



## Sodium-carbonate co-substituted hydroxyapatite ceramics

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### Abstract

Powders of sodium-carbonate co-substituted hydroxyapatite, having sodium content in the range of 0.25–1.5 wt.% with a 0.25 wt.% step, were prepared by a precipitation-solid state reaction route. Compacts of the powders were sintered in a  $\text{CO}_2$  flow (4 mL/min) at 1100 °C for 2 h. The sintered ceramics contained sodium and carbonate ions in the ranges of 0–1.5 wt.% and 1.3–6 wt.%, respectively, which are typical impurity concentrations in biological apatite. A relationship between sodium and carbonate contents and the type of carbonate substitution was found. The total carbonate content progressively increased with the sodium content. The obtained ceramics showed an AB-type carbonate substitution. However, the substitution became more B-type as the sodium content increased. As a result, the carbonation was almost B-type (94 %) for the highest sodium content (1.5 wt.%).

**Keywords:** sodium-carbonate co-substituted hydroxyapatites, sintering, characterization

### I. Introduction

Biological apatite based on hydroxyapatite, HA, has a number of substitutions in cationic and anionic sublattices. The substitutions significantly affect the chemical and physico-chemical properties of the apatite, like mineralization and demineralization processes of calcified tissues and susceptibility to caries of teeth. Sodium ( $\text{Na}^+$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions are some of the major substituents occurring at levels of *ca* 0.9 wt.% and 5–8 wt.% [1–4].

As nanosize of crystals and their separation from the organic matrix cause difficulties in the apatite examination, synthetic carbonated hydroxyapatites, CHAs, are typically used as structural models for studying the growth and dissolution processes of biological crystals. Such studies also result in the development of bioactive materials for medical purposes [5–13]. The effect of sodium substitution in HA has extensively been studied [14–18], however, the simultaneous sodium-carbonate substitutions have not been examined as often. Besides, only limited combinations of the sodium and carbonate concentrations have been reported [19–24].

The sodium and carbonate ions have been introduced into HA in various ways. These have been (i) precipitation, with addition of sodium and carbonate into the mother solution containing soluble salts [19,20]; (ii) wet precipitation combined with a preliminary mechanical activation of parent reactants [24] or with firing powder samples in a wet carbon dioxide atmosphere [23]; (iii) synthesis at a high temperature and moderate pressure [22].

A recent *in vivo* study revealed that sodium-free CHA enhanced bone in-growth and coverage [25]. However, an *in vitro* study of sodium-carbonate HA showed that the co-substitution brought little enhance in osteoblast proliferation or phenotype expression compared to HA [25,26]. The processing routes indicated above may result in different physico-chemical characteristics, structural perturbations and, particularly, in  $\text{CO}_3^{2-}$  distributions in the lattice (A-, AB-, and B-types of substitution [5,10]) of sodium-bearing CHAs designed as the same product. This may cause contradicting biological behaviour of such compounds.

In this study, a relationship between sodium and carbonate concentrations in a wide range in biological crystals, and modes of carbonate distribution for each designed combination of the substituents was found in substituted apatite ceramics prepared by a simple reliable route.

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**Table 1. Elemental analysis of the sodium-substituted carbonated ceramics**

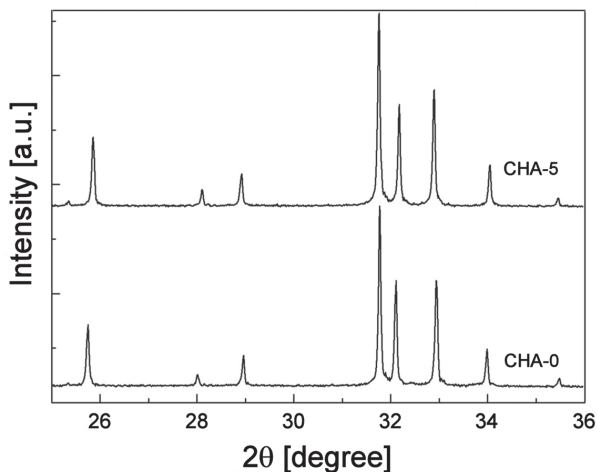
Sample notation	Na [wt.%]	Ca [wt.%]	PO <sub>4</sub> [wt.%]	C [wt.%]	H [wt.%]
CHA-0	0	40.6	54.6	0.27	0.15
CHA-1	0.25	40.3	54.4	0.53	0.15
CHA-2	0.50	40.1	53.0	0.78	0.13
CHA-3	0.75	39.6	52.6	0.90	0.11
CHA-4	1.00	39.5	52.5	1.10	0.11
CHA-5	1.25	39.5	52.0	1.08	0.10
CHA-6	1.50	38.2	52.0	1.20	<0.1

## II. Materials and methods

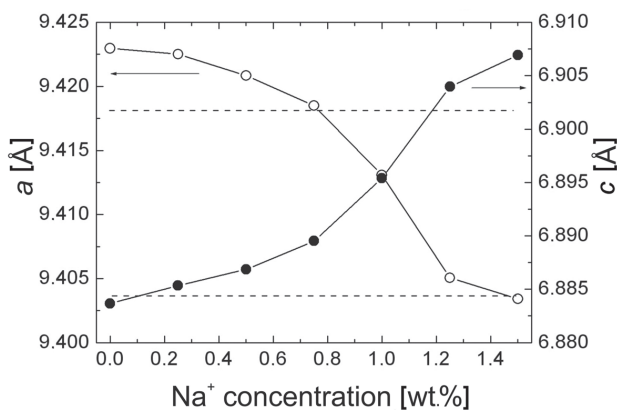
An initial powder of carbonated hydroxyapatite (CHA) was prepared through the reaction of calcium carbonate, CaCO<sub>3</sub>, (Merck, Germany, analytical grade) and a solution of the phosphate acid, H<sub>3</sub>PO<sub>4</sub>, (Merck) [2,27]. Sodium dopants were introduced into the CHA powder by soaking the powder in a solution of sodium hydrocarbonate, NaHCO<sub>3</sub>, at 60 °C until the sol-

vent was completely evaporated. The concentration of solution was varied so that the amount of sodium in the ceramics resulted from firing of compacts of such soaked powders was from 0.25–1.5 wt.% with a step of 0.25 wt.%. The compacts in the form of pellets (3 mm height and 10 mm diameter) were prepared in a steel mold by uniaxial pressing under 120 MPa. The compacts were sintered in a muffle in a dry CO<sub>2</sub> flow (4 mL/min) at 1100 °C for 2 h. Six batches of sintered compacts were prepared with five samples of each sodium concentration.

Calcium and sodium amounts in the samples were determined by atomic absorption spectroscopy (Thermo Electron Corporation, M-series AA spectrometer). Corresponding amounts of orthophosphate were found by colorimetry using the molybdenum blue method (Varian Cary Win UV spectrophotometer,  $\lambda = 725$  nm). Carbon and hydrogen contents were measured by the burning method (EA 1110 CHNS-0 elemental analyser). Structural analysis was performed using a Philips APDW 40C diffractometer and a copper K <sub>$\alpha$</sub>  radiation ( $\lambda = 0.154$  nm) with a nickel filter through 20–70° diffraction angles ( $2\theta$ ). IR spectra were recorded by employing a BIO-RAD 175 spectrometer at a 2 cm<sup>-1</sup> resolution and the KBr technique, operating in the transmittance mode between wave numbers of 400–4000 cm<sup>-1</sup>.



**Figure 1. XRD patterns of ceramics without sodium (CHA-0) and with 1.25 wt.% of sodium (CHA-5)**



**Figure 2. Lattice constants of ceramics with varying sodium concentration (the dotted horizontal lines are the reference values of HA)**

## III. Results and discussion

Compositions of the sintered ceramics, with given sodium concentrations, are listed in Table 1. The pivotal result is the interrelation between the sodium and carbon concentrations: the higher the value for sodium, the higher is the carbon content. The comparison of the XRD patterns for ceramics with no sodium and a high sodium content shows no changes in the crystallographic apatite structure (Fig. 1). However, the lattice constants substantially change (Fig. 2). Starting from the reference values of HA (the  $a$  constant is a little enhanced compared to the reference value because the ceramics was sintered in the CO<sub>2</sub> atmosphere [23,28]), the  $a$  constant gradually decreased, and the  $c$  constant gradually increased as the sodium content in-

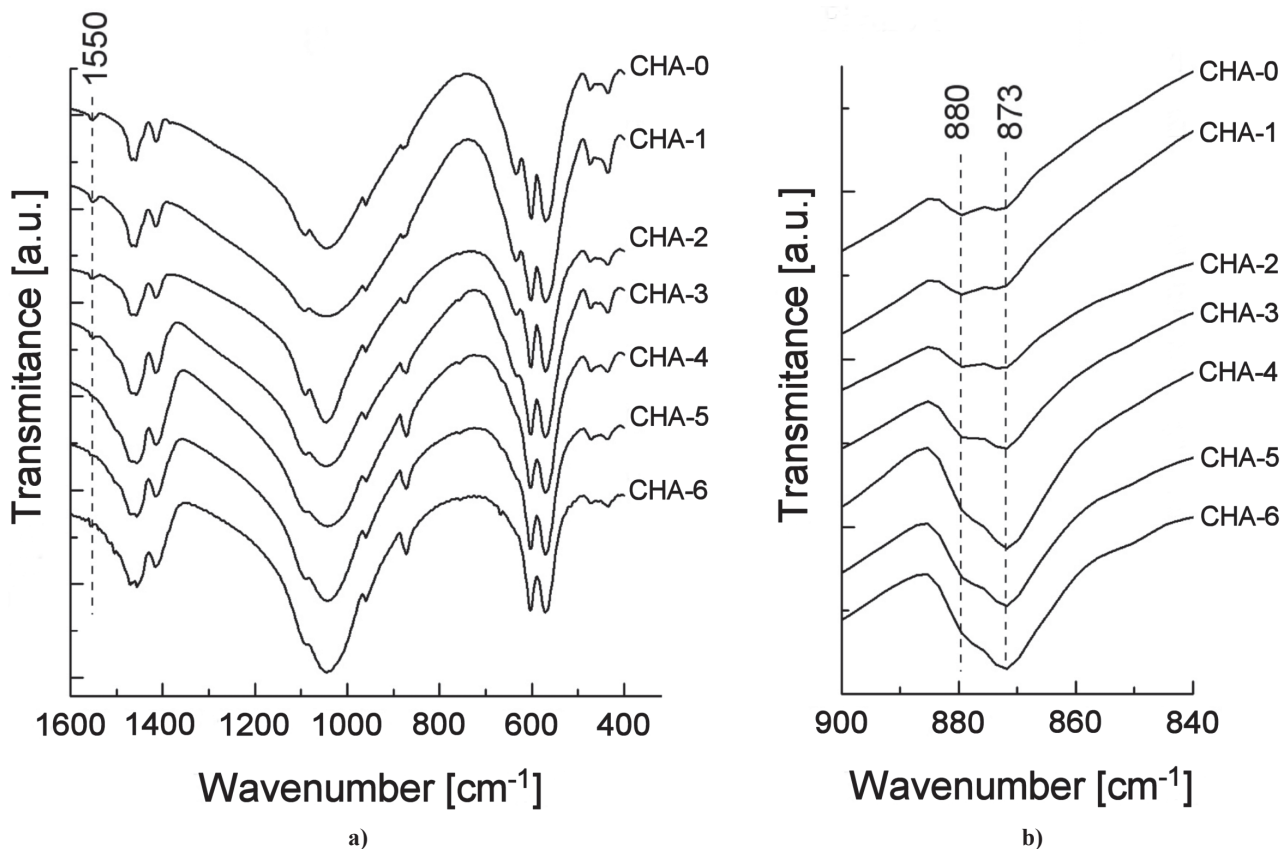


Figure 3. Fragments of IR spectra for ceramics with different sodium contents: 0 wt.% (CHA-0), 0.25 wt.% (CHA-1), 0.5 wt.% (CHA-2), 0.75 wt.% (CHA-3), 1.0 wt.% (CHA-4), 1.25 wt.% (CHA-5) and 1.5 wt.% (CHA-6)

creased in the ceramics. Most probably, this is not a result of the  $\text{Na}^+$  for  $\text{Ca}^{2+}$  substitution as the effective ionic radii of  $\text{Na}^+$  (0.99 Å) and  $\text{Ca}^{2+}$  (1.00 Å) are very close [29]. The change in lattice constants could be

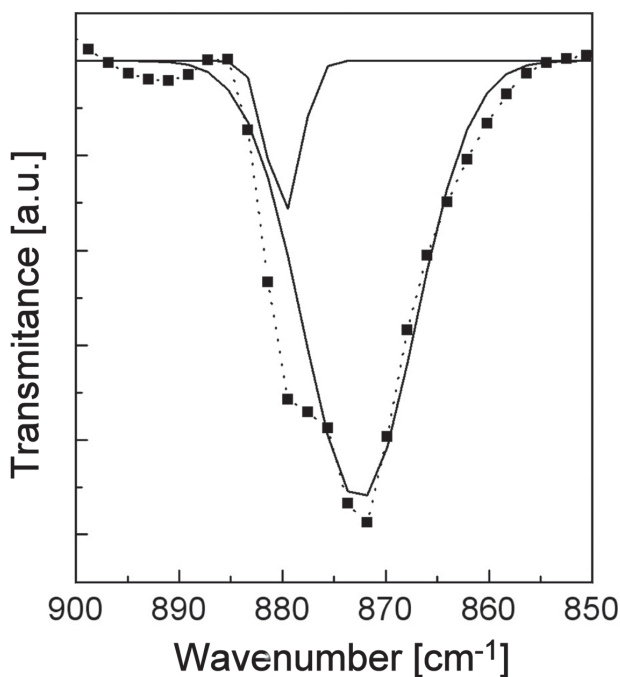


Figure 4. Deconvolution of the band at  $\sim 875 \text{ cm}^{-1}$  (sample CHA-3) performed using Gauss functions and the Fityk program

caused by increased carbonate content in these ceramics (Table 1). However, the presence of carbonate may differently affect the lattice constants in CHA depending on the substitution site [5,10].

IR spectra of all sintered ceramics displayed typical absorbance bands of CHA (Fig. 3a):  $\text{PO}_4^{3-}$  bands at  $478 \text{ cm}^{-1}$  ( $\nu_2$ ),  $563$  and  $603 \text{ cm}^{-1}$  ( $\nu_4$ ),  $965 \text{ cm}^{-1}$  ( $\nu_1$ ),  $1055$ ,  $1075$ ,  $1085$  and  $1105 \text{ cm}^{-1}$  ( $\nu_3$ ); two resolved peaks or shoulders at about  $634$  and  $3571 \text{ cm}^{-1}$  of vibrational and stretching modes of  $\text{OH}^-$ , respectively; a broad vibrational band with a pick at about  $3400 \text{ cm}^{-1}$  and a sharp one at  $1640 \text{ cm}^{-1}$  of adsorbed water; clear peaks and more or less resolved shoulders at  $1410$ ,  $1450$ ,  $1460$ ,  $1475$ ,  $1500$ ,  $1515 \text{ cm}^{-1}$  and, particularly, at  $1545$  and  $1570 \text{ cm}^{-1}$  in the  $\nu_3 \text{CO}_3^{2-}$  region and at about  $875 \text{ cm}^{-1}$  ( $\nu_3 \text{CO}_3^{2-}$ ) indicated an AB-type CHA [10,13,22]. The sodium doping mainly affected the carbonate content in the CHAs. Fragments of IR spectra associated with  $\text{CO}_3^{2-}$  absorbance are depicted in Fig. 3. Comparative analysis of the spectra reveals that the prominent absorbance at  $1550 \text{ cm}^{-1}$ , associated with carbonates in A-positions, becomes weaker as the sodium content in the CHA increases (Fig. 3a). In the end, the absorbance disappears in spectra of ceramics with a sodium content above 1 wt.%. This is consistent with the decrease in hydrogen content (Table 1) and weakening of the  $\text{OH}^-$  band (at  $634 \text{ cm}^{-1}$ ) in the spectra which may be attributed to the increasing occupation of A-site with carbonates as the sodium content increase. Analysis (decon-

volution performed using Gauss functions and the Fityk program - an example is shown in Fig. 4) of the  $\nu_2\text{CO}_3^{2-}$  domain sheds some light on this fact. Deconvolution of the band at about  $875\text{ cm}^{-1}$  for two peaks at  $880$  and  $873\text{ cm}^{-1}$  (Fig. 3b) associated with carbonates in A- and B-sites, respectively [10], reveals that, though decreasing in relative intensity as the sodium content increases, the band at  $880\text{ cm}^{-1}$  is present in each of the spectra, i.e. all sintered ceramics are CHA of an AB-type.

The areas under  $\nu_3$  and (or)  $\nu_2\text{CO}_3^{2-}$  domains increased as the amount of sodium increased. This results from increasing carbonate content in the ceramics. The relative distribution of carbonates in the lattice was also evaluated. For this, the area of the  $\nu_2\text{CO}_3^{2-}$  region was used because several bands in the  $\nu_3\text{CO}_3^{2-}$  domain are associated with the both types of  $\text{CO}_3^{2-}$ . The baseline for the  $\nu_2\text{CO}_3^{2-}$  range was determined as it was suggested earlier [30]. The total  $\text{CO}_3^{2-}$  concentration in each ceramics, represented by the area of  $\nu_2\text{CO}_3^{2-}$  absorbance (the area approach fits better such a representation than the peak height way [31]), was calculated using the corresponding content of carbon (Table 1) and assuming that the latter entirely results from  $\text{CO}_3^{2-}$ . Using the whole area under the  $\nu_2\text{CO}_3^{2-}$  range and the areas of the deconvoluted peaks (at  $880$  and  $873\text{ cm}^{-1}$ ) compiling this area, the distribution of the carbonates in A- and B-sites was calculated as the ratios of corresponding areas for each ceramics (Fig. 5). It can be seen that, as the content of the sodium substituent increases: i) the total carbonate amount also increases and ii) the amount and the accumulation rate of carbonate in B-sites are much higher than those in A-sites. These result in formation of almost B-carbonated ceramics for higher sodium concentrations (e.g. 94 % for 1.5 wt.% of  $\text{Na}^+$ , Fig. 5). The increase in carbonation on B-site led to stronger corresponding absorbances and broadening (detected increase of the areas) of the  $\nu_2$  and  $\nu_3\text{CO}_3^{2-}$ -regions (Fig. 3a). The overlap of the broadened B-carbonate absorbances in the  $\nu_3$  region with the band at  $1550\text{ cm}^{-1}$  gives a worse resolution in this region of the spectra. As a result, the band at  $1550\text{ cm}^{-1}$  gradually transforms to a shoulder and final-

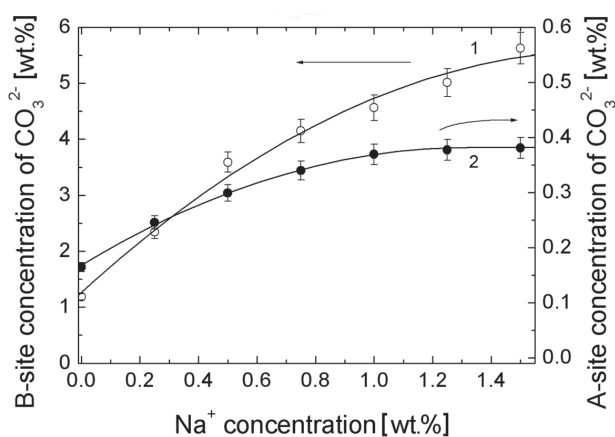


Figure 5. Distribution of carbonates in the A- and B-sites of the lattice in CHA ceramics doped with sodium

ly disappears at above 1 wt.% of  $\text{Na}^+$  (Fig. 3a) despite the presence and even slight increase of the carbonate content in A-sites (Fig. 5, curve 2).

The carbonate content in the sintered ceramics is in the range of 1.3–6.0 wt.% for sodium concentration in the range of 0–1.5 wt.%, respectively (Fig. 5). Such combinations of the sodium and carbonate co-substitution are characteristic of bone [2–4]. Thus, the prepared ceramics are supposed to manifest enhanced biological behaviour compared to unsubstituted calcium phosphates or only carbonated HA materials [25].

A reason of the transition of an A-B type apatite to a mainly B-type apatite with  $\text{Na}^+$ -substitution observed in the study may be associated with lower defect formation energy of the later ( $-71\text{ kJ/mol}$ ) compared to that of the former ( $-518.7\text{ kJ/mol}$ ) [32] resulting in a more stable structure.

#### IV. Conclusions

1. Sodium-carbonate co-substituted HA ceramics were prepared through the introduction of sodium by a diffusion way into a nanocrystalline HA powder and sintering compacts of the sodium-doped powder in a  $\text{CO}_2$  flow at high temperature. Ceramics with 0–1.5 wt.% sodium contained 1.3–6.0 wt.% carbonate, respectively. All ceramics were carbonated in both A- and B- sites.
2. The total carbonate concentration in ceramics increased progressively with the sodium content. A distribution of carbonates in A- and B-sites of the lattice for variety of sodium contents was obtained. The higher the sodium content, the higher was the carbonate concentration in B-sites compared to that in A-sites. As a result, about 94 % of the total carbonate in the lattice was accumulated in B-sites at 1.5 wt.% of sodium.
3. The combination of sodium and carbonate contents in the ceramics was within the typical values of natural bone, and so the ceramics can be considered as prospective biomaterials.

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