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Standard enthalpy of formation of neodymium fluorbritholites

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Abstract

Neodymium-bearing silicate-fluorapatites $Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)_xF_2$ with $1 \leq x \leq 6$ have been synthesized by solid state reaction at high temperature. The heat of solution in 46 wt% nitric acid has been measured at 298 K with a differential calorimeter. From the measurements on several compositions of the solid solution, the mixing enthalpy has been determined. In order to determine the enthalpies of formation, a thermochemical cycle was proposed and complementary experiences were performed to obtain the formation enthalpy of the monosubstituted britholite $Ca_9Nd(PO_4)_5(SiO_4)F_2$. This quantity was combined with the mixing enthalpies to obtain the formation enthalpies of the remaining britholites. The stability of the solid solution decreases as the rate of substitution increases.

Keywords: Britholites; Heat of solution; Heat of formation

1. Introduction

Apatite which is the most widespread phosphate mineral in crustal rocks, is remarkable for its structure allowing a wide chemical variability [1]. This large array of substitutions exhibited by apatite minerals appears both in the cationic and anionic sites. Most of the apatites are isomorphous to fluorapatite $Ca_{10}(PO_4)_6F_2$, crystallising in the hexagonal system (space group $P6_3/m$). The quasi-compact arrangement of the anion groups (PO_4) forms the skeleton of the apatite and exhibits two types of channels. The first is occupied by four Ca cations with Ch symmetry, placed on the ternary axis and called Ca(I). The second is occupied, on its periphery, by six Ca cations with Cs site symmetry and is called Ca(II). The Ca(II) cations are located on two equilateral triangles at level 1/4 and 3/4 centred on the six-fold axis. F^- anions are located in the centre of these triangles.

Britholites are apatites issued from a coupled substitution (Ca^{2+}; $PO_4{}^{3-}$) ↔ (Ln^{3+}; $SiO_4{}^{4-}$) where Ln represents a rare earth. These minerals are found in high-temperature geological settings such as metamorphic rocks in Oklo [2] and Hoggar [3] or volcanic ejecta [4]. Apatite-group minerals having Si/P ratio near 0 or 6 are found in nature, but complete solid solution between calcium–phosphate apatite and silicate britholite has only been demonstrated with synthesised samples [5]. These minerals reveal a structure stability and durability under radiation conditions either in geologic environment or in probes [6,7]. Britholites resistance to irradiation is greatly influenced by the chemical composition, being mainly correlated to the substitution rate on the cationic site, to the PO_4/SiO_4 ratio and to the nature of the anion: a better behaviour towards irradiation has been observed when britholite does not contain more than one SiO_4 group per unit-cell and when it is fluor-rich [8,9]. Consequently, low silicate fluorbritholites are potential candidates for actinides immobilisation, and the study of the thermodynamic stability of such apatites or apatite like compounds is the focus of some recent research [10,11].

This study deals with thermodynamic stability of the solid solution $Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)_xF_2$ where $0 \leq x \leq 6$, with the aim to contribute to potential use of these apatites in nuclear waste science. Neodymium was chosen because the ionic radii of Nd^{3+} and Pu^{3+} are almost identical [9], and so should be similarly accommodated in the apatite structure.

The first part of this paper deals with the solution calorimetry in nitric acid (46%, w/w) of neodymium-bearing

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silicate-fluorapatites. The second part presents the determination of mixing enthalpies of these products leading to the enthalpies of formation.

2. Synthesis

Samples with $x = 0$, 1, 2, 3, 4, 4.5, 5 and 6 were prepared by solid state reaction at high temperature as described in a previous work [12]. A stoichiometric mixture of $CaF_2/Nd_2O_3/CaCO_3/Ca_2P_2O_7/SiO_2$ was reacted, according to the following equation:

$$CaF_2 + \frac{x}{2}Nd_2O_3 + 3CaCO_3 + \frac{(6-x)}{2}Ca_2P_2O_7 + xSiO_2$$
$$\rightarrow Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)xF_2 + 3CO_3$$

The reagents used are of analytical quality (purity >99.9%) and the silica is amorphous.

By varying the ratio $j = Si/(Si + P) = x/6$, one can obtain up to six neodymium and silicate groups per unit cell. However, a preliminary treatment is necessary. It consists in heating the mixture at 1173 K for several hours in order to decompose the carbonate. Intermediate grindings are then carried out to obtain a homogeneous mixture, which is then pilled and sintered at 1673 K. Several grinding-calcination cycles are required to obtain well-crystallized apatites [12].

The purity and crystallinity of the studied products are checked by X-ray diffraction and infrared spectroscopy. X-ray diffraction patterns have been obtained from powdered samples with a CPS 120 INEL diffractometer ($K\alpha_1$, cobalt, internal standard: α-Al_2O_3). These patterns show that the samples are well crystallized and contain a pure apatite phase. The lattice volume increases linearly with the rate of substitution according to the Vegard's law, indicating that neodymium – silicate bearing – fluoroapatites form a continuous solid solution. Infrared experiments were performed on pellets obtained by mixing 1.5 mg of product in 300 mg of KBr for IR spectroscopy. The spectra have been recorded between 400 and 4000 cm^{-1} using a Perkin-Elmer 7700 FTIR spectrometer; they confirm the tetrahedral SiO_4 and PO_4 groups substitution. Characterization results are reported in detail in the previous paper [12].

3. Thermochemical study

3.1. Calorimetry

Solution enthalpies were measured at 298 K with a Calsol differential solution calorimeter described elsewhere [13]. The reliability of Calsol was checked with the dissolution of tris-hydroxy-methylaminomethane in 0.1 mol dm^{-3} hydrochloric solution. Its corresponding enthalpy has been determined by many authors with a high accuracy (-29.773 ± 0.008) kJ mol^{-1} [14] (-29.765 ± 0.004) kJ mol^{-1} [15]. The value measured at 298 K (-30.19 ± 0.05) kJ mol^{-1}, differs from that published by no more than 1.4%.

3.2. Neodymium fluorbritholite solution enthalpies

Several trials were carried out to choose the most convenient solvent for the synthesized britholites. HF or HF + HNO_3 mixtures were good candidates as acidic mixtures. Fluorine is needed to break silicates entities but calcium and neodymium fluorides may precipitate. It was observed experimentally that these britholites dissolve completely in 46 wt% nitric acid, for concentrations of solute less than around 10^{-4} mol l^{-1}, as described in a previous presentation [16]. Table 1 gives the molar enthalpy measured by dissolving a few milligrams (2–10 mg) of britholites in 50 ml of acid solution.

The constrained least square method described elsewhere [17] was applied to the experimental results to obtain solution

Table 1
Standard enthalpies of solution at 298 K of neodymium-fluorbritholites in 46% (w/w) HNO_3 (aq)

x(Nd)	m (mg)	$\Delta_{sol}H$ (J)	$\Delta_{sol}H$ (kJ mol^{-1})
0	2.26	−0.53	−238.44
	3.70	−0.95	−259.06
	3.80	−0.99	−264.31
	7.33	−1.95	−268.48
	8.43	−2.49	−299.06
1	2.31	−1.23	−532.81
	4.38	−2.50	−570.28
	7.22	−3.90	−540.80
	9.16	−4.79	−523.44
	10.42	−5.95	−570.82
2	2.92	−2.14	−733.25
	3.82	−2.72	−712.61
	5.11	−3.53	−689.95
	6.54	−4.57	−698.99
	8.24	−5.19	−630.07
3	2.29	−2.01	−876.49
	4.15	−3.50	−842.53
	4.30	−3.79	−883.27
	6.75	−5.79	−859.10
	8.37	−7.33	−875.28
4	2.70	−2.87	−1062.45
	3.63	−3.93	−1083.83
	4.20	−4.17	−993.74
	8.22	−8.62	−1048.42
	9.72	−10.02	−1031.09
4.5	2.81	−2.90	−1030.68
	4.68	−5.13	−1095.49
	5.88	−6.11	−1038.66
	9.45	−10.25	−1084.44
	10.10	−10.26	−1016.33
5	2.63	−3.05	−1159.05
	3.55	−4.17	−1174.51
	4.24	−4.92	−1160.60
	6.15	−7.03	−1143.30
	8.02	−9.40	−1172.03
6	2.77	−3.21	−1158.49
	4.74	−5.50	−1159.98
	6.42	−7.51	−1169.15
	7.09	−7.99	−1127.40
	7.83	−8.80	−1123.24

Table 2
Solution enthalpies at infinite dilution and mixing enthalpies

x	j	$\Delta_{\mathrm{sol}}^{\infty}H^{\circ}(j)$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}^{\infty}H^{\circ}(j)$ (kJ mol^{-1})
0	0	−245.4 ± 4.9	0
1	0.17	−500,6 ± 10.0	−113 ± 8
2	0.33	−657.6 ± 13.2	−128 ± 10
3	0.5	−798.7 ± 15.9	−127 ± 11
4	0.67	−959.1 ± 19,1	−145 ± 14
4.5	0.75	−1038.6 ± 20.7	−153 ± 16
5	1.83	−1102.7 ± 22.1	−146 ± 17
6	1	−1098.7 ± 21.9	0

enthalpies at infinite dilution $\Delta_{\mathrm{sol}}^{\infty}H^{\circ}(j)$ (Table 2). For each rate of substitution $x = 6j$, the mixing enthalpies $\Delta_{\mathrm{mix}}H^{\circ}(j)$ referenced to the end members of the solid solution ($x = 0$ and $x = 6$) are calculated according the following expression and reported in Table 2 and Fig. 1:

$$\Delta_{\mathrm{mix}}H^{\circ}(j) = [\Delta_{\mathrm{sol}}^{\infty}H^{\circ}(j) - j\,\Delta_{\mathrm{sol}}^{\infty}H^{\circ}(j=1) - (1-j)\Delta_{\mathrm{sol}}^{\infty}H^{\circ}(j=0)].$$

Statistical errors on mixing enthalpies 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 of the reference compounds.

Dissolution was carried with very few quantities of britholite, less than 12 mg. The molar ratio britholite/acid is about 10^{-5}. Hence the dissolution was carried out at very great dilution. Due to the low pH of the acid solution, only H_4SiO_4 and H_3PO_4 are present in the solution as silicate and phosphate entities. Consequently, one can propose the following reaction scheme for the dissolution of the fluorbritholite containing one neodymium and one silicate per formula unit:

$$\mathrm{Ca_9Nd(PO_4)_5(SiO_4)F_2} + 19\{\mathrm{HNO_3}\}_{\mathrm{sln}} \rightarrow \{\mathrm{H_4SiO_4} + \mathrm{CaF_2} + \mathrm{Nd(NO_3)_3} + 5\mathrm{H_3PO_4} + 8\mathrm{Ca(NO_3)_2}\}_{\mathrm{sln}} \tag{I}$$

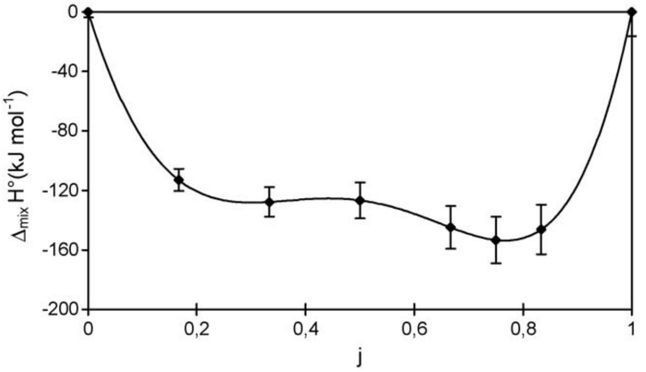

Fig. 1. Variation of the mixing enthalpy of the fluorbritholites vs. the rate of substitution j.

3.3. Enthalpy of formation of the monosubstituted fluorbritholite $Ca_9Nd(PO_4)_5(SiO_4)F_2$

Direct measurement of the standard formation enthalpy of such compounds is impossible. Consequently, for a given product, one has to imagine a succession of reactions, the “sum” of which leads to the formation reaction. Several possibilities exist. However only those containing steps for which the enthalpy can be measured experimentally or calculated from literature data can be considered, because they allow calculation of $\Delta_f H$. For britholite containing one neodymium and one silicate, $Ca_9Nd(PO_4)_5(SiO_4)F_2$, the following sequence of equations can be written:

$$\{\mathrm{H_4SiO_4} + \mathrm{CaF_2} + \mathrm{Nd(NO_3)_3} + 5\mathrm{H_3PO_4} + 8\mathrm{Ca(NO_3)_2}\}_{\mathrm{sln}} \rightarrow \mathrm{Ca_9Nd(PO_4)_5(SiO_4)F_2} + 19\{\mathrm{HNO_3}\}_{\mathrm{sln}} \tag{–I}$$

$$19\{\mathrm{HNO_3}; 4.109\mathrm{H_2O}\}_{\mathrm{l}} \rightarrow \tfrac{19}{2}\mathrm{H_2(g)} + \tfrac{19}{2}\mathrm{N_2(g)} + 28.5\mathrm{O_2(g)} + 78.071\mathrm{H_2O} \tag{II}$$

$$8\mathrm{Ca(s)} + 8\mathrm{N_2(g)} + 40\mathrm{O_2(g)} + 32\mathrm{H_2(g)} \rightarrow 8[\mathrm{Ca(NO_3)_2}; 4\mathrm{H_2O}]\mathrm{(s)} \tag{III}$$

$$8[\mathrm{Ca(NO_3)_2}; 4\mathrm{H_2O}]\mathrm{(s)} + \mathrm{sln} \rightarrow \{8\mathrm{Ca(NO_3)_2} + 32\mathrm{H_2O}\}_{\mathrm{sln}} \tag{IV}$$

$$\mathrm{Nd(s)} + \tfrac{3}{2}\mathrm{N_2(g)} + \tfrac{15}{2}\mathrm{O_2(g)} + 6\mathrm{H_2(g)} \rightarrow [\mathrm{Nd(NO_3)_3}; 6\mathrm{H_2O}]\mathrm{(s)} \tag{V}$$

$$[\mathrm{Nd(NO_3)_3}; 6\mathrm{H_2O}]\mathrm{(s)} + \mathrm{sln} \rightarrow \{\mathrm{Nd(NO_3)_3} + 6\mathrm{H_2O}\}_{\mathrm{sln}} \tag{VI}$$

$$\tfrac{15}{2}\mathrm{H_2(g)} + 10\mathrm{O_2(g)} + 5\mathrm{P(s)} + 3.78\mathrm{H_2O} \rightarrow 5\{\mathrm{H_3PO_4}; 0.756\mathrm{H_2O}\}_{\mathrm{l}} \tag{VII}$$

$$5\{\mathrm{H_3PO_4}; 0.756\mathrm{H_2O}\}_{\mathrm{l}} + \mathrm{sln} \rightarrow \{5\mathrm{H_3PO_4} + 3.78\mathrm{H_2O}\}_{\mathrm{sln}} \tag{VIII}$$

$$\mathrm{Ca(s)} + \mathrm{Si(s)} + \tfrac{3}{2}\mathrm{O_2(g)} + \mathrm{H_2(g)} + \mathrm{F_2(g)} + 3.416\mathrm{H_2O} \rightarrow \mathrm{CaSiO_3} + 2\{\mathrm{HF}; 1.708\mathrm{H_2O}\}_{\mathrm{l}} \tag{IX}$$

$$\mathrm{CaSiO_3(s)} + 2\{\mathrm{HF}\}_{\mathrm{sln}} + \{\mathrm{H_2O}\}_{\mathrm{sln}} \rightarrow \{\mathrm{H_4SiO_4} + \mathrm{CaF_2}\}_{\mathrm{sln}} \tag{X}$$

$$2\{\mathrm{HF}; 1.708\mathrm{H_2O}\}_{\mathrm{l}} + \mathrm{sln} \rightarrow 2\{\mathrm{HF} + 1.708\mathrm{H_2O}\}_{\mathrm{sln}} \tag{XI}$$

$$38\mathrm{H_2O} \rightarrow 38\mathrm{H_2} + 19\mathrm{O_2} \tag{XII}$$

$$\{44.196\mathrm{H_2O}\}_{\mathrm{sln}} \rightarrow 44.196\mathrm{H_2O} + \mathrm{sln} \tag{XIII}$$

$$9\mathrm{Ca(s)} + \mathrm{Nd(s)} + 5\mathrm{P(s)} + \mathrm{Si(s)} + 12\mathrm{O_2(g)} + \mathrm{F_2} \rightarrow \mathrm{Ca_9Nd(PO_4)_5(SiO_4)F_2}$$

In addition to the dissolution reaction already mentioned (step (I)), this scheme involves several other steps, which include processes of dissolution or dilution in acid solution (steps (IV), (VIII), (X) and (XI)). Their corresponding enthalpies were measured in the same solvent in a similar study on lanthanum oxybritholites [17]. The solution enthalpy of the step (VI) is also measured in the present work. The remaining steps involve the reactions of formation of well-known products or entities, the corresponding enthalpies were taken from literature and are reported in Table 3.

The enthalpy of formation of the britholite containing one neodymium and one silicate $Ca_9Nd(PO_4)_5(SiO_4)F_2$ is then deduced as $-13{,}430$ kJ mol^{-1}.

3.4. Enthalpies of formation of the solid solution

The enthalpy of formation of each britholite can be expressed through the mixing enthalpy. The mixing process of a calcium fluorapatite $Ca_{10}(PO_4)_6F_2$ and the fluorbritholite $Ca_4Nd_6(SiO_4)_6F_2$ leading to 1 mol of a britholite containing x silicates can be expressed as follows:

$$\left(\frac{1-x}{6}\right)\mathrm{Ca_{10}(PO_4)_6F_2} + \frac{x}{6}\mathrm{Ca_4Nd_6(SiO_4)_6F_2} \xrightarrow{\Delta_{\mathrm{mix}}H^{\circ}(x)} \mathrm{Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)_xF_2}$$

Table 3
Standard enthalpies of formation and solution enthalpies of compounds

	$\Delta_f H^\circ$ (298 K) (kJ mol^{-1})	References	$\Delta_{sol} H^\circ$ (298 K) (kJ mol^{-1})	References
HNO_3; $4.109H_2O$	−201.29	[19]	–	–
$Ca(NO_3)_2$; $4H_2O$	−2132.33	[19]	30.41	[17]
$Nd(NO_3)_3$; $6H_2O$	−3047.58	[19]	31.50	[a]
H_3PO_4; $0.756H_2O$	−1271.85	[19]	−1.19	[17]
$CaSiO_3$ (α)	−1628.40	[20]	−158.74	[17]
H_2O	−285.83	[21]	0	[22]
HF; $1.708H_2O$	−316.85	[19]	00.17	[17]

[a] Present work.

Table 4
Enthalpies of formation of some characteristic compositions of the solid solution

x	Neodymium fluorbritholite	$\Delta_f H^\circ$ (kJ mol^{-1})
0	$Ca_{10}(PO_4)_6F_2$	−13548
1	$Ca_9Nd(PO_4)_5(SiO_4)F_2$	−13430
2	$Ca_8Nd_2(PO_4)_4(SiO_4)_2F_2$	−13214
3	$Ca_7Nd_3(PO_4)_3(SiO_4)_3F_2$	−12982
4	$Ca_6Nd_4(PO_4)_2(SiO_4)_4F_2$	−12769
4.5	$Ca_{5.5}Nd_{4.5}(PO_4)_{5.5}(SiO_4)_{4.5}F_2$	−12662
5	$Ca_5Nd_5(PO_4)_1(SiO_4)_5F_2$	−12539
6	$Ca_4Nd_6(SiO_4)_6F_2$	−12162

Consequently:

$$\begin{aligned}&\Delta_f H^\circ(Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)_xF_2)\\&\quad=[\Delta_{mix}H^\circ+\tfrac{x}{6}\Delta_f H^\circ(Ca_4Nd_6(SiO_4)_6F_2)\\&\qquad+\left(\tfrac{1-x}{6}\right)\Delta_f H^\circ(Ca_{10}(PO_4)_6F_2)]\end{aligned}\tag{8}$$

Hence, if we know the formation enthalpy of anyone britholite, say the monosubstituted one, and the enthalpy of formation of the calcium fluorapatite, the formation enthalpy of the britholite containing six neodymium and silicates $Ca_4Nd_6(SiO_4)_6F_2$ can easily be calculated, and so the formation enthalpy of all the other britholites.

Using the enthalpy of formation of the calcium fluorapatite $\Delta_f H^\circ(Ca_{10}(PO_4)_6F_2) = -13{,}548$ kJ mol^{-1} [23], the formation enthalpies of the remaining britholites are calculated through (Eq. (8)) combining mixing enthalpies, and the formation enthalpy of the fluorbritholite monosubstitued. The results are reported in Table 4.

4. Discussion

The enthalpy of formation of britholites decreases as the double substitution (Ca^{2+}; $PO_4{}^{3-}$) ↔ (Nd^{3+}; $SiO_4{}^{4-}$) increases. The slightly substituted britholites are the most stable. These thermodynamic results are in agreement with those of Carpena et al. [2,8,9] reporting the stability of the monosubstituted fluorobritholites with respect to radiation and to alteration by streaming water.

The mixing enthalpies at 298 K are negative; the solid solution is more stable than the corresponding mixture of the end members. The mixing enthalpy curve shows two minima, suggesting the presence of two phenomena. It may be assumed that one of them is related to the anionic substitution and the other to the cationic one, each one giving a peculiar contribution to the measured mixing enthalpy. As with alkali-earth-substituted Ca-fluorapatite [23], it may be also suggested that the presence of two minima in mixing enthalpy curve is related to the preferable occupancy of one of the two cationic sites. Reitveld X-ray investigation and calorimetric measurements on other britholites will provide more information on the substitution mechanism. The latest measurements are actually performed on lanthanum britholites and will be submitted in forthcoming paper.

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