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α-BaCaAlF$_7$

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α-Barium calcium aluminium heptafluoride is a member of the isotypic complex fluorides of general formula BaCaMF$_7$ (M = Al, Ga, Cr). The crystal structure is made up of triple layers which extend parallel to the (001) plane, and are stacked along [001], with a stacking unit of c/2. The central unit of one triple layer consists of edge-sharing ${}^2_\infty$[CaF$_{8/2}$] polyhedra, forming a distorted fluorite-type arrangement. On both sides of this layer, isolated [AlF$_6$] octahedra are attached by edge-sharing with the central unit. The triple layers are held together by 11-coordinate Ba atoms that are located between the layers.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Al—F) = 0.002 Å
R factor = 0.019
wR factor = 0.043
Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Complex fluorides are interesting host lattices for doping with rare-earth or transition metal ions to obtain luminescent materials with slightly different characteristics, compared to the widely used oxides (Rubio, 1991; Kubel *et al.*, 1997; Joubert *et al.*, 2001).

Numerous phases in the pseudobinary system MF$_2$–AlF$_3$ with M = Ca, Sr, Ba have been reported, and the corresponding structures solved and refined from either single-crystal or powder data [M = Ca: CaAlF$_5$ (Hemon & Courbion, 1991) and Ca$_2$AlF$_7$ (Domesle & Hoppe, 1980); M = Sr: two polymorphs of SrAlF$_5$ (Von der Muehll *et al.*, 1971; Kubel, 1998; Weil *et al.*, 2001) and Sr$_5$Al$_2$F$_{16}$ (Weil, 2001); M = Ba: four polymorphic forms of BaAlF$_5$ (Domesle & Hoppe, 1982*a*; Le Bail *et al.*, 1990; Weil *et al.*, 2001), three polymorphic forms of Ba$_3$AlF$_9$ (Renaudin *et al.*, 1990; Renaudin *et al.*, 1991; Le Bail, 1993) and Ba$_3$Al$_2$F$_{12}$ (Domesle & Hoppe, 1982*b*)], whereas the number of structurally well-characterized compounds in the pseudo-ternary system MF$_2$–M'F$_2$–AlF$_3$ (M, M' = Ca, Sr, Ba) is restricted to only three representatives,

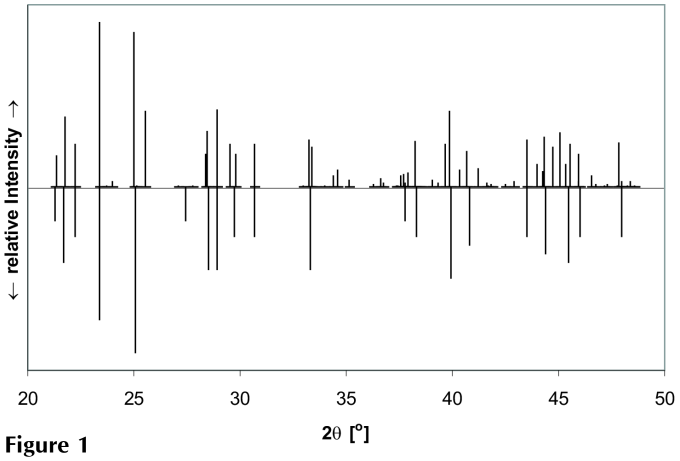

Figure 1
Powder patterns of α-BaCaAlF$_7$. Top: calculated from single-crystal data; bottom: PDF entry # 27-0090 (ICDD, 2001); 2θ values are for Cu $K\alpha_1$ radiation.

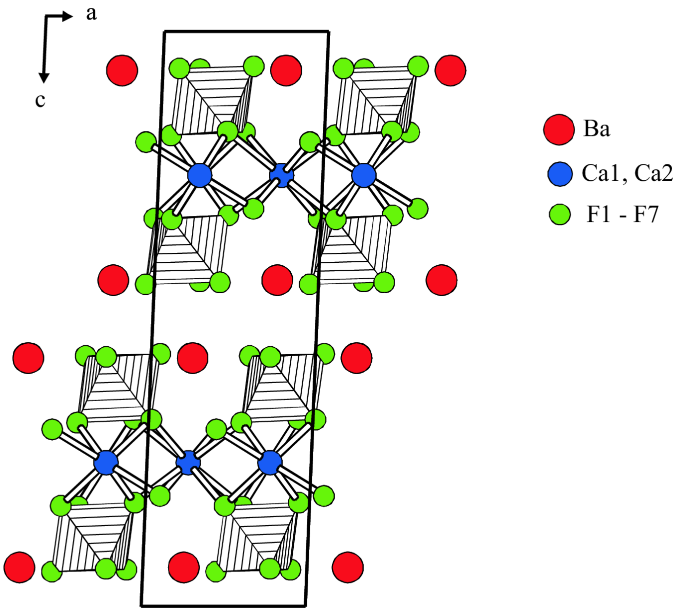

Figure 2
Projection of the crystal structure along [010]; the unit cell and the [AlF$_6$] octahedra are outlined.

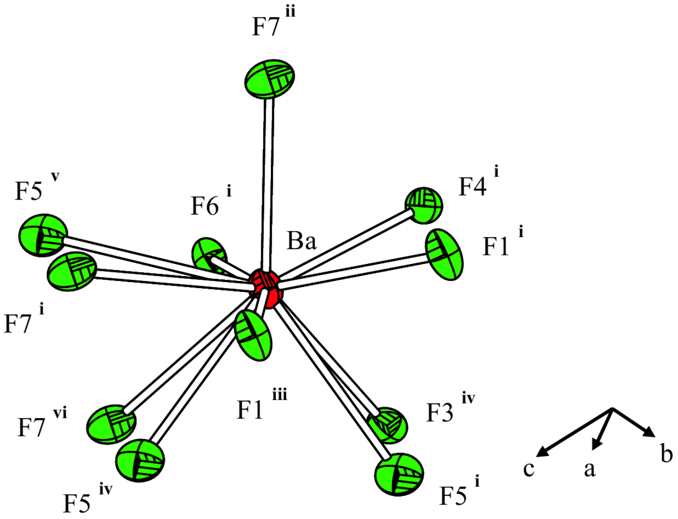

Figure 3
Displacement ellipsoid plot of the coordination environment of the Ba atom, with ellipsoids drawn at the 75% probability level.

with composition Ba$_{0.43}$Sr$_{0.57}$AlF$_5$ (Kubel, 1998), Sr$_{0.92}$Ca$_{0.08}$AlF$_5$ and Sr$_{0.67}$Ca$_{0.33}$AlF$_5$ (Weil *et al.*, 2001) (all single-crystal data). Additionally, two more phases with composition SrCaAlF$_7$ and BaCaAlF$_7$ have been reported, each with three polymorphic forms denoted as α, β and γ (Hoffman, 1972). For four modifications (all SrCaAlF$_7$ polymorphs and α–BaCaAlF$_7$), non-indexed powder data are given and their Eu$^{\rm II}$ activation was measured. The latter phase is a very interesting candidate as a luminescent material, since it shows a high Eu$^{\rm II}$ emission line. Fig. 1 shows that the phase previously described as α-BaCaAlF$_7$ is identical to the title compound. Except for an impurity line at $2\theta = 27.4°$, the entry in the powder diffraction file (PDF # 27-0090; ICDD, 2001) is in agreement with the powder pattern calculated on the basis of the single-crystal structure refinement.

α-BaCaAlF$_7$ is isotypic with BaCaGaF$_7$ and BaCaCrF$_7$ (Holler & Babel, 1985). In accordance with the slightly smaller ionic radius of Al$^{\rm III}$ (0.54 Å) with respect to Ga$^{\rm III}$ and Cr$^{\rm III}$ (both 0.62 Å, values from Shannon, 1976), the unit-cell volume of the title compound is slightly smaller (Al: 544 Å^3; Ga: 553 Å^3; Cr: 556 Å^3). The structure is built up from triple layers, which extend parallel to (001) and consist of a central unit and two side units (Fig. 2). The central unit is composed of edge-sharing ${}^{2}_{\infty}[\mathrm{CaF}_{8/2}]$ polyhedra with distorted square antiprisms as the corresponding coordination polyhedra. Although the intrapolyhedral geometry differs significantly from that of a cube found in the ideal fluorite structure, this arrangement can be considered as part of a distorted CaF$_2$ structure. This assumption is confirmed by comparable distances d(Ca1—Ca2) of 3.703 (1) and 3.902 (1) Å, as well as the average Ca—F distance of 2.372 Å and the values of the a and b axes, with respect to the distances and the lattice parameter in CaF$_2$ itself [d(Ca—Ca) = 3.869 Å, d(Ca—F) = 2.369 Å and a = 5.471 Å; values from Zhurova *et al.* (1996)]. The side units are made up from isolated [AlF$_6$] octahedra which share common edges with the central fluorite-type ${}^{2}_{\infty}[\mathrm{CaF}_{8/2}]$ layer. The average Al—F distance of 1.808 Å is in the typical range for [AlF$_6$] octahedra found in other complex aluminium fluorides. The largest deviation from the ideal octahedral angle is 6.6°. Two triple layers are stacked along [001] with a stacking unit of c/2 and are held together by 11-coordinated Ba atoms. The resulting [BaF$_{11}$] polyhedron might be described as a distorted tricapped rectangular prism (Fig. 3), with an average Ba—F distance of 2.850 Å. The F atoms exhibit either a coordination number (CN) of 3, resulting in a distorted trigonal planar environment (F1, F2 and F4), or CN = 4, with a distorted tetrahedral coordination geometry (F3, F5, F6 and F7).

Experimental

A mixture of 457 mg BaF$_2$ (Riedel-de Haën, 97%), 41 mg CaF$_2$ (Merck, Suprapur) and 44 mg AlF$_3$ (CERAC, 99.9%), corresponding to a molar ratio of 5:1:1, was added to 1 g ZnCl$_2$ (Aldrich, 98%) and placed in a platinum crucible. The reaction mixture was then heated under atmospheric conditions to 873 K over a period of 2 h. The flux was kept at that temperature for 2 h and then cooled to 473 K over a period of 12 h. After cooling to room temperature, the solidified melt was leached with demineralized water. Colourless plates of the title compound were isolated from the residue. Additionally, tetragonal plates of matlockite-type BaFCl (Sauvage, 1974) were found in the crystal mixture.

Crystal data

BaCaAlF$_7$
M_r = 337.40
Monoclinic, $P2/n$
a = 5.3664 (5) Å
b = 5.3846 (6) Å
c = 18.8262 (19) Å
β = 92.319 (2)°
V = 543.55 (10) Å^3
Z = 4
D_x = 4.123 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3828 reflections
θ = 3.2–30.5°
μ = 8.49 mm^{-1}
T = 293 (2) K
Plate, colourless
0.12 × 0.08 × 0.06 mm

Data collection

Siemens SMART area detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.429$, $T_{\max} = 0.630$
5719 measured reflections
1603 independent reflections
1477 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 30.5°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.044$
$S = 1.11$
1603 reflections
93 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0157P)^2 + 1.3785P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0038 (3)

Table 1
Selected geometric parameters (Å).

Ba—F4$^{\rm i}$	2.5498 (16)	Ca1—F4$^{\rm x}$	2.2282 (17)
Ba—F1$^{\rm i}$	2.6763 (17)	Ca1—F4	2.2282 (17)
Ba—F7$^{\rm ii}$	2.7542 (17)	Ca1—F3$^{\rm vii}$	2.3880 (16)
Ba—F1$^{\rm iii}$	2.7831 (17)	Ca1—F3$^{\rm xi}$	2.3880 (16)
Ba—F5$^{\rm i}$	2.7860 (17)	Ca1—F6$^{\rm xii}$	2.4102 (16)
Ba—F6$^{\rm i}$	2.8244 (16)	Ca1—F6$^{\rm xiii}$	2.4102 (16)
Ba—F5$^{\rm iv}$	2.8660 (18)	Ca1—F2$^{\rm xiv}$	2.4609 (18)
Ba—F7$^{\rm i}$	2.9510 (17)	Ca1—F2$^{\rm xv}$	2.4609 (18)
Ba—F5$^{\rm v}$	3.0058 (18)	Ca2—F4$^{\rm xii}$	2.2392 (17)
Ba—F7$^{\rm vi}$	3.0102 (17)	Ca2—F4	2.2392 (17)
Ba—F3$^{\rm iv}$	3.1421 (17)	Ca2—F2	2.3868 (16)
Al—F1$^{\rm vii}$	1.7535 (19)	Ca2—F2$^{\rm xii}$	2.3868 (16)
Al—F2$^{\rm vii}$	1.8038 (17)	Ca2—F6$^{\rm xvi}$	2.4231 (17)
Al—F7	1.8047 (18)	Ca2—F6$^{\rm xvii}$	2.4231 (17)
Al—F3	1.8083 (18)	Ca2—F3$^{\rm viii}$	2.4389 (17)
Al—F5$^{\rm viii}$	1.8133 (18)	Ca2—F3$^{\rm xi}$	2.4389 (17)
Al—F6$^{\rm ix}$	1.8614 (18)		

Symmetry codes: (i) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, 1-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}+x, 1-y, z-\frac{1}{2}$; (v) $\frac{1}{2}-x, y-1, \frac{1}{2}-z$; (vi) $\frac{1}{2}+x, -y, z-\frac{1}{2}$; (vii) $1-x, 1-y, 1-z$; (viii) $-x, 1-y, 1-z$; (ix) $-x, -y, 1-z$; (x) $\frac{3}{2}-x, y, \frac{3}{2}-z$; (xi) $\frac{1}{2}+x, 1-y, \frac{1}{2}+z$; (xii) $\frac{1}{2}-x, y, \frac{3}{2}-z$; (xiii) $1+x, y, z$; (xiv) $x, y-1, z$; (xv) $\frac{3}{2}-x, y-1, \frac{3}{2}-z$; (xvi) $\frac{1}{2}-x, 1+y, \frac{3}{2}-z$; (xvii) $x, 1+y, z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *SHELXL*97.

References

Domesle, R. & Hoppe, R. (1980). *Z. Kristallogr.* **153**, 317–328.
Domesle, R. & Hoppe, R. (1982*a*). *Z. Anorg. Allg. Chem.* **495**, 16–26.
Domesle, R. & Hoppe, R. (1982*b*). *Z. Anorg. Allg. Chem.* **495**, 27–28.
Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Hemon, A. & Courbion, C. (1991). *Acta Cryst.* C**47**, 1302–1303.
Hoffman, M. V. (1972). *J. Electrochem. Soc.* **119**, 905–909.
Holler, H. & Babel, D. (1985). *Z. Anorg. Allg. Chem.* **523**, 89–98.
ICDD (2001). *The Powder Diffraction File*. International Centre for Diffraction Data, 12 Campus Boulevard, Newton Square, PA 19073–3273, USA.
Joubert, M. F., Guyot, Y., Jacquier, B., Chaminade, J. P. & Garcia, A. (2001). *J. Fluorine Chem.* **107**, 235–240.
Kubel, F., Hagemann, H. & Bill, H. (1997). *Mater. Res. Bull.* **32**, 263–269.
Kubel, F. (1998). *Z. Anorg. Allg. Chem.* **624**, 1481–1486.
Le Bail, A., Férey, G., Mercier, A. M., de Kozak, A. & Samouël, M. (1990). *J. Solid State Chem.* **89**, 282–291.
Le Bail, A. (1993). *J. Solid State Chem.* **103**, 287–291.
Renaudin, A., Férey, G., de Kozak, A. & Samouël, M. (1990). *Eur. J. Solid State Inorg. Chem.* **27**, 571–580.
Renaudin, A., Férey, G., de Kozak, A. & Samouël, M. (1991). *Eur. J. Solid State Inorg. Chem.* **28**, 373–381.
Rubio, O. J. (1991). *J. Phys. Chem. Solids*, **52**, 101–174.
Sauvage, M. (1974). *Acta Cryst.* B**30**, 2786–2787.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Von der Muehll, R., Anderson, S. & Galy, J. (1971). *Acta Cryst.* B**27**, 2345–2353.
Weil, M., Zobetz, E., Werner, F. & Kubel, F. (2001). *Solid State Sci.* **3**, 441–453.
Weil, M. (2001). *Z. Anorg. Allg. Chem.* **627**, 2669–2672.
Zhurova, E. A., Maximov, B. A., Simonov, V. I. & Sobolev, B. P. (1996). *Kristallografiya*, **41**, 438–443.