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Crystal structure of the Fe-member of usovite

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Crystals of the title compound, with the idealized composition $\text{Ba}_2\text{CaFeAl}_2\text{F}_{14}$, dibarium calcium iron(II) dialuminium tetradecafluoride, were obtained serendipitously by reacting a mixture of the binary fluorides BaF_2 , CaF_2 and AlF_3 in a leaky steel reactor. The compound crystallizes in the usovite structure type ($\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$), with Fe^{2+} cations replacing the Mg^{2+} cations. The principal building units are distorted $[\text{CaF}_8]$ square-antiprisms (point group symmetry 2), $[\text{FeF}_6]$ octahedra (point group symmetry $\bar{1}$) and $[\text{AlF}_6]$ octahedra that are condensed into undulating ${}^2[\text{CaFeAl}_2\text{F}_{14}]^{4-}$ layers parallel (100). The Ba^{2+} cations separate the layers and exhibit a coordination number of 12. Two crystal structure models with a different treatment of the disordered Fe site [mixed Fe/Ca occupation, model (I), *versus* underoccupation of Fe, model (II)], are discussed, leading to different refined formulae $\text{Ba}_2\text{Ca}_{1.310(15)}\text{Fe}_{0.690(15)}\text{Al}_2\text{F}_{14}$ [model (I)] and $\text{Ba}_2\text{CaFe}_{0.90(1)}\text{Al}_2\text{F}_{14}$ [model (II)].

1. Chemical context

Fluoridoaluminates with alkaline earth cations exhibit a rich crystal chemistry (Babel & Tressaud, 1985; Weil *et al.*, 2001). They are suitable host materials for optical applications as has been shown by luminescence excitation studies of SrAlF_5 or CaAlF_5 doped with Pr^{3+} and Mn^{2+} (van der Kolk *et al.*, 2004). In order to prepare large single crystals of a related fluoridoaluminate with composition BaCaAlF_7 , a different preparation route was chosen in comparison with the reported crystal-growth procedure. Instead of using a ZnCl_2 melt (Werner & Weil, 2003), a carbon tool steel container shielded

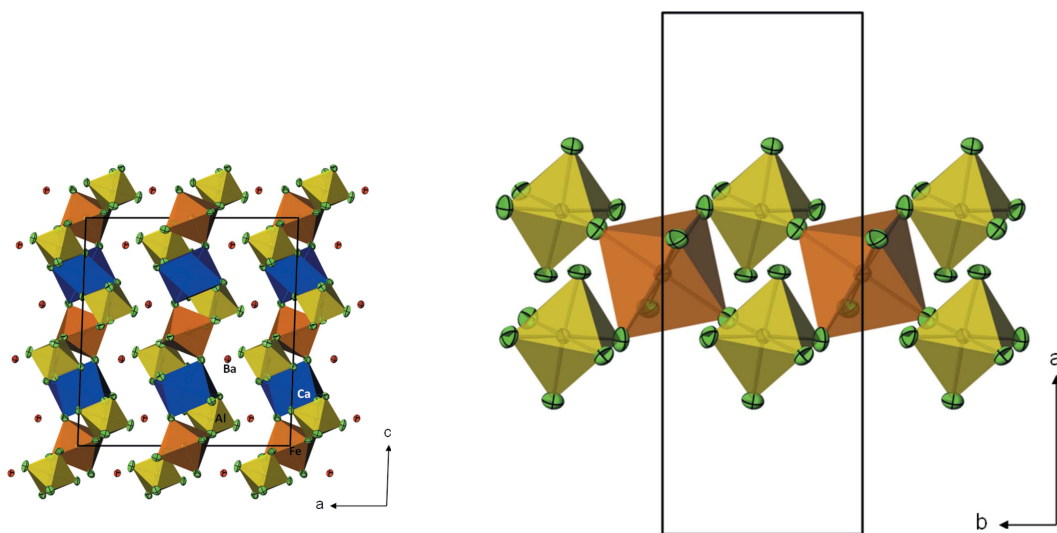


Figure 1
 $[\text{AlF}_6]$ octahedra (yellow, with F atoms green) and $[\text{FeF}_6]$ octahedra (orange) are linked into crosslinked double chains parallel to $[010]$. Displacement ellipsoids are drawn at the 74% probability level.

Table 1
Selected bond lengths (Å) for model (I).

For model (II), bond lengths are the same within their standard uncertainties.

Ba—F7	2.696 (2)	Ca2—F4	2.376 (2)
Ba—F4 ⁱ	2.730 (2)	Ca2—F4 ^{ix}	2.376 (2)
Ba—F1 ⁱ	2.755 (2)	Ca2—F5 ^x	2.544 (2)
Ba—F2 ⁱⁱ	2.765 (2)	Ca2—F5 ^{iv}	2.544 (2)
Ba—F5 ⁱⁱⁱ	2.766 (2)	Fe1—F7 ^x	2.015 (2)
Ba—F5 ^{iv}	2.827 (2)	Fe1—F7 ⁱ	2.015 (2)
Ba—F3 ^{iv}	2.889 (2)	Fe1—F2 ^{xi}	2.131 (2)
Ba—F1 ^v	2.889 (2)	Fe1—F2 ^{viii}	2.131 (2)
Ba—F3	2.974 (2)	Fe1—F3 ^x	2.216 (2)
Ba—F6 ⁱⁱⁱ	3.101 (2)	Fe1—F3 ⁱ	2.216 (2)
Ba—F6 ^{iv}	3.158 (2)	Al—F4 ^{xii}	1.780 (2)
Ba—F1 ^{vi}	3.233 (3)	Al—F1	1.780 (3)
Ca2—F7 ^{vii}	2.235 (2)	Al—F6 ^{iv}	1.790 (2)
Ca2—F7 ⁱ	2.235 (2)	Al—F2 ^{iv}	1.799 (2)
Ca2—F6 ⁱⁱⁱ	2.369 (2)	Al—F5 ⁱⁱⁱ	1.843 (2)
Ca2—F6 ^{viii}	2.369 (2)	Al—F3 ⁱⁱⁱ	1.846 (2)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + 1, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x, -y + 1, z + \frac{1}{2}$; (vii)

with a molybdenum foil was used for solid state reactions between a mixture of the binary fluorides (Weil & Kubel, 2002). However, during one of these experiments it turned out that the container was not completely lined by the molybdenum foil which consequently led to a reaction with the container wall and an incorporation of iron into parts of the reaction products. Crystal structure analysis of selected crystals from this reaction batch revealed an Fe-containing phase that crystallizes isotypically with the mineral usovite, $\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$ (Litvin *et al.*, 1980).

Compounds with the usovite-type structure are represented by the general formula $\text{Ba}_2(M^{\text{II}}1)(M^{\text{II}}2)(M^{\text{III}}3)_2\text{F}_{14}$ ($M^{\text{II}}1 = \text{Ca, Cd, Mn}$; $M^{\text{II}}2 = \text{Mg, Co, Mn, Cu, Cd, Fe}$; $M^{\text{III}}3 = \text{Al, V, Fe, Cr, Ga, Mn}$) and crystallize with four formula units in the space group $C2/c$. Most of the usovite-type representatives known so far were prepared and structurally determined by Babel, Tressaud and co-workers over the last three decades (Holler *et al.*, 1984, 1985; Kaiser *et al.*, 2002; Le Lirzin *et al.*, 1990, 1991, 2008; Qiang *et al.*, 1988).

2. Structural commentary

The principal building units of the usovite crystal structure are distorted $[\text{BaF}_{12}]$ polyhedra, $[(M^{\text{II}}1)\text{F}_8]$ square-antiprisms (point group symmetry 2) and $[(M^{\text{II}}2)\text{F}_6]$ octahedra (point group symmetry $\bar{1}$), as well as rather regular $[(M^{\text{III}}3)\text{F}_6]$ octahedra. The $[(M^{\text{II}}2)\text{F}_6]$ and $[(M^{\text{III}}3)\text{F}_6]$ octahedra are connected by corner-sharing into infinite crosslinked double chains $\infty[(M^{\text{II}}2)\text{F}_2\text{F}_{4/2}(M^{\text{III}}3)_2\text{F}_8\text{F}_{4/2}]$ extending parallel to $[010]$ (Fig. 1). Neighbouring chains are linked by the $[(M^{\text{II}}1)\text{F}_8]$ square-antiprisms into undulating (100) layers with composition $\infty^2[(M^{\text{II}}1)(M^{\text{II}}2)(M^{\text{III}}3)_2\text{F}_{14}]^{4-}$, with the Ba^{2+} cations separating the individual layers (Fig. 2).

The unit-cell volume of the title compound $[1067.9 (2) \text{ \AA}^3]$ is slightly larger than that of usovite $\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$ (1027.9 Å; Litvin *et al.*, 1980) due to the replacement of the Mg^{2+} cations (ionic radius = 0.72 Å; Shannon, 1976) by the

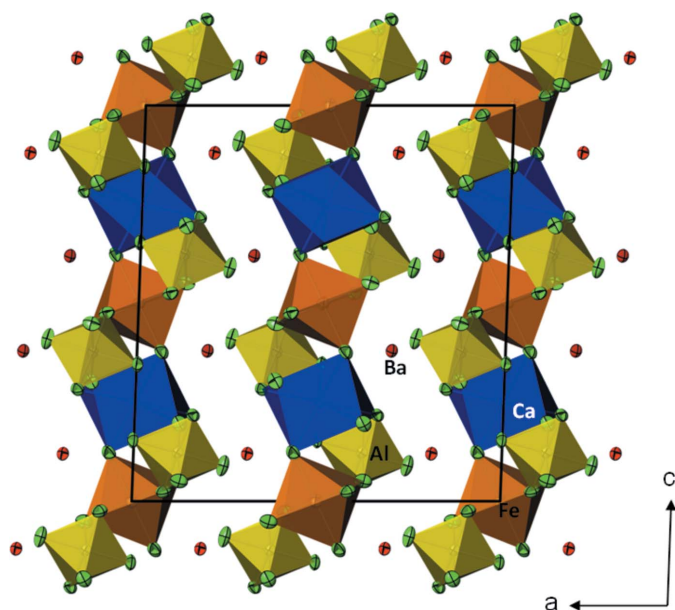


Figure 2
The crystal structure of the usovite-type title compound, emphasizing the formation of the layered $\infty^2[\text{CaFeAl}_2\text{F}_{14}]^{4-}$ framework parallel to (100), separated by Ba^{2+} cations. Displacement ellipsoids are drawn at the 74% probability level. The colour code is as in Fig. 1, with $[\text{CaF}_8]$ polyhedra in blue and Ba atoms in red.

larger Fe^{2+} cations (ionic radius = 0.78 Å; Shannon, 1976) at the $M^{\text{II}}2$ site. This is also reflected by the bond lengths within the individual coordination polyhedra (Table 1). Whereas the Ba—F, Ca—F and Al—F distances remain nearly unaltered between the two structures, the Mg—F and Fe—F distances show remarkable differences. The Mg—F distances in the usovite structure range from 1.939 to 2.041 Å, the corresponding Fe—F distances in the title structure from 2.015 (2) to 2.216 (2) Å, with a mean distance of 2.123 Å. The latter is in reasonable agreement with the mean $\text{Fe}^{\text{II}}-\text{F}$ distance of 2.106 Å in the isotypic crystal structure of $\text{Ba}_2\text{CaFeV}_2\text{F}_{14}$ (Kaiser *et al.*, 2002). However, the mean bond lengths in both the title structure and $\text{Ba}_2\text{CaFeV}_2\text{F}_{14}$ are considerably longer than that of 2.074 Å in the structure of the binary compound FeF_2 (Jauch *et al.*, 1993).

A similar increase of the $M-\text{F}$ bond lengths of the $[(M^{\text{II}}2)\text{F}_6]$ octahedra was also observed for a series of other usovite-type structures and was associated with an occupational disorder of the $M^{\text{II}}2$ site. For these models, either a mutual substitution of Ca^{2+} (on the $M^{\text{II}}1$ site) with corresponding divalent transition metal ions on the $M^{\text{II}}2$ site, or partial replacement of the divalent transition metal ions by Ca^{2+} at the $M^{\text{II}}2$ site was considered, resulting in stoichiometric compounds and Ca-rich compounds, respectively (Kaiser *et al.*, 2002). In the case of the title compound, a model with mutual substitution of Ca^{2+} and Fe^{2+} on the $M^{\text{II}}1$ and $M^{\text{II}}2$ sites could be ruled out during refinement. However, a model with an incorporation of Ca^{2+} on the Fe^{2+} site resulted in a ratio of $\text{Ca}:\text{Fe} = 0.155 (7):0.345 (7)$ for this site [model (I); overall refined formula for the compound: $\text{Ba}_2\text{Ca}_{1.310 (15)}\text{Fe}_{0.690 (15)}\text{Al}_2\text{F}_{14}$] and converged with the same reliability

Table 2
Bond-valence sum calculations for model (I) in valence units.

Atom	Assumed valence state	Bond-valence sum	Deviation from assumed valence state in valence units	Bond-valence sum under consideration of mixed Fe:Ca1 occupancy*
Ba	2	1.94	0.06	1.94
Fe1	2	1.73	0.27	2.00
Ca2	2	1.95	0.05	1.95
Al	3	2.97	0.03	2.97
F1	1	0.96	0.04	0.96
F2	1	0.99	0.01	1.03
F3	1	0.93	0.07	0.96
F4	1	1.00	0	1.00
F5	1	0.99	0.01	0.99
F6	1	0.92	0.08	0.92
F7	1	0.97	0.03	1.03

Note: (*) calculated with the weighted average Fe:Ca ratio of 0.77:0.23 at the $M2$ site.

factors and remaining electron densities as the model without an incorporation of Ca^{2+} and underoccupation of the Fe^{2+} site only [model (II); Table 3]. The refined formula for this model is $Ba_2Ca_2Fe_{0.90(1)}Al_2F_{14}$. Bond lengths and angles of the two models are the same within the corresponding standard uncertainties (Table 1).

Kaiser *et al.* (2002) have discussed in detail the pros and cons of the incorporation of Ca^{2+} (ionic radius = 1.0 Å; Shannon, 1976) at the $M^{II}2$ site for various usovite-type structures. Strong arguments supporting an $M^{II}2$ site with mixed Fe/Ca occupation are the resulting bond-valence sums

(Brown, 2002) that deviate significantly from the expected values of 2 if only Fe^{2+} ions are considered to be present at the $M^{II}2$ site (Table 2). Contrariwise, the bond-valence sums are in excellent agreement with the expected value if a mixed Fe/Ca occupancy is taken into account. The corresponding numbers are listed in Table 2 and were calculated with the weighted average occupancy ratio of Fe:Ca = 0.77:0.23 that was estimated by the program *VaList* (Wills, 2010). This ratio is in good agreement with the occupancy ratio from the refinement [model (I): Fe:Ca = 0.69:0.31]. The resulting global instability index (Brown, 2002) of 0.04 valence units for model (I) suggests a very tightly bonded structure with little strain. Any strain inherent in the usovite structure is obviously relieved by the substitution of Ca^{2+} on the $M^{II}2$ site.

On the other hand, an $M^{II}2$ site without an incorporation of Ca^{2+} would result in an underoccupation of Fe^{2+} [model (II)] and consequently requires the presence of an element in a higher oxidation state (here most probably Fe^{3+}) to compensate the negative charge of -2 of the $[Ba_2CaAl_2F_{14}]$ framework. Although in this case rather a decrease of $M^{II}2-F$ bond lengths should be expected (contrary to the findings of the current study), it cannot completely ruled out that Fe^{3+} ions are present at this site. As a matter of fact, based on diffraction data alone, there is a clear tendency towards model (I) but no definite answer whether Fe is partly replaced by Ca on the $M^{II}2$ site [model (I)] or is statistically occupied by Fe^{2+} and small amounts of Fe^{3+} [model (II)]. Complementary analytical techniques like Mössbauer spectroscopy will be needed in future to shed some light on this problem.

Table 3
Experimental details.

	Model (I)	Model (II)
Crystal data		
Chemical formula	$Ba_2Ca_{1.31}Fe_{0.69}Al_2F_{14}$	$Ba_2CaFe_{0.90}Al_2F_{14}$
M_r	685.68	684.98
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	293	293
a, b, c (Å)	13.7387 (12), 5.2701 (5), 14.759 (3)	13.7387 (12), 5.2701 (5), 14.759 (3)
β (°)	92.074 (14)	92.074 (14)
V (Å ³)	1067.9 (2)	1067.9 (2)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	9.21	9.33
Crystal size (mm)	0.43 × 0.11 × 0.07	0.43 × 0.11 × 0.07
Data collection		
Diffractometer	Nonius CAD-4 four-circle diffractometer	Nonius CAD-4 four-circle diffractometer
Absorption correction	ψ scan (North <i>et al.</i> , 1968)	ψ scan (North <i>et al.</i> , 1968)
T_{min}, T_{max}	0.329, 0.901	0.329, 0.901
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5922, 1564, 1490	5922, 1564, 1490
R_{int} ($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.055 0.703	0.055 0.703
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.078, 1.09	0.032, 0.078, 1.10
No. of reflections	1564	1564
No. of parameters	95	96
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	2.31, -2.03	2.32, -2.03

Computer programs: *CAD-4 Software* (Enraf-Nonius, 1989), *HELENA* implemented in *PLATON* (Spek, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ATOMS for Windows* (Dowty, 2006) and *pubCIF* (Westrip, 2010).

3. Synthesis and crystallization

The binary fluorides AlF_3 (Merck, Patinal), CaF_2 (Merck, Suprapur) and BaF_2 (Riedel de Haen, pure) were mixed in the stoichiometric ratio 1:1:1 and thoroughly ground in a ball mill, pressed into tablets and placed in a carbon tool steel container shielded with a molybdenum foil. $\text{NH}_4\text{F}\cdot\text{HF}$ (100 mg, Fluka, p.A.) were added to the mixture to increase the HF pressure, to expel the remaining oxygen and to adjust a slightly reducing atmosphere during the reaction. The reactor was then closed and heated to 1173 K in the course of 20 h, kept at that temperature for 24 h, and then cooled slowly to 973 K at a rate of 10 K h^{-1} , kept at this temperature for 24 h and finally cooled to room temperature overnight. After opening the reactor it became evident that parts of the molybdenum foil were torn apart accompanied by a severe attack of the inner container wall. Single crystals of the title compound were separated from the obtained colourless to light-green bulk material. X-ray powder diffraction of the bulk revealed the formation of $\alpha\text{-BaCaAlF}_7$ as the main phase and the title compound as a minority phase. Some additional reflections were also present that could not be assigned to any known phases.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Coordinates of usovite (Litvin *et al.*, 1980) were used as starting parameters for refinement. The model converged rather smoothly with $R1 = 0.034$ and $wR2 = 0.089$. However, negative residual electron density at the Fe atom pointed to an underoccupation and/or a statistical disorder of the $M^{II}2$ site with a lighter element present. In fact, free refinement of the site occupation factor for this site resulted in only 90% occupancy and significant better reliability factors (see Table 3). The same procedure applied for all other atoms resulted in full occupancy within the twofold standard uncertainty. For the final models, full occupancy was therefore considered for all atoms except Fe. Model (I) accounts for an incorporation of Ca^{2+} at the Fe site under consideration of full occupancy; in model (II), the site occupation factor of the Fe site was refined freely without contribution of Ca^{2+} at this site. The remaining electron densities (Table 3) are virtually the same for both models. They are associated with truncation effects close to the heavy Ba sites,

with the maximum electron density 0.68 \AA^{-3} and the minimum electron density 0.96 \AA^{-3} away from the Ba atom.

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supporting information

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Crystal structure of the Fe-member of usovite

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Computing details

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989) for modelI; *CAD-4 Software* (Enraf-Nonius, 1989) for modelII. Cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989) for modelI; *CAD-4 Software* (Enraf-Nonius, 1989) for modelII. For both compounds, data reduction: *HELENA* implemented in *PLATON* (Spek, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *ATOMS for Windows* (Dowty, 2006) for modelI; *Atoms for Windows* (Dowty, 2006) for modelII. For both compounds, software used to prepare material for publication: *publCIF* (Westrip, 2010).

(modelI) Dibarium calcium iron(II) dialuminium tetradecafluoride

Crystal data

Ba₂CaFeAl₂F₁₄

$M_r = 685.68$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 13.7387$ (12) Å

$b = 5.2701$ (5) Å

$c = 14.759$ (3) Å

$\beta = 92.074$ (14)°

$V = 1067.9$ (2) Å³

$Z = 4$

$F(000) = 1233$

$D_x = 4.265$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 16.0$ – 28.7 °

$\mu = 9.21$ mm⁻¹

$T = 293$ K

Lath, colourless

$0.43 \times 0.11 \times 0.07$ mm

Data collection

Nonius CAD-4 four-circle diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: ψ scan (North *et al.*, 1968)

$T_{\min} = 0.329$, $T_{\max} = 0.901$

5922 measured reflections

1564 independent reflections

1490 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.8$ °

$h = -19 \rightarrow 19$

$k = -7 \rightarrow 7$

$l = -20 \rightarrow 20$

3 standard reflections every 240 min

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.078$

$S = 1.09$

1564 reflections

95 parameters

0 restraints

Primary atom site location: isomorphous structure methods

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 2.0371P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.31$ e Å⁻³

$$\Delta\rho_{\min} = -2.03 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0022 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ba	0.308721 (14)	0.46574 (4)	0.379963 (13)	0.01408 (12)	
Fe1	0.0000	0.5000	0.0000	0.0122 (2)	0.690 (15)
Ca1	0.0000	0.5000	0.0000	0.0122 (2)	0.310 (15)
Ca2	0.0000	0.44616 (15)	0.2500	0.01239 (19)	
Al	0.38007 (8)	0.50390 (18)	0.12342 (7)	0.0111 (2)	
F1	0.25596 (18)	0.4521 (4)	0.0896 (2)	0.0240 (5)	
F2	0.08574 (15)	0.1721 (4)	0.97491 (13)	0.0184 (4)	
F3	0.37359 (16)	0.2100 (4)	0.55132 (14)	0.0197 (4)	
F4	0.00268 (16)	0.0837 (4)	0.15434 (15)	0.0190 (4)	
F5	0.34180 (14)	0.2933 (4)	0.71743 (13)	0.0157 (4)	
F6	0.12186 (16)	0.2677 (4)	0.80391 (15)	0.0207 (4)	
F7	0.43370 (17)	0.0715 (4)	0.37866 (16)	0.0208 (4)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.01226 (15)	0.01401 (16)	0.01593 (15)	-0.00069 (5)	-0.00023 (9)	0.00074 (5)
Fe1	0.0106 (4)	0.0124 (3)	0.0136 (4)	0.0004 (2)	-0.0005 (3)	-0.0029 (2)
Ca1	0.0106 (4)	0.0124 (3)	0.0136 (4)	0.0004 (2)	-0.0005 (3)	-0.0029 (2)
Ca2	0.0131 (4)	0.0124 (4)	0.0118 (4)	0.000	0.0019 (3)	0.000
Al	0.0114 (5)	0.0096 (3)	0.0123 (5)	-0.0007 (3)	-0.0004 (4)	0.0005 (3)
F1	0.0130 (11)	0.0219 (11)	0.0366 (14)	-0.0017 (8)	-0.0069 (10)	-0.0007 (9)
F2	0.0218 (10)	0.0183 (9)	0.0148 (8)	0.0033 (8)	-0.0016 (7)	-0.0026 (7)
F3	0.0269 (11)	0.0140 (8)	0.0184 (9)	-0.0003 (8)	0.0027 (8)	-0.0032 (7)
F4	0.0100 (9)	0.0247 (9)	0.0224 (10)	-0.0014 (8)	0.0000 (7)	-0.0087 (8)
F5	0.0155 (9)	0.0173 (8)	0.0145 (8)	-0.0037 (7)	0.0027 (6)	0.0004 (7)
F6	0.0220 (10)	0.0161 (8)	0.0243 (10)	0.0037 (8)	0.0035 (8)	0.0076 (8)
F7	0.0183 (11)	0.0239 (10)	0.0206 (10)	0.0009 (9)	0.0052 (8)	-0.0067 (8)

Geometric parameters (\AA , $^\circ$)

Ba—F7	2.696 (2)	Ca2—F4	2.376 (2)
Ba—F4 ⁱ	2.730 (2)	Ca2—F4 ^{ix}	2.376 (2)

Ba—F1 ⁱ	2.755 (2)	Ca2—F5 ^x	2.544 (2)
Ba—F2 ⁱⁱ	2.765 (2)	Ca2—F5 ^{iv}	2.544 (2)
Ba—F5 ⁱⁱⁱ	2.766 (2)	Fe1—F7 ^x	2.015 (2)
Ba—F5 ^{iv}	2.827 (2)	Fe1—F7 ⁱ	2.015 (2)
Ba—F3 ^{iv}	2.889 (2)	Fe1—F2 ^{xi}	2.131 (2)
Ba—F1 ^v	2.889 (2)	Fe1—F2 ^{viii}	2.131 (2)
Ba—F3	2.974 (2)	Fe1—F3 ^x	2.216 (2)
Ba—F6 ⁱⁱⁱ	3.101 (2)	Fe1—F3 ⁱ	2.216 (2)
Ba—F6 ^{iv}	3.158 (2)	Al—F4 ^{xii}	1.780 (2)
Ba—F1 ^{vi}	3.233 (3)	Al—F1	1.780 (3)
Ca2—F7 ^{vii}	2.235 (2)	Al—F6 ^{iv}	1.790 (2)
Ca2—F7 ⁱ	2.235 (2)	Al—F2 ^{iv}	1.799 (2)
Ca2—F6 ⁱⁱⁱ	2.369 (2)	Al—F5 ⁱⁱⁱ	1.843 (2)
Ca2—F6 ^{viii}	2.369 (2)	Al—F3 ⁱⁱⁱ	1.846 (2)
F7—Ba—F4 ⁱ	64.22 (7)	F6 ⁱⁱⁱ —Ca2—F6 ^{viii}	100.95 (11)
F7—Ba—F1 ⁱ	158.04 (7)	F7 ^{vii} —Ca2—F4	139.26 (9)
F4 ⁱ —Ba—F1 ⁱ	97.60 (7)	F7 ⁱ —Ca2—F4	73.58 (8)
F7—Ba—F2 ⁱⁱ	89.56 (7)	F6 ⁱⁱⁱ —Ca2—F4	133.25 (7)
F4 ⁱ —Ba—F2 ⁱⁱ	65.13 (7)	F6 ^{viii} —Ca2—F4	109.76 (8)
F1 ⁱ —Ba—F2 ⁱⁱ	70.80 (7)	F7 ^{vii} —Ca2—F4 ^{ix}	73.58 (8)
F7—Ba—F5 ⁱⁱⁱ	102.89 (6)	F7 ⁱ —Ca2—F4 ^{ix}	139.26 (9)
F4 ⁱ —Ba—F5 ⁱⁱⁱ	63.11 (6)	F6 ⁱⁱⁱ —Ca2—F4 ^{ix}	109.76 (8)
F1 ⁱ —Ba—F5 ⁱⁱⁱ	77.18 (7)	F6 ^{viii} —Ca2—F4 ^{ix}	133.25 (7)
F2 ⁱⁱ —Ba—F5 ⁱⁱⁱ	113.14 (6)	F4—Ca2—F4 ^{ix}	73.00 (12)
F7—Ba—F5 ^{iv}	94.51 (6)	F7 ^{vii} —Ca2—F5 ^x	86.30 (7)
F4 ⁱ —Ba—F5 ^{iv}	134.23 (6)	F7 ⁱ —Ca2—F5 ^x	110.96 (8)
F1 ⁱ —Ba—F5 ^{iv}	107.32 (7)	F6 ⁱⁱⁱ —Ca2—F5 ^x	165.39 (7)
F2 ⁱⁱ —Ba—F5 ^{iv}	159.58 (6)	F6 ^{viii} —Ca2—F5 ^x	70.35 (7)
F5 ⁱⁱⁱ —Ba—F5 ^{iv}	85.46 (4)	F4—Ca2—F5 ^x	61.35 (7)
F7—Ba—F3 ^{iv}	108.42 (7)	F4 ^{ix} —Ca2—F5 ^x	71.46 (7)
F4 ⁱ —Ba—F3 ^{iv}	168.26 (6)	F7 ^{vii} —Ca2—F5 ^{iv}	110.96 (8)
F1 ⁱ —Ba—F3 ^{iv}	87.26 (7)	F7 ⁱ —Ca2—F5 ^{iv}	86.30 (7)
F2 ⁱⁱ —Ba—F3 ^{iv}	106.93 (6)	F6 ⁱⁱⁱ —Ca2—F5 ^{iv}	70.35 (7)
F5 ⁱⁱⁱ —Ba—F3 ^{iv}	128.56 (6)	F6 ^{viii} —Ca2—F5 ^{iv}	165.39 (7)
F5 ^{iv} —Ba—F3 ^{iv}	52.84 (6)	F4—Ca2—F5 ^{iv}	71.46 (7)
F7—Ba—F1 ^v	58.57 (7)	F4 ^{ix} —Ca2—F5 ^{iv}	61.35 (7)
F4 ⁱ —Ba—F1 ^v	122.79 (7)	F5 ^x —Ca2—F5 ^{iv}	120.53 (9)
F1 ⁱ —Ba—F1 ^v	138.03 (11)	Fe1 ^{ix} —Ca2—Ca1 ^{ix}	0.0
F2 ⁱⁱ —Ba—F1 ^v	113.81 (7)	F4 ^{xii} —Al—F1	175.02 (12)
F5 ⁱⁱⁱ —Ba—F1 ^v	128.75 (7)	F4 ^{xii} —Al—F6 ^{iv}	93.99 (12)
F5 ^{iv} —Ba—F1 ^v	53.35 (7)	F1—Al—F6 ^{iv}	90.60 (11)
F3 ^{iv} —Ba—F1 ^v	50.92 (7)	F4 ^{xii} —Al—F2 ^{iv}	93.23 (11)
F7—Ba—F3	59.03 (6)	F1—Al—F2 ^{iv}	88.30 (12)
F4 ⁱ —Ba—F3	90.21 (6)	F6 ^{iv} —Al—F2 ^{iv}	94.65 (11)
F1 ⁱ —Ba—F3	111.82 (7)	F4 ^{xii} —Al—F5 ⁱⁱⁱ	87.88 (10)
F2 ⁱⁱ —Ba—F3	52.19 (6)	F1—Al—F5 ⁱⁱⁱ	90.20 (12)
F5 ⁱⁱⁱ —Ba—F3	153.12 (6)	F6 ^{iv} —Al—F5 ⁱⁱⁱ	90.11 (11)

F5 ^{iv} —Ba—F3	113.88 (6)	F2 ^{iv} —Al—F5 ⁱⁱⁱ	175.02 (11)
F3 ^{iv} —Ba—F3	78.06 (7)	F4 ^{xii} —Al—F3 ⁱⁱⁱ	88.87 (11)
F1 ^v —Ba—F3	61.81 (7)	F1—Al—F3 ⁱⁱⁱ	86.45 (11)
F7—Ba—F6 ⁱⁱⁱ	149.96 (6)	F6 ^{iv} —Al—F3 ⁱⁱⁱ	176.00 (12)
F4 ⁱ —Ba—F6 ⁱⁱⁱ	127.50 (6)	F2 ^{iv} —Al—F3 ⁱⁱⁱ	87.98 (11)
F1 ⁱ —Ba—F6 ⁱⁱⁱ	50.94 (6)	F5 ⁱⁱⁱ —Al—F3 ⁱⁱⁱ	87.19 (10)
F2 ⁱⁱ —Ba—F6 ⁱⁱⁱ	120.41 (6)	Al—F1—Ba ^v	114.10 (11)
F5 ⁱⁱⁱ —Ba—F6 ⁱⁱⁱ	68.78 (5)	Al—F1—Ba ⁱ	96.30 (9)
F5 ^{iv} —Ba—F6 ⁱⁱⁱ	56.89 (6)	Ba ^v —F1—Ba ⁱ	138.03 (11)
F3 ^{iv} —Ba—F6 ⁱⁱⁱ	63.59 (6)	Al—F1—Ba ⁱⁱⁱ	90.11 (11)
F1 ^v —Ba—F6 ⁱⁱⁱ	103.02 (6)	Ba ^v —F1—Ba ⁱⁱⁱ	111.43 (8)
F3—Ba—F6 ⁱⁱⁱ	137.04 (6)	Ba ⁱ —F1—Ba ⁱⁱⁱ	95.98 (7)
F7—Ba—F6 ^{iv}	58.76 (6)	Al ^{iv} —F2—Ca1 ^{xiii}	136.08 (11)
F4 ⁱ —Ba—F6 ^{iv}	67.12 (6)	Al ^{iv} —F2—Fe1 ^{xiii}	136.08 (11)
F1 ⁱ —Ba—F6 ^{iv}	127.71 (7)	Ca1 ^{xiii} —F2—Fe1 ^{xiii}	0.0
F2 ⁱⁱ —Ba—F6 ^{iv}	130.73 (6)	Al ^{iv} —F2—Ba ^{xiv}	106.09 (9)
F5 ⁱⁱⁱ —Ba—F6 ^{iv}	50.92 (6)	Ca1 ^{xiii} —F2—Ba ^{xiv}	117.51 (8)
F5 ^{iv} —Ba—F6 ^{iv}	67.24 (5)	Fe1 ^{xiii} —F2—Ba ^{xiv}	117.51 (8)
F3 ^{iv} —Ba—F6 ^{iv}	118.00 (6)	Al ^{vi} —F3—Ca1 ^v	125.67 (12)
F1 ^v —Ba—F6 ^{iv}	82.68 (7)	Al ^{vi} —F3—Fe1 ^v	125.67 (12)
F3—Ba—F6 ^{iv}	117.62 (5)	Ca1 ^v —F3—Fe1 ^v	0.0
F6 ⁱⁱⁱ —Ba—F6 ^{iv}	97.89 (5)	Al ^{vi} —F3—Ba ^{iv}	94.81 (9)
F7—Ba—F1 ^{vi}	105.96 (6)	Ca1 ^v —F3—Ba ^{iv}	131.32 (9)
F4 ⁱ —Ba—F1 ^{vi}	113.22 (7)	Fe1 ^v —F3—Ba ^{iv}	131.32 (9)
F1 ⁱ —Ba—F1 ^{vi}	68.57 (8)	Al ^{vi} —F3—Ba	97.28 (9)
F2 ⁱⁱ —Ba—F1 ^{vi}	48.35 (6)	Ca1 ^v —F3—Ba	98.63 (7)
F5 ⁱⁱⁱ —Ba—F1 ^{vi}	144.90 (6)	Fe1 ^v —F3—Ba	98.63 (7)
F5 ^{iv} —Ba—F1 ^{vi}	111.48 (6)	Ba ^{iv} —F3—Ba	101.94 (7)
F3 ^{iv} —Ba—F1 ^{vi}	58.64 (6)	Al ^{xv} —F4—Ca2	107.90 (10)
F1 ^v —Ba—F1 ^{vi}	84.02 (7)	Al ^{xv} —F4—Ba ^v	142.62 (11)
F3—Ba—F1 ^{vi}	46.95 (6)	Ca2—F4—Ba ^v	109.17 (8)
F6 ⁱⁱⁱ —Ba—F1 ^{vi}	94.27 (6)	Al ^{vi} —F5—Ca2 ^{iv}	99.49 (9)
F6 ^{iv} —Ba—F1 ^{vi}	163.69 (5)	Al ^{vi} —F5—Ba ^{vi}	116.54 (9)
F7 ^x —Fe1—F2 ^{xi}	85.92 (8)	Ca2 ^{iv} —F5—Ba ^{vi}	103.29 (7)
F7 ⁱ —Fe1—F2 ^{xi}	94.08 (8)	Al ^{vi} —F5—Ba ^{iv}	96.93 (8)
F7 ^x —Fe1—F2 ^{viii}	94.08 (8)	Ca2 ^{iv} —F5—Ba ^{iv}	117.45 (8)
F7 ⁱ —Fe1—F2 ^{viii}	85.92 (8)	Ba ^{vi} —F5—Ba ^{iv}	121.50 (7)
F7 ^x —Fe1—F3 ^x	82.86 (8)	Al ^{iv} —F6—Ca2 ^{viii}	133.22 (12)
F7 ⁱ —Fe1—F3 ^x	97.14 (8)	Al ^{iv} —F6—Ba ^{vi}	100.10 (9)
F2 ^{xi} —Fe1—F3 ^x	95.71 (8)	Ca2 ^{viii} —F6—Ba ^{vi}	113.52 (8)
F2 ^{viii} —Fe1—F3 ^x	84.29 (8)	Al ^{iv} —F6—Ba ^{iv}	102.40 (9)
F7 ^x —Fe1—F3 ⁱ	97.14 (8)	Ca2 ^{viii} —F6—Ba ^{iv}	101.02 (7)
F7 ⁱ —Fe1—F3 ⁱ	82.86 (8)	Ba ^{vi} —F6—Ba ^{iv}	102.46 (6)
F2 ^{xi} —Fe1—F3 ⁱ	84.29 (8)	Ca1 ^v —F7—Fe1 ^v	0.0
F2 ^{viii} —Fe1—F3 ⁱ	95.71 (8)	Ca1 ^v —F7—Ca2 ^{xvi}	120.98 (11)
F7 ^{vii} —Ca2—F7 ⁱ	145.63 (12)	Fe1 ^v —F7—Ca2 ^{xvi}	120.98 (11)
F7 ^{vii} —Ca2—F6 ⁱⁱⁱ	80.29 (8)	Ca1 ^v —F7—Ba	113.91 (9)
F7 ⁱ —Ca2—F6 ⁱⁱⁱ	78.02 (8)	Fe1 ^v —F7—Ba	113.91 (9)

F7 ^{vii} —Ca2—F6 ^{viii}	78.02 (8)	Ca2 ^{xvi} —F7—Ba	120.86 (10)
F7 ⁱ —Ca2—F6 ^{viii}	80.29 (8)		

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

(modell)*Crystal data*

Al₂Ba₂CaF₁₄Fe_{0.90}
M_r = 684.98
 Monoclinic, *C2/c*
 Hall symbol: $-C\ 2yc$
a = 13.7387 (12) Å
b = 5.2701 (5) Å
c = 14.759 (3) Å
 β = 92.074 (14)°
V = 1067.9 (2) Å³
Z = 4

F(000) = 1240
D_x = 4.260 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 16.0–28.7°
 μ = 9.33 mm⁻¹
T = 293 K
 Lath, colourless
 0.43 × 0.11 × 0.07 mm

Data collection

Nonius CAD-4 four-circle
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.329, *T_{max}* = 0.901
 5922 measured reflections

1564 independent reflections
 1490 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
 θ_{\max} = 30.0°, θ_{\min} = 2.8°
 $h = -19 \rightarrow 19$
 $k = -7 \rightarrow 7$
 $l = -20 \rightarrow 20$
 3 standard reflections every 240 min
 intensity decay: none

Refinement

Refinement on *F*²
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.078$
S = 1.10
 1564 reflections
 96 parameters
 0 restraints

Primary atom site location: isomorphous
 structure methods
 $w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 1.6437P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.32\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -2.03\text{ e \AA}^{-3}$
 Extinction correction: *SHELXL*,
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0022 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of *F*² against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on *F*², conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative *F*². The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. *R*-factors based on *F*² are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ba	0.308719 (14)	0.46574 (4)	0.379962 (12)	0.01408 (12)	
Ca	0.0000	0.44617 (15)	0.2500	0.01239 (19)	
Al	0.38008 (8)	0.50390 (18)	0.12340 (7)	0.0111 (2)	
Fe	0.0000	0.5000	0.0000	0.0114 (3)	0.901 (5)
F1	0.25596 (18)	0.4521 (4)	0.0896 (2)	0.0240 (5)	
F2	0.08572 (15)	0.1721 (4)	0.97492 (13)	0.0184 (4)	
F3	0.37360 (16)	0.2100 (4)	0.55132 (14)	0.0197 (4)	
F4	0.00267 (15)	0.0837 (4)	0.15434 (15)	0.0190 (4)	
F5	0.34178 (14)	0.2932 (4)	0.71742 (13)	0.0157 (4)	
F6	0.12185 (16)	0.2677 (4)	0.80392 (14)	0.0207 (4)	
F7	0.43372 (16)	0.0715 (4)	0.37867 (16)	0.0208 (4)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.01226 (16)	0.01399 (16)	0.01592 (15)	-0.00069 (5)	-0.00023 (9)	0.00074 (5)
Ca	0.0131 (4)	0.0124 (4)	0.0118 (4)	0.000	0.0019 (3)	0.000
Al	0.0114 (5)	0.0096 (3)	0.0123 (5)	-0.0007 (3)	-0.0003 (4)	0.0005 (3)
Fe	0.0098 (4)	0.0115 (3)	0.0128 (4)	0.0004 (2)	-0.0005 (3)	-0.0030 (2)
F1	0.0129 (11)	0.0219 (11)	0.0366 (14)	-0.0017 (8)	-0.0068 (10)	-0.0007 (9)
F2	0.0219 (10)	0.0184 (9)	0.0148 (8)	0.0032 (8)	-0.0016 (7)	-0.0026 (7)
F3	0.0270 (11)	0.0140 (8)	0.0184 (9)	-0.0004 (8)	0.0027 (8)	-0.0031 (7)
F4	0.0100 (9)	0.0247 (9)	0.0224 (10)	-0.0013 (8)	0.0000 (7)	-0.0086 (8)
F5	0.0156 (9)	0.0172 (8)	0.0145 (8)	-0.0038 (7)	0.0027 (6)	0.0004 (7)
F6	0.0221 (10)	0.0160 (8)	0.0243 (10)	0.0037 (8)	0.0036 (8)	0.0076 (8)
F7	0.0182 (11)	0.0238 (9)	0.0207 (10)	0.0008 (8)	0.0053 (8)	-0.0067 (8)

Geometric parameters (\AA , $^\circ$)

Ba—F7	2.696 (2)	Ca—F4	2.376 (2)
Ba—F4 ⁱ	2.730 (2)	Ca—F4 ^{ix}	2.376 (2)
Ba—F1 ⁱ	2.755 (2)	Ca—F5 ^x	2.544 (2)
Ba—F2 ⁱⁱ	2.766 (2)	Ca—F5 ^{iv}	2.544 (2)
Ba—F5 ⁱⁱⁱ	2.767 (2)	Fe—F7 ⁱ	2.015 (2)
Ba—F5 ^{iv}	2.826 (2)	Fe—F7 ^x	2.015 (2)
Ba—F3 ^{iv}	2.889 (2)	Fe—F2 ^{viii}	2.131 (2)
Ba—F1 ^v	2.889 (2)	Fe—F2 ^{xi}	2.131 (2)
Ba—F3	2.974 (2)	Fe—F3 ^x	2.216 (2)
Ba—F6 ⁱⁱⁱ	3.101 (2)	Fe—F3 ⁱ	2.216 (2)
Ba—F6 ^{iv}	3.159 (2)	Al—F4 ^{xii}	1.779 (2)
Ba—F1 ^{vi}	3.232 (3)	Al—F1	1.780 (3)
Ca—F7 ^{vii}	2.235 (2)	Al—F6 ^{iv}	1.790 (2)
Ca—F7 ⁱ	2.235 (2)	Al—F2 ^{iv}	1.799 (2)
Ca—F6 ⁱⁱⁱ	2.369 (2)	Al—F5 ⁱⁱⁱ	1.843 (2)
Ca—F6 ^{viii}	2.369 (2)	Al—F3 ⁱⁱⁱ	1.846 (2)

F7—Ba—F4 ⁱ	64.22 (7)	F7 ⁱ —Ca—F4 ^{ix}	139.26 (9)
F7—Ba—F1 ⁱ	158.04 (7)	F6 ⁱⁱⁱ —Ca—F4 ^{ix}	109.75 (8)
F4 ⁱ —Ba—F1 ⁱ	97.60 (7)	F6 ^{viii} —Ca—F4 ^{ix}	133.25 (7)
F7—Ba—F2 ⁱⁱ	89.56 (7)	F4—Ca—F4 ^{ix}	73.01 (12)
F4 ⁱ —Ba—F2 ⁱⁱ	65.12 (7)	F7 ^{vii} —Ca—F5 ^x	86.30 (7)
F1 ⁱ —Ba—F2 ⁱⁱ	70.80 (7)	F7 ⁱ —Ca—F5 ^x	110.95 (8)
F7—Ba—F5 ⁱⁱⁱ	102.89 (6)	F6 ⁱⁱⁱ —Ca—F5 ^x	165.38 (7)
F4 ⁱ —Ba—F5 ⁱⁱⁱ	63.12 (6)	F6 ^{viii} —Ca—F5 ^x	70.34 (7)
F1 ⁱ —Ba—F5 ⁱⁱⁱ	77.18 (7)	F4—Ca—F5 ^x	61.35 (7)
F2 ⁱⁱ —Ba—F5 ⁱⁱⁱ	113.14 (6)	F4 ^{ix} —Ca—F5 ^x	71.47 (7)
F7—Ba—F5 ^{iv}	94.51 (6)	F7 ^{vii} —Ca—F5 ^{iv}	110.95 (7)
F4 ⁱ —Ba—F5 ^{iv}	134.23 (6)	F7 ⁱ —Ca—F5 ^{iv}	86.30 (7)
F1 ⁱ —Ba—F5 ^{iv}	107.33 (6)	F6 ⁱⁱⁱ —Ca—F5 ^{iv}	70.34 (7)
F2 ⁱⁱ —Ba—F5 ^{iv}	159.58 (6)	F6 ^{viii} —Ca—F5 ^{iv}	165.38 (7)
F5 ⁱⁱⁱ —Ba—F5 ^{iv}	85.46 (4)	F4—Ca—F5 ^{iv}	71.47 (7)
F7—Ba—F3 ^{iv}	108.42 (6)	F4 ^{ix} —Ca—F5 ^{iv}	61.35 (7)
F4 ⁱ —Ba—F3 ^{iv}	168.26 (6)	F5 ^x —Ca—F5 ^{iv}	120.54 (9)
F1 ⁱ —Ba—F3 ^{iv}	87.26 (7)	F4 ^{xii} —Al—F1	175.02 (12)
F2 ⁱⁱ —Ba—F3 ^{iv}	106.93 (6)	F4 ^{xii} —Al—F6 ^{iv}	94.00 (11)
F5 ⁱⁱⁱ —Ba—F3 ^{iv}	128.56 (6)	F1—Al—F6 ^{iv}	90.60 (11)
F5 ^{iv} —Ba—F3 ^{iv}	52.85 (6)	F4 ^{xii} —Al—F2 ^{iv}	93.23 (11)
F7—Ba—F1 ^v	58.57 (7)	F1—Al—F2 ^{iv}	88.31 (12)
F4 ⁱ —Ba—F1 ^v	122.79 (7)	F6 ^{iv} —Al—F2 ^{iv}	94.65 (11)
F1 ⁱ —Ba—F1 ^v	138.03 (11)	F4 ^{xii} —Al—F5 ⁱⁱⁱ	87.88 (10)
F2 ⁱⁱ —Ba—F1 ^v	113.81 (7)	F1—Al—F5 ⁱⁱⁱ	90.18 (12)
F5 ⁱⁱⁱ —Ba—F1 ^v	128.76 (7)	F6 ^{iv} —Al—F5 ⁱⁱⁱ	90.11 (11)
F5 ^{iv} —Ba—F1 ^v	53.36 (6)	F2 ^{iv} —Al—F5 ⁱⁱⁱ	175.02 (10)
F3 ^{iv} —Ba—F1 ^v	50.92 (7)	F4 ^{xii} —Al—F3 ⁱⁱⁱ	88.87 (11)
F7—Ba—F3	59.02 (6)	F1—Al—F3 ⁱⁱⁱ	86.45 (11)
F4 ⁱ —Ba—F3	90.21 (6)	F6 ^{iv} —Al—F3 ⁱⁱⁱ	175.99 (12)
F1 ⁱ —Ba—F3	111.81 (7)	F2 ^{iv} —Al—F3 ⁱⁱⁱ	87.98 (10)
F2 ⁱⁱ —Ba—F3	52.19 (6)	F5 ⁱⁱⁱ —Al—F3 ⁱⁱⁱ	87.19 (10)
F5 ⁱⁱⁱ —Ba—F3	153.12 (6)	F7 ⁱ —Fe—F2 ^{viii}	85.92 (8)
F5 ^{iv} —Ba—F3	113.88 (6)	F7 ^x —Fe—F2 ^{viii}	94.08 (8)
F3 ^{iv} —Ba—F3	78.06 (7)	F7 ⁱ —Fe—F2 ^{xi}	94.08 (8)
F1 ^v —Ba—F3	61.81 (6)	F7 ^x —Fe—F2 ^{xi}	85.92 (8)
F7—Ba—F6 ⁱⁱⁱ	149.97 (6)	F7 ⁱ —Fe—F3 ^x	97.13 (8)
F4 ⁱ —Ba—F6 ⁱⁱⁱ	127.50 (6)	F7 ^x —Fe—F3 ^x	82.87 (8)
F1 ⁱ —Ba—F6 ⁱⁱⁱ	50.94 (6)	F2 ^{viii} —Fe—F3 ^x	84.30 (8)
F2 ⁱⁱ —Ba—F6 ⁱⁱⁱ	120.42 (6)	F2 ^{xi} —Fe—F3 ^x	95.70 (8)
F5 ⁱⁱⁱ —Ba—F6 ⁱⁱⁱ	68.77 (5)	F7 ⁱ —Fe—F3 ⁱ	82.87 (8)
F5 ^{iv} —Ba—F6 ⁱⁱⁱ	56.89 (6)	F7 ^x —Fe—F3 ⁱ	97.13 (8)
F3 ^{iv} —Ba—F6 ⁱⁱⁱ	63.59 (6)	F2 ^{viii} —Fe—F3 ⁱ	95.70 (8)
F1 ^v —Ba—F6 ⁱⁱⁱ	103.02 (6)	F2 ^{xi} —Fe—F3 ⁱ	84.30 (8)
F3—Ba—F6 ⁱⁱⁱ	137.04 (6)	Al—F1—Ba ^v	114.10 (11)
F7—Ba—F6 ^{iv}	58.77 (6)	Al—F1—Ba ⁱ	96.30 (9)
F4 ⁱ —Ba—F6 ^{iv}	67.12 (6)	Ba ^v —F1—Ba ⁱ	138.03 (10)

F1 ⁱ —Ba—F6 ^{iv}	127.71 (7)	Al—F1—Ba ⁱⁱⁱ	90.11 (11)
F2 ⁱⁱ —Ba—F6 ^{iv}	130.72 (6)	Ba ^v —F1—Ba ⁱⁱⁱ	111.43 (8)
F5 ⁱⁱⁱ —Ba—F6 ^{iv}	50.93 (5)	Ba ⁱ —F1—Ba ⁱⁱⁱ	95.98 (7)
F5 ^{iv} —Ba—F6 ^{iv}	67.24 (5)	Al ^{iv} —F2—Fe ^{xiii}	136.08 (11)
F3 ^{iv} —Ba—F6 ^{iv}	118.00 (6)	Al ^{iv} —F2—Ba ^{xiv}	106.08 (9)
F1 ^v —Ba—F6 ^{iv}	82.69 (7)	Fe ^{xiii} —F2—Ba ^{xiv}	117.52 (8)
F3—Ba—F6 ^{iv}	117.62 (5)	Al ^{vi} —F3—Fe ^v	125.66 (11)
F6 ⁱⁱⁱ —Ba—F6 ^{iv}	97.89 (5)	Al ^{vi} —F3—Ba ^{iv}	94.81 (9)
F7—Ba—F1 ^{vi}	105.96 (6)	Fe ^v —F3—Ba ^{iv}	131.32 (9)
F4 ⁱ —Ba—F1 ^{vi}	113.22 (7)	Al ^{vi} —F3—Ba	97.27 (9)
F1 ⁱ —Ba—F1 ^{vi}	68.57 (8)	Fe ^v —F3—Ba	98.64 (7)
F2 ⁱⁱ —Ba—F1 ^{vi}	48.36 (6)	Ba ^{iv} —F3—Ba	101.94 (7)
F5 ⁱⁱⁱ —Ba—F1 ^{vi}	144.89 (5)	Al ^{xv} —F4—Ca	107.92 (10)
F5 ^{iv} —Ba—F1 ^{vi}	111.48 (6)	Al ^{xv} —F4—Ba ^v	142.62 (11)
F3 ^{iv} —Ba—F1 ^{vi}	58.64 (6)	Ca—F4—Ba ^v	109.17 (8)
F1 ^v —Ba—F1 ^{vi}	84.02 (7)	Al ^{vi} —F5—Ca ^{iv}	99.48 (9)
F3—Ba—F1 ^{vi}	46.95 (6)	Al ^{vi} —F5—Ba ^{vi}	116.53 (9)
F6 ⁱⁱⁱ —Ba—F1 ^{vi}	94.27 (6)	Ca ^{iv} —F5—Ba ^{vi}	103.28 (7)
F6 ^{iv} —Ba—F1 ^{vi}	163.69 (5)	Al ^{vi} —F5—Ba ^{iv}	96.94 (8)
F7 ^{vii} —Ca—F7 ⁱ	145.64 (12)	Ca ^{iv} —F5—Ba ^{iv}	117.45 (7)
F7 ^{vii} —Ca—F6 ⁱⁱⁱ	80.29 (8)	Ba ^{vi} —F5—Ba ^{iv}	121.51 (7)
F7 ⁱ —Ca—F6 ⁱⁱⁱ	78.04 (8)	Al ^{iv} —F6—Ca ^{viii}	133.22 (12)
F7 ^{vii} —Ca—F6 ^{viii}	78.04 (8)	Al ^{iv} —F6—Ba ^{vi}	100.10 (9)
F7 ⁱ —Ca—F6 ^{viii}	80.29 (8)	Ca ^{viii} —F6—Ba ^{vi}	113.52 (8)
F6 ⁱⁱⁱ —Ca—F6 ^{viii}	100.95 (11)	Al ^{iv} —F6—Ba ^{iv}	102.40 (9)
F7 ^{vii} —Ca—F4	139.26 (9)	Ca ^{viii} —F6—Ba ^{iv}	101.01 (7)
F7 ⁱ —Ca—F4	73.57 (8)	Ba ^{vi} —F6—Ba ^{iv}	102.45 (6)
F6 ⁱⁱⁱ —Ca—F4	133.25 (7)	Fe ^v —F7—Ca ^{xvi}	120.99 (11)
F6 ^{viii} —Ca—F4	109.75 (8)	Fe ^v —F7—Ba	113.91 (9)
F7 ^{vii} —Ca—F4 ^{ix}	73.57 (8)	Ca ^{xvi} —F7—Ba	120.85 (10)

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