

Structure of LiSrAlF_6

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Abstract. Lithium strontium hexafluoroaluminate, LiSrAlF_6 , $M_r = 235.53$, trigonal, $P\bar{3}1c$, $a = 5.071$ (6), $c = 10.189$ (1) Å, $V = 226.93$ (5) Å³, $Z = 2$, $D_x = 3.45$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 117.53$ cm⁻¹, $F(000) = 216$, $T = 296$ K, $R = 0.024$ for 163 observations with $F_o^2 \geq 3\sigma(F_o^2)$. Each of the cations occupies a distorted octahedral site. The symmetry of the Al site is reduced from O_h to D_3 in part by rotation of the trigonal fluorine faces, one relative to the other, by 67.2° .

Introduction. The compound LiSrAlF_6 has been reported to function as a tunable, room-temperature laser material when doped with the ion Cr^{3+} (Payne, Chase, Smith, Kway & Newkirk, 1989). Its slope efficiency, 36%, and optical properties differ markedly from the characteristics of the highly efficient and isostructural laser material Cr^{3+} : LiCaAlF_6 (Payne, Chase, Newkirk, Smith & Krupke, 1988). In this paper we describe structural features that influence these properties.

Experimental. LiSrAlF_6 was prepared by grinding a mixture of LiF (99.3%, AESAR), SrF_2 (reagent grade), and AlF_3 (99.5%, ALFA) containing an excess of 10 mol % LiF and AlF_3 to compensate for volatilization losses during crystal growth. The sample was placed in a Pt tube and hydrofluorinated for 3 h at 873 K to reduce the oxygen content. Crystals were grown in a horizontal zone-melting apparatus by melting a zone of the sample at 1053 K under an Ar atmosphere and translating the induction coil at a rate of 2.67 mm h⁻¹. A colorless, rectangular crystal of dimensions 0.12 × 0.15 × 0.08 mm was physically separated from the sample and mounted on a glass fiber with epoxy for data collection with a Rigaku AFC6R diffractometer equipped with Mo $K\alpha$ radiation. Lattice parameters were determined by automatic centering and least-squares analysis of 15 reflections in the range $30 \leq 2\theta \leq 50^\circ$. Intensity data were collected by using the ω - 2θ scan technique; intensities of three standard reflections measured after each block of 200 data exhibited an average fluctuation of 1.7%. A total of 1019 data with $F_o^2 \geq 3\sigma(F_o^2)$ were obtained from

1586 reflections measured to $(\sin\theta_{\max})/\lambda = 1.32$ Å⁻¹ in the range $-7 \leq h \leq 7$, $0 \leq k \leq 7$ and $-16 \leq l \leq 16$.

All calculations were performed on a MicroVAX II computer with programs from the TEXSAN crystallographic software package (Molecular Structure Corporation, 1989). The Sr, Al, and Li atoms were placed by comparison with the isostructural compound LiCaAlF_6 (Viebahn, 1971). The position of the F atom was determined by examining a difference electron density map. Following refinement of the structure with isotropic thermal parameters, the data were corrected for absorption (transmission coefficients = 0.889–1.141) with the program DIFABS (Walker & Stuart, 1983) and subsequently averaged ($R_{\text{int}} = 0.063$). Final least-squares refinement on F with 237 unique reflections having $F_o^2 \geq 3\sigma(F_o^2)$ and 17 variables affords the final residuals $R = 0.024$ and $wR = 0.024$ where the function $\sum w(|F_o| - |F_c|)^2$ is minimized with weights derived from counting statistics [$w = 1/\sigma^2(F)$]. The isotropic extinction coefficient = 5.34×10^{-7} (Zachariasen, 1968), $S = 1.21$, and $\Delta/\sigma = 0.01$. Analysis of the final difference electron density map reveals a maximum peak = 0.62 e Å⁻³ that corresponds to 0.31% of an Sr atom. Final atomic parameters are listed in Table 1; other data have been deposited.*

Discussion. A sketch of the structure is shown in Fig. 1. The compound is isostructural with the material LiCaAlF_6 ; each crystallizes as an ordered derivative of the structure type Li_2ZrF_6 (Brunton, 1973). As a consequence of a larger crystal radius, the volume of the unit cell of the Sr analog is 22.42 Å³ greater than that of the Ca analog. Other important differences are discussed below.

Selected interatomic distances and angles are listed in Table 2. The Sr atom occupies the center of a trigonally elongated octahedral environment as evi-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the the British Library Document Supply Centre as Supplementary Publication No. SUP 53255 (4 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates for LiSrAlF_6

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	B_{eq} (\AA^2)
Li	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{4}$	1.5 (3)
Sr	0	0	0	0.84 (1)
Al	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	0.73 (4)
F	0.3879 (4)	0.0328 (4)	0.1485 (1)	1.39 (5)

Table 2. Selected bond distances (\AA) and bond angles ($^\circ$) for LiSrAlF_6

Sr—F	2.424 (2)	Li—F	2.020 (2)
Al—F	1.799 (1)		
F—Sr—F	94.93 (5)	F—Li—F	94.72 (9)
F—Al—F	94.2 (1)		74.49 (8)
	85.6 (1)		96.12 (5)
	90.24 (6)		

denced by consideration of the F—Sr—F angle, $94.93(5)^\circ$, involving F atoms from adjacent irregular close packed planes. The Sr—F distance, $2.421(1) \text{\AA}$, compares to the length, 2.46\AA , computed from crystal radii for an Sr atom bound to six, three-coordinate F atoms (Shannon & Prewitt, 1969).

The Li atom occupies a highly distorted octahedral environment (*cf.* Table 2). The Li—F distance, $2.020(2) \text{\AA}$, compares to similar interactions in the compounds LiCaAlF_6 , $2.009(3)$; LiSbF_6 , $2.032(6)$ (Burns, 1962); and Li_2ZrF_6 , $2.025(1) \text{\AA}$.

The AlF_6 unit exhibits D_3 symmetry with an Al—F distance of $1.799(1) \text{\AA}$. This distance is similar to the six-coordinate Al environments in the compounds LiCaAlF_6 , $1.800(3)$; SrAlF_5 , 1.79 and 1.81 (Von der Mühl, Andersson & Galy, 1971); and $\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12}$, $1.807(3) \text{\AA}$ (Geller, 1971). The heights of the AlF_6 groups along the trigonal axis in LiSrAlF_6 and LiCaAlF_6 are statistically equivalent. The largest distortions from O_h symmetry arise from the relative rotations of the two trigonal F faces. As viewed along the c axis (Fig. 2), the angle of rotation between the two faces in LiSrAlF_6 is 67.2° which compares with the angle of 63.4° observed in the derivative LiCaAlF_6 . These rotations and resulting angular distortions (*cf.* Table 2) are consistent with the emission lifetimes for Cr^{3+} ions doped onto these sites. The lifetime for $\text{Cr}^{3+}:\text{LiSrAlF}_6$ is $67 \mu\text{s}$ while that for $\text{Cr}^{3+}:\text{LiCaAlF}_6$ is $205 \mu\text{s}$ (Payne, Chase & Wilke, 1989). The larger static distortion of the AlF_6 unit from O_h symmetry in the compound LiSrAlF_6 contributes to a greater relaxation of the Laporte selection rule; hence, a shorter lifetime is observed.

The nature of the distortion at the Al site is best appreciated by examination of the projection shown in Fig. 3. From comparison of the positions of the F atoms in the structure of LiSrAlF_6 with those in an ideal close-packed layer, it is seen that the F hollows occupied by Sr atoms are expanded relative to the

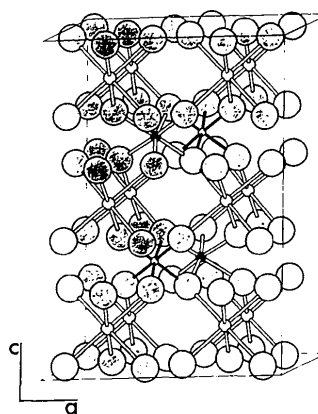


Fig. 1. Sketch of the unit cell of LiSrAlF_6 as viewed approximately along the a axis. The small open circles with unshaded bonds represent Sr atoms, the open circles with shaded bonds represent Al atoms, the small filled circles with unshaded bonds represent Li atoms, and the largest shaded circles represent F atoms.

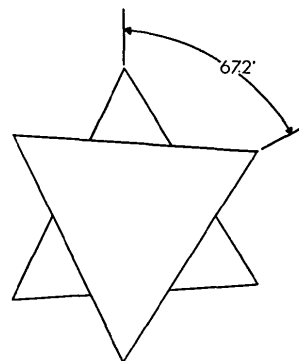


Fig. 2. Drawing of AlF_6 group exhibiting relative orientation of trigonal F faces.

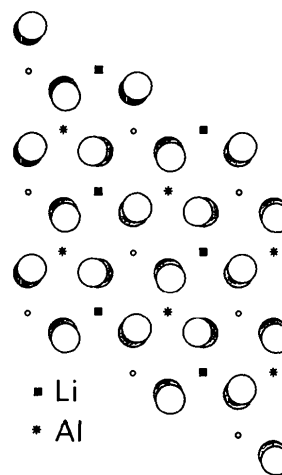


Fig. 3. Comparison of idealized F closest packing with F packing in the structure of LiSrAlF_6 by projection onto (001). The large and small circles represent F and Sr atoms, respectively. The large shaded circles represent the positions of F atoms in an ideal close-packed layer.

ideal packing and are displaced towards the Al atoms. This displacement probably arises from the larger electrostatic interaction of the ions Al³⁺ and F⁻ in comparison with the interactions between Sr²⁺ and F⁻ and Li⁺ and F⁻; each F⁻ anion is 3-coordinate, binding to Sr²⁺, Li⁺, and Al³⁺. From inspection of Fig. 1, it is seen that the displacements will occur in an opposite sense relative to the trigonal axis for adjacent F layers, affording the observed distortions of the AlF₆ units. Because the potential well for the Sr–F interaction is probably wider and softer than that of the Ca–F interaction it is not surprising that a larger displacement toward the Al³⁺ ion and a more distorted AlF₆ group in the Sr derivative are observed.

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Reaction of PhCCo₃(CO)₉ with Bis(dimethylphosphino)ethane and Structure of PhCCo₃(CO)₅(dmpe)₂·(toluene). Observation of Phosphine Bridging and Chelation

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Abstract. Tri- μ -carbonyl-dicarbonyl-mono-(μ_3 -benzylidene)-1,2-ethanediylbis(dimethylphosphino)-tricobalt(1)(3Co–Co) toluene solvate, [PhCCo₃(CO)₅(dmpe)₂].toluene (where dmpe = Me₂PCH₂CH₂PMe₂), C₂₄H₃₇Co₃O₅P₄·C₇H₈, *M_r* = 798.39, monoclinic, *P*2₁/*c*, *a* = 9.861 (2), *b* = 11.172 (2), *c* = 32.935 (5) Å, β = 82.91 (1)°, *V* = 3600.5 (10) Å³, *Z* = 4, *D_x* = 1.473 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 15.74 cm⁻¹, *F*(000) = 1648, *T* = 295 K, *R* = 0.0758 for 3810 independent reflections. The cobalt atoms are in a triangular array with a capping μ_3 -benzylidene ligand completing the *nido* polyhedral core. One dmpe ligand bridges a pair of cobalt atoms while the second dmpe ligand chelates

the unique cobalt atom. Three μ_2 -carbonyl groups are observed due to the high degree of phosphine substitution.

Introduction. Olefin hydroformylation using PhCCo₃(CO)₉ has been extensively studied because it was believed that the capping μ_3 -benzylidene ligand might stabilize the triangular array of cobalt atoms against fragmentation and, thus, promote metal cluster catalysis (Pittman & Ryan, 1978; Ryan, Pittman & O'Connor, 1977). However, other studies suggest that clusters based on RCCo₃(CO)₉ (where *R* = Ph or Me) readily decompose under reducing conditions to give mononuclear cobalt species which are responsible for the observed catalytic activity (Murata & Matsuda, 1980; Withers & Seyferth, 1983). Stabili-

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