

β -Ba₃AlF₉, a Complex Structure Determined from Conventional X-Ray Powder Diffraction

A. LE BAIL

*Laboratoire des Fluorures, CNRS-URA 449, Faculté des Sciences,
Université du Maine, 72017 Le Mans Cedex, France*

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β -Ba₃AlF₉ crystallizes in the *Pnc2* space group with lattice parameters $a = 7.5318(3)$ Å, $b = 14.8674(7)$ Å, and $c = 14.5732(7)$ Å, $Z = 8$. The structure is determined *ab initio* from conventional X-ray powder data. Direct methods allowed the location of 7 Ba atoms; the structure was completed, via difference Fourier and Rietveld refinement methods, to a total of 29 independent atoms (equalling the most complex structure determined from a combination of synchrotron and neutron powder data) and 74 refined atomic coordinates. The structure is built up from a tridimensional network of [FBa₄] tetrahedra sharing corners and/or edges where isolated [AlF₆] octahedra are inserted. A relationship between the Ba₃Al cationic subnetwork and the structure of β -V₃S is disclosed. A reversible phase transition is detected (492°C on heating, 476°C on cooling); its character has yet to be established. © 1993 Academic Press, Inc.

Introduction

The most complex structure determined *ab initio* from powder diffraction data is currently that of Ga₂(HPO₃)₃ · 4H₂O (1). To produce the complete solution, the complementary use of synchrotron X-ray and neutron-diffraction powder methods was necessary (29 atoms in general position in the asymmetric unit cell, 86 atomic coordinates to be refined). The structure of β -Ba₃AlF₉, with comparable complexity (29 independent atoms, 74 refined atomic coordinates), is determined here from conventional X-ray powder data.

β -Ba₃AlF₉ is a high temperature form stabilized by quenching, and previously characterized by an unindexed X-ray powder pattern (2). Its existence was confirmed re-

cently (3) by isolation of a single crystal allowing one to establish an orthorhombic cell by X-ray techniques study and to index the powder pattern. The space group was not identified in other terms than "P-type." The bad quality of this crystal prevented a structural determination. Such a problem was previously encountered for β - and γ -BaAlF₅, whose structures were determined from conventional X-ray powder data and for which the quality of the refinements was improved from neutron powder data (4). The same methodology is applied here to β -Ba₃AlF₉.

Experimental

The sample was prepared as described in Ref. (3). Starting from a stoichiometric

mixture led to contamination by $\text{Ba}_5\text{AlF}_{13}$, isostructural with $\text{Sr}_{10}\text{Al}_2\text{F}_{25}\text{Cl}$ (5). $\beta\text{-Ba}_3\text{AlF}_9$ was obtained almost pure starting from 2.9 BaF_2 and 1 AlF_3 . This could be explained by differences in vapor pressure of AlF_3 and BaF_2 at the quenching (in water) temperature (860°C in a sealed tube). A DSC experiment (Perkin Elmer DSC4, Ar flow, $10^\circ\text{C} \cdot \text{min}^{-1}$), coupled with X-ray powder diffraction, disclosed a sharp reversible transition with hysteresis. The thermal events culminated at 492°C on heating (endothermic) and 476°C on cooling (exothermic). DTA analysis (Q1500D-MOM, Ar flow, $5^\circ\text{C} \cdot \text{min}^{-1}$) confirmed the transition and made it possible to retrieve a decomposition process emphasized in (3) occurring in a broad temperature range (522–575°C). A mixture of $\text{Ba}_5\text{AlF}_{13}$ and $\text{Ba}_5\text{Al}_3\text{F}_{19}$ was established to be still present at 815°C. A thermal event culminating at 840°C was interpreted as the reappearance of Ba_3AlF_9 .

X-ray powder diffraction data for structure determination were collected at $25 \pm 2^\circ\text{C}$ on a PW1380 Philips horizontal goniometer, equipped with a graphite monochromator in the reflected beam, automated with a DACO system. Choosing a 0.1° receiving slit ensured obtaining reflections with $0.12^\circ(2\theta)$ as minimal full width at half maximum. Measurement was over $10^\circ \leq 2\theta \leq 110^\circ$ using $\text{CuK}\alpha_{1,2}$ X-rays by steps of 0.02° , counting 32 sec per step.

Structure Determination

The cell proposed in Ref. (3) was confirmed. The space group, deduced from careful inspection of systematic absences, could be either $Pnc2$ or $Pncm$ ($Pmna$). Integrated intensities were obtained by iterating the Rietveld decomposition formula (6) (a process called the "Le Bail method" (7) in Ref. (1)) using the ARITB program (8). The contribution of the $\text{Ba}_5\text{AlF}_{13}$ impurity to the pattern was imposed from its known struc-

ture. Among the 1077 extracted reflections ($R_P = 5.18\%$, $R_{WP} = 6.36\%$, background subtracted), 634 were retained because they had no neighboring reflection at less than $0.02^\circ(2\theta)$ and were used as input data for the SHELXS-86 program (9). The structure determination was successful using the direct methods with the $Pnc2$ space group. Two hundred one phases were observed for $|E|$ values greater than 1.2 and refined using 3822 unique triplets and 177 negative quartets (SHELX-86 combined figure of merit 0.091). The solution produced an E -map with seven peaks that were two or three times larger than the next ones. They were assigned as barium atoms and this model was entered into the ARIT4 program (10) for Rietveld refinements. Scattering and anomalous dispersion factors were taken from the "International Tables for X-Ray Crystallography" (11). Alternating Fourier syntheses and Rietveld refinements revealed progressively the positions of 3 aluminum and 19 fluorine atoms, giving a total of 29 independent atoms in the asymmetric unit.

The final Rietveld X-ray data analysis is shown in Fig. 1. The final cycle of least-squares refinement contained terms for 116 parameters (98 for $\beta\text{-Ba}_3\text{AlF}_9$) and con-

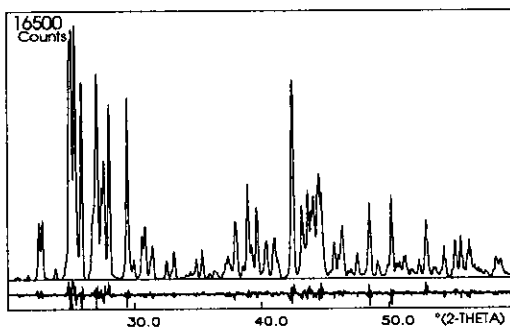


FIG. 1. Small part of the final calculated and observed-calculated difference profile plots for the X-ray Rietveld refinement of $\beta\text{-Ba}_3\text{AlF}_9$. This part contains 2000 points, and respectively 240 and 46 reflections for $\beta\text{-Ba}_3\text{AlF}_9$ and the $\text{Ba}_5\text{AlF}_{13}$ impurity.

verged to final agreement factors $R_B = 2.9\%$, $R_P = 6.8\%$, $R_{WP} = 8.4\%$, $R_{EXP} = 3.8\%$ (the two phases confused, background subtracted, see Ref. (6) for description of the R factors; R_F for β - Ba_3AlF_9 was 2.2%). The peak shapes, for the main phase, were fitted according to Eq. 1 in Ref. (7) with parameters $U_1 = 0.17(1)$, $V_1 = -0.17(1)$, $W_1 = 0.093(4)$, $U_2 = -0.28(8)$, $V_2 = 0.3(1)$, $W_2 = 1.32(3)$, $C = 0.083(2)$, $D = 0.045(8)$, $a = 120$, $b = 59$. A slight preferred

TABLE I
FRACTIONAL COORDINATES AND B_{iso} (Å)
FOR β - Ba_3AlF_9

	x	y	z	B_{iso}
Ba(1)	0.5101(8)	0.1449(2)	0 ^a	1.14(8)
Ba(2)	0.7687(6)	0.0941(2)	0.4335(4)	1.15(8)
Ba(3)	0.7489(7)	0.2751(2)	0.2230(4)	1.19(9)
Ba(4)	0.2443(7)	0.1904(2)	0.3043(4)	1.27(8)
Ba(5)	0.2604(8)	0.3919(2)	0.1003(4)	1.50(9)
Ba(6)	0	0	0.1494(4)	1.6(2)
Ba(7)	0	0	0.8285(4)	1.2(2)
Al(1)	0.9812(45)	0.6946(11)	0.5148(17)	2.6(3)
Al(2)	$\frac{1}{2}$	0	0.7911(22)	2.6(3)
Al(3)	$\frac{1}{2}$	0	0.2001(21)	2.6(3)
F(1)	0.1175(40)	0.7724(21)	0.9205(23)	2.6(2)
F(2)	0.9610(47)	0.1901(18)	0.5569(18)	2.6(2)
F(3)	0.7923(39)	0.7379(19)	0.4643(21)	2.6(2)
F(4)	0.1351(44)	0.1918(25)	0.1130(22)	2.6(2)
F(5)	0.1658(41)	0.6460(20)	0.5722(20)	2.6(2)
F(6)	0.0916(33)	0.4178(18)	0.4908(24)	2.6(2)
F(7)	0.4334(45)	0.1144(19)	0.7961(24)	2.6(2)
F(8)	0.3274(42)	0.5367(19)	0.3851(23)	2.6(2)
F(9)	0.3494(47)	0.5239(20)	0.2094(21)	2.6(2)
F(10)	0.6844(44)	0.9887(19)	0.2849(22)	2.6(2)
F(11)	0.4754(48)	0.8755(20)	0.1818(20)	2.6(2)
F(12)	0.6472(39)	0.5062(25)	0.6063(22)	2.6(2)
F(13)	0.0772(38)	0.1550(21)	0.7531(19)	0.6(2)
F(14)	0.8698(29)	0.9220(17)	0.4343(18)	0.6(2)
F(15)	0.9198(36)	0.1264(19)	0.2723(22)	0.6(2)
F(16)	0.4611(38)	0.7172(15)	0.8609(19)	0.6(2)
F(17)	0.4274(36)	0.8006(18)	0.4956(31)	0.6(2)
F(18)	$\frac{1}{2}$	0	0.5784(17)	0.6(2)
F(19)	0	0	0.6168(22)	0.6(2)

Note. B_{iso} is the isotropic temperature factor. One B_{iso} value was refined for all Al atoms; the same for F(1) to F(12) and F(13) to F(19) atoms.

^a The origin along the c axis is arbitrarily fixed by this coordinate.

TABLE II
SELECTED BOND DISTANCES AND ANGLES
FOR β - Ba_3AlF_9

Bond distances			
Al(1)-F(1)	1.78(5)	Al(2)-F(7) ($\times 2$)	1.77(5)
Al(1)-F(2)	1.87(5)	Al(2)-F(8) ($\times 2$)	1.97(5)
Al(1)-F(3)	1.73(5)	Al(2)-F(9) ($\times 2$)	1.68(5)
Al(1)-F(4)	1.65(5)	Al(3)-F(10) ($\times 2$)	1.87(5)
Al(1)-F(5)	1.78(5)	Al(3)-F(11) ($\times 2$)	1.88(5)
Al(1)-F(6)	1.79(5)	Al(3)-F(12) ($\times 2$)	1.76(5)
Bond angles			
F(1)-Al(1)-F(2)	82(4)	F(7)-Al(2)-F(7)	175(4)
F(1)-Al(1)-F(3)	93(4)	F(7)-Al(2)-F(8)	84(4)
F(1)-Al(1)-F(4)	165(4)	F(7)-Al(2)-F(8)	93(4)
F(1)-Al(1)-F(5)	91(4)	F(7)-Al(2)-F(9)	91(4)
F(1)-Al(1)-F(6)	106(4)	F(7)-Al(2)-F(9)	92(4)
F(2)-Al(1)-F(3)	89(4)	F(8)-Al(2)-F(8)	92(3)
F(2)-Al(1)-F(4)	83(4)	F(8)-Al(2)-F(9)	176(4)
F(2)-Al(1)-F(5)	92(4)	F(8)-Al(2)-F(9)	89(4)
F(2)-Al(1)-F(6)	171(4)	F(9)-Al(2)-F(9)	90(4)
F(3)-Al(1)-F(4)	86(4)	F(10)-Al(3)-F(10)	97(4)
F(3)-Al(1)-F(5)	176(4)	F(10)-Al(3)-F(11)	96(4)
F(3)-Al(1)-F(6)	91(4)	F(10)-Al(3)-F(11)	95(4)
F(4)-Al(1)-F(5)	91(4)	F(10)-Al(3)-F(12)	171(4)
F(4)-Al(1)-F(6)	89(4)	F(10)-Al(3)-F(12)	92(4)
F(5)-Al(1)-F(6)	87(4)	F(11)-Al(3)-F(11)	164(4)
		F(11)-Al(3)-F(12)	83(4)
		F(11)-Al(3)-F(12)	84(4)
		F(12)-Al(3)-F(12)	78(4)

Note. Bond distances in Å, bond angles in °.

orientation was found to occur in the [011] direction and was taken into account with a March correction (12); the refined parameter took the value 0.971(2).

Description of the Structure and Discussion

The final structural parameters, and selected bond lengths and angles, are given in Tables I and II, respectively. From the well established bond lengths in fluoaluminates, the Al-F distances for isolated $[AlF_6]$ octahedra rarely deviate from 1.80 ± 0.04 Å. Numerous values are out of this range in Table II. Therefore, the present result is not accurate; however, it may be considered as acceptable from the crystal chemistry point of view and because there are few other ways to investigate the structure.

Fluorine anions F(1) to F(12) show the usual octahedral arrangement about the

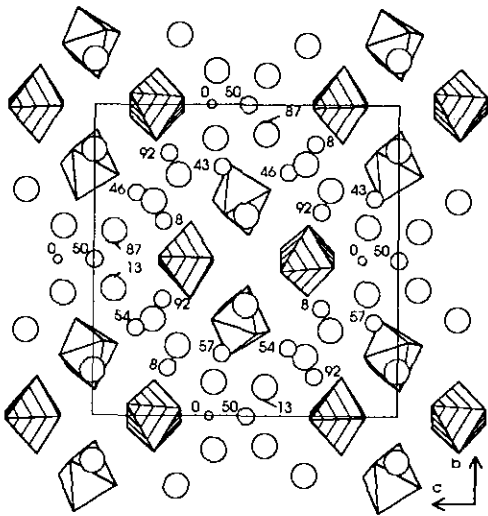


FIG. 2. Polyhedral representation of the structure of β - Ba_3AlF_9 viewed parallel to the $[100]$ direction. The aluminum-centered octahedra are depicted; they are either at $x \approx 0$ (unhatched) or $x \approx \frac{1}{2}$ (hatched). Heights in units of $a/100$ are given for F(13) to F(19). The FBa_4 tetrahedra are not represented; they may easily be located as they involve F(13) to F(18) shown as medium-size open spheres, the barium atoms (largest circles) being either at $x \approx 0$ or $\frac{1}{4}$ or $\frac{1}{2}$ or $\frac{3}{4}$ (see Fig. 3). F(19) atoms are shown as the smallest circles.

aluminum atoms (Fig. 2). Each Ba atom has 9 to 12 neighboring fluorine atoms, forming polyhedra not having well defined shapes. The fluorines F(13) to F(18) are at the center of $[\text{FBa}_4]$ tetrahedra as found in the fluorine structure-type adopted by BaF_2 . Finally, F(19) is coordinated to three Ba cations. The structure is built up from a rather complex tridimensional network of $[\text{FBa}_4]$ tetrahedra sharing edges and/or vertices into which isolated $[\text{AlF}_6]$ octahedra are inserted. However, the simplest description of the structure is obtained by looking at the cationic subnetwork. In this way one observes that the β - V_3S structure (13) (space group $P4_2/nbc$) is almost exactly reproduced by the Ba_3Al arrangement. Then, it is possible to describe β - Ba_3AlF_9 as Hyde and Andersson (14) described β - V_3S , by Ba_{4+4} tetraedersterns (tetracapped tetra-

hedra) and Ba_4Al_4 stellae quadrangulae (showing a smaller topological distortion from a cube than the tetraederstern). Only a part of the Ba_4 tetrahedra involved in this description (Fig. 3) are occupied by fluorine atoms. As a consequence of the relationship, the cationic subnetwork is pseudocentric (taking the origin at $0, \frac{1}{4}, \frac{1}{4}$; however, the pseudo-inversion center clearly does not apply to most of the fluorine atoms) and the structure is pseudotetragonal, which might lead to easy microtwinning and explain the bad quality of the crystals supporting a phase transition on cooling. Close structural relationships have previously been shown to exist between the Ba-Al cationic subnetwork of α -, β -, and γ - BaAlF_5 and respectively the CrB, SrAg, and FeB structure-types (4).

The two other known polymorphs, α - Ba_3AlF_9 (denoted form Ib in (15), originally α in (2)) and Ba_3AlF_9 -I (16), have in common a short cell parameter ($\approx 5.6 \text{ \AA}$) and present a clear structural relationship. They are quite different from β - Ba_3AlF_9 , which

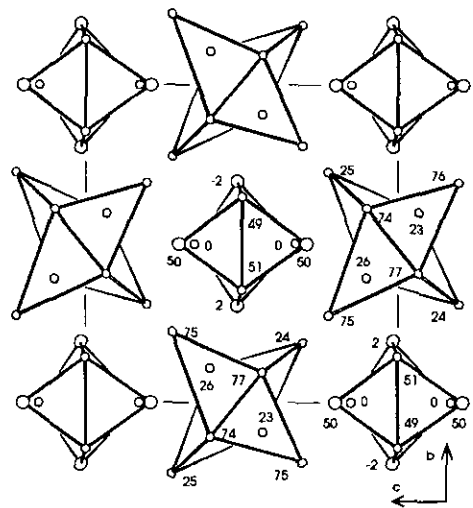


FIG. 3. The Ba_3Al cationic subnetwork of β - Ba_3AlF_9 , related to the β - V_3S structure, with Ba_{4+4} tetraedersterns (at the middle of the edges) and Ba_4Al_4 stellae quadrangulae. Small circles are Ba; large circles are Al atoms (heights in units of $a/100$).

appears to be 2% more dense; nevertheless, all three polymorphs are characterized by isolated $[\text{AlF}_6]$ octahedra and $[\text{FBa}_4]$ tetrahedra. If other polymorphs were synthesized, it would not be very surprising if one showed analogies with $\alpha\text{-V}_3\text{S}$.

The character of the reversible transition at 492 and 476°C has to be established. Owing to the *Pnc2* acentric space group and the close relationship with a tetragonal centrosymmetric compound, a ferroelectric–paraelectric transition is a possibility. A thermodiffraction study is planned which could also reveal the actual structure of Ba_3AlF_9 above 840°C, since the quenching operation cannot reveal this.

Turning back to considerations about feasibility of complex structure determination from powder data, it may be concluded that careful work together with the application of efficient algorithms has made it possible to determine a structure from conventional X-ray powder data as complex as any other unknown structure determined previously from synchrotron data. Like $\text{Ga}_2(\text{HPO}_3)_3 \cdot 4\text{H}_2\text{O}$ (1), $\beta\text{-Ba}_3\text{AlF}_9$ closes the gap between structures that can be refined and those that can be determined. None of these currently most complex structures, according to a criterion arbitrarily based on the full number of independent atoms, has made use of sophisticated recent efforts to facilitate the determination of structures because of high degree of overlapping (maximization and likelihood ranking (17), iterative Patterson squaring (18) or alternative methods (19, 20)). Instead, "brute force" was applied with success to the full data set (with equipartitioning) or to an expurgated one by simple elimination of reflections which overlap too much (conserving, however, slightly more than 50% reflections at 1 Å resolution). Both cases make use of one of the more sophisticated methods of extracting useful information from a powder pattern: iterating the Rietveld decomposition formula.

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