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Synthesis of silicon-substituted hydroxylapatite

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Silicon-substituted hydroxylapatite was prepared to produce a biomaterial with improved bioactivity *via* aliovalent anion substitution, which leads to the instability of apatite $Ca_5(PO_4)_3OH$ at $T > 900$ °C and to the formation of a $Ca_3(PO_4)_2$ phase.

Synthetic hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is extensively used in modern medicine as a bone restorative material due to its close chemical similarity to the natural tissue. HA ceramics is almost inert in contact with living bone; the reason is a low solubility of hydroxylapatite ($IP_{HA} \sim 10^{-119}$ M^{18}).[1] Many researches are focused on the biphasic ceramics of HA and more soluble tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) ($IP_{TCP} \sim 10^{-25}$ M^5). Another approach to improve the bioactivity of HA is to modify its chemical composition in order to make the composition closer to a carbonate-containing bone mineral.[2–5] Note that 'bioactivity' is a complex term including (*a*) the dissolution of a material in acidic media and (*b*) the formation of a new apatite layer on the surface of a material from supersaturated body fluids.

The clinical application of glass ceramics developed by Hench[1] in the $CaO–Na_2O–SiO_2–P_2O_5$ system demonstrates a great advantage of the incorporation of silicon in a biomaterial. It is known that silanol (–SiOH) groups promote the nucleation of the new apatite layer on the surface of the material leading to fast bone bonding process. Several attempts have been made to synthesise the Si-incorporated hydroxylapatite (Si-HA),[2–5] but only Gibson *et al.*[3] reported the formation of the thermally stable (with respect to decay into tricalcium phosphates – TCP and secondary phases) product. The purpose of this study was to synthesise Si-doped HA and to examine its high-temperature stability.

The Si-HA was prepared by a conventional precipitation technique using $Ca(NO_3)_2$ and KH_2PO_4 solutions (at 80 °C, 5 h). Amorphous calcium phosphate (ACP) formed at the first step was treated with tetraethyl orthosilicate (TEOS) solution:

$$10Ca(NO_3)_2 + (6-2x)KH_2PO_4 + xSi(OEt)_4 + xK_2SO_4 + 14KOH \rightarrow \qquad (1)$$
$$Ca_{10}(PO_4)_{6-2x}(SiO_4)_x(SO_4)_x(OH)_2 + 20KNO_3 + 4xEtOH + (12-4x)H_2O$$

A sulfate-containing component was used to balance the net charge in apatite structure through aliovalent anion substitution:

$$2PO_4^{3-} \leftrightarrow SiO_4^{4-} + SO_4^{2-} \qquad (2)$$

Another set of experiments was performed with previously synthesised pure HA: the crystals were modified with TEOS on their surface (with or without K_2SO_4):

$$Ca_{10}(PO_4)_6(OH)_2 + xSiO_4^{4-} \rightarrow \qquad (3)$$
$$Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x} + xOH^- + xPO_4^{3-}$$

All as-prepared samples were thermally treated at 950–1300 °C to analyse the high-temperature stability of Si-doped HA. Specimens were analysed by powder X-ray diffraction [XRD; DRON-3M, 'Bourevestnik', USSR; $\lambda(CuK\alpha) = 1.54183$ Å], scanning (SEM; Supra 50 VP, Leo, Germany) and transmission (TEM; Jem-2000 FXII, Jeol, Japan) electron microscopy and IR spectroscopy (400–4000 cm^{-1}, PE-1600 FTIR, Perkin–Elmer, USA).

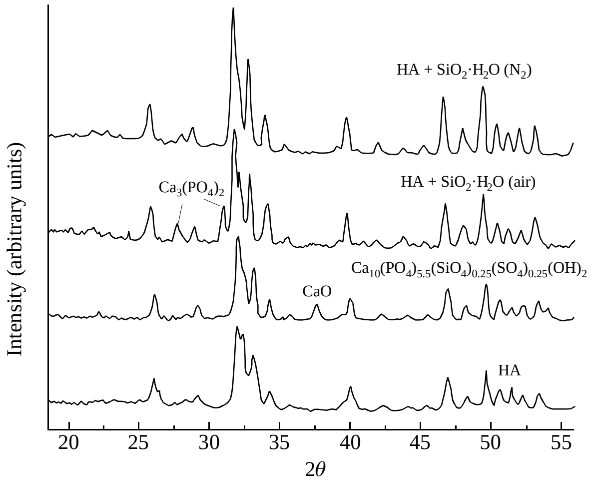

Figure 1 XRD patterns of Si-HA samples after annealing at 1300 °C.

It was found that hydrated silica inhibited the crystallization of HA. One could observe an increase in X-ray peaks width with increasing concentration of TEOS. High temperature treatment of the samples $Ca_{10}(PO_4)_{6-2x}(SiO_4)_x(SO_4)_x(OH)_2$ with $x > 0.25$ prepared by reaction (1) at 1300 °C led to HA decomposition and to the formation of $Ca_3(PO_4)_2$ and CaO as secondary phases (Figure 1). Silicon was reported to stabilise the α-TCP phase promoting the decomposition of HA.[5] The crystal structure of α-TCP is related to HA unit cell, and the solubility of Ca_2SiO_4 in α-TCP is about 4 wt.% according to the known phase diagram.[6] To conclude, the solubility of calcium silicate in the HA structure cannot be much higher than the TCP limit.

An increase in HA unit cell (hexagonal $P6_3/m$) parameters after silicon doping is consistent with the ionic radii of silicate and phosphate (bond length Si–O = 1.66 Å, P–O = 1.55 Å):

$Ca_{10}(PO_4)_6(OH)_2$, $a = b = 9.415(3)$ Å, $c = 6.877(2)$ Å;
$Ca_{10}(PO_4)_{5.5}(SiO_4)_{0.25}(SO_4)_{0.25}(OH)_2$, $a = b = 9.439(4)$ Å, $c = 6.899(3)$ Å.

IR-spectroscopic data of HA and Si–HA samples revealed another mechanism of charge compensation: partial substitution of CO_3^{2-} for PO_4^{3-} and formation of $Ca_{10}(PO_4)_{6-2x}(SiO_4)_x(CO_3)_x(OH)_2$ seems preferable over substitution for SO_4^{2-}. In the spectra of the samples it was possible to observe the peaks corresponding to the CO_3^{2-} groups at 874, 1418 and 1482 cm^{-1} (Figure 2). The decomposition of carbonate-containing hydroxylapatite at $T > 700$ °C leads to the formation of $Ca_3(PO_4)_2$. Only one very week peak of SiO_4^{2-} groups at 890 cm^{-1} could be detected at Si–HA samples. The silicon content of the samples prepared by reaction (3) did not exceed 2 wt.% according to quantitative X-ray fluorescence analysis.

The TEM micrographs of as-precipitated powders of HA and Si–HA are shown in Figure 3, where submicron-sized particles can be observed. Note that silicon doping switches the crystal shape from uniaxial to elongated. The excess of silicon was presented in the form of a separate amorphous $SiO_2 \cdot yH_2O$ phase.

The bioactivity of thermally stable Si–HA ceramics was evaluated *in vitro* in the media of simulated body fluids (SBF): (pH 7.4; Tris buffer) 142 mM Na^+, 5 mM K^+, 1.5 mM Mg^{2+}, 2.5 mM Ca^{2+}, 147.8 mM Cl^-, 27 mM HCO_3^-, 1 mM HPO_4^{2-}, SO_4^{2-}; at 37 °C. The surface of the samples immersed in SBF for 1–10 days were examined with SEM. The formation of the new apatite layer (thickness of about 1 μm after 7 days) on the surface of ceramic pellets was evidenced. Moreover, higher dissolution of Si–HA powders in comparison with pure HA was observed during the experiments in buffered solutions at pH 4.5.

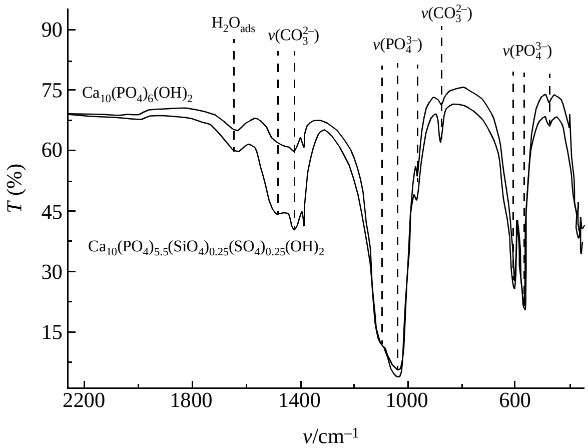

Figure 2 IR spectra of as-precipitated Si-HA samples.

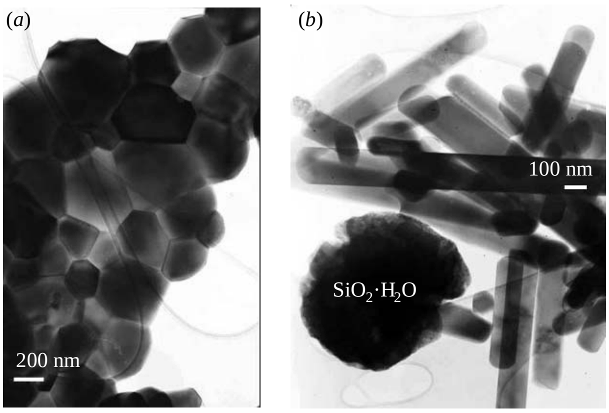

Figure 3 TEM micrographs of HA and Si-HA samples.

The increasing dissolution can be related to intrinsic microstrains of HA crystals due to significant difference in the effective ionic radii of PO_4^{3-} and SiO_4^{4-} groups. The accommodation of the lattice to the induced strains can be implemented *via* the surface segregation of silicate ions.

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