

# Effect of ion concentration on mechanosynthesis of carbonated chlorapatite nanopowders



Abbas Fahami <sup>a,\*</sup>, Bahman Nasiri-Tabrizi <sup>b,\*\*</sup>, Gary W. Beall <sup>c,d</sup>, Belinda Pingguan-Murphy <sup>b</sup>

<sup>a</sup> Ingram School of Engineering and Materials Science, Engineering and Commercialization Program, Texas State University, San Marcos, 78666 TX, USA

<sup>b</sup> Department of Biomedical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

<sup>c</sup> Texas State University, Department of Chemistry and Biochemistry, 601 University Drive, San Marcos, 78666 TX, USA

<sup>d</sup> Physics Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

## ARTICLE INFO

### Article history:

Received 10 November 2014

Accepted 24 January 2015

Available online 7 February 2015

### Keywords:

Bioceramics

X-ray techniques

FTIR

Electron microscopy

Nanoparticles

## ABSTRACT

Carbonated chlorapatite nanopowders (n-CCAp) with different degrees of substitution were successfully synthesized by the one-step mechanochemical process. Results demonstrated that the formation of n-CCAp was influenced strongly by the carbonate content ( $x$ ). From X-ray analysis, crystallite size, crystallinity degree, and unit cell volume of n-CCAp decreased significantly as carbonate content ( $x$ ) increased from 0 to 2. Conversely, the lattice strain and the volume fraction of grain boundaries grew considerably. Microscopic analysis showed the average particle size of the synthesized powders was  $15 \pm 10$  nm. The influence of carbonate concentration on mechanosynthesis of pure n-CCAp utilizing a facile solid-state process has not been reported yet; it has potential application for biomedical engineering.

© 2015 Elsevier B.V. All rights reserved.

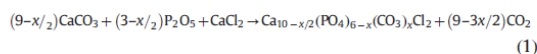
## 1. Introduction

Minor amounts of carbonate are valuable and certainly essential constituents of the hydroxyapatite of human dental enamel and cortical bone [1]. Perhaps the greatest fascinating trait of the apatites is their extraordinary ability to undergo isomorphous substitution by a large variety of cations and anions. The incorporation of carbonate into the apatite structure can happen by substitution for the monovalent anion (A-type substitution of one  $\text{CO}_3^{2-}$  for two  $\text{X}^-$ ) or by substitution for phosphate (B-type substitution  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$ ), the latter of which requires loss of both monovalent anions and cations to preserve charge neutrality [2]. These kind of apatite structures form a bioactive apatite with higher dissolution and osteoclast mediated resorption properties [3]. Furthermore, the presence of carbonate into the apatite structure leads to a decline in crystallinity, a change in crystal morphology, and an enhancement of chemical reactivity due to the weak bonding due to carbonates geometry [4–6]. In fact, the carbonated apatite boosts the local concentration of calcium and phosphate ions that are necessary for new bone formation [7]. For all these reasons, the production of carbonated hydroxyapatite and carbonated fluorapatite is of great value and has been broadly scrutinized using different synthesis processes such as precipitation, sol–gel, solid-state reaction, and hydrothermal treatment [8].

In the present study, the effect of carbonate concentration on mechanochemical synthesis of pure n-CCAp was examined for the first time. The synthesis of pure n-CCAp reported here can be a promising candidate for using in biomedical applications.

## 2. Materials and methods

Calcium carbonate ( $\text{CaCO}_3$ , Merck), calcium chloride ( $\text{CaCl}_2$ , Merck), and phosphorous pentoxide ( $\text{P}_2\text{O}_5$ , Merck) were used as precursor materials. Mechanical activation was done in a high-energy planetary ball mill for 10 h using hardened chromium steel vials (vol. 125 ml) and balls (20 mm in diameter) under a high-purity argon atmosphere (99.99% purity). The total powder mass, the weight ratio of ball-to-powder (BPR), and rotational speed were 7 g, 15:1, and 600 rpm, respectively. The designed degree of substitution of  $\text{PO}_4^{3-}$  by  $\text{CO}_3^{2-}$  was demonstrated by the  $x$  value in the general formula of B-type CCAp ( $\text{Ca}_{10-x/2}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{Cl}_2$ ), where  $x$  values were chosen equal to 0.0, 0.5, 1.0, and 2 and so the synthesized nanopowders were designated as CCA0, CCA0.5, CCA1, and CCA2, respectively. The general form of the mechanochemical reaction is as follows:



The details of powder components and mole ratio are summarized in Table 1. Phase evaluation was performed by X-ray diffraction (Philips X-ray diffractometer (XRD), Cu-K $\alpha$  radiation, 40 kV,

\* Corresponding author. Tel.: +15129600009; fax: +15122453675.

\*\* Corresponding author. Tel.: +60 379674491; fax: +60 379674579.

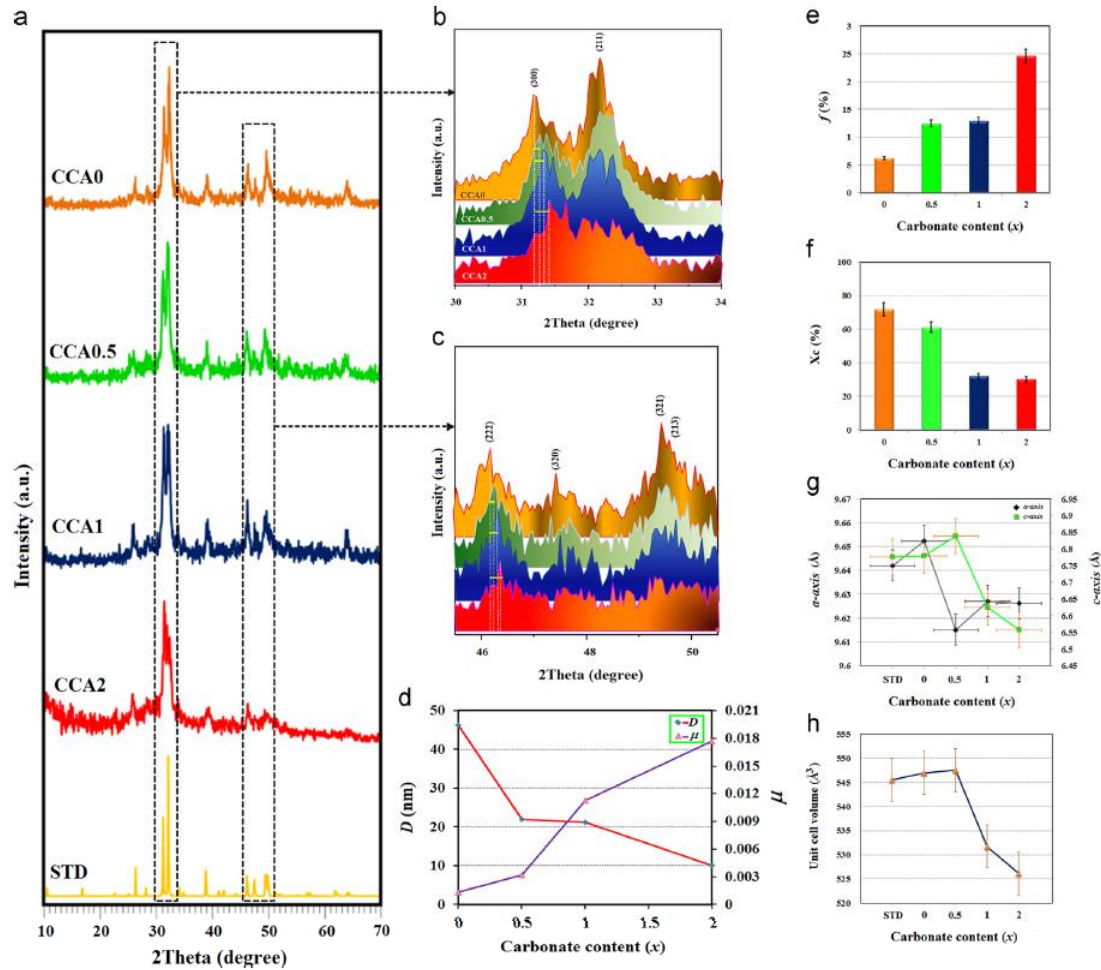
E-mail addresses: fahami@txstate.edu (A. Fahami), bahman\_nasiri@hotmail.com (B. Nasiri-Tabrizi).

<http://dx.doi.org/10.1016/j.matlet.2015.01.149>

0167-577X/© 2015 Elsevier B.V. All rights reserved.

**Table 1**  
Details of powder components and mole ratio.

Series	Degree of substitution ( $\text{Ca}_{10-x/2}(\text{PO}_4)_6-x(\text{CO}_3)_x\text{Cl}_2$ )	Powder component	Mole ratio	Phase composition
CCA0	0	$\text{CaCO}_3\text{-P}_2\text{O}_5\text{-CaCl}_2$	9:3:1	$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$
CCA0.5	0.5	$\text{CaCO}_3\text{-P}_2\text{O}_5\text{-CaCl}_2$	8.75:2.75:1	$\text{Ca}_{9.75}(\text{PO}_4)_5.5(\text{CO}_3)_{0.5}\text{Cl}_2$
CCA1	1	$\text{CaCO}_3\text{-P}_2\text{O}_5\text{-CaCl}_2$	8.5:2.5:1	$\text{Ca}_{9.5}(\text{PO}_4)_5(\text{CO}_3)\text{Cl}_2$
CCA2	2	$\text{CaCO}_3\text{-P}_2\text{O}_5\text{-CaCl}_2$	8:2:1	$\text{Ca}_9(\text{PO}_4)_4(\text{CO}_3)_2\text{Cl}_2$



**Fig. 1.** (a) XRD patterns, (b) magnitude XRD profiles  $2\theta=30\text{--}34^\circ$  and (c)  $2\theta=45.5\text{--}50.5^\circ$ , (d) crystallite size and lattice strain, (e) volume fraction of grain boundary, (f) crystallinity degrees, and (g) the lattice parameters and (h) unit cell volume of the samples milled for 10 h with different degrees of substitution.

30 mA,  $0.02^\circ \text{ s}^{-1}$  step scan, and  $10^\circ \leq 2\theta \leq 70^\circ$ ). The functional groups of n-CCAp were assessed using Fourier transformed infrared spectroscopy (Perkin-Elmer Spectrum 65 FT-IR Spectrometer, USA) in the range of  $4000\text{--}400 \text{ cm}^{-1}$ . Microstructural appraisal of n-CCAp was executed using SEM (SEM, VEGA Tescan easyprobe) and TEM (HT-7700, Hitachi, Japan) that operated at the acceleration voltage of 18 and 60 kV, respectively.

### 3. Results and discussion

The XRD patterns of the samples milled for 10 h with different degrees of substitution are shown in Fig. 1a. From these profiles, all the peaks belonged to the characteristic peaks of apatite (JCPDS027-0074). However, with increasing the carbonate concentration, some noticeable characteristics can be seen; first, the intensity of the characteristic

Link to Full-Text Articles :

<http://www.sciencedirect.com/science/article/pii/S0167577X1500172X>