



Crystallization behavior of tantalum and chlorine co-substituted hydroxyapatite nanopowders



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ABSTRACT

The crystallization behavior of tantalum and chlorine co-substituted hydroxyapatite nanopowders was examined. Results showed that combined processing by mechanical alloying and annealing is conducive to the structural changes and crystal growth. A series of nanocrystalline tantalum and chlorine co-substituted hydroxyapatite (Ta/Cl-HA) with different dopant contents were synthesized as a result of the progressive mechanochemical reaction. During the subsequent annealing, crystallization of the as-milled powders occurred, leading to a significant increase in the fraction of crystalline phase. TEM images revealed that the crystallized and doped nanopowders composed of crystalline nanoneedles with an average size of 61 ± 26 nm.

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Introduction

Bioceramics are an important class of ceramics that range in biocompatibility from ceramic oxides to bioresorbable ceramic materials [1]. Among them, calcium phosphate is the most important inorganic constituent of biological tissues, and synthetic calcium phosphate has been widely used as biomaterials [2]. The two general biomedical applications of calcium phosphate can be outlined: (i) using them in powder form as filling materials to impart bioactivity to various biocomposites and hybrid biomaterials; (ii) manufacturing of either dense compacts or porous scaffolds, possessing the sufficient mechanical properties [3]. However, insertion of implants to replace the injured parts often gives discomfort for patients, due to brittleness and inadequate biological properties of the ceramic implants [4]. Most studies have shown that the incorporation of ions such as Na^+ , Ag^+ , K^+ , Mg^{2+} , Zn^{2+} , Cd^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , La^{3+} , In^{3+} , Bi^{3+} , Ga^{3+} , Eu^{3+} , Y^{3+} , Pb^{4+} , V^{5+} , AsO_4^{3-} , VO_4^{3-} , SO_4^{3-} , CO_3^{2-} , SiO_4^{3-} , F^- , Cl^- , Br^- , and O^{2-} can improve the crystal structure, crystallinity, surface charge, the solubility and other vital properties, leading to major changes in biological response upon implantation [5–7]. Accordingly, these substituted apatites can be

used for repairing and replacing diseased and damaged parts of musculoskeletal systems, and also as a drug or gene delivery agent, as a bioactive coating on metallic osseous implants, biomagnetic particles and fluorescent markers [8].

In the apatite lattice, monovalent anions (F^- , Cl^-) substitute OH^- ions in the anion channel without charge imbalance. Besides, the anionic complexes can substitute the phosphate group and a large number of monovalent, bivalent, trivalent, tetravalent, and pentavalent metal cations can replace for calcium, suggesting the apatite is able to incorporate almost half of the elements of the periodic system in its atomic structure [9–13]. Hence, over the past decade, many studies have been devoted to the synthesis of substituted apatites by various methods such as wet chemical precipitation [14], co-precipitation [15], emulsion method [16], sol–gel synthesis [17], hydrothermal reaction [18], mechanochemical method [19], and microwave irradiation technique [20]. Among them, powder synthesized using a mechanochemical route usually possesses a well-defined structure due to the perturbation of surface-bonded species as a result of pressure, which enhancing the thermodynamic and kinetic reactions between solids [21,22]. Indeed, the mechanochemical process has the advantages of simplicity and reproducibility of a solid-state procedure to perform mass production and the basic characteristics of an ordinary wet reaction to generate a powder with an appropriate microstructure [23–26].

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Although the incorporation of tantalum (Ta^{5+}) into the apatite structure improves its biological responses [27,28], to our knowledge, the crystallization behavior of the Ta/Cl–HA nanopowders and its effect on the crystal structure have not previously been investigated. Therefore, the present study establishes for the first time the role of subsequent annealing on the phase transitions and morphological changes of nanosize Ta and Cl co-substituted HA. Besides, the structural features were assessed to figure out the possible doping mechanism.

Experimental procedures

Raw materials

Calcium hydroxide ($\text{Ca}(\text{OH})_2$, ≥ 96 wt%), phosphoric acid (H_3PO_4 , ≥ 85 wt% in H_2O), and tantalum (V) chloride (TaCl_5 , 99.99 wt%) were used as the raw materials. All chemicals were purchased from Sigma–Aldrich Co., USA and used without further purification.

Explanation

Depending on the milling conditions, the mechanical activation is classified in two categories: (i) gradual mode in which the reaction may extend to a very small volume during each collision and (ii) mechanically induced self-sustaining reaction (MSR) wherein a self-propagating combustion reaction can be initiated, if the reaction enthalpy is sufficiently high [29]. In the second mode of reaction, which can be predicted by calculating the adiabatic temperature (T_{ad}), the incidence of the combustion reaction results in a rapid rise in temperature of the milling medium, and provides appropriate conditions for a quick transformation. The reaction mechanism can be predicted by calculating the adiabatic temperature or by describing this property ($-\Delta H_{298}/\sum C_p$). For self-sustaining mode reaction to take place it is necessary that these quantities be at least $T_{\text{ad}} > 1800$ K and $-\Delta H_{298}/\sum C_p > 2000$ K [30]. Here, it can be hypothesized that the mode of the reaction is progressive due to the lack of high exothermic reactions. This reaction involves the following steps: (i) the reactive absorption of atmospheric carbon dioxide during milling, and (ii) the mechanically induced reaction of the mixed powders. It should be noted that this assessment is provided according to the following assumptions: (i) milling vial is sealed and isolated (ii) all the reactions occur in the standard conditions ($\Delta G = \Delta G^\circ$) (iii) the activity coefficient is equal to 1, and (iv) the reactions occur in the same physical conditions. During the subsequent annealing, the crystallinity degree is expected to increase significantly due to the crystallization and removal of carbonaceous materials.

Mechanical activation

A series of Ta/Cl–HA powders with different dopant contents and general formula $\text{Ca}_{10-2.5x}\text{Ta}_x(\text{PO}_4)_6(\text{OH})_{2-y}\text{Cl}_y$ were synthesized by mechanical activation of the desired amounts of the

reagents (see Table 1), using a high-energy planetary ball mill (Retsch, PM100) with zirconia vials (50 ml) and balls (10 mm diameter) for 3 h without using any process control agent (PCA). In the apatite formula, the values x and y define the deviation from the complete stoichiometry, within the intervals $0 \leq x \leq 0.5$ and $0 \leq y \leq 1.5$. In all the experiments, the $(\text{Ca} + \text{Ta})/\text{P}$ ratio was fixed at 1.67. On the other hand, the $\text{Ta}/(\text{Ca} + \text{Ta})$ ratio ranged from 0 to 0.1. The ball-to-powder (BPR) weight ratio, total powder mass and rotational speed were 8:1, 4 g, and 500 rpm, respectively. The grinding was suspended for 10 min after 45 min run to avoid excess temperature increase inside the mill vials.

Thermally induced crystallization

To appraise the effect of the subsequent annealing on the crystallization behavior and structural evolution, the mechano-synthesized powders were separately filled in a quartz boat and annealed under atmospheric pressure at 800°C for 1 h. The heating rate from room temperature up to the desired temperature was fixed at $10^\circ\text{C min}^{-1}$. Fig. 1 shows a schematic illustration of the strategy for the fabrication and crystallization of Ta/Cl–HA nanopowders.

Characterization techniques

Phase analysis was performed with a X-ray diffractometer (XRD, PANalytical Empyrean, Netherlands) using a $\text{Cu-K}\alpha$ radiation at 30 kV and 35 mA over a 2θ range from 10° to 70° . To examine the XRD profiles, *Rietveld refinement* and “PANalytical X’Pert HighScore” software were also employed and the patterns were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS), which involved card #24-0033 for HA, #27-0074 for chlorapatite (CA), #01-072-1651 for CaCO_3 (CC), and #01-072-0010 for $\text{Ca}_2\text{PO}_4\text{Cl}$ (CCP). The phase percentages (W_p) in the synthesized powders were determined from the relative intensity ratio of the representing major phases, using Eq. (I) [27].

$$W_p = \frac{(I)_p}{\sum_{i=1}^n (I)_i} \times 100 \quad (\text{I})$$

where $(I)_p$ and $(I)_i$ are the intensity of the major peak of the phase and intensity of major peaks of all phases.

Considering that the phase constitution and transformation characteristics appear to be critically dependent on crystallite size (D) and lattice strain (η), the measurement of these features in the mechanically alloyed powders is very essential. Hence, the crystallite size and lattice strain of the samples were calculated using the well-known equation [31]:

$$B \cos\theta = \frac{0.9\lambda}{D} + \eta \sin\theta \quad (\text{II})$$

where λ , D , η and θ are the wavelength of the X-ray used (0.154056 nm), crystallite size, internal micro-strain and the Bragg angle ($^\circ$), respectively. Note that B in the above equation is the peak width (in radians) after subtracting the peak width due to

Table 1
Details of the powder components.

Sample	Powder components (g)			Ta/(Ca + Ta) ratio	(Ca + Ta)/P ratio	^a N Ta _{ions} × 10 ²³	^b N Cl _{ions} × 10 ²³
	Ca(OH) ₂	H ₃ PO ₄	TaCl ₅				
TaCl0	2.23	1.77	–	0	1.67	0	0
TaCl25	2.06	1.68	0.26	0.025	1.67	0.004	0.02
TaCl50	1.91	1.60	0.49	0.050	1.67	0.008	0.04
TaCl100	1.65	1.46	0.89	0.100	1.67	0.01	0.07

^a N Ta_{ions}, number of Ta ions.

^b N Cl_{ions}, number of Cl ions.

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