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Hypothetical AlF_3 crystal structures

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Abstract

Applying a structure prediction computer programme (*GRINSP* = Geometrically Restrained INorganic Structure Prediction), the occurrence of 6-connected 3D networks was investigated, through AlF_6 octahedra exclusive corner sharing. The five known AlF_3 varieties were reproduced (α-, β-, η-, κ- and τ-AlF_3) and seven hypothetical models were predicted. Among these still to be synthesized AlF_3 phases, one can recognize two known structure types ($TlCa_2Ta_5O_{15}$, $Ba_4CoTa_{10}O_{30}$) and some easy to imagine intergrowths; however, a few others are completely unexpected, though simple. A comparison of the ab initio total energies of all the structures is provided, leading to the conclusion that the virtual models could well be viable.

Keywords: Crystal structure prediction; Inorganic; AB_3 compounds; Corner-sharing octahedra; aluminium fluorides; Monte Carlo simulation; Computer modelling; Ab initio energy calculations

1. Introduction

Contrarily to AB_2 compounds with corner-sharing tetrahedra (especially zeolites), it has been a long time since the last AB_3 structure built up from corner-sharing octahedra was disclosed. An answer to the following question may be of interest to solid state chemists: is it still possible to find new AB_3 structures of that kind? The prediction of the stoichiometry and of the bond topology (i.e., the approximate atomic arrangement) of the stable compounds was long considered as being more difficult than to calculate accurate static and dynamic properties of a crystal, once accurate atomic coordinates and cell dimensions were known [1]. However, generators of so-called structure candidates [2] are developing and improving. A fabulous inorganic example consists in the more than 1,000,000 zeolite models gathered into the hypothetical zeolites database [3–4]. Concerning organic molecules, the progress has been established by several recent blind tests [5]. An efficient theory of materials should help us to reduce the number of false structure candidates, and to establish serious databases which would include both known and virtual crystal structures, the latter being eventually confirmed. Using such databases would allow to reduce the structure determination steps to a simple identification (possibly by search-match techniques using the powder pattern) followed by a refinement. Unfortunately, a completely efficient theory is still lacking, so that we are condemned to overload databases of virtual structures with huge quantities of models that will never be confirmed. Science must go on, even with imperfect theories, so that a second database of hypothetical compounds was built in 2003 [6], including zeolites as well as other predicted oxides (phosphates, borosilicates, titanosilicates, etc.) and fluorides. This database is essentially filled in structure candidates by the Geometrically Restrained Inorganic Structure Prediction (*GRINSP*) software [7].

The aim of this work is to provide models with the AlF_3 composition, built up from AlF_6 octahedra sharing exclusively their corners, by using *GRINSP*. Three-dimensional AB_3 compounds based on corner-sharing octahedra were examined by the Automated Assembly of Secondary Building Units approach, developed by Mellot-Draznieks

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et al. [8–9], using *Cerius*2 [10] and *GULP* [11] in a sequence of simulated annealing plus minimization steps for the aggregation of large structural motifs, but no completely new structure type was predicted, apparently, and not all known structures were listed (τ-AlF_3 was lacking). From the present study, 12 different AlF_3 structure types will be described, the conditions of the simulations are discussed below.

2. Prediction conditions

The knowledge assumed in this study is limited to the Al–F, F–F and Al–Al ideal first neighbour distances, and the exclusive corner-sharing connection mode. More generally, *GRINSP* makes use of the common geometrical characteristics of a well-defined group of crystal structures (N-connected 3D nets with $N = 3, 4, 5, 6$ and possible combinations of two N values), allowing to explore the possible models, retrieving those already known (a proof of efficiency), and listing those yet to be synthesized, in a selected range of cell parameters.

Exploring AB_3 models needed 230 days of calculation on a single 2.4 GHz processor PC, 1 day per space group (SG). *GRINSP* is a Monte Carlo (MC) software, applying a pseudo-random number sequence to the heuristic solution of the structural problem. Once a SG is selected, a first Al atom is placed in a box (with cell parameters relations in agreement with the SG) whose dimensions are selected at random, at a Wyckoff position selected at random. One then checks if the model is not already fulfilling all requirements: one Al atom should have six Al first neighbours in the approximated range 3.5 ± 0.6 Å, themselves not distant outside of the range 4.2–6.7 Å, as second neighbours. The fact that distances are given a large tolerance range allows many solutions to be captured which may not correspond to regular polyhedra at this stage. In other words, the model may stay far above the local minima of interest. If the model is not already completed, a second Al atom is inserted randomly at a new (or identical) Wyckoff position, at random in the free space (delimited by the distance ranges above) in the neighbourhood of the first atom and of its equivalents, if any. Then this new model is checked again, etc., until a full agreement with the geometrical specifications is reached. If after some trials, no satisfying model is found, a new first Al will be placed, and so on. For a given set of cell parameters, 300,000 MC events were performed, and at least 20,000 sets of random cell parameters were explored for each SG. In this first step, atoms do not move (this is not a simulated annealing approach), their possible positions are tested and checked, then they are retained or not. The cell is progressively filled up to completely respect the geometrical restraints, if possible. The total number of Al atoms placed is not predetermined. For that search, the cell parameters were not larger than 16 Å (known phases have cell parameters all smaller than 13 Å).

In a second step the F atoms were added at the midpoints of the Al–Al first neighbours and it was verified by distance and cell improvements (by the MC method as well) that regular AlF_6 polyhedra could really be built, i.e., that there was a deep local minima existing close to this previously selected rough arrangement of Al atoms. The cost function allowing to establish a minimum is based on the verification of the provided ideal distances Al–F (1.81 Å), F–F (2.56 Å) and Al–Al (3.5 Å) first neighbours. The total R factor is defined by the equation:

$$R = \sqrt{[(R_1 + R_2 + R_3)/(R_{01} + R_{02} + R_{03})]},$$

where R_n and R_{0n} for $n = 1, 2, 3$ are defined by the expressions:

$$R_n = \Sigma[w_n(d_{0n} - d_n)]^2,$$

$$R_{0n} = \Sigma[w_n d_{0n}]^2,$$

where the d_{0n} values for $n = 1-3$ are the ideal first interatomic distances Al–F ($n = 1$), F–F ($n = 2$) and Al–Al ($n = 3$), whereas the d_n values are the corresponding observed distances in the structural model for these atom pairs. The selected w_n being $w_1 = 2.0$, $w_2 = 0.61$ and $w_3 = 0.23$, attributing more weight to the respect of the Al–F first distances. Models were retained if $R < 0.03$, they may need further optimizations by using bond valence rules, or energy calculation (as shown below), however, in many cases the predicted cell parameters differ by less than 3% from the real ones when the real compounds are built up from ideal polyhedra, which was the case with dense SiO_2 polymorphs or zeolites previously studied by *GRINSP* [7] and AlF_3 phases. During this second step, the atoms are moving, but no jump is allowed because a jump would break the coordinations established at the first step. This is a simple routine for local optimization. The change in the cell parameters from the rough structure candidate to the final model may be quite considerable (up to 30%). During the optimization, the original SG may not be conserved, so that the final structure is always proposed in the P1 SG, presented in a CIF file. The final choice of the real symmetry has to be done by using a programme able to detect missing symmetries, like *PLATON* [12].

One given model can be identified in different SGs with slightly different or equal R values. For the automatic recognition that a model is known or was already obtained in previous predictions, tools are needed. An algorithm for the efficient comparison of periodic structure (*CMPZ*) was recently presented [13]. The way GRINSP recognizes a structure type is by comparing the coordination sequence (CS) [14] of any model with a list of previously established ones (as well as with the other CS already stored during the current run). CS originally developed for zeolites was extended to the N-connected frameworks inside of the *GRINSP* algorithm. Only one model was retained corresponding to one structure type, selecting the model with best R value and higher symmetry.

GRINSP is available via http://www.cristal.org/grinsp/. The software is free of charge for non-profit organizations and is delivered with the Fortran source code under the GNU Public Licence. Parallelization of the code is in project.

3. Known 6-connected 3D nets, AlF_3 examples

When restricting considerations to the AB_3 stoichiometry, among the various families of structures, there is one where each A atom is connected to six others (through B atoms) so that the A atoms lie at the points of a 3D 6-connected net. Examining the existing 6-connected 3D nets, one can distinguish nine different frameworks. The first framework, and simplest of such structures corresponds, in its most symmetrical configuration, to A atoms placed at the vertex of a primitive cubic lattice, the B atoms being at the middle of the edges, and represents the structure of crystalline ReO_3, more generally named as the perovskite structure type (though perovskite is a mineral formulated $CaTiO_3$). Many of the main structure types belonging to that family characterized by 6-connected 3D nets can be found in the crystal chemistry of aluminium fluorides. The stable perovskite-like form of AlF_3 crystallizes with a rhombohedral structure, SG $R\bar{3}c$, and transforms reversibly to the cubic ReO_3-type polymorph at 725 K [15]. The rhombohedral form is referred usually as α-AlF_3. A metastable form, called β-AlF_3 is closely related to that of hexagonal tungsten bronze (HTB), a second framework in this family. The distortion leads to an orthorhombic cell with b/a ratio quite close to $\sqrt{3}$, pseudo-hexagonal, generating systematic twinning, in SG *Cmcm* [16]. This β-form transforms slowly and irreversibly to the cubic perovskite polymorph. A third framework is observed crystallizing in the cubic pyrochlore structure for which two aluminium fluoride equivalents have been reported, $Al(OH,F)_3$ [17] and η-AlF_3 [18]. The fourth framework is the tetragonal tungsten bronze (TTB) for which a κ-AlF_3 phase was described [18]. The fifth one was described only as an aluminium fluoride and named τ-AlF_3 [19] (it was later given another designation: θ-AlF_3 [18]), which is maybe the more complex structure with intrications of tetrahedra of octahedra (as in the pyrochlore structure) and infinite chains. Two other 6-connected frameworks not known with AlF_3 formula are typified by the structures of $Ca_2TlTa_5O_{15}$ [20] and $Ba_4CoTa_{10}O_{30}$ [21]. It was shown that these structures can be derived from the ReO_3 type by fourling and twinning operations [22], as well as HTB and intergrowth tungsten bronze (ITB). Many intergrowths could be imagined by increasing the number of perovskite planes which is equal to two, between two hexagonal ring regions in $TlCa_2Ta_5O_{15}$. Finally, two frameworks built up from octahedra of different sizes may be listed: $Na_4Ca_4Al_7F_{33}$ [23] with an $M_{11}F_{33}$ corner-sharing net of CaF_6 and AlF_6 octahedra, and $Rb_2NaAl_6F_{21}$ [24] with an M_7F_{21} net of NaF_6 and AlF_6 octahedra.

In a strict classification of AB_3 nets built from corner-connected ideal octahedra, Herzig and Zemann [25] retained only the perovskite, HTB and pyrochlore structure types because the representatives of TTB, and the other structures, were containing some extra-framework ions. Their comparative study in 1993 was incomplete, since τ-AlF_3 [19] published in 1992 escaped to their attention; moreover, the TTB AlF_3 free of extra-framework ion was obtained in 1995.

Table 1
Comparison of AlF_3 predicted cell parameters with observed ones

	Predicted/*observed*				R	FD	Z	N	SG	Ref	PCOD entry No.
	a (Å)	b (Å)	c (Å)	$\overline{\Delta}$(%)							
α-AlF_3 (perov)	5.111		12.504	2.59	0.0062	21.21	6	1			1000048
	4.931		*12.446*						$R\bar{3}c$	[15]	
β-AlF_3 (HTB)	6.984	12.107	7.213	0.91	0.0035	19.67	12	1			1000049
	6.931	*12.002*	*7.134*						*Cmcm*	[16]	
η-AlF_3 (pyr)	9.667			0.84	0.0046	17.71	16	1			1000017
	9.749								$Fd\bar{3}m$	[17]	
κ-AlF_3 (TTB)	11.539		3.615	1.46	0.0098	20.78	10	2			1000050
	11.403		*3.544*						$P4/mbm$	[18]	
τ-AlF_3 (or θ-)	10.210		7.241	0.48	0.0159	21.17	16	3			1000014
	10.184		*7.174*						$P4/nmm$	[19]	

$\overline{\Delta}$ (%) = average discrepancy on the cell parameters.
FD = framework density (number of Al atoms reported to a volume of 1000 Å^3).
SG = Space group of the real structure.
Z = number of AlF_3 formula per cell.
N = number of Al atoms with different coordination sequences.
R = quality factor regarding the ideal Al–F, F–F and Al–Al first neighbour interatomic distances.
Perov, perovskite; HTB, hexagonal tungsten bronze; pyr, pyrochlore; TTB, tetragonal tungsten bronze.

Table 2
AlF_3 virtual polymorphs proposed by GRINSP corresponding to known structure types

Structure type	FD	*a* (Å)	*b* (Å)	*c* (Å)	*SG*		*Z*	*N*	*R*	Ref	PCOD entry
					Starting	Final					
$TlCa_2Ta_5O_{15}$	20.67	6.992	3.607	9.539	*Pmmm*	*Pmmm*	5	2	0.0035	[20]	1300007
$Ba_4CoTa_{10}O_{30}$	21.15	9.504	13.780	3.615	*Iba2*	*Cm2m*	10	2	0.0093	[21]	1300008

Results from GRINSP for known Al/F-based 6-connected 3D nets are reported in Table 1. The atomic coordinates for these models were deposited at the Predicted Crystallography Open Database (PCOD: http://www.crystallography.net/pcod) [6] in CIF format as well as three-dimensional drawings in VRML language. The models can be obtained by using the PCOD entry number as keyword, or the formulation, cell parameters, volume, etc.

4. AlF_3 polymorphs "yet to be synthesized", predicted by GRINSP

One should treat apart structures which are not yet existing with AlF_3 formulation but are known for other compositions. Table 2 gives the cell parameters predicted by GRINSP for possible AlF_3 polymorphs adopting the structures of $Ca_2TlTa_5O_{15}$ [20] and $Ba_4CoTa_{10}O_{30}$ [21].

Up to $R<0.02$, five unknown structure types are disclosed by GRINSP which could well constitute "yet to be synthesized" AlF_3 compounds. Two of them (noted V-1, V-2) have even R values smaller than for the known metastable compound τ-AlF_3 ($R=0.0159$), and the three others (noted V-3, V-4 and V-5) present R values only slightly higher. V-1 is a simple HTB-perovskite intergrowth (Fig. 1) with one more perovskite layer than into the $TlCa_2Ta_5O_{15}$ structure type. Tetrahedra of octahedra, like in the pyrochlore or the τ-AlF_3 structure types are recognized into the V-2 model (Fig. 2), they are separated by perovskite planes, so that the structure looks like an intergrowth between pyrochlore and perovskite. The projection of the V-3 structure suggests octahedra face sharing, but it is an illusion (Fig. 3). In spite of tunnels delimited by rings of six octahedral sharing corners, this model shows the highest density of the series with $R<0.02$. The V-4 model is exclusively built up from tetrahedra of octahedra (Fig. 4), just as the pyrochlore structure type, but with a denser packing (framework densities are respectively 21.7 and 17.7 Al atoms per 1000 Å^3), so that no ring larger that four octahedra exists in V-4, nor any remarkable cavity as can be found in the pyrochlore structure. One of the reviewers identified V-4 as corresponding to the Fischer's sphere packing 6/4/*t*41 and having the RCSR symbol *why* (See http://okeeffe-ws1.la.asu.edu/RCSR/home.htm). The V-5 model presents HTB channels intercrossed at 90° in subsequent layers in the *ab* plane, indeed the framework density is equal to that of the β-AlF_3 HTB-like model (FD~19.7). The shortest F–F distances in these models are larger than 2.42 Å. For R values larger than 0.02, problems arise generally, like too

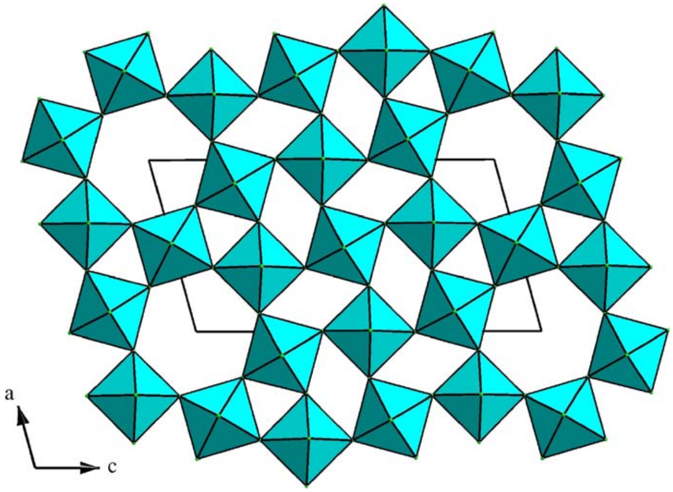

Fig. 1. Virtual AlF_3 model V-1, intergrowth HTB–perovskite (three layers).

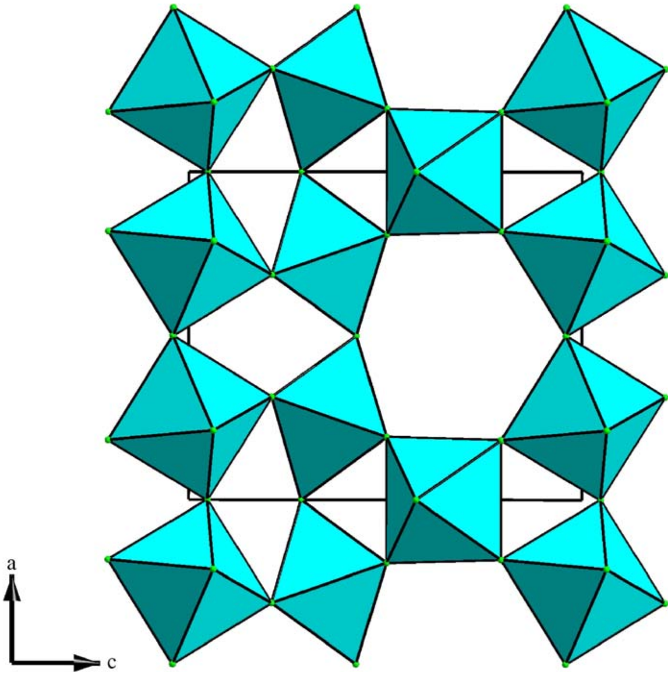

Fig. 2. Virtual AlF_3 model V-2, intergrowth pyrochlore–perovskite.

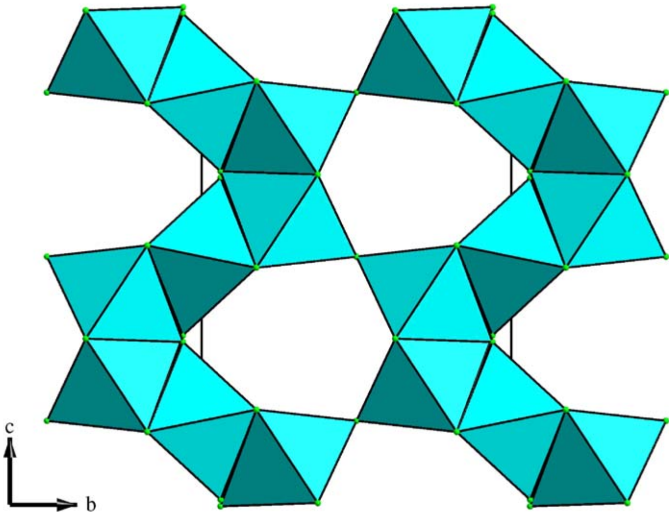

Fig. 3. Virtual AlF_3 model V-3.

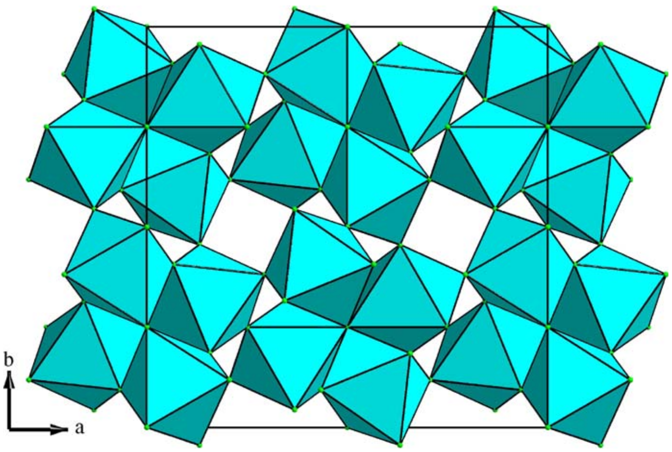

Fig. 4. Virtual AlF_3 model V-4, dense packing of tetrahedra of octahedra, exclusively.

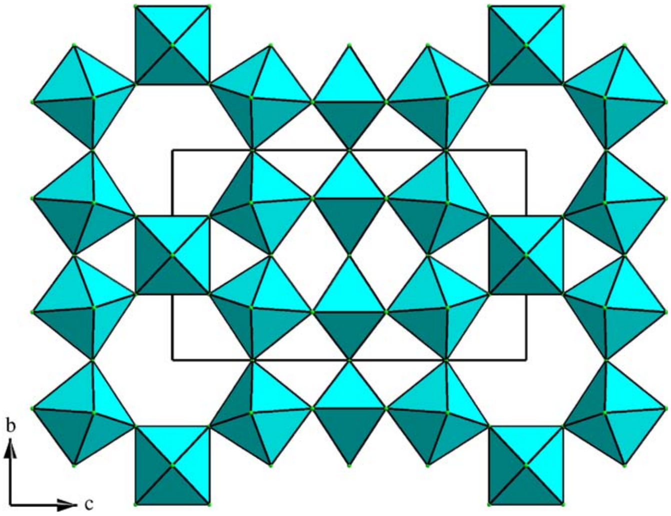

Fig. 5. Virtual AlF_3 model V-5, HTB tunnels intercrossed at 90° in the *ab* plane.

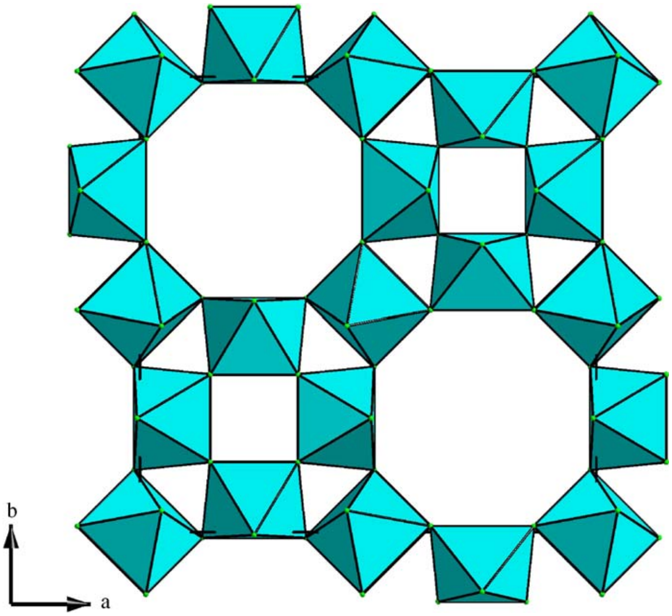

Fig. 6. Virtual AlF_3 model V-6, not viable due to a high level of octahedra distortion and too short *F–F* distances.

short interatomic distances for a small part of them, and some octahedra may become distorted. For instance, in spite of an interesting channel with rings of eight octahedra, the V-6 model has the largest framework density of the whole series (FD = 23.6) because of the excessive proximity of the octahedra along the *c*-axis (leading to irrealistic interlayer distances Al–Al = 3.195 Å, and to F–F distances as short as 1.8 Å) (see Figs. 5 and 6). However, the occurrence of structures built up from such layers cannot be excluded if they were isolated, and if the AB_6 octahedra would accept some distortion. Five additional models with $0.02 < R < 0.03$ appeared not viable either and are not listed here; however, they can be found into the PCOD with entry numbers 1300009–1300013. Only one of them (PCOD1300011) was found to have an FD equal to that of the pyrochlore, but some F–F distances would be too short, close to 2.2 Å. Finally, one of these rejected models is isostructural to $Na_4Ca_4Al_7F_{33}$ [23], replacing the Ca atoms by Al ones (PCOD1300011, with $R = 0.0283$). Indeed, the GRINSP software can produce trigonal prisms instead of octahedra for $R > 0.02$ (Table 3).

5. Ab initio calculations

Ab initio comparison of the total energies of the predicted structures with the real ones was performed using the *WIEN2K* code [26] which is a full potential (Linearized) Augmented Plane Wave code for periodic systems, renown for its accuracy. Computations were

Table 3
AlF_3 virtual polymorphs proposed by GRINSP (unknown structure types)

Virtual AlF_3	FD	a (Å)	b (Å)	c (Å)	β (°)	SG		Z	N	R	PCOD entry
						Starting	Final				
V-1	21.27	6.992	7.218	13.513	105.22	$P2_1/m$	$P2_1/m$	14	3	0.0042	1300001
V-2	20.43	6.889	6.889	8.252	90.00	$P\bar{4}m2$	$Pmm2$	8	2	0.0054	1300002
V-3	22.37	5.207	6.960	7.402	90.00	$Pnc2$	$Pmna$	6	2	0.0160	1300003
V-4	21.71	10.505	10.505	6.678	90.00	$I4_1/a$	$I4_1/a$	16	1	0.0181	1300004
V-5	19.74	7.125	7.125	11.977	90.00	$P4_2/mmc$	$P4_2/mmc$	12	2	0.0191	1300005
V-6	23.65	12.601	12.601	6.391	90.00	$P4/nmm$	$P4/nmm$	12	2	0.0233	1300006

FD = framework density (number of Al atoms in 1000 Å^3).
SG = starting higher symmetry space group in which the initial model of Al-only atoms were obtained, and final space group deduced by PLATON after including the F atoms and optimizing.
Z = number of AlF_3 formula per cell.
N = number of Al atoms with different coordination sequences.
R = quality factor regarding the ideal Al–F, F–F and Al–Al first neighbour interatomic distances.

performed on the Beowulf-type parallel computer in Le Mans (cluster of five AMD64 dual-core nodes with 16 Go of RAM each). Sphere sizes (R_{mt}) of 1.60 a.u. for F and Al were used. The basis set was determined by a large cutoff corresponding to $R_{\mathrm{mt}}K_{\max} = 7$. The full Brillouin Zone was sampled with 100 k-points and we used the Generalized Gradient Approximation of Perdew et al. [27] for the description of exchange and correlation effects within density functional theory. It was checked on the three lowest energy structures that an increase of the number of k-points up to 10000, of $R_{\mathrm{mt}}K_{\max}$ up to 10.5 or a decrease of R_{mt} down to 1.5 a.u. would not change the ordering of the total energies, although evidently changing by a few digits their absolute values.

In principle, no adjustment of cell parameters is necessary when dealing with the existing AlF_3 phases, contrary to the hypothetical models being somewhat uncertain. However, in order to maintain some coherency in the study, all structures (real or virtual) were volume-optimized. The procedure did not yield changes greater than 1% versus the original values. For instance, the cell volume for α-AlF_3 was decreased by 0.29% by this process. Volume optimization should be considered as insufficient for predicted structure candidates which would deserve the individual optimization of the independent cell parameters as well as atomic positions. However, this is not totally automated in the current version of *WIEN2K* and judged too time-consuming. For the so-called pyrochlore structure we simply replaced the OH in the naturally occurring structure by *F* atoms.

Results are presented in Table 4. One sees that the predicted structures are interclassed with the known ones, with of course the ideal α-AlF_3 structure having the lowest energy although not by a very large amount. This leads to the conclusion that these predicted structures might be synthesized in the future. The classification does not follow exactly the one deduced from R values; however, plotting ΔE against R shows a small correlation.

Table 4
Total energies obtained with the WIEN2 K ab initio code for natural and predicted structures for AlF_3

Phase or structure type	Total energy per electron in Ry	ΔE	R
α-AlF_3 (perovskite)	−36.1856793	0.	0.0062
V-1	−36.1851923	0.0004870	0.0042
$TlCa_2Ta_5O_{15}$-like	−36.1844875	0.0011918	0.0035
β-AlF_3 (HTB)	−36.1844544	0.0012249	0.0035
$Ba_4CoTa_{10}O_{30}$-like	−36.1844253	0.0012540	0.0093
κ-AlF_3 (TTB)	−36.1843461	0.0013332	0.0098
η-AlF_3 (pyrochlore-like)	−36.1842524	0.0014269	0.0046
V-3	−36.1839795	0.0016998	0.0160
V-4	−36.1839778	0.0017015	0.0181
V-2	−36.1839340	0.0017453	0.0054
V-5	−36.1835532	0.0021261	0.0191
τ-AlF_3 (or θ-)	−36.1815946	0.0040847	0.0159

The energies (in Ry) are divided by the number of electrons in the cell for comparison purposes. For the sake of clarity, ΔE is calculated by difference with the total energy of α-AlF_3.

6. Extending to more hypothetical MF_3 ($M = \mathrm{Fe, Cr}$) compounds

Even more difficult is the prediction of the synthesis conditions for making these predicted crystal structures to appear. We can already be sure that most predictions inside of the PCOD will be vain, never confirmed, because the synthesis route may depend on a precursor (organometallic, hydrate, amorphous compound) which itself is yet unknown, or because the prediction is simply false. The latest discovered AlF_3 phase, τ-AlF_3 [19], was obtained from the thermolysis of either $[(CH_3)_4N]AlF_4 \cdot H_2O$ or amorphous $AlF_3 \cdot xH_2O$ ($x < 0.5$). Its structure determination was only possible from powder diffraction data, after the preparation of a pure-enough sample obtained from the

Table 5
Estimated cell parameters for virtual FeF_3 and CrF_3 compounds

Model	a (Å)	b (Å)	c (Å)	β (°)	R	PCOD entry
V-1-Fe	7.357	7.543	14.362	105.82	0.0026	1300021
V-1-Cr	7.298	7.415	14.027	105.08	0.0026	1300031
V-2-Fe	7.324	7.324	8.812	90.	0.0056	1300022
V-2-Cr	7.204	7.204	8.677	90.	0.0056	1300032
V-3-Fe	7.441	7.864	5.552	90.	0.0156	1300023
V-3-Cr	7.327	7.736	5.466	90.	0.0156	1300033
V-4-Fe	11.211	11.211	7.117	90.	0.0176	1300024
V-4-Cr	11.042	11.042	6.991	90.	0.0176	1300034
V-5-Fe	7.544	7.544	12.784	90.	0.0186	1300025
V-5-Cr	7.439	7.439	12.585	90.	0.0189	1300035
τ-Fe	10.875	10.875	7.720	90.	0.0158	1300026
τ-Cr	10.726	10.726	7.603	90.	0.0158	1300036

above organometallic phase. The route from the amorphous phase always led to a mixture with dominant β-AlF_3. There is no doubt that if the predictions presented here had been available by the end of the 1980s, the structure would have been solved earlier. These considerations suggest that a list of cell parameters for possible MF_3 isostructural compounds (including those corresponding to τ-AlF_3) would be of interest (Table 5). The models were built by using the ideal M–F distances 1.930 and 1.900 Å, respectively, for the virtual FeF_3 and CrF_3 compounds (VF_3 and GaF_3 compounds would have very similar cell parameters with FeF_3 and CrF_3, respectively). Physical properties prediction (magnetic behaviour, etc.) for these hypothetical compounds remains to be done. At least structure prediction would help to solve the structures if the samples occur only in powder form, as is frequently the case for metastable compounds obtained after decomposition of a precursor.

7. Conclusions

In spite of being based on the most simple approach, verifying ideal interatomic distances, the cost function applied in this study allows to reproduce the existing crystal structures with less than 3% discrepancy on the cell parameters. However, GRINSP will be able of this performance only in cases where the polyhedra are ideal ones (which is the case for SiO_4 tetrahedra or AlF_6 octahedra). It seems that the question asked in the introduction was given a positive answer : new AB_3 structures built up from corner-sharing octahedra can be expected to be disclosed in the future. The question how to obtain them has the following answer: try all ways of synthesis, especially study the decomposition of hydrated, hydroxy-hydrated or organometallic materials, expecting to obtain metastable compounds.

The present tour for predicting octahedra corner-sharing AB_3 compounds is not exhaustive. Probably more structures would be obtained if the cell parameters limit at 16 Å and the maximum of 64 Al atoms per cell were extended to larger values. In the current conditions, no viable framework with larger porosity than the pyrochlore structure was found.

Accurate prediction of both structures and properties appears to be one of the main scientific challenge of the XXIth century, probably finding some equilibrium between these 1,000,000 models for SiO_2 and 12 models for AlF_3, or the more than 1000 titanosilicates recently added into the PCOD. The usefulness of databases of predicted structures will be increased when powder patterns are calculated and used by search-match software for identification purposes. This is in project, as soon as enough structures are incorporated into the PCOD, containing less than 3000 models up to now. Finally, investigations of the possible physical properties of the FeF_3 and CrF_3 hypothetical models (or with other compositions) could be worth trying, especially for the magnetic aspects, just to see if efforts in order to realize the predictions may have some interest.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.06.010.

References

[1] F.C. Hawthorne, Acta Crystallogr. B 50 (1994) 481–510.
[2] J.C. Schön, M. Jansen, Angew Chem. Int. Ed. Eng. 35 (1996) 1286–1304.
[3] M.M.J. Treacy, I. Rivin, E. Balkovsky, K.H. Randall, M.D. Foster, Micropor. Mesopor. Mater. 74 (2004) 121–132.
[4] M.D. Foster, M.M.J. Treacy, Hypothetical zeolites, http://www.hypotheticalzeolites.net/
[5] G.M. Day, W.D.S. Motherwell, H.L. Ammon, S.X.M. Boerrigter, R.G. Della Valle, E. Venuti, A. Dzyabchenko, J.D. Dunitz, B. Schweizer, B.P. van Eijck, P. Erk, J.C. Facelli, V.E. Bazterra, M.B. Ferraro, D.W.M. Hofmann, F.J.J. Leusen, C. Liang, C.C. Pantelides, P.G. Karamertzanis, S.L. Price, T.C. Lewis, H. Nowell, A. Torrisi, H.A. Scheraga, Y.A. Arnautova, M.U. Schmidt, P. Verwer, Acta Crystallogr. B 61 (2005) 511–527.
[6] A. Le Bail, Predicted crystallography open database, http://www.crystallography.net/pcod/
[7] A. Le Bail, J. Appl. Crystallogr. 38 (2005) 389–395.
[8] C. Mellot-Draznieks, J.M. Newsam, A.M. Gorman, C.M. Freeman, G. Férey, Angew. Chem. Int. Ed. 39 (2000) 2270–2275.
[9] C. Mellot-Draznieks, S. Girard, G. Férey, C. Schön, Z. Cancarevic, M. Jansen, Chem. Eur. J. 8 (2002) 4103–4113.
[10] Cerius2, Version 4.2, Molecular Simulations Inc., Cambridge, UK, 2000.
[11] J.D. Gale, J. Chem. Soc., Faraday Trans. 93 (1997) 629–637.
[12] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.
[13] R. Hundt, J.C. Schön, M. Jansen, J. Appl. Crystallogr. 39 (2006) 6–16.
[14] W.M. Meier, H.J. Moeck, J. Solid State Chem. 27 (1979) 349–355.
[15] P. Daniel, A. Bulou, M. Rousseau, J. Nouet, J.L. Fourquet, M. Leblanc, R. Burriel, J. Phys.: Condens. Matter 2 (1990) (5663–4677).
[16] A. Le Bail, C. Jacoboni, M. Leblanc, R. De Pape, H. Duroy, J.L. Fourquet, J. Solid State Chem. 77 (1988) 96–101.
[17] J.L. Fourquet, M. Riviere, A. Le Bail, M. Nygrens, J. Grins, Eur. J. Solid State Inorg. Chem. 25 (1988) 535–540.

[18] N. Herron, D.L. Thorn, R.L. Harlow, G.A. Jones, J.B. Parise, J.A. Fernandez-baca, T. Vogt, Chem. Mater. 7 (1995) 75–83.

[19] A. Le Bail, J.L. Fourquet, U. Bentrup, J. Solid State Chem. 100 (1992) 151–159.

[20] M. Ganne, M. Dion, A. Verbaere, M. Tournoux, J. Solid State Chem. 29 (1979) 9–13.

[21] B. Jasper-Toennies, Hk. Mueller-Bushbaum, Monats. Chem. Verw. Tl. 115 (1984) 1151–1157.

[22] B.-O. Marinder, Acta Chem. Scand. 45 (1991) 659–668.

[23] A. Hemon, G. Courbion, J. Solid State Chem. 84 (1990) 153–164.

[24] A. Le Bail, Y. Gao, C. Jacoboni, Eur. J. Solid State Inorg. Chem. 26 (1989) 281–288.

[25] P. Herzig, J. Zemann, Z. Kristallogr. 205 (1993) 85–97.

[26] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, K. Schwarz, Techn. Universtät, Wien, Austria, 2001, ISBN 3-9501031-1-2.

[27] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.