 837 (2007).
11. F. Ren, R. Xin, X. Ge, Y. Leng, *Acta Biomater.*, **5**, 3141 (2009).
12. D. Shepherd, S. M Best, *Biomed. Mater.,* **8**, 025003 (2013).
13. R. J. Friederichs, H. F. Chappell, D. V. Shepherd, S. M. Best, *J. R. Soc. Interface*, **12**, 20150190 (2015).
14. I. R. Zerbo, A. L. J. J. Bronckers, G. deLange, E. H. Burger, *Biomater.*, **26**, 1445 (2005)
15. A. Ito, R. Z. LeGeros, *Key Eng. Mater.*, **377**, 85 (2008).
16. S. Kannan, F. Goetz-Neunhoeffer, J. Neubauer, J. M. F. Ferreira, *J. Am. Ceram. Soc.*, **94**, 230 (2011).
17. S. Pina, P. M. C. Torres, J. M. F. Ferreira, *J. Mater. Sci.: Mater. Med.*, **21**, 431 (2010).
18. D. Rabadjieva, S. Tepavitcharova, R. Gergulova, K. Sezanova, R. Titorenkova, O. Petrov, E. Dyulgerova, *J. Mater. Sci: Mater. Med.*, **22**, 2187 (2011).
19. D. Rabadjieva, S. Tepavitcharova, K. Sezanova, R. Gergulova, *J. Solution Chem.*, **45**, 1620 (2016).
20. T. Kokubo, *J. Non-Cryst. Solids*, **120**, 138 (1990);
21. M. Yashima, A. Sakai, T. Kamiyama, A. Hoshikawa, *J. Solid State Chem.*, **175**, 272 (2003).
22. S. Kannan, F. Goetz-Neunhoeffer, J. Neubauer, J. M. F. Ferreiraw, *J. Am. Ceram. Soc.*, **92**, 1592 (2009).
23. S. Kannan, F. Goetz-Neunhoeffer, J. Neubauer, J. M. F. Ferreiraw, *J. Am. Ceram. Soc.*, **91**, 1 (2008).
24. B. Dickens, L. W. Schroeder, W. E. Brown, *J. Solid State Chem.*, **10**, 232 (1974)
25. D. M.C. Huminicki, F. C. Hawthorne, *Reviews in Mineralogy and Geochemistry*, 48, 123 (2002).
26. T. Ben Hamed, A. Boukhris, A. Badri, M. Ben Amara, *Acta Cryst.*, **E73**, 817 (2017).
27. J. H. Roderic, J. B. Jones, *Am. Mineral.*, **61**, 987 (1976).
28. L. Fanfani, A. Nunzi, P.F. Zanazzi, *Mineral. Mag.*, **38**, 687 (1972).