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Investigation of the β´- to α-phase transformation temperature of $(Ca_{1-x}Mg_x)_3(PO_4)_2$ solid solutions

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Abstract. Tricalcium phosphate $Ca_3(PO_4)_2$ (TCP), an osteoconductive as well as bioresorbable phase, has found application as bone cement and bone implant material. TCP was found to crystallize in three polymorphic modifications: β-TCP below 1180 °C, α-TCP between 1180 °C and 1430 °C, and α`-TCP above 1430 °C [1]. It is mainly β-TCP and α-TCP that have gained acceptance in biomedical applications. At the moment β-TCP ceramics are used for non-load-bearing applications in oral surgery. In this investigation we were able to detect an additional but reversible phase transformation from β- to β´-TCP at 1000 °C. The influence of partial Mg^{2+} substitution of Ca^{2+} in the solid solution series of β´-TCP $(Ca_{1-X}Mg_X)_3(PO_4)_2$ was determined at 1025 °C ± 10 °C in air. The temperatures for β´- to α-TCP phase transformation were investigated in a manner differentiated according to the different Mg^{2+} contents.

Introduction

Bioceramics are used very widely in implantation surgery. Further improvement of the available materials is required with respect to degradation behaviour and the possibility of deposing organic or biological substances, which favour the healing process after implantation.
The calcium phosphate must be degradable in order for it to be displaced by newly generated bone but should also possess enough mechanical stability to fill the diseased or damaged part of the skeletal system. It is the poor strength of β-tricalcium-phosphate ceramics (TCP) that is preventing their application for load-bearing purposes. It was assumed that phase transformation of β-TCP to α-TCP is reducing mechanical strength. Mg-doping is known [2, 3] to be a very effective method to stabilize the β-modification of TCP. In this investigation, we were able to show that a combination of differential thermal analysis and XRD-investigation of quenched TCP powders is a very effective method of determining the phase transforma-

tion temperatures of β'-TCP to α-TCP. The CaO-rich part of the system M_3P-C_3P as described by Ando et al. [2] could possibly be redrawn so as to include our data.

Experimental methods

Synthesis

Syntheses of pure TCP were carried out by solid-state reaction in a chamber furnace at 1025 °C ± 10 °C in air. The starting materials - high purity $(NH_4)_2HPO_4$ (>99 %, Fluka) and $CaCO_3$ (99.99%, Fluka) - were mixed in proper molar ratios, homogenized in an agate disc mill and sintered for 2.5 hours at 1025 °C. For the synthesis of several members of the β-$(Ca_{1-X}Mg_X)_3(PO_4)_2$ solid solution series, CaO was partly replaced by MgO (>98 %, Fluka). Phase composition of the air-quenched solid solutions was examined at room temperature by quantitative X-ray powder diffraction (XRPD) in combination with Rietveld refinement.

XRD investigation

All samples were characterized by XRD powder methods with CuK_α radiation. A SIEMENS D5000 diffractometer equipped with a diffracted-beam graphite monochromator was used for recording the data. The following adjustments were applied in continuous step mode with fixed slits (table 1).

Table 1. Instrument parameter for quantitative X-ray powder diffraction analysis.

Generator: 30 mA/40 kV	Detector slit: 0.2 mm
Tube: Long fine focus	Detector: scintillation
X-ray: CuK_α	Step/Time: 0.02 °/4 s
Slits: fixed = 0.5 °	Range: 5-75 °2θ

Rietveld refinement of synthesis products

All powders were proven to be single-phase by Rietveld refinement of the XRD pattern. For the Rietveld refinements the software TOPAS 2.1 (Bruker AXS) with fundamental parameters approach was utilized. Refined parameters were "scale factor", "zero displacement", "background as Chebychev polynomial of 5th grade", "crystallite size", "microstrain" and "lattice parameters". Occupancy factors were included in the case of the refinement of the Mg-doped solid solutions of β-TCP, whereby a scattering factor of P^{5+} was assumed for phosphorous in tetrahedral coordination with oxygen. All parameters were refined simultaneously.

The following table 2 summarizes the ICSD-codes of the structural data (ICSD, 1995), which were used for the Rietveld refinement of synthesized phases together with all possible secondary phases.

Table 2. ICSD-data used for Rietveld refinement and quantification.

Phase	Starting data	
	ICSD-Code	Authors
β-C_2P (Calcium phosphate)	73712	Boudin et al. (1983) [4]
HAP (Hydroxyapatite)	87668	Wilson et al. (1999) [5]
β-TCP (Whitlockite)	6191	Dickens et al. (1974) [6]
α-TCP (Tricalcium phosphate)	923	Mathew et al. (1982) [7]

Rietveld quantification

Accuracy (absolute error E_a) and precision (standard deviation s) of Rietveld quantification were verified on three different synthetic mixtures which were prepared from pure HAP and β -TCP. Eight independent measurements led to determination of the values as plotted in table 3. The determined maximum value for precision does not exceed 1.6 ma.%. The values for accuracy of β -TCP in the mixes were always higher than 1.2 ma.%.

Table 3. Calculated quantities and precision of ß-TCP in the synthetic mixes of ß-TCP and HAP

β-TCP in mix	Calculated β-TCP [ma.%]
100	99.9 ± 0.1
75	76.1 ± 1.6
50	50.5 ± 1.5
25	26.6 ± 1.4
0	0.2 ± 0.2

All other quantification results are average values from at least five independent preparations followed by Rietveld refinement of XRD-patterns. From the statistical evaluation of different synthesized samples there could be obtained data relative to purity of calibration samples and to the determination limits of all possible minor phases, these being in every case lower than 0.24 ma.%.

Differential Temperature Analysis

Differential Temperature Analysis (DTA) of the synthesized powders (with 0 and 3 mole % Mg^{2+}) of the solid solution β-$(Ca_{1-X}Mg_X)_3(PO_4)_2$ was performed with a Simultaneous Differential Technique module in nitrogen atmosphere (flow rate: 100 ml N_2/min) (SDT 2960, TA instruments). A heating- and cooling-rate of 5 °C/min was utilized up to 1450 °C. Samples with more than 3 mole% of Mg^{2+} were investigated in a vertical tube furnace for 45 minutes

in air and quenched in H_2O to stabilize α-TCP. The quenched samples were ground and investigated by XRD and by Rietveld refinement.

Results

Substitution of Ca^{2+} by Mg^{2+} in the β-TCP structure at 1025 °C ± 10 °C is correlated with a decrease of lattice parameter a and cell volume V, which is plotted in figure 1. Refinement from lattice parameters led to the composition of the end member of the solid solution. At a temperature of 1025 °C ± 10 °C up to 14 mole% of Ca^{2+} can be replaced by Mg^{2+} in the β-$(Ca_{1-X}Mg_X)_3(PO_4)_2$. For the described synthesis conditions, the Mg-rich end member of the solid solution has the formula $(Ca_{0.86}Mg_{0.14})_3(PO_4)_2$ [8]. Above 14 mole%, stanfieldite ($C_3M_3P_2$) can be detected in the synthesized samples as secondary phase. Additionally, the occupation factor of the Ca(4) and Ca(5) sites of the β-TCP structure by Mg^{2+} ions could be calculated by Rietveld refinement of the XRD data. The change of lattice parameters can be attributed to the stepwise occupation by Mg^{2+} on the two different Ca^{2+} sites.

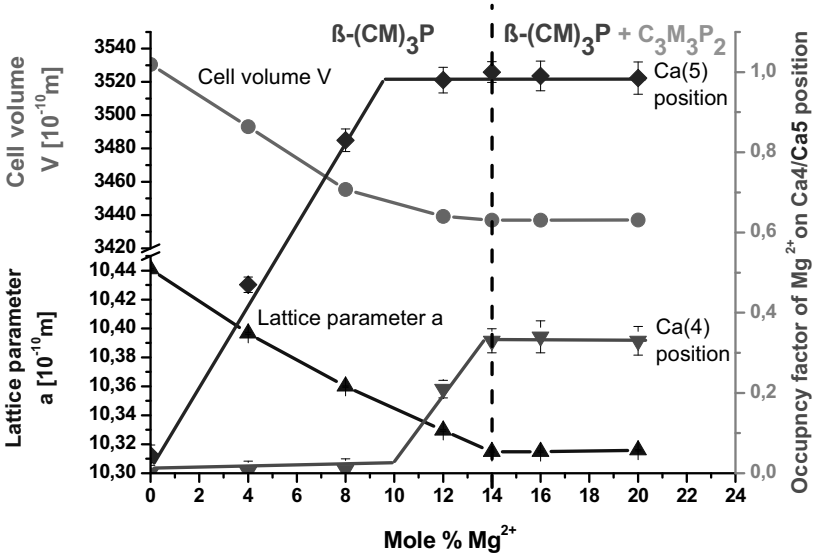

Figure 1. Lattice parameter a, cell volume V of β-$(Ca_{1-X}Mg_X)_3(PO_4)_2$ and refined occupancy factors of Mg^{2+} on Ca4 and Ca5 position with increasing Mg-content synthesized at 1025 °C.

In figure 2, there are summarized the determined temperatures of β`- to α-TCP transformation and melting temperature. The data regarding transformation temperatures and/or melting temperatures acquired in the course of this investigation are plotted into the phase diagram $Ca_3P_2O_8$ – $Mg_3P_2O_8$ as included in Ando [2] and are marked as triangles and circles. Investigation of the quenched samples always resulted in two phases, α-TCP and β-TCP, which

indicates that there exist, in every case, two phases in equilibrium. Transformation temperature was set at the lowest temperature when α-TCP was detected by XRD analysis for the specific solid solution member of $(Ca_{1-X}Mg_X)_3(PO_4)_2$.
As plotted in figure 2, temperature of β´- to - α-TCP transformation can be increased from 1150 °C (Mg^{2+}-free) to 1540 °C by means of Mg^{2+}-substitution on Ca^{2+} sites of 8 mole %. Samples with substitution above 10 mole % Mg^{2+} are not affected by the β´- to α-TCP transformation since, in these cases, the melting points were reached before transformation could take place. The formed melt can fill up existing pores, which leads to denser ceramic. Higher temperatures during sintering process result in denser TCP ceramics and thus in improved mechanical properties. Sintering of TCP ceramics with Mg content can be performed at much higher temperatures.

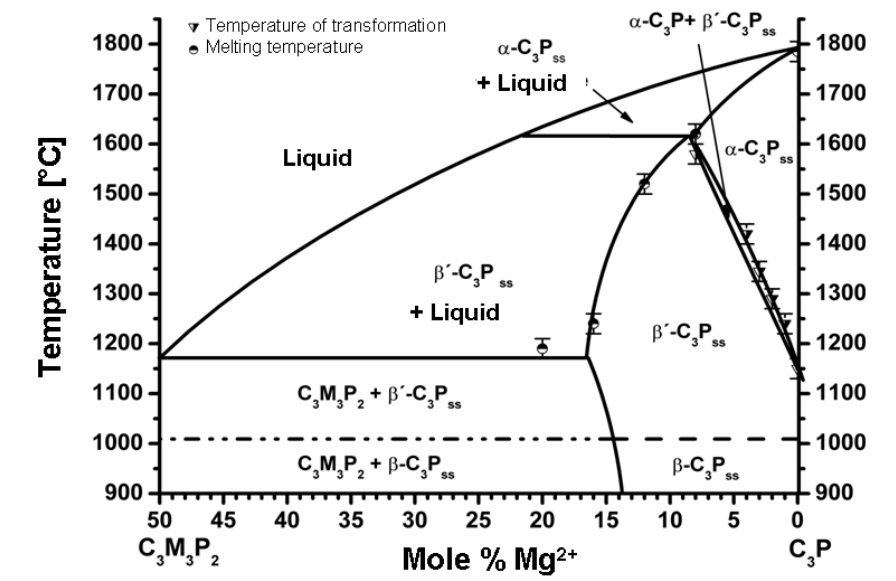

Figure 2. Redrawn phase diagram (as per [2]) with the determined β´-α transformation temperatures differentiated in terms of Mg-content in $(Ca_{1-X}Mg_X)_3(PO_4)_2$.

Conclusion

Phase transformation of β´- to α-TCP is a reconstructive process. For this reason, α- to β´-TCP transformation is strongly retarded. Transformation temperature of β´- to α-TCP can be increased by substitution with Mg^{2+} up to temperatures of 1540 °C for $(Ca_{0.92}Mg_{0.8})_3(PO_4)_2$, as has been established by the described investigations. But there could also be detected another reversible phase transformation, namely from β- to β´-TCP, at 1000 °C. It is assumed that this is responsible for the low mechanical properties determined for β-TCP ceramics. This phase transformation may cause microcracks and therefore low strength properties in

spite of Mg-doping. In the last analysis, it is this that is tending to restrict the application of β-TCP ceramics to non-load-bearing indications as bone implant material.

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