

**Materials based on double calcium phosphates and alkaline metals
 $\text{Ca}_{3-x}\text{M}_{2x}(\text{PO}_4)_2$ (M=Na,K) for biomedical applications obtained by the 3D-printing technology**

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Abstract

Bioceramics as bone grafts have to demonstrate special biological properties, such as gradual dissolution in liquid media of organism (resorption) and replacement by newly formed bone. Bone mineral has a composition very similar to $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (hydroxyapatite-HA), but, additionally, contains several ionic substitutions [1]. Since the resorption rate of HA is too low to induce massive bone growth, biphasic calcium phosphate ceramics, combinations of $\beta\text{-Ca}_3(\text{PO}_4)_2$ (tricalcium phosphate) and HA, are commonly used as bioactive implants [2]. Another way to improve resorptivity of such materials is chemical modification of HA or $\text{Ca}_3(\text{PO}_4)_2$, e.g. by Ca/M (=alkaline metal) substitution leading to formation of CaMPO_4 compounds with rhenanite structure.

The main objective of this study was to create materials with defined 3D-structure and better resorption properties compared to HA. We have chosen double phosphates of calcium and alkaline metals $\text{Ca}_{(3-x)}\text{M}_{2x}(\text{PO}_4)_2$ ($x=0\div 1$, M=Na, K) with crystal structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ ($x<0.15$) and $\beta\text{-CaNaPO}_4$ ($x=1$) as the components of ceramics and multiphase composites. The phase diagrams of the systems $\text{Ca}_3(\text{PO}_4)_2\text{-CaNaPO}_4$ and $\text{Ca}_3(\text{PO}_4)_2\text{-CaKPO}_4$ have been studied.

Phase diagram of $\text{Ca}_3(\text{PO}_4)_2\text{-CaNaPO}_4$ was verified according to that one after Ando [3]. Phase «A» - a solid solution near the composition $\text{Ca}_5\text{Na}_2(\text{PO}_4)_4$, was considered as a superlattice of $\alpha\text{-CaNaPO}_4$ with doubled a lattice parameter and tripled c . It was determined that single-phase $\alpha\text{-CaNaPO}_4$ cannot be kept under cooling down at any rate, even by quenching, due to fast $\alpha\text{-CaNaPO}_4$ to $\beta\text{-CaNaPO}_4$ transformation. This transformation accompanied by significant volume change can negatively affects the ceramics causing formation of cracks. Also, kinetics of $\alpha\leftrightarrow\beta$ transformation in pure $\text{Ca}_3(\text{PO}_4)_2$ was explored, and critical cooling rate to produce single-phase $\alpha\text{-Ca}_3(\text{PO}_4)_2$ was determined. "Dangerous" temperature region in sense of the rapid transformation was found to be located near 800-900 °C.

Phase diagram of $\text{Ca}_3(\text{PO}_4)_2\text{-CaKPO}_4$ system has been constructed for the first time. The main feature of it compared to the sodium system is an area of solid solution, called us by «B», at the vicinity of the composition with $x=0.33$ considered as a superstructure of $\alpha\text{-CaKPO}_4$. The solid solution «B» is transformed to apatite-like phase called us by «X» under cooling.

Solubility of the ceramic materials was investigated. The solubility of materials with high amount of high-temperature rhenanite phases is increased in comparison with materials based on $\beta\text{-Ca}_3(\text{PO}_4)_2$.

To obtain three-dimensional structure Fused Deposition Modeling (FDM) was used. Form with a specified structure was prepared with FDM 3D-printer, after that ceramic with a given structure was prepared with negative replica technique.

References

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