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A novel approach to the synthesis of silicocarnotite

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ABSTRACT

In this letter, we present a new approach to the synthesis of silicocarnotite – a promising bioceramic material. This approach is based on selecting a precursor with a crystalline structure close to that of silicocarnotite in an attempt to reduce the transformation temperatures. In the synthesis route that we suggest, silicocarnotite forms from mechanochemically synthesized nanosized silicon-substituted apatite. The main advantages of this route are lower temperatures and shorter annealing times required for the synthesis of the target phase in comparison with the direct solid-state synthesis, aqueous precipitation or sol–gel method. It was shown that the silicocarnotite phase is obtainable by annealing the mechanochemically synthesized silicon-substituted apatite for 5 h at a temperature as low as 1000 °C. According to the differential scanning calorimetry, the phase transition from silicon-substituted apatite to silicocarnotite occurs at 970 °C. In this work, complete assignment of the absorption bands of the IR spectrum of silicocarnotite to particular bond vibrations is reported for the first time.

1. Introduction

Calcium phosphate bioceramic is used in bone tissue engineering because of similarity in composition with the bone mineral, excellent bioactivity, ability to promote cellular functions and expression, and osteoconductivity [1–3]. In 1970, Carlisle found high levels of silicate uniquely localized in the calcification front and suggested that silicon ions are involved in the calcification process of young bones [4]. Since the mid-1990s, silicon-containing or silicon–substituted calcium phosphates have received increasing attention from researchers and, more recently, from clinicians [5–10].

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) is one of the widely used materials for bone and dental tissue reconstitution because of its biocompatibility with hard tissues, high osteoconductivity, and bioactivity [11,12]. However, simulated body fluid immersion tests showed that silicocarnotite $Ca_5(PO_4)_2SiO_4$ (SC) has a greater *in vitro* apatite-forming ability than HA [13]. SC demonstrates better biocompatibility and biodegradability and higher osteogenic activity and osteoconductivity than the HA bioceramics [14]. It was concluded that the effect of the SC bioceramics on tendon-to-bone healing is also more pronounced. When doped with metal ions, SC is a promising phosphor for light-emitting diodes [15].

SC is a synthetic inorganic compound, which can be obtained by high-temperature treatment of calcium-phosphate compounds with silicon-containing additions. The available synthesis methods of SC along with the required synthesis parameters are listed in Table 1. Although SC can be obtained from different reactants, pure SC has been synthesized only from a stoichiometric mixture of tricalcium phosphate and dicalcium silicate [17,18]. In that case, two-stage annealing of the reaction mixtures has been used. The purpose of the first annealing stage was to transform low-temperature phases of the mixture (β-$Ca_3(PO_4)_2$ and γ-Ca_2SiO_4) to high-temperature phases (α'-$Ca_3(PO_4)_2$ and α-Ca_2SiO_4), which produce the so-called R-phase [18]. The transformation of the R-phase to SC takes place upon cooling at 1310 °C. As this reaction is a slow diffusion-controlled process, the second annealing stage was necessary to eliminate non-equilibrium intermediate phases.

As can be seen from Table 1, the available synthesis methods of SC are both time- and energy-consuming. A solution to these problems can be found by selecting a precursor with a crystalline structure close to that of SC. Considering the fact that the HA hexagonal and SC orthorhombic lattices have the same weight per unit volume [21], silicon-substituted apatite (HA–Si) appears to be a promising candidate to be selected as a precursor because it has silicate tetrahedrons in its structure. However, the maximum

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Table 1
Synthesis methods and conditions of SC.

Method	Initial reactants	Annealing temperature, duration	SC purity	Reference
Solid-state reaction	$Ca_2P_2O_7/Ca_3(PO_4)_2$, $CaSiO_3/SiO_2$, $CaCO_3$	1200 °C, 3 h/1300–1400 °C	SC as a minor phase/not specified	[16]
	$Ca_3(PO_4)_2$, Ca_2SiO_4	1550 °C, 6 days + 1155 °C, 24 h	pure	[17]
	$Ca_3(PO_4)_2$, Ca_2SiO_4	1550 °C, 2 h + 1400 °C, 4 h	pure	[18]
Sol–gel method	$Ca(OH)_2$, H_3PO_4, SiO_2 sol	120 °C, 12 h + 1200 °C, 2 h	negligible concentrations of other phases	[19]
	$Ca(NO_3)_2 \cdot 4H_2O$, $C_6H_{15}PO_4$, $Si(OCH_2CH_3)_4$	60 °C, 72 h + 120 °C, 48 h + 1400 °C, 6 h	negligible concentration of HA	[13]
Aqueous precipitation	$Ca(OH)_2$, H_3PO_4, $Si(OCOCH_3)_4$	1100 °C, 15 h	32 wt% of HA + 14 wt% of β-$Ca_3(PO_4)_2$	[20]

Table 2
Elemental composition of the powder after mechanochemical synthesis.

	C*	O*	Al*	Si	P	Ca	Fe
Concentration of element (at%)	8.3(2)	68.6(8)	0.1(1)	3.3(1)	5.5(1)	14.2(1)	≤0.1

* – elements contained in the substrate.

amount of silicon that can be substituted in HA–Si is 1.2 mol, while the formation of the SC structure requires a precursor containing 2 mol of silicon. Our previous investigations showed that mechanochemically synthesized nanosized HA–Si can contain up to 2 mol of silicon owing to its defect structure [22]. In such a structure, the phase transition to SC upon annealing should occur at temperatures lower than those required in schemes using other precursors or reaction mixtures. These considerations have allowed us to propose a fast and energy-saving synthesis route of SC.

2. Material and methods

The silicon-substituted apatite powder was synthesized by mechanical activation of the reaction mixture at room temperature and a relative humidity of 15%. $CaHPO_4$ (VECTON, Russia), CaO (REACHEM, Russia) powders and amorphous $SiO_2 \cdot 0.7H_2O$ (REACHEM, Russia) with a specific surface area of 420 m^2/g were taken as reactants. The reactants were mixed in the ratios corresponding to the following equation:

$$4.0CaHPO_4 + 6.0CaO + 2SiO_2 \cdot 0.7H_2O \rightarrow 2Ca_5(PO_4)_2SiO_4 + 3.4H_2O \quad (1)$$

Mechanical activation of the mixture (mechanochemical synthesis) was carried out in a planetary ball mill AGO-2 with water-cooled steel vials. The rotation speed of the vials was 1200 rpm. Further details of the milling operations can be found in Ref. [22]. In order to avoid contamination of the synthesized powder by the material of the balls and vials, their surface was lined with the same powder prior to the synthesis. For this, a milling cycle was conducted, in which the powder was allowed to adhere to the surface of the balls and vials.

The product of the mechanochemical synthesis was annealed in a high-temperature electrical furnace PVK-1.4-8 at 1000 and 1300 °C for 5 h using a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was performed using NETZSCH STA 449 F1 Jupiter device in argon–oxygen mixture (80:20) at a heating rate of 10 °C/min using a platinum crucible.

FTIR spectra were obtained with a Tensor 27 spectrometer using the KBr pellet method.

TEM images were obtained using a JEOL JEM 2010 Transmission Electron Microscope.

The elemental analysis carried out using a Hitachi-3400S Scanning Electron Microscope equipped with an Energy-Dispersive Spectroscopy unit (NORAN Spectral System 7).

XRD patterns were recorded on a D8 Advance powder diffractometer with Θ–Θ geometry equipped with a one-dimensional Lynx-Eye detector and a K_β filter using Cu Kα radiation. XRD patterns were collected in the interval $10° < 2\Theta < 70°$ with a step size of $\Delta 2\Theta = 0.0195°$ and a counting time of 35.4 s per step.

The crystallite size, lattice parameters and concentrations was estimated by the Rietveld method [23] using software for the profile and structural analysis Topas 4.2 (Bruker AXS, Germany). The instrumental contribution was calculated by the method of fundamental parameters [24]. The initial structure information was taken from Refs. [21,25].

3. Results and discussion

According to the elemental analysis (Table 2), the ratios of Ca/P/Si in the mechanochemically synthesized powder are close to the ratios of these elements in the SC compound, namely 5/2/1. As lining of the balls and vials was used, the powder obtained by the mechanochemical synthesis contained only traces of iron introduced as contamination during milling.

The XRD pattern of the powder obtained by the mechanochemical synthesis is presented in Fig. 1. All broad reflections belong to apatite, in which the silicate group partially substitutes for the phosphate group (HA–Si phase) [22]. Although the stoichiometric ratios of the initial components corresponded to SC, the structure that formed during the mechanochemical synthesis was the apatite structure. Calculations show that the average grain size of the HA–Si phase is 17 nm (Table 3). TEM observations confirm that the synthesized product consists of nanoparticles (Fig. 2a, b). Such a small grain size indicates that the apatite nuclei with a defect structure are formed in conditions created by high-energy ball collisions during the treatment in a planetary ball mill.

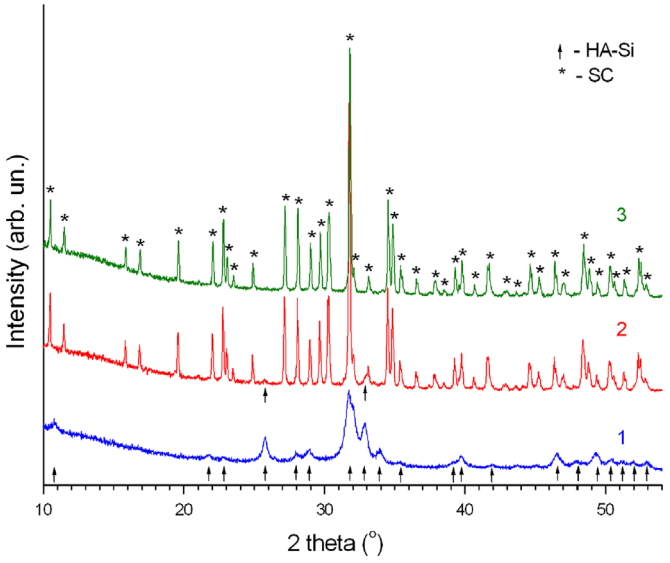

Fig. 1. XRD patterns of the mechanochemically synthesized powder (1) and the products of its annealing at 1000 °C (2) and 1300 °C (3).