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BRIEF COMMUNICATION

Crystal Structure Determination of $Li_2Ca_4Si_4O_{13}$

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We synthesized the compound $Li_2Ca_4Si_4O_{13}$, $M_r = 494.5$, triclinic, space group $P\bar{1}$, $a = 10.450(3)$, $b = 8.231(3)$, $c = 7.170(2)$ Å, $\alpha = 77.71(2)°$, $\beta = 90.06(2)°$, $\gamma = 109.25(2)°$, $V = 567.3(5)$ Å^3, $Z = 2$. The structure is composed of two types of silicate anions: isolated $(SiO_4)^{-4}$ tetrahedra and infinite chains $(Si_3O_9)^{-6}$ along the [001] axis with three tetrahedra in the repeat unit. Calcium-distorted octahedra form infinite ribbons along the [001] axis. These ribbons are joined in the plane (010) by silicate chains $(Si_3O_9)^{-6}$ to form a layer of Ca octahedra and silicate anions. The isolated tetrahedra $(SiO_4)^{-4}$ join two different ribbons related by a center of symmetry. The structure is completed by Li^+ ions in distorted tetrahedral sites.

INTRODUCTION

Several lithium calcium silicate phases are known (1, 2), but the structure of only one of them, Li_2CaSiO_4, has been reported (2). It is a typical orthosilicate and contains isolated an $(SiO_4)^{4-}$ tetrahedron as the silicate anion. Moreover, considerable attention has been focused on the crystal chemistry of mixed anion silicates (3), compounds that contain more than one kind of silicate anion in the structure. Pucharovskii (4) reviewed the minerals and synthetic analogs with mixed anion silicates and reported the mineral joesmithite, whose conformation consisted of isolated tetrahedra $(SiO_4)^{-4}$ and infinite metasilicate chains $(Si_2O_6)^{-6}$ similar to pyroxenes. In a previous paper (5) we reported preliminary structural information on the silicate anion of the title compound. The present paper reports the crystal structure of this compound, whose formula may be written more accurately as $Li_2Ca_4(SiO_4)(Si_3O_9)$ with mixed anion silicates formed by isolated silicium tetrahedra and chains of $(Si_3O_9)^{-6}$.

EXPERIMENTAL

Li_2CO_3, $CaCO_3$, and SiO_2 were mixed intimately in the ratio 1 : 4 : 4 and heated in an electric furnace, initially in the range 500–900°C for several hours to eliminate CO_2 and finally above 1000°C to obtain a very homogeneous glass on quenching in water. Small glass samples were folded in platinum foil and heated in a vertical electrical furnace controlled to ±3°C; after at least 20 days the samples were quenched in mercury to room temperature.

A crystal of approximately 0.2 × 0.1 × 0.01 mm was mounted on an R3M Nicolet single crystal diffractometer. The unit-cell constants were refined from the positions of 30 carefully measured reflections in the range $20° < 2\theta < 30°$. Systematic absences were consistent with space group $P\bar{1}$ or $P1$. Data were collected using the $\theta/2\theta$ scan mode, using monochromated Mo$K\alpha$ radiation over the range $2\theta_{max} = 50°$ and $h = -13$ to 13, $k = -10$ to 10, and $l = 0$ to 9. Reflections ($n = 2156$) were observed with $(I) > 3\sigma(I)$. Intensities of two standard reflections measured at 50-min intervals showed no significant deviations from the mean. Intensities were reduced to F_0 by applying Lorentz polarization and absorption corrections. Structure was solved by Patterson and successive Fourier syntheses. Anisotropic least-squares refinement minimizing $\Sigma\, w\,(|F_0|-|F_c|)^2$, $w = 1/\sigma^2(F_0)$, converted to $R = 0.039$ and $wR = 0.041$, with a goodness of fit of 1.49. In the final least-squares cycle the maximum ratio of shift to e.s.d. was less than 0.008. Final difference synthesis maximum and minimum peaks were 0.68 and $-0.62\ e \cdot$ Å^{-3}. Scattering factors were taken from International Tables

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TABLE 1
Summary of Data Collection and Processing Parameters

Crystal Data

$Li_2Ca_4Si_4O_{13}$
$M_r = 494.5$
Triclinic, space group $P\bar{1}$
$a = 10.450(3)$ Å $\alpha = 77.71(2)°$
$b = 8.231(3)$ Å $\beta = 90.06(2)°$
$c = 7.170(2)$ Å $\gamma = 109.25(2)°$
$V = 567.3(5)$ Å^3 $Z = 2$
$Dx = 2.89$ g/cm^3 $\mu = 2.35$ mm^{-1}
Crystal size 0.2 × 0.1 × 0.01 mm

Data collection and refinement

Mo$K\alpha$($\lambda = 0.71069$ Å), graphite monochromator
$2\theta/\theta$ scans
$2\theta_{max} = 50°$
$F(000) = 492.00$
2156 observed reflections [$I > 3\sigma(I)$]
$R = 0.039$
$wR = 0.041$
$S = 1.49$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\ \rho_{max} = 0.68\ e \cdot$ Å^3
$\nabla\ \rho_{min} = -0.62\ e \cdot$ Å^3

TABLE 2
Atom Coordinates ($\times 10^4$) and Temperature Factors (A^2 × 10^3)

Atom	x	y	z	U^a
Li(1)	1140(10)	−4184(13)	2276(22)	39(5)
Li(2)	4087(9)	4098(11)	−2487(17)	24(3)
Ca(1)	3942(1)	7923(1)	−5710(1)	8(1)
Ca(2)	−30(1)	1942(1)	835(1)	8(1)
Ca(3)	5973(1)	2105(1)	758(1)	9(1)
Ca(4)	55(1)	−1968(1)	−5700(1)	8(1)
Si(1)	1790(1)	5728(2)	−2666(2)	7(1)
Si(2)	2786(1)	842(2)	743(2)	6(1)
Si(3)	3044(1)	3830(2)	2829(2)	6(1)
Si(4)	2806(1)	933(2)	6380(2)	6(1)
O(1)	3429(3)	2927(4)	4951(5)	11(1)
O(2)	1435(3)	3501(4)	2849(5)	11(1)
O(3)	3403(3)	5886(4)	−2716(5)	8(1)
O(4)	1588(3)	6646(4)	−4859(5)	11(1)
O(5)	3472(4)	2730(4)	1393(5)	11(1)
O(6)	1637(3)	6771(4)	−1000(5)	12(1)
O(7)	1199(3)	−89(4)	1341(5)	9(1)
O(8)	3023(4)	1561(4)	8413(5)	10(1)
O(9)	3842(3)	−93(4)	6201(5)	10(1)
O(10)	681(3)	3753(4)	−2130(5)	11(1)
O(11)	3734(3)	−333(4)	1354(5)	10(1)
O(12)	1226(3)	29(4)	6182(5)	9(1)
O(13)	3991(3)	5869(4)	2270(5)	8(1)

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

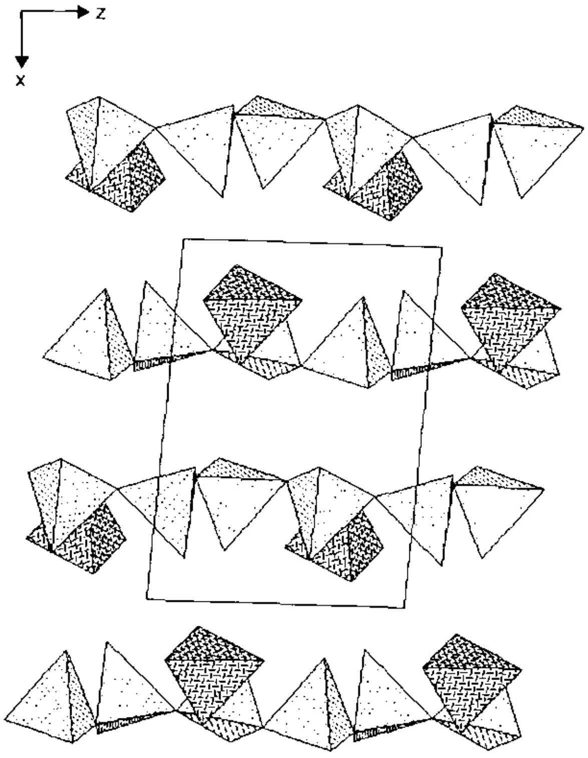

FIG. 1. Silicate anion in the structure $Li_2Ca_4(SiO_4)(Si_3O_9)$.

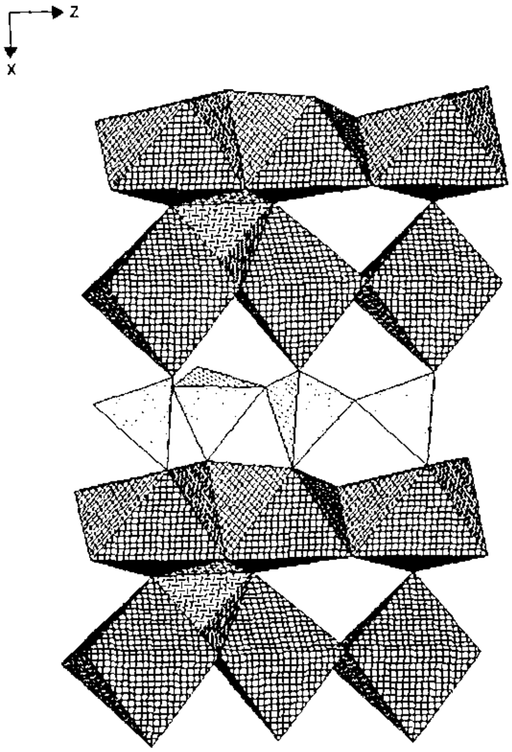

FIG. 2. Projection (010) of one layer ($y = 0.2$) of the structure.

for X-ray Crystallography (1974). All calculations were carried out using the PC version of SHELXTL (6).

DISCUSSION

Details of data collection and processing parameters are listed in Table 1. Final atomic parameters are given in Table 2.[2] The structure $Li_2Ca_4Si_4O_{13}$ contains two types of silicate anions: isolated (orthosilicate) $(SiO_4)^{-4}$ tetrahedra and infinite (metasilicate) chains $(Si_3O_9)^{-6}$, which run along the [001] axis. The latter may be classified according to Liebau as Dreier single chains (3). The structural motifs of silicate anions are illustrated in Fig. 1.

The four crystallographically independent Ca^{+2} ions have a distorted octahedral environment and form infinite ribbons extending to the [001] axis by sharing edges and corners. The ribbons associated by center of symmetry are arranged on two levels along [010] at $y = 0.8$ and $y = 0.2$. This ribbons are joined in the plane (010) by silicate chains $(Si_3O_9)^{-6}$ to form a layer of Ca octahedra and silicate anions. The isolated tetrahedra $(SiO_4)^{-4}$ join two different ribbons related by center of symmetry. The projection of the structure of such packing at $y = 0.2$ is represented in Fig. 2.

The structure is completed by Li^+ ions in distorted tetrahedral sites.

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[2] Tabulations of bond distances and bond angles are available from the authors on request.