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Crystal Structure of the Metastable Form of Aluminum Trifluoride β-AlF_3 and the Gallium and Indium Homologs

A. LE BAIL, C. JACOBONI, M. LEBLANC, R. DE PAPE, H. DUROY, AND J. L. FOURQUET

Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences, Route de Laval, 72017 Le Mans Cedex, France

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The crystal structure of the metastable phase β-AlF_3, which is related to the hexagonal tungsten bronze structure, has been solved by X-ray powder and single-crystal diffraction methods. The crystal habit is pseudo-hexagonal with systematic twinning (rotation of 120° around the c axis), but the true symmetry is orthorhombic with space group $Cmcm$, $Z = 12$, $a = 6.931(3)$, $b = 12.002(6)$, $c = 7.134(2)$ Å ($R = 0.044$ and $R_w = 0.051$ from 929 independent reflections). The network is built from very regular AlF_6 octahedra rotated by approximately 7.2° from the positions of the ideal HTB structure. A similar network, with the same propagation of the tilting, was observed in the compound $(H_2O)_{0.33}FeF_3$ and in the metastable polymorphs of CrF_3 and of VF_3. Our reinvestigation of the structures of β-GaF_3 and β-InF_3 using powder data shows that they are isotypic with the aluminum compound, with $a = 7.210(1)$, $b = 12.398(2)$, $c = 7.333(1)$ and $a = 7.875(2)$, $b = 13.499(4)$, $c = 7.956(2)$ Å, respectively.

Introduction

The stable form of aluminum fluoride crystallizes with a rhombohedral structure, space group $R\bar{3}$ (*1, 2*) and transforms reversibly to a cubic ReO_3-type polymorph at 725 K (*3*). We will refer to this rhombohedral form as the "α" form by analogy with the stable forms of gallium and indium trifluoride, whose structures are very similar to that of α-AlF_3 (*2*). A metastable form, called β-AlF_3 (*4*), observed by several authors was obtained by dehydrating α-$AlF_3 \cdot 3H_2O$ (*4, 5*) or from the thermal decomposition of NH_4AlF_4 (*7*).

Several discrepancies in the literature led us to reexamine these compounds. Although the published powder diffraction patterns are very similar, the reported hexagonal (*4, 6*) and tetragonal (*7, 8*) indexings are incompatible. In addition the exact composition has not been fully characterized. One group of authors (*5*) assumes that the preparation of α-$AlF_3 \cdot 3H_2O$ by dehydration leads to an oxyfluoride $Al(OH,F)_3$ due to hydrolysis.

In this paper we have tried to resolve these ambiguities for the aluminum phase, and to characterize the related β-phases of gallium and indium previously prepared by thermal decomposition of the ammonium salts $(NH_4)_3MF_6$ (*6*).

Preparations

β-AlF_3 was prepared by two different methods, by dehydration of α-$AlF_3 \cdot 3H_2O$, which results in polycrystalline samples

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and by crystal growth from a chloride flux (*9*).

The trihydrate was heated (5°/min) to 220°C under vacuum (10^{-5} Torr) to give an amorphous material. The fluorine content was carefully checked by titration of the HF evolved after pyrohydrolysis and the aluminum content was determined by complexometric titration. The F/Al ratio was found to be 2.98 ± 0.03. This amorphous material remains slightly hydrated and can be formulated as $AlF_3 \cdot xH_2O$ ($x < 0.5$). Further heating to 450°C under high vacuum or an inert atmosphere is necessary to obtain pure crystalline β-AlF_3. Chemical analysis yielded a F/Al ratio of 2.99 ± 0.03. When heated at 500°C for 12 hr in a sealed platinum tube under an inert atmosphere, β-AlF_3 irreversibly transforms to the stable α-form. AlF_3 undergoes no perceptible hydrolysis under these mild conditions of dehydration. The pyrohydrolysis experiments used to check the amount of fluorine in AlF_3 require more severe conditions: at least 620°C and a partial pressure of water equal to 1 atm.

Crystals of β-AlF_3 were grown from a chloride flux according to the scheme:

$$7RbCl + \tfrac{3}{2}CoCl_2 + CoF_2 + 4\alpha\text{-}AlF_3 \rightarrow \beta\text{-}AlF_3.$$

The crystals are colorless needles with hexagonal sections, some of them up to 5 mm long and 1 mm thick. Chemical analysis confirmed the composition ($\%Al_{calc} = 32.1$, $\%Al_{obs} = 32.7$).

The phases β-GaF_3 and β-InF_3 were prepared by the method of Beck *et al.* (*8*). Pure β-GaF_3 was obtained by heating 1.5 g of $(NH_4)_3GaF_6$ (5°/min) to 420°C under an argon flow. The sample was then quenched. For β-InF_3 a first step (10°C/min to 275°C) gave $NH_4In_3F_{10}$ (*10*) which was then heated under vacuum at 275°C for 2 days. Chemical analysis confirmed the compositions MF_3:

	$\%M_{calc}$	$\%M_{obs}$	$\%F_{calc}$	$\%F_{obs}$
Ga	55.02	53.3(7)	44.98	44.8(3)
In	66.29	65.2(7)	33.71	31.7(3)

The three β-phases are metastable and transform on heating to the corresponding α-phases. The conversion temperatures, not discernable by differential thermoanalysis, were roughly determined by trial and error to be 500°C for β-AlF_3, 550°C for β-GaF_3, and 400°C for β-InF_3. The transformation results in a large decrease in volume of 11.9, 14.3, and 13.8%, respectively.

Structural Determination of β-AlF_3

A small needle was selected for the crystallographic determination. A preliminary study by standard photographic methods suggested LAUE symmetry $6/mmm$ and the only observed reflection condition was $00l$ with $l = 2n$, leading to three possible space groups: $P6_322$, $P6_3/m$, or $P6_3$.

However, a study of the crystal on an Enraf–Nonius CAD4 automated four-circle diffractometer revealed that the hexagonal equivalence conditions were not fulfilled, particularly for the reflections hkl with l odd. The only condition of equivalence observed was $hkl = \bar{h}kl$. The refinement of the structure starting from the hexagonal tungsten bronze (HTB) model (*11*) did not converge ($R = 0.12$ for 1103 reflections); however, the residual drops to 0.049 for the 596 reflections with $l = 2n$ which represent 90% of the total intensity. This indicates that the HTB model provides an approximate description of the structure.

At this stage, we considered the possibility that β-AlF_3 could be isostructural with orthorhombic $(H_2O)_{0.33}FeF_3$ (*12*), space group *Cmcm*, whose crystals adopt a pseudo-hexagonal habit with frequent (110) twinning. Recently, the same structure was encountered for the metastable forms of CrF_3 and VF_3 (*13*).

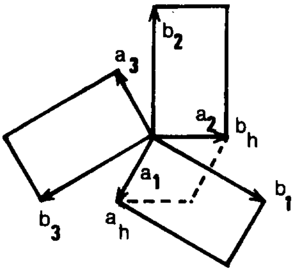

FIG. 1. Arrangement of the three twinned orthorhombic domains.

In order to overcome possible problems due to twinning in the single-crystal study, we recorded an X-ray powder diffractogram which was analyzed by means of a modified Rietveld program (*14, 15*). All previously mentioned space groups were tested; only the refinement in space group *Cmcm* was able to reproduce satisfactorily the intensities of the reflections with l odd. The residual values for the refinement are $R_I = 0.056$, $R_{\mathrm{prof}} = 0.090$ assuming isotropic thermal motion. These results confirm the hypothesis of twinning; as shown in Fig. 1 the lowering of symmetry is compatible with the existence of three orthorhombic domains rotated by 120° around the common c axis.

This model leads to a strict superposition of all reflections and the total intensities depend upon the volumes of the three domains. Consideration of the diffraction planes $H_1 = (h, k, l)$, $H_2 = (-h/2 + k/2, -3h/2 - k/2, l)$, $H_3 = (-h/2 - k/2, 3h/2 - k/2, l)$, which are related to each other by the pseudo-threefold axis and the corresponding intensities for each domain, shows that the nine intensities reduce to three independent values I_1, I_2, I_3 and that the intensities of the polycrystal (I') are related to the volumes (v) of the domains by:

$$\begin{vmatrix} I_1' \\ I_2' \\ I_3' \end{vmatrix} = \begin{vmatrix} I_1 & I_2 & I_3 \\ I_3 & I_1 & I_2 \\ I_2 & I_3 & I_1 \end{vmatrix} * \begin{vmatrix} v_1 \\ v_2 \\ v_3 \end{vmatrix}. \qquad (1)$$

In order to test this twinning hypothesis in the space group *Cmcm*, a new set of data was collected from another crystal on a Siemens AED2 four-circle diffractometer. Table I shows the experimental details. An absorption correction was applied. As all of the intensities are superposed, the determination of the relative volumes of the three domains using Eq. (1) could not be performed without the fact that the reflections $h\ 0\ l$ with l odd corresponding to the orthorhombic axis of a given domain, say the domain 1, are forbidden in the space group *Cmcm* ($I_1 = 0$). Only the two other domains contribute to these reflections with their planes ($h/2$, $3h/2$, l) and ($-h/2$, $3h/2$, l); for instance, the (2 0 3) polycrystal reflection is the sum of the (1 3 3) and (−1 3 3) reflections from domains 2 and 3. Moreover the intensities of these reflections are equal ($I_2 = I_3$). Thanks to these additional relations, the resolution of Eq. (1) was possi-

TABLE I

DETAILS OF THE DATA COLLECTION ON β-AlF$_3$

Molecular weight: 83.95 g
Space group: *Cmcm*

$a = 6.931(3)$ Å $\quad V = 593.44$ Å^3
$b = 12.002(6)$ Å $\quad \rho_{\mathrm{obs}} = 2.843(5)$ g · cm^{-3} (flotation method)
$c = 7.134(3)$ Å $\quad \rho_{\mathrm{calc}} = 2.82$ g · cm^{-3}
$Z = 12$

Radiation: Mo$K\alpha$ (graphite monochromatized); $\mu(\mathrm{Mo}K\alpha) = 7.60$ cm^{-1}
$T = 20$°C
Scanning: $\omega/2\theta$ Angular range: $5.71 \leq 2\theta \leq 79.98$
Region of reciprocal space: Four independent sets
Crystal shape: Needle with hexagonal section ($14 \times 7 \times 5 \times 10^{-6}$ mm^3)
Absorption correction: By the Gauss method
Minimum and maximum transmission factors: 0.9259, 0.9573
Number of measured reflections: 4150
Number of independent reflections after merging in *mmm:* 981
Number of independent reflections with $\sigma(I)/I <$ 0.33 used in the refinement: 929

TABLE II

FINAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR β-AlF$_3$

Atom	Site	x	y	z	$U_{11}{}^a$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq} (Å^2)
Al1	4b	0	1/2	0	55(3)	42(3)	43(3)	−2(2)	0	0	0.368
Al2	8d	1/4	1/4	0	40(2)	57(3)	44(2)	−3(2)	−5(1)	8(2)	0.371
F1	8f	0	2125(1)	5257(2)	40(4)	107(5)	112(5)	10(4)	0	0	0.681
F2	16h	3161(1)	1054(1)	9800(1)	83(3)	61(3)	141(4)	−4(2)	−12(3)	23(2)	0.750
F3	4c	0	5177(2)	1/4	155(8)	128(8)	49(6)	0	0	0	0.870
F4	8g	2297(2)	2352(1)	1/4	133(5)	141(6)	40(4)	0	0	−2(4)	0.826

[a] The vibrational coefficients relate to the expression $T = \exp\{-2\pi^2(h^2a^{*2}u_{11} + k^2b^{*2}u_{22} + l^2c^{*2}u_{33} + 2klb^*c^*u_{23} + 2hla^*c^*u_{13} + 2hka^*b^*u_{12})\}$.

ble. From the intensities of the 14 strongest associated triplets (h 0 l) with l odd, the proportions of the three domains were found to be $v_1 = 0.567 \pm 0.004$, $v_2 = 0.180 \pm 0.060$, $v_3 = 0.253 \pm 0.060$, with excellent precision. All of the intensities were then transformed to "single-crystal" intensities using the linear equations:

$$\begin{vmatrix} I_1' \\ I_2' \\ I_3' \end{vmatrix} = \begin{vmatrix} v_1 & v_2 & v_3 \\ v_2 & v_3 & v_1 \\ v_3 & v_1 & v_2 \end{vmatrix} * \begin{vmatrix} I_1 \\ I_2 \\ I_3 \end{vmatrix}.$$

The corrected data were merged in the Laue group *mmm* ($R_{int} = 0.044$). The same procedure, when applied to the first crystal data, gave the proportions: $v_1 = 0.30$, $v_2 = 0.34$, $v_3 = 0.35$, but unfortunately these very similar values are unsuitable for an accurate correction of the raw data, because the v-matrix is nearly singular.

All calculations were performed with the SHELX 76 (*16*) program. Atomic scattering factors and the values of $\Delta f'$ and $\Delta f''$ were taken from "The International Tables for X-Ray Crystallography" (*17*) for Al^{3+} and F$^-$. The refinement was started with the model from the powder work and rapidly converged to $R = 0.044$ and $R_w = 0.051$,[1] with anisotropic thermal parameters for all the atoms varied. Weights were calculated as $w = 14.0356\{\sigma(F) + 1.95 \times 10^{-4} F^2\}$ and the secondary extinction coefficient took the value 468(60) × 10^{-5}. It is notable that better R and R_w values (0.033 and 0.035, respectively) can be obtained without significant changes in the refined parameters by limiting the data set at $2\theta_{max} = 66°$ (606 independent reflections instead of 929), which is a feature of many reported structure determinations.

Figure 2 shows a perspective view of the structure. Table II presents the final results, and distances and angles are listed in Table III. The AlF$_6$ octahedra are very regular and the mean distance Al–F is very close to the sum of the Al^{3+} and F$^-$ ionic radii.

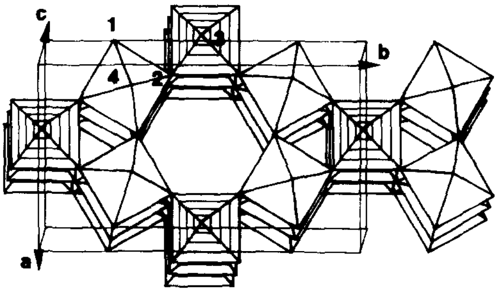

FIG. 2. Perspective view of the structure of β-AlF$_3$. Al$_1$F$_6$ octahedra are hatched and the F atoms are numbered.

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[1] F_o and F_c values may be obtained by request to J. L. Fourquet.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR β-AlF_3 (CRYSTAL)

4× Al_1–F_2	1.801(1)	*1.874(10)*	$d(Al_1$–$F)$ =	1.799	*1.880*
2× Al_1–F_3	1.796(1)	*1.878(3)*	$d(F$–$F)$ =	2.545	*2.652*
2× Al_2–F_1	1.800(1)	*1.891(3)*	$d(Al_2$–$F)$ =	1.799	*1.881*
2× Al_2–F_2	1.800(1)	*1.870(12)*	$d(F$–$F)$ =	2.544	*2.660*
2× Al_2–F_4	1.798(1)	*1.882(5)*			
Al_1–F_3–Al_1	166.4	*154.8*	F_2–Al_1–F_2	89.9	*87.7*
Al_2–F_4–Al_2	165.5	*153.9*	F_2–Al_1–F_3	89.7	*89.7*
Al_2–F_1–Al_2	148.7	*144.8*	F_1–Al_2–F_2	89.8	*89.1*
Al_1–F_2–Al_2	148.3	*146.5*	F_1–Al_2–F_4	89.9	*88.6*
			F_2–Al_2–F_4	89.8	*89.5*

Note. The values for GaF_3 (powder) are given in italics.

Discussion

The accurate determination of the volumes of the twin domains, the regularity of the AlF_6 octahedra, and the consistency of the anisotropic thermal motion with the tilting scheme of the octahedra are very strong arguments for the true symmetry of β-AlF_3 being orthorhombic, despite the apparent hexagonal symmetry which leads to a b/a ratio of 1.732.

Other evidence comes from the isotypy with $(H_2O)_{0.33}FeF_3$ and the powder diffraction results for β-AlF_3 and β-GaF_3. For the latter phase a successful refinement of the structure by means of the same profile method (*14*, *15*) and starting from the same model leads to a rather different b/a ratio of 1.720, thus demonstrating directly the lowering of symmetry. Table IV shows the final atomic parameters for β-GaF_3 and Table III lists distances and angles; as for β-AlF_3 the framework is built from very regular octahedra.

The aluminum and gallium β-phases, and probably the indium one, undergo the same mode of tilting: the mean rotation angles with respect to an ideal HTB structure are 7.2° and 12.9° for the Al and Ga compounds, respectively. The indium phase is highly hygroscopic and readily transforms in $InF_3 \cdot 3H_2O$. We have indexed the powder diffraction pattern by analogy with the other β phases. The unit cell parameters (a = 7.875(2), b = 13.499(4), c = 7.956(2) Å) were obtained by a least-squares method and give a b/a ratio of 1.714.[2]

It is notable that very few structures of HTB-type fluorides have been fully solved from single-crystal data. Examples are $(H_2O)_{0.33}FeF_3$ and $Cs_{0.4}Zn_{0.4}Fe_{1.6}F_6$ (space group $P2_1$) (*18*). Recent investigations by electron microscopy on A_xVF_3 bronzes (*19*) also suggest that the presumed hexagonal symmetry is probably a pseudo-one.

TABLE IV

FINAL ATOMIC COORDINATES FOR β-GaF_3

	x	y	z	B_{eq} (Å^2)
Ga1	0	$\frac{1}{2}$	0	0.98(3)
Ga2	$\frac{1}{4}$	$\frac{1}{4}$	0	—
F1	0	0.210(1)	0.539(2)	1.72(6)
F2	0.320(1)	x/3[a]	0.961(1)	—
F3	0	0.533(1)	$\frac{1}{4}$	—
F4	0.216(2)	0.222(1)	$\frac{1}{4}$	—
H_2O[b]	0	0.06(1)	$\frac{1}{4}$	—

a = 7.210(1) Å; b = 12.398(2) Å; c = 7.333(1) Å

R_1 = 0.037

R_P = 0.087

R_{wp} = 0.098

[a] Constrained parameter.

[b] In 4c sites, with an occupancy factor of 0.22(2) due to zeolitic hydration during the data collection.

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[2] Our results on the unit cell of β-MF_3 (M = Al, Ga, In) disagree with those of Shinn *et al.* (*7*) and Beck *et al.* (*8*) who claimed a tetragonal symmetry.

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