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X-Ray Diffraction Studies on the Thermal Stability of Calcium-Strontium Hydroxyapatite Solid Solutions Syntheszed in the Presence of Diethylamine

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ABSTRACT: Calcium-Strontium hydroxyapatite (HAP) solid solutions in the presence and absence of diethylamine (DEA) were prepared by the method of co-precipitation from basic media. The samples were heated at 773.15K in a furnace. Characterization of the samples by x-ray powder diffractometry, atomic absorption spectroscopy (AAS) and UV- visible spectrometry revealed that calcium –strontium HAP solid solutions at an elevated temperature of 773.15K were unstable and underwent transformation into other phosphates possibly beta tricalcium phosphate(β-TCP). Solid solutions synthesized in the presence of DEA show remarkable stability and enhanced crystallinity at that temperature. The stability was probably due to the added organic molecule which acted as a template.

KEYWORDS: Apatites, solid solutions, templates.

INTRODUCTION

Being the most common member of the apatite family, Calcium HAP ($Ca_{10} (PO_4)_6 (OH)_2$) is not only the major constituent of mineral phosphate, but the major inorganic constituent of bones and teeth (Van-Wazer, 1961; Sowerby and Emeleus,1975; Bigi *et al.,* 1980; Andress Verges *et al.,* 1983). Fundamental studies and clinical applications have demonstrated that HAP biomaterials are biocompatible and osteoconductive (Baud *et al.,*1973; Wei *et al.,* 2003). The synthesis and isomorphous substitution reactions of HAP have been widely investigated by several researchers. (Baud *et al.,* 1973; Kousoukos and Nancolas, 1981; Bartels *et al.,* 1982; Thomas *et al.,* 1989; Inikori, 1991; Ajibola, 1995). During investigations of cation-exchange characteristics of various synthetic HAP it has been discovered that cations having ionic radii close to that of calcium tend to replace Ca^{2+} in the apatite structure (Patel,1979; Young,1980; Thomas *et al.,* 1989; Inikori, 1991; Ajibola, 1995). .Preorganized architectures consisting of funtionalized surfaces act as templates for the nucleation and growth of inorganic materials (Kresge *et al.,* 1992; Pathak *et al.,* 2004; Ayi *et al.,* 2005). The templates are frequently used to promote the formation of a desired structure during the synthesis of inorganic materials and it is understood that the templating agents, normally organic nitrogen-containing bases, may serve as structure directing agents, as buffers or as void fillers (Pathak *et al.,* 2004). X-ray diffraction technique has been used by several researchers to investigate the individual effect of some elements on the formation and some properties of apatite in synthetic and biological systems formed (Baud *et al.,* 1973; Kousoukos and Nancolas, 1981; Bartels *et al*1982; Andress Verges *et al.,* 1983; Thomas *et al.,* 1989; Inikori, 1991; Ajibola, 1995). This paper reports the synthesis of Ca-Sr HAP solid solutions and also investigates for the firs time the stability of solid solution formed at an elevated temperature of 773.5K in the a presence of DEA .

EXPERIMENTAL

Solid solutions of $Ca_{10-x} Sr_x (PO_4)_6 (OH)_2$ where the compositional parameter x runs from 0 to 10, were synthesized from aqueous media by method of Co-precipitation (Baud *et al.,*1973;Kousoukos and Nancolas,1981;Bartels *et al* ;Collins, 1959; Thomas *et al.,*1989). 0.30M orthophosphoric acid solution (350 ml) was added drop wise at a rate of one drop per second into a mixed boiling solution of $Ca(OH)_2$ and $Sr(NO_3)_2$. The mixture was constantly stirred while the addition lasted. The pH of the mediating solutions were maintained at 12 with ammonia solution. The mixed metal ions in solution were in such a way that the total concentration was exactly 0.50M (i.e in the Ca-Sr matal ion ratio of;1:5 to 5:1). Precipitates obtained were filtered, washed with cold water followed by acetone and dried at 105^0C for 1 hr. The dried samples were later heated in a furnace at 773.15K for about six hours. Solid solutions of

Ca_{10-x} Sr_x $(PO_4)_6$ $(OH)_2$ in the presence of DEA were also synthesized in the same way as described above, but 0.05M DEA solution was added to the mixed metal solution of $Ca(OH)_2$ and Sr $(NO_3)_2$. The precipitates were treated in the same way as the solid solutions free DEA.

X-ray Analysis

X-ray powder diffraction patterns of the precipitates were taken using a Philips powder diffractometer (MD-10). Nickel filtered Copper K_α radiation = 0.154nm was employed at room temperature in the 2θ range of 0 to $80^{0.}$

Chemical Analysis

The Calcium and strontium content were determined by atomic absorption spectroscopy while the content of phosphorous was obtained by colorimetric method (Sowerby and Emeleus, 1975; Bigi *et al.,* 1980; Inikori, 1991; Thomas *et al.,* 1989; Ajibola, 1995).

RESULTS

Table 1 shows the lattice parameters of calcium-strontium HAP solid solutions and calcium-strontium HAP solid solutions precipitated in the presence of DEA respectively and heated in each at 773.15K for six hour. The mole-atom ratios of metal to phosphorus of calcium-strontium HAP solid solutions precipitated in the presence of DEA and without DEA are shown in Table 2.

The variation of lattice constants with strontium substitution for calcium HAP solid solutions in the presence of DEA is shown in Figure 1. The plots of lattice constant against atom percent strontium for calcium-strontium HAP solid solutions in the presence of DEA are linear within the limits of experimental error as shown by equations of the lines in Figure 1 and in Figure 2 in the absence of DEA. The plots have been included to facilitate the visualization of the near linear variation and scatter of the points in both cases respectively.

Table 1. Lattice parameters (Å) of calcium-strontium HAP solid solutions in the range 0-100% strontium and after heating at 773.15K.

Sr content (Atom%)	**Without DEA**		**With DEA**	
	a(= b)	**C**	**a(= b)**	**C**
0	7.82	6.90	9.25	6.48
20	10.22	6.56	9.31	6.90
40	11.50	6.52	9.43	6.94
50	10.47	6.70	9.51	7.00
60	10.47	6.70	9.54	7.06
80	8.94	7.12	9.61	7.14
100	9.63	6.14	9.63	7.20

Table 3. Metal-Phosphorus ratios of Ca_{10}-x Srx $(PO4)_6$ in the range 0-100% strontium.

Sr content (Atom%)	$\frac{(Ca+Sr)}{P}$ **(Without DEA)**	$\frac{(Ca+Sr)}{P}$ **(With DEA)**	**Theoretical value**
0	1.69	1.63	1.67
20	1.82	1.65	1.67
40	1.80	1.65	1.67
50	2.00	1.69	1.67
60	2.20	1.62	1.67
80	1.50	1.6.2	1.67
100		1.69	1.67

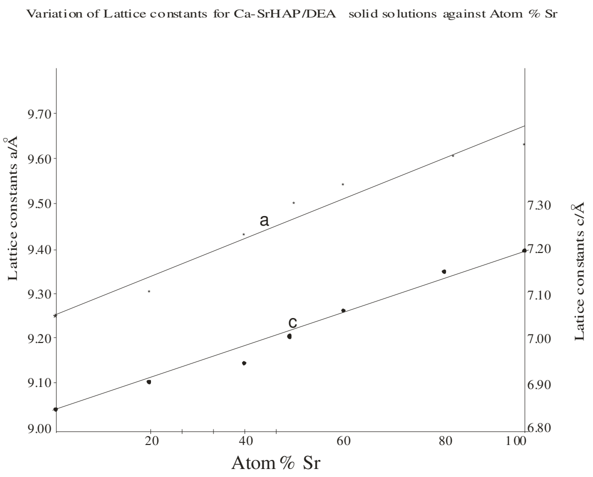

Figure1: Variation of Lattice constants for Ca-SrHAP/DEA solid solutions against Atom % Sr.
(a)$y = 9.25 + 0.005x$ $\delta = 0.05$; (c) $y = 6.82 + 0.004x$ $\delta = 0.0$

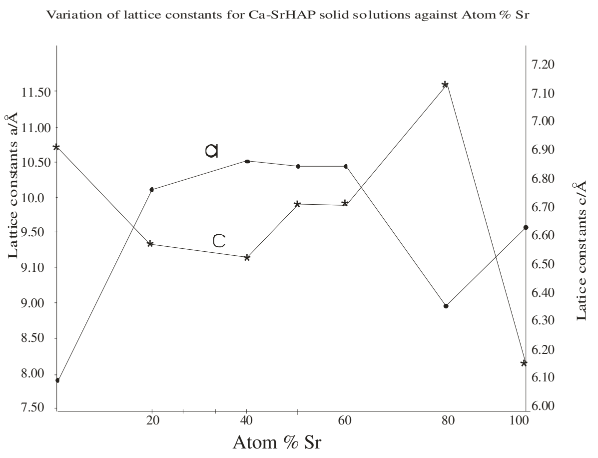

Figure 2: Variation of Lattice constants for Ca-SrHAP solid solutions against Atom % Sr**.**

DISCUSSION

X-ray powder diffraction studies

The X-ray powder patterns for the calcium-strontium HAP solid solutions synthesized in the presence of DEA and heated show that the samples contain single phases. This suggests that even at such elevated temperature the apatitic lattices remain intact and thus the apatite samples are stable. As mentioned earlier, this may not be unconnected with the presence of the DEA, which is believed to be responsible for the stability of the apatite samples at such temperature. Incorporation of the strontium in the HAP lattice produces a sharpening of the x-ray diffraction peaks and enhancement of peak. Peak sharpening and intensity enhancement suggest that there is an increase in crystallite size and a concomitant increase in crystallinity (Thomas *et al.,* 1989; Ajibola, 1995; Inikori, 1992). Lattice parameters of these samples increase with increased strontium substitution as shown in Table 2, which is consistent with the larger ionic radius of strontium (1.13Å). The increase in lattice constant is most evident on the c axis. Such a dilation with the proportion of strontium atom percent is in agreement with those reported elsewhere (Andrez-Vergess *et al.,* 1983; Collins,1959). The plot of the cell parameters a and c of this solid solutions against atom percent strontium (Figure 1) shows that the a and c axis vary linearly with increasing strontium incorporation which follows the Vegard's law (Kousoukos and Nancolas,1981;Andrez-Vergess *et al.,*1983 Thomas *et al.,* 1989; Ajibola,1995;Inikori,1992).

Such an effect could not be accounted for by surface adsorption and it has been suggested that strontium shows a preference for the six-fold position in the HAP lattice (Patel,1979;Bigi *et al.,*1980). It has also been reported that the proportionality between unit cell lattice parameters and the strontium concentration of precipitates obtained from the interaction between strontium ions and HAP suggests that solid solutions are formed during crystallization reactions rather than discrete calcium-strontium apatites (Baravelli, 1984).

The x-ray powder patterns obtained for calcium-strontium HAP samples heated show peak enhancement or broadening. This suggests that the samples contain mixed phases (more than one compound present). As earlier revealed this may not be unconnected with the fact that when heated lattices of the solid solutions are destroyed and the apatite becomes destabilized and transformed into other phosphates. The β -tricalciumphosphate and it derivatives are likely to predominate at such elevated temperature (Legeros, 1977). With the exception of the end members, the solid solutions in the entire range heated at 773.15K for six hours are thermally destabilized.

The mole - atom ratios

The values for the mole-atom ratios obtained from atomic absorption spectrometry and colorimetric analysis for calcium-strontium HAP synthesized in the presence of DEA and heated at 773.15K for six hours range from 1.62 –1.69 (Theoretical value = 1.67). The values observed are characteristics of apatitic solid solutions (Table 3). For calcium- strontium HAP samples (free from DEA) the values for mole-atom ratios cannot be reasonably related to the theoretical value of 1.67 for the apatitic solid solutions (Table 4). This suggests that the formation of phosphate groups other than apatites is favored at elevated temperatures.

CONCLUSION

It has been established that calcium-strontium HAP solid solutions synthesized in aqueous medium in the presence of DEA are stabilized when heated at 773.15K for six hours. The stability of the apatite at such elevated temperature is linked to the presence of the DEA molecule which improves the crystallinity of the apatite. This assertion is corroborated by the fact that calcium-strontium HAP solid solutions devoid of DEA when heated at 773.15K for six hours tend to disintegrate and undergo transformation into other phosphate groups (i.e. formation of mixed β – calcium phosphate and other phosphates are favored). These templated apatites may serve as important biomaterials for bone and teeth implants if further characterization are done on them.

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