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Sr_2LiSiO_4F: Synthesis, Structure, and Eu^{2+} Luminescence

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The structure and Eu^{2+} luminescence of the compound Sr_2LiSiO_4F are described. Crystal data: FW = 293.26, $P2_1/m$ (No. 11), monoclinic, $a = 6.5825(9)$, $b = 5.4158(8)$, $c = 6.9266(6)$ Å, $\beta = 112.525(8)°$, $V = 228.09(5)$ Å^3, $Z = 2$, $R = 0.049$, $R_w = 0.058$ for 760 averaged reflections. The structure contains two crystallographically distinct Sr atoms; both are 10-coordinate and bound by eight O atoms and two F atoms. The Li atom occupies a distorted square pyramid, and the Si atom a slightly distorted tetrahedron. When doped with the lanthanide ion Eu^{2+}, the compound exhibits a bright green emission with a maximum intensity at 531 nm.

Introduction

Inorganic oxoanion halides have for some time been of technological use and interest as fluorescent lamp phosphors,[1] laser hosts,[2] and X-ray storage media.[3] Despite this utility, synthetic examples of such materials remain rather uncommon. In this contribution we describe the preparation and structure of the new compound Sr_2LiSiO_4F. To our knowledge, it is the first synthetic example of an alkaline-earth silicate fluoride to be structurally characterized by single-crystal X-ray methods.

We have been attracted to the synthesis of oxoanion halides by the possibility of observing unusual optical properties as well as moderately low melting points that are desirable for the growth of large single crystals.

Experimental Section

A powder sample of Sr_2LiSiO_4F was prepared from the molar quantities of 2 $SrCO_3$ (AESAR, 99.9%), 1 SiO_2 (ALFA, 99.98%), and 1 LiF (AESAR, 99.9%). The mixture of carbonate and SiO_2 was heated at 873 K for 1 h; then the fluoride was added, and the sample was reground and heated in a Pt crucible at 1273 K for 12 h under an Ar atmosphere. A crystal was obtained for X-ray structure analysis from a stoichiometric melt. The melt was contained in a Pt crucible and slowly cooled from 1223 to 873 K at 6 K/h and then rapidly cooled at 50 K/h to room temperature. A colorless, transparent crystal of dimensions 0.10 × 0.12 × 0.10 mm was selected and mounted on a glass fiber with epoxy for structure determination. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement with 19 automatically centered reflections in the range $30 \le 2\theta \le 36°$. The cell constants correspond to a monoclinic cell; Laue symmetry $2/m$ was determined on the diffractometer. Intensity data were collected over the range of indices $0 \le h \le 10$, $0 \le k \le 8$, $-11 \le l \le 11$ by using the ω scan technique to a maximum 2θ value of 70°; from 1070 measured reflections a total of 760 were observed [$F_o^2 \ge 3\sigma F^2$]. The intensities of three representative reflections measured after every block of 200 data varied by an average of 2% during the collection.

The structure was solved by using the TEXSAN software package.[4] The crystal was found to form in the centrosymmetric space group $P2_1/m$. The positions of the Sr and Si atoms were derived from the direct methods program SHELXS,[5] while the remaining atoms F, O, and Li were located from difference electron density maps. After a full-matrix least-squares refinement of the model with isotropic displacement coefficients on each atom, an absorption correction was applied by using the program DIFABS[6] (transmission factors = 0.51−1.29). The data were averaged ($R_{int} = 0.066$), and the model was refined with anisotropic displacement coefficients on each atom. Final least-squares refinement resulted in the residuals $R = 0.049$ and $R_w = 0.058$. The largest peak in the final difference electron density map corresponds to 0.38% of the Sr1 atom. Crystal data are outlined in Table 1; atomic parameters are listed in Table 2.

The melting characteristics were examined by differential thermal analysis at Harrop Ind., Inc. The sample was heated in a Pr crucible under an Ar atmosphere at 10 °C/min.

The luminescence measurement was performed on a powder sample nominally doped with 2 mol % Eu^{2+}; the doping level was chosen to provide a bright emission that would be easily detectable. The preparative procedure was that described above [Eu_2O_3 (99.99%, MOLYCORP)], except for the final heating where the sample was placed in an atmosphere having a molecular ratio of 25 N_2:1 H_2. Steady-state, room-temperature luminescence spectra were obtained on a computer-controlled right-angle spectrometer. Excitation light from an Oriel 300-W Xe lamp was passed through a 50-cm water filter, focused initially onto the slits of a Cary Model 15 prism monochromator and then onto the sample. Luminescence was collected at a near right angle to excitation, dispersed through an Oriel 22500 $^1/_8$-m monochromator, and detected with a

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Table 1. Crystallographic Data for Sr_2LiSiO_4F

chem formula	Sr_2LiSiO_4F
fw, u	293.26
crystal system	monoclinic
space group	$P2_1/m$ (No. 11)
a, Å	6.5825(9)
b, Å	5.4158(8)
c, Å	6.9266(6)
V, Å^3	228.09(5)
β, deg	112.525(8)
Z	2
ϱ_{calc}, g cm^{-3}	4.270
radiation	Mo Kα[a]
temp, K	298
linear abs coeff μ, cm^{-1}	228.82
transm factors	0.51−1.29
R, R_w[b]	0.049, 0.058

[a] Graphite monochromated; $\lambda = 0.710\ 69$ Å. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Positional and Equivalent Displacement Parameters (B_{eq}) for Sr_2LiSiO_4F

	site sym	x	y	z	B_{eq}
Sr1	m	0.1597(2)	$^1/_4$	0.3722(1)	0.50(3)
Sr2	m	0.6342(2)	$^1/_4$	0.8985(1)	0.57(3)
Si	m	0.6547(5)	$^1/_4$	0.3351(4)	0.29(8)
F	$\bar{1}$	0	0	0	1.0(2)
O1	m	0.405(1)	$^1/_4$	0.158(1)	0.7(2)
O2		0.2252(8)	−0.009(1)	0.7117(8)	0.9(2)
O3	m	0.665(1)	$^1/_4$	0.572(1)	1.2(3)
Li	m	0.141(3)	$^1/_4$	-0.125(3)	1.1(7)

Hamamatsu R636 photomultiplier tube. The signal was collected and amplified with a Keithley Model 602 picoammeter and then converted to a digital signal for computer acquisition. Spectrometer control and data acquisition were achieved with computer programs written in this laboratory. The excitation spectrum was corrected by using rhodamine B as a quantum counter. The emission spectrum was corrected with a tungsten lamp that has been calibrated at Eppley Laboratories, Inc.

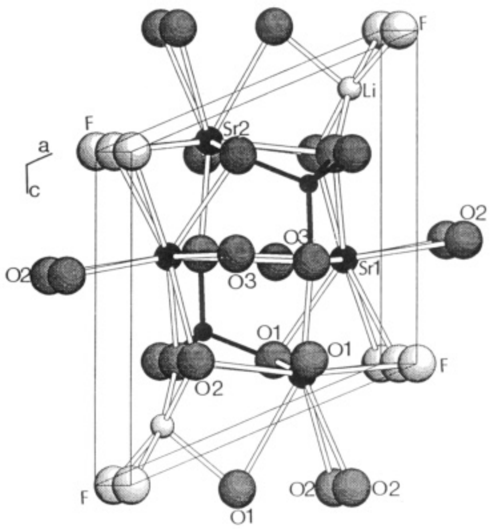

Figure 1. Unit cell diagram of Sr_2LiSiO_4F as viewed along the b axis. Here, and in ensuing figures, large circles represent O and F atoms; O atoms are more heavily shaded. Large filled circles represent Sr atoms, and small filled circles represent Si atoms. Medium, lightly shaded circles represent Li atoms.

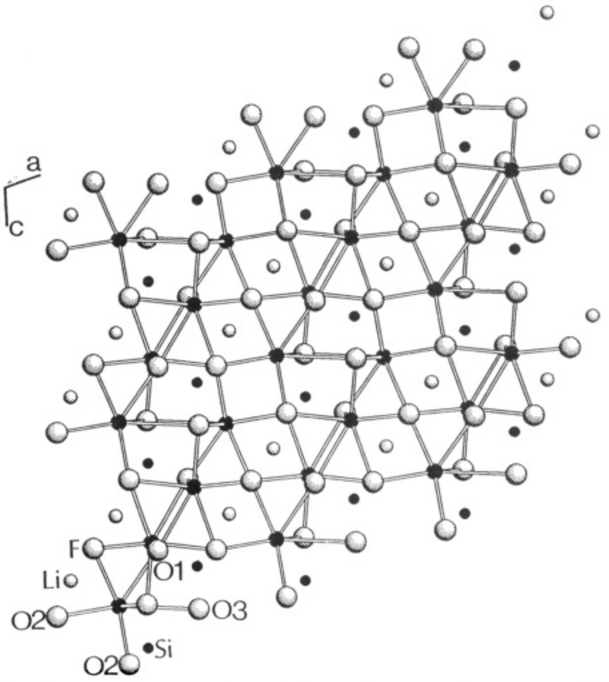

Figure 2. Framework resulting from condensation of Sr polyhedra.

Results and Discussion

Structure. A view of the contents of the unit cell is given in Figure 1. The structure contains two types of 10-coordinate Sr atoms, a 5-coordinate Li atom, and a 4-coordinate Si atom. The Sr-centered polyhedra share faces and vertices to form a three-dimensional framework that contains distorted square-pyramidal and tetrahedral interstices occupied by the Li and Si atoms, respectively (Figure 2). The Li- and Si-centered polyhedra share vertices to form a thick, two-dimensional substructure that extends parallel to the plane (100). As indicated by the formula, the SiO_4 groups are isolated one from the other, while the Li-centered square pyramids are linked through the F atoms (Figure 3). Atom Sr1 is bound by one O1, four O2, three O3, and two F atoms in an environment that is best described as a distorted bicapped square antiprism. Atom Sr2 is bound by three O1, four O2, one O3, and two F atoms in an environment that is best described as a distorted bicapped dodecahedron. The uniqueness of each of these polyhedra may be appreciated by considering their associations with the other metal atoms in the structure. Both are surrounded by four Si atoms, but the Sr1-centered site shares only edges O2···O2, O1···O3, and O2···O3 (×2), while the Sr2-centered polyhedron shares vertex O3, edge O1···O2(×2), and face O1···O2···O2. Similarly, both polyhedra share O and F atoms with four adjacent Li atoms but in a different manner. The Sr1-centered site shares edges O2···O2 and O2···F(×2) and the face F···F···O1, and the Sr2-centered site shares edge F···F and faces O1···O2···F(×2) and O2···O2···O1. The Sr1 environment is bound by 17 neighboring Sr atoms—8 Sr1 and 9 Sr2—while the Sr2 environment is bound by 15 Sr atoms—9 Sr1 and 6 Sr2. The details of the connectivities of these polyhedra through vertices, triangular faces, and quadrilateral faces are summarized in Table 3.

Interatomic distances and angles are listed in Table 4. The average Sr1−O, 2.77 ± 0.18 Å, and Sr2−O distances, 2.74 ± 0.17 Å, compare to Sr−O distances of 2.711 ± 0.05 and 2.859 ± 0.07 Å for 10-coordinate Sr atoms in α′-Sr_2SiO_4.[7] The Sr−F bond distances for Sr1, 2.7404(8), and Sr2, 2.6132(9) Å, compare to the value of 2.67 Å obtained from Shannon radii.[8]

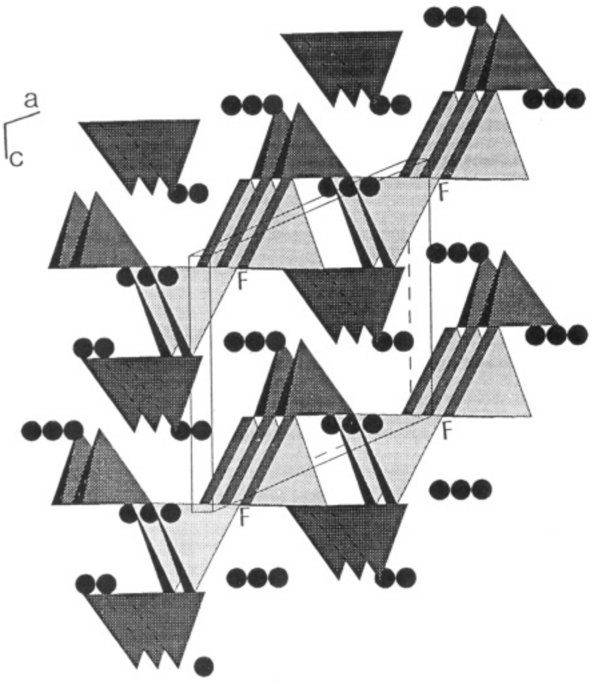

Figure 3. Polyhedral view of Si- and Li-centered polyhedra. Heavily shaded polyhedra represent SiO_4 groups and lightly shaded polyhedra represent LiO_3F_2 groups.

Table 3. Shared Polyhedral Vertices and Faces for Sr1- and Sr2-Centered Polyhedra

centered polyhedron	shared vertex or face	bound atom
Sr1	F (×2)	Sr1
	O3 (×2)	
	O2···O3 (×2)	
	O3···O3 (×2)	
Sr2	O1	Sr1
(Sr1)	O2 (×4)	(Sr2)
	O1···O3···F (×2)	
	O2···O2···O3	
	O2···O2···F···F	
Sr2	O1 (×2)	Sr2
	F (×2)	
	O1···O2···O2···F	
	O1···O2···O1···O2	

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Sr_2LiSiO_4F

Sr1−O1	2.575(9)	O1−Sr1−O2	126.2(2)
−O2 × 2	2.627(5)		128.1(2)
−O2 × 2	2.708(5)	O1−Sr1−O3	76.7(2)
−O3 × 2	2.912(3)		56.7(2)
−O3 × 1	3.071(8)	O2−Sr1−O3	57.6(2)
−F × 2	2.7404(8)		117.2(2)
			149.1(2)
			82.6(2)
			140.2(2)
		F−Sr1−O1	63.7(1)
		F−Sr1−O2	116.7(1)
			167.9(1)
			92.6(1)
			64.5(1)
			112.5(1)
		O2−Sr1−O2	64.5(2)
			105.58(9)
			75.7(1)
		O3−Sr1−O3	68.5(1)
			136.8(3)
		F−Sr1−F	59.21(2)
Sr2−O1 × 2	2.734(1)	O1−Sr2−O2	125.1(2)
−O1 × 1	2.756(9)		69.9(2)
−O2 × 2	2.817(5)		113.5(2)
−O2 × 2	2.866(5)		55.3(2)
−O3 × 1	2.343(9)	O1−Sr2−O3	84.2(2)
−F × 2	2.6132(9)	O1−Sr2−O3	86.9(4)
			69.9(2)
		F−Sr2−O1	125.3(2)
			120.2(1)
		F−Sr2−O2	92.9(2)
			169.7(1)
		F−Sr2−O3	81.3(2)
		O1−Sr2−O1	164.1(3)
			92.8(2)
		O2−Sr2−O2	124.47(8)
			96.5(1)
		F−Sr2−F	62.41(2)
Si−O1	1.631(7)	O1−Si−O2	106.2(3)
−O2 ×2	1.621(6)	O1−Si−O3	113.5(5)
−O3	1.619(9)	O2−Si−O2	107.2(5)
		O2−Si−O3	111.7(3)
Li−O1	2.06(2)	O1−Li−O2	102.7(7)
−O2 ×2	2.01(2)	F−Li−O1	87.2(7)
−F ×2	2.01(2)	F−Li−O2	92.5(2)
			169.4(9)
		O2−Li−O2	88.4(8)
		F−Li−F	84.6(9)

The Li atom is coordinated to one O1, two F, and two O2 atoms. The rectangular base of the pyramid is comprised of the F and O2 atoms, and the apex is represented by atom O1. A displacement of the Li atom above the basal plane toward the apex is indicated by the angle F−Li−O2 = 169.4(9)°. The average Li−O distance, 2.03 ± 0.03 Å, compares to the Li−O distances for 5-coordinate Li atoms in $SrLiBO_3$,[9] 2.06 ± 0.10 Å, and $BaLiBO_3$,[10] 2.05 ± 0.11 Å.

The Si atom binds to one O1, one O3, and two O2 atoms. The average Si−O distance, 1.623 ± 0.005 Å, is normal, and all O−Si−O angles are near the tetrahedral value.

The bond valence method[11,12] was used to calculate a valence of 1.0 for the F atom; it appears that this atom has been correctly identified in the structure analysis. All other atoms have calculated valences within 3% of standard integral values, except for atoms Sr1 and O3 where valences of 1.8 and 1.9, respectively, indicate a lack of bonding electron density.

On heating a sample of the title compound, a single, broad endotherm commencing at 820 °C and extending to 920 °C is observed via differential thermal analysis. The sample fully melts at 920 °C. We have been unable to identify the phase(s) in a powder quenched from 900 °C. These results may be consistent with a peritectic reaction, but a definite conclusion cannot be made without identification of the quenched material.

Luminescence. The composition $Sr_{1.98}Eu_{0.02}LiSiO_4F$ exhibits an intense green emission under ultraviolet excitation (Figure 4). Excitation and emission maxima occur at 348 and 531 nm, respectively. Wanmaker and Verriet have reported[13] a similar green emission for Eu^{2+}:$Ca_3SiO_4Cl_2$ at 510 nm, and Nicholson and Burrus have reported[14] emission from Eu^{2+}:$Sr_2Si_3O_8Cl_4$ at 500

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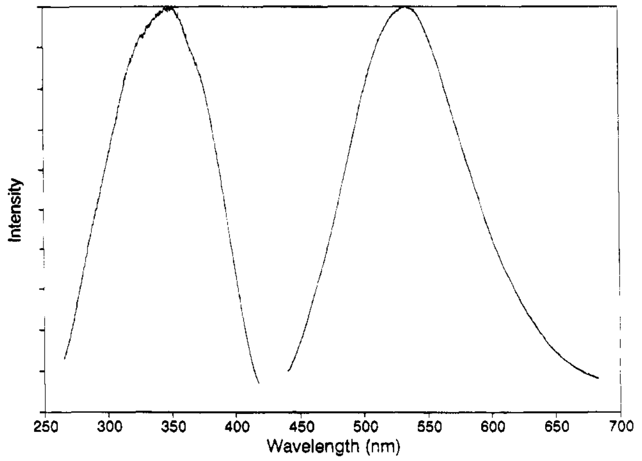

Figure 4. Emission and excitation spectra of the luminescence of $Sr_{1.98}Eu_{0.02}LiSiO_4F$ at 298 K. λ_{exc} = 348 nm for emission and λ_{em} = 531 nm for excitation.

nm. The position of the excitation band is similar to those observed for many blue-emitting Eu^{2+} phosphors, and it is consistent with the weak crystal field to be expected for a 10-coordinate silicate fluoride site. The broad emission peak is attributable to the allowed transition $4f^65d^1 \rightarrow 4f^7$. Obviously, the long-wavelength emission results from a sizable Stokes shift rather than a low-energy position of the excited state. Thermal quenching data (Figure 5) are similar to those of the more efficient, green Eu^{2+} emission observed in simple silicates.[15] The room-temperature spectrum provides little information concerning the distribution of Eu^{2+} ions over the two nonequivalent Sr dopant sites. While the sites are structurally distinct, they are likely to be electronically comparable. Similar Eu^{2+} excitation and emission characteristics may be expected from each site, leading to the symmetric peaks observed in the spectrum (Figure 4). Of course, the presence of a single, luminescent center cannot be excluded.

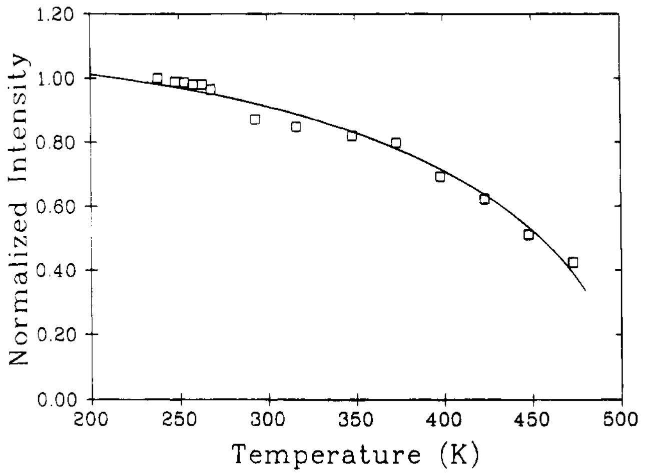

Figure 5. Temperature dependence of the fluorescence intensity of $Sr_{1.98}Eu_{0.02}LiSiO_4F$.

Work is ongoing to more fully characterize the phase change and luminescence properties of this new host.

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Supporting Information Available: Listings of complete crystal data and anisotropic displacement coefficients (2 pages). Ordering information is given on any current masthead page.

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