

Synthesis from solutions and properties of various metal fluorides and fluoride salts

Gwenaël Corbel, Georges Courbion, Françoise Le Berre, Marc Leblanc*,
Jean-Marc Le Meins, Vincent Maisonneuve, Nicolas Mercier

Laboratoire des Fluorures, UMR, 6010, Faculté des Sciences, Université du Maine, Avenue Olivier-Messiaen, 72085 Le Mans Cedex 09, France

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Abstract

Parts of the recent advances in the search of new fluorides or fluoride salts, at the Laboratoire des Fluorures in Le Mans, are presented. Hydrothermal synthesis in sub-critical or super-critical conditions is mainly used to obtain rare earth (RE), Al, Ga, In or 3d transition fluorides or fluoride salts (borates, carbonates, phosphates or silicates). Open structures are obtained by low temperature crystallisation from solutions (δ -(H₃O)RE₃F₁₀·xH₂O) and, probably, by decomposition of hybrid organic–inorganic fluorides D-MF₅ (D = diprotonated aliphatic diamine), prepared by micro-wave heating of the solutions. Non-centrosymmetric phases are evidenced in fluoride carbonates and fluoride borates: K₄RE₂(CO₃)₃F₄ and M₂(BO₃)(OH)_{0.75}F_{0.25}; the magnetic properties of several iron fluoride phosphates are found to be governed by super or super-superexchange interactions. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fluoride synthesis started in Le Mans with Prof. R. De Pape in 1965. Solid state experiments were first performed and numerous compounds of the now classical fluoride families were investigated [1]. Simultaneously, the chloride flux method [2] was developed in order to grow crystals for analyses in physics: vibrational modes, resonance, etc.

Later, hydrothermal synthesis in super-critical water was shown to be efficient to grow metastable phases, anhydrous or hydrated [3]. Iron fluorides were particularly studied and the concept of magnetic frustration established after the structural and magnetic characterisation of ordered mixed cation or mixed valence fluorides [4]. Hydrothermal synthesis was also used in sub-critical conditions and mixed anion fluorides were evidenced: oxide–fluorides [5], fluoride phosphates with hybrid organic–inorganic frameworks [6].

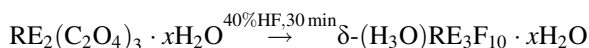
The recent trends in fluoride synthesis involve mainly the low temperature crystallisation from solutions with the hydrothermal method or with micro-wave heating. Fluorides and mixed anion fluorides (fluoride salts), obtained in sub-critical or super-critical solvents, are mainly concerned.

Open structures or UV transparent materials are actively sought; several physical properties, such as ionic conductivity and magnetism, are investigated.

In this paper, the original phases which were studied in Le Mans will be mainly discussed. Rare earth (RE), group III and 3d transition metal fluorides will be presented separately.

2. Rare earth fluorides

A new family of hydrated hydronium fluorides was discovered in 1997 [7,8]: the δ -(H₃O)RE₃F₁₀·xH₂O compounds, together with the ammonium, potassium and rubidium phases. Their crystallisation occurs for the heavy RE cations and Y³⁺ from room temperature to a maximum temperature which increases with the element number (Table 1). One of the preparation reactions is



The cubic structure, derived from a diamond type stacking of octahedral RE₆F₃₂ units, built from REF₈ square antiprisms, presents large cavities surrounded by ten RE₆F₃₂ units (Fig. 1). A zeolitic behaviour of water molecules and cation exchange properties are observed.

* Corresponding author. Tel.: +33-2-4383-3560; fax: +33-2-4383-3506.
E-mail address: marc.leblanc@univ-lemans.fr (M. Leblanc).

Table 1
Synthesis temperature (°C) of rare earth or yttrium fluorides by hydrothermal method or solid state technique

Fluorides/rare earth element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Reference
δ -(H ₃ O)RE ₃ F ₁₀ ·xH ₂ O												30	50	80	100	30	[7]
γ -ThRE ₂ F ₁₀ ·xH ₂ O										50	30	75		85		85	[9]
RE(CO ₃)F bastnaesite	700	700	700	700			700										
BaRE(CO ₃) ₂ F huangoite	700	700	700	700		700	700										[11]
Ba ₃ RE ₂ (CO ₃) ₃ F ₂ cebaite	700	700	700	700		700	700										[11]
Ba ₂ RE(CO ₃) ₃ F zhonghuacerite	700	700	700	700		700											[12]
Ba ₂ RE(CO ₃) ₂ F ₃							700	700			700				700		[10]
Na ₃ RE ₂ (CO ₃) ₄ F	700		700														[14]
Na ₂ RE(CO ₃)F ₃							350										[17]
KRE(CO ₃)F ₂							700	700									[19]
K ₄ RE ₂ (CO ₃) ₃ F ₄	180	180	700	700		700	700	700									[20]
RE ₃ (BO ₃) ₂ F ₃ (solid state)						900	900	850									[26]
Na _{1.3} RE _{8.7} (SiO ₄) ₆ O _{1.4} F _{0.6}		700															
Na ₂ MgRE ₂ (Si ₄ O ₁₂)F ₂						700	700	700									[28]

Attempts to produce a neutral network M₃F₁₀ by the substitution of RE³⁺ and alkaline A⁺ or H₃O⁺ by Th⁴⁺ lead to new cubic phases γ -ThRE₂F₁₀·xH₂O (RE = Ho, Er, Yb), which present also a zeolitic behaviour of water molecules [9].

Together with monazite, bastnaesite is a very important mineral for rare earth resources. In spite of this economical interest, few families of fluoride carbonate minerals had been discovered and accurately described before we started in 1991. Since then, the hydrothermal method in super-critical conditions proved to be very efficient to grow crystals and to evidence new structural families [10–21].

A list of these rare earth fluoride carbonates is given in Table 1. Most of the phases exist for the light (and large) RE³⁺ cations and only one structure type, Ba₂RE(CO₃)₂F₃,

is found for heavy RE³⁺ cations. Four of these families were known minerals (their names are indicated) and a new mineral lukechangite-(Ce), ideally Na₃Ce₂(CO₃)₄F, was discovered [22] after our synthesis and description of Na₃La₂(CO₃)₄F. The crystal structures of huangoite, cebaite and zhonghuacerite are now revised.

Apart from bastnaesite and Ba₂RE(CO₃)₂F₃, fluoride carbonates can be described from the stacking of dense, lacunar or sheared infinite “flat-lying” carbonate layers [23] (Fig. 2); the resulting structural correlations are discussed [21]. A polar orientation of one C–O bond of the carbonate groups implies non-centrosymmetry and large second harmonic generation coefficients. Such a condition is fulfilled in the K₄RE₂(CO₃)₃F₄ family. In this last structure, RE³⁺ cations adopt a ninefold co-ordination (F + 6O + 2F) (Fig. 3); they are surrounded by three carbonate groups of the carbonate layer planes. Similar arrangements are curiously observed in Ce⁴⁺ oxycarbonate K₄Ce(CO₃)₃O·2H₂O [24] and Ce⁴⁺ peroxy-carbonate K₄Ce(CO₃)₃O₂·2H₂O [25]. K₄Ce(CO₃)₃O·2H₂O is prepared at low temperature in sub-critical conditions.

Triangular groups are also found in borates, which present frequently, a good transparency for UV radiations. Only one structural family was evidenced for rare earth cations, RE₃(BO₃)₂F₃ [26]. The synthesis is achieved in the solid state and a luminescence study of Eu₃(BO₃)₂F₃ indicates an anionic disorder between BO₃³⁻ and 3F⁻; the formula is better expressed by Eu₃(BO₃)_{2+x}F_{3-3x} [27].

Non-centrosymmetry is also generated with a polar orientation of tetrahedral groups. Consequently, fluoride silicates were investigated. Hydrothermal experiments lead frequently to the well known apatite type and only one new structural family appears: Na₂MgRE₂(Si₄O₁₂)F₂ [28]. It is interesting to note that the Ce³⁺ oxide fluoride apatite Na_{1.3}Ce_{8.7}(SiO₄)₆(O_{1.4}F_{0.6}) (unpublished results) is stable in super-critical conditions while this phase was not obtained by solid state reaction [29], as a reason of the oxidation of Ce³⁺ to Ce⁴⁺ at high temperature.

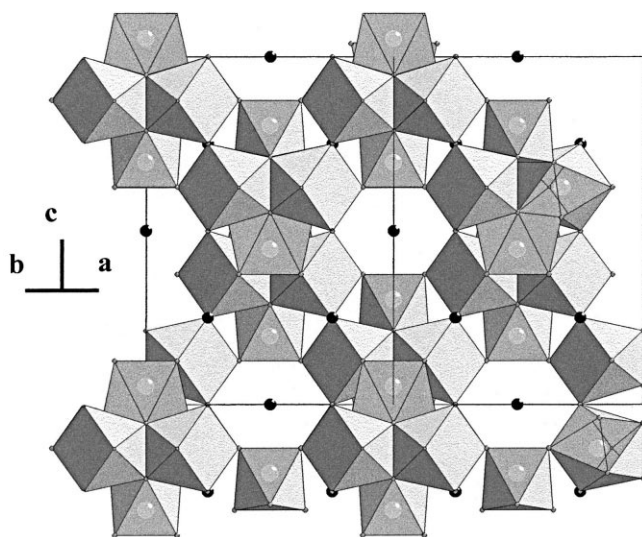


Fig. 1. [1 1 0] projection of the structure of (H₃O)Yb₃F₁₀·H₂O. For sake of clarity, water molecules in the tunnels are omitted.

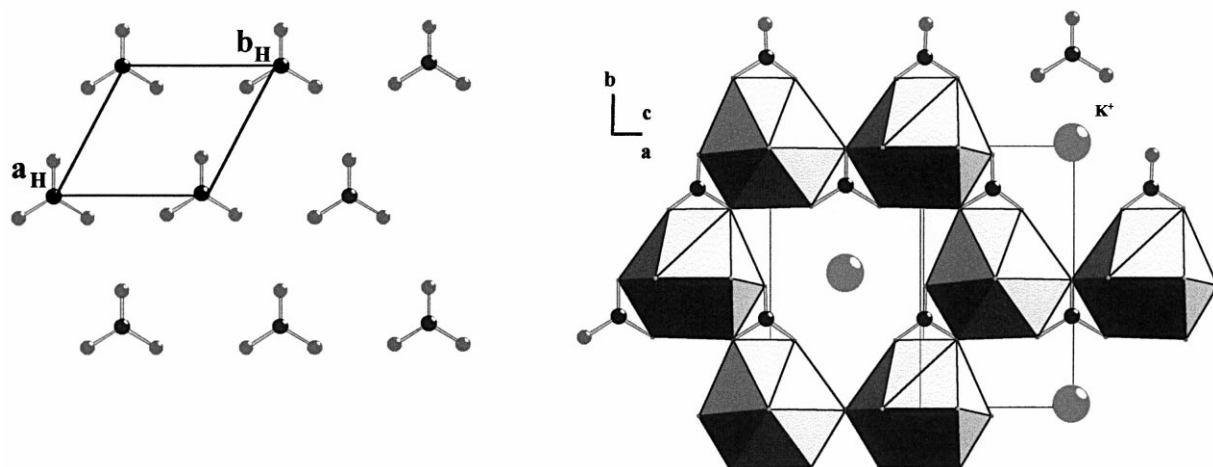


Fig. 2. “Flat-lying” layer of carbonate groups (left) together with K^+ cations and RE^{3+} co-ordination polyhedra in $K_4RE_2(CO_3)_3F_4$ (right).

3. Al, Ga, In and main group transition metal fluorides

The main interest of the work on group III metals and 3d transition metals concerns the evidence of the first 3d metal fluoride carbonates [13] and the synthesis of hybrid organic–inorganic fluorides by a promising micro-wave heating technique [30]. The experimental temperatures are given in Tables 2 and 3. The elaboration of the fluoride phosphates $Na_2M_2(PO_4)_2F_3$ [31] by various methods will be also mentioned and the importance of the solvent composition in the hydrothermal route will be emphasised.

3.1. Divalent M^{II} fluorides

Super-critical conditions and large fluoride concentration in the solution favour the crystal growth of a new class of fluoride carbonates which involves the 3d transition metals. Two structural types appear, $BaCu(CO_3)F_2$ [13,18] (Table 2) and $KCu(CO_3)F$ [15]. $CuCO_3$ layers, separated by BaF_2 or KF sheets, are found in both phases, resulting in a strong anisotropy of the indices of refraction.

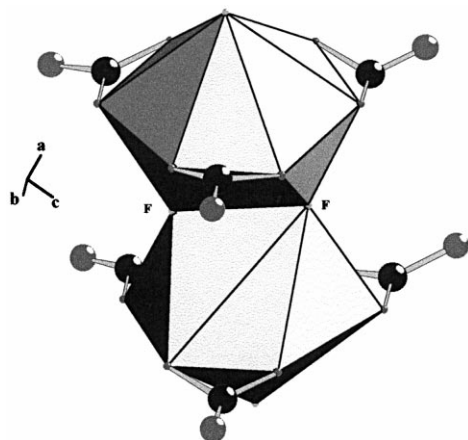


Fig. 3. Connection of two RE^{3+} co-ordination polyhedra by F–F edges in $K_4RE_2(CO_3)_3F_4$.

Similar layers of “flat-lying” triangles are found in $Zn_2(BO_3)_5(OH)_{0.75}F_{0.25}$ [32], crystallised in sub-critical conditions (Table 2 and Fig. 4). As a consequence, $KCu(CO_3)F$ and $Zn_2(BO_3)(OH)_{0.75}F_{0.25}$ are non-centrosymmetric. Until now, the growth of large crystals of fluoride borates is impossible; microcrystalline powders of $Zn_2(BO_3)(OH)_{0.75}F_{0.25}$ (Table 2) and $M_3(BO_3)(OH, F)_3$ nocerines only are obtained, at any temperature between 180 and 700°C.

3.2. Trivalent M^{III} fluorides

Micro-wave heating of solutions was originally used for mineralisation and, later, for the crystallisation of oxide powders; a recent review paper is given in [33]. We have shown very recently that fluorides can be also prepared by this way. Several series of hybrid organic–inorganic fluorides are now evidenced [30,34]. Generally, experiments last for 1–4 h at 190°C in ethanol. Surprisingly, single crystals suitable for crystal structure determination can grow within this very short time of synthesis. $D \cdot MF_5$ series, together with $D_2 \cdot MF_7 \cdot H_2O$ phases (D = diprotonated aliphatic 1.6, 1.8, 1.10, 1.12 diamines and $M^{3+} = Al, Ga, V, Cr, Fe$) have been obtained (Fig. 5). Upon heating under argon atmosphere, decomposition of the $D \cdot MF_5$ compounds occurs in two steps. The intermediate hybrid phases are thought to involve the formation of Al–N bonds and are expected to be mesoporous.

It must be noted that two fluoride carbonates, $La(CO_3)F$ and $Ce(CO_3)F$, mentioned in #2 and Table 1, and the fluoride borate $Zn_2(BO_3)(OH)_{0.75}F_{0.25}$ can be obtained by this micro-wave route at 180°C in concentrated K_2CO_3 or H_3BO_3 solutions (unpublished results).

Mixed anion compounds are often of technological interest; they exhibit ferroelectricity, ionic conductivity, ... This last property is encountered in the fluoride phosphate $Na_3Al_2(PO_4)_2F_3$ in the crystalline and vitreous states [35]. Several other fluoride phosphates, including either

Table 2
Synthesis temperature of the M^{II} fluorides by hydrothermal method

Fluorides/ M^{II}	Mn	Fe	Co	Ni	Cu	Zn	Reference
KM(CO ₃)F					700		[15]
BaM(CO ₃)F ₂	700		700	700	700	700	[13]
M ₂ (BO ₃)(OH) _{0.75} F _{0.25}						180	[32]
M ₃ (BO ₃)(OH, F) ₃		350	700	250–700			

Table 3
Synthesis temperature of M^{III} fluorides by hydrothermal, solid state (S), chloride flux (F) methods or by recrystallisation from a glass (G). Aliphatic diamines are diprotonated and are symbolised by D

Fluorides/ M^{III}	Al	Ga	In	Sc	V	Cr	Mn	Fe	Reference
D-MF ₅ (micro-wave)	190		190		190	190		190	[30]
D ₂ MF ₇ ·H ₂ O (micro-wave)			190						[34]
Ba ₃ M(CO ₃)F ₇				700					[16]
Na ₃ M ₂ (PO ₄) ₂ F ₃	700 S680 F700 G500	180			630	S800		S800 F 700 G470	[31]

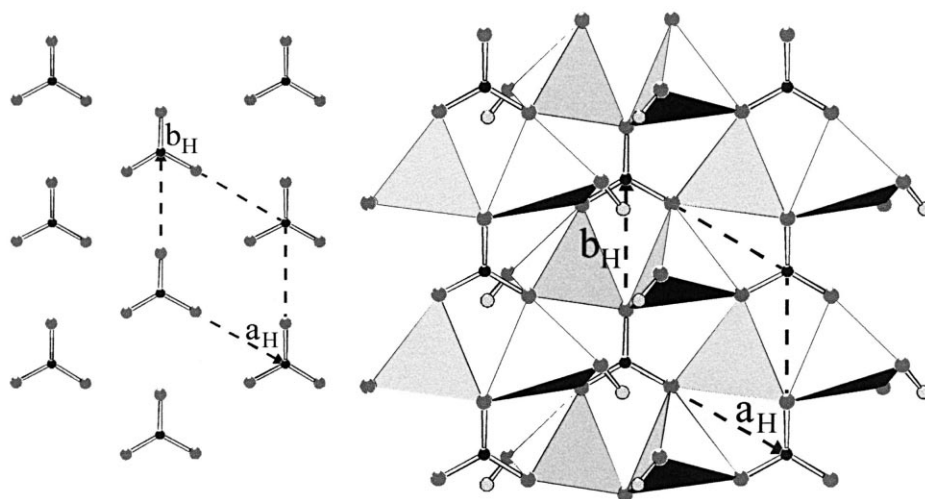


Fig. 4. Flat-lying layer of borate groups (left) together with ZnO₃(OH, F) tetrahedra in Zn₂(BO₃)(OH)_{0.75}F_{0.25} (right).

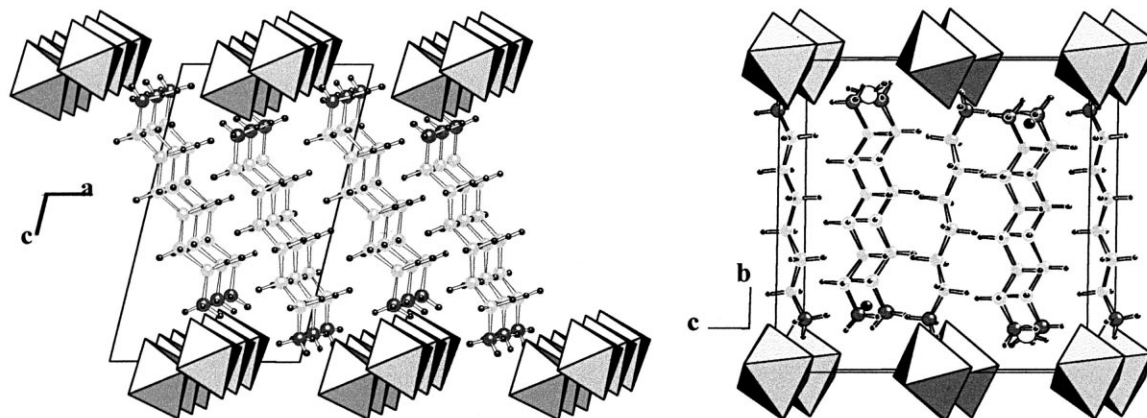


Fig. 5. Perspective view of [H₃N(CH₂)₆NH₃] \cdot AlF₅ (left) and [H₃N(CH₂)₆NH₃]₂ \cdot InF₇ \cdot H₂O (right).

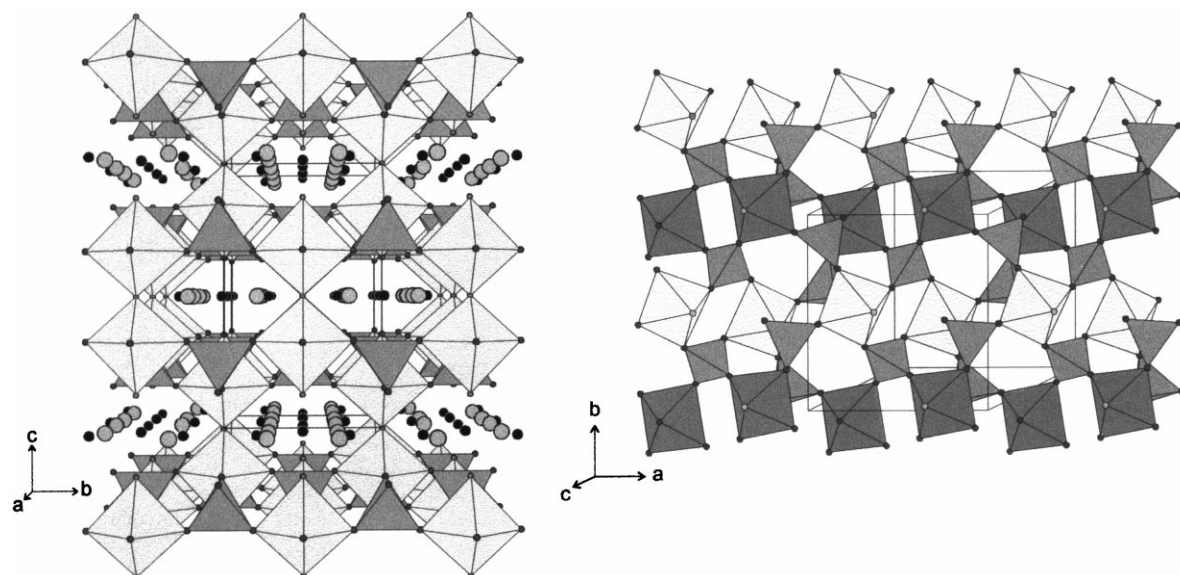


Fig. 6. Perspective view [48] of α - $\text{Na}_3\text{Al}_2(\text{PO}_4)_2\text{F}_3$ (left) and [0 0 1] projection of a layer of $\text{Sr}_2\text{Fe}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}_2$ (right).

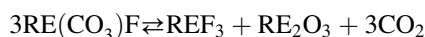
diamagnetic or paramagnetic M^{III} cations, were studied. The magnetic behaviour is governed by the cation topology and by the presence of super-superexchange interactions [36] or superexchange interactions, as observed in $\text{SrFe}(\text{PO}_4)\text{F}_2 \cdot \text{H}_2\text{O}$ [37].

Several methods of synthesis are used for the synthesis of fluoride phosphates and it is remarkable that the $\text{Na}_3\text{M}_2(\text{PO}_4)_2\text{F}_3$ phases ($\text{M}^{3+} = \text{Al}, \text{Ga}, \text{V}, \text{Cr}, \text{Fe}$) (Fig. 6) can be obtained by solid state reaction, by hydrothermal or chloride flux methods and also by recrystallisation from a glass of identical composition [31]. Nevertheless, the main synthesis route remains the high-temperature (700°C) and high-pressure (200 MPa) hydrothermal method which allows the growth of crystals suitable for X-ray diffraction. Sr^{2+} (or Ba^{2+}), Fe^{3+} in $\text{HF}-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ solutions were especially studied in hydrothermal conditions. The results clearly show the importance of the initial $\text{H}_3\text{PO}_4/\text{HF}$ molar ratio on the composition of the final products: $\text{Sr}_2\text{Fe}_2(\text{HPO}_4)(\text{PO}_4)_2\text{F}_2$ (Fig. 6), $\text{SrFePO}_4\text{F}_2$, $\text{BaFePO}_4\text{F}_2$, $\text{BaFe}(\text{P}_2\text{O}_7)\text{F}_2$ [38–42]. Extreme cases are observed, such as SrFeP_2O_7 or $\text{Sr}_2\text{Fe}_2\text{F}_{10} \cdot \text{H}_2\text{O}$. The nature of the 3d cations seems also to play an important role. In similar conditions, the results with $\text{M} = \text{Al}^{3+}$ and $\text{M} = \text{Fe}^{3+}$ are quite different [43] as a reason, probably, of the difference of the Lewis acidity. The charge of the clusters during the crystallisation process should be taken into account in order to explain the formation of the solids.

4. Conclusion

Hydrothermal or solvothermal reactions in sub-critical or super-critical conditions lead to numerous fluorides or fluoride salts (borates, carbonates, phosphates or silicates). High pressure prevents from decomposition reactions with

gas formation occurring



As a consequence, several fluoride carbonates grow at a temperature (700°C) which is much higher than their decomposition temperature ($\approx 300^\circ\text{C}$) under atmospheric pressure.

Hydrothermal synthesis implies that $\text{OH}^- \leftrightarrow \text{F}^-$ substitution occurs; however, the OH^-/F^- ratio decreases when the temperature is increased. Such a substitution was observed in $\text{Al}_2[(\text{OH})_{0.5}\text{F}_{0.5}]_6 \cdot \text{H}_2\text{O}$; the powder sample was obtained at $T < 100^\circ\text{C}$ [44–46]. Crystals of $\text{Al}_2[(\text{OH})_{0.5}\text{F}_{0.5}]_6 \cdot \text{H}_2\text{O}$ were recently obtained in super-critical conditions ($T = 700^\circ\text{C}$, $P = 2000 \times 10^5 \text{ Pa}$) from Al_2O_3 , H_3BO_3 in 5MHF (the growth temperature is much higher than the dehydration and decomposition temperatures under atmospheric pressure, 210 and 450°C , respectively) (unpublished results). The octahedral crystals are now investigated by Raman spectroscopy and compared with AlF_3 crystals grown in HF solutions at the same temperature, in order to analyse the extent of the $\text{OH}^- \leftrightarrow \text{F}^-$ substitution. It is surprising that the OH^-/F^- ratio is frequently equal to a ratio of integers: $\text{Al}_2[(\text{OH})_{0.5}\text{F}_{0.5}]_6 \cdot \text{H}_2\text{O}$, $\text{Zn}_2(\text{BO}_3)(\text{OH})_{0.75}\text{F}_{0.25}$, $\text{Na}_2\text{Eu}(\text{CO}_3)\text{F}_{2.5}(\text{OH})_{0.5}$ [47], synthesised at low temperature (180°C). Such an order was ruled out by neutron diffraction in $\text{Al}_2[(\text{OH})_{0.5}\text{F}_{0.5}]_6 \cdot \text{H}_2\text{O}$. However, this question of OH^-/F^- order deserves attention and will be examined in the near future by NMR or Raman spectroscopy.

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