

## Structural Effects of Silicon Substitution on Hydroxyapatite Structure with High Substitution Ratio By Rietveld's Analysis

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### Abstract

The silicon-substituted hydroxyapatite (Si-HA) with three different Si-substitution levels were synthesized via aqueous precipitation method, in the absence of any surfactants and organic solvents. The composition of the Si-substituted HA phases and effect of silicon substitution on the crystal structure were investigated by Rietveld refinements from powder X-ray diffraction data. The results show that the final compounds are oxyhydroxyapatites, a chemical formula for the Si-substituted HA phases with indication of the incorporated silicate amount is proposed.

**Indexing terms/Keywords:** Si-substituted hydroxyapatite, X-ray diffraction, Rietveld refinement.

### Introduction

Recently, Rietveld analysis was shown to be very useful for determining the spatial coordinates of atoms within the crystal structures of polycrystallines. Rietveld analysis can precisely determine the crystal structure in one step, it's an accurate method which can precisely determine each parameter of simulating functions fitting the integrated intensity obtained from the structural model to measured diffraction intensity. Although powder diffraction provides less information than the single crystal method, the new Rietveld analysis system Fullprof has solved this problem by development of a mathematical algorithm.

Synthetic, pure and substituted, hydroxyapatite (HA) is well established as bone replacement material in orthopedics and dentistry, due to its bioactivity and biocompatibility with the human bone [1]. Previous studies showed that the traditional HA materials lacked the ability to induce osteogenesis [2,3], while the silicon (Si) element was usually used as a functional element to improve the bioactivity of the apatite materials [4–6] and enhance the reactivity of pure hydroxyapatite [7,8]. The composition of SiHA can be described as  $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-x}$  [9]. Several authors have worked on this subject, assuming that Si or  $\text{SiO}_4^{4-}$ , replaces P or  $\text{PO}_4^{3-}$ , respectively, at the 6 h positions, with the subsequent loss of charge equilibrium [10]. In the present study, a pure hydroxyapatite HA and a series of silicon-substituted hydroxyapatite ceramics ( $\text{Si}_x\text{HA}$ ), with high substitution ratio ( $x=1.4$ ; 1.6 and 1.8), were synthesized via an aqueous precipitation method. The as-obtained X-ray diffraction data were used for Rietveld refinement analysis to study the structural effect of silicon substitution ratio on hydroxyapatite structure.

### Materials and Methods

A pure HA and SiHA were prepared following the aqueous precipitation method described in our previous works [11,12] using calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and tetraethoxysilane ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ) (TEOS) solutions as reagents.

The crystalline phases of powders were determined using X-ray diffraction (XRD) they were identified by means of a XPERT-PROPW3050/60 (Theta/Theta) using  $\text{CuK}\alpha$  radiation and operating at 45 kV and 40 mA and counting



time of 0.5°/mn. Crystalline phases detected in the patterns were identified by comparison to standard patterns from the ICDD-PDF.

### Rietveld refinements

Rietveld analysis can obtain accurate structural parameters directly from the complicated X-ray powder diffraction patterns without peak separation. For each reflection, Rietveld analysis multiplies the function, which can simulate the shape of the reflection peak to integrated intensity obtained from the structure model, and then refine the function parameters to fit the measured reflection intensity by using the least-squares method. The experimental profiles were fitted with the most suitable pseudo-Voigt analytical function. For both the  $K\alpha_1$  and  $K\alpha_2$  profiles, the line broadening function  $B(2\theta)$  may be represented by the pseudo-Voigt function:

$$pV(x) = \eta L(x) + (1 - \eta)G(x). \quad (1)$$

The  $L(x)$  and  $G(x)$  are, respectively, the Lorentzian and Gaussian components.

The objective function to be minimized in the program is the weighted sum of squares :

$$S = \sum w_i [y_i(o) - y_i(c)]^2 \quad (2)$$

where  $w_j$  is the weight based on counting statistics,  $y_i(c)$  consists of contributions from nearby diffraction peaks and the background, and  $y_i(o)$  is the observed intensity.

Calculating the distortion of the  $PO_4$  tetrahedrons can do an estimation of the structure distortion. The tetrahedral distortion index was obtained from the calculated data using the relation:

$$TDI = \frac{\sum_{i=1}^6 |OPO_i - OPO_m|}{6}$$

where  $OPO_i$  denotes the six angles between P and the four O atoms of the phosphate tetrahedron and  $OPO_m$  the average angle.

**Table 1. Lattice parameters and unit cell volume**

Samples	a=b(Å)	c(Å)	V(Å <sup>3</sup> )
HA	9.4159	6.8819	528.4002
Si <sub>1,4</sub> HA	9.4366	6.9111	532.9788
Si <sub>1,6</sub> HA	9.4384	6.9131	533.3455
Si <sub>1,8</sub> HA	9.4387	6.9132	533.3903

### Results

The structural study was carried out by powder X-ray (XRD) and the Rietveld refinements were carried out using the program Fullprof. The refinements were performed using the atomic position set no 176 [13].

The pseudo-Voigt profile function of Thompson [14] was employed to model the peak shape of the Bragg reflections. The refinement procedure was started by refining: the scale factor, zero point of detector, 1<sup>st</sup> background parameter (polynomial function of sixth order) and lattice parameters; then gradually more parameters were opened; the peak profile (pseudo-Voigt) parameters, atomic coordinates and isotropic displacement parameters B. In the final step the individual anisotropic thermal parameters (ATPs) could be improved. Attempts to refine the ATPs of the hydrogen atom were not successful, then Isotropic displacement parameter is Kept fixed at the value 1.5.

The lattice parameters of HA, Si-HA samples and the unit cell volume are listed in table 1. It can be seen that the unit cell parameters and unit cell volume of Si-HA are larger than that of pure HA. This can be understood considering that the average lengths of the Si-O and P-O bonds are 1.62 and 1.51 Å, respectively. Therefore, the substitution of PO<sub>4</sub><sup>3-</sup> by SiO<sub>4</sub><sup>4-</sup> is assumed to contribute to the increase in the lattice parameters of the Si-HA materials. Both a and c parameters increase as the level of Si substitution increases. These changes also appear logical considering that the ionic radius of Si<sup>4+</sup> (0.042 nm) is larger than that of P<sup>5+</sup> (0.035 nm).

Atomic coordinates, occupancies and agreement factors for HA and Si<sub>x</sub>HA are collected in Tables 2. Tables 3 collects the anisotropic displacement parameters for HA and SiHA. In order to study the effect of Si incorporation into the PO<sub>4</sub> tetrahedrons, the P-O distances and angles were calculated from the atomic coordinates. Table 4 collects distances for different atoms and Tables 5 collects bonding angles and distortions indexes (TDI) calculated from the six O-P-O angles of the PO<sub>4</sub> tetrahedron. No significant differences result in P-O distances due to the Si incorporation. Only a small increase of TDI can be observed.

## Discussion

The Si or SiO<sub>4</sub><sup>4-</sup>, incorporation into the apatite structure at the P or PO<sub>4</sub><sup>3-</sup>, position has been studied by several authors. Gibson et al. have reported on the higher bioactivity [7], sintering behavior [15] and chemical characterization [9] of these compounds. These authors have reported on aqueous precipitated apatites and the effect of the Si is noticeable by the SiHA behavior. The main structural evidences reported so far are the decrease and increase of "a" and "c" parameters, respectively, absence of secondary phases and small tetrahedron distortion changes. The results obtained in this work agree with it, except for the behavior of the "c" parameter. In our samples, both "a" and "c" parameters increase with Si incorporation, pointing out a difference in the chemical composition respect to aqueous precipitated SiHA.

Despite of the SiO<sub>4</sub><sup>4-</sup> substitution for PO<sub>4</sub><sup>3-</sup>, the P-O distances and O-P-O angles show that PO<sub>4</sub> tetrahedrons are significantly modified. Table 5 shows that the P-O distances do not show significant differences, and only a small increase of the tetrahedron distortion can be observed in Si<sub>x</sub>HA.

**Table 2. Atomic coordinates and occupancies for samples HA and Si<sub>x</sub>HA**

	<b>Wyckoff</b>	<b>X</b>	<b>Y</b>	<b>Z</b>	<b>Occ</b>	<b>B<sub>iso</sub></b>
	<b>HA pure</b>	<b>R<sub>p</sub>=9,99</b>	<b>R<sub>f</sub>=1,82</b>	<b>R<sub>wp</sub>=12,8</b>	<b>R<sub>exp</sub>=9,43</b>	<b>χ<sup>2</sup>=1,84</b>
<b>O1</b>	6h	0.32590	0.48244	¼	5.9154	2.4421
<b>O2</b>	6h	0.58394	0.46367	¼	5.8946	1.3273
<b>O3</b>	12i	0.33818	0.25338	0.06712	12.1170	1.6715
<b>O(H)</b>	4e	0.00000	0.00000	0.22352	2.0015	3.3422
<b>H</b>	4e	0.00000	0.00000	0.16450	1.9402	1.5000
<b>Ca1</b>	4f	1/3	2/3	0.00112	4.0060	1.8642
<b>Ca2</b>	6h	0.24844	0.99304	¼	5.9143	1.2372

<b>P</b>	6h	0.39802	0.36911	1/4	5.9393	1.0943
	<b>Si<sub>1,4</sub>HA</b>	<b>R<sub>P</sub>=25,1</b>	<b>R<sub>F</sub>=7,68</b>	<b>R<sub>wp</sub>=25,4</b>	<b>R<sub>exp</sub>=16,82</b>	<b>χ<sup>2</sup>=2,26</b>
<b>O1</b>	6h	0.32754	0.48383	1/4	6.00006	0.05135
<b>O2</b>	6h	0.58140	0.46124	1/4	6.00079	0.03121
<b>O3</b>	12i	0.34276	0.25799	0.06842	12.00482	0.01420
<b>O(H)</b>	4e	0.00000	0.00000	0.19710	1.88938	0.52970
<b>H</b>	4e	0.00000	0.00000	0.05879	0.52489	1.50000
<b>Ca1</b>	4f	1/3	2/3	0.00128	4.09191	0.43415
<b>Ca2</b>	6h	0.25018	0.99057	1/4	5.97685	0.05784
<b>P</b>	6h	0.39842	0.37037	1/4	4.63177	0.00746
<b>Si</b>	6h	0.39842	0.37037	1/4	1.33823	0.00746
	<b>Si<sub>1,6</sub>HA</b>	<b>R<sub>P</sub>=20.4</b>	<b>R<sub>wp</sub>=20,6</b>	<b>R<sub>exp</sub>=13,83</b>	<b>χ<sup>2</sup>=2,25</b>	
<b>O1</b>	6h	0.32866	0.48458	1/4	6.09427	0.94419
<b>O2</b>	6h	0.58862	0.46507	1/4	6.14295	0.43129
<b>O3</b>	12i	0.34244	0.25966	0.06915	11.87898	0.78382
<b>O(H)</b>	4e	0.00000	0.00000	0.19372	1.83971	1.00040
<b>H</b>	4e	0.00000	0.00000	0.05979	0.30133	1.50000
<b>Ca1</b>	4f	1/3	2/3	0.00166	4.08905	0.75790
<b>Ca2</b>	6h	0.24592	0.99224	1/4	5.95157	1.90140
<b>P</b>	6h	0.39731	0.36821	1/4	4.41332	1.21855
<b>Si</b>	6h	0.39731	0.36821	1/4	1.57664	1.21855
	<b>Si<sub>1,8</sub>HA</b>	<b>R<sub>P</sub>=21,8</b>	<b>R<sub>wp</sub>=22,0</b>	<b>R<sub>exp</sub>=14,25</b>	<b>χ<sup>2</sup>=2,28</b>	
<b>O1</b>	6h	0.32825	0.48342	1/4	6.02098	1.16676
<b>O2</b>	6h	0.58906	0.46413	1/4	6.01776	0.89039
<b>O3</b>	12i	0.34273	0.25740	0.07005	12.09045	0.48416
<b>O(H)</b>	4e	0.00000	0.00000	0.19319	1.79933	2.04065
<b>H</b>	4e	0.00000	0.00000	0.06070	0.11548	1.50000
<b>Ca1</b>	4f	1/3	2/3	0.00159	4.12904	0.90180
<b>Ca2</b>	6h	0.24630	0.97990	1/4	6.12515	0.60398
<b>P</b>	6h	0.39800	0.36870	1/4	4.22196	0.05029
<b>Si</b>	6h	0.39800	0.36870	1/4	1.69053	0.05029

The PO<sub>4</sub><sup>3-</sup>/SiO<sub>4</sub><sup>4-</sup> substitution is non-iso-electronic. Therefore, we need to know the OH<sup>-</sup>/O<sup>2-</sup> ratio at the 4e position. The maximum theoretical occupancy for O and H at this position is 2. Sample HA shows 2.00 and 1.94 for O and H, respectively. Considering that the H atoms are forming the hydroxyls, our results show that there are 1.94 H atoms per unit cell that, combined with 1.94 O atoms, will result in the same amount of OH. The composition at the 4e Wyckoff position in HA was calculated to be (OH)<sub>1.94</sub>O<sub>0.06</sub>.

Table 3. Anisotropic displacement parameters for HA and Si<sub>x</sub>HA

	<b>B<sub>11</sub></b>	<b>B<sub>22</sub></b>	<b>B<sub>33</sub></b>	<b>B<sub>12</sub></b>	<b>B<sub>13</sub></b>	<b>B<sub>23</sub></b>
<b>HA : Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub></b>						
<b>O1</b>	0.00879	0.01597	0.00391	0.01477	0.00000	0.00000
<b>O2</b>	0.01400	0.00091	0.00008	0.00501	0.00000	0.00000
<b>O3</b>	0.01300	0.00530	0.00078	0.01042	0.00116	0.00769
<b>O(H)</b>	0.00545	0.00545	0.03762	0.00273	0.00000	0.00000
<b>Ca1</b>	0.00763	0.00763	0.00809	0.00381	0.00000	0.00000
<b>Ca2</b>	0.00482	0.00151	0.01071	0.00103	0.00000	0.00000
<b>P</b>	0.00367	0.00325	0.00762	0.00215	0.00000	0.00000
<b>Si<sub>1,4</sub>HA : Ca<sub>10</sub>(PO<sub>4</sub>)<sub>4,6</sub>(SiO<sub>4</sub>)<sub>1,4</sub>(OH)<sub>0,6</sub></b>						
<b>O1</b>	0.00155	0.00291	0.02685	0.00965	0.00000	0.00000
<b>O2</b>	0.00743	0.00748	0.02212	0.00528	0.00000	0.00000
<b>O3</b>	0.00904	0.01590	0.01997	0.02009	0.00087	0.03051
<b>O(H)</b>	0.00191	0.00191	0.00814	0.00095	0.00000	0.00000
<b>Ca1</b>	0.00100	0.00100	0.00489	0.00050	0.00000	0.00000
<b>Ca2</b>	0.00160	0.00077	0.00378	0.00082	0.00000	0.00000
<b>P</b>	0.00094	0.00328	0.00370	0.00018	0.00000	0.00000
<b>Si</b>	0.00094	0.00328	0.00370	0.00018	0.00000	0.00000
<b>Si<sub>1,6</sub>HA : Ca<sub>10</sub>(PO<sub>4</sub>)<sub>4,4</sub>(SiO<sub>4</sub>)<sub>1,6</sub>(OH)<sub>0,4</sub></b>						
<b>O1</b>	0.00762	0.03431	0.03628	0.00810	0.00000	0.00000
<b>O2</b>	0.00467	0.02730	0.00803	0.00106	0.00000	0.00000
<b>O3</b>	0.00402	0.00390	0.02066	0.00794	0.00114	0.02321
<b>O(H)</b>	0.00209	0.00209	0.00348	0.01045	0.00000	0.00000
<b>Ca1</b>	0.00225	0.00225	0.00323	0.00112	0.00000	0.00000
<b>Ca2</b>	0.01389	0.00533	0.01174	0.00579	0.00000	0.00000
<b>P</b>	0.00566	0.00045	0.00197	0.00020	0.00000	0.00000
<b>Si</b>	0.00566	0.00045	0.00197	0.00020	0.00000	0.00000
<b>Si<sub>1,8</sub>HA : Ca<sub>10</sub>(PO<sub>4</sub>)<sub>4,2</sub>(SiO<sub>4</sub>)<sub>1,8</sub>(OH)<sub>0,2</sub></b>						
<b>O1</b>	0.00549	0.05523	0.00599	0.00886	0.00000	0.00000
<b>O2</b>	0.00327	0.00816	0.00781	0.00072	0.00000	0.00000
<b>O3</b>	0.00505	0.03481	0.00617	0.00041	0.00037	0.05430
<b>O(H)</b>	0.00710	0.00710	0.01620	0.00355	0.00000	0.00000
<b>Ca1</b>	0.00293	0.00293	0.00614	0.00146	0.00000	0.00000
<b>Ca2</b>	0.00876	0.00576	0.00757	0.00340	0.00000	0.00000
<b>P</b>	0.01023	0.00897	0.00274	0.00902	0.00000	0.00000
<b>Si</b>	0.01023	0.00897	0.00274	0.00902	0.00000	0.00000

The SiHA sample shows a similar amount of vacancies but differs in the hydroxylation degree respect to HA. From the data collected in Table 2 and following the same procedure as above, the 4e position of Si<sub>x</sub>HA is calculated as:

$(\text{OH})_{0.52}\text{O}_{1.36}\text{V}_{0.11}$ ;  $(\text{OH})_{0.30}\text{O}_{1.54}\text{V}_{0.16}$  and  $(\text{OH})_{0.16}\text{O}_{1.64}\text{V}_{0.20}$  for Si<sub>1,4</sub>HA, Si<sub>1,6</sub>HA and Si<sub>1,8</sub>HA, respectively. V represent vacancies formed at this position.

In the case of HA, the fact that the sites of the O1, O2 and P atoms show some vacancies, whereas the sites of O3 maintain significantly high occupancy, undoubtedly show evidence for replacement of PO<sub>4</sub><sup>3-</sup> by CO<sub>3</sub><sup>2-</sup> ions in the apatite lattice [16].

**Table 4.Distance (Å) for different atoms**

	<b>HA</b>	<b>Si<sub>1,4</sub>HA</b>	<b>Si<sub>1,6</sub>HA</b>	<b>Si<sub>1,8</sub>HA</b>
<b>Ca1-O1</b>	2.4137	2.4169	2.4139	2.4207
<b>Ca1-O2</b>	2.4607	2.4679	2.4562	2.4473
<b>Ca1-O3</b>	2.8329	2.8114	2.8217	2.8130
<b>Ca2-O1</b>	2.6774	2.6714	2.7059	2.5880
<b>Ca2-O2</b>	2.3528	2.3624	2.3656	2.3670
<b>Ca2-O3</b>	2.4971	2.5498	2.5425	2.6177
<b>Ca2-O3(2)</b>	2.3100	2.3251	2.3404	2.3130
<b>Ca2-O(H)</b>	2.3797	2.4341	2.3904	2.4460
<b>P-O1</b>	1.5246	1.5198	1.5290	1.5227
<b>P-O2</b>	1.5161	1.4953	1.5638	1.5617
<b>P-O3</b>	1.5731	1.5551	1.5331	1.5412
<b>Average distance P-O</b>	1.5379	1.5234	1.5419	1.5418

**Table 5.Bonding angles and distortions indexes (TDI) for PO<sub>4</sub> tetrahedrons**

<b>Angles</b>	<b>Bonding angles</b>			
	<b>HA</b>	<b>Si<sub>1,4</sub>HA</b>	<b>Si<sub>1,6</sub>HA</b>	<b>Si<sub>1,8</sub>HA</b>
<b>O1-Ca1-O3</b>	67.77(3)	69.14	68.88	68.70
<b>O2-Ca1-O3</b>	55.96 (3)	55.86	56.10	54.84
<b>O1-Ca2-O3</b>	71.97 (4)	72.25	72.42	72.53
<b>O2-Ca2-O3</b>	76.22 (4)	74.51	74.61	75.63
<b>O1-P-O3</b>	110.74 (6)	110.92	111.42	111.27
<b>O1-P-O2</b>	112.12 (7)	111.11	112.02	112.62
<b>O1-P-O3(2)</b>	107.54 (10)	107.05	107.36	107.96
<b>O3-P-O3(2)</b>	106.26 (7)	109.27	107.64	107.60
<b>O2-P-O3</b>	108.37 (5)	107.22	107.02	106.88
<b>O2-P-O3(2)</b>	106.15 (8)	105.25	105.12	104.93
<b>Average angle O-P-O</b>	108.53	108.47	108.43	108.54
<b>TDI</b>	1.78 x 10 <sup>-2</sup>	1.81 x 10 <sup>-2</sup>	2.02 x 10 <sup>-2</sup>	2.08 x 10 <sup>-2</sup>

Therefore, we can estimate unit cell formulas as described in Table 6:

**Table 6. Chemical formulas of the samples after refinement**

<b>Samples</b>	<b>General chemical formulas</b>	<b>Detailed chemical formulas</b>
<b>HA</b>	$\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2-y}\text{O}_y$	$\text{Ca}_{10}(\text{PO}_4)_{5,93}(\text{CO}_3)_{0,07}(\text{OH})_{1,94}\text{O}_{0,006}$
<b>Si<sub>1,4</sub>-HA</b>		$\text{Ca}_{10}(\text{PO}_4)_{4,66}(\text{SiO}_4)_{1,34}(\text{OH})_{0,52}\text{O}_{1,36}\text{V}_{0,11}$
<b>Si<sub>1,6</sub>-HA</b>		$\text{Ca}_{10}(\text{PO}_4)_{4,41}(\text{SiO}_4)_{1,58}(\text{OH})_{0,3}\text{O}_{1,53}\text{V}_{0,16}$
<b>Si<sub>1,8</sub>-HA</b>	$\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-y-z}\text{O}_y\text{V}_z$	$\text{Ca}_{10}(\text{PO}_4)_{4,22}(\text{SiO}_4)_{1,7}(\text{OH})_{0,16}\text{O}_{1,64}\text{V}_{0,2}$

## Conclusions

In the present study, a pure hydroxyapatite HA and a series of silicon-substituted hydroxyapatite ceramics (Si<sub>x</sub>HA), with x = 1.4; 1.6 and 1.8, were synthesized by an aqueous precipitation method. The Rietveld analysis for different samples shows a slight disruption of hydroxyapatite structure without deformation. The insertion of silicon atoms into HA matrix lead to an increase in unit cell parameters (a and c) suggesting the substitution of phosphates by silicates. The calculation of tetrahedral distortion index TDI confirms that the HA structure is slightly affected by the substitution phenomena.

Finally, the Rietveld refinement revealed that the as-prepared samples are not hydroxyapatite and silicon-hydroxyapatite as expected, but rather carbonated oxy-hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_{5,93}(\text{CO}_3)_{0,07}(\text{OH})_{1,94}\text{O}_{0,06}$  and silicated oxy-hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{SiO}_4)_x(\text{OH})_{2-y-z}\text{O}_y\text{V}_z$  respectively.

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