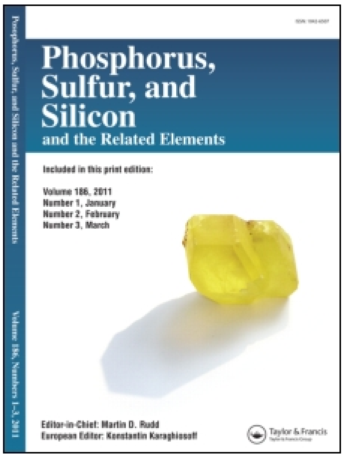

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SYNTHESIS OF CALCIUM-STRONTIUM PHOSPHATE FLUOR-HYDROXYAPATITES BY NEUTRALISATION

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SYNTHESIS OF CALCIUM-STRONTIUM PHOSPHATE FLUOR-HYDROXYAPATITES BY NEUTRALISATION

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In this work, the method of neutralisation was used for the first time for the preparation of calcium-strontium fluor-hydroxyapatites. Ca-Sr fluor-hydroxyapatites were prepared by neutralisation of a solution containing phosphoric acid and ammonium fluoride by an aqueous suspension of calcium oxide and strontian at room temperature. Apatites with various amounts of strontium and fluoride were prepared and characterized by X-ray diffraction. They had the general formula $Ca_{10-x}Sr_x(PO_4)_6(OH)_{2-y}F_y$ ($0 \leq x \leq 10$, $0 \leq y \leq 2$). The cell parameters and the crystal size were determined from X-ray diagrams. The apatites were better crystallized when the amount of strontium increased and no effect of fluorine ions on the crystal size was detected. After heating at 600°C, the cell parameters increased with the amount of strontium; raising the amount of fluoride decreased the "a" value and increase the "c" value. These results show that it is possible to prepare calcium-strontium fluor-hydroxyapatites at room temperature by an easy and non-polluting method.

Keywords: fluoride; strontium; apatite; synthesis; neutralization; heat treatment

INTRODUCTION

The term apatite refers to a family of mineral compounds the great majority of which crystallize in the hexagonal system with the space group $P6_3/m$. Their chemical formula is $M_{10}(XO_4)_6(Y)_2$. Studies concerning them are very numerous, not only from a fundamental point of view, their applications have also been widely investigated. The apatitic structure

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accepts many substitutions which can be total or partial. **M** can be a cation: monovalent (Na^+, etc.), divalent (Ca^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}, Ba^{2+}, etc.), trivalent (La^{3+}, Eu^{3+}, etc.) or a vacancy; $\mathbf{XO_4}$ can be a cationic group: monovalent (CO_3F^-, etc.), divalent (HPO_4^{2-}, CO_3^{2-}, etc.), trivalent (AsO_4^{3-}, PO_4^{3-}, etc.), or tetravalent (SiO_4^{4-}, etc.); **Y** can be a anion: monovalent (OH^-, F^-, Cl^-, Br^-, I^-, etc.), divalent (CO_3^{2-}, O^{2-}, S_2^{2-}, etc.) or a vacancy[1,2]. These substitutions confer on apatites various properties, in multiple fields and each one requires a specific method of preparation to be established. This has been the subject of many studies. Industrial development requires simple methods, easy to set up, with controlled cost and leading to products of quality corresponding to the desired applications.

One compound of the apatite family has been more particularly studied: it is calcium phosphate hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$. Indeed the chemical composition of this compound is very close to the mineral part of bones and teeth in vertebrate ones. It can also be a model compound for natural apatites which crystallized two billion years ago, during nuclear reactions. These apatites have, during all these years, confined radioactive elements [3,4]. The substitution of strontium for calcium in apatites presents a great interest in both the preparation of biomaterials and the storage of nuclear waste. Indeed, strontium is an element which plays a part in osseous mineralisation[5,6] and which is also occurs as radioactive waste[7,8]. The substitution of strontium ions for calcium ions within the structure of calcium phosphate hydroxyapatite can be partial or total. The methods of preparation described for these mixed Sr-Ca compounds involve solid-solid reactions at high temperature[9], double decomposition[10,11], hydrothermal[12] and hydraulic[13] cements, etc.

An industrial method of preparation of calcium phosphate hydroxyapatite consists of the neutralization of a suspension of lime by a phosphoric acid solution according to the following reaction[14]:

$$10\,CaO + 6\,H_3PO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 8\,H_2O$$

One of the great advantages of this process, in addition to being easy to carry out at room temperature, is the fact that the by-product of the reaction is water. It is thus non-polluting and its application has already been described[3] for calcium phosphate hydroxyapatites $Ca_{10}(PO_4)_6(OH)_2$, In this work, the process was adapted to study the possibility of synthesizing mixed apatites, in particular involving the substitution of strontium ions for calcium and fluoride ions for hydroxyl.

MATERIALS AND METHODS

The method of neutralization used was derived from the general method for the preparation of phosphocalcium apatite by partially or completely replacing calcium oxide CaO by anhydrous strontian $Sr(OH)_2$, and adding a measured quantity of fluoride ions to the reaction mixture. According to the proportion of strontium, calcium and fluoride ions, apatites with the following chemical formula were performed:

$$Ca_{10-x}Sr_x(PO_4)_6(OH)_{2-y}F_y \quad (0 \le x \le 10 \text{ and } 0 \le y \le 2)$$

First, CaO lime and anhydrous strontian $Sr(OH)_2$ were respectively prepared by heating calcium carbonate $CaCO_3$ to 900°C and hydrated strontian $Sr(OH)_2,8H_2O$ to 150°C. Various mixtures of CaO and $Sr(OH)_2$ were prepared (table I), corresponding to various Sr/(Ca+Sr) atomic ratios, while maintaining the total atomic ratio (Ca+Sr)/P equal to 1.67, i.e. that of a stoichiometric apatite.

TABLE I Composition of the various calcium strontium mixtures preparing

mixing	*1*	*2*	*3*	*4*	*5*
m_{CaCO3} (g)	10.059	8.047	5.030	2.012	0
$m_{Sr(OH)2,8H2O}$ (g)	0	5.369	13.423	21.476	26.845
$CaCO_3$ (wt %)	100.0	60.0	27.3	8.6	0
$Sr(OH)_2,8H_2O$ (wt %)	0	40.0	72.7	91.4	100.0
Sr/(Sr+Ca)	0	0.2	0.5	0.8	1.0

Synthesis of calcium-strontium hydroxyapatites

$$Ca_{10-x}Sr_x(PO_4)_6(OH)_2$$

Each of the five mixtures, described in table I, was introduced into a vessel containing 150 ml of water and magnetically stirred. Then, a solution (50 ml) prepared with 6.917 g of phosphoric acid H_3PO_4 and water was slowly introduced at room temperature. A precipitate was immediately formed. When the total quantity of the acidic solution has been added, the suspension was matured at room temperature for 2 hours.

Synthesis of calcium-strontium fluor-hydroxyapatites

$Ca_{10-x}Sr_x(PO_4)_6(OH)_{2-y}F_y$

Only apatites containing one fluoride ion and one hydroxide ion per cell (y = 1) were studied. Each mixture, described in table I, was introduced into a vessel containing 150 ml of water and 3.459 g of phosphoric acid under stirring. Then, a solution (50 ml) prepared with water, 3.459 g of phosphoric acid and 0.441 g of ammonium fluoride NH_4F was slowly introduced at room temperature.

Synthesis of calcium-strontium fluorapatites

$Ca_{10-x}Sr_x(PO_4)_6F_2$

The same protocol was used for the preparation of fluor-hydroxyapatites, but in this case the solution introduced into the vessel was prepared with 0.883 g of NH_4F.

For all preparations, after precipitation, the suspension was filtered and the solid washed with water. Finally, the solid was analyzed by X-ray diffraction (Inel C.P.S. 120). A part of the sample was progressively heated to 900°C and also characterized by X-ray diffraction. Alumina was used to precisely determine the position of the diffraction lines.

RESULTS AND DISCUSSION

All the X-ray diagrams of the solids precipitated and filtered at room temperature (see figures 1 and 2) show the presence of a single and pure apatitic phase. Its crystalinity increased with the strontium content (see figures 1 and 2). This increase of the crystallization state has already been detected for calcium-strontium hydroxyapatites using hydraulic cements[13]. For a fixed amount of strontium, the amount of fluoride ions does not seem to modify the crystallization state of the apatitic phase. The X-ray diagrams obtained, after several hours acquisition, enable us to determine the dimension of the crystallites using the formula of Scherrer (1918):

$$L_{hkl} = \frac{0,94 \times \lambda}{\sqrt{\Delta_{hkl}^2 - \Delta_0^2} \times \cos\theta}$$

0.94: Scherrer's constant,

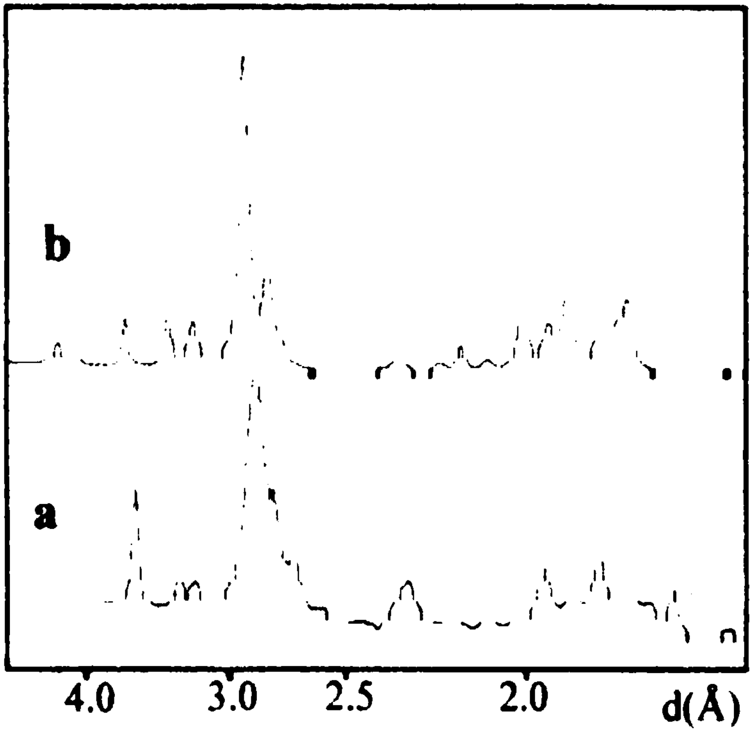

FIGURE 1 X-ray diagrams of (a) a $Ca_{10}(PO_4)_6(OH)_2$ hydroxyapatite and (b) a $Sr_{10}(PO_4)_6(OH)_2$ hydroxyapatite prepared at 20°C

L_{hkl}: apparent size in the direction perpendicular to the plane of the diffraction line (hkl),

λ: wavelength of the X-ray radiation,

θ: angle of diffraction of the hkl diffraction line (in radians), Δ_{hkl}: width at half height of the hkl difraction line,

Δ_0: width at half height of the same diffraction line for an ideally crystallised hydroxyapatite (the values of Δ_0 are 0.0012821 and 0.0014 for the diffraction lines 002 and 310 respectively).

The results of our measurements on the 002 and 310 diffraction lines are reported in table II. The crystallite size increased with the strontium content. This was observed in both hydroxyapatites and fluorapatites. The fluoridation of the hydroxyapatites does not seem to have any effect on the

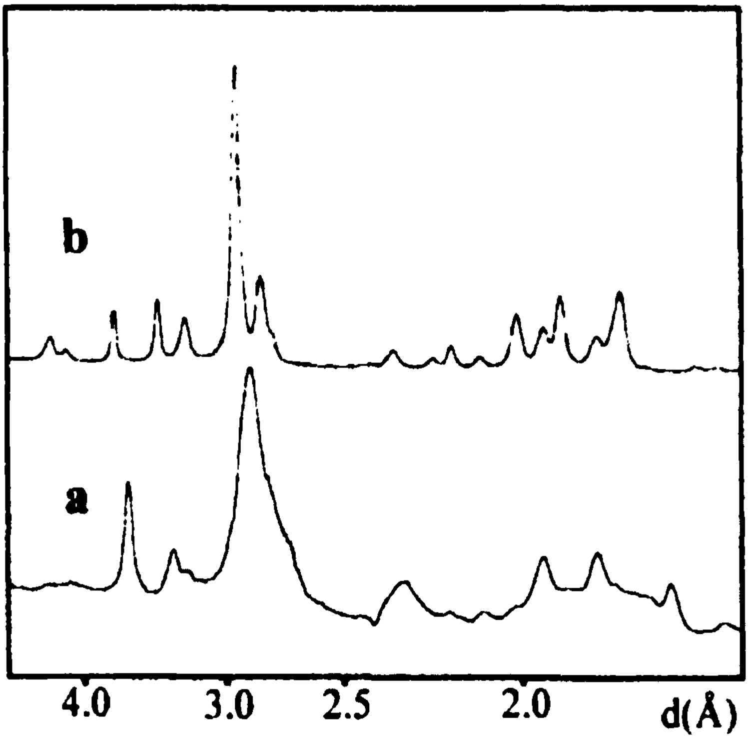

FIGURE 2 X-rays diagrams of (a) a $Ca_{10}(PO_4)_6F_2$ fluorapatite and (b) a $Sr_{10}(PO_4)_6F_2$ fluorapatite prepared at 20°C

crystallite size, a small reduction was observed with calcium apatites and an increase with strontium apatites.

TABLE II Crystallite sizes of various apatites (± 3 Å)

	L_{002}(Å)	L_{310}(Å)
$Ca_{10}(PO_4)_6(OH)_2$	234	67
$Sr_{10}(PO_4)_6(OH)_2$	261	128
$Ca_{10}(PO_4)_6F_2$	176	58
$Sr_{10}(PO_4)_6F_2$	303	140

After heating the apatites, the X-ray diagrams show a clear improvement of the crystallisation state (figure 3). The values of the lattice parameters "a" and "c" of the various apatites are presented in tables III, IV and V.

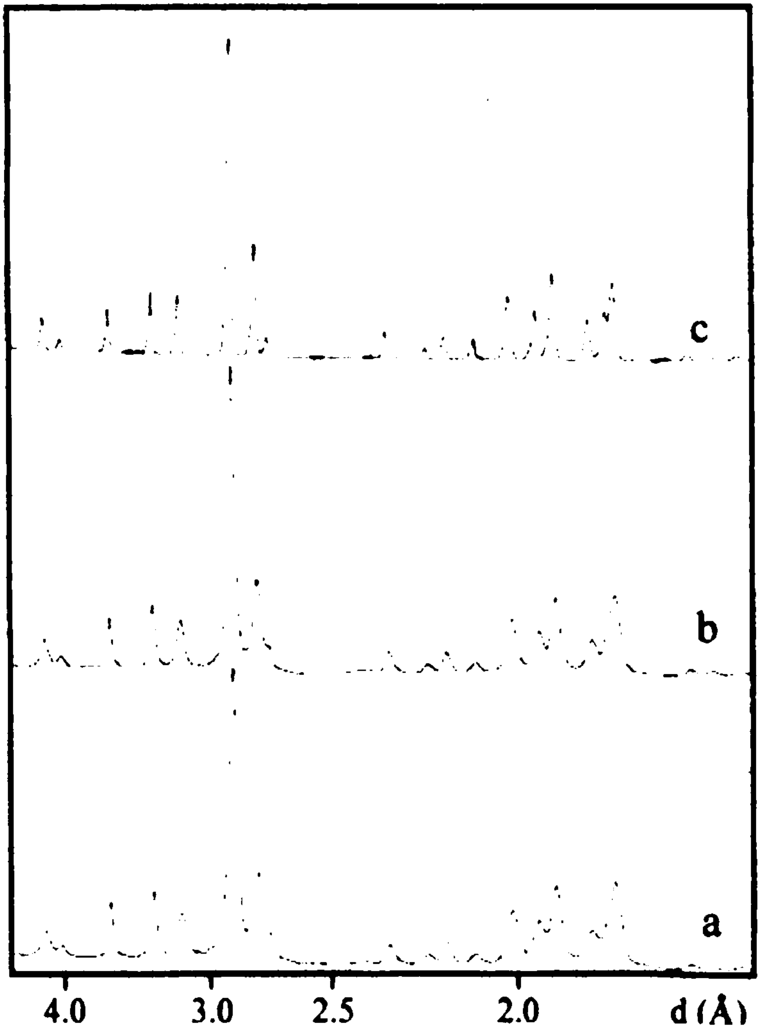

FIGURE 3 X-ray diagrams of a strontium fluorapatite $Sr_{10}(PO_4)_6F_2$ heated to various temperatures (a: 150, b: 600 and c: 900°C)

TABLE III Experimental and theoretical values of cell parameters "a" and "c" of the calcium-strontium hydroxyapatites (± 0.001 Å)

$Sr/(Sr+Ca)$	$a_{exp}(Å)$	$a_{th}(Å)$	$c_{exp}(Å)$	$c_{th}(Å)$
0	9.417	9.418	6.878	6.881
0.2	9.495	9.486	6.959	6.961
0.5	9.594	9.588	7.076	7.081
0.8	9.700	9.690	7.200	7.200
1.0	9.761	9.760	7.283	7.280

TABLE IV Experimental and theoretical values of cell parameters "a" and "c" of the calcium-strontium fluor-hydroxyapatites (± 0.001 Å)

$Sr/(Sr+Ca)$	$a_{exp}(Å)$	$a_{th}(Å)$	$c_{exp}(Å)$	$c_{th}(Å)$
0	9.393	9.393	6.880	6.883
0.2	9.472	9.461	6.973	6.962
0.5	9.570	9.563	7.114	7.081
0.8	9.673	9.666	7.212	7.201
1.0	9.723	9.734	7.302	7.280

TABLE V Experimental and theoretical values of cell parameters "a" and "c" of the calcium-strontium fluorapatites (± 0.001 Å)

$Sr/(Sr+Ca)$	$a_{exp}(Å)$	$a_{th}(Å)$	$c_{exp}(Å)$	$c_{th}(Å)$
0	9.369	9.367	6.881	6.884
0.2	9.434	9.436	6.966	6.963
0.5	9.544	9.539	7.083	7.082
0.8	9.639	9.641	7.200	7.201
1.0	9.712	9.710	7.283	7.280

An increase in the value of the crystallographic parameters $a_{exp}$and c_{exp} was observed each time the atomic ratio Sr/(Sr+Ca) increased. Moreover, the experimental values were close to the theoretical values. These observations can be allotted to a substitution of Ca^{2+} by Sr^{2+} and OH^- and F^-in the apatitic structure. The theoretical parameters were calculated starting from the following.

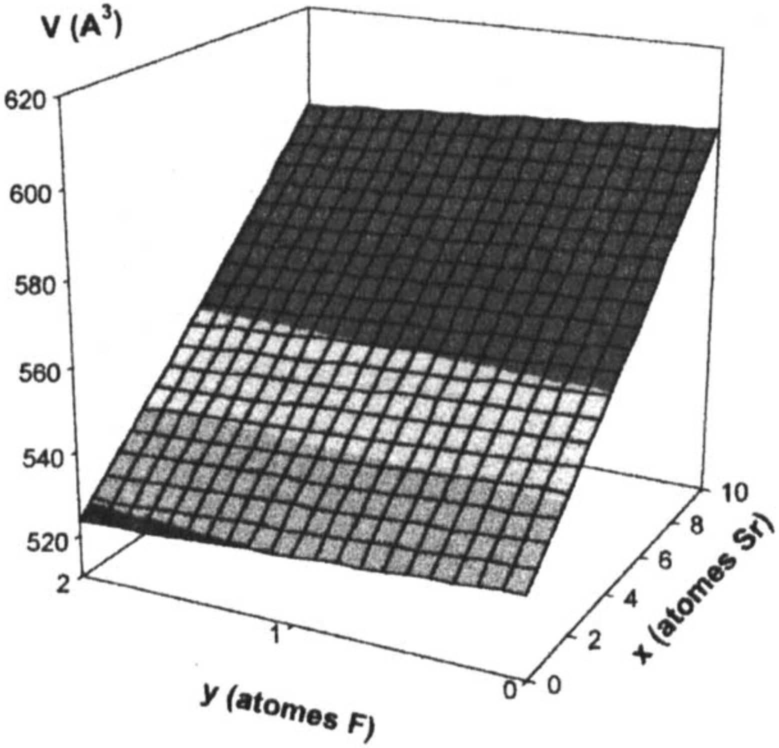

FIGURE 4 Variations of the volume of the apatitic cell vs the number of inserted flourine and strontium ions in the apatitic cell (See Color Plate at the back of this issue)

$$a\ (x,y) = 0.00015\ xy + 0.0340\ x - 0.0255\ y + 9.418 \qquad (1)$$

$$c\ (x,y) = -0.00015\ xy + 0.0015\ y + 0.0399\ x + 6.881 \qquad (2)$$

With × and y representing the number of fluorine and strontium atoms respectively that we want insert into the apatitic cell. The variations of volume V(x,y) (figure 4) and the c/a distortion (figure 5) of the apatitic cell can then be given by:

$$V(x,\ y) = (a\ (x,\ y))^2\ .\ c(x,\ y)\ .\ \sin 120°$$

$$\frac{c}{a} = \frac{-0.00015xy + 0.0399x + 0.0015y + 6.881}{0.00015xy + 0.0340x - 0.0255y + 9.418}$$

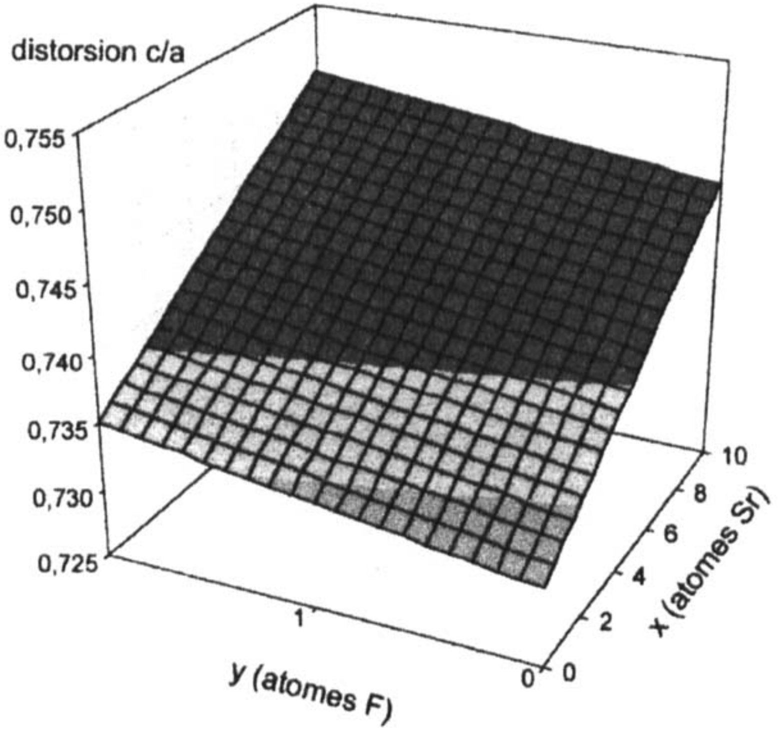

FIGURE 5 Variations of the distorsion c/a of the apatitic cell vs the number of inserted flourine and strontium ions in the apatitic cell (See Color Plate at the back of this issue)

The insertion of the strontium atoms in the lattice induces an increase of the cell parameters "a" and "c" and the correlated increase of the cell volume. On the other hand for a fixed strontium content, the cell volume decreases when the number of inserted fluoride atoms increases. Indeed, the insertion of fluorine in the cell of a calcium-strontium hydroxyapatite induces a diminution of these crystallographic parameters. In the same way, the variations of the cell parameters make it possible to explain the variations of the c/a ratio of the apatitic cell. It is possible to determine the number of fluorine and strontium atoms which enter in a calcium phosphorus hydroxyapatite starting from the values of these cell parameters. The values of x and y are given by the following relations:

$$x^2 + \alpha x + \beta = 0$$

with

$$\alpha = 125.12727 - 13.636364\ (a + c) \tag{3}$$

$$\beta = -17235.682 + 136.36364\ a + 2318.1818\ c \tag{4}$$

$$y^2 + \gamma\ y + \delta = 0$$

with

$$\gamma = 975.88889 - 41.666667\ (a + c) \tag{5}$$

$$\delta = -39395.611 + 11083.333\ a - 94444.4444\ c \tag{6}$$

The couples of values x and y which are solutions of these equations and pertaining to the field of solid-solution solid $0 \leq x \leq 10$ and $0 \leq y \leq 2$ are given by the following relations:

$$x = \frac{1}{2}\ (-\alpha - (\alpha^2 - 4\ \beta)^{1/2}) \tag{7}$$

$$y = \frac{1}{2}\ (-\gamma + (\gamma^2 - 4\ \delta)^{1/2}) \tag{8}$$

Conversely, it is possible to determine the content of strontium and fluorine of an apatite by knowing its crystallographic parameters. From the previous results and equations 7 and 8, it is thus possible to determine the chemical composition of a calcium-strontium fluor-hydroxyapatite by knowing the value of the crystallographic parameters.

This point was checked by preparing an apatite randomly chosen, measuring its crystallographic parameters and comparing the chemical composition calculated from equation 7 and 8 to the real composition. The apatite which was randomly chosen was an apatite with the chemical formula: $Ca_{8.5}Sr_{1.5}(PO_4)_6(OH)_{1.7}F_{0.3}$. It was prepared by the neutralisation route and heated at 900°C. Its crystallographic parameters, were a = 9.461 Å and c = 6.939 Å. Using the equations 7 and 8, the calculated x and y values were respectively 1.45 ± 0.03 and 0.24 ± 0.07 and agree with the initial formula.

CONCLUSIONS

The process of apatite synthesis by precipitation at room temperature is an easy method to implement and very little (or not) polluting. Calcium-strontium fluor-hydroxyapatites $Ca_{10-x}Sr_x(PO_4)_6(OH)_{2-y}F_y$ were synthesized with this process for × values in the range 0 to 10 and for y values in the range 0 to 2. The results deduced from the characterizations carried out on these apatites showed them to form solid solutions, over the whole range. The amount of strontium and fluorine ions can be calculated simply from the cell parameters "a" and "c" of the considered apatite. Reciprocally, an easy determination of the parameters "a" and "c" of a $Ca_{10-x}Sr_x(PO_4)_6(OH)_{2-y}F_y$ apatite is possible if the amounts of strontium and fluoride ions in the apatite are known. These very interesting preliminary results make it possible to consider the use of this method for the synthesis of many other mixed apatites.

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