

# Structural analysis of a series of strontium-substituted apatites

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## Abstract

A series of Sr-substituted hydroxyapatites,  $(\text{Sr}_x\text{Ca}_{1-x})_5(\text{PO}_4)_3\text{OH}$ , where  $x = 0.00, 0.25, 0.50, 0.75$  and  $1.00$ , were made by a standard wet chemical route and investigated using X-ray diffraction (XRD), Rietveld refinement and Raman spectroscopy. We report apatites manufactured by two synthesis routes under  $90^\circ\text{C}$ , and only the fully Sr-substituted sample had a small amount of an impurity phase, which is believed to be strontium pyrophosphate. Lattice parameters ( $a$  and  $c$ ), unit cell volume and density were shown to increase linearly with strontium addition and were consistent with the addition of a slightly larger and heavier ion (Sr) in place of Ca. XRD Lorentzian peak widths increased to a maximum at  $x = 0.50$ , then decreased with increasing Sr content. This indicated an increase in crystallite size when moving away from the  $x = 0.50$  composition ( $d \approx 9.4$  nm). There was a slight preference for strontium to enter the Ca(II) site in the mixed apatites (6 to 12% depending on composition). The position of the Raman band attributed to  $\nu_1 \text{PO}_4^{3-}$  at around  $963 \text{ cm}^{-1}$  in hydroxyapatite decreased linearly to  $949 \text{ cm}^{-1}$  at full Sr-substitution. The full width at half maximum of this peak also correlated well and increased linearly with increasing crystallite size calculated from XRD.

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**Keywords:** Raman; Apatite; Strontium; XRD; Rietveld

## 1. Introduction

It is known that strontium and other divalent cations with a similar charge-to-size ratio to calcium can readily substitute in the lattice of hydroxyapatite. Also it has been reported that there is immiscibility in this system and complete solid-solution cannot occur, although this may be due to poor sample preparation [1]. Apatites have many applications, from optoelectronics [2] to waste immobilization [3] and biomaterials [4]. Strontium is also beneficial for biological applications for bone regeneration due to the recent success of treatments such as strontium ranelate [5], which stimulates bone formation, decreases bone resorption and reduces the risk of vertebral fractures in postmenopausal osteoporosis. Both calcium- and strontium-hydroxyapatite are hexagonal (space group  $P6_3/m$ ) [6,7]. No complete systematic studies have been performed on this system manufactured by a wet chemical route to our knowledge, and

samples are typically only analysed by X-ray diffraction (XRD). Heijligers et al. [1] performed a structural study of Sr–Ca apatites made by solid state synthesis using XRD but had significant tristrontium phosphate present for compositions above 80% Sr-substitution. Bigi et al. looked at the structure of 0, 20 and 60% substitution of Sr for Ca in hydroxyapatite [8].

Raman microspectrometry is powerful investigative tool, as the probe is 10–100 times smaller than similar micro-infrared spectroscopic techniques. It is useful for biological samples due to its non-invasive and non-destructive nature, and fluorescence is minimized. No special sample preparation is required as the technique is performed in reflection and hence artefacts from the preparation process are eliminated. Complex studies can be performed, such as at interfaces and line-scans of cross-sections. The functional groups present in biological and synthetic apatites, such as phosphate ( $\text{PO}_4^{3-}$ ), hydroxyl ( $\text{OH}^-$ ), acidic phosphate ( $\text{HPO}_4^{2-}$ ), carbonate ( $\text{CO}_3^{2-}$ ) and fluoride ( $\text{F}^-$ ), can be probed, and peak width, position and multiplicity correlated with composition and structure.

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The purpose of this study was to investigate the crystal-line structure of a series of apatites, where Ca is progressively substituted for Sr, by XRD, Rietveld refinement and Raman spectroscopy.

## 2. Experimental

### 2.1. Synthesis

Strontium-substituted hydroxyapatites were synthesized by a wet chemical route. Two reaction routes were used [9].

#### 2.1.1. Route 1

**Solution A preparation.** Calcium nitrate 4-hydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and/or strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) were dissolved in 200 ml of distilled water. Table 1 gives the weights used for each apatite composition. The pH of the solution was adjusted to 11 using 30% ammonia solution, then 400 ml of distilled water was added to the solution. The solution was constantly stirred.

**Solution B preparation.** Diammonium hydrogen orthophosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) was dissolved in 120 ml of distilled water. The amount of  $(\text{NH}_4)_2\text{HPO}_4$  used is given in Table 1. The pH of the solution was adjusted to 11 using ammonia solution; however, no hydroxides precipitated, which have lower solubility than amide salts, tricalcium phosphate and apatite. Distilled water (160 ml) was then added to the constantly stirred solution. The solution was filtered using a Buchner funnel, as described [9].

**Solution A–solution B mix.** Solution B was added dropwise to the constantly stirred solution A over a period of approximately 2 h. The pH was kept at around 11. A precipitate formed and was stirred for 1 h, before being left overnight. The precipitate was centrifuged and washed twice with distilled water. Finally, the precipitate was dried for 20 h at 85 °C. The dried material was crushed using a Gyro-mill and sieved with a 38 µm sieve into coarse and fine fractions.

#### 2.1.2. Route 2

**Solution A preparation.** Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and strontium hydroxide ( $\text{Sr}(\text{OH})_2$ ) were dissolved in 500 ml of distilled water. Table 2 gives the weights used for each apatite composition.

**Solution B preparation.** Orthophosphoric acid solution (85%  $\text{H}_3\text{PO}_4$ ) was diluted in 500 ml of distilled water. The amount of  $\text{H}_3\text{PO}_4$  used is given in Table 2.

**Solution A–solution B mix.** Solution B was added dropwise to the constantly stirred solution A over a period of 2 h. The pH of the mixture was adjusted to about 11 with a 30% ammonia solution, if needed. The precipitate formed was stirred for 1 h, before being left overnight. The precipitate was centrifuged and washed twice with distilled water. Finally, the precipitate was dried for 20 h at 85 °C. The dried material was powdered using a Gyro-mill and sieved with a 38 µm sieve.

### 2.2. XRD

A Phillips powder diffractometer with a copper ( $\text{Cu K}\alpha$ ) X-ray source (Phillips PW 1700 series diffractometer, Philips, Eindhoven, the Netherlands) was used to characterize the glass samples. The powdered samples (<38 µm particle size) were scanned between  $2\theta$  values of 10 and 80° with a step size of  $2\theta = 0.04^\circ$  in order to determine the crystal structure of each apatite. This step size results in a  $d$ -spacing deviation of around 0.009 Å at  $20^\circ 2\theta$ , consistent with the errors reported in the refinement below. These parameters gave sufficient resolution for the refinement, with the most intense peaks occurring in the  $2\theta = 30\text{--}35^\circ$  region. XRD was then carried out and the results analysed using software containing a database of standard diffraction files. Rietveld refinement was performed with GSAS [10] and EXPGUI [11] software using a 10-term shifter-Chebyshev background function. Initial atomic coordinates and unit cell dimensions were taken from previously published data [6,7]. Parameters varied in the refinement were atomic coordinates ( $x$ ,  $y$  and  $z$ ), unit cell parameters ( $a$  and  $c$ ), displacement parameters ( $U_{\text{iso}}$ ), peak intensity scaling and peak profile parameters related to particle size and stress. For the mixed apatites, the fractional occupancies of both divalent cation sites were initially set at the stoichiometric values, then refined to total unity as there is some evidence that strontium preferentially substitutes onto the Ca(II) site [8]. To determine the Bragg peak widths, the Bragg reflection at around  $2\theta = 25.9^\circ$ , corresponding to the 002  $hkl$  reflection, was Lorentzian deconvoluted with Microcal Origin software.

### 2.3. Raman

The Raman system used consisted of a Renishaw RM 2000 spectrometer (Renishaw LC, UK) connected to a Leica microscope with an objective ( $\times 50$ ). A 785 nm 300 mW line focus laser with 100 mW power at the sample

Table 1  
Experimental weights (in g) for route 1 synthesis for the series  $(\text{Sr}_x\text{Ca}_{1-x})_5(\text{PO}_4)_3\text{OH}$ , where  $x = 0.00$  and 1.00

Sr ( $x$ )	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	wt.%	mol.%	$\text{Sr}(\text{NO}_3)_2$	wt.%	mol.%	$(\text{NH}_4)_2\text{HPO}_4$	wt.%	mol.%
1.00	–	–	–	42.34	72.76	62.50	15.85	27.24	37.50
0.50	23.62	38.95	31.25	21.17	34.91	31.25	15.85	26.14	37.50
0.25	35.42	57.27	46.87	10.58	17.11	15.62	15.85	25.63	37.51
0.00	47.23	74.87	62.50	–	–	–	15.85	25.13	37.50

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