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Standard enthalpies of formation of “A” type carbonate phosphobaryum hydroxyapatites

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Abstract Phosphobaryum carbonate hydroxyapatites $Ba_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$ with $0 \leq x \leq 1$, were synthesized in this study by solid gas reaction at a high temperature. Carbonate content was determined by thermogravimetric analysis and X-ray diffraction. The heat of the solution in a 3 wt% nitric acid solution was measured at 298 K using an isoperibol calorimeter. The combination of the enthalpies of solution with the enthalpies of formation of the reactants allowed us to determine the standard enthalpies of formation of the studied apatites. The result showed a decrease in formation enthalpy with the carbonate amount introduced in the lattice, suggesting an increase in stability of these compounds as the ratio of the substitution increases.

Keywords Carbonate apatites · Heat of solution · Enthalpy of formation

Introduction

Apatites crystallizing in $P6_{3/m}$ are inorganic compounds with a general formula $M_{10}(XO_4)_6Y_2$, where M is mostly a divalent cation (Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+}, Pd^{2+}, etc.), XO_4 is a trivalent or tetravalent anion ($PO_4{}^{3-}$, $VO_4{}^{3-}$, $AsO_4{}^{3-}$, $SiO_4{}^{4-}$, etc.), and Y is a monovalent or bivalent anion (F^-, Cl^-, Br^-, OH^-, $CO_3{}^{2-}$). Their crystalline structures can accommodate a great variety of other substitutions and vacancies both in anionic and cationic sites which make these materials as highly effective ion exchange matrixes [1]. Carbonate apatites are the main mineral components of human and animal hard tissues (bones and teeth) [2–4]. It has been established that the carbonate ion can be accommodated either in hydroxyl position or as a substituent for the phosphate group; consequently, the carbonate apatites are respectively known as “A” and “B” type ones [5, 6]. Such substitutions have a strong influence on physico-chemical properties of the apatites. Many studies have been reported on synthesis, structure determination, on one hand, the dissolution behaviour and the thermal stability on the other hand [7–11].

This article deals with the elaboration and characterisation of “A” type phosphobaryum carbonate hydroxyapatites $Ba_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$. Calorimetric study has been performed to determine the formation enthalpy of these compounds. The latter quantity is associated to the formation entropy to give the Gibbs energy. However, for such kind of compounds the enthalpy factor is much more important, and so, comparison of their stability can be made on the basis of their formation enthalpy [12].

Synthesis

“A” type phosphobaryum carbonate apatites were prepared in two steps. The first one consists in synthesizing phosphobaryum hydroxyapatite by solid-state reaction at a high temperature [13]. A stoichiometric mixture of $Ba_3(PO_4)_2$ and $BaCO_3$ was finely crushed in acetone and heated for 12 h at 1000 °C under pure Argon atmosphere, then ignited at 1100 °C for 2 h under wet Argon atmosphere ($P_{H_2O} = 0.47 \cdot 10^5$ Pa). The synthesis was achieved by thermal ignition at 900 °C in wet atmosphere over a week with several crushing operations in acetone to avoid the

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formation of hydroxyl deficient apatites. The synthesis can be schematized by the following reaction:

$$Ba_3(PO_4)_{2(sd)}+Ba(CO_3)_{(sd)}+H_2O_{(g)} \rightarrow Ba_{10}(PO_4)_6(OH)_{2(sd)}+CO_{2(g)}$$

The second step consists in heating baryum hydroxyapatite in CO_2 gas flow as it was described in a previous study [11]. Various amounts of carbonate were introduced into the lattice by varying both the duration of gas flowing (from half an hour to six days) and the temperature of synthesis (from 700 to 1000 °C). Carbonation occurred according to the following reaction:

$$Ba_{10}(PO_4)_6(OH)_{2(sd)}+xCO_{2(g)} \rightarrow Ba_{10}(PO_4)_6(OH)_{2(1-x)}(CO_3)_{x(sd)}+xH_2O_{(g)}$$

The reagents used are of analytical quality (over 99.9% of purity) manufactured by Merck, Fluka and Air Liquide.

Characterisation

Purity and crystallinity of the various products are checked by infrared spectroscopy and X-ray diffraction.

IR spectroscopy

Infrared spectra were recorded using a Perkin-Elmer 7700 FT-IR spectrometer between 400 and 4000 cm^{-1} in KBr pellets. They exhibit the characteristic absorbance bands of carbonate groups substituting hydroxyl ions in the tunnel, which appear at 874, 1433 and 1514 cm^{-1}, suggesting the formation of "A" type carbonate apatite [5].

Superposition of spectrum of apatites having the compositions 0.290, 0.744 and 1 mol of carbonate per unit cell is given in Fig. 1, which shows that the higher the

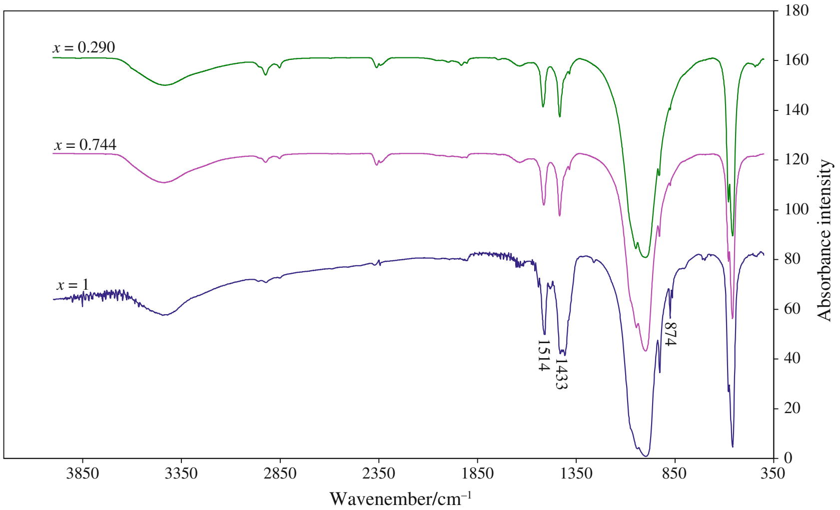

Fig. 1 Infrared spectrum of A-type CO_3^{2-} phosphobaryum hydroxyapatites

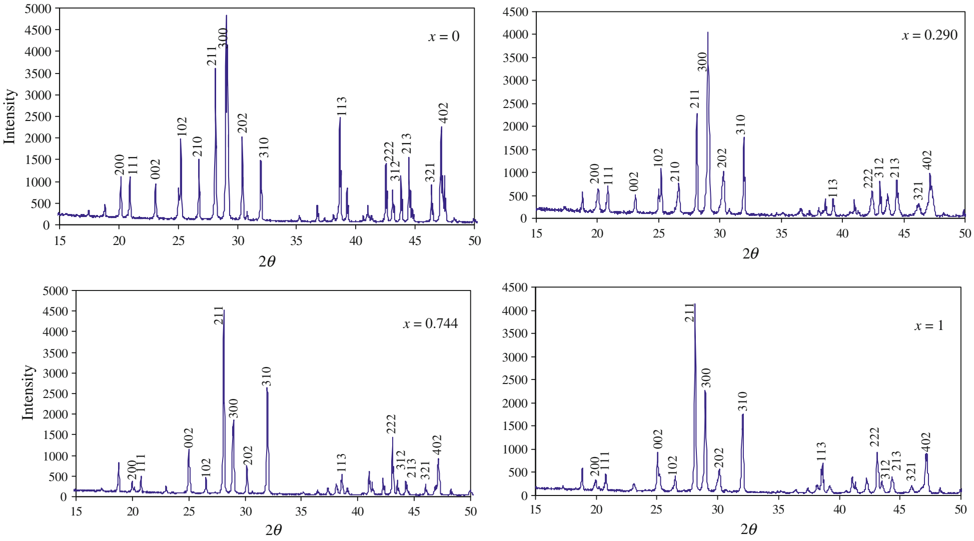

Fig. 2 X-ray diffraction patterns of "A" type carbonate phosphobaryum apatites with $x = 0.297$, 0.739, 1 and 0 (hydroxyapatite)

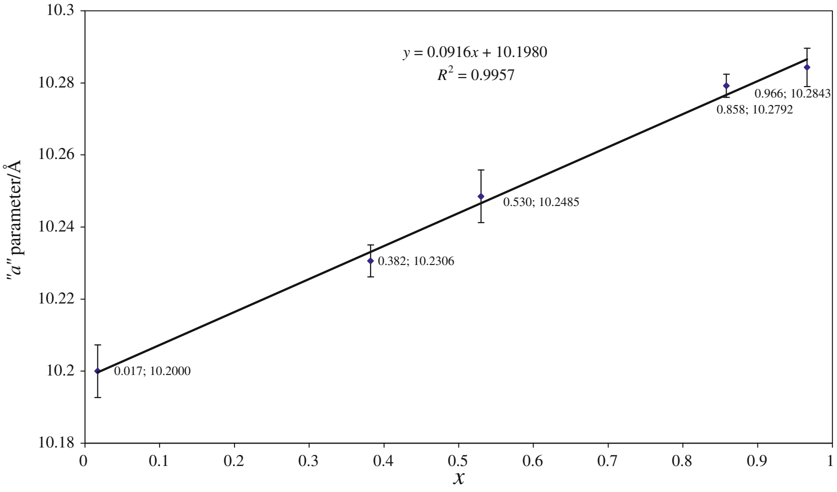

Fig. 3 Calibration curve showing the variation of “a” parameter versus x

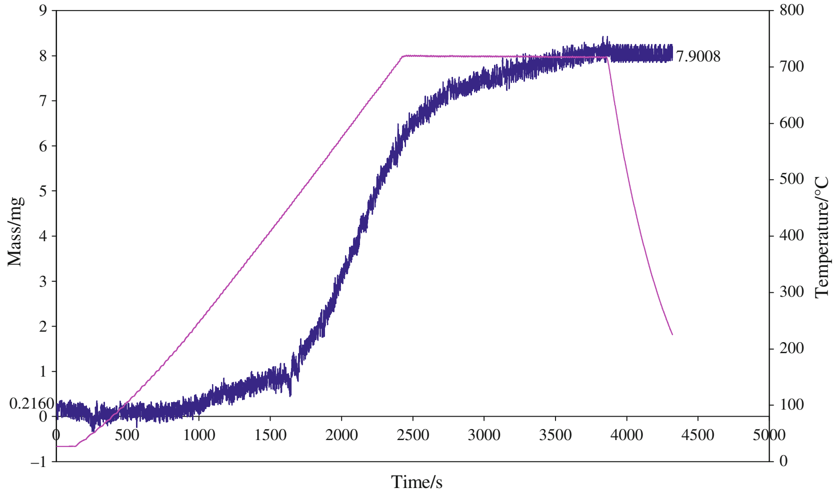

Fig. 4 Thermogravimetric curve carbonation of 604.745 mg of $Ba_{10}(PO_4)_6(OH)_2$

carbonate content, the higher the corresponding bands' intensity.

X-ray diffraction

X-ray diffraction patterns have been obtained from powdered samples with a D8 ADVANCE Bruker diffractometer using copper radiations ($K\alpha_1 = 1.5406$ Å; $K\alpha_2 = 1.5445$ Å). Figure 2 shows well-crystallized phases of substituted apatites and non-substituted hydroxyapatite. The lattice constants of the structure were refined by the cell parameter program “ERACEL”.

Measurement of carbonate content in apatites

Carbonate amounts have been determined using a calibration curve. Samples of compositions $x = 0.017$, 0.382, 0.530, 0.858 and 0.966 have been obtained by recording thermogravimetrically the weight variation of pure hydroxyapatite, under CO_2 flow. The correlation of the a values determined by X-ray diffraction, with the carbonate content, shows a linear variation allowing us to determine the CO_3^{2-} content of the samples prepared for calorimetric experiments. The

Table 1 Lattice parameters and the corresponding carbonate amount x

a/Å	c/Å	x	V/Å^3
10.1971(15)	7.7209(13)	−0.010(90)	695.337
10.2079(36)	7.7051(21)	0.107(84)	695.545
10.2149(37)	7.7048(22)	0.184(81)	696.559
10.2247(37)	7.7082(20)	0.290(78)	697.877
10.2436(23)	7.7077(14)	0.497(75)	701.786
10.2663(44)	7.7356(23)	0.744(77)	706.084
10.2761(28)	7.7185(18)	0.851(79)	705.867
10.2807(44)	7.7014(26)	0.902(81)	704.927
10.2942(38)	7.7246(24)	1.049(87)	708.915

Table 2 Standard enthalpies of solution at 298 K of "A" type carbonate phosphobaryum hydroxyapatites in 3 wt% HNO_3 and the corresponding error 'ε'

Chemical formula	m/mg	d/mm	$-\Delta H_i$/J	ε_i/J	$-\Delta_{sol}H$/kJ/mol
$Ba_{10}(PO_4)_6(OH)_2$	88.6	48.5	15.53	0.34	347.29 ± 7.11
	105.2	57.5	18.41	0.35	
	79.0	44.5	14.25	0.34	
	168.6	90.5	28.98	0.39	
	58.7	34.0	10.89	0.33	
	74.6	44.5	14.25	0.34	
	169.2	93.5	29.94	0.39	
	177.0	95.0	30.42	0.39	
$Ba_{10}(PO_4)_6(OH)_{1.786}(CO_3)_{0.107}$	151.5	81.0	25.93	0.38	327.11 ± 7.61
	125.1	66.5	21.29	0.36	
	93.7	48.5	15.53	0.34	
	75.6	40.0	12.81	0.33	
	173.0	88.5	28.34	0.39	
	226.4	113.0	36.18	0.42	
$Ba_{10}(PO_4)_6(OH)_{1.632}(CO_3)_{0.184}$	125.6	58.5	18.73	0.35	317.49 ± 5.68
	98.4	43.5	13.93	0.38	
	184.5	93.5	29.94	0.39	
	140.2	63.5	20.33	0.35	
	170.1	88.0	28.18	0.38	
	158.3	77.5	24.81	0.37	
	192.0	103.5	33.14	0.41	
	161.3	85.5	27.38	0.38	
$Ba_{10}(PO_4)_6(OH)_{1.420}(CO_3)_{0.290}$	155.8	73.5	23.53	0.37	308.87 ± 5.27
	174.0	86.0	27.54	0.38	
	165.2	81.5	26.10	0.38	
	185.8	87.0	27.86	0.38	
	195.2	97.0	31.06	0.40	
	234.2	115.0	36.82	0.42	
	105.4	50.0	16.01	0.34	
	134.6	66.0	21.13	0.36	
$Ba_{10}(PO_4)_6(OH)_{1.006}(CO_3)_{0.497}$	209.5	96.5	30.90	0.40	294.07 ± 4.62
	183.7	83.5	26.74	0.38	
	251.6	117.5	37.62	0.43	
	240.6	112.0	35.86	0.42	
	222.0	103.0	32.98	0.41	
	117.9	54.5	17.45	0.35	
	193.4	88.5	28.34	0.38	
	184.0	84.0	26.90	0.38	
$Ba_{10}(PO_4)_6(OH)_{0.512}(CO_3)_{0.744}$	118.1	52.0	16.65	0.13	288.84 ± 5.62
	189.5	87.5	28.02	0.21	
	209.9	95.5	30.58	0.23	
	80.7	36.5	11.69	0.09	
	180.4	81.5	26.10	0.20	
	197.8	87.5	28.02	0.16	
	131.2	60.0	19.21	0.21	
	96.8	43.5	13.93	0.11	
$Ba_{10}(PO_4)_6(OH)_{0.298}(CO_3)_{0.851}$	77.8	36.0	11.52	0.33	295.71 ± 4.23
	103.7	60.5	19.37	0.35	

Table 2 continued

Chemical formula	*m*/mg	*d*/mm	$-\Delta H_i$/J	ε_i/J	$-\Delta_{sol}H$/kJ/mol
	151.4	72.0	22.57	0.36	
	216.7	106.5	32.34	0.39	
	241.2	115.0	35.86	0.41	
	258.5	127.0	38.42	0.42	
	206.8	102.0	30.74	0.38	
	80.0	38.0	11.53	0.31	
	99.4	49.0	14.41	0.31	
	122.9	60.0	17.61	0.32	
	165.6	83.0	24.33	0.35	
$Ba_{10}(PO_4)_6(OH)_{0.196}(CO_3)_{0.902}$	115.6	56.5	18.09	0.35	295.85 ± 5.39
	138.5	68.5	21.93	0.36	
	170.5	78.5	25.13	0.37	
	106.3	52.5	16.81	0.34	
	185.4	84.5	27.06	0.38	
	210.5	92.0	29.46	0.39	
	154.4	77.0	24.65	0.37	
	127.8	54.5	17.45	0.35	
	87.4	36.0	11.53	0.33	
$Ba_{10}(PO_4)_6(CO_3)_1$	125.4	61.5	19.69	0.35	298.83 ± 6.30
	85.7	41.5	13.29	0.33	
	119.8	55.5	17.77	0.35	
	162.9	74.0	23.69	0.36	
	177.0	80.5	25.77	0.37	
	99.3	48.0	15.37	0.34	
	75.0	38.5	12.33	0.33	
	202.5	92.0	29.46	0.39	

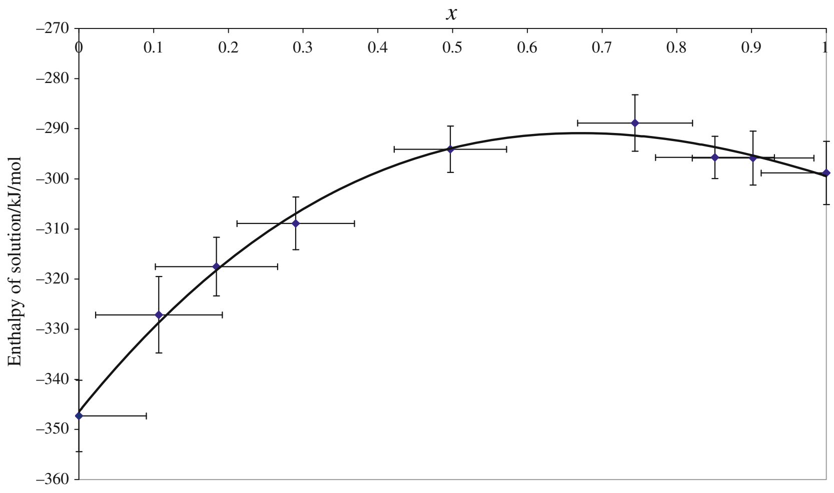

Fig. 5 Standard enthalpies of solution at 298 K of “A” type carbonate phosphobaryum hydroxyapatites versus the rate of CO_3^{2-} ions per unit cell

calibration curve, Fig. 3, leads to $a = 10.1980$ Å for $x = 0$. Experimental *a* parameter for hydroxyapatite is $a = 10.1971(15)$ Å which is very close to the literature value (10.190(3) Å [13]). The calibration curve equation has been determined by the least square method. Figure 4 gives an example of TG curve recorded on 604.745 mg of hydroxyapatite heated in CO_2 gas flow after 12 h of purging time. The amount of carbonate determined from the thermogram is $x = 0.966$. This value differs from that determined by considering the difference of weight before and after the treatment

Table 3 Mass, *d* shift, enthalpy of dissolution and the corresponding error 'ε' for $BaCO_3$ in 3 wt% HNO_3 at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
64.1	29.0	9.28	0.33
183.3	48.5	15.53	0.34
230.2	62.0	19.85	0.35
335.0	72.0	23.05	0.36
151.2	40.0	12.81	0.33

$\Delta_{sol}H = -15.57 \pm 0.58$ kJ/mol

Table 4 Mass, *d* shift, enthalpy of dissolution and the corresponding error 'ε' for $Ba(OH)_2$ in 3 wt% HNO_3 at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
93.5	40.5	12.97	0.33
177.1	72.0	23.05	0.36
245.9	106.0	33.94	0.41
127.7	54.0	17.29	0.35
211.0	85.5	27.37	0.38
319.5	122.5	39.22	0.44
270.5	110.5	35.38	0.42

$\Delta_{sol}H = -41.12 \pm 0.76$ kJ/mol

Table 5 Mass, *d* shift, enthalpy of dissolution and the corresponding error 'ε' for $Ba_3(PO_4)_2$ in 3 wt% HNO_3 at 298 K

m/mg	d/mm	$-\Delta H_{mes}$/J	ε/J
93.5	41.5	13.29	0.33
167.6	72.0	23.05	0.36
198.2	83.0	26.58	0.38
74.2	34.0	10.89	0.33

$\Delta_{sol}H = -82.67 \pm 3.46$ kJ/mol

Table 6 Standard enthalpies of solution and enthalpies of formation of solids involved in complementary reactions

	$\Delta_{sol}H°$ (298 K)/kJ/mol	Ref	$\Delta_f H°$ (298 K)/kJ/mol	Ref
$BaCO_3$	-15.57 ± 0.58	[a]	-1213.0	22
$Ba(OH)_2$	-41.12 ± 0.76	[a]	-944.7	22
$Ba_3(PO_4)_2$	-82.67 ± 3.46	[a]	-4120	18

[a] Present work

by 3.2%. For the other experiments, this difference is around 2.8%. The X-ray diffraction patterns of the treated powders show thin and intense peaks suggesting a good homogeneity of the samples.

Table 1 gives the lattice parameters of the samples together with the volume and the corresponding carbonate amount per unit cell. The error on *x* was determined taking into account the dispersion of experimental values around the calibration line, using a statistical treatment developed by Linnig and Mandel [14]. The slight increase in the volume of unit cell with the carbonate ratio (1.3%) did not allow us to determine accurately the mixing volume because of the error on the lattice parameters and *x*.

Table 7 Standard enthalpies of formation at 298 K of "A" type phosphobaryum carbonate hydroxyapatites

Chemical formula	$-\Delta_f H$/kJ/mol
$Ba_{10}(PO_4)_6(OH)_2$	13246
$Ba_{10}(PO_4)_6(OH)_{1.786}(CO_3)_{0.107}$	13295
$Ba_{10}(PO_4)_6(OH)_{1.632}(CO_3)_{0.184}$	13323
$Ba_{10}(PO_4)_6(OH)_{1.420}(CO_3)_{0.290}$	13357
$Ba_{10}(PO_4)_6(OH)_{1.006}(CO_3)_{0.497}$	13421
$Ba_{10}(PO_4)_6(OH)_{0.512}(CO_3)_{0.744}$	13484
$Ba_{10}(PO_4)_6(OH)_{0.298}(CO_3)_{0.851}$	13503
$Ba_{10}(PO_4)_6(OH)_{0.196}(CO_3)_{0.902}$	13514
$Ba_{10}(PO_4)_6(CO_3)_1$	13538

Thermochemical study

Calorimetry

The calorimeter used is an isoperibol one. It has been previously described in detail [10, 11, 15]. The energy released or absorbed during the dissolution induces a variation of the temperature of the reactional medium, which is measured by means of a thermistance connected to a Wheatstone bridge and recorded versus time.

Chemical calibration of the device was carried out by a standard reaction [11]. Experiments consist in dissolving various amounts of trihydroxymethyl aminomethane $(HOCH_2)_3CNH_2$ or "THAM" in 350 mL of 0.1 mol kg^{-1} hydrochloric aqueous solution. The calibration coefficient ($C = 0.3202 \pm 0.0024$ J mm^{-1}) was determined through the proportionality between *d* shift recorded between the base lines of the thermogram and the energy amount calculated by considering the standard molar enthalpy of that reaction as -29.74 kJ mol^{-1} [16].

The reliability of the calorimeter was checked by dissolving potassium chloride KCl in water and tribaryum phosphate $Ba_3(PO_4)_2$ in a 3 wt% nitric acid solution at 298 K. The resulting molar dissolution enthalpies of these products are 17.57 ± 0.11 and -82.67 ± 3.46 kJ mol^{-1}. These values are in good agreement with the literature data: (17.584 ± 0.017 kJ mol^{-1}) [17] and (-84.8 ± 2.1 kJ mol^{-1}) [18], respectively.

Enthalpy of solution

A 3 wt% nitric acid solution was used as a solvent for the carbonate phosphoapatites. Measurement of the solution enthalpies was carried out in the 350 cm^3 of acid solution in which CO_2 gas was continuously bubbled to avoid the retention of CO_2 produced by the reaction. Different quantities of the apatites were dissolved under stirring, and the molar dissolution enthalpies were determined according to a mathematical treatment in which the statistical weight (ω_i) of an experimental result depends on the corresponding variance. This procedure leads to derive the dissolution enthalpy as

$$\Delta_{\mathrm{sol}}\mathrm{H} = \frac{\sum \omega_i \cdot \Delta\mathrm{H}_i m_i}{\sum \omega_i \cdot m_i^2} = A(\mathrm{J\,g^{-1}}) \qquad (1)$$

where (ω_i) is the reciprocal of the variance of ΔH_i ($\omega_i = 1/\sigma_{\Delta H_i}{}^2$), and ΔH_i is the energy resulting from dissolving m_i (mg). This calculation is detailed in references [19, 20]. However, (ω_i) can be taken as equal to the reciprocal of the square of the error, since the latter is proportional to the square root of the variance. Application of this formula has been preceded by a statistical treatment on the results obtained with the same device, which has shown that the intercept of the line giving ΔH_i as a function of m_i is statistically negligible.

According to Eq. 1, the more precise the ΔH_i measurement, the less important the statistical weight in calculation of $\Delta_{\mathrm{sol}}H$. This procedure leads to a lower error on $\Delta_{\mathrm{sol}}H$ than the error on the mean value of $\Delta_{\mathrm{sol}}H$ calculated from simple division of ΔH_i by m_i.

ΔH_i was calculated by the product $\Delta H_i = C{\cdot}d_i$ where C is the calibration coefficient. According to Guedens et al. [21], $\Delta(\Delta H_i)$ or ε_i can be calculated through the following relationship:

$$\left[\frac{\Delta(\varepsilon_i)}{\Delta H_i}\right]^2 = \left[\frac{\Delta C}{C}\right]^2 + \left[\frac{\Delta d}{d}\right]^2 \qquad (2)$$

in which $(\Delta C/C) = 7.5.10^{-3}$ and $\Delta d = 1$ mm. The results are reported in Table 2. $\Delta_{\mathrm{sol}}H$ is the proportionality factor between the energy released and the weight m ($y_i = A{\cdot}m_i$), and so the propagation of error leads to

$$\sigma^2(A) = \sum_i \left(\frac{\partial A}{\partial m_i}\right)^2 \sigma^2(m_i) + \sum_i \left(\frac{\partial A}{\partial y_i}\right)^2 \sigma^2(y_i) \qquad (3)$$

Neglecting the error on (m_i) and taking into account the A expression, Eq. 1, one can derive the variance on A, $\sigma^2(A)$, as:

$$\sigma^2(A) = \frac{1}{\sum_i m_i^2/\sigma^2(y_i)} \qquad (4)$$

$\sigma^2(y_i)$ represents the dispersion of y_i values around the mean value $\bar{y}_i$. This supposes several measurement of y_i (or ΔH_i) for the same value of mass m_i. In the present case, if we consider y_i value, reported in Table 2, as the mean of two values differing from $\bar{y}_i$ by ε_i, then this leads to $\sigma^2(y_i) = 2\varepsilon_i^2$ and allows us to calculate $\sigma^2(A)$ for each series of measurements. The error on A factor was calculated by the product $\Delta A = t{\cdot}\sigma(A)$ where t is the student factor for (N-1) degrees of freedom, and N is the number of dissolution experiments of each apatite compound. Molar enthalpies of solution are gathered in the right column of Table 2, and variation of this quantity over x is reported in Fig. 5 together with the error segments.

Enthalpy of formation

The direct measurement of the standard enthalpy of formation of these products is impossible. However, this

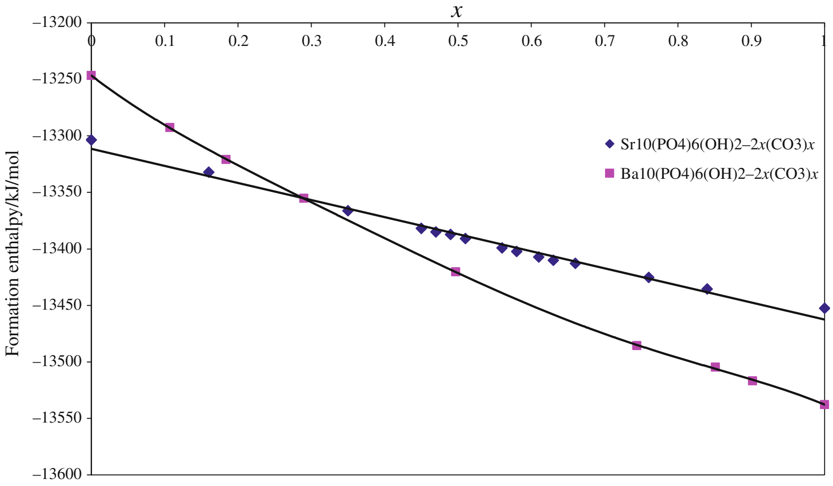

Fig. 6 Comparative results of the standard formation enthalpy evolution of “A” type carbonate phosphobaryum and phosphostrontium apatites solid solutions versus x

quantity can be calculated through a thermochemical cycle involving a succession of steps, for which the "sum" corresponds to the enthalpy of formation of the compounds. For this kind of apatites, the following sequence of processes can be considered:

$$10Ba(NO_3)_2 + 6H_3PO_4 + xCO_{2\,(g)} + (2\text{-}x)H_2O \rightarrow Ba_{10}(PO_4)_6(OH)_{(2\text{-}2x)}(CO_3)_{x\,(sd)} + 20HNO_3 \quad (1)$$

$$x[BaCO_{3\,(sd)} + 2HNO_3 \rightarrow Ba(NO_3)_2 + CO_{2\,(g)} + H_2O] \quad (2)$$

$$(1\text{-}x)[Ba(OH)_{2\,(sd)} + 2HNO_3 \rightarrow Ba(NO_3)_2 + 2H_2O] \quad (3)$$

$$3Ba_3(PO_4)_{2\,(sd)} + 18HNO_3 \rightarrow 9Ba(NO_3)_2 + 6H_3PO_4 \quad (4)$$

$$xBaCO_{3\,(sd)} + (1\text{-}x)Ba(OH)_{2\,(sd)} + 3Ba_3(PO_4)_{2\,(sd)} \rightarrow Ba_{10}(PO_4)_6(OH)_{(2\text{-}2x)}(CO_3)_{x\,(sd)}$$

In addition to the dissolution reaction of the apatite already mentioned (step 1), this scheme includes processes of dissolution of baryum carbonate (step 2), baryum hydroxide (step 3) and tribaryum phosphate (step 4). Their corresponding enthalpies were measured in the same solvent and under the similar conditions as the apatites, and the results are shown in Tables 3, 4 and 5. Table 6 gathers both dissolution and formation enthalpies of the reactants products.

The combination of the measurement results with those from the literature enables us to determine the enthalpy of formation. Values are reported in Table 7 and Fig. 6. Error on this quantity cannot be determined because of the lack of errors on literature data. One can notice a decrease in the enthalpy of formation when the amount of carbonate increases. For comparison, the results obtained with the strontium carbonate apatites are also reported in Fig. 6.

Discussion and conclusions

Enthalpy of formation of "A" type phosphobaryum carbonate hydroxyapatites $Ba_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$ decreases with the quantity of carbonate introduced in the lattice. The excess volume in the solid solution was too low, and so, the entropy was negligible in comparison to the enthalpy factor. Such a phenomenon has been observed with the "A" type carbonate apatite containing strontium [11]. Introduction of carbonate increases the stability of these types of compounds.

The drawing of $\Delta_f H$ over x is linear for strontium products and nonlinear for baryum apatites (Fig. 6). This behaviour can be related to the difference between the formation enthalpies of limit products. This difference is lower for the strontium (149 kJ mol^{-1}) than for the baryum apatites (291 kJ mol^{-1}), and so, the lattice enthalpies of the limit products for strontium apatites are closer. Consequently, replacement of two hydroxyl ions by one carbonate does not affect appreciably the lattice enthalpy of the strontium hydroxyapatite. This is not the case for the baryum hydroxyapatite because of the large difference between the lattice enthalpies of the limit products.

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References

1. Petkova V. Serafimova E. Petrova N. Pelovski Y. Thermochemistry of triboactivated natural and NH4-exchanged clinoptilolite mixed with Tunisian apatite. J Therm Anal Calorim. 2010. doi:10.1007/s10973-010-1224-8.
2. Hench LL. Bioceramics: from concept to clinic. J Am Ceram Soc. 1991;74:1487–510.
3. Onishi A, Thomas PS, Stuart BH, Guerbois JP, Forbes S. Tg–Ms characterisation of pig bone in an inert atmosphere. J Therm Anal Cal. 2007;88:405–9.
4. Devièse T, Colombini MP, Regert M, Stuart BH, Guerbois JP. TGMS analysis of archaeological bone from burials of the late Roman period. J Therm Anal Calorim. 2010;99:811–3.
5. Bonel G. Contribution à l'étude de la carbonatation des apatites II. Synthèse et étude des propriétés physico-chimiques des apatites carbonatées de type B. III. Synthèse et étude des propriétés physico-chimiques d'apatites carbonatées dans deux types de sites. Evolution des spectres infrarouge en fonction de la composition des apatites. Ann Chim Sci Mat. 1972;7:127–44.
6. Roux P, Bonel G. Sur la préparation de l'apatite carbonatée de type A à haute température par évolution sous pression de gaz carbonique. Ann Chim Sci Mat. 1977;2:159–65.
7. Ntahomvukiye I, Khattech I, Jemal M. Synthèse, characterisation et thermochimie d'apatites calco-plombeuses fluorées $Ca_{(10-x)}Pb_x(PO_4)_6F_2$, $0 \leq x \leq 10$. Ann Chim Sci Mat. 1997;22:435–46.
8. Ardhaoui K, Coulet MV, Ben Chérifa A, Carpena J, Rogez J, Jemal M. Standard enthalpy of formation of neodymium fluorbritholites. Thermochim Acta. 2006;444:190–4.
9. Ardhaoui K, Rogez J, Ben Chérifa A, Jemal M, Satre P. Standard enthalpy of formation of lanthanum oxybritholites. J Therm Anal Calorim. 2006;86:553–9.
10. Bel Hadj Yahia F, Jemal M. Synthesis, structural analysis and thermochemistry of B-type carbonate apatites. Thermochim Acta. 2010;505:22–32.
11. Jebri S, Boughzala H, Bechrifa A, Jemal M,. Structural analysis and thermochemistry of "A" type phosphostrontium carbonate hydroxyapatites. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-1598-2.
12. Jemal M. Thermochemistry and relative stability of apatite phosphates. Phos Res Bull. 2002;15:119–24.
13. Khattech I. Synthèse, caractérisation et étude thermochimique de phosphates à base de métaux alcalino-terreux. Thesis, Tunis El Manar University; 1996.
14. Linnig FJ, Mandel J. Which measure of precision? The evaluation of the precision of analytical methods involving linear calibration curves. Anal Chem. 1964;36:25–9.
15. Ben Chérifa A, Jemal M. Sur la réaction de dissolution des phosphates dans les acides: enthalpie de dissolution du phosphate tricacique β dans l'acide nitrique. Ann Chim Sci Mat Fr. 1985; 10:543–8.
16. Hill JO, Öjelund G, Wadsö I. Thermochemical results for "tris" as a test substance in solution calorimetry. J Chem Thermodyn. 1969;1:111–6.
17. Wadsö I, Goldberg RN. Standards in isothermal microcalorimetry. Pure Appl Chem. 2001;73:1625–39.

18. Khattech I, Lacout JL, Jemal M. Synthèse et thermochimie de phosphates d'alcalino-terreux. I. Enthalpie standard de formation du phosphate tribarytique et de l'apatite phosphobarytique chlorée. Ann Chim Fr. 1996;21:251–8.
19. Sands DE. Weighting factors in least squares. J Chem Educ. 1974;51:473–4.
20. Pattengill MD, Sands DE. Statistical significance of linear last-squares parameters. J Chem Educ. 1979;56:244–7.
21. Guedens WJ, Yperman J, Mullens J, Van Poucke LC. Statistical analysis of errors: a practical approach of an undergraduate chemistry lab. J Chem Educ. 1993;70:776–9.
22. Lide David R, editor. Handbook of chemistry and physics. 87th ed. Boca Raton: CRC Press; 2006/2007.