Inorg. Chem. **1995,** *34,* 1308−1310

Articles

The New Orthosilicate $Li_4SrCa(SiO_4)_2$: Structure and Eu^{2+} Luminescence

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Received October 20, 1994[⊗]

The structure and Eu^{2+} luminescence of the compound $Li_4SrCa(SiO_4)_2$ are described. Crystal data: fw = 339.63, orthorhombic, $a = 4.983(2)$ Å, $b = 9.930(2)$ Å, $c = 14.057(2)$ Å, $V = 695.5(4)$ Å^3, $Z = 4$, *Pbcm* (No. 57), $R = 0.056$, $R_w = 0.063$ for 996 averaged reflections. The structure is a condensed system of Sr-centered distorted bicapped square antiprisms, Ca-centered distorted octahedra, and Li- and Si-centered distorted tetrahedra. When doped with the lanthanide Eu^{2+}, the material produces a blue photoluminescence with maximum intensity at 430 nm.

Introduction

While attempting to prepare derivatives of the silicate fluoride Sr_2LiSiO_4F,[1] we have identified the new, complex orthosilicate $Li_4SrCa(SiO_4)_2$. Silicates have, for some time, been important in the development of the earth sciences and the technology of cement. In addition, a few examples, such as Zn_2SiO_4, Mg_2SiO_4, and Y_2SiO_5, have found use as phosphors,[2-4] laser crystals,[5,6] or scintillators[7] when doped with a suitable transition-metal or lanthanide ion. In this contribution, we describe the crystal structure of the title compound and its luminescence characteristics when doped with the ion Eu^{2+}.

Experimental Section

Synthesis. A powder sample of $Li_4SrCa(SiO_4)_2$ was prepared from the molar quantities of 2 Li_2CO_3 (AESAR, 99.9%), 1 $SrCO_3$ (AESAR, 99.9%), 1 $CaCO_3$ (AESAR, 99.9%), and 2 SiO_2 (ALFA, 99.98%). The mixture of carbonates and SiO_2 was heated at 873 K for 1 h; then the sample was reground and heated at 1273 K for 12 h. A crystal was obtained for X-ray structure analysis from a stoichiometric melt that was contained in a Pt crucible and slowly cooled from 1280 to 773 K at 6 K/h, followed by rapid cooling at 50 K/h to room temperature.

Crystallographic Study. A colorless, transparent crystal of dimensions 0.12 × 0.12 × 0.15 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 $30 \leq 2\theta \leq 36°$. The cell constants correspond to an orthorhombic cell; Laue symmetry *mmm* was determined on the diffractometer. Intensity data were collected over the range of indices $0 \leq h \leq 16$, $0 \leq k \leq 23$, $-8 \leq l \leq 8$ by using the ω scan technique to a maximum 2θ value of 73°, and from 3686 measured reflections a total of 2006 were observed $[F_o^2 \geq 3\sigma(F_o^2)]$. The intensities of three representative reflections measured after every block of 200 data varied by an average of 2% during the collection.

Table 1. Crystallographic Data for $Li_4SrCa(SiO_4)_2$

chem formula	$Li_4SrCa(SiO_4)_2$	Z	4
fw	339.63	ϱ_{calcd}	243 g cm^{-3}
space group	*Pbcm* (No. 57)	λ	0.710 69 Å
a	4.983(1) Å	T	298 K
b	9.930(2) Å	linear abs coeff μ	85.89 cm^{-1}
c	14.057(2) Å	$R(F_o)^a$	0.056
V	695.5 (4) Å^3	$R_w(F_o)^b$	0.063

^{a} $R = \Sigma||F_o - |F_c/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The structure was solved by using the TEXSAN crystallographic software package.[8] The crystal was found to form in the centrosymmetric space group *Pbcm*. The positions of the Sr, Ca, and Si atoms were derived from the direct methods program SHELXS,[9] while the remaining atoms 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[10] (transmission factors = 0.87 −1.11). The data were averaged ($R_{int} = 0.10$), 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 0.59% of the Sr atom. Crystal data are outlined in Table 1, and atomic positional parameters are listed in Table 2.

The luminescence measurement was performed with a powder sample nominally doped with 2 mol % Eu^{2+}. The preparative procedure was that described above [Eu_2O_3 (99.99%, MOLYCORP)], except the final heating was done in an atmosphere of 25:1 N_2:H_2. The room-temperature luminescence spectrum was obtained on a computer-controlled, right-angle spectrometer. Excitation provided by an Oriel 300-W Xe lamp was passed through a 50-cm water filter, focused 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

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) Akella, A.; Keszler, D. A. *Chem. Mater.*, submitted for publication.

(2) Kotera, Y. *J. Jpn. Soc. Color. Mater.*, **1985**, *58*, 80.

(3) Blasse, G. *Mater. Chem. Phys.* **1987**, 253.

(4) Morrel, A.; El Khiati, N. *J. Electrochem. Soc.* **1993**, *140*, 2019. Welker, T. *J. Luminesc.* **1991**, *48 & 49*, 49.

(5) Petricevic, V.; Gayen, S. K.; Alfano, R. R. *Appl. Opt.* **1988**, *27*, 4162; Verden, H. R.; Thomas, L. M.; Andrauskas, D. M.; McCollum, T.; Pinto, A. *Appl. Phys. Lett.* **1988**, *53*, 2593.

(6) Bagdasarov, Kh. S.; Kaminskii, A. A.; Kevorkov, A. M.; Prokhorov, A. M.; Sarkisov, S. E.; Terosyan, T. A. *Dokl. Akad. Nauk SSSR* **1973**, *212*, 1326.

(7) Blasse, G. *Chem. Mater.* **1994**, *9*, 1465.

(8) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0. Molecular Structure Corp., The Woodlands, TX 77381, 1989.

(9) Sheldrick, G. SHELXS86. In *Crystallographic Computing 3*; Sheldrick, G., Kruger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985, 175.

(10) Walker, N.; Stuart, D. *Acta Crystallgr., Sect. A* **1983**, *39*, 158.

0020-1669/95/1334-1308$09.00/0

Table 2. Positional and Equivalent Displacement Parameters (B_{eq}) for $Li_4SrCa(SiO_4)_2$

	site sym	*x*	*y*	*z*	$B_{eq}{}^a$ (Å^2)
Sr	*m*	0.0553(2)	0.23147(8)	$^3/_4$	0.72(3)
Ca	2	$^1/_2$	0	$^1/_2$	0.43(5)
Si1	*m*	0.4732(4)	−0.0253(2)	$^3/_4$	0.31(7)
Si2	2	0.0174(4)	$^1/_4$	0	0.36(7)
O1	*m*	−0.421(1)	0.3128(6)	$^3/_4$	0.5(2)
O2	*m*	−0.203(1)	−0.0001(6)	$^3/_4$	0.6(2)
O3		0.3338(8)	0.0448(4)	0.6558(3)	0.5(1)
O4		0.2090(8)	0.3350(4)	0.9274(3)	0.6(1)
O5		−0.1782(9)	0.1503(4)	0.5616(3)	0.6(2)
Li1		−0.041(2)	−0.0022(9)	0.8731(7)	0.1(1)
Li2		0.521(2)	0.225(1)	0.6275(8)	0.71(2)

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

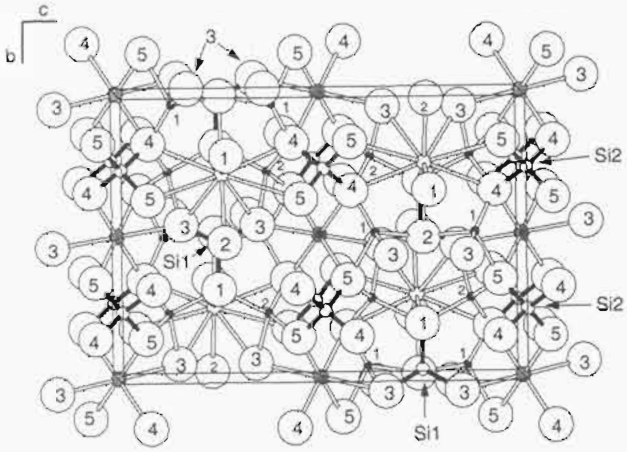

Figure 1. Unit-cell drawing of $Li_4SrCa(SiO_4)_2$. The view is along the *a* axis. Large open circles represent O atoms, small filled circles Li atoms, medium shaded circles Ca atoms, medium open circles with open bonds Sr atoms, and medium open circles with filled bonds Si atoms, here and in Figure 2.

with a 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.

Results and Discussion

A view of the contents of the unit cell is given in Figure 1. The structure contains a 10-coordinate Sr atom, a 6-coordinate Ca atom, two nonequivalent 4-coordinate Li atoms, and two nonequivalent 4-coordinate Si atoms. The O environment about the Sr atom is best described as a distorted bicapped square antiprism, and the polyhedron about the Ca atom is a distorted octahedron. Each of the Li and Si atoms occupies a distorted tetrahedron. While it is difficult to describe the structure in terms of a closest packing of spheres, it is useful to note the layered stacking of the metal atoms. These atomic sheets extend in the *ab* plane and stack along [001]. The repeat sequence is •••(Ca, Si2)••(Li1, Li2)••(Sr, Si1)••(Li1, Li2)••, i.e., atoms Ca and Si2 commix in one plane, atoms Li1 and Li2 in another, and atoms Sr and Si1 in another.

The Sr-centered polyhedra condense only in the *ab* plane, and this occurs by sharing vertices O1 and O2. In contrast the Ca-centered octahedra are completely isolated from one another. The two polyhedra, however, are connected by sharing vertices O3, O4, and O5. Again, within the *ab* planes, the Sr and Si1 atoms share vertices O1 and O2 and an edge O3••O3, while the Ca and Si2 atoms share vertices O4 and O5. The Si1 atoms also share O3 vertices with the Ca atom, and Si2 atoms bridge the O4••O5 edges of the Sr-centered polyhedra. Each Sr-centered polyhedron is capped by 8 Li atoms. Two each of atoms Li1 and Li2 span edges and triangular faces. Likewise, the Ca-centered octahedron is surrounded by 8 Li atoms. Four of these share vertices O3 and O4, and the others bridge edges O3••O5 and O4••O5. Interestingly, there is no metal atom directly bridging the two triangular faces O3••O4••O5 of the octahedra. The Li-centered tetrahedra share all of their vertices to form a thick, two-dimensional substructure of formula $(Li_2O_4)^{6-}$ that extends parallel to the *ab* plane (Figure 2). Sr and Si1 atoms occupy sites within the slabs, and the Ca and Si2 atoms occupy sites between the slabs.

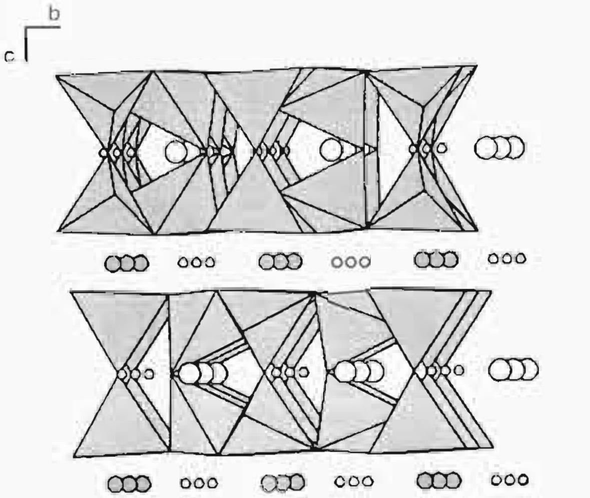

Figure 2. Polyhedral drawing of condensed Li−O system. Tetrahedra represent LiO_4 units.

The overall structure bears some resemblance to that of Li_2CaSiO_4.[11] Although the Ca atom occupies an 8-coordinate, distorted dodecahedral site in this structure, the metal atoms occupy layers in a manner similar to that of the title structure. The Ca and Si atoms occupy one layer and the Li atoms another. Likewise, the Li-centered tetrahedra condense into a two-dimensional system by sharing vertices.

Selected interatomic distances and angles are listed in Table 3. The average Sr−O distance is 2.76 ± 0.16 Å, which compares to Sr−O distances of 2.70 ± 0.22 and 2.86 ± 0.19 Å for the two 10-coordinate Sr atoms in α′-Sr_2SiO_4.[12] The average Ca−O distance is 2.384 ± 0.026 Å, which compares to Ca−O distances of 2.30−2.44 Å for the 6-coordinate Ca atoms in Ca_2SiO_4.[13] The Ca site symmetry is C_2; modest deviation from orthogonality is seen with the O3−Ca−O4 angle = 93.0(2)°, while the angle O3−Ca−O5 = 77.3(1)° represents a more severe distortion.

Atom Li1 binds to one each of atoms O2, O3, O4, and O5, and atom Li2 binds to one each of atoms O1, O3, O4, and O5. As noted above, the two-dimensional Li−O substructure (Figure 2) results from a sharing of all of the tetrahedral vertices. The Li1 and Li2 atoms share O3, O4, and O5, two Li1 atoms share O2, and two Li2 atoms share O1. The average Li1−O distance is 1.94 ± 0.04 Å, and the average Li2−O bond distance is 1.99 ± 0.07 Å. Each compares to the Li−O distances for 4-coor-

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(11) Gard, J. A.; West, A. R. *J. Solid State Chem.* **1973**, *7*, 422−427.

(12) Catti, M.; Gazzoni, G.; Ivaldi, G.; Zanini, G. *Acta Crystallogr., Sect B* **1983**, *39*, 674.

(13) Udagawa, S.; Urabe, K.; Natsume, M.; Yano, T. *Cement Concr. Res.* **1980**, *10*, 139−144.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $Li_4SrCa(SiO_4)_2$

Sr−O1	2.505(6)	O1−Sr−O1	144.0(2)
Sr−O1	2.734(6)	O1−Sr−O2	79.6(2)
Sr−O2	2.635(6)		86.6(2)
Sr−O2	2.766(6)	O1−Sr−O3	135.8(1)
Sr−O3 × 2	2.667(4)	O1−Sr−O4	98.1(1)
Sr−O4 × 2	2.804(4)	O1−Sr−O5	73.7(1)
Sr−O5 × 2	3.003(4)	O2−Sr−O2	166.2(1)
		O2−Sr−O3	69.4(1)
		O2−Sr−O4	116.95(8)
		O2−Sr−O5	64.95(8)
		O3−Sr−O3	59.5(2)
		O3−Sr−O4	70.8(1)
		O3−Sr−O5	116.9(1)
			65.0(1)
		O4−Sr−O4	125.6(2)
		O4−Sr−O5	171.3(1)
		O5−Sr−O5	123.8(2)
Ca−O3 × 2	2.384(4)	O3−Ca−O3	180
Ca−O4 × 2	2.414(2)	O3−Ca−O4	93.0(2)
Ca−O5 × 2	2.355(4)		87.0(1)
		O3−Ca−O5	77.3(1)
		O4−Ca−O4	180
		O4−Ca−O5	97.7(1)
		O5−Ca−O5	180
Si1−O1	1.629(6)	O1−Si1−O2	108.1(3)
Si1−O2	1.633(6)	O1−Si1−O3	110.4(2)
Si1−O3 × 2	1.649(4)	O2−Si1−O3	110.6(2)
		O3−Si1−O3	106.8(3)
Si2−O4 × 2	1.632(4)	O4−Si2−O4	108.4(3)
Si2−O5 × 2	1.637(4)	O4−Si2−O5	109.3(2)
		O4−Si2−O5	111.5(2)
		O5−Si2−O5	106.9(3)
Li1−O2	1.91(1)	O2−Li1−O3	102.3(5)
Li1−O3	1.966(9)	O2−Li1−O4	100.4(4)
Li1−O4	1.98(1)	O2−Li1−O5	106.0(5)
Li1−O5	1.90(1)	O3−Li1−O5	104.7(4)
		O4−Li1−O5	108.2(5)
Li2−O1	1.95(1)	O1−Li2−O3	106.6(5)
Li2−O3	2.06(1)	O1−Li2−O4	101.9(5)
Li2−O4	2.05(1)	O3−Li2−O4	101.0(5)
Li2−O5	1.91(1)	O3−Li2−O5	96.5(5)

dinate Li atoms in Li_2CaSiO_4,[8] 1.969 ± 0.014 Å, and Li_2O,[14] 1.997 Å.

Atom Si1 binds one O1, one O2, and two O3 atoms. Atom Si2 binds two O4 and two O5 atoms. The average Si1−O distance is 1.640 ± 0.010 Å, and the average Si2−O bond distance is 1.635 ± 0.003; each is normal, and all O−Si−O values are near the tetrahedral value.

The composition $Li_4Sr_{1.98}Eu_{0.02}Ca(SiO_4)_2$ produces blue emission under ultraviolet excitation. Excitation and emission maxima occur at 335 and 430 nm, respectively (Figure 3). The breadth of the bands is consistent with transitions between a $4f^7$ ground state and a $4f^65d^1$ excited state. Similar behavior has been reported[15] for Eu^{2+}-doped samples of the simple orthosilicates Ca_2SiO_4 and Sr_2SiO_4. The emission, however, occurs at longer wavelengths. For Ca_2SiO_4, the maximum intensity is at 500 nm, and Sr_2SiO_4 exhibits a maximum at 550 nm with a shoulder near 500 nm. The higher emission energy of the title compound may derive from the high concentration of Li atoms in the structure. These small atoms, surrounding the polyhedra of the emission centers, likely constrain the distortion of the excited state which leads to a smaller Stokes shift.[16]

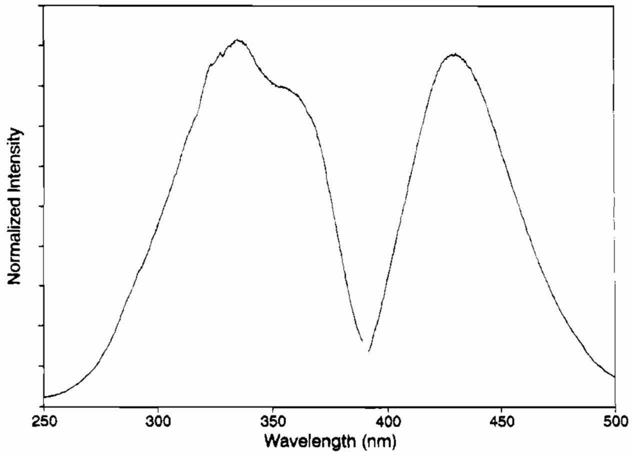

Figure 3. Emission and excitation spectra of the luminescence of $Li_4Sr_{1.98}Eu_{0.02}Ca(SiO_4)_2$ at 298 K. (λ_{exc} = 335 nm for emission, λ_{em} = 430 nm for excitation.)

Acknowledgment. This research was supported by the National Science Foundation (DMR92-21372). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the work.

Supplementary Material 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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(14) Zintl, E.; Harder, A.; Dauth, B. *Z. Electrochem.* **1934**, *40*, 588.

(15) Blasse, G.; Wanmaker, W. L.; Ter vrugt, J. W.; Bril, A. *Philips Res. Rep.* **1968**, *23*, 189.

(16) Blasse, G. *J. Solid. State. Chem.* **1979**, *27*, 3.