SYNTHESIS AND INVESTIGATION OF TRICALCIUM PHOSPHATE POLYMORPHS

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ABSTRACT

Calcium phosphates (CPs) are the main inorganic part of biological hard tissues such as bones or teeth and play an essential role in human life. Due to the similarity to the mineral phase of bones and excellent biocompatibility, different synthetic CPs have been widely applied as biomaterials for bone repair. These materials are used in biomedical applications in different forms varying from thin coatings on metallic implants to sintered bioceramics. Tricalcium phosphate ($Ca_3(PO_4)_2$, TCP) is one of the representative biomaterials, which finds an application in bone cements and bone implants due to its excellent resorbability and osteoconductivity.

There are three known polymorphs of TCP: the low-temperature β-TCP and the high-temperature forms α- and α'-TCP. The last one is not suitable for practical applications, because it exists only at temperatures above 1430 °C and transforms to α-TCP on cooling below the transition temperature. In contrast, β-TCP is stable at room temperature and transforms at about 1125 °C to α-TCP phase, which can be retained during the cooling to room temperature. However, thermal quenching is often required for the synthesis of pure α-TCP without β-TCP secondary phase, which forms during the cooling of the sample, since phase transition from β- to α-TCP is reversible. Commonly, the synthesis of both α- and β-TCP polymorphs is performed by thermal treatment of a precursor with appropriate Ca to P molar ratio (1.5:1). Usually β-TCP powders are synthesized by solid-state reaction or wet precipitation method at temperatures about 800 °C or higher. The most common approach to the synthesis of α-TCP is thermal transformation of crystalline β-TCP at temperatures above 1125 °C. However, α-TCP can be also synthesized from amorphous CP at such low temperatures as 600−700 °C with further transformation to β-TCP at about 900 °C. Thereby, α-TCP can be obtained at low and high temperatures – below the temperature of formation of β-TCP and above the temperature of transition of β-TCP to α-TCP.

α- and β-TCP crystallize in the monoclinic and rhombohedral crystal systems, respectively. Theoretical densities of α- and β-TCP are 2.866 and 3.066 g cm^{-3}, respectively. These structural differences between α- and β-polymorphs are responsible for their different chemical and biological properties, such as solubility and biodegradability. The solubility of both structures is intermediate between orthophosphates, however α-TCP is much more reactive in aqueous solutions than β-TCP and easily hydrolyzes with a formation of calcium deficient hydroxyapatite, which is similar to bone hydroxyapatite. These differences in chemical properties of TCP polymorphs define their different practical applications. α-TCP is widely used as a major powder component of various bone cements, whereas β-TCP is an important component of mono- or biphasic bioceramics and composites. Both of these materials promote bone growth where implanted and support the proliferation of fibroblasts, osteoblasts and other bone cells.

In our work, we investigated phase-selective synthesis of TCP polymorphs, effect of doping with foreign ions on phase transformations between polymorphs and effect of doping on physical and biological properties of TCP.

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