JOURNAL OF SOLID STATE CHEMISTRY 114, 512–515 (1995)

Crystal Structure Determination of $Li_2Ca_2Si_5O_{13}$

M. E. Villafuerte-Castrejón,* A. Dago,† U. Caldiño,‡ and R. Pomes†,[1]

*Materials Research Institute, Universidad Nacional Autónoma de México, P.O. Box 70-360, Mexico 04510 Distrito Federal, Mexico; †National Center for Scientific Research, P.O. Box 6990, Havana, Cuba; and ‡Department of Physics, Universidad Autonoma Metropolitana-Iztapalapa, P.O. Box 55534, 09340 Mexico Distrito Federal, Mexico

Received December 14, 1993; in revised form May 13, 1994; Accepted May 18, 1994

$Li_2Ca_2Si_5O_{13}$, M_r = 441.56, triclinic, space group $P\bar{1}$, a = 7.495(1), b = 7.749(2), c = 10.191(2) Å, α = 83.28(2)°, β = 68.87(2)°, γ = 75.87(2)°, V = 535.1(2) Å^3, Z = 2. This structure contains a complex double-chain silicate anion composed of 4- and 5-membered rings of silicate tetrahedra. Lithium is tetrahedrally coordinated and pairs of tetrahedra sharing one edge form binuclear units. Distorted calcium octahedra form an infinite column, each octahedron sharing four edges with four adjacent octahedra.

INTRODUCTION

The system Li_2O–CaO–SiO_2 is of some interest in glasses, glass–ceramics, and solid electrolytes. Several crystalline lithium calcium silicates are known (1) but the structure of only one, Li_2CaSiO_4, has been reported (2). It is a typical orthosilicate, containing isolated SiO_4^{4-} tetrahedra as the silicate anion. The phase diagram for the region Li_2SiO_3–Li_2CaSiO_4–SiO_2 has been determined (1) and several phases have been synthesized. The silicate anion constitution of two of these, $Li_2Ca_4Si_4O_{13}$ and $Li_2Ca_2Si_5O_{13}$, has been described (3). In this paper we report the crystal structure of $Li_2Ca_2Si_5O_{13}$.

EXPERIMENTAL

Mixtures of Li_2CO_3, $CaCO_3$, and SiO_2 in the ratio 1 : 3 : 6 were mixed intimately by grinding under acetone. The composition was melted in a Pt crucible at 1100°C for 2 days and at the end of the reaction time quenched to room temperature. The glass obtained was wrapped in Pt foil and crystallized at 995 ± 5°C for 48 days and quenched to room temperature by dropping the Pt envelope in a glass with mercury. Full details of the crystal growth were published by Villafuerte and others (4, 5).

A crystal was selected and cut down to a semispherical shape of 0.2 mm. Three dimensional X ray diffraction intensities were collected on a R3M/E Nicolet single-crystal diffractometer. The unit-cell constants were refined from the positions of 37 carefully measured reflections in the range 25° < 2θ < 40°, space group $P\bar{1}$. Data were collected using the $\theta/2\theta$ scan mode, using monochromated Mo$K\alpha$ radiation over the range $2\theta_{max}$ = 55° and h = −8 to 8, k = −8 to 8, and l = 0 to 8. Reflections (n = 1106) were observed with [$I > 3\sigma(I)$]. Intensities of two standard reflections measured at 50-min intervals showed no significant deviations from mean. Intensities were reduced to F_o by applying Lorentz polarization and absorption corrections. Structure was solved by Patterson and successive Fourier syntheses. Anisotropic least-

TABLE 1
Summary of Data Collection and Processing Parameters

Crystal data	
$Li_2Ca_2Si_5O_{13}$	
M_r = 441.56	
Triclinic, space group $P\bar{1}$	
a = 7.495(1) Å	α = 83.28(2)°
b = 7.749(2) Å	β = 68.87(2)°
c = 10.191(2) Å	γ = 75.87(2)
V = 535.1(2) Å^3	Z = 2
Dx = 2.75 g/cm^3	D_{obs} = 2.7 g/cm^3
μ = 1.66 mm^{-1}	
Crystal size 0.2 × 0.1 × 0.01 mm	
Data collection and refinement	
Mo$K\alpha$ (λ = 0.71069 Å), graphite monochromator	
2θ/θ scans	
2θmax = 55°	
F(000) = 440	
1106 observed reflections [$I > 3\sigma(I)$]	
R = 0.038	
wR = 0.037	
S = 1.198	
(Δ/σ)max = 0.009	
$\Delta\rho_{max}$ = 0.88 e Å^3	
$\nabla\rho_{min}$ = −0.82 e Å^3	

[1] To whom correspondence should be addressed.

0022-4596/95 $6.00

TABLE 2
Atom Coordinates (× 10^4) and Temperature Factors (Å^2 × 10^3) for $Li_2Ca_2Si_5O_{13}$ with e.s.d.'s in Parentheses

Atom	x	y	z	U^a
Li(1)	8245(17)	−787(16)	1233(14)	24(5)
Li(2)	1651(16)	4095(14)	7473(12)	18(5)
Ca(1)	4529(2)	8562(2)	3905(1)	11(1)
Ca(2)	242(2)	1673(2)	6058(1)	11(1)
Si(1)	1462(3)	2292(2)	2637(2)	9(1)
Si(2)	3153(3)	4502(2)	4080(2)	9(1)
Si(3)	7344(3)	2322(2)	2655(2)	8(1)
Si(4)	7817(3)	3071(2)	−381(2)	8(1)
Si(5)	6356(3)	6990(2)	387(2)	9(1)
O(1)	2538(6)	6607(5)	4244(4)	11(2)
O(2)	2220(6)	4978(5)	−68(4)	10(2)
O(3)	−2992(6)	585(5)	3629(4)	11(2)
O(4)	2774(6)	3291(6)	5504(4)	12(2)
O(5)	7800(6)	1761(6)	1034(4)	13(2)
O(6)	5506(6)	3986(6)	3108(4)	12(2)
O(7)	6535(6)	7748(6)	1700(4)	11(2)
O(8)	292(6)	7668(6)	1661(4)	12(2)
O(9)	7102(6)	8216(6)	−1034(5)	13(2)
O(10)	1956(6)	3964(6)	3163(5)	14(2)
O(11)	1595(6)	599(6)	3674(5)	12(2)
O(12)	−758(6)	3067(5)	2575(5)	12(2)
O(13)	4142(6)	6873(6)	680(5)	15(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $U(i, j)$ tensor.

TABLE 3
Bond Lengths (Å) for $Li_2Ca_2Si_5O_{13}$ with e.s.d.'s in Parentheses

Li(1)–O(3)	2.539(13)	Li(2)–O(4)	1.985(13)
Li(1)–O(5)	1.919(13)	Li(2)–O(7)	2.048(12)
Li(1)–O(7)	1.817(14)	Li(2)–O(8)	2.128(14)
Li(1)–O(8)	1.855(13)	Li(2)–O(12)	2.137(14)
Ca(1)–O(1)	2.292(5)	Ca(2)–O(1)	2.285(5)
Ca(1)–O(3)	2.451(6)	Ca(2)–O(3)	2.449(6)
Ca(1)–O(3)	2.632(6)	Ca(2)–O(4)	2.390(5)
Ca(1)–O(4)	2.402(5)	Ca(2)–O(8)	2.309(5)
Ca(1)–O(7)	2.268(4)	Ca(2)–O(11)	2.431(5)
Ca(1)–O(11)	2.444(5)	Ca(2)–O(11)	2.423(5)
Si(1)–O(9)	1.631(4)	Si(2)–O(1)	1.595(4)
Si(1)–O(10)	1.626(6)	Si(2)–O(4)	1.607(4)
Si(1)–O(11)	1.592(4)	Si(2)–O(6)	1.655(4)
Si(1)–O(12)	1.646(5)	Si(2)–O(10)	1.652(6)
Si(3)–O(3)	1.591(4)	Si(4)–O(2)	1.621(5)
Si(3)–O(5)	1.651(5)	Si(4)–O(5)	1.662(5)
Si(3)–O(6)	1.609(4)	Si(4)–O(8)	1.576(4)
Si(3)–O(12)	1.634(5)	Si(4)–O(13)	1.593(6)
Si(5)–O(2)	1.625(4)		
Si(5)–O(7)	1.583(6)		
Si(5)–O(9)	1.632(4)		
Si(5)–O(13)	1.600(5)		

TABLE 4
Selected Bond Angles (deg.) in $Li_2Ca_2Si_5O_{13}$ with e.s.d.'s in Parentheses

O(9)–Si(1)–O(12)	106.5(3)	O(10)–Si(2)–O(6)	106.2(2)
O(9)–Si(1)–O(11)	110.3(2)	O(10)–Si(2)–O(4)	107.9(3)
O(9)–Si(1)–O(10)	111.4(3)	O(10)–Si(2)–O(1)	108.1(3)
O(11)–Si(1)–O(10)	111.4(2)	O(6)–Si(2)–O(4)	109.2(2)
O(12)–Si(1)–O(11)	113.0(2)	O(6)–Si(2)–O(1)	107.9(2)
O(12)–Si(1)–O(10)	104.0(2)	O(4)–Si(2)–O(1)	117.0(2)
O(12)–Si(3)–O(6)	105.5(2)	O(13)–Si(4)–O(8)	112.0(3)
O(12)–Si(3)–O(5)	105.0(2)	O(13)–Si(4)–O(2)	109.6(2)
O(12)–Si(3)–O(3)	115.6(3)	O(13)–Si(4)–O(5)	108.0(3)
O(6)–Si(3)–O(5)	110.6(3)	O(8)–Si(4)–O(2)	112.8(2)
O(6)–Si(3)–O(3)	113.4(2)	O(8)–Si(4)–O(5)	109.3(2)
O(5)–Si(5)–O(3)	106.5(3)	O(2)–Si(4)–O(5)	104.8(3)
O(2)–Si(5)–O(3)	109.7(3)		
O(2)–Si(5)–O(9)	106.3(2)		
O(2)–Si(5)–O(7)	109.2(3)		
O(13)–Si(5)–O(9)	109.4(3)		
O(13)–Si(5)–O(7)	110.7(2)		
O(9)–Si(5)–O(7)	111.4(3)		

squares refinement minimizing $\Sigma\, w\,(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ converged to $R = 0.038$ and $wR = 0.037$, with a goodness of fit of 1.19. In the final least-squares

TABLE 5
Anisotropic Temperature Factors (Å^2 × 10^3) $Li_2Ca_2Si_5O_{13}$ with e.s.d.'s in Parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li(1)	15(7)	20(7)	43(8)	−1(6)	−13(6)	−9(5)
Li(2)	17(6)	13(6)	20(7)	−2(5)	−2(5)	−4(5)
Ca(1)	8(1)	14(1)	11(1)	−2(1)	−2(1)	−3(1)
Ca(2)	8(1)	12(1)	12(1)	−1(1)	−3(1)	−3(1)
Si(1)	7(1)	12(1)	9(1)	−1(1)	−3(1)	−2(1)
Si(2)	7(1)	9(1)	11(1)	−1(1)	−3(1)	−3(1)
Si(3)	5(1)	9(1)	9(1)	−1(1)	−2(1)	−1(1)
Si(4)	5(1)	11(1)	8(1)	−1(1)	−1(1)	−2(1)
Si(5)	7(1)	10(1)	10(1)	−2(1)	−2(1)	−2(1)
O(1)	13(1)	10(2)	9(2)	−1(2)	−3(2)	−1(2)
O(2)	10(2)	8(2)	13(2)	−1(2)	−6(2)	−1(2)
O(3)	11(2)	8(2)	12(3)	−1(2)	−2(2)	−3(2)
O(4)	10(2)	14(2)	12(3)	−3(2)	−5(2)	−4(2)
O(5)	16(2)	15(3)	10(3)	−2(2)	−6(2)	−2(2)
O(6)	4(2)	9(2)	18(3)	−3(2)	2(2)	−1(2)
O(7)	11(2)	14(2)	12(3)	−1(2)	−5(2)	−6(2)
O(8)	6(2)	18(3)	9(3)	−6(2)	2(2)	−1(2)
O(9)	14(2)	9(2)	11(3)	2(2)	1(2)	−1(2)
O(10)	14(2)	13(2)	17(3)	1(2)	−8(2)	−4(2)
O(11)	11(2)	10(2)	14(3)	2(2)	−3(2)	−3(2)
O(12)	8(2)	12(2)	15(3)	−1(2)	−4(2)	−1(2)
O(13)	10(2)	19(3)	16(3)	−1(2)	−3(2)	15(2)

Note. The anisotropic temperature factor exponent takes the form $-2\pi(h^2a^{*2}U_{11} + k^2\,b^{*2}\,U_{22} + \ldots + 2hka^*b^*U_{12})$.

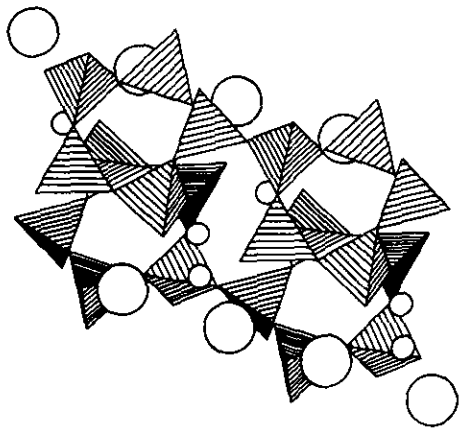

FIG. 1. Silicate anion in the structure $Li_2Ca_2Si_5O_{13}$.

cycle the maximum ratio of shift to e.s.d. was less than 0.009. Final difference synthesis of maximum and minimum peaks was 0.88 and -0.82 e Å^{-3}, respectively. Scattering factors were taken from *International Tables for X ray Crystallography* (1974). All calculations were carried out using the complex program SHELXTL-Plus (6).

DISCUSSION

Details of data collection and processing parameters are listed in Table 1. Final atomic parameters are given in Table 2 and selected bond distances and angles in Tables 3 and 4, respectively. Anisotropic temperature factors are given in Table 5.

The silicate anion of this phase has a complex double-chain structure, Fig. 1. The basic building block is a five-membered ring of silicate tetrahedra. Adjacent rings link up by sharing opposite corners to form infinite chains. These chains link up in pairs to form double chains. The repeat unit in the double chain contains two five-membered rings with a four-membered ring formed at their points of contact. It has the constitution $(Si_{10}O_{26})^{12-}$ and according to Liebau may be classified as looped branched double drierkette (7). Lithium is tetrahedrally coordinated and pairs of tetrahedra sharing one edge form binuclear

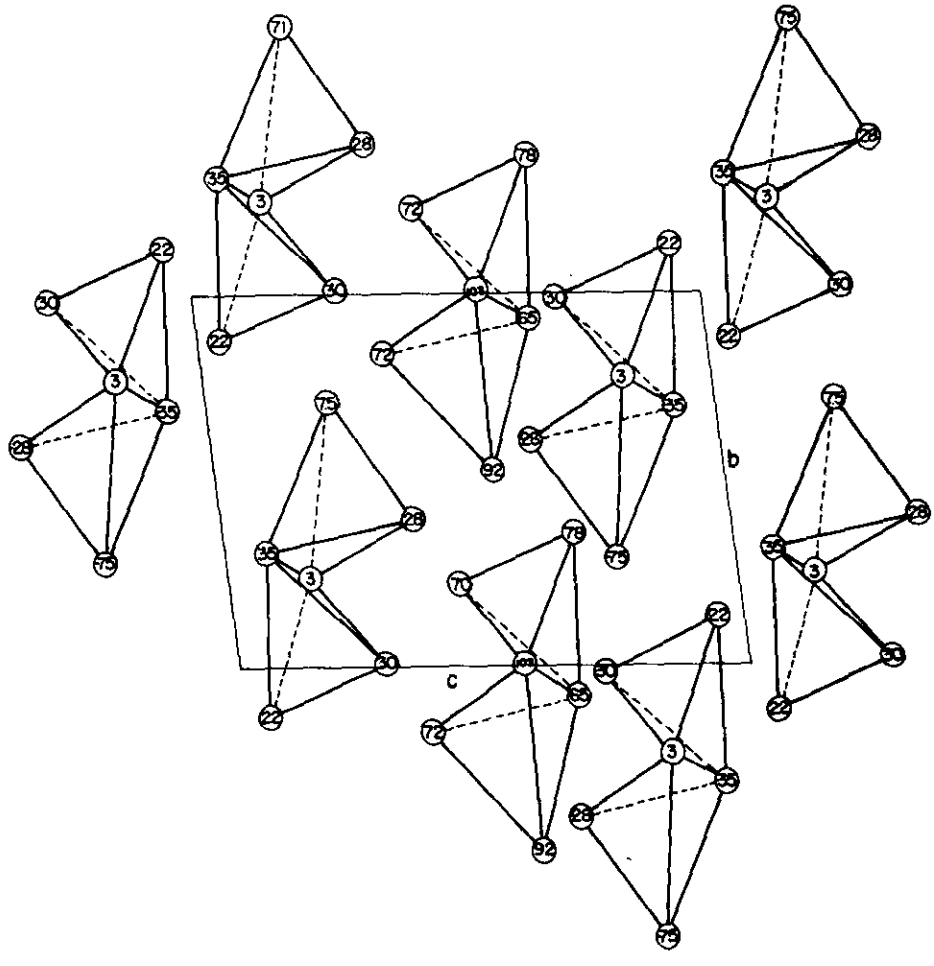

FIG. 2. A projection down the a axis of $Li_2Ca_2Si_5O_{13}$ showing the binuclear units of lithium oxygen tetrahedra.

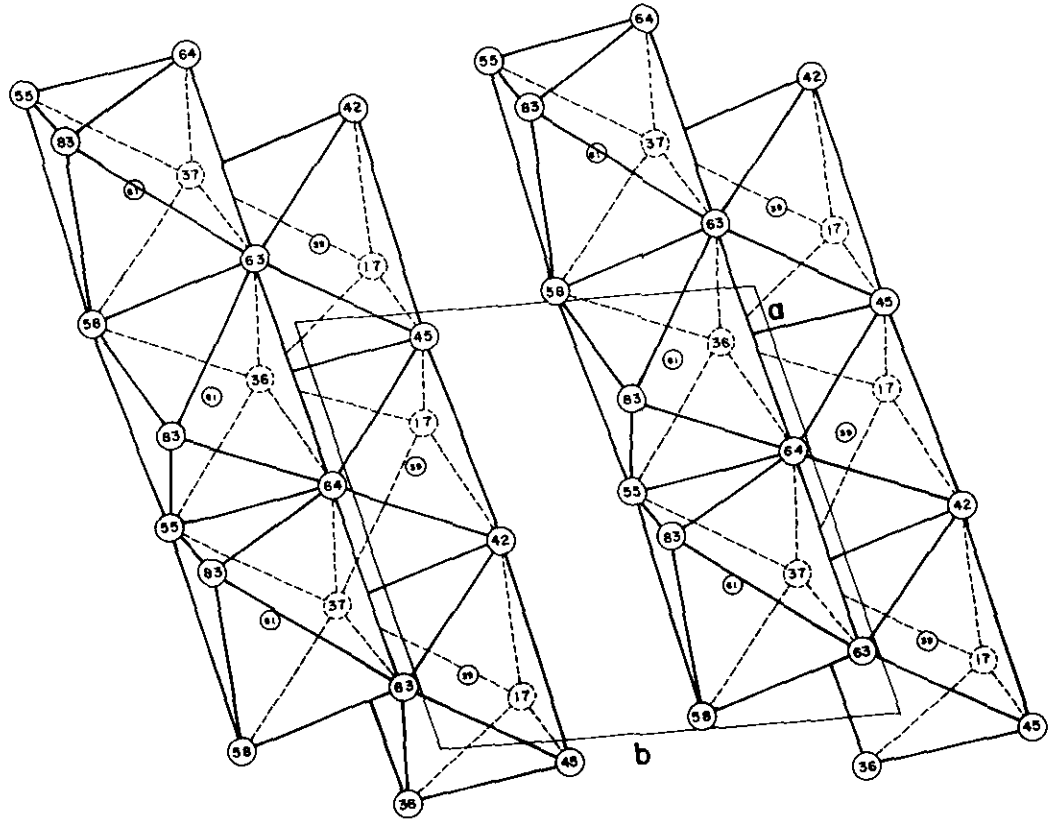

FIG. 3. Solid double chain of calcium octahedra in $Li_2Ca_2Si_5O_{13}$.

units (Fig. 2). Distorted calcium octahedra form an infinite column, each octahedron sharing four edges with four adjacent octahedra (Fig. 3). To complete the structure Ca^{+2} ions in distorted octahedrons form a solid double chain by sharing trigonal faces.

REFERENCES

1. West, A. R., *J. Am. Ceram. Soc.* **61,** 152 (1978).
2. Gard, J. A., and West, A. R., *J. Solid State Chem.* **7,** 422 (1973).
3. Villafuerte Castrejón, M. E., Rendon Diazmirón, L. E., Campana, C., and West, A. R., *J. Mater. Sci. Lett.* **2,** 355 (1983).
4. Villafuerte Castrejón, M. E., Rendón Diazmiron, L. E., and Campana, C., "International Crystallography Congress, Ottawa, Canada, 1981." [Collected abstract]
5. Villafuerte Castrejón, M. E., Rendón Diazmirón, L. E., and Campana, C., "European Crystallographic Congress, Jerusalem, Israel, 1982." [Collected abstract]
6. Sheldrick, G. M., "SHELXTL-Plus." Siemens Analytical X-ray Instruments, Madison, WI, 1991.
7. Liebau, F., *Rev. Mineral.* **5,** 1 (1980).