Structural analysis and thermochemistry of "A" type phosphostrontium carbonate hydroxyapatites

Sonia Jebri · Habib Boughzala · Ali Bechrifa ·
Mohamed Jemal

Abstract "A" type phosphostrontium carbonate hydroxyapatites, having the general formula $Sr_{10}(PO_4)_6(OH)_{(2-2x)}$ $(CO_3)_x$ with $0 \leq x \leq 1$, were synthesised by solid gas reaction at high temperature. The samples were characterised by X-ray diffraction and infrared spectroscopy. Analysis of carbonate was achieved by coulometry and Rietveld refinement of the structure. Using an isoperibol calorimeter, the heat of solution of these products was measured at 298 K in 9 wt% nitric acid solution. Thermochemical cycle was proposed and complementary experiences were performed to reach the standard enthalpies of formation of these compounds. The results showed a decrease of the enthalpy of formation with the amount of carbonate introduced in the lattice, suggesting an increase of stability due to this kind of substitution.

Keywords Carbonate apatites · Isoperibol calorimeter · Heat of solution · Formation enthalpies

Introduction

Apatites are a large class of mineral compounds with the general formula $M_{10}(PO_4)_6X_2$, where M is generally a divalent cation and X can be a hydroxyl, carbonate or a halide. They crystallise in the hexagonal system space group $P6_3/m$ and form the major part of the sedimentary phosphate ores and of the mineral matter of the calcified tissues [1, 2]. Apatites have been used as catalysts, laser materials, gas sensors and ion conductors [3–6]. Their chemical composition and structural behaviour differ slightly from those of human hard tissues [7]. Consequently they can offer an excellent biocompatibility for bone and teeth implantations [8–10]. Physico-chemical properties of the apatites are modified and affected by a wide range of cationic and anionic substitutions [11–15]. Substitution of CO_3^{2-} to PO_4^{3-} or OH^- can occur in the apatite lattice, leading to a "B" or "A" type carbonate apatites, respectively [16, 17].

A bibliographic survey showed that no work had been interested in the themochemical study of "A" type phosphostrontium carbonate hydroxyapatites. This article deals with synthesis, characterisation and determination of the dissolution and formation enthalpies of these compounds.

Samples synthesis and characterization

Sample preparation

"A" type carbonate apatites were prepared in tow steps. The first one consists in synthesising phosphostrontium hydroxyapatite $Sr_{10}(PO_4)_6(OH)_2$ by double decomposition in an aqueous medium. Experiments consist in adding, drop by drop, during 3 h, a solution of diammonium hydrogen phosphate (0.2 M) into a boiling solution of strontium nitrate (0.2 M) [18]. The pH of precipitation has to be adjusted to about 11.5 by adding ammoniacal solution (28 wt%). The obtained precipitate was washed and dried

S. Jebri · A. Bechrifa (✉) · M. Jemal
Faculty of Science, Chemistry Department, Applied
Thermodynamic Laboratory,
Tunis El Manar University, Tunis 2092, Tunisia
e-mail: ali.bechrifa@fst.rnu.tn

H. Boughzala
Faculty of Science, Chemistry Department, Laboratory of
Crystallochemistry and materials, Tunis El Manar University,
Tunis 2092, Tunisia

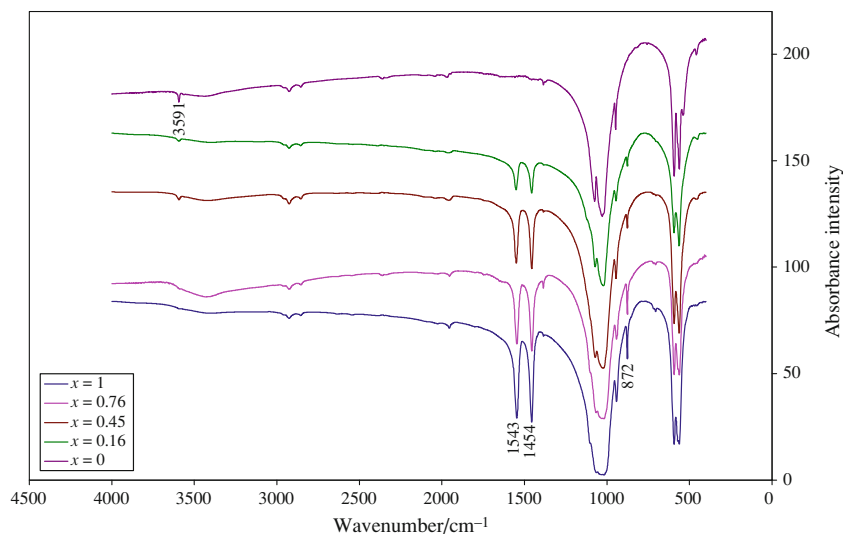**Fig. 1** Infrared spectrum of four samples of A-type CO_3^{2-} apatites compared to that of the hydroxyapatite

Table 1 Crystallographic data and refinement details

Data collection	Initial structural parameters	Profile and structure refinement
Radiation: Cu, λ ($K\alpha_1/\alpha_2$)	Mineral name: Belovite	Background: Chebychev
Temperature/K: 298(2)	Formula: $Sr_5(PO_4)_3(OH)$	Profile function: Pseudo-Voigt
2θ range/°: 5–110	Space group: $P6_3/m$	GOF: 3.5
Scan mode: θ–2θ	Cell parameters:	R_{exp}: 1.94
	$a = 9.745$; $c = 7.265$	
Step width/°: 0.016		R_{wp}: 6.78
Time per step/s: 1.0	$V = 597.49$	R_p: 4.99

**Fig. 2** Calculated (2θ range: 10–100°) and recorded (2θ range: 5–100°) X-ray diffraction pattern and their difference
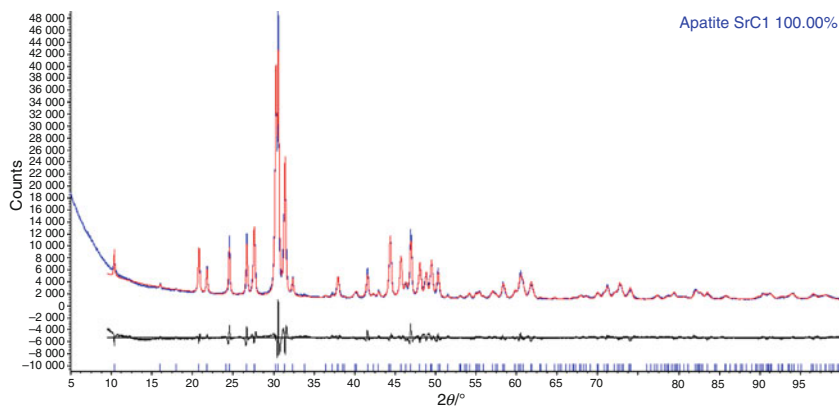
overnight at 70 °C, then ignited at 800 °C for 24 h under wet Argon atmosphere. The synthesis can be schematized by the following reaction:

$$10Sr(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH$$
$$\rightarrow Sr_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O$$
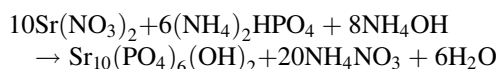
The purity and crystallinity of the obtained samples were checked by X-ray diffraction and IR spectroscopy.

The second step of the synthesis consists in heating the strontium hydroxyapatite in CO_2 gas flow. Various amounts of carbonate were introduced in the lattice by varying both the time of gas flowing (half hour to 6 days) and the temperature of synthesis (700 to 1000 °C). Carbonatation occurred according to the following reaction:

$$Sr_{10}(PO_4)_6(OH)_2(sd) + x\, CO_2(g)$$
$$\rightarrow Sr_{10}(PO_4)_6(OH)_{2(1-x)}(CO_3)_x(sd) + xH_2O\ (g)$$
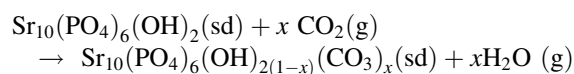
The reagents were Merck and Fluka products used for analysis (over 99% of purity).

Characterisation and control

Control of purity of the synthesised products was achieved by X-ray diffraction and infrared spectroscopy. Determination of carbonate amount was performed by coulometry and Rietveld refinement of the structure.

Rietveld analytical results of the products having the carbonate compositions: 0.55, 0.56, 0.76 and 0.84 were compared to the coulometry results, the later are: 0.59, 0.69, 0.74 and 0.76, respectively. A convergence was observed for some products.

Table 2 Carbonate content, lattice parameters and volume of pure and substituted hydroxyapatites

x	$a/\text{Å}$	$c/\text{Å}$	$V/\text{Å}^3$
0	9.745(1)	7.265(1)	597.5(3)
0.16	9.772(1)	7.288(1)	602.7(4)
0.35	9.7943(4)	7.2759(3)	604.5(1)
0.45	9.816(1)	7.2658(7)	606.32(2)
0.47	9.8271(7)	7.2630(5)	607.4(1)
0.49	9.819(4)	7.2713(3)	607.2(1)
0.51	9.8074(6)	7.2734(5)	605.8(1)
0.55	9.861(1)	7.2502(9)	610.62(2)
0.56	9.845(2)	7.2501(1)	608.6(2)
0.58	9.8334(5)	7.2680(4)	608.6(1)
0.61	9.833(2)	7.256(1)	607.4(2)
0.63	9.868(2)	7.2461(9)	611.1(2)
0.66	9.850(1)	7.2528(8)	609.5(2)
0.76	9.877(1)	7.2463(8)	612.2(2)
0.84	9.883(1)	7.2435(8)	612.8(2)
1	9.872(2)	7.2626(2)	612.9(5)
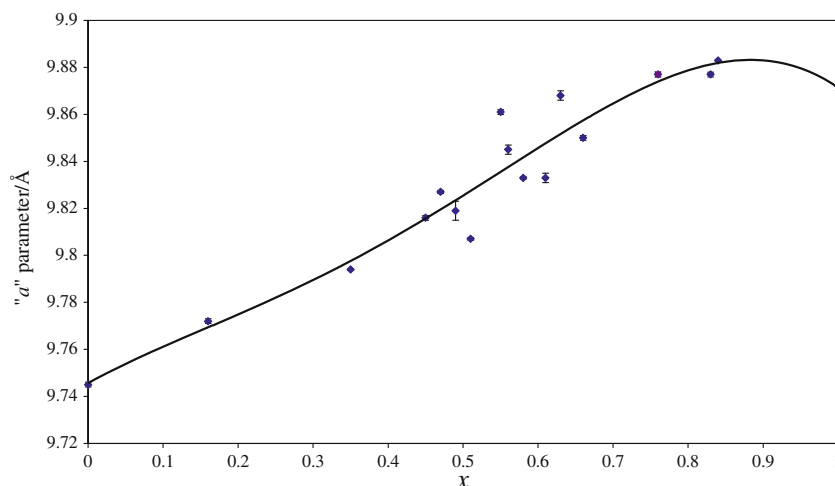
IR spectroscopy

Infrared experiments were performed on pellets obtained by mixing 1.5 mg of the product in 300 mg of KBr for IR spectroscopy. The spectra were recorded between 400 and 4000 cm^{-1} using a Perkin-Elmer 7700 FT-IR spectrometer. They showed absorption bands of "A" type carbonate apatites and the absence of impurities which may exist in the solid such as HPO_4^{2-} (1180–1200 cm^{-1}) and $P_2O_7^{4-}$ (1200–1250 cm^{-1}). As shown previously [16], infrared bands characterising carbonate groups substituting hydroxyl ions in the tunnels appear at 1543, 1454 and 872 cm^{-1}. The superimposing of spectra in Fig. 1 showed that the intensity of these bands increase with the amount of carbonate introduced in the lattice, while the one corresponding to hydroxyl (3591 cm^{-1}) decreases until disappearance.

X-ray diffraction

Powder X-ray diffraction was carried out with D8 ADVANCE Bruker diffractometer using copper radiations. The Rietveld refinement of the diffraction profile and the crystal structure using the atomic coordinates suggested by the ICSD data base (record No. 2855) allow quantifying the carbonate substituting the hydroxyl in the apatitic cell. The refinement of the analysed samples was realised using TOPAS program [19]. The unit cell parameters, the grain size, the atomic coordinates as well as the occupancy rates of the hydroxyl site and the carbon were refined taking into account the oxygen of the carbonate group.

Moreover, to avoid divergence, some constraints were applied respecting the electrical neutrality and crystallographic site multiplicities. Fixed at a common value of 1.5, no thermal displacement parameter was refined. Convergence was reached after few cycles with suitable final agreement factors.

Fig. 3 Variation of the "a" crystallographic parameter versus x

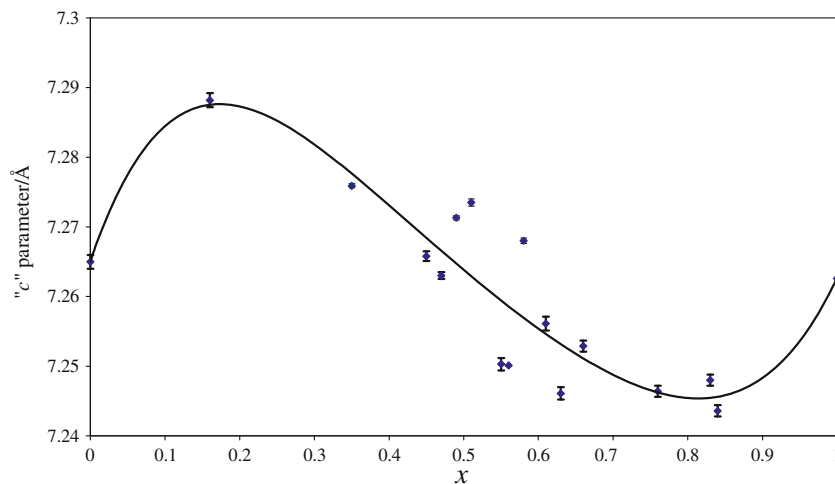**Fig. 4** Variation of the "c" crystallographic parameter versus x

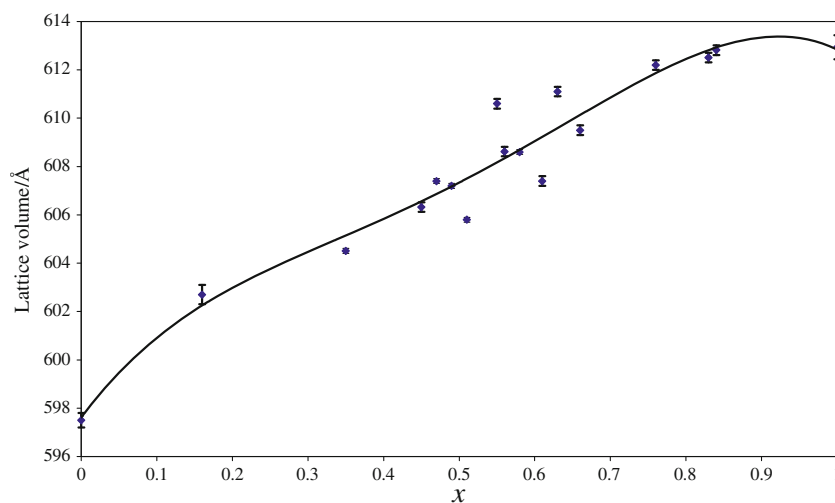**Fig. 5** Variation of the lattice volume of the apatites over the carbonate content

Table 1 summarises the data collection, the initial structural parameters, the profile and the structure refinement details. The best agreement between the observed and the calculated profiles and the differential curve of a treated product having 0.56 mol of carbonate ions per unit cell is presented by Fig. 2.

Table 2 and Figs. 3, 4 show the variation of the lattice parameters versus the rate of carbonate substitution x. One can notice an increase in "a" parameter and a slight variation of "c" parameter with the introduction of carbonate ions in the tunnels. This results in an increase in the volume of the lattice as shown in Fig. 5.

Thermochemical study

Calorimetric technique

Heat amounts were determined using an isoperibol calorimeter. The device was previously described in detail [20,

21]. The heat effect produced in the calorimetric cell was manifested by the variation of the temperature of the reaction medium which was detected by a thermistance probe acting as one of the four branches of a Wheatstone bridge. The balance voltage was amplified by a Keithley multimeter then recorded over time.

The solid to be dissolved or the liquid to be diluted was carefully introduced in a thin-walled glass bulb which was manufactured at one of the extremities of a Pyrex tube (5 mm diameter). Experiment started by searching a quasi-steady state in which the electrical current was practically null and the baseline deviated slightly from the vertical line. The reaction was started by breaking the bulb using a

Table 3 Molar enthalpies of KCl and $Sr_3(PO_4)_2$, respectively, in water and HNO_3 9 wt% at 298 K

Product	Present work	Literature
KCl	17.57 ± 0.11 kJ mol^{-1}	17.54 ± 0.01 kJ mol^{-1} [26]
$Sr_3(PO_4)_2$	-102.40 ± 0.65 kJ mol^{-1}	-101.1 ± 1.5 kJ mol^{-1} [27]

Table 4 Standard enthalpy of solution of the compounds in (HNO_3; $35.35H_2O$) and the corresponding error 'ε'

Chemical formula	m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J	$-\Delta_{sol}H$/kJ mol^{-1}
$Sr_{10}(PO_4)_6(OH)_2$	40.3	32.5	10.40	0.08	380.33 ± 3.35
	107.7	86.0	27.53	0.21	385.4 ± 3.4 [28]
	81.5	62.0	19.85	0.15	
	170.5	134.0	43.54	0.33	
	208.9	176.0	56.35	0.43	
	137.4	112.5	36.02	0.27	
$Sr_{10}(PO_4)_6(OH)_{1.68}(CO_3)_{0.16}$	115.7	90.5	28.98	0.22	382.06 ± 2.64
	124.7	98.5	31.53	0.24	
	134.5	102.5	32.82	0.25	
	75.0	59.0	18.89	0.14	
	110.4	88.5	28.33	0.22	
	91.0	73.0	23.37	0.18	
	64.8	51.5	16.45	0.13	
$Sr_{10}(PO_4)_6(OH)_{1.30}(CO_3)_{0.35}$	121.3	97.0	31.06	0.24	384.14 ± 2.68
	134.1	103.5	33.14	0.25	
	160.6	128.5	41.14	0.31	
	67.3	54.0	17.29	0.13	
	89.1	73.0	23.37	0.27	
	105.4	87.0	27.86	0.21	
	146.0	113.0	36.28	0.28	
$Sr_{10}(PO_4)_6(OH)_{1.10}(CO_3)_{0.45}$	88.6	72.5	23.21	0.18	387.75 ± 2.71
	138.0	113.0	36.18	0.28	
	115.9	92.5	29.61	0.23	
	145.1	115.5	36.98	0.28	
	77.7	62.5	20.01	0.15	
	128.7	104.0	33.30	0.25	
	100.7	80.0	25.61	0.19	
$Sr_{10}(PO_4)_6(OH)_{1.06}(CO_3)_{0.47}$	133.0	106.0	33.94	0.25	388.27 ± 3.08
	110.7	87.0	27.86	0.21	
	96.1	76.0	24.33	0.19	
	70.1	55.0	17.61	0.13	
	125.6	110.0	35.22	0.27	
	82.7	67.0	21.45	0.16	
$Sr_{10}(PO_4)_6(OH)_{1.02}(CO_3)_{0.49}$	127.6	101.0	32.34	0.25	390.12 ± 2.44
	70.1	57.5	18.41	0.14	
	103.9	82.0	26.25	0.20	
	86.0	69.5	22.25	0.17	
	117.2	95.0	30.42	0.23	
	39.3	31.0	09.93	0.07	
	144.3	115.0	36.82	0.28	
	50.4	41.5	13.29	0.10	
$Sr_{10}(PO_4)_6(OH)_{0.98}(CO_3)_{0.51}$	102.1	84.0	26.89	0.20	390.29 ± 2.73
	127.9	105.5	33.78	0.26	
	110.4	88.5	28.34	0.22	
	91.0	73.0	23.37	0.18	
	64.8	53.5	17.13	0.13	
	143.3	116.5	37.30	0.28	
	81.2	64.0	20.49	0.16	

Table 4 continued

Chemical formula	m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J	$-\Delta_{sol}H$/kJ mol^{-1}
$Sr_{10}(PO_4)_6(OH)_{0.88}(CO_3)_{0.56}$	68.4	56.5	18.09	0.14	391.35 ± 2.73
	99.9	79.5	25.45	0.19	
	81.1	66.0	21.13	0.16	
	90.1	73.5	23.53	0.18	
	111.7	92.5	29.62	0.23	
	119.8	96.5	30.90	0.24	
	139.2	110.0	35.22	0.27	
$Sr_{10}(PO_4)_6(OH)_{0.84}(CO_3)_{0.58}$	113.1	90.0	28.82	0.22	392.06 ± 2.45
	130.7	103.0	32.98	0.25	
	151.7	119.5	38.26	0.29	
	120.0	96.5	30.90	0.24	
	89.8	73.5	23.53	0.18	
	98.6	79.0	25.29	0.19	
	67.1	57.0	18.25	0.14	
	139.0	111.5	35.70	0.27	
$Sr_{10}(PO_4)_6(OH)_{0.78}(CO_3)_{0.61}$	77.6	64.0	20.53	0.16	393.67 ± 2.51
	117.2	95.5	30.63	0.23	
	56.7	47.0	15.07	0.11	
	91.7	75.0	24.06	0.18	
	146.5	120.0	38.49	0.29	
	126.5	104.0	33.36	0.25	
	68.4	56.0	17.96	0.14	
	40.2	34.5	11.07	0.08	
$Sr_{10}(PO_4)_6(OH)_{0.74}(CO_3)_{0.63}$	42.0	35.0	11.23	0.08	394.67 ± 2.52
	143.8	119.0	38.17	0.29	
	65.8	55.0	17.64	0.13	
	115.1	95.5	30.63	0.23	
	159.8	134.5	43.14	0.33	
	79.1	66.0	21.17	0.16	
	127.2	103.0	33.04	0.25	
	93.5	75.5	24.22	0.18	
$Sr_{10}(PO_4)_6(OH)_{0.68}(CO_3)_{0.66}$	65.1	54.5	17.48	0.13	397.67 ± 2.54
	101.1	85.0	27.26	0.21	
	84.5	71.0	22.77	0.17	
	129.1	108.0	34.64	0.26	
	171.6	142.5	45.71	0.35	
	70.2	57.5	18.44	0.14	
	146.1	122.0	39.13	0.30	
	141.4	117.0	37.53	0.29	
$Sr_{10}(PO_4)_6(OH)_{0.48}(CO_3)_{0.76}$	76.7	64.5	20.69	0.16	404.22 ± 2.50
	162.3	136.0	43.62	0.33	
	124.7	102.5	32.88	0.25	
	63.3	51.0	16.36	0.12	
	94.2	78.5	25.18	0.19	
	139.7	117.0	37.53	0.29	
	69.7	58.0	18.60	0.14	
	36.6	32.0	10.26	0.08	
	114.5	102.0	32.72	0.25	

Table 4 continued

Chemical formula	m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J	$-\Delta_{sol}H$/kJ mol^{-1}
$Sr_{10}(PO_4)_6(OH)_{0.32}(CO_3)_{0.84}$	150.1	128.0	41.06	0.31	409.35 ± 2.61
	131.2	110.5	35.44	0.27	
	64.0	56.5	17.61	0.14	
	89.4	78.0	25.02	0.19	
	183.7	154.0	49.39	0.38	
	72.5	64.0	20.53	0.16	
	115.5	97.5	31.27	0.24	
	48.1	40.5	12.99	0.10	
$Sr_{10}(PO_4)_6(CO_3)_1$	127.5	106.0	34.00	0.26	422.23 ± 2.82
	159.7	133.5	42.82	0.33	
	97.9	81.0	25.98	0.20	
	115.4	94.5	30.31	0.23	
	65.2	56.5	18.12	0.14	
	130.3	110.5	35.44	0.27	
	84.1	69.5	22.29	0.17	

Fig. 6 Standard enthalpy of solution at 298 K of A-type carbonate apatites versus the rate of CO_3^{2-} ion per unit cell
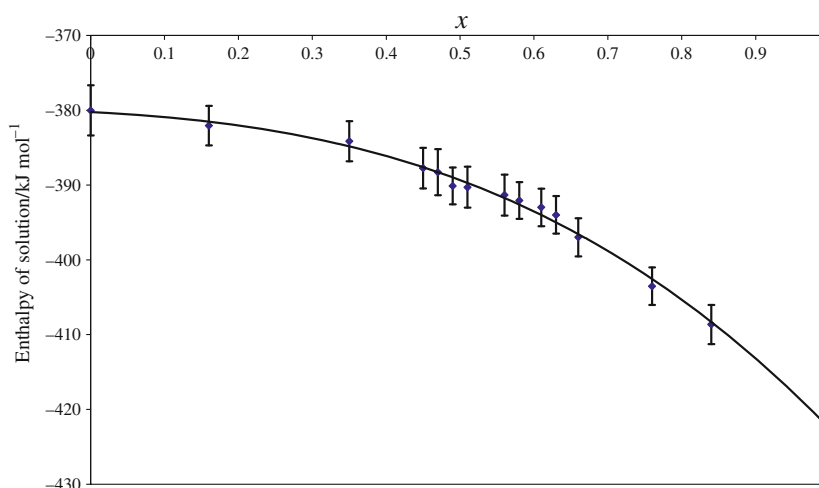
thin glass baton and the heat effect dissipated in the medium results in a deviation of the signal, which then became parallel to the previous baseline. The shift between the base lines is proportional to the corresponding heat effect. Chemical calibration was carried out by dissolving various amounts of the trihydroxymethyl aminonomethane $(HOCH_2)_3CNH_2$ or "THAM" in 350 mL of 0.1 mol kg^{-1} hydrochloric aqueous solution. The energy (E_i) corresponding to each amount (m_i) was calculated taking into account the mass of the solid and the key value for the standard enthalpy of dissolution of THAM ($\Delta H_m°(T_0) = -29.74$ kJ mol^{-1}) [22]. The energy released, E, was plotted versus the shift d (mm) recorded between the two base lines. Statistical treatment [23] showed that the energy can be expressed as: $E = A \cdot d$, where the mean calibration coefficient is:

$$A = \frac{\sum d_i E_i}{\sum d_i^2} = 0.3202 \pm 0.0024 \, \text{J mm}^{-1}$$

The reliability of the device was tested by measuring the solution enthalpies of potassium chloride (KCl) in water and tristronsium phosphate $Sr_3(PO_4)_2$ in nitric acid solution 9 wt% at 25 °C. Various amounts of these products were dissolved in the corresponding solvent under stirring and the molar dissolution enthalpies were determined according a mathematical treatment in which the statistical weight (ω_i) of an experimental result depends on the corresponding variance. This procedure led to express the dissolution enthalpy as:

$$\Delta_{sol}H = \frac{\sum \omega_i \Delta H_{mes} m_i}{\sum \omega_i m_i^2}$$

where ω_i is the reciprocal of the variance and ΔH_{mes} the energy resulting from dissolving m_i (mg). This calculation is detailed in Refs. [24, 25]. However, ω_i can be taken as equal the reciprocal of the square of the error since the later is proportional to the square root of the variance. Table 3 gathers the deduced molar enthalpy of each product. These quantities are in good agreement with values found in literature. This agreement showed that the calorific capacity of the solvent and the calorimeter accessories are close for the calibration and reliability experiments. This is not surprising because the solvents are water or diluted aqueous solution.

Enthalpy of solution

Dissolution of the apatites, at 25 °C, were carried out in 350 cm^3 of nitric acid solution 9 wt% (HNO_3; $35.35H_2O$) in which CO_2 gas was continuously bubbled to avoid the retention of CO_2 produced by the reaction. Table 4 gathers the mass of product (mg), the corresponding shift "d", the measured enthalpies and the error on these measurements which can be expressed as: $\varepsilon_i = 0.0024d_i$ (J). The right column of the table reports the molar dissolution enthalpy which is compared to literature value for hydroxyapatite [28]. Figure 6 shows the variation of the standard enthalpy of dissolution of the studied compounds versus the rate of CO_3^{2-} ion per unit cell.

Table 5 Mass, 'd' shift, enthalpy of dissolution and the corresponding error 'ε' of $SrCO_3$ in HNO_3 9 wt% at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
67.6	31.0	9.93	0.07
103.0	42.0	13.45	0.10
146.9	56.0	17.93	0.14
193.4	67.5	21.61	0.16
245.1	85.0	27.23	0.21

$\Delta_{sol}H_m = -17.99 \pm 0.17$ kJ mol^{-1}

Table 6 Mass, 'd' shift, enthalpy of dissolution and the corresponding error 'ε' of $Sr(OH)_2$ in HNO_3 9 wt% at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
30.2	67.5	21.61	0.16
16.9	37.0	11.85	0.09
45.9	109.0	34.90	0.27
51.9	120.5	38.58	0.29
60.9	140.5	44.99	0.34
27.1	59.0	18.89	0.14
38.6	85.5	27.38	0.21

$\Delta_{sol}H_m = -87.86 \pm 0.62$ kJ mol^{-1}

Enthalpy of formation

Direct measurement of the standard formation enthalpy of such compounds is impossible. However, it is possible to reach this quantity by considering a thermochemical cycle involving a succession of steps, the final balance of which

Table 7 Mass, 'd' shift, enthalpy of dissolution and the corresponding error 'ε' of $Sr_3(PO_4)_2$ in HNO_3 9 wt% at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
142.3	99.0	31.70	0.24
65.9	48.0	15.37	0.12
115.5	81.5	26.10	0.20
226.6	151.5	48.51	0.37
131.7	92.5	29.62	0.23
159.7	113.0	36.18	0.28
179.0	130.5	41.78	0.32
96.4	68.5	21.93	0.17

$\Delta_{sol}H_m = -102.22 \pm 0.65$ kJ mol^{-1}

Table 8 Standard enthalpies of solution and formation of entities involved in the complementary reactions

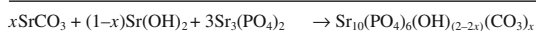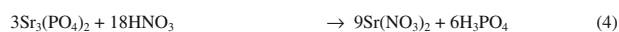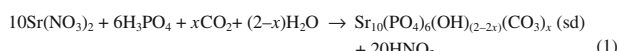|	$\Delta_{sol}H_m°$(298 K)/ kJ mol^{-1}	Ref	$\Delta_f H_m°$(298 K)/ kJmol^{-1}	Ref
$SrCO_3$	-17.99 ± 0.17	a	-1220.1	[29]
$Sr(OH)_2$	-87.86 ± 0.62	a	-959.0	[29]
$Sr_3(PO_4)_2$	-102.22 ± 0.65	a	-4110	[27]

[a] Present work

Table 9 Standard enthalpies of formation at 298 K calculated according to the proposed cycle

Chemical formula	$-\Delta_f H_m$/kJ mol^{-1}
$Sr_{10}(PO_4)_6(OH)_2$	13,303
$Sr_{10}(PO_4)_6(OH)_{1.68}(CO_3)_{0.16}$	13,332
$Sr_{10}(PO_4)_6(OH)_{1.30}(CO_3)_{0.35}$	13,366
$Sr_{10}(PO_4)_6(OH)_{1.10}(CO_3)_{0.45}$	13,382
$Sr_{10}(PO_4)_6(OH)_{1.06}(CO_3)_{0.47}$	13,385
$Sr_{10}(PO_4)_6(OH)_{1.02}(CO_3)_{0.49}$	13,387
$Sr_{10}(PO_4)_6(OH)_{0.98}(CO_3)_{0.51}$	13,391
$Sr_{10}(PO_4)_6(OH)_{0.88}(CO_3)_{0.56}$	13,399
$Sr_{10}(PO_4)_6(OH)_{0.84}(CO_3)_{0.58}$	13,402
$Sr_{10}(PO_4)_6(OH)_{0.78}(CO_3)_{0.61}$	13,407
$Sr_{10}(PO_4)_6(OH)_{0.74}(CO_3)_{0.63}$	13,410
$Sr_{10}(PO_4)_6(OH)_{0.68}(CO_3)_{0.66}$	13,413
$Sr_{10}(PO_4)_6(OH)_{0.48}(CO_3)_{0.76}$	13,425
$Sr_{10}(PO_4)_6(OH)_{0.32}(CO_3)_{0.84}$	13,435
$Sr_{10}(PO_4)_6(CO_3)_1$	13,452
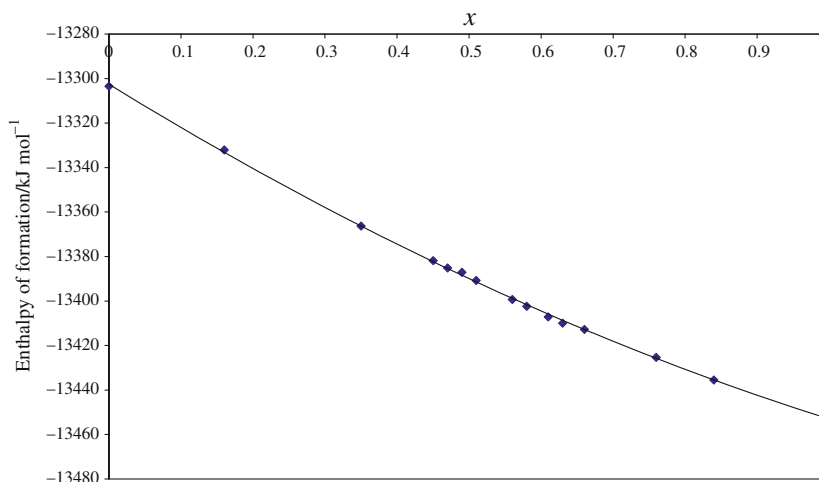
represents the formation reaction of the particular product. Let $Sr_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$ the general formula of the apatites, the thermochemical cycle proposed is represented by the following sequence of steps:

$$10Sr(NO_3)_2 + 6H_3PO_4 + xCO_2 + (2-x)H_2O \rightarrow Sr_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x \text{ (sd)} + 20HNO_3 \quad (1)$$

$$x[SrCO_3 + 2HNO_3 \rightarrow Sr(NO_3)_2 + CO_2 + H_2O] \quad (2)$$

$$(1-x)[Sr(OH)_2 + 2HNO_3 \rightarrow Sr(NO_3)_2 + 2H_2O] \quad (3)$$

$$3Sr_3(PO_4)_2 + 18HNO_3 \rightarrow 9Sr(NO_3)_2 + 6H_3PO_4 \quad (4)$$

$$xSrCO_3 + (1-x)Sr(OH)_2 + 3Sr_3(PO_4)_2 \rightarrow Sr_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$$

In addition to the dissolution reaction of the apatite in nitric acid already mentioned (step 1), this scheme involves processes of dissolution of strontium carbonate, strontium hydroxide and tristrontium phosphate (steps 2, 3, 4). Their corresponding enthalpies were measured according to the experimental procedure previously described. The results are shown in Tables 5, 6 and 7. Table 8 gathers both the dissolution and formation enthalpies of these products.

The combination of measurements with those of the literature led to the enthalpy of formation. Table 9 indicates the values of the enthalpies of formation calculated according to the proposed cycle. One can notice a decrease in the enthalpy of formation when the amount of carbonate increases (Fig. 7). The uncertainties on these values can not been determined because the literature values are given without any error.

Discussion and conclusions

The variation of the standard enthalpy of dissolution of the studied apatites as a function of CO_3^{2-} ratio showed that the higher the carbonate amount the lower the energy released by the acid dissolution. Introduction of carbonate in the lattice seems to strengthen the crystal edifice.

Moreover, the formation enthalpy decreased with the quantity of carbonate, so it can be deduced that this kind of substitution seemed to increase the stability of the apatite. This seems to be correlated with the creation of vacancies induced in the hydroxyl site.

Finally, these results are in agreement with those of the thermal decomposition of these compounds. TG experiments performed on these products showed that the higher the carbonate content, the higher the decomposition temperature. Structural study will provide more information about the effect of such substitution on the stability of these compounds.

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