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Preparation and Crystal Structure of Li_2CaSiO_4 and Isostructural Li_2CaGeO_4

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Li_2CaSiO_4 and Li_2CaGeO_4 are isostructural. They have body-centered tetragonal unit cells, with dimensions $a = 5.047 \pm 0.005$, $c = 6.486 \pm 0.006$ Å, and $a = 5.141 \pm 0.002$, $c = 6.595 \pm 0.002$ Å, respectively, and space group $I\bar{4}2m$. Their crystal structures, refined to $R = 0.076$ and 0.051, respectively, comprise columns, parallel to [001], of alternating (CaO_8) dodecahedra and (SiO_4) [or (GeO_4)] tetrahedra that are linked by sharing edges. Neighboring columns are joined at their corners to form a three-dimensional network, enclosing channels parallel to [001] that contain lithium. The lithium atoms are in distorted (LiO_4) tetrahedra joined at the corners to form sheets perpendicular to [001].

Li_2CaSiO_4 was first prepared by Maslova and Lileev (*1*) who also measured its refractive indices. The system Li_4SiO_4–Ca_2SiO_4 was studied by Schwarz and Haacke (*2*) but their work was mainly confined to a plot of liquidus temperatures along the join. Little further systematic work on the system Li_2O–CaO–SiO_2 or on the corresponding germanate system has been reported.

Li_2CaSiO_4

Preparation, Properties and Unit Cell

Li_2CaSiO_4 was best prepared by reacting an equimolar mixture of Li_2SiO_3 and $CaCO_3$ in a platinum crucible at ca. 900°C for 1–2 days. It formed as small (1–10 μm), irregularly shaped, white crystals of moderately low birefringence. Powder X-ray diffraction patterns were recorded with a Guinier-de Wolff focusing camera; powder intensities and accurate *d*-spacings were measured with a Philips diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Indexed powder data are given in Table I. Difficulty was experienced in obtaining consistent values for the intensities of some reflections. For instance, those subsequently indexed as 110 and 220 varied considerably in intensity from sample to sample, although the 330 intensity was quite consistent. A flat plate photograph taken of a powder flake showed little evidence of preferred crystal orientation. For the structure refinement, powder traces of several samples of Li_2CaSiO_4 were recorded using a scanning speed of $\frac{1}{4}°2\theta$/min. The peak areas were measured by cutting out the peaks from each trace and weighing. The traces were normalized by equating their summed peak areas, and the mean area of each peak was calculated. Intensities were assumed to be proportional to the mean peak areas and were scaled to give a value of 100 for the strongest reflection.

The unit cell was determined by electron diffraction of single crystals, using an AEI type EM802 electron microscope equipped with a 60° double-tilt specimen stage (*3*). The procedures used have been described in detail by Gard (*4*). Three series of diffraction patterns were recorded from crystals tilted through large angles around various rows of reflections. The distances between spots along the tilt axis of each series corresponded to *d*-spacings of 3.57, 3.23 and 2.52 Å, respectively. The spots on all the patterns fell on primitive or centered rectangular nets, and the tilt axes were subsequently identified with the *hh*0, 00*l* and *h*00 rows of the reciprocal lattice, respectively. A complete three-dimensional picture of the reciprocal lattice was constructed from

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TABLE I

INDEXED POWDER DATA, OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Li_2CaSiO_4 AND Li_2CaGeO_4

	Li_2CaSiO_4					Li_2CaGeO_4				
$h\,k\,l$	d_{obs} (Å)	I	d_{calc} (Å)	$\lvert F_o\rvert$	$\lvert F_c\rvert$	d_{obs} (Å)	I	d_{calc} (Å)	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1 0 1	3.987	2	3.9832	4.9	2.2	4.08	41	4.0546	35.4	34.2
1 1 0	3.576	66^a	3.5688	—	—	3.654	84	3.6352	80.7	84.7
0 0 2	3.243	13	3.2430	32.2	33.0	3.307	23	3.2975	66.8	63.2
2 0 0	2.526	6	2.5235	20.7	20.8	2.577	13	2.5705	46.1	48.2
1 1 2	2.402	100	2.4001	63.1	62.3	2.445	100	2.4424	96.5	91.5
2 1 1	2.130	22	2.1317	23.9	24.8	2.173	9	2.1710	23.9	23.7
2 0 2	1.9877	33	1.9916	40.2	42.3	2.028	42	2.0273	77.1	73.9
1 0 3			1.9873	20.7	20.4			2.0213	8.2	9.0
2 2 0	1.7826	17^a	1.7844	—	—	1.8178	25	1.8176	95.6	95.9
3 0 1	1.6286	5	1.6284	21.8	23.0	—	—	1.6586	—	—
0 0 4			1.6215	13.6	15.2	1.6488	2	1.6488	47.0	41.7
3 1 0	1.5963	6	1.5960	25.6	23.0	1.6262	8	1.6257	44.7	50.0
2 2 2	1.5630	11	1.5634	33.0	32.1	1.5918	16	1.5918	54.9	53.4
2 1 3			1.5613	9.0	8.1			1.5889	24.6	26.9
1 1 4	1.4762	11^a	1.4763	—	—	1.5014	13	1.5015	61.9	54.4
3 1 2	1.4317	28	1.4320	44.2	41.1	1.4584	29	1.4581	68.1	67.0
3 2 1	1.3626	16	1.3683	7.5	7.2	1.3900	25^b	1.3937	—	—
2 0 4			1.3642	48.6	52.4			1.3878	—	—
3 0 3	1.3273	2	1.3277	19.0	13.8	1.3517	3	1.3515	36.7	37.0
4 0 0	1.2617	5^a	1.2618	—	—	1.2852	5	1.2852	63.4	64.1
4 1 1	1.2026	4	1.2028	14.9	14.5	1.2255	7	1.2252	23.6	23.8
2 2 4	1.1990		1.2000	21.1	23.7	1.2209		1.2212	47.3	42.6
3 3 0	1.1890	4	1.1896	38.8	42.9	1.2117	5	1.2117	67.4	62.2
4 0 2	1.1747	8	1.1759	29.1	26.6	1.1970	4^b	1.1975	—	—
3 2 3			1.1750	19.6	15.1			1.1963	—	—
3 1 4	1.1358	10	1.1375	32.5	31.8	1.1574	11	1.1576	52.0	50.3
4 2 0	1.1273	5	1.1285	30.0	30.2	1.1491	5	1.1496	43.9	47.2
2 1 5			1.1247	9.1	11.2	1.1434		1.1441	18.5	19.9
3 3 2	1.1159	5	1.1168	34.1	27.6	1.1370	5	1.1374	50.3	48.0
0 0 6	1.0800	2^a	1.0810	—	—	—	—	1.0992	—	—
4 2 2	1.0645	6	1.0659	26.4	27.2	1.0856	8	1.0855	46.2	45.1
4 1 3			1.0652	9.3	7.8			1.0846	16.4	14.2
1 1 6	1.0329	4	1.0346	31.2	31.3	1.0517	4	1.0521	45.3	50.1
4 0 4	0.9947	4	0.9958	26.6	26.4	1.0130	4	1.0137	36.5	40.7
2 0 6			0.9937	13.3	17.2			1.0106	29.9	26.2
5 1 0	0.9887	4^a	0.9898	—	—	1.0080	4	1.0082	45.5	45.4
3 3 4	—	—	0.9592	—	—	0.9764	1	0.9764	26.1	28.5
3 2 5	0.9510	6	0.9515	6.5	6.8	—	—	0.9682	—	—
5 1 2	0.9458		0.9467	25.1	24.8	0.9640	7	0.9642	43.4	39.0
4 2 4	0.9256	7	0.9263	23.8	25.4	0.9420	11	0.9430	41.9	42.2
2 2 6			0.9246	22.0	26.4			0.9406	41.8	43.8

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[a] These reflections were omitted from the structure refinement, because their intensities were not reproducible from sample to sample.

[b] These reflections were also omitted from the structure refinement, because they overlapped those of CaO impurity, and accurate intensities could not be obtained.

projections down the three tilt axes. All reflections could be indexed on a body-centered tetragonal unit cell with $a = 5.047 \pm 0.005$, $c = 6.486 \pm 0.006$ Å. The only systematically absent reflections were those imposed by the body centering, i.e., with odd values of $(h+k+l)$ absent. Space groups fulfilling this condition are $I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$ and $I4/mmm$. Further selection was not possible, as intensities on the electron-diffraction patterns were not sufficiently reliable to distinguish the Laue groups $4/m$ from $4/mmm$. Atomic cell contents are $Li_4Ca_2Si_2O_8$, corresponding to a theoretical density of 2.93 g/cm^3. The observed density, measured on ca. 2.0 g of material with a Beckmann gas displacement pycnometer, is 3.03 g/cm^3.

Crystal Structure

Consideration of the possible space groups suggested that the general positions of $I\bar{4}$ [No. 82, Ref. (*5*)], or the special (*i*) positions of $I\bar{4}2m$ (No. 121) or of $I\bar{4}m2$ (No. 119) could represent the eight oxygen atoms of two $(SiO_4)^{4-}$ tetrahedra, with Si atoms on the origin and the body center. In space groups $I\bar{4}$ and $I\bar{4}2m$, suitable sites for the four lithiums would be $\{\frac{1}{2}, 0, (\frac{1}{4}, \frac{3}{4})\}$ and $\{0, \frac{1}{2}, (\frac{1}{4}, \frac{3}{4})\}$, at the centers of somewhat flattened tetrahedra, and for the two calcium ions $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, each coordinated to eight oxygens; suitable choice of coordinates for the oxygen atoms give reasonable Si–O, Li–O and Ca–O distances. No plausible sites for the Li atoms could be found for $I\bar{4}m2$, however, so it was rejected.

Thirty-four independent reflections were used in the structure refinement after multiple peaks had been divided in proportion to $n|F_{\text{calc}}|^2$, where n is the multiplicity. Using the least squares method, the structure refined in space group $I\bar{4}$ to $R = 0.074$ (where

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|)$$

and in $I\bar{4}2m$ to $R = 0.076$. The slight reduction in R-value for $I\bar{4}$ has little if any significance, as there is an extra variable permitting a difference

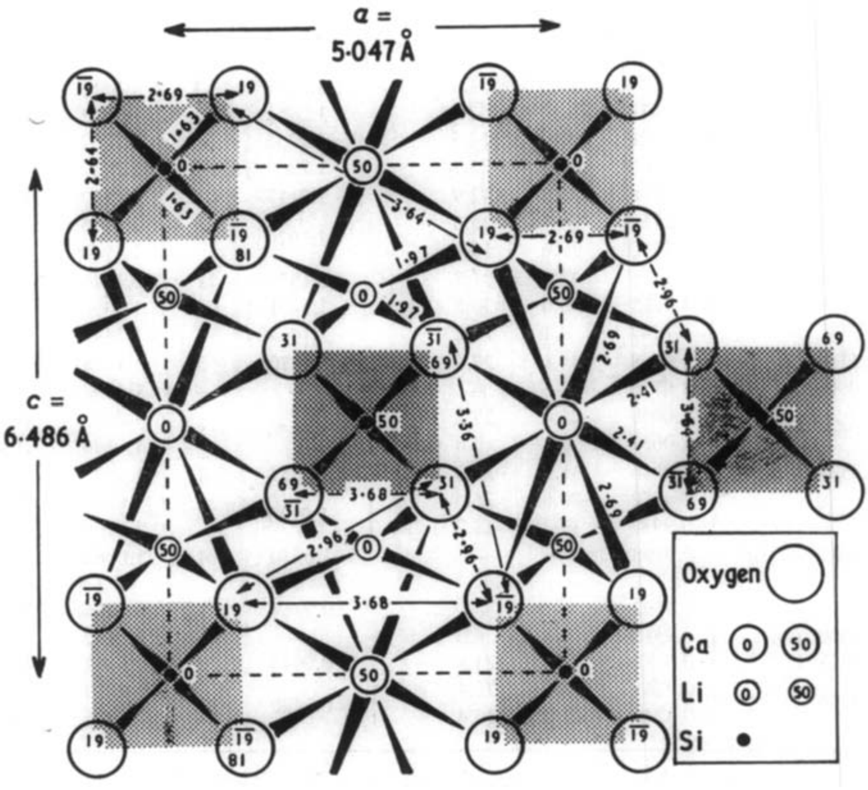

FIG. 1. Projection of the crystal structure of Li_2CaSiO_4 down [010]. (---) Unit cell axes; y coordinates are given as percentages. Oxygen coordination of each cation is shown, with typical bond lengths in Å; O–O distances in the coordination polyhedra are also indicated for clarification of Table III.

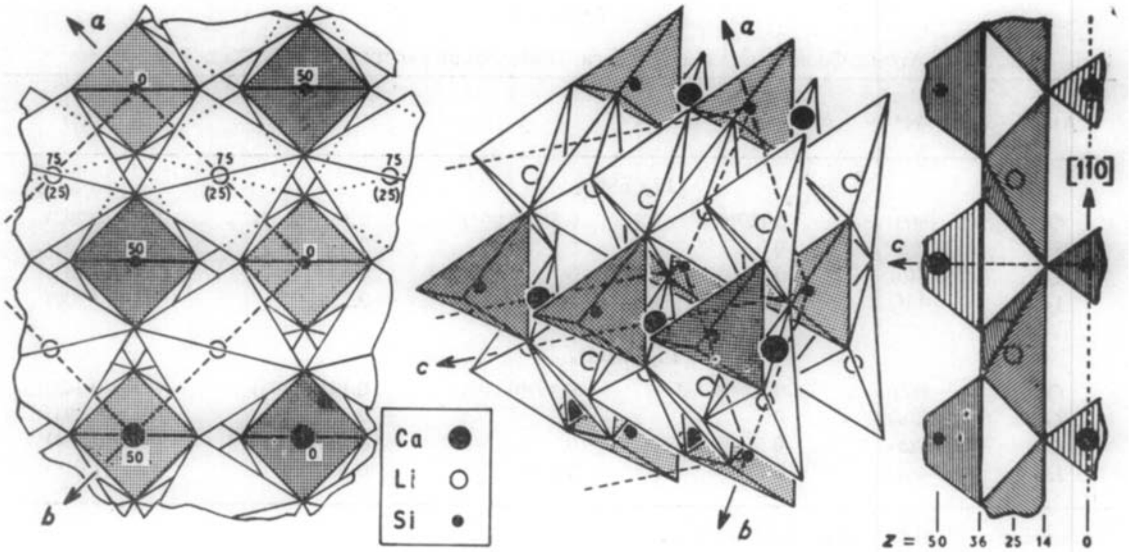

FIG. 2. Projections of the crystal structure of Li_2CaSiO_4 down [001] (left) and [110] (right), and a perspective view (center) approximately along [331]. (---) Unit cell axes; z coordinates are given as percentages. All (SiO_4) tetrahedra, and also the (LiO_4) tetrahedra in the [110] projection (right) are shaded. In the [001] projection (left), (· · ·) obscured edges of some of the lower (LiO_4) tetrahedra; the z-heights of two Ca atoms are given, but the other Ca atoms are omitted to show the heights of Si atoms. (LiO_4) tetrahedra are joined only at the corners, to form sheets at $z = 25$ and 75%; adjacent sheets are cross-linked by tetrahedral Si and 8 coordinate Ca atoms at $z = 0$ and 50%.

between the x and the y coordinates for oxygen. Consequently, Li–O distances would be less for half of the lithiums than for the other half in $I\bar{4}$, but there is no good crystallo-chemical reason for the difference. The space group $I\bar{4}2m$ is therefore preferable. Coordinates and isotropic temperature factors for the refinement in $I\bar{4}2m$ are listed in Table I, and interatomic distances and bond angles in Table III. Projections of the crystal structure are shown in Figs. 1 and 2. Fig. 1 also shows typical cation to oxygen, and oxygen to oxygen distances in the various coordination polyhedra.

Li_2CaGeO_4

A similar method was used to prepare Li_2CaGeO_4, using Li_2GeO_3 and $CaCO_3$ as starting materials. The unit cell was found by electron diffraction to be body-centered tetragonal with $a = 5.141 \pm 0.002$, $c = 6.595 \pm 0.006$ Å. Powder traces of five specimens were recorded and mean peak areas were used for the structure refinement; no difficulty was encountered in obtaining reproducible intensity values. Using 34 independent reflections, the structure refined in space group $I\bar{4}2m$ to $R = 0.051$, showing that Li_2CaSiO_4 and Li_2CaGeO_4 are isostructural. Relevant X-ray and crystallographic data are given in Tables I, II and III.

Discussion of the Structures

The most numerous cation is lithium, sited at the centers of distorted $(LiO_4)^{7-}$ tetrahedra. These tetrahedra share corners to form two intersecting sets of chains, parallel to [110] and [1$\bar{1}$0], respectively, and each with a repeat unit of two tetrahedra (i.e., "Zweierketten"). They therefore comprise rather open, two-dimensional sheets, parallel to (001) and of constitution $(Li_2O_4)^{6-}$, in which all the corners, but no edges, of the tetrahedra are shared. Adjacent sheets are joined, via silicon, by sharing corners with $(SiO_4)^{4-}$ tetrahedra, and also via calcium in distorted dodecahedra. However, the sheets are sufficiently open to permit each $(CaO_8)^{14-}$ dodecahedron to share an edge with each of two $(SiO_4)^{4-}$ tetrahedra on the *outer* faces of two adjacent sheets. Alternatively, then, the structure may be regarded as comprising columns of alternating, edge-sharing (SiO_4) tetrahedra and (CaO_8) dodecahedra; the columns are linked by their corners to neighboring columns to form a three-dimensional network, enclosing channels parallel to [001] that contain the lithiums.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS, WITH ESD'S IN PARENTHESES

Atom	N[a]	x	y	z	B_{iso} (Å^2)
		Li_2CaSiO_4			
O	8(*i*)	0.189(0.003)	0.189(0.003)	0.142(0.002)	0.905(0.292)
Si	2(*a*)	0	0	0	0.533(0.164)
Ca	2(*b*)	0	0	0.500	0.564(0.124)
Li	4(*d*)	0	0.500	0.250	3.319(0.909)
		Li_2CaGeO_4			
O	8(*i*)	0.199(0.003)	0.199(0.003)	0.146(0.003)	0.144(0.345)
Ge	2(*a*)	0	0	0	0.684(0.094)
Ca	2(*b*)	0	0	0.500	0.428(0.174)
Li	4(*d*)	0	0.500	0.250	1.679(1.019)

[a] Number of positions and Wyckoff notation.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES, ESD'S IN PARENTHESES

Li_2CaSiO_4				Li_2CaGeO_4		
		d	*n*[g]			*d*
Si–O	1.626(0.014)	⟨1,1,.75⟩	4	Ge–O	1.731(0.016)	⟨1,1,.74⟩
O–O	2.685(0.020)	⟨110⟩	2[a]	O–O	2.879(0.022)	⟨110⟩
O–Si–O	111.3(07)$^{\circ e}$			O–Ge–O	112.5(0.8)°	
O–O	2.640(0.020)	⟨1,0,.75⟩	4	O–O	2.800(0.026)	⟨1,0,.74⟩
O–Si–O	108.5(0.7)$^{\circ e}$			O–Ge–O	108.0(0.8)°	
Li–O	1.969(0.014)	⟨1,.60,.35⟩	4	Li–O	1.973(0.016)	⟨1,.66,.35⟩
O–O	3.677(0.020)	⟨1,.60,0⟩	2	O–O	3.702(0.022)	⟨1,.66,0⟩
O–Li–O	138.1(0.6)$^{\circ e}$			O–Li–O	139.5(0.7)°	
O–O	2.957(0.020)	⟨1,.25,.43⟩	4[b]	O–O	2.954(0.024)	⟨1,.21,.42⟩
O–Li–O	97.4(0.6)$^{\circ e}$			O–Li–O	96.9(0.7)°	
Ca–O	2.686(0.015)	⟨1,1,1.9⟩	4	Ca–O	2.737(0.020)	⟨1,1,1.8⟩
Ca–O	2.408(0.014)	⟨1,1,.45⟩	4	Ca–O	2.388(0.017)	⟨1,1,.48⟩
O–O	3.361(0.021)	⟨1,1,4.0⟩	4[c]	O–O	3.373(0.030)	⟨1,1,4.9⟩
O–O	3.644(0.020)	⟨1,0,.45⟩	4[c]	O–O	3.641(0.025)	⟨1,0,.48⟩
Li_2O	Li–O	1.997	Li_2PdO_2	Li–O	1.990[f]	
[Ref. (6)]	O–O	3.261	[Ref. (7)]	O–O	3.74	
				O–O	2.98	
				O–O	3.12	

[a,b] O–O edges shared with a (CaO_8) dodecahedron.

[c] In addition to these O–O edges, each (CaO_8) dodecahedron has two edges of type *a* and eight edges of type *b*.

[d] Approximate direction (in axial coordinates) of line joining centers of atoms.

[e] Distance and direction of oxygen atoms involved are given immediately above.

[f] Li assumed to be equidistant from its tetrahedral oxygens.

[g] n = number of similar bonds or edges in the appropriate polyhedron.

Ca–O bond distances fall into two groups: four oxygens at 2.69 Å (2.74 Å for Li_2CaGeO_4) form the common ⟨110⟩ edges of two (SiO_4) [or (GeO_4)] tetrahedra and one (CaO_8) dodecahedron; the other four at 2.41 Å (2.39 Å for Li_2CaGeO_4) directly link adjacent (CaO_8) dodecahedra. The (LiO_4) tetrahedra are evidently flattened in the [001] direction because of the attraction of Ca for the four oxygens at 2.69 Å; resistance of (LiO_4) tetrahedra to excessive flattening, and repulsion between Si^{4+} and Ca^{2+} probably account for this Ca–O bond being longer than the other. The slight elongation of the ⟨110⟩ edges of (SiO_4) [or (GeO_4)] tetrahedra may be caused by the almost direct pull of the two Ca ions at 2.41 Å.

Although the oxygen arrangement does not approximate to either hexagonal or cubic close packing, the structure may be considered in terms of layers, parallel to (001), of loosely packed oxygen atoms with interleaved cations. Each oxygen has two Li^+, two Ca^{2+} and one Si^{4+} as the nearest cations.

Comparison of Li_2CaSiO_4 with other oxides containing tetrahedrally coordinated lithium shows that $(LiO_4)^{7-}$ tetrahedra are quite versatile in the ways that they can coalesce. Li_2O itself has a three-dimensional antifluorite structure with all tetrahedral edges shared (*6*), Li_2PdO_2 has $(LiO)_\infty^-$ sheets with four shared edges in each tetrahedron (*7*), while only the corners are joined in the $(LiO_2)_\infty^{3-}$ sheets of Li_2CaSiO_4. The degree and manner of sharing of the $(LiO_4)^{7-}$ tetrahedra appears to be related to the overall Li:O ratio.

Acknowledgments

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