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LiBaAlF$_6$ and the crystal chemistry of Li$A^{II}B^{III}$F$_6$ phases

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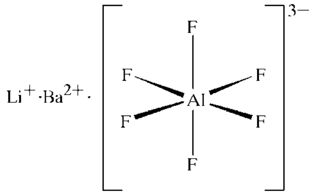
Lithium barium hexafluoroaluminate (LBAF), LiBaAlF$_6$, is a new member of the large family of compounds of formula Li$A^{II}B^{III}$F$_6$. These materials display a variety of structures depending on the sizes of the *A* and *B* cations. LiBaAlF$_6$, which is isomorphous with LiBaCoF$_6$, belongs to the monoclinic $P2_1/c$ subset and has a three-dimensional network structure consisting of distorted LiF$_4^{3-}$ tetrahedra corner-sharing with AlF$_6^{3-}$ octahedra and BaF$_{12}$ polyhedra. All of the atoms reside on general positions. An analysis of the ionic radii of the *A* cations *versus* formula volumes for the known members of the family yields a structure map that reasonably segregates the compounds by space group. The data obtained are thus suitable for predicting new isomorphic crystal structures.

Comment

It is often possible to predict a new structure by analogy. The Li$A^{II}B^{III}$F$_6$ family is one of the well studied sets of fluoride structures. The fluorides with cation pairs ($A^{II}B^{III}$) PdAl (Bachmann & Mueller, 1993), YbAl (Koehler, 1999), CaAl (Bolotina *et al.*, 1993), CaCr (Rupp *et al.*, 1993), CdCo, CaNi, CaCo and SrNi (Fleischer & Hoppe, 1982) and SrAl (Schaffers & Keszler, 1991) crystallize in the space group $P\overline{3}c$. These crystals have layered structures in which face-sharing B^{III}F$_6^{3-}$ and LiF$_6^{5-}$ octahedra alternate with layers of divalent cations. Both the first and second coordination environments of A^{II} are octahedral. Distorted anionic 3^6 grids are located in perpendicular planes (001) and (110). LiSmAlF$_6$ is characterized by the hexagonal space group $P6_322$ (Koehler & Mueller, 1991). In contrast with those crystals with a $P\overline{3}c$ structure, the SmF$_6^{4-}$ polyhedron is prismatic rather than octahedral.

A decrease in the radius of the divalent cation results in a change of symmetry to tetragonal $P4_2/mnn$ in the case of LiMgCoF$_6$, LiNiCoF$_6$ and LiZnCoF$_6$ (Fleischer & Hoppe, 1982). All cations in these crystals have octahedral coordination environments, and the Li and Mg atoms are located on common sites. Increasing the radii of the di- and trivalent cations also causes changes in the space group. Fluorides with $A^{II}B^{III}$ cation pairs, such as SrCo, SrFe and BaCo (Fleischer & Hoppe, 1982) and BaCr (Babel, 1974), are characterized by the monoclinic space group $P2_1/c$. Despite their identical space group and the closely similar atom positions in their unit cells, the structures of the strontium-containing fluorides differ from those of the barium fluorides. The coordination environment of Sr is a distorted square antiprism, while the Li atoms have an octahedral environment. In contrast, the Ba atoms are characterized by a coordination number of 12 and the Li atoms have a coordination number of 4 in the barium fluorides. The tetrahedral Li-centred polyhedron is distorted due to the presence of one additional longer bond (*ca* 2.65 Å) with an F atom of the second coordination sphere.

The previously unreported title compound, LiBaAlF$_6$, (I), belongs to the monoclinic $P2_1/c$ subset of this family. The three-dimensional network structure, consisting of Li-centred distorted tetrahedra corner-sharing with Al-centred octahedra and Ba-centred polyhedra, is analogous to that of LiBaCoF$_6$ (Fig. 1). The large Ba polyhedron (distorted bicapped pentagonal prism) compresses the lithium coordination environment and transforms it from octahedral to tetrahedral. It might seem that the small volume of the Al polyhedra could provoke an increase of the Li coordination environment up to octahedral, but this is not the case.



(I)

The dependence of the formula volumes on the Shannon (1976) radii of divalent cations with coordination number 6 for the known Li$A^{II}B^{III}$F$_6$ phases (Fig. 2*a*) shows a fairly good segregation of the different structures by space group. One can see a real possibility of structure prediction for some new crystals by analogy with known isomorphic structures. Nevertheless, there are some areas of overlap, making it difficult to predict the LiBaAlF$_6$ structure based on these data alone. Moreover, the structures of LiSrNiF$_6$ and LiSrCoF$_6$ differ despite the small differences in the Ni and Co radii.

It is possible to calculate the radii in these structures by a different method. All F$\cdots$F distances in the coordination polyhedra were averaged and halved in order to estimate the anionic fluoride radius. Subtracting the anionic radius obtained in this manner from the mean cation–anion distance allows one to determine the cationic radius. There is good agreement between the Shannon ionic radii and the calculated values in the case of trivalent cation octahedra (Table 1). In the case of polyhedra with divalent cations, the situation is different. The anionic radii of fluoride found *via* the F$\cdots$F

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distances are larger than the tabulated values, making the cationic radii smaller than the tabulated radii. This indicates that the divalent cations pull the fluoride anions together more weakly than do the trivalent cations. According to the Shannon data, the $\mathrm{Ni}^{\mathrm{III}}$ ionic radius is larger than those of $\mathrm{Co}^{\mathrm{III}}$ and $\mathrm{Fe}^{\mathrm{III}}$, which does not correlate with their relative positions in the periodic table. The increase of di- and trivalent cation radii in $\mathrm{Li}A^{\mathrm{II}}B^{\mathrm{III}}\mathrm{F}_6$ crystals is accompanied by a gradual increase in the formula volume and causes a symmetry change. Trigonal symmetry is the most prevalent for the fluorides considered here. In compounds with a small B^{III} radius and a rather large A^{II} radius, a reorganization from a trigonal structure to a hexagonal one ($\mathrm{LiSmAlF}_6$) may take place. A small increase in the trivalent cation radius when passing from $\mathrm{LiSrNiF}_6$ to $\mathrm{LiSrCoF}_6$ causes a significant lowering of symmetry down to monoclinic. This may mean that the gradual increase in the size of the trivalent cation octahedron leads to compression of the strained divalent cation polyhedron. When the difference between the tabulated radius of $\mathrm{Sr}^{\mathrm{II}}$ and the calculated radius reaches a maximum (0.48 Å), as in the case of $\mathrm{LiSrNiF}_6$, the structure becomes reorganized back to trigonal. The increase of the A^{II} radius in the monoclinic structures ($\mathrm{LiSrCoF}_6 \rightarrow \mathrm{LiBaCoF}_6$) causes a reorganization of the structures of the Li, Sr and Ba coordination polyhedra without a change of space group. The analogous structure map with our calculated A^{II} radii plotted against formula volume is shown in Fig. 2(*b*). For a small cationic radius the volume increases sharply with increasing radius. Once the cationic radius becomes similar to the anionic radius, realignment of the unit cell occurs without a significant volume change. This map also provides good segregation of space groups.

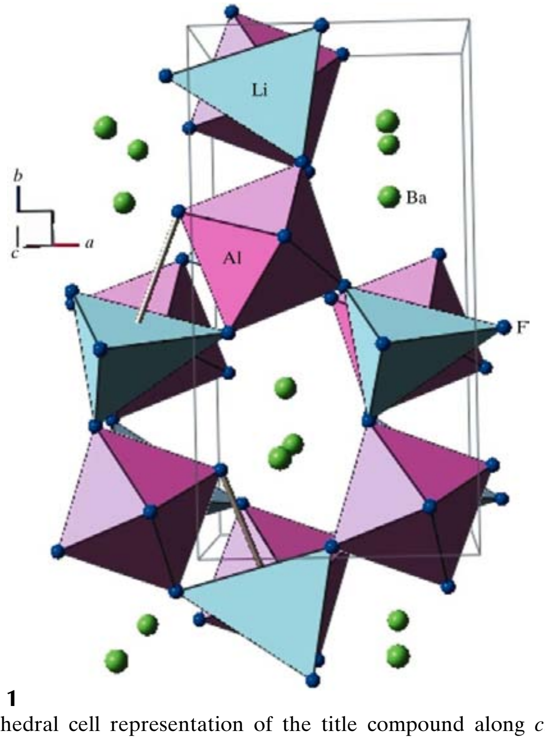

Figure 1
A polyhedral cell representation of the title compound along *c*. AlF_6 polyhedra are light-coloured, LiF_4 polyhedra are dark-coloured and Ba cations are shown as circles. The fifth Li$\cdots$F contacts are shown as thick lines.

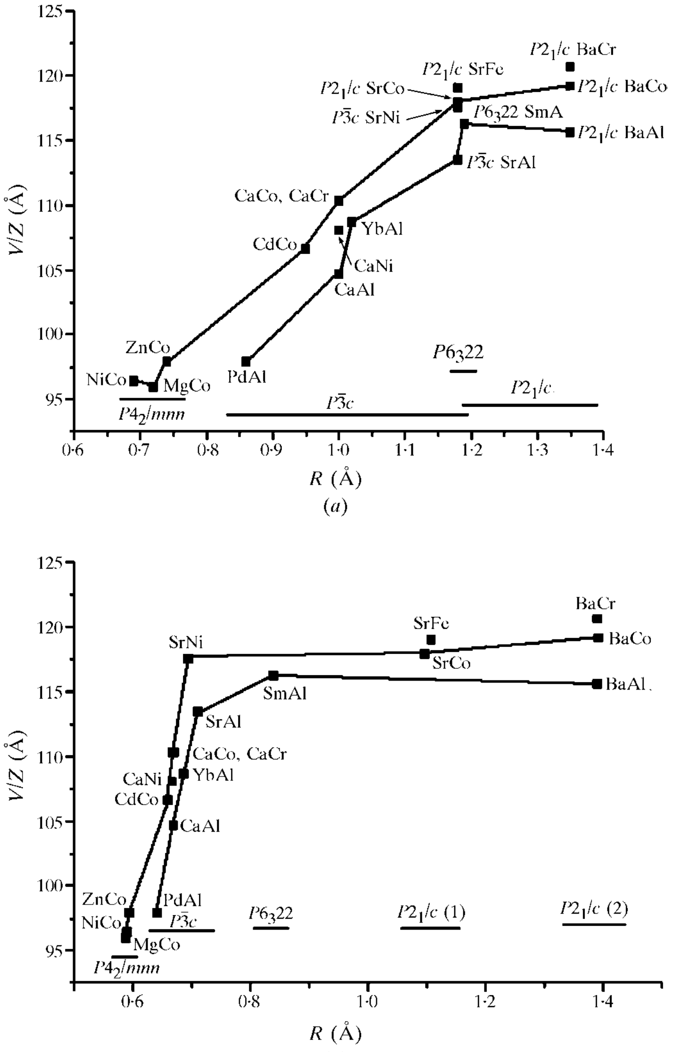

Figure 2
(*a*) A structure map showing the dependence of the formula volumes *V*/*Z* on the Shannon (1976) radii of A^{II} cations of coordination number 6, and the distribution of the space groups of known $\mathrm{Li}A^{\mathrm{II}}B^{\mathrm{III}}\mathrm{F}_6$ structures. (*b*) A structure map showing the dependence of the formula volumes *V*/*Z* on the calculated radii of A^{II} cations of varied coordination number (as shown in Table 1), and the distribution of the space groups.

In conclusion, the structure determination of $\mathrm{LiBaAlF}_6$ completes a data set for the construction of correlations between ionic radii, unit-cell parameters and space groups for crystals in the $\mathrm{Li}A^{\mathrm{II}}B^{\mathrm{III}}\mathrm{F}_6$ family, making it possible to predict reliably in many cases the structure type of new isomorphic crystals of similar compounds.

Experimental

Lithium barium hexafluoroaluminate (LBAF), $\mathrm{LiBaAlF}_6$, was grown from the melt by the Bridgman method in quartz crucibles. Double fluorides of 99.99% purity were used as starting reagents. $\mathrm{LiBaAlF}_6$ melts congruently at 1113–1133 K. The partial AlF_3 pressure was determined to be ~1 bar at this temperature (1 bar = 100 000 Pa). Because of the high volatility of this component, an excess ~2 wt.%

Table 1
Comparison of the ionic radii and formula volumes of $\mathrm{Li}A^{\mathrm{II}}B^{\mathrm{III}}\mathrm{F}_6$ compounds.

Compound	Space group	V/Z (Å^3)	M^{2+} radius (Å) (Shannon, 1976)	M^{2+} radius (Å) (calculated)	Li	Al	Ni	Co	Fe	Cr
$\mathrm{LiMgCoF}_6$	$P4_2/mnn$	95.92	0.72	0.589	0.589			0.565		
$\mathrm{LiNiCoF}_6$		96.42	0.69	0.590	0.590			0.559		
$\mathrm{LiZnCoF}_6$		97.98	0.74	0.594	0.594			0.569		
$\mathrm{LiPdAlF}_6$	$P\bar{3}c$	97.84	0.86	0.641	0.583	0.530				
$\mathrm{LiCdCoF}_6$		106.61	0.95	0.660	0.593			0.548		
$\mathrm{LiCaAlF}_6$		104.67	1.00	0.669	0.589	0.528				
$\mathrm{LiCaNiF}_6$		108.04	1.00	0.667	0.595		0.545			
$\mathrm{LiCaCoF}_6$		110.29	1.00	0.671	0.600			0.548		
$\mathrm{LiCaCrF}_6$		110.30	1.0	0.668	0.594					0.558
$\mathrm{LiYbAlF}_6$		108.63	1.02	0.687	0.591	0.529				
$\mathrm{LiSrAlF}_6$		113.46	1.18	0.711	0.592	0.527				
$\mathrm{LiSrNiF}_6$		117.57	1.18	0.697	0.611		0.544			
$\mathrm{LiSmAlF}_6$	$P6_322$	116.23	1.20	0.840	0.591	0.529				
$\mathrm{LiSrCoF}_6$	$P2_1/c$	117.93	1.26	1.096†	0.600			0.564		
$\mathrm{LiSrFeF}_6$		119.07	1.26	1.108†	0.605				0.567	
$\mathrm{LiBaAlF}_6$		115.59	1.61	1.390‡	0.362§	0.530				
$\mathrm{LiBaCoF}_6$		119.18	1.61	1.392‡	0.360§			0.556		
$\mathrm{LiBaCrF}_6$		120.68	1.61	1.391‡	0.359§					0.558
r_{cation}, average					0.595 0.36§	0.529	0.545	0.558		
r_{anion}, average				1.63 1.48†‡	1.43 1.53§	1.28	1.32	1.35	1.36	1.35

† Sr coordination number is 8. ‡ Ba coordination number is 12. § Li coordination number is 4. Notes: Li^+, Al^{3+}, Ni^{3+}, Co^{3+}, Fe^{3+} and Cr^{3+} Shannon radii for an octahedral environment are, respectively, 0.76 (0.594 for tetrahedral coordination environment), 0.535, 0.56, 0.545, 0.55 and 0.615 Å.

of AlF_3 was added to the original composition. Crystal growth was carried out in a graphite container placed inside the silica ampoule. All operations were carried out in a dry-box to avoid oxygen-containing impurities. To suppress decomposition, CF_4 was added to the reactor. The experiments were carried at a surplus pressure (approximately 0.1 bar). The axial temperature gradient was 10–20 K cm^{-1} and the ampoule pulling rate varied from 0.5 to 5 mm d^{-1}. The crystal composition was analyzed using an EDS microprobe to 0.5% coincidence in composition.

Crystal data

$\mathrm{LiBaAlF}_6$
$M_r = 285.26$
Monoclinic, $P2_1/c$
$a = 5.3372$ (10) Å
$b = 10.150$ (2) Å
$c = 8.535$ (2) Å
$\beta = 90.34$ (3)°
$V = 462.35$ (17) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 8.82$ mm^{-1}
$T = 296$ (2) K
0.22 × 0.18 × 0.18 mm

Data collection

Bruker–Nonius X8-APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.159$, $T_{\max} = 0.210$
4624 measured reflections
1638 independent reflections
1607 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.035$
$S = 1.17$
1638 reflections
83 parameters
$\Delta\rho_{\max} = 1.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}

Analysis of the X-ray data using *XPREP* (Bruker, 2004) indicated three possible space groups, *viz*. $P2_1/c$, Pc and $P2_1$. The structure was refined in $P2_1/c$ to a final wR_2 of 0.0352 and R_1 of 0.0141 for 1607 reflections (1638 unique; $R_{\mathrm{int}} = 0.0173$), 83 parameters. The corresponding data for the Pc group are: 2319 unique reflections, $R_{\mathrm{int}} = 0.0156$, $wR_2 = 0.0335$, $R_1 = 0.0128$ for 2260 reflections, 164 parameters; the Flack (1983) parameter was 0.22 (3). There is a problem in the latter case with the anisotropic refinement of atom Li1. The TWIN, BASF and ISOR instructions (*SHELXTL*; Sheldrick, 2008) for Li1 resulted in $wR_2 = 0.0319$, $R_1 = 0.0124$, 165 parameters, twinning 0.52:0.48. The R_1 value for the $P2_1$ space group is larger than either of the other cases. Therefore, the crystal structure corresponds to either the centrosymmetric $P2_1/c$ group or noncentrosymmetric Pc group. By analogy with the case of $\mathrm{LiBaCoF}_6$, we chose the $P2_1/c$ space group.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Version 6.12; Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3143). Services for accessing these data are described at the back of the journal.

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