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Standard enthalpies of formation and mixing of hydroxy- and fluorapatites[☆]

M. Jemal *, A. Ben Cherifa, I. Khattech, I. Ntahomvukiye

Faculté des Sciences, Département de chimie, Campus universitaire, 1060 Tunis, Tunisia

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Abstract

Ca, Sr, Cd and Pb hydroxy- (Hap) and fluorapatites (Fap) and (caCd) and (CaPb) Hap have been synthesized and spectroscopically and chemically characterized, then dissolved in 9 wt% nitric acid using an isoperibol calorimeter. Dissolution of secondary products and other entities lead to standard enthalpies of formation of single-cation products. These values are, respectively, −13.305, −13.373, −8.648 and −8.261 kJ mol^{-1} for Haps, and −13.545, −13.604, −8.795 and −8.529 kJ mol^{-1} for Faps. Replacement of OH by F decreases the lattice volume and increases the stability of the structure. In the Hap and Fap series, the smaller the lattice volume, the worse the stability, except for Pb products. Dissolution of solid solution Haps leads to enthalpies of mixing of the limit products. The results are in agreement with the preferable occupancy of site II by Cd or Pb up to 40% and 45%, respectively.

Keywords: Fluorapatite; Heat of mixing; Heat of solution; Hydroxyapatite

1. Introduction

Apatites form a well-known family of phosphates crystallizing in the hexagonal system $P6_3/m$. The majority of apatites are calcium compounds. Hydroxyapatites form the inorganic phase of calcified tissues, whereas fluorapatites are the mineral of phosphate ores.

In spite of their abundance, thermochemical studies on apatites have not received much attention. According to Vieillard and Tardy's compilation [1], the most recent

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* Corresponding author.

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research concerning the pure products date from the beginning of the 1970s, but there are no thermochemical data on the solid solutions.

The present paper deals with the synthesis and characterization of Ca, Sr, Cd and Pb pure hydroxy- and fluorapatites and of $Ca_{10-x}M_x(PO_4)_6(OH)_2$ where M is Cd and Pb. These products were dissolved in 9 wt% nitric acid solution, and the enthalpy of formation or mixing deduced.

2. Experimental

2.1. Synthesis procedure

Single-cation apatites

CaHap was prepared either by rapid neutralization of a saturated $Ca(OH)_2$ solution by H_3PO_4[2], or by a "reverse method" which consists of a dropwise addition of a diammonium phosphate into a $Ca(NO_3)_2$ solution at pH 9. The solid was then ignited at 900°C in flowing water vapor [3, 4].

SrHap, CdHap and PbHap were prepared by a "direct method" which consists of dropping, over 3 h, a solution of metal nitrate into a boiling solution of diammonium phosphate at a pH in the range 9–11.5. The solid was then ignited at 700, 600 or 400°C, respectively, in flowing water vapor [5–7]

Calcium, strontium and lead fluorapatites were also synthesized by the direct method, slightly modified by adding ammonium fluoride to the phosphate solution. After washing, the solid was ignited in vacuum or in inert gas flow at 900 or 400°C [3, 4]. It was not possible to synthesize CdFAp either by this method or by solid–solid reaction [8].

Solid solution

(CaCd)Hap and (CaPb)Hap were synthesized according to the procedure described previously by dropwise mixing of a solution of the two corresponding nitrates. Varying the proportion of nitrates in the mixture allows the formula of the solid to be modified over the whole range of composition.

The purity of each product was checked by X-ray diffractometry, IR spectroscopy and chemical analysis.

2.2. Calorimetric technique

The calorimetric device was of isoperibol type, described previously in detail [3]. The sensor was a thermistor of 2002 Ω at 25°C, forming one of the four arms of a Wheatstone bridge. The balance voltage was amplified, then reocrded versus time. The device was also provided with a stirrer and a resistance for calibration by Joule effect. The solid to be dissolved, or liquid to be diluted, was carefully injected at the botton of a thin-walled sphere formed at one of the extremities of a pyrex tube (external diameter, 5 mm). After a period during which the baseline did not move significantly from the horizontal, the reaction was started by breaking the globe with a thin glass rod. This induces a shift, the magnitude of which depends on the heat effect involved. After about 2 min, the reaction stops, and the baseline becomes parallel to the earlier one.

The apparatus was tested by a well-known calibration reaction, namely the dissolution of trihydroxymethylaminomethane (or TRIS) in HCl solution (0.1 mol per kg solution). Eight samples weighing from 40 to 200 mg and accurately measured were progressively dissolved in 350 ml solution. The data were processed by a least-squares method suggested by Sands [9] and Pattengill and sands [10], in which the statistical weight associated with each result is inversely proportional to the corresponding variance. The enthalpy deduced (-29.6 ± 0.2 kJ mol^{-1}) is in good agreement with those found by other authors (-29.765 ± 0.004) [11] (-29.773 ± 0.008) [12]. At the end of successive additions, the TRIS concentration did not exceed 0.03 mol l^{-1}. The sensitivity of the device does not allow the dilution effect resulting from the increase in solute concentration to be detected.

3. Results and discussion

3.1. Enthalpy of solution

After calibration by Joule effect (3 runs), dissolution of apatite samples was carried out as with TRIS. Samples of solid were dissolved in 350 ml of 9wt% HNO_3 solution. The results are shown in Tables 1 and 2.

3.2. Standard enthalpy of formation

Determination of the enthalpies of formation of single-cation apatites was carried out by imagining a succession of reactions the “summation” of which leads to $\Delta_{\mathrm{for}}H^{\ominus}(T_0)$ of the product under discussion. These successions involve several steps, some of which are dissolution reactions, others being dilution processes in the same acid solution. These reactions were achieved under the same conditions.

As the dissolution implies nitric acid, one of the main steps in each succession will be the dissolution of metallic nitrate. If $M(NO_3)_2 \cdot nH_2O$ refers to the formula of the latter and $HNO_3 \cdot 35.35H_2O$ to the starting solvent, the general scheme for hydroxyapatite would be

$$\{10M(NO_3)_2 + 6H_3PO_4 + 2H_2O\}_{\mathrm{in\ sln}} \rightarrow M_{10}(PO_4)_6(OH)_2(s) + 20\{HNO_3\}_{\mathrm{in\ sln}} \tag{1}$$

$$10M + 10N_2 + 5[6+n]O_2 + 10nH_2 \rightarrow 10[M(NO_3)_2 \cdot nH_2O](s) \tag{2}$$

$$10[M(NO_3)_2 \cdot nH_2O](s) + \{\mathrm{sln}\} \rightarrow 10\{M(NO_3)_2 + nH_2O\}_{\mathrm{in\ sln}} \tag{3}$$

$$20[HNO_3 \cdot 35.35H_2O] \rightarrow 10H_2 + 10N_2 + 30O_2 + 707H_2O \tag{4}$$

$$9H_2 + 6P + 12O_2 + (6 \times 0.756)H_2O \rightarrow 6\{H_3PO_4 \cdot 0.756H_2O\} \tag{5}$$

$$6\{H_3PO_4 \cdot 0.756H_2O\} + \{\mathrm{sln}\} \rightarrow \{6H_3PO_4 + 4.536H_2O\}_{\mathrm{in\ sln}} \tag{6}$$

Table 1
Enthalpies of solution of hydroxy and fluorapatites in $HNO_3 \cdot 35.35H_2O$

Expt. No.	m/g	ε/(J mm^{-1})	D/mm	$\Delta_{sol}H$/J	$\Delta_{sol}H$/(J g^{-1})
1	0.17789	−0.307	206.5	−63.374	−356.254
2	0.13016	−0.319	148.0	−47.155	−362.281
3	0.04365	−0.315	51.0	−16.046	−367.617
4	0.07454	−0.316	85.5	−26.991	−362.099
5	0.15703	−0.317	182.0	−57.645	−367.093
6	0.09789	−0.319	111.0	−35.459	−362.231
7	0.05834	−0.320	65.5	−20.951	−359.124
8	0.11701	−0.319	133.0	−42.487	−363.103
		$\langle \Delta_{sol}H(Ca_{10}(PO_4)_6(OH)_2) \rangle = -326.87 \pm 1.70$ J g^{-1}			
1	0.07103	−0.308	60.5	−18.663	−262.751
2	0.13580	−0.314	111.0	−34.850	−256627
3	0.16736	−0.313	139.0	−43.463	−259.699
4	0.08119	−0.312	68.0	−21.188	−260.974
5	0.10627	−0.317	88.0	−28.061	−264.051
8	0.15964	−0.306	132.0	−40.374	−252.906
9	0.18214	−0.313	154.0	−48.157	−264.397
		$\langle \Delta_{sol}H(Sr_{10}(PO_4)_2(OH)_2) \rangle = -258.96 \pm 2.08$ J g^{-1}			
1	0.13594	−0.309	80.5	−24.874	−182.975
2	0.16023	−0.309	91.0	−28.156	−175.723
3	0.06173	−0.312	35.0	−10.910	−176.734
4	0.24602	−0.309	142.0	−43.847	−178.224
5	0.11116	−0.309	64.0	−19.789	−178.019
6	0.20080	−0.309	116.5	−35.997	−179.269
7	0.17775	−0.310	104.0	−32.222	−181.276
		$\langle \Delta_{sol}H(Cd_{10}(PO_4)_6(OH)_2) \rangle = -179.11 \pm 0.98$ j g^{-1}			
1	0.57741	−0.313	80.0	−25.057	−43.395
2	0.43535	−0.312	61.0	−19.019	−43.686
3	0.54056	−0.314	75.0	−23.538	−43.543
4	0.51433	−0.310	72.0	−22.287	−43.333
6	0.79476	−0.310	113.5	−35.201	−44.291
7	1.00069	−0.315	138.0	−43.486	−43.456
		$\langle \Delta_{sol}H(Pb_{10}(PO_4)_6(OH)_2) \rangle = -43.41 \pm 0.21$ J g^{-1}			
1	0.18739	−0.326	111.0	−36.202	−193.190
2	0.07018	−0.326	42.5	−13.861	−197.507
3	0.13363	−0.329	78.0	−25.651	−191.957
4	0.21049	−0.322	126.0	−40.620	−192.976
5	0.10181	−0.326	61.0	−19.820	−195.285
6	0.17859	−0.326	108.0	−35.780	−196.978
7	0.15554	−0.328	91.5	−30.053	−193.215
		$\langle \Delta_{sol}H(Ca_{10}(PO_4)_6F_2) \rangle = -195.68 \pm 1.01$ J g^{-1}			
1	0.11762	−0.304	59.0	−17.915	−152.312
2	0.15263	−0.303	75.0	−22.700	−148.729
3	0.20153	−0.306	98.0	−29.965	−148.685
4	0.17508	−0.312	80.0	−24.947	−142.487
7	0.26203	−0.299	137.0	−41.019	−156.544

Table 1 *(continued)*

Expt. No.	m/g	ε/(J mm^{-1})	D/mm	$\Delta_{sol}H$/J	$\Delta_{sol}H$/(J g^{-1})
8	0.23058	−0.307	116.5	−35.785	−155.196
		$\langle\Delta_{sol}H(Sr_{10}(PO_4)_6)F_2\rangle = -150.72 \pm 1.79$ J g^{-1}			
1	0.47864	−0.293	120.0	−35.208	−73.559
2	0.36029	−0.296	92.0	−27.226	−75.568
5	0.31259	−0.296	79.0	−23.382	−74.799
6	0.34178	−0.303	82.0	−24.875	−72.781
7	0.37574	−0.298	92.5	−27.564	−73.360
8	0.32792	−0.297	83.0	−24.654	−75.182
		$\langle\Delta_{sol}H(Pb_{10}(PO_4)_6F_2)\rangle = -74.96 \pm 0.73$ J g^{-1} [a]			

Key: ε is the mean calibration constant; D is the shift recorded between the two base lines (see text).

[a] This value was determined by dissolving the product in ($HNO_3 \cdot 2.86H_2O$).

Table 2
Standard enthalpies of solution of hydroxy- and fluorapatites in $HNO_3 \cdot 35.35H_2O$

	CaHap	SrHap	CdHap	PbHap	CaFap	SrFap	PbFap
$\Delta_{sol}H^\ominus(298)$/ (kJ mol^{-1})	−364.3 ±1.7	−383.3 ±3.1	−309.5 ±1.7	−116.2 ±0.6	−197.3 ±1.2	−223.7 ±2.6	−200.9 ±1.9 [a]

[a] Determined by dissolving the product in ($HNO_3 \cdot 2.86H_2O$).

$$\{(10n + 2.536)H_2O\}_{\text{in sln}} \rightarrow (10n + 2.536)H_2O + \{\text{sln}\} \tag{7}$$

$$(10n - 2)H_2O \rightarrow (10n - 2)H_2 + (5n - 1)O_2 \tag{8}$$

$$10M + 6P + 13O_2 + H_2 \rightarrow M_{10}(PO_4)_6(OH)_2(s)$$

For fluorapatites, the first step is the dissolution of apatite (1) (see below), and steps (2), (3), (4) and (5) remain the same. However, one has to take into account the involvement of hydrogen fluoride, so two other steps must be considered, (9) and (10). Finally, steps (7) and (8) in the Hap scheme have to be replaced by steps (7′) and (8′) in order to balance the "summation". These additional and replacement steps are successively listed below

$$\{10M(NO_3)_2 + 6H_3PO_4 + 2HF\}_{\text{in sln}} \rightarrow M_{10}(PO_4)_6F_2(s) + 20\{HNO_3\}_{\text{in sln}} \tag{1′}$$

$$\{(10n + 7.952)H_2O\}_{\text{in sln}} \rightarrow (10n + 7.952)H_2O + \{\text{sln}\} \tag{7′}$$

$$10nH_2O \rightarrow 10nH_2 + 5nO_2 \tag{8′}$$

$$2(HF \cdot 1.708H_2O) + \{\text{sln}\} \rightarrow \{2HF + 3.416H_2O\}_{\text{in sln}} \tag{9}$$

$$H_2 + F_2 + 3.416H_2O \rightarrow 2[HF \cdot 1.708H_2O] \tag{10}$$

Standard enthalpies of formation of metallic nitrates (step (2) are taken from the literature [13–15]. They are listed together with standard enthalpies of solution of these nitrates (step (3)) in Table 3.

Standard enthalpies of formation for various entities (from the literature) and enthalpies of dilution of H_2O (7, 7′) and of concentrated H_3PO_4 (6) and HF (9) solutions are listed in Table 4.

Taking into account all these data, one can calculate the enthalpies of formation of the various single-cation apatites. Table 5 gathers these enthalpies in addition to lattice parameters and the volume and ionic radii of cations.

Table 3
Standard enthalpies of formation and standard enthalpies of solution of metal nitrates in $HNO_3 \cdot 35.35H_2O$

	$Ca(NO_3)_2 \cdot 4H_2O$	$Sr(NO_3)_2$	$Cd(NO_3)_2 \cdot 4H_2O$	$Pb(NO_3)_2$
$\Delta_{for}H^{\ominus}(298)$/kJ mol^{-1}	−2132.33	−978.20	−1650	−447.19
$\Delta_{sol}H^{\ominus}(298)$/kJ mol^{-1}	33.3 ± 0.2	13.9 ± 0.1	21.55 ± 0.25	20.8 ± 0.1

Table 4
Standard enthalpies of formation and enthalpies of dilution for H_2O, H_3PO_4 and HF solutions

	H_2O	$HNO_3 \cdot 35.35H_2O$	$H_3PO_4 \cdot 756H_2O$	$HF \cdot 1.708H_2O$
$\Delta_{for}H^{\ominus}(298)$/kJ mol^{-1}	−285.81	−206.82	−1271.85	−316.85
$\Delta_{dil}H^{\ominus}(298)$/kJ mol^{-1}	≈0	–	−7.87 ± 0.04	−4.52 ± 0.04

Table 5
Standard enthalpies of formation and lattice parameters and volumes for hydroxy- and fluorapatites

M (Ion r/Å)	$M_{10}(PO_4)_6(OH)_2$				$M_{10}(PO_4)_6F_2$			
	$\Delta_{for}H^{\ominus}(298)$/ (kJ mol^{-1})	a/Å	c/Å	V/Å^3	$\Delta_{for}H^{\ominus}(298)$ (kJ mol^{-1})	a/Å	c/Å	V/Å^3
Ca (0.99)	−13,305[a]	9.425	6.885	530	−13,545	9.370	6.881	524
Sr (1.16)	−13,373	9.762	7.283	602	−13,604	9.714	7.289	596
Cd (0.97)	−8,648	9.334	6.647	502 Ref. [19]	−8,795[b]	9.30	6.63	497 Ref. [20]
Pb (1.21)	−8,261	9.877	7.426	628	−8,529	9.75	7.30	602 Ref. [20]

[a] Values from literature are in the range −13.648– −13.750 kJ mol^{-1} [16–18].

[b] This value was obtained by extrapolating the line giving the formation enthalpy of (CaCdFap) solid solution versus composition, to pure Fap.

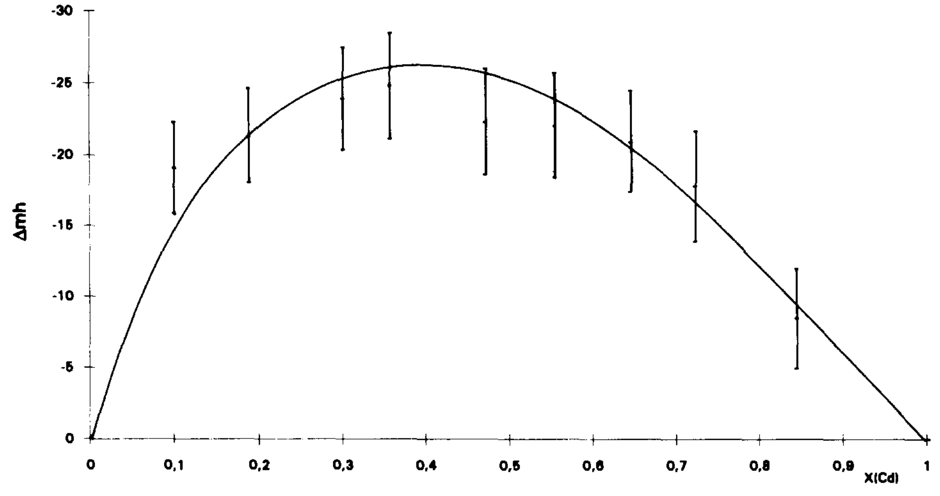

Fig. 1. Standard mixing enthalpy of (CaCd)Hap solid solutions.

It should be noticed that for the same single cation, replacement of OH by F decreases the formation enthalpy by −240, −231, −148 and $-268\,\mathrm{kJ\,mol^{-1}}$ respectively, and so contributes to better stabilization of the structure. However, disregarding the heavy metal products, the smaller the ionic radius of the cation, the smaller the lattice volume, and the worse the stability of the structure.

3.3. Solid solution

Dissolution of Fap or Hap solid solutions provides the mixing enthalpy of the limit products. This is possible by subtracting the heat of solution of the solid solution from the enthalpies of dissolution of the limit products, according to

$$\Delta_{m}H^{\ominus}(T_0) = X_1\Delta_{sol}H_1^{\ominus}(T_0) + X_2\Delta_{sol}H_2^{\ominus}(T_0) - \Delta_{sol}H_{ss}^{\ominus}(T_0)$$

Fig. 1 shows the variation in the standard mixing enthalpy of (CaCd) and (CaPb) hydroxy solid solutions. One can notice the non-symmetrical shape of the (CaCd) curve which seems to have a minimum at about 40% Cd. This result, which was not observed on the lattice volume curve (not shown), is in agreement with the non-statistical distribution of Cd in the lattice. Cd atoms begin to subsitute for Ca, preferably at site II, and the discrepancy of Cd atom distribution in that site from the statistical distribution increases on increasing the ratio Cd/(Ca + Cd) up to the value of 0.4 [19]. A similar conclusion can be deduced from the (CaPb)Hap results, Figs. 2a and 2b, with the difference that in the latter case preferable occupancy of site II by lead atoms is attested by X-ray diffractometry (Fig. 2a and Ref. [21]) and confirmed by thermochemical results (Fig. 2b). This preference goes to 45% Pb atoms [21].

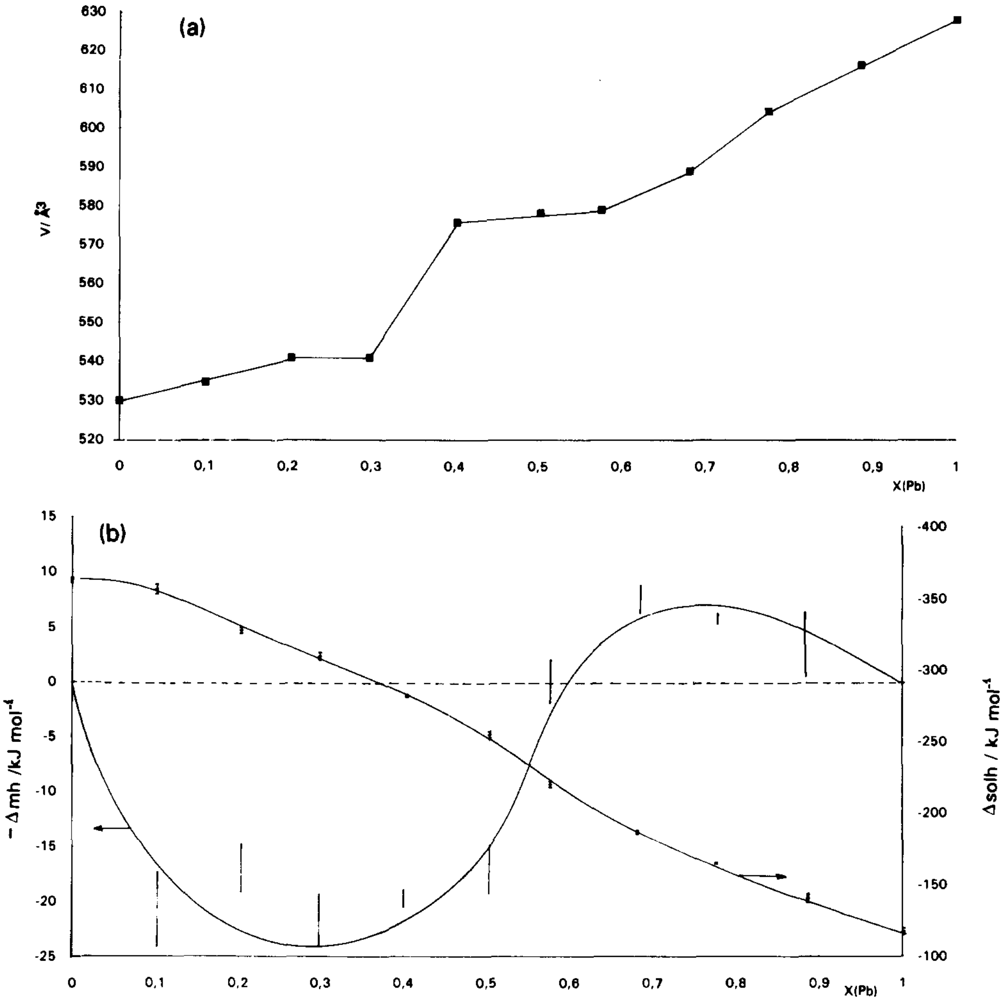

Fig. 2a. Lattice volume of (CaPb)Hap solid solutions. 2b. Standard enthalpies of solution and mixing enthalpy for (CaPb)Hap solid solutions.

References

[1] P. Vieillard and Y. Tardy, in J.O. Nriagu and P.B. Moore (Eds.), Phosphate Minerals, Springer Verlag, New York, 1984.
[2] A. Ben Cherifa, I. Khattech and M. Jemal, Ann. Chim., 13 (1988) 57.
[3] A. Ben Cherifa, Thèse de Spécialité, Université de Tunis II, 1988. A. Ben Cherifa, B. Omezzine and M. Jemal, J. Soc. Chim. Tun., 11 (1984) 53.
[4] A. Ben Cherifa, S. Somrani and M. Jemal, J. Chim. Phys., 88 (1991) 1893.
[5] I. Khattech, J.L. Lacout and M. Jemal, Adv. Mater. Res., submitted.
[6] A. Ben Cherifa, M. Jemal, A. Nounah and J.L. Lacout, Thermochim. Acta, 237 (1994) 285.
[7] I. Ntahomvukiye, I. Khattech and M. Jemal, Ann. Chim. Fr., in press.

[8] A. Ben Cherifa, A. Nounah, J.L. Lacout and M. Jemal, Adv. Mater. Res, submitted.
[9] D.E. Sands, J. Chem. Educ., 51 (7) (1974) 473.
[10] M.D. Pattengill and D.E. Sands, J. Chem. Educ. 56, 4 (1976) 244.
[11] N. Nichols, R. Skold and I. Wandsö, Chem. Scr., 9 (1979) 110.
[12] C.E. Vanderzee, D.H. Waugh, N.C. Haas and D.A. Wigg, J. Chem. Thermodyn., 12(1980) 27.
[13] Handbook of Chemistry and Physics, 66th edn., CRC Press Edition, USA, 1985–86.
[14] R.H. Perry and D.W. Green (Eds.), Perry's Chemical Engineers' Hanmdbook, 6th edn., International Student Edition, McGraw Hill, NY. USA, 1984.
[15] N.B.S. Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
[16] A.J. Gottschall, J. South Africa, 11 (1958) 45.
[17] F.G. Smirnova and V. Illarionov, J. Inorg. Chem., 7 (1962) 920.
[18] J.K. Jacques, J. Chem. Soc., (1963) 3820.
[19] A. Nounah, Thèse de Doctorat, I.N.P Toulouse, 1992.
[20] E.R. Friedler and F.A. Hummel, Am. Mineral, 55 (1970) 170.
[21] A. Bigi, A. Ripamonti, S. Bruckner, M. Gazzano, N. Roveri and A. Thomas, Acta Crystallogr. Sect. B, 45 (1989) 247.