Progress in Natural Science: Materials International (xxxx) xxxx–xxxx

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Progress in Natural Science: Materials International

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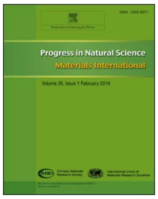

Original Research

Mechanochemical preparation and structural characterization of Ta-doped chlorapatite nanopowders[☆]

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ARTICLE INFO

Keywords:
Mechano-synthesis
Structural features
Lattice constants
XRD-Rietveld refinement
Ta-doped ClA

ABSTRACT

Nanocrystalline tantalum-doped chlorapatite (Ta-doped ClA) was successfully synthesized using a facile mechanochemical method. In the absence of the dopant, milling for 3 h led to the formation of a poorly crystalline hydroxyapatite, while in its presence of the Ta dopant, Ta-doped ClA nanopowders were produced as a result of an oncoming reaction. The results indicated that lattice micro-strain, crystallite size, crystallinity level, phase percentage and hexagonal lattice constants of the substituted apatite nanopowders were dramatically affected by the doping concentration. The *a*-axis and unit cell volume increased with the increase in the doping concentration, owing to the ionic radius difference of Cl^- and OH^- ions. From the TEM observations, the doped powders consisted of nanoneedles with a mean size of 60 ± 20 nm in length and 14 ± 4 nm in width.

1. Introduction

Apatites are the materials with various applications in bone replacement and ceramic membranes, environmental remediation and catalysis [1]. Among the types of apatites, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is broadly used in biomedical applications [2]. But the inherent brittleness and lower strength of HA place the obstacles to load-supporting applications [3]. The atomic doping or replacement in synthetic apatites is one of the strategies to overcome the intrinsic weaknesses of bioceramic implants [4–9]. The Ca^{2+} sites in HA can be replaced by a variety of monovalent (Na^+, K^+, Ag^+), divalent (Mg^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Ga^{2+}, Eu^{2+} etc.), trivalent (Al^{3+}, Bi^{3+}, Y^{3+}, La^{3+} etc.), tetravalent (Zr^{4+}) and pentavalent (Nb^{+5}, V^{+5}, Ta^{+5}) cations. Besides, the OH^- in the anion channel can be substituted by monovalent anions without any charge imbalance and the bivalent anions (e.g., CO_3^{2-}, SO_4^{2-}, HPO_4^{2-}, SeO_3^{2-}, SeO_4^{2-}) can also replace the phosphate, by balancing the charge of the calcium and hydroxide groups [10–13].

The main replacement in bioapatites is carbonates (CO_3^{2-}), as the bone minerals contain a large amount of carbonates. Given that the $Ca–PO_4$ bond is stronger than the $Ca–CO_3$ bond, this substitution increases the solubility of synthetic apatite [14]. On the other hand, the bone mineral is accompanied by minor groups and trace elements like Cl^-, which has a crucial role in biological reactions connected to bone metabolism [15]. The importance of Cl^- incorporation can be linked to its aptitude to create acidic environments on the bone periphery, leading to increased activity of osteoclasts in bone resorption [16]. In addition to their application in bone tissue engineering, metal-doped HA can be utilized for various biomedical applications [17–23]. Therefore, many researchers have tried to prepare substituted apatites with different sizes and geometrical shapes by different kinds of chemical preparation procedures [8,9]. For instance, Landi et al. [24] investigated the insertion of magnesium ions into the apatite lattice by wet-chemical synthesis, which is highly regarded for the development of synthetic bone. Furthermore, the substitution of Zn^{2+}, Ag^+, Cu^{2+} and Ti^{4+} in the apatite lattice are repeatedly been investigated due to the significant role of these cations in different metabolic processes and in prevention of microbial infections in many biomedical applications [25,26]. In contrast to the solid-state processes through which heterogeneous particles are typically formed, powders produced by mechanochemical reactions generally have highly homogenous configuration [27]. This change may be caused by the turbulence of surface-bonded species, which increases the thermodynamic and kinetic reactions between the particles of reactants [28,29]. In fact, the mechanochemical synthesis offers several benefits such as lower temperature, less processing stages, ease of scale-up, as well as lower costs for nanomaterials preparation over traditional processing techniques [30].

[☆] Peer review under responsibility of Chinese Materials Research Society.

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http://dx.doi.org/10.1016/j.pnsc.2016.11.010
Received 21 December 2015; Received in revised form 7 November 2016; Accepted 14 November 2016

Please cite this article as: Nasiri-Tabrizi, B., Progress in Natural Science: Materials International (2016), http://dx.doi.org/10.1016/j.pnsc.2016.11.010

Table 1
Description and powder components of pure and doped samples.

Sample	Powder components	($Ca_{10-2.5x}Ta_x$ $(PO_4)_6$ $(OH)_{2-2x}Cl_{2x}$)	(Ca+Ta)/P ratio
S0	$Ca(OH)_2$–H_3PO_4	x=0	1.67
S25	$Ca(OH)_2$–H_3PO_4–$TaCl_5$	x=0.25	1.67
S50	$Ca(OH)_2$–H_3PO_4–$TaCl_5$	x=0.5	1.67
S100	$Ca(OH)_2$–H_3PO_4–$TaCl_5$	x=1	1.67

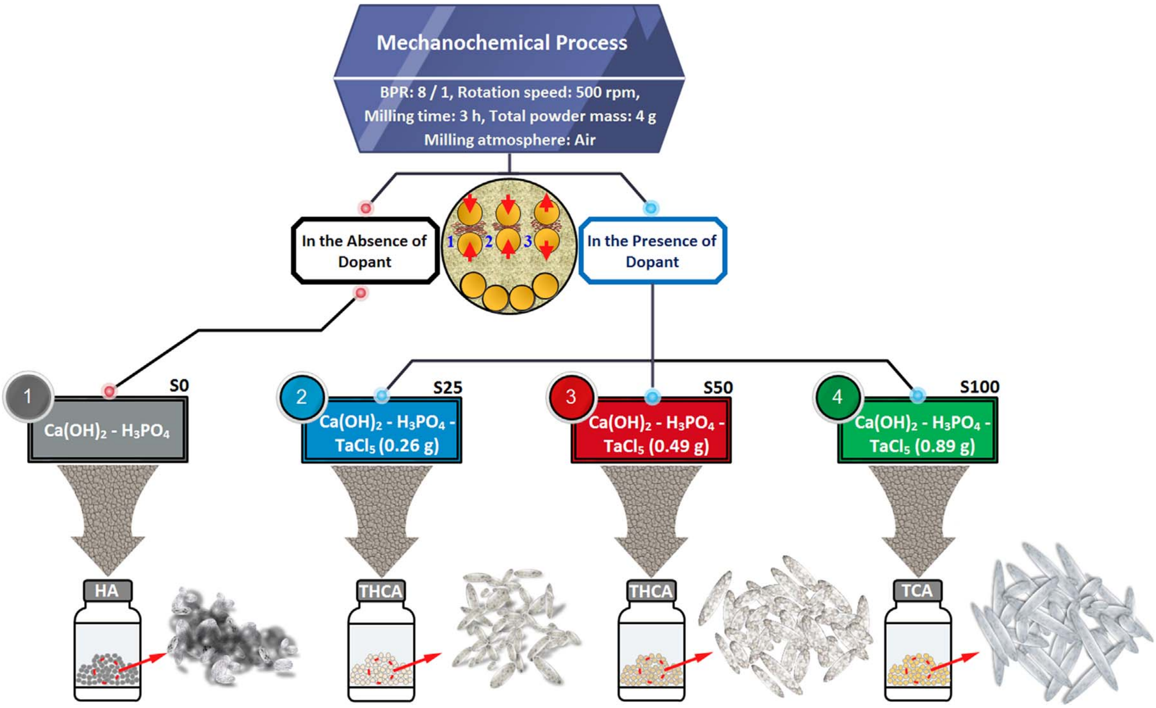

Fig. 1. A schematic outline of the mechanochemical preparation of Ta-doped ClA nanopowders.

It has been found that the insertion of Ta^{5+} into the apatite lattice enhances its biological features by increasing the cell adhesion and proliferation. This cationic substitution also increases the mechanical properties of synthetic HA compared to the undoped bulk ceramic [31,32]. It has recently been found that Ta can replace Ca in HA lattice for Ta contents $< 4.5\%$. For higher amounts of dopant, a deviation from the stoichiometric composition was detected and the unwanted phase became visible [32]. Despite the unique features, only a few studies have been focused on doping of apatites with Ta^{5+}. Therefore, in this work, the mechanochemical preparation of Ta-doped ClA and its structural evolution during mechanical activation are investigated.

2. Experimental procedures

$TaCl_5$ (99.99 wt%), $Ca(OH)_2$ (≥96 wt%) and H_3PO_4 (≥85 wt% in H_2O) were obtained from Sigma-Aldrich Co. (USA) and utilized as reactants without additional purification. To synthesize Ta-doped ClA nanopowders ($Ca_{10-2.5x}Ta_x(PO_4)_6(OH)_{2-2x}Cl_{2x}$), the desired amounts of the raw materials were combined and mechanically activated in a high energy mechanical milling (Retsch, PM100) for 3 h using zirconia grinding-bowl (vol. 50 ml) and balls (diameter of 10 mm) at room temperature. The description and powder components of the pure and doped specimens are presented in Table 1. In the apatite formula, the level of substitution of Ca^{2+} by Ta^{5+}, is represented by the variable x in the chemical formula of the substituted apatite, and was selected as 0, 0.25, 0.50 and 1.00. Therefore, the resultant nanopowders were labeled as S0, S25, S50, and S100, respectively. The rotational speed, total powder mass, ball-to-powder (BPR) weight ratio, and (Ca+Ta)/P ratio were 500 rpm, 4g, 8:1, and 1.67, respectively. Fig. 1 presents a schematic outline of the mechanochemical preparation of Ta-doped ClA nanopowders.

The phase of the nanopowders was identified using PANalytical Empyrean X-ray diffractometer (XRD, Netherlands) by a $Cu\text{-}K_\alpha$ radiation over a 2θ range from 10° to 70°. "*Rietveld refinement*" and "*X'Pert HighScore*" software were utilized to examine the XRD profiles, wherein the reflections were matched against standards (#27-0074 for chlorapatite (ClA). The structural properties of the as-prepared products were determined using the following equation [33]: