

## Effect of Mg<sup>2+</sup> Content on Lattice Parameter and Phase Transformation Temperature of $\beta$ - $\alpha$ TCP

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**INTRODUCTION:** Tricalcium phosphate Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (TCP), an osteoconductive as well as bioresorbable phase, has found application as bone cement and bone implant material. TCP can crystallize in three polymorphic modifications:  $\beta$ -TCP below 1180 °C,  $\alpha$ -TCP between 1180 °C and 1430 °C, and  $\alpha'$ -TCP above 1430 °C [1]. Mainly  $\beta$ -TCP and  $\alpha$ -TCP have reached acceptance in biomedical applications. At the moment  $\beta$ -TCP ceramics are used for non load-bearing applications in oral surgery. In this investigation the determination of the influence of partial Mg<sup>2+</sup> substitution of Ca<sup>2+</sup> in the solid solution series of  $\beta$ -TCP (Ca<sub>1-x</sub>Mg<sub>x</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was determined at 1025 °C  $\pm$  10 °C in air. The temperatures for  $\beta$ - $\alpha$ -phase transformation were determined in dependence of the Mg<sup>2+</sup> content.

**EXPERIMENTAL METHODS:** Syntheses of  $\beta$ -TCP powders were carried out by solid-state reaction in a chamber furnace at 1025 °C  $\pm$  10 °C in air. The starting materials - high purity (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (>99 %, Fluka), MgO (>98 %, Fluka) and CaCO<sub>3</sub> (99.99%, Fluka) - were mixed in proper molar ratios, homogenized in an agate disc mill, and dried at 195 °C. After further homogenization in a disc mill, the samples were sintered for 2.5 hours at 1025 °C. Phase composition was examined by quantitative X-ray powder diffraction (XRPD) in combination with Rietveld refinements. All powders were proven to be single-phase  $\beta$ -TCP. Rietveld refinement was performed using the structural models (ICSD Database) of all possible occurring secondary phases listed in Table 1.

Table 1: ICSD data for Rietveld refinements

Phase	Mineral/name	ICSD-Code
$\beta$ -Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	$\beta$ -C <sub>2</sub> P	73712
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	HAP (Hydroxyapatite)	87668
$\beta$ -Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	$\beta$ -TCP (Whitlockite)	6191
$\alpha$ -Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	$\alpha$ -TCP	923
(CaMg) <sub>3</sub> P <sub>2</sub> O <sub>8</sub>	Stanfieldit	23642

Refined parameters were scale factor, zero displacement, background as Chebyshev polynomial of 5th grade, crystallite size, micro

strain and lattice parameters. Occupancy factors were included in case of refinement of the Mg-doped solid solutions of  $\beta$ -TCP, whereby the scattering factor of P<sup>5+</sup> was assumed for phosphorous in tetrahedral coordination.

**RESULTS:** Substitution of Ca<sup>2+</sup> by Mg<sup>2+</sup> in the  $\beta$ -TCP structure at 1025 °C  $\pm$  10 °C is correlated with a decrease of the lattice parameters. Refinement from lattice parameters led to the composition of the end member of the solid solution. At a temperature of 1025 °C  $\pm$  10 °C up to 14 mole% of Ca<sup>2+</sup> can be replaced by Mg<sup>2+</sup> in the  $\beta$ -Ca<sub>1-x</sub>Mg<sub>x</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. For the described synthesis conditions the Mg-rich end member of the solid solution has the formula (Ca<sub>0.86</sub>Mg<sub>0.14</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>[2]. Additionally the occupation factor of the Ca(4) and Ca(5) sites of the  $\beta$ -TCP structure by Mg<sup>2+</sup> ions could be calculated by Rietveld refinement of the XRD data. The course of lattice parameters can be attributed to the stepwise occupation by Mg<sup>2+</sup> on the two different Ca<sup>2+</sup> sites. Rietveld refinement has proven to be a very powerful tool in terms of characterization of the synthesized TCP samples and optimization of the synthesis conditions.

Transformation temperature of  $\beta$ - $\alpha$  TCP can be increased from 1150 °C (Mg<sup>2+</sup>-free) to 1540 °C with a Mg<sup>2+</sup>-substitution on Ca<sup>2+</sup> sites of 8 mole %. Samples with higher substitution than 10 mole % Mg<sup>2+</sup> are not affected by the  $\alpha$ - $\beta$  transformation since the melting points were reached before transformation could take place. The formed melt fills up existing pores and thus lead to completely dense ceramic. Higher temperatures during sintering process lead to denser TCP ceramics and thus better mechanical properties. Sintering of Mg-containing TCP ceramics can be performed at much higher temperatures.

**REFERENCES:** <sup>1</sup> Elliott, J.C. 1994 *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates* <sup>2</sup> Enderle, R., Götz-Neunhoeffler, F., Göbbels, M., Müller, F., Greil, P. 2005 Influence of Magnesium-doping on the phase transition temperature of  $\beta$ -TCP ceramics; *Biomaterials*; **26**(17): 3377-3769