

STANDARD ENTHALPY OF FORMATION OF LANTHANUM OXYBRITHOLITES

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Lanthanum-bearing silicate-oxyapatites or britholites, $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}$ with $1 \leq x \leq 6$, have been synthesized by solid state reaction at high temperature. They were characterized by X-ray diffraction and IR spectroscopy. Using two microcalorimeters, the heat of solution of these compounds have been measured at 298 K in a solution of nitric and hydrofluoric acid. A strained least squares method was applied to the experimental results to obtain the solution enthalpies at infinite dilution, and the mixing enthalpy in two steps. In the first step the mixing enthalpy obtained is referenced to the britholite monosubstituted and to the oxysilicate. The mixing enthalpy referenced to the oxyapatite and to the oxysilicate is then extrapolated. In order to determine the enthalpies of formation of all the terms of the solution, thermochemical cycles were proposed and complementary experiments were performed. The results obtained show a decrease of the enthalpy of formation with the amount of Si and La introduced in the lattice. This was explained by the difference in the bond energies of (Ca–O, P–O) and (La–O, Si–O).

Keywords: britholites, enthalpy of formation, solution calorimetry, thermodynamics

Introduction

The composition of apatite compounds is $\text{M}_{10}(\text{XO}_n)\text{Z}_2$; with $M = \text{Ba, Ca, Cd, Na, Pb, Sr}$ or vacancy; $X = \text{As, C, P, Si, S, V}$ and $Z = \text{F}^-, \text{OH}^-, \text{O}^{2-}$ or vacancy [1]. This large array of substitution exhibited by apatite minerals is due to its crystallographic structure. Most apatites crystallise in the hexagonal system with space group $\text{P6}_3/\text{m}$. Apatite structure can be described as a nearly compact stacking of XO_4 groups, forming a skeleton with two types of channels. The first one is occupied by four M cations (site I with a C_3 point symmetry) placed along the ternary axis. The second one is occupied on its periphery by six M cations (site II with a C_s point symmetry). Z anions which appear on columns parallel to the c axis, are generally located near the mirror plans at $z = 1/4$ and $3/4$.

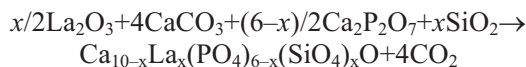
Britholites are apatites with a coupled cation-anion substitution ($\text{Ca}^{2+}; \text{PO}_4^{3-} \leftrightarrow \text{Ln}^{3+}; \text{SiO}_4^{4-}$) where Ln is a rare earth. These minerals are found in high-temperature geological settings such as in Oklo [2] and in Hoggar [3]. They have revealed a great structure stability and durability under radiation conditions as well in geological environment as in test conditions [4, 5]. It was then naturally thought to consider britholites as candidates for immobilization of some actinides issued

from nuclear wastes. In addition, Ln -apatite type silicates are good oxide conductors [6], so, the study of such apatites or apatite-type products are becoming the focus of some recent researches [7, 8].

This work deals with the thermodynamic stability of the solid solution $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}$ with $0 \leq x \leq 6$, in order to contribute with numerical data to a potential valorisation of these apatites. This paper presents the synthesis and the characterization of the samples of lanthanum-bearing silicate-oxyapatites which will be dissolved quantitatively thereafter in acidic solution in a calorimeter. In addition, a computation of the enthalpies of formation deduced from the dissolution results and the mixing enthalpies will be presented.

Synthesis

The samples were prepared by solid state reaction at high temperature under oxidizing medium. A stoichiometric mixture of $\text{La}_2\text{O}_3/\text{CaCO}_3/\text{Ca}_2\text{P}_2\text{O}_7/\text{SiO}_2$ was heated in order to prepare britholites, according to the following equation:



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where $0 < x \leq 6$. By varying the ratio $j = \text{Si}/(\text{Si} + \text{P})$, where $0 < j < 1$, one can obtain up to six lanthanum and silicate groups per unit cell. However, a preliminary treatment is necessary. It consists in heating the mixture at 1173 K during several hours in order to decompose the carbonate. Intermediate grinding is then carried out leading to a homogeneous mixture which is then pilled and sintered at 1673 K. Many grinding-calcination cycles are required to obtain well-crystallized apatites [9].

Characterization

The purity and the crystallinity of the products were checked by X-ray diffraction and infrared spectroscopy. The X-ray diffraction patterns were obtained from powdered samples using a Siemens D5000 diffractometer (Cu anticathode) and infrared spectra were recorded using a Perkin-Elmer 7700FTIR spectrometer between 4000 and 400 cm^{-1} in KBr pellets.

X-ray diffraction patterns show that every compound is a pure apatite phase crystallizing in the hexagonal system $P6_3/m$. Hence, lanthanum silicate bearing oxyapatites form a continuous solid solution [9]. Figure 1 shows the variation of the lattice parameters *vs.* the rate of substitution *x*. One can notice the increase of both the parameters with the simultaneous introduction of lanthanum and silicate ions. This result is not surprising as the average length of Si–O bond (1.62 \AA) is larger than the average length of the P–O bond (1.51 \AA), and as lanthanum cation radius (1.03 \AA) is slightly bigger than the calcium cation radius (0.99 \AA). The coupled substitution leads to an increase in the cell parameters which seems to be in agreement with the Vegard's law.

The infrared spectra exhibit only characteristic transmittance bands of phosphate and silicate groups. It is interesting to notice the lack of the bands (3560 cm^{-1}) and ($1200\text{--}1250 \text{ cm}^{-1}$) corresponding respectively to the vibration modes of the OH^- and $\text{P}_2\text{O}_7^{4-}$ groups. It is well known that these groups could be formed as impurities in such products.

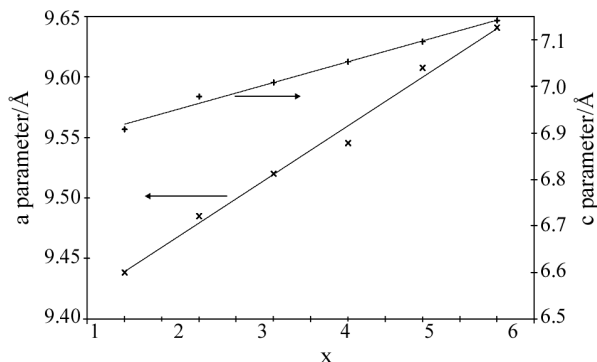


Fig. 1 Variation of the \times – *a* and $+$ – *c* crystallographic parameters *vs.* *x*

Thermochemical study

Calorimetric technique

Solution enthalpies were measured at room temperature using two differential calorimeters named C-80 (Setaram) [10, 11] and Calsol [12]. These devices allow observing either quick or slow kinetic phenomena. Due to its 100 cm^3 -polytetrafluoroethylene-cell, the Calsol provides a wide spectra of experiments: the solute/solvent ratio can be varied in a wide range and experiments requiring HF solvent can be performed. Experiments not requiring HF addition were performed in the stainless steel vessel of the C-80. The C-80 and Calsol were calibrated with the dissolution of trihydroxymethyl aminomethane in 0.1 mol L^{-1} hydrochloric solution, which has been extensively used as a test reaction in solution calorimetry. Its corresponding enthalpy has been determined by many authors with a high accuracy: (-29.773 ± 0.008) [13], $(-29.765 \pm 0.004) \text{ kJ mol}^{-1}$ [14]. The results, $(-29.16 \pm 0.04) \text{ kJ mol}^{-1}$ for the C-80 and $(-30.19 \pm 0.05) \text{ kJ mol}^{-1}$ for the Calsol, are in good agreement with those published in literature.

Lanthanum oxybritholite solution enthalpies

Many experiments were performed to find the most suitable solvent and the best experimental conditions. In a previous study on neodymium fluor-britholites [15], 46 mass% nitric acid was used as solvent. It was surprising that no added fluor was necessary to dissolve silicate entities. Indeed, the fluor was already present in the structure of fluorapatite, and moved firstly into the solvent to produce locally a HF concentration near the reacting interface. For the oxybritholites no fluor is present in the structure and consequently hydrofluoric acid is added to nitric acid to allow the dissolution of silicates. However, an important quantity of fluor or solute leads to the precipitation of calcium and lanthanum fluorides [15]. Then, samples only from 2 to 12 mg were dissolved in the PTFE-cell of the Calsol calorimeter in 50 cm^3 of solvent. The hydrofluoric acid was added in the ratio of two mols of acid for one mol of britholite. Table 1 gathers the results of the measurements.

Determination of the mixing enthalpies in the solid solution

The strained least squares method was applied to the experimental results to obtain solution enthalpies at infinite dilution $\Delta_{\text{sol}}^{\infty} H(j)$ for each substitution rate $x=6j$ and then the mixing enthalpies $\Delta_{\text{mix}} H(j)$ referenced to the end members of the solution. This treatment consists in minimizing the function

Table 1 Standard enthalpies of solution at 298 K of oxybritholites in the solvent based on HF–HNO₃. A mass (*m*) of a few milligrams of britholite having the rate of substitution *x* is dissolved in 50 mL of acids (columns 2 and 3). Molar solution enthalpies are reported in column 4

<i>x</i>	<i>m</i> /mg	$\Delta_{\text{sol}}H/\text{J}$	$\Delta_{\text{sol}}H/\text{J g}^{-1}$
1	3.05	-2.24	-743.33
	4.34	-3.15	-724.65
	6.12	-4.41	-720.15
	8.42	-6.12	-726.65
	10.86	-7.95	-732.44
2	2.22	-1.55	-702.19
	4.73	-3.32	-702.38
	7.11	-5.168	-726.84
	8.74	-6.33	-724.77
3	10.42	-7.36	-706.46
	2.63	-2.05	-779.99
	4.44	-3.39	-765.69
	6.14	-4.78	-778.52
	10.30	-7.96	-772.99
4	11.30	-8.74	-773.59
	2.60	-2.18	-836.52
	4.52	-3.74	-826.89
	5.56	-4.71	-846.46
	8.28	-6.92	-835.17
5	10.55	-8.69	-824.02
	2.26	-1.89	-834.12
	5.53	-4.64	-839.28
	8.09	-6.82	-843.29
	8.78	-7.44	-846.03
6	10.60	-8.98	-847.99
	4.05	-3.90	-962.49
	5.45	-5.22	-958.41
	7.63	-7.24	-949.19
6	9.74	-9.36	-961.13
	10.61	-10.23	-964.52

$$A = \sum_j \sum_i [\Delta_{\text{sol}} H(n_i, j) - \Delta_{\text{sol}} H(\text{model})]^2 \quad (1)$$

where $\Delta_{\text{sol}} H(n_i, j)$ is the solution enthalpy for the experience *i* corresponding to a final concentration z_i of the solute having the *j* ratio. As the volume of the solvent is identical for all the experiments, this concentration is directly proportional to the mol number n_i of the solute.

During preliminary experiments the concentration range of the solute in the solvent has been so chosen that the evolutions of the solution enthalpies are linear. This domain concerns the strong dilution since the mass ratio britholites/acid is about 1/1000. The results are then described by a ruled surface as:

$$\Delta_{\text{sol}} H(\text{model}) = a(j)n_i + \Delta_{\text{sol}}^{\infty} H(j) \quad (2)$$

We expect that the mixing enthalpy in the solid solution is represented by a polynomial depending only on the rate of substitution *j* as

$$\Delta_{\text{mix}} H(j) = j(1-j) \sum_{k=0}^4 \lambda_k j^k \quad (3)$$

The mixing enthalpy is calculated through the solution enthalpies at infinite dilution taking as references the end members of the solid solution $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ ($j=0$) and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$ ($j=1$). So:

$$\Delta_{\text{mix}} H(j) = \Delta_{\text{sol}}^{\infty} H(j) - j\Delta_{\text{sol}}^{\infty} H(1) - (1-j)\Delta_{\text{sol}}^{\infty} H(0) \quad (4)$$

It is assumed that the mixing enthalpy does not depend on the concentration z_i (or molar number n_i) of the solute in the solvent and can be calculated for each concentration z_i . This impose a condition between the slopes $a(j)$ which become then correlated by:

$$a(j) = (1-j)a(0) + ja(1)$$

This relation is obtained by equalizing the mixing enthalpies calculated at infinite dilution ($z=0$) and that calculated at all the concentrations z in the solvent. This correlation makes the mathematical treatment more realistic as experimental data are all together associated. The solid solution is then globally treated.

Moreover, it should be noticed that calcium oxyapatite is not stable in air at room temperature. It transforms into oxyhydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{O}$ in contact with steam [16, 17]. Consequently this apatite was not synthesized and so, the corresponding solution enthalpy was not measured. The mixing enthalpy was then referenced to $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{O}$ ($j=1/6$; $v=0$) and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$ ($j=1$; $v=1$). Using the variable change

$$v = (6/5j - 1/5) \text{ where } -1/5 < v < 1 \quad (5)$$

$$\Delta_{\text{mix}} H(v) = [\Delta_{\text{sol}}^{\infty} H(v) - v\Delta_{\text{sol}}^{\infty} H(v=1) - (1-v)\Delta_{\text{sol}}^{\infty} H(v=0)] \quad (6)$$

The mixing enthalpy referenced to $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ ($j=0$) and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$ ($j=1$) is deduced. Considering Eq. (1), Eq. (2) and the variable change in Eq. (5), *A* is expressed as:

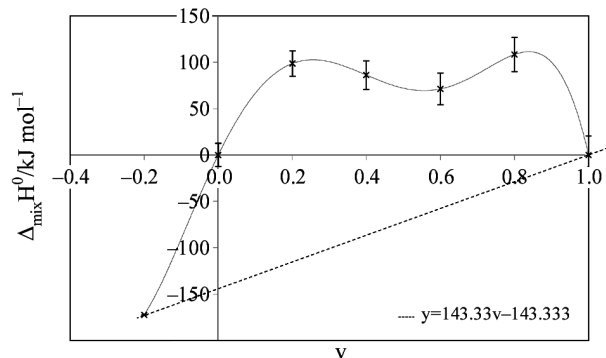
$$A = \sum_i [\Delta_{\text{sol}} H(n_i, v=0) - a(v=0)n_i - \Delta_{\text{sol}}^{\infty} H(v=0)]^2 + \sum_i [\Delta_{\text{sol}} H(n_i, v=1) - a(v=1)n_i - \Delta_{\text{sol}}^{\infty} H(v=1)]^2 + \sum_i \sum_{v=1/5}^{4/5} [\Delta_{\text{sol}} H(n_i, v) - a(v)n_i - \Delta_{\text{sol}}^{\infty} H(v)]^2 \quad (7)$$

This *A* function is minimized through the resolution of a nine-equation-system of nine variables which are $a(v=0)$, $a(v=1)$, $\Delta_{\text{sol}}^{\infty} H(v=0)$, $\Delta_{\text{sol}}^{\infty} H(v=1)$, λ_0 , λ_1 , λ_2 , λ_3 and λ_4 . The nine equations are:

$$\frac{\partial A}{\partial a(v=0)} = \frac{\partial A}{\partial a(v=1)} = \frac{\partial A}{\partial \Delta_{\text{sol}}^{\infty} H(v=0)} = \frac{\partial A}{\partial \Delta_{\text{sol}}^{\infty} H(v=1)} = \frac{\partial A}{\partial \lambda_k} = 0$$

Table 2 Minimization parameters

Variable	Value/kJ mol ⁻¹
$a(v=0)$	$2.87 \cdot 10^6$
$a(v=1)$	$-7.71 \cdot 10^6$
$\Delta_{\text{sol}}^{\infty} H(v=0)$	-805
$\Delta_{\text{sol}}^{\infty} H(v=1)$	-1457
λ_0	-819
λ_1	461
λ_2	3792
λ_3	-5186

**Fig. 2** Variation of the mixing enthalpy of the oxybritholites solid solution vs. v

where $0 \leq k \leq 4$. The nine-equation-system was solved by a standard code for each value of k , from variance calculations. The calculated results approach at most the experimental data for $k_{\text{max}}=3$. So

$$\Delta_{\text{mix}}H(v) = v(1-v) \sum_{k=0}^3 \lambda_k(v)^k$$

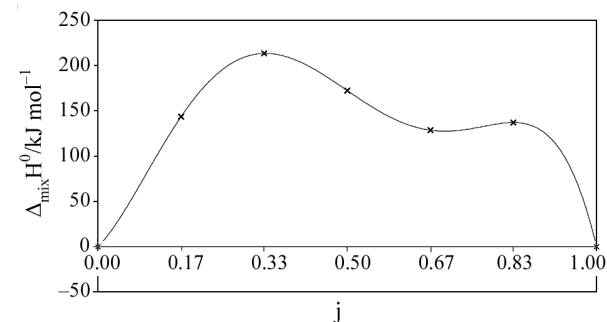
The results are gathered in Table 2 and the corresponding mixing enthalpy is plotted vs. v in Fig. 2. Statistical errors are calculated with the method proposed by Guedens *et al.* [18] taking into account the experimental errors on the dissolution enthalpies of the solid solution and the references. By extrapolation the mixing enthalpy of calcium oxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{O}$) is deduced as -172 kJ mol^{-1} . The equation of the ruled surface describing the experimental results and the solution enthalpies at infinite dilution are reported in Table 3. The mixing enthalpy of the solid solution can then be calculated in the j space, i.e. with the references $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ ($j=0$) and $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$ ($j=1$) using the variable change $v=(6/5j-1/5)$ where $-1/5 < v < 1$. The corresponding values are reported in Table 4 and plotted in Fig. 3.

Dissolution mechanism

The dissolutions were carried out at great dilution of the solute in the solvent. The pH of the acid solution

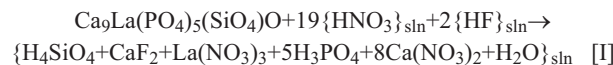
Table 3 Solution enthalpy slopes and solution enthalpies at infinite dilution

x	j	$a(j)/\text{kJ solute mol}^{-1}$	$\Delta_{\text{sol}}^{\infty} H^{\circ}/\text{kJ mol}^{-1}$
1	0.17	$2.87 \cdot 10^6$	-805
2	0.33	$7.54 \cdot 10^5$	-836
3	0.5	$-1.36 \cdot 10^6$	-994
4	0.67	$-3.48 \cdot 10^6$	-1125
5	0.83	$-5.59 \cdot 10^6$	-1218
6	1	$-7.71 \cdot 10^6$	-1457

**Fig. 3** Variation of the mixing enthalpy of the solid solution oxybritholites vs. j **Table 4** Mixing enthalpy of the lanthanum oxybritholite solid solution

x	j		$\Delta_{\text{mix}}H/\text{kJ mol}^{-1}$
0	0	$\text{Ca}_{10}(\text{PO}_4)_6\text{O}$	0
1	0.17	$\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{O}$	144
2	0.33	$\text{Ca}_8\text{La}_2(\text{PO}_4)_4(\text{SiO}_4)_2\text{O}$	214
3	0.5	$\text{Ca}_7\text{La}_3(\text{PO}_4)_3(\text{SiO}_4)_3\text{O}$	172
4	0.67	$\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{O}$	129
5	0.83	$\text{Ca}_5\text{La}_5(\text{PO}_4)_1(\text{SiO}_4)_5\text{O}$	137
6	1	$\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$	0

is very low, consequently only H_4SiO_4 and H_3PO_4 are present in the solution as silicate and phosphate entities, respectively. And so the following reaction scheme can be proposed for the dissolution of the oxybritholite containing one lanthanum and one silicate per formula unit:



Enthalpy of formation of the monosubstituted oxybritholite $\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{O}$

Direct measurement of the standard formation enthalpy of such compounds is impossible. Consequently, for a given compound, one has to imagine a set of reactions, the 'sum' of which leads to the reaction of formation. As with apatite-like compounds,

Table 5 Standard enthalpies of formation and solution enthalpies of well-known compounds and entities

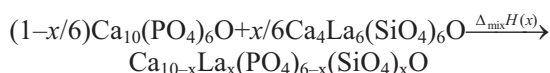
	$\Delta_f H^0(298\text{K})/\text{kJ mol}^{-1}$	Reference	$\Delta_{\text{sol}} H(298\text{K})/\text{kJ mol}^{-1}$	Reference
HNO ₃ ; 4.109H ₂ O	-201.29	[21]		
Ca(NO ₃) ₂ ; 4H ₂ O	-2132.33	[21]	30.41	present work
La(NO ₃) ₃ ; 6H ₂ O	-3063.65	[21]	22.24	present work
H ₃ PO ₄ ; 0.756H ₂ O	-1271.85	[21]	-1.19	present work
CaSiO ₃ (α)	-1628.40	[22]	-158.74	present work
H ₂ O	-285.83	[21]	0	[23]
HF; 1.708H ₂ O	-316.85	[21]	00.17	present work

previously studied [19, 20], several possibilities exist. However only are considered those containing steps for which the enthalpy can be measured experimentally or calculated from literature data, because they allow calculation of $\Delta_f H$. For oxybritholite containing one lanthanum and one silicate, Ca₉La(PO₄)₅(SiO₄)O, the suitable following set can be retained below.

In addition to the dissolution reaction already mentioned in step I, this scheme involves several other steps, which include processes of dissolution or of dilution in acidic solution (steps II, VI, VIII, X and XII). Their corresponding enthalpies were measured in the same solvent. The reactions corresponding to steps II and XII were performed in the Calsol calorimeter. Those of steps VI, VIII and X were performed in the C-80 calorimeter. The other steps involve the reactions of formation of well-known compounds or entities, the corresponding enthalpies were taken from literature and reported in Table 5. The enthalpy of formation of the britholite containing one lanthanum and one silicate Ca₉La(PO₄)₅(SiO₄)O is then deduced as -13438 kJ mol⁻¹.

Enthalpies of formation along the solid solution

The enthalpies of formation along the solid solution can be expressed through the mixing enthalpy. The mixing reaction of calcium oxyapatite Ca₁₀(PO₄)₆O and oxy-silicate Ca₄La₆(SiO₄)₆O leading to one mol of a britholite containing x silicates can be written as follows:



Consequently:

$$\begin{aligned} \Delta_f H^0(\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}) = \\ [\Delta_{\text{mix}} H + x/6\Delta_f H^0(\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}) + \\ (1-x/6)\Delta_f H^0(\text{Ca}_{10}(\text{PO}_4)_6\text{O})] \end{aligned} \quad (8)$$

From the calculated enthalpy of formation of the monosubstituted britholite and the enthalpy of formation of the oxyapatite, the enthalpies of formation of all the terms of the solid solution can be obtained. The enthalpy of formation of the oxyapatite was deduced from the empirical estimation of Bogach *et al.* [24], according to which the enthalpy of formation of a phosphocalcic apatite Ca₁₀(PO₄)₆Z₂ is expressed as a

{H ₄ SiO ₄ +CaF ₂ +La(NO ₃) ₃ +5H ₃ PO ₄ +8Ca(NO ₃) ₂ +H ₂ O} _{sln}	→	Ca ₉ La(PO ₄) ₅ (SiO ₄)O+19{HNO ₃ } _{sln} +2{HF} _{sln}	[-I]
2{HF+1.708H ₂ O} _{sln}	→	2{HF; 1.708H ₂ O} ₁ +sln	[II]
19{HNO ₃ ; 4.109H ₂ O} ₁	→	19/2H ₂ (g)+19/2N ₂ (g)+28.5O ₂ (g)+78.071H ₂ O	[III]
2{HF; 1.708H ₂ O} ₁	→	F ₂ +H ₂ +3.416H ₂ O	[IV]
8Ca(s)+8N ₂ (g)+40O ₂ (g)+32H ₂ (g)	→	8[Ca(NO ₃) ₂ ; 4H ₂ O](s)	[V]
8[Ca(NO ₃) ₂ ; 4H ₂ O](s)+sln	→	{8Ca(NO ₃) ₂ +32H ₂ O} _{sln}	[VI]
La(s)+3/2N ₂ (g)+15/2O ₂ (g)+6H ₂ (g)	→	[La(NO ₃) ₃ ; 6H ₂ O](s)	[VII]
[La(NO ₃) ₃ ; 6H ₂ O](s)+sln	→	{La(NO ₃) ₃ +6H ₂ O} _{sln}	[VIII]
15/2H ₂ (g)+10O ₂ (g)+5P(s)+3.78H ₂ O	→	5{H ₃ PO ₄ ; 0.756H ₂ O} ₁	[IX]
5{H ₃ PO ₄ ; 0.756H ₂ O} ₁ +sln	→	{5H ₃ PO ₄ +3.78H ₂ O} _{sln}	[X]
Ca(s)+Si(s)+3/2O ₂ (g)+H ₂ (g)+F ₂ (g)+3.416H ₂ O	→	CaSiO ₃ +2{HF; 1.708H ₂ O} ₁	[XI]
CaSiO ₃ (s)+2{HF} _{sln} +{H ₂ O} _{sln}	→	{H ₄ SiO ₄ +CaF ₂ } _{sln}	[XII]
2{HF; 1.708H ₂ O} ₁ +sln	→	2{HF+1.708H ₂ O} _{sln}	[XIII]
37H ₂ O	→	37H ₂ +18.5O ₂	[XIV]
{39.78H ₂ O} _{sln}	→	39.78H ₂ O+sln	[XV]
9Ca(s)+La(s)+5P(s)+Si(s)+25/2O ₂ (g)	→	Ca ₉ La(PO ₄) ₅ (SiO ₄)O	

linear function of the enthalpy of formation of the CaZ_2 compound as:

$$\Delta_f H^0(\text{Ca}_{10}(\text{PO}_4)_6\text{Z}_2) = 1.1431\Delta_f H^0(\text{CaZ}_2) - 12191 \quad [\text{kJ mol}^{-1}] \quad (9)$$

Taking into account the enthalpy of formation of CaO , $-635.1 \text{ kJ mol}^{-1}$ [21], Eq. (9) leads to the value $-12917 \text{ kJ mol}^{-1}$ for the oxyapatite. The enthalpies of formation of all the terms of the solid solution are calculated through Eq. (8), and the results are gathered in Table 6 for the particular discrete compositions from $x=0$ to 6.

Discussion

The mixing enthalpy of the solid solution $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_{6-x}(\text{SiO}_4)_x\text{O}$ is positive. At high temperature the mixing Gibbs energy $\Delta_{\text{mix}}G$ is negative, as these britholites were synthesized by solid-state reaction. Consequently $\Delta_{\text{mix}}S > 0$, suggesting that britholites have a great degree of disorder. Berastegui *et al.* [25] demonstrated in a previous study on the ionic conductivity in germanate oxyapatites $\text{La}_{9.33}(\text{GeO}_4)_6\text{O}_2$ that one dimensional channels along the c axis in the oxyapatite structure are pathways for oxygen ions O^{2-} diffusion which is enhanced by the presence of anion vacancies. Nakayama *et al.* [26] reported that this ionic conductivity exists even at low temperature (30°C) in oxysilicates, $\text{Ln}_x(\text{SiO}_4)_6\text{O}_{1.5x-12}$ ($\text{Ln}=\text{La, Pr, Nd, Sm, Gd}$ or Dy ; $x=8-9.33$). Bouhaouss *et al.* [27] proposed a mechanism for O^{2-} ions conduction in lanthanum containing vanadocalcic oxyapatites in which La^{3+} ions in $\text{Ca}(\text{II})$ sites increase the size of screw channels leading to more important polarizability. Therefore, the oxybritholite studied in this work may exhibit a great mobility of oxygen ions along the channels enhanced by the presence of vacancies along the c axis and of lanthanum ions on its periphery. This might contribute importantly to the positive mixing entropy.

On the other hand, Table 6 shows a decrease of the enthalpy of formation as the substitution rate increases, indicating an increase in stability of oxybritholites. This can be explained by the difference between the energy bonds, D_{298}^0 , Si-O bond energy ($D_{298}^0=799.6 \text{ kJ mol}^{-1}$) is higher than P-O bond energy ($D_{298}^0=599.1 \text{ kJ mol}^{-1}$). Similarly La-O bond is stronger than Ca-O ; D_{298}^0 equals 799 and $402.1 \text{ kJ mol}^{-1}$ respectively [28]. Consequently the double substitution (La ; Si) for (Ca ; P) contributes to strengthen the crystal edifice and so to increase to stability of the solid solution. Moreover the reported value for the enthalpy of formation of the lanthanum silicate with an oxyapatite-like structure $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$

Table 6 Enthalpies of formation of lanthanum-bearing silicate-oxyapatites

x		$\Delta_f H^0/\text{kJ mol}^{-1}$
0	$\text{Ca}_{10}(\text{PO}_4)_6\text{O}$	-12917
1	$\text{Ca}_9\text{La}(\text{PO}_4)_5(\text{SiO}_4)\text{O}$	-13438
2	$\text{Ca}_8\text{La}_2(\text{PO}_4)_4(\text{SiO}_4)_2\text{O}$	-14033
3	$\text{Ca}_7\text{La}_3(\text{PO}_4)_3(\text{SiO}_4)_3\text{O}$	-14738
4	$\text{Ca}_6\text{La}_4(\text{PO}_4)_2(\text{SiO}_4)_4\text{O}$	-15446
5	$\text{Ca}_5\text{La}_5\text{PO}_4(\text{SiO}_4)_5\text{O}$	-16102
6	$\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$	-16904

($-14611 \text{ kJ mol}^{-1}$) [7], is in the same order of magnitude than the values found in this work but differs from that of the oxybritholite containing six lanthanum and oxysilicates $\text{Ca}_4\text{La}_6(\text{SiO}_4)_6\text{O}$ ($-16904 \text{ kJ mol}^{-1}$). The later seems to be more stable. That difference in stability may be the consequence of the presence of vacancies in the cation sites in La-silicate.

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References

- 1 J. C. Elliott, Structure and chemistry of the apatites and other calcium orthophosphates, Elsevier, 1994, p. 63.
- 2 J. Carpena and V. Sère, From the natural to synthetic analogue: interest of Oklo for the synthesis of stable crystalline matrices, in Proceedings of the fourth joint EC-CEA final meeting, Saclay 1995, p. 225.
- 3 J. Carpena, J. R. Kiénast, K. Ouzegane and C. Jehanno, Geol. Soc. Amer. Bull., 100 (1988) 1237.
- 4 P. Trocellier, Ann. Chim. Sci. Mat., 25 (2000) 321.
- 5 R. C. Ewing, W. J. Weber and F. W. Clinard Jr., Progress in Nuclear Energy, 29 (1995) 63.
- 6 S. Tao and J. T. S. Irvine, Mater. Res. Bull., 36 (2001) 1245.
- 7 A. S. Risbud, K. B. Helean, M. C. Wilding, P. Lu and A. Navrotsky, J. Mater. Res., 16 (2001) 2780.
- 8 R. El Ouenzerfi, M. T. Cohen-Adad, C. Goutaudier and G. Panczer, Solide State Ionics, 176 (2005) 225.
- 9 L. Boyer, J. Carpena and J. L. Lacout, Solid State Ionics, 95 (1997) 121.
- 10 K. Ardhaoui, A. Ben Cherifa and M. Jemal, Setaram News, 10 (2003) 7.
- 11 K. Ardhaoui, A. Ben Cherifa and M. Jemal, J. Therm. Anal. Cal., 81 (2005) 251.
- 12 M. Ganteaume, M. Coten and M. Decressac, Thermochem. Acta, 178 (1991) 81.
- 13 J. O. Hill, G. Ojelung and I. Wadsö, J. Chem. Thermodyn., 1 (1969) 118.
- 14 C. E. Vanderzee, D. H. Waugh, N. C. Haas and D. A. Wigg, J. Chem. Thermodyn., 12 (1980) 27.

- 15 V. Coulet, A. Ben Cherifa, J. Rogez, J. Carpena, M. Jemal and J. C. Mathieu, Interactions dans la solution solide $\text{Ca}_{10-n}\text{La}_n(\text{PO}_4)_{6-n}(\text{SiO}_4)_n\text{F}_2$ ($0 \leq n \leq 6$), 32^{ème} Journées de Calorimétrie et d'Analyse Thermique, Hammamet, Tunisie 2001, p. 95.
- 16 J. C. Trombe and G. Montel, C. R. Acad. Sc. Paris, 273C (1971) 462.
- 17 C. J. Liao, F. H. Lin, K. S. Chen and J. S. Sun, Biomaterials, 20 (1999) 1807.
- 18 Guedens, J. Yperman, J. Mullens, L. C. Van Pouck and E. J. Pauwels, J. Chem. Educ., 70 (1993) 776.
- 19 A. Ben Cherifa and M. Jemal, J. Therm. Anal. Cal., 68 (2002) 1035.
- 20 S. Ben Abdelkader, A. Ben Cherifa, M. V. Coulet, I. Khattech, J. Rogez and M. Jemal, J. Therm. Anal. Cal., 77 (2004) 863.
- 21 Selected values of chemical thermodynamic properties, Tech. Note, N. B.S Circular, U. S Dept. Commerce, 1973.
- 22 I. Barin and G. Platzki, Thermochemical Data of Pure Substances, 3rd Ed., New York 1995.
- 23 A. Ben Cherifa, Thesis, Université de Tunis, 1988.
- 24 V. V. Bogach, S. V. Dobrydnev and V. S. Beskov, Russian J. Inorg. Chem., 46 (2001) 1011.
- 25 P. Berastegui, S. Hull, F. J. Garcia Garcia and J. Grins, J. Solid State Chem., 168 (2002) 294.
- 26 S. Nakayama, M. Sakamoto, M. Higuchi, K. Kodaira, M. Sato, S. Kakita, T. Suzukie and K. Itohe, J. Eur. Ceram. Soc., 19 (1999) 507.
- 27 A. Bouhaouss, A. Laghzizil, A. Bensaoud, M. Ferhat, G. Lorent and J. Livage, International J. Inorg. Mater., 3 (2001) 743.
- 28 Handbook of Chemistry and Physics, 85th Edition, 2004–2005, p. 52.

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