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The crystal structure of $LiAlSi_2O_6$ III (high-quartz solid solution)

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Auszug

Die Gitterkonstanten von $LiAlSi_2O_6$ III sind $a = 5{,}217 \pm 0{,}001$ Å, $c = 5{,}464 \pm 0{,}002$ Å; die Raumgruppe ist $P6_222$ (oder $P6_422$), $Z = 1$, $D_{\text{beob}} = 2{,}395$, $D_{\text{ber}} = 2{,}399$ g/cm³. Die Atomabstände sind auf 0,001 Å für (Si,Al)—O und 0,005 Å für Li—O bestimmt worden. $R = 0{,}051$. Es konnte bestätigt werden, daß sich die Struktur vom Hochtemperatur-Quarz ableitet, in den Li eingebaut wird. Die Verteilung von Si und Al in den Tetraedern ist vollständig zufällig. Die Li-Atome befinden sich in den dreizähligen Punktlagen parallel zur c-Achse, wobei das einzige Li-Atom der Elementarzelle die eine der drei Lagen nach Zufall besetzt; es ist in Vierer-Koordination. Jedes Li-Tetraeder hat je eine Kante mit zwei (Si,Al)-Tetraedern gemeinsam. Der Abstand (Si,Al)—Li ist mit $2{,}609 \pm 0{,}001$ Å außerordentlich kurz. Für die ungewöhnlich geringe thermische Ausdehnung von $LiAlSi_2O_6$ III wird eine Erklärung gegeben.

Abstract

$LiAlSi_2O_6$ III (high-quartz solid solution) was found to be hexagonal, space group $P6_222$ (or $P6_422$), $a = 5.217 \pm 0.001$, $c = 5.464 \pm .002$ Å, $Z = 1$, $D_o = 2.395$ and $D_c = 2.399$ g/cm³. The bond lengths were determined with an accuracy of 0.001 Å for Si,Al—O bonds and 0.005 Å for Li—O bonds. The final R value was 5.1%. The structure was confirmed to be a stuffed derivative of high quartz. The distribution of Si and Al in the tetrahedra is completely random. Lithium atoms are 4-coordinated and stuffed into interstitial positions parallel to the c axis. They occupy an equipoint of rank 3. There is only one lithium atom per unit cell, randomly distributed among the three equivalent sites. Each lithium tetrahedron shares two edges with two Si,Al tetrahedra. The Si,Al—Li distance, 2.609 ± 0.001 Å, is exceptionally short. An explanation for the unusually low thermal-expansion behavior of $LiAlSi_2O_6$ III is given.

Introduction

Three different polymorphs have been reported in the literature for the spodumene composition $LiAlSi_2O_6$. They were sometimes called α, β, and γ spodumene. In order to preserve the use of the designations α, β, and γ for polymorphs connected by displacive transformations, LI and PEACOR (1968) proposed the term $LiAlSi_2O_6$ I for the monoclinic form (the mineral spodumene, sometimes called α spodumene), $LiAlSi_2O_6$ II for the tetragonal form (the high-temperature form, sometimes called β spodumene) and $LiAlSi_2O_6$ III for the hexagonal form (another high-temperature form, sometimes called γ spodumene). The term $LiAlSi_2O_6$ III is especially useful because the nomenclature used in the literature for this hexagonal form has been very confusing, indeed. It has been called by the following different names: (1) β eucryptite solid solution by ROY and OSBORN (1949) and SKINNER and EVANS (1960), or β eucryptite-like structure by KALININA and FILIPOVICH (1965), (2) β quartz solid solution by KARSTETTER and VOSS (1967), (3) β eucryptite β quartz solid solution by EPPLER (1963), (4) optically negative β spodumene or silica *O* by ROY *et al.* (1950) and ROY (1959) and (5) γ spodumene by MUNOZ (1966).

When glass of spodumene composition is heat treated, the first crystallization product is hexagonal $LiAlSi_2O_6$ III. As the temperature or time of the heat treatment increases, $LiAlSi_2O_6$ III transforms into tetragonal $LiAlSi_2O_6$ II. This way of preparing $LiAlSi_2O_6$ III is very common and has been mentioned in many papers in the literature. Another method of preparation of $LiAlSi_2O_6$ III involves the use of high pressure and temperature. MUNOZ (1966) synthesized $LiAlSi_2O_6$ III from $LiAlSi_2O_6$ II by this method.

Attention is focused on $LiAlSi_2O_6$ III because of its very low thermal-expansion behavior. It is one of the principal crystalline phases that can be formed in low-expansion, lithium-bearing glass-ceramic materials. This paper is concerned with the crystal-structure analysis of $LiAlSi_2O_6$ III and an explanation of its low thermal-expansion behavior based on its structure.

Experimental

Single crystals were grown by heat treating a freshly-drawn glass fiber of composition $LiAlSi_2O_6$ at 977 °C for half an hour. The crystals thus grown were not sufficient in volume for a wet chemical analysis. However, the glass from which the crystals were grown was chemically analyzed. The analysis showed that the exact chemical composition of the glass was $0.94\ Li_2O - 1.00\ Al_2O_3 - 4.00\ SiO_2$, which is very close to a 1:1:4 mole ratio. Parts of the single crystals were ground to spherical shapes. Several such single crystals were selected for use with the precession and Weissenberg methods. A spherical crystal, mounted on the a^* axis and having a diameter of 0.275 mm, was used for both intensity measurements and the accurate determination of lattice constants. A zero-level Weissenberg photograph was taken for this crystal. An x-ray tube with a contaminated copper target was used deliberately to record more data due to the presence of many different characteristic radiations, namely W$L\alpha_1$, Fe$K\alpha$, Cu$K\beta$, Cu$K\alpha_1$, and Cu$K\alpha_2$. All the data from this Weissenberg photograph were refined by the least-squares program LCLSQ written by BURNHAM (1962). The refined lattice parameters obtained thereby, plus some other data are as follows:

Space group: $P6_222$ (or its enantiomorph $P6_422$)

$a = 5.217 \pm 0.001$, $c = 5.464 \pm 0.002$ Å
$Z = 1$ $LiAlSi_2O_6$
$D_o = 2.395$, $D_c = 2.399$ g/cm^3
$\mu = 74.95$ cm^{-1} for Cu$K\alpha$ radiation.

A second batch of glass having composition $LiAlSi_2O_6$ was prepared. Chemical analysis showed that the composition was $0.98\ Li_2O - 1.00\ Al_2O_3 - 4.00\ SiO_2$. Part of the glass was finely ground and the glass powder completely crystallized to the hexagonal $LiAlSi_2O_6$-III phase by heat treatment at 750 °C for ten days. Powder-diffractometer data were refined by the least-squares method. The lattice constants thus obtained were $a = 5.213$ and $c = 5.451$ Å. These results agree well with the single-crystal data, another indication that the single crystals are close to composition $LiAlSi_2O_6$. No

Table 1. *A comparison of lattice constants of* $LiAlSi_2O_6$ III *and its solid solution from different sources*

	Single crystal (this paper)	Powder (this paper)	Powder (MUNOZ)	Powder (TOROPOV *et al.*)	Powder (ROY *et al.*)	Powder (EVANS)*
Composition	Li_2O—Al_2O_3—$4SiO_2$	Li_2O—Al_2O_3—$4SiO_2$	Li_2O—Al_2O_3—$4SiO_2$	Li_2O—Al_2O_3—$3.7SiO_2$	unknown (1—1—8 ~ 1—1—4)	Li_2O—Al_2O_3—$4SiO_2$
a	5.217 Å	5.213 Å	5.216 Å	5.232 Å	5.205 Å	5.23 Å
c	5.464	5.451	5.450	5.458	5.434	2 × 5.44

* No diffraction data were given. The values of the constants were taken directly from a diagram.

accurate lattice constants of $LiAlSi_2O_6$ III are given in the literature. However, all the diffraction data available in the literature for both $LiAlSi_2O_6$ III and its solid solution were indexed and refined. The results are listed in Table 1 along with our data for comparison.

The intensities were collected from the spherical crystals having a diameter of 0.275 mm and mounted for rotation about the a^* axis. They were measured with a manually operated Supper diffractometer (equi-inclination Weissenberg geometry) with a scintillation counter and $CuK\alpha$ radiation. The associated electronics included pulse-height-analysis circuitry. Both the *hkl* and *khl* reflections were collected from the zero to the fifth levels, and the average, after correction for Lorentz-polarization factors, was calculated. All the *hkl* intensities agreed well with *khl* data. Absorption ($\mu R = 1.0$) and secondary-extinction corrections (ZACHARIASEN, 1963) were applied. There were a total of 81 independent reflections (excluding extinguished ones), of which 71, or 87.7%, were measured. Among the 71 reflections measured, three were too small to be observed. Since $LiAlSi_2O_6$ III is noncentrosymmetric, the structure factors for the unobserved reflections were taken to be two-thirds that of the minimum observed reflection.

Determination and refinement of structure

$LiAlSi_2O_6$ III has the same space group as that of high quartz and its lattice constants are close to those of high quartz. Thus, it was suspected that $LiAlSi_2O_6$ III was a stuffed derivative of high quartz, so its F_o values were compared with the corresponding F_c values for high quartz (YOUNG, 1962). Since a fairly reasonable agreement was obtained, a least-squares refinement of the positional parameters alone was started by using the atomic positions from high quartz, omitting the lithium atoms, and assuming complete disorder for silicon and aluminum. The overall temperature factor was taken to be 0.5. The refinement converged at $R = 13.4\%$.

The following ionic states were assigned to each element in $LiAlSi_2O_6$ III: for lithium, Li^{+1}; for oxygen, O^{-1}; and for both aluminum and silicon, $\frac{1}{3}(2Si^{+2} + Al^{+1})$. These assignments were based on the following considerations: (1) The overall charges must remain balanced for $LiAlSi_2O_6$ III, (2) The bonding in $LiAlSi_2O_6$ III was assumed to be half ionic and half covalent, (3) The silicon atoms in the high quartz structure occupy a 3-fold position. If $LiAlSi_2O_6$ III is a stuffed derivative of high quartz, the two silicon and one aluminum atoms in a unit cell have to occupy the 3-fold position, or aluminum and silicon atoms have to be completely disordered. In addition, since $LiAlSi_2O_6$ III was formed at a relatively high temperature and quenched to room temperature, the silicon and aluminum atoms are probably disordered. This was later verified by the refinement.

Refinement of the structure was carried out on the IBM 7090 using the SFLSQ2 least-squares program of Prewitt (1962). The weighting scheme recommended by Cruickshank (1965) was used. All the independent reflections measured, including the unobserved ones, were used.

The isotropic refinement was also carried out omitting the lithium atoms. The R value dropped to 7.6%. A comparison of F_o and F_c at this stage revealed that several reflections were affected by primary extinction. The 011 reflection, whose raw intensity was the largest, was found to be affected most. This was the only reflection which was later excluded from the final refinements.

Even before the three-dimensional difference synthesis was computed, the lithium atoms were located by the geometrical method described as follows. There is only one lithium atom per unit cell; this could occupy an equipoint of rank 3, 6, 12 or 24. Statistically, each of such equipoints would contain 1/3, 1/6, 1/12 or 1/24 lithium atom respectively. Since the ionic state of the lithium atom was assumed to be Li^{+1}, there should be only two electrons per lithium atom. The number of electrons at each possible site which lithium might occupy would be 0.67, 0.33, 0.17 or 0.08. However, there are nine electrons at each oxygen site and twelve electrons at each Si,Al site, as computed from the ionic states assigned to them. Thus, it becomes increasingly difficult to distinguish a lithium peak in an electron-density map from the background fluctuation if lithium occupies an equipoint of rank 6 or higher. Based on this consideration, a search for the lithium atom was started at an equipoint of rank 3. There are four different equipoints of rank 3 in space group $P6_222$, of which one is occupied by the Si,Al atom. This leaves only three equipoints for consideration. Each of these possible lithium equipoints was tested for the Si,Al—Li, Li—O distances and the O—Li—O angles. The test results were listed in Table 2. An examination of the results clearly indicated that the lithium atom may occupy the equipoint 3*a* at 000. At this site, lithium is 4-coordinated, the Si,Al—Li distance being 2.609 Å, Li—O 2.068 Å and the average O—Li—O angle 110.8°. These values match very closely those of the Li tetrahedra of

Table 2. *Interatomic distances and angles for possible lithium location in different three-fold positions*

Atom pair	$3a$, 000	$3d$, $\frac{1}{2}0\frac{1}{2}$	$3b$, $00\frac{1}{2}$
Li—O	2.068 Å	2.282 Å	2.610 Å
O—O	2.601	2.737	3.729
	3.696	4.102	4.102
	3.714	4.167	4.876
average	3.337	3.669	4.236
O—Li—O	77.9°	73.7°	91.2°
	126.6	127.9	103.6
	127.8	131.8	138.2
average	110.8	111.1	111.0
minimum Si,Al—Li	2.609 Å	2.740 Å	2.771 Å

$LiAlSi_2O_6$ II (LI and PEACOR, 1968), namely Si,Al—Li 2.628 and 2.710 Å, Li—O 2.081 Å, average O—Li—O angle 110.5°. In addition, the lithium tetrahedron shares edges with the Si,Al tetrahedra and the shared edge is the shortest for both the Li and Si,Al tetrahedra. This correct lithium position was later confirmed by the three-dimensional difference synthesis.

Table 3. *Final atom parameters*
(those of high quartz in parentheses)

	x	y	z
Si,Al	$\frac{1}{2}$	0	0
	($\frac{1}{2}$)	(0)	(0)
O	.2057 ± .0006	(.4114)	$\frac{1}{2}$
	(x)*	($2x$)	($\frac{1}{2}$)
Li	0	0	0

* x: .2068 ± .0007, YOUNG (1962); .197, WYCKOFF (1926).

Table 4
Isotropic temperature factors and atom parameters at the end of isotropic refinement

	x	y	z	B
Si,Al	$\frac{1}{2}$	0	0	.29 ± .05 Å^2
O	.2055 ± .0008	(.4110)	$\frac{1}{2}$	1.65 ± .10
Li	0	0	0	1.45 ± .88

Further isotropic refinement was carried out with the correct lithium position included. The R value remained 7.6⁰/₀ and the isotropic temperature factor of lithium changed from 1.37 to 1.38, which agrees well with the corresponding value of $LiAlSi_2O_6$ II (LI and PEACOR, 1968). Since there is only one lithium per unit cell and lithium is a very light atom, the improvement of R value by inserting the lithium atom is very small. In addition, any such improvement may well be cancelled by the presence of primary extinction in several strong reflections, especially the 011 reflection. Thus, it seems that the temperature factor would be a good indicator for the presence of lithium. In order to test this assumption, lithium was introduced in the two remaining 3-fold equipoints and refined isotropically. For the equipoint 3b at $00\frac{1}{2}$, the R value increased slightly to 8.4⁰/₀ and the lithium temperature factor also increased from 1.37 to 3.07. For the equipoint 3d at $\frac{1}{2}0\frac{1}{3}$, the R value increased further to 8.6⁰/₀ and the lithium temperature factor jumped from 1.37 to 5.31. In the final isotropic refinement, excluding the 011 reflection, the R value decreased slightly to 6.9⁰/₀ and the lithium temperature factor was 1.45. Refinement with anisotropic temperature factors was then carried out. The final R value was 5.1⁰/₀.

Table 5. *Final anisotropic temperature factors**
(those of high quartz in parentheses)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B**
Si,Al	.0042 ± 10 (.0274 ± 8)	.0028 ± 11 (.0190 ± 10)	.0018 ± 7 (.0102 ± 4)	.0014 (.0)	.0 (.0)	.0 (.0)	.30 Å² (1.80)
O	.0176 ± 16 (.0552 ± 37)	.0188 ± 28 (.0507 ± 40)	.0186 ± 16 (.0341 ± 12)	.0094 (.0)	.0089 ± 17 (−.0230 ± 24)	.0 (.0)	1.89 (4.48)
Li	.0046 ± 169	.0103 ± 293	.0510 ± 216	.0052	.0	.0	2.48

* By symmetry $\beta_{12} = {}^1/_2\,\beta_{22}$, $\beta_{13} = \beta_{23} = 0$ for Si,Al and Li; $\beta_{12} = {}^1/_2\,\beta_{22}$, $\beta_{23} = 0$ for oxygen.

** An equivalent isotropic temperature factor defined by HAMILTON (1959).

Table 6. *Thermal-ellipsoid data*
(those of high quartz in parentheses)

Atom	Principal thermal axes	Root-mean-square displacement	Angle between principal thermal axis and the following coordinate axis		
			a	*b**	*c*
Si,Al	1	.0526 ± .0108 Å (.1244 ± .0023)	90.0 ± .0° (90.0 ± 1.7)	90.0 ± .0° (90.0 ± .0)	0.0 ± .0° (0.0 ± 1.1)
	2	.0539 ± .0106 (.1345 ± .0035)	90.0 ± .0 (90.0 ± 2.9)	180.0 ± .0 (180.0 ± 1.6)	90.0 ± .0 (90.0 ± .0)
	3	.0695 ± .0091 (.1699 ± .0033)	0.0 ± .0 (0.0 ± 3.3)	90.0 ± .0 (90.0 ± 2.9)	90.0 ± .0 (90.0 ± 1.7)
O	1	.0957 ± .0139 (.1317 ± .0080)	34.1 ± 4.0 (47.1 ± 1.7)	90.0 ± .0 (111.5 ± 4.0)	55.9 ± 4.0 (50.6 ± 3.0)
	2	.1394 ± .0103 (.2294 ± .0076)	90.0 ± .0 (90.0 ± 6.3)	180.0 ± .0 (150.0 ± 6.1)	90.0 ± .0 (120.0 ± 6.1)
	3	.1918 ± .0083 (.2851 ± .0072)	55.9 ± 4.0 (42.9 ± 1.7)	90.0 ± .0 (70.1 ± 7.1)	145.9 ± 4.0 (126.1 ± 4.9)
Li	1	.0521 ± .2720	0.0 ± 0.0	90.0 ± .0	90.0 ± .0
	2	.1034 ± .1454	90.0 ± .0	180.0 ± .0	90.0 ± .0
	3	.2778 ± .0588	90.0 ± .0	90.0 ± .0	180.0 ± .0

* Indicates reciprocal-lattice direction.

Table 7. *Observed and calculated structure factors*

hkl	F_o	$3.382\|F_c\|$	A_c	B_c
003	45.35	46.44	13.73	0
006	292.76	304.25	89.95	0
010	190.52	178.58	-52.79	0
012	94.63	87.64	25.91	0
013	80.71	67.81	-20.05	0
014	139.66	128.99	38.13	0
015	219.46	217.92	64.42	0
016	72.21	74.58	-22.05	0
020	225.71	218.17	64.50	0
021	180.44	164.27	-48.56	0
022	139.80	123.30	36.45	0
023	388.39	407.82	120.56	0
024	78.31	74.69	22.08	0
025	39.84	41.33	-12.22	0
026	160.58	163.13	48.23	0
030	212.67	201.61	-59.60	0
031	149.54	138.79	41.03	0
032	266.37	258.36	76.38	0
033	14.17	0.28	0.08	0
034	192.15	182.18	53.86	0
035	95.28	100.87	29.82	0
040	266.25	284.43	84.09	0
041	66.01	61.70	18.24	0
042	38.72	37.76	-11.16	0
043	222.99	218.02	64.45	0
044	48.96	44.71	-13.22	0
050	47.97	50.24	14.85	0
051	138.36	137.30	40.59	0
052	126.32	124.38	36.77	0
110	205.61	179.11	-52.95	0
111	14.17	1.73	- 0.26	0.44
112	391.11	418.46	-61.85	-107.13
113	57.27	52.70	-15.58	0
114	279.98	283.68	-41.93	72.63
115	97.48	92.88	-13.73	-23.78
116	78.62	76.36	-22.57	0
120	91.92	80.02	23.66	0
121	259.15	243.51	-49.78	-52.01
122	208.63	199.46	-16.66	56.56
123	192.15	184.15	-54.26	4.38
124	154.18	150.43	-15.40	-41.72
125	147.84	143.64	-26.35	33.30
130	136.90	129.28	-38.22	0
131	255.12	256.76	-10.08	75.23
132	162.60	156.23	-42.55	-17.95
133	46.45	37.06	-10.88	1.33
134	122.51	120.15	-29.45	19.85
135	144.34	155.07	- 9.44	-44.86
140	75.07	67.60	-19.98	0
141	144.66	147.59	-33.65	-27.77
142	158.46	151.30	-11.83	43.14
143	58.41	57.42	-16.52	- 3.92
150	54.13	70.17	-20.74	0
220	374.17	385.14	113.86	0
221	56.58	56.57	8.36	-14.48
222	56.33	57.83	- 8.55	-14.81
223	193.74	195.04	57.66	0
224	23.68	24.53	- 3.63	6.28
225	32.61	34.81	5.15	8.91
230	129.23	123.39	-36.48	0
231	176.93	171.55	48.71	-14.11
232	133.76	135.43	38.30	-11.67
233	21.26	17.45	- 5.03	1.16
234	124.71	131.23	37.16	11.13
240	177.92	182.30	53.89	0
241	50.78	51.83	-15.26	1.42
242	46.63	51.15	14.81	3.06
330	14.17	14.67	4.34	0
331	107.67	111.38	-16.46	28.52
332	127.67	133.27	-19.70	-34.12

It is interesting to compare the intensity data and the precisions of the structures of $LiAlSi_2O_6$ III and II. For $LiAlSi_2O_6$ III, the number of independent intensities measured is 87.7% of the total number of independent reflections, the number of reflections per parameter at the final anisotropic refinement is 6.4, and the R value is 5.1%. These values match closely the corresponding values of 86.8%, 6.7 and 6.2% in $LiAlSi_2O_6$ II. It is strongly suspected that this 1% gain in R value, and especially the impressive improvement of the standard deviations of the bond distances and angles of $LiAlSi_2O_6$ III over II, is due to the secondary-extinction correction which is the only difference in data correction for the two compounds.

The final positional parameters for all atoms, together with those for high quartz, are listed in Table 3. The final isotropic temperature factors and the atom parameters at the end of isotropic refinement are listed in Table 4. The individual anisotropic temperature factors are listed in Table 5. The thermal-ellipsoid data are listed in Table 6 and the observed and calculated structure factors are listed in Table 7.

Discussion of the structure

The bond distances, angles and their standard deviations were computed with BUSING, MARTIN and LEVY's "Function and error program" (1964). The results are listed in Tables 8 and 9. The projections of the structure on (001) and (100) are shown in Figs. 1 and 2.

The Si,Al tetrahedra

The structure consists of a three-dimensional aluminosilicate framework. The distribution of Si and Al in the tetrahedra is completely random. There is only one symmetry-independent Si,Al tetrahedron.

Table 8. *Interatomic distances in* $LiAlSi_2O_6$ III

Atom pair	Distance	Standard deviation	Atom pair	Distance	Standard deviation
(*a*) Si,Al tetrahedron			(*b*) Lithium tetrahedron		
Si,Al—O(1)$_2$	1.641 Å	.001 Å	Li—O(1)$_2$	2.068 Å	.005 Å
Si,Al—O(1)$_3$	1.641	.001	Li—O(1)$_3$	2.068	.005
Si,Al—O(1)$_5$	1.641	.001	Li—O(1)$_5$	2.068	.005
Si,Al—O(1)$_6$	1.641	.001	Li—O(1)$_6$	2.068	.005
O(1)$_2$—O(1)$_3$	2.706	.008	O(1)$_2$—O(1)$_3$	3.696	.009
O(1)$_2$—O(1)$_5$	2.730	.004	O(1)$_2$—O(1)$_5$	3.713	.012
O(1)$_2$—O(1)$_6$	*2.601*	.004	O(1)$_2$—O(1)$_6$	*2.601*	.004
O(1)$_3$—O(1)$_5$	*2.601*	.004	O(1)$_3$—O(1)$_5$	*2.601*	.004
O(1)$_3$—O(1)$_6$	2.730	.004	O(1)$_3$—O(1)$_6$	3.713	.012
O(1)$_5$—O(1)$_6$	2.706	.008	O(1)$_5$—O(1)$_6$	3.696	.009
(*c*) Miscellaneous distances					
Si,Al(1)$_1$—Si,Al(1)$_2$	3.181 Å	.001 Å	Si,Al—Li(1)$_2$	3.181 Å	.001 Å
Si,Al(1)$_1$—Si,Al(1)$_3$	4.871	.001	Li(1)$_1$—Li(1)$_2$	3.642	.001
Si,Al—Li(1)$_1$	2.609	.001	Li(1)$_1$—Li(1)$_3$	5.464	.002

Table 9. *Interatomic angles in* $LiAlSi_2O_6$ III

Atoms	Angle	Standard deviation
(*a*) Si,Al tetrahedron		
O(1)$_2$—Si,Al—O(1)$_3$	111.1°	.3°
O(1)$_2$—Si,Al—O(1)$_5$	112.6	.1
O(1)$_2$—Si,Al—O(1)$_6$	104.9	.4
O(1)$_3$—Si,Al—O(1)$_5$	104.9	.4
O(1)$_3$—Si,Al—O(1)$_6$	112.6	.1
O(1)$_5$—Si,Al—O(1)$_6$	111.1	.3
(*b*) Lithium tetrahedron		
O(1)$_2$—Li—O(1)$_3$	126.65°	.04°
O(1)$_2$—Li—O(1)$_5$	127.7	.1
O(1)$_2$—Li—O(1)$_6$	77.9	.1
O(1)$_3$—Li—O(1)$_5$	77.9	.1
O(1)$_3$—Li—O(1)$_6$	127.7	.1
O(1)$_5$—Li—O(1)$_6$	126.65	.04
(*c*) Rhombus formed by edge-sharing between Si,Al and lithium tetrahedron		
O(1)$_3$—Si,Al—O(1)$_5$	104.9°	.4°
O(1)$_3$—Li—O(1)$_5$	77.9	.1
Si,Al—O(1)$_3$—Li	88.6	.2
Si,Al—O(1)$_5$—Li	88.6	.2
(*d*) Miscellaneous angles		
Si,Al(1)$_1$—O—Si,Al(1)$_2$	151.6°	.4°

The Si,Al tetrahedron is very similar to those in $LiAlSi_2O_6$ II (Li and Peacor, 1967), as seen by the comparison in Table 10. The Si,Al—O bond distance is 1.641 ± 0.001 Å. This value is in good agreement with that of 1.643 ± 0.006 Å which is the average Si,Al—O distance for $LiAlSi_2O_6$ II. According to Smith and Bailey (1963), however, the average Si,Al—O bond distance with complete disorder of Si and Al and one third of Al is about 1.655 Å. This discrepancy may be attributed to the edge sharing between Si,Al and Li tetrahedra which is the case for both $LiAlSi_2O_6$ III and II but is very rare for natural aluminosilicate structures.

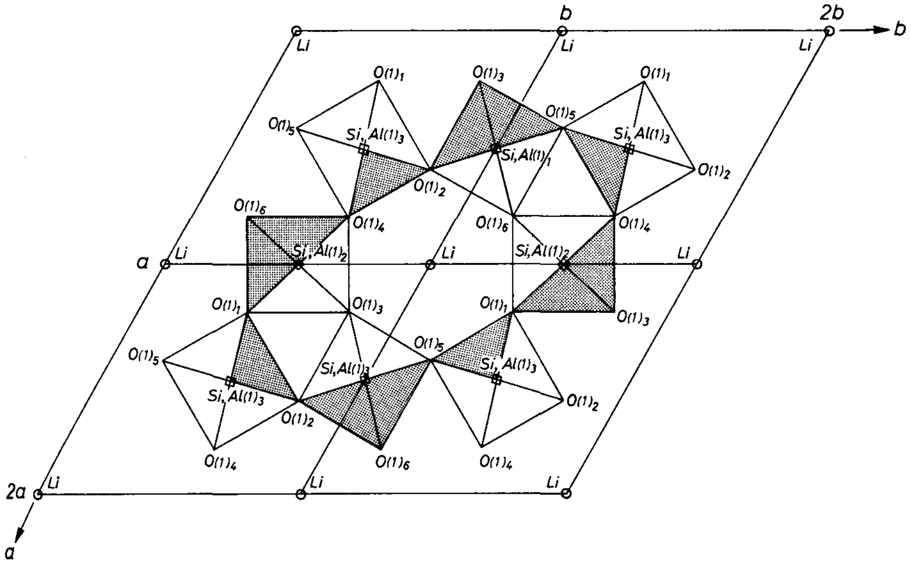

Fig. 1. The projection of $LiAlSi_2O_6$ III on (001)

The Si,Al tetrahedra form interconnecting 6- and 8-membered rings. The channels created by 6-membered rings are parallel to the three crystallographic axes. The neighboring 6-membered rings share one or no common tetrahedron. Wherever the two neighboring 6-membered rings do not share any common tetrahedron, eight out of the twelve Si,Al tetrahedra form an 8-membered ring. At the center of this 8-membered ring there is a channel parallel to the *c* axis which is occupied by the lithium atoms. For every 6-membered ring, the 6 Si,Al tetrahedra are arranged in a double-helical fashion. A large cavity which has 6-fold coordination with oxygen is formed within each ring. The details of the geometry of this distorted octa-

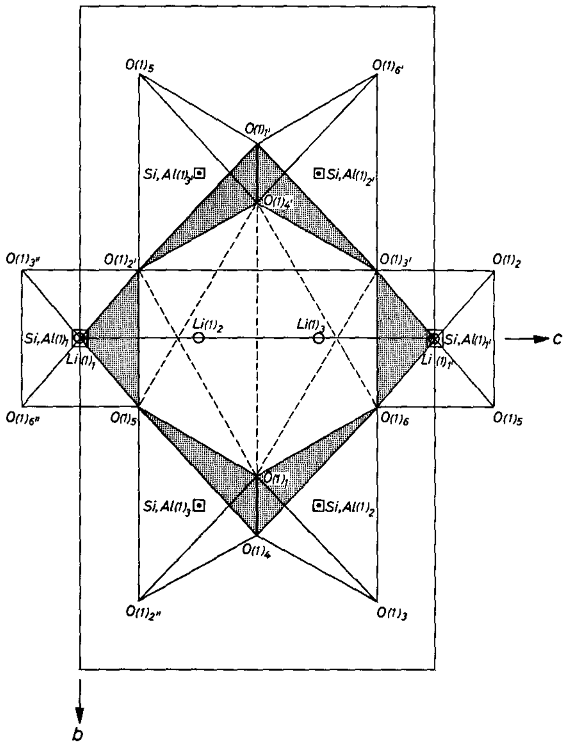

Fig. 2. The projection of $LiAlSi_2O_6$ III on (100)

hedron are listed in Table 11. The average distance from the center of the cavity to the six nearby oxygen atoms is 2.40 Å, with a range from 2.28 to 2.66 Å.

Lithium coordination

The structure is a stuffed derivative of the high-quartz structure. Lithium atoms are stuffed in interstitial positions and occupy equipoints of rank 3. There is only one lithium atom per unit cell. As mentioned earlier, Si and Al atoms are completely disordered. Thus, in order to maintain the charge balance, the distribution of this one lithium over three equivalent sites of the 3-fold positions must be completely random. The distances among the three equivalent lithium sites, i.e., 000, $00\frac{1}{3}$, and $00\frac{2}{3}$ are 1.821 ± 0.001 and 3.642 ± 0.001 Å. The value of 1.821 Å is too short for a lithium-lithium distance. Hence, all the actual lithium-lithium distances are 3.642 Å or longer.

Table 10. *A comparison of bond distances and angles for high quartz,* **$LiAlSi_2O_6$ III** *and* **$LiAlSi_2O_6$ II**

	$LiAlSi_2O_6$ III	$LiAlSi_2O_6$ II		high quartz
Tetrahedron		No. 1	No. 2	(YOUNG, 1962)
T—O				
average	1.641 ± .001 Å	1.647 ± .006 Å	1.640 ± .006 Å	1.594 ± .006 Å
range	1.641 to 1.641	1.633 to 1.665	1.637 to 1.643	1.594 to 1.594
O—T—O				
average	109.5 ± .3°	109.4 ± .3°	109.5 ± .4°	109.4 ± .5°
range	104.9 to 112.6	100.9 to 112.6	103.4 to 114.0	106.8 to 111.5
O—O				
average	2.679 ± .005 Å	2.686 ± .008 Å	2.677 ± .009 Å	2.603 ± .010 Å
range	2.601 to 2.730	2.552 to 2.728	2.574 to 2.746	2.559 to 2.634
sharing edge	2.601 ± .004	2.522 ± .008	2.574 ± .008	
Li—T	2.609 ± .001	2.628 ± .037	2.710 ± .040	
Lithium tetrahedron				
Li—O				
average	2.068 ± .005 Å	2.081 ± .041 Å		
range	2.068 to 2.068	1.933 to 2.269		
O—Li—O				
average	110.8 ± .1°	110.5 ± 1.9°		
range	77.9 to 127.7	74.1 to 139.4		
O—O				
average	3.337 ± .008 Å	3.339 ± .009 Å		
range	2.601 to 3.696	2.552 to 3.843		
sharing edge	2.601 ± .004	2.628 ± .037, 2.710 ± .040		
T—O—T				
average	151.6 ± .4°	149.4 ± .5°		152.8 ± .5°
range	151.6 to 151.6	143.6 to 154.0		152.8 to 152.8

Table 11. *Distances and angles in irregular octahedron for a large cavity*

Atoms	Distances and angles	Atoms	Distances and angles
X—O (X is at the center of the cavity)		O—X—O (90°)	
X—O(1)$_1$	2.661 Å	O(1)$_1$—X—O(1)$_2$	65.9°
X—O(1)$_2$	2.276	O(1)$_1$—X—O(1)$_3$	65.9
X—O(1)$_3$	2.276	O(1)$_1$—X—O(1)$_5$	114.1
X—O(1)$_4$	2.661	O(1)$_1$—X—O(1)$_6$	114.1
X—O(1)$_5$	2.276	O(1)$_2$—X—O(1)$_4$	114.1
X—O(1)$_6$	2.276	O(1)$_2$—X—O(1)$_5$	73.7
average	2.404	O(1)$_2$—X—O(1)$_6$	127.9
		O(1)$_3$—X—O(1)$_4$	114.1
O—O (same length for regular octahedron)		O(1)$_3$—X—O(1)$_5$	127.9
		O(1)$_3$—X—O(1)$_6$	73.7
O(1)$_1$—O(1)$_2$	2.706 Å	O(1)$_4$—X—O(1)$_5$	65.9
O(1)$_1$—O(1)$_3$	2.706	O(1)$_4$—X—O(1)$_6$	65.9
O(1)$_1$—O(1)$_5$	4.148		
O(1)$_1$—O(1)$_6$	4.148	O—X—O (180°)	
O(1)$_4$—O(1)$_2$	4.148	O(1)$_1$—X—O(1)$_4$	180.0°
O(1)$_4$—O(1)$_3$	4.148	O(1)$_2$—X—O(1)$_3$	131.9
O(1)$_4$—O(1)$_5$	2.706	O(1)$_5$—X—O(1)$_6$	131.9
O(1)$_4$—O(1)$_6$	2.706		

The lithium tetrahedron is irregular. The Li—O bond distance is 2.068 ± 0.005 Å. The O—Li—O tetrahedral angles range from 77.9° to 127.8° with an average of 110.8 ± 0.1°. These values agree very well with those of $LiAlSi_2O_6$ II (LI and PEACOR, 1968). A comparison of lithium tetrahedra between $LiAlSi_2O_6$ III and II is also listed in Table 10. Each Li tetrahedron shares two edges with two Si,Al tetrahedra. Statistically, each Si,Al tetrahedron shares two edges with two one third Li tetrahedra, or there is a two thirds possibility for each Si,Al tetrahedron sharing an edge with one Li tetrahedron. As would be expected from PAULING's rule (1960), the shared edge, 2.601 ± 0.004 Å, is the shortest for both the Li and Si,Al tetrahedra, as shown in italics in Table 8. The corresponding O—O distance in the Si tetrahedron of high quartz (YOUNG, 1962) is also the shortest, as seen by the comparison in Table 14. This may indicate that a favorable condition for edge sharing exists in high-quartz structure. According to PAULING, this edge shortening indicates that the structure has appreciable ionic character. This seems to support the assumption made earlier that the structure is half ionic and half covalent. A comparison of $LiAlSi_2O_6$ III with five other lithium compounds whose structures are also accurately determined, is listed in Table 15. Included in this table are $LiAlSi_2O_6$ II (LI and PEACOR, 1968) and γ $LiAlO_2$ (MAREZIO, 1965). They represent the only two lithium compounds so far reported in literature having Li tetrahedra sharing edges with other cation tetrahedra. Among these three Li compounds, i.e., $LiAlSi_2O_6$ III, $LiAlSi_2O_6$ II, and γ $LiAlO_2$, $LiAlSi_2O_6$ III has the shortest Si,Al—Li distance, 2.609 ± 0.001 Å. As can be seen in Table 15, this distance is close to the unusually short B—Li distance of 2.601 Å reported in $LiBO_2$ (ZACHARIASEN, 1964) where Li is 5-coordinated and the Li polyhedra share edges with trigonally coordinated boron. Since the ionic radius of Si,Al is much larger than that of B, the repulsion between Si,Al and Li would be greater than that existing between B and Li. It is this strong repulsive force existing between Si,Al and Li that may be responsible for the high-temperature transformation from $LiAlSi_2O_6$ III to II. After the transformation, the Si,Al—Li distance increases from 2.609 to 2.625 and 2.710 Å, while the magnitude of shared edge decreases from 2.601 to 2.552 and

Table 12

Distances and angles in 4-membered rings formed by Li *and* Si,Al *tetrahedra*

Atoms	Distances and angles
(*a*) Li and Si,Al rhombus (exactly coplanar)	
Li—Si,Al(1)$_1$	3.181 Å
Li—Si,Al(1)$_3$	3.181
Si,Al(1)$_3$—Si,Al(1)$_2$	3.181
Si,Al(1)$_2$—Si,Al(1)$_1$	3.181
Si,Al(1)$_1$—Si,Al(1)$_2$—Si,Al(1)$_3$	89.5°
Si,Al(1)$_2$—Si,Al(1)$_3$—Li	90.5
Si,Al(1)$_3$—Li—Si,Al(1)$_1$	89.5
Li—Si,Al(1)$_1$—Si,Al(1)$_2$	90.5
(*b*) Pentagon formed by Li and the bridging oxygen atoms (almost coplanar)	
O(1)$_1$—O(1)$_3$	2.705 Å
O(1)$_3$—O(1)$_6$	2.730
O(1)$_6$—Li	2.068
Li—O(1)$_4$	2.068
O(1)$_4$—O(1)$_1$	2.730
O(1)$_1$—O(1)$_3$—O(1)$_6$	99.5°
O(1)$_3$—O(1)$_6$—Li	105.3
O(1)$_6$—Li—O(1)$_4$	126.6
Li—O(1)$_4$—O(1)$_1$	105.3
O(1)$_4$—O(1)$_1$—O(1)$_3$	99.5

Table 13. *Additional tetrahedral sites for lithium in 6-fold positions*

	$6h$, $x0\frac{1}{2}$ $x = .1415$	$6e$, $00j$ $j = .3649$	$3a$, 000
Li—O	2.223 Å	2.151 Å	2.068 Å
	2.000	2.000	
average	2.111	2.075	2.068
O—O	4.090 Å		
	3.717	3.717 (2) Å	3.714 (2) Å
	3.699 (2)	3.699 (2)	3.696 (2)
	2.602 (2)	2.602 (2)	2.601 (2)
average	3.402	3.339	3.337
O—Li—O	136.7°	136.7°	
	133.8	126.0 (2)	127.8° (2)
	122.2 (2)	119.5	126.6 (2)
	75.9 (2)	77.5 (2)	77.9 (2)
average	111.1	110.5	110.8
Si,Al—Li	3.311 Å	3.317 Å	
	3.179	3.181	3.181 Å
	2.501	2.641	2.609

Table 14. *A comparison of* Si,Al *tetrahedra for* $LiAlSi_2O_6$ III *and high quartz*

	$LiAlSi_2O_6$ III	high quartz
Si,Al—O(1)$_2$	1.641 Å	1.594 Å
Si,Al—O(1)$_3$	1.641	1.594
Si,Al—O(1)$_5$	1.641	1.594
Si,Al—O(1)$_6$	1.641	1.594
O(1)$_2$—(1)$_3$	2.706	2.615
O(1)$_2$—O(1)$_5$	2.730	2.635
O(1)$_2$—O(1)$_6$	*2.601*	*2.558*
O(1)$_3$—O(1)$_5$	*2.601*	*2.558*
O(1)$_3$—O(1)$_6$	2.730	2.635
O(1)$_5$—O(1)$_6$	2.706	2.615
O(1)$_2$—Si,Al—O(1)$_3$	111.1°	110.2°
O(1)$_2$—Si,Al—O(1)$_5$	112.6	111.5
O(1)$_2$—Si,Al—O(1)$_6$	104.9	106.7
O(1)$_3$—Si,Al—O(1)$_5$	104.9	106.7
O(1)$_3$—Si,Al—O(1)$_6$	112.6	111.5
O(1)$_5$—Si,Al—O(1)$_6$	111.1	110.2

2.574 Å. As will be discussed later, this strong repulsion existing between Si,Al and Li also plays an important role in controlling the thermal expansion. In reference to the Li—O distance, the Li compounds may be divided into two groups according to whether Li polyhedra share edges with other cation polyhedra, as can be seen by the comparison of six Li compounds in Table 15. In the first group where Li polyhedra share edges with other cation polyhedra, the Li—O distances are generally longer than the average value of 1.98 Å reported in the *International tables for x-ray crystallography*, Vol. III (1962). Included in this group are $LiAlSi_2O_6$ III, $LiAlSi_2O_6$ II, γ $LiAlO_2$ and $LiBO_2$ and the corresponding average Li—O distances are 2.068, 2.081, 2.003 and 2.068 Å. This lengthening of Li—O distance in this group may be attributed to the very short distance between Li and cation which is, in turn, due to the edge sharing between Li and cation polyhedra. The strong repulsive force operating between Li and cation tends to push the two oxygen atoms on the shared edge apart which may result in the increase of Li—O distance. For the second group, where Li polyhedra do not share edges with other cation polyhedra, the Li—O distances are shorter than those of first group. For example, the average Li—O distances in $Li_2SO_4 \cdot H_2O$ (LARSON, 1965) and $LiGaO_2$ (MAREZIO, 1965) are 1.947 and 1.985 Å respectively.

Table 15. *A comparison of some interesting aspects for several lithium compounds*

	$LiAlSi_2O_6$ III	$LiAlSi_2O_6$ II	γ $LiAlO_2$	$LiBO_2$	$Li_2SO_4 \cdot H_2O$	$LiGaO_2$
Li coordination	4	4	4	5	4	4
Li–O distance						
average	2.068 Å	2.081 Å	2.003 Å	2.068 Å	1.947 Å	1.985 Å
range	2.068 to 2.068	1.933 to 2.269	1.948 to 2.059	1.945 to 2.473	1.907 to 2.001	1.949 to 2.001
Cation coordination	4 Si,Al	4 Si,Al	4 Al	3 B	4 S	4 Ga
Edge sharing between Li and cation polyhedra	yes	yes	yes	yes	no	no
Length of shared edge	2.601 Å	2.552, 2.574 Å	2.737 Å	2.334 Å	—	—
Minimum Li cation distance	2.608	2.628, 2.710	2.656	2.601	2.974	3.057

It is noted that each Li tetrahedron forms two 4-membered rings with Si,Al tetrahedra. These two rings are symmetry equivalent. The details of the 4-membered ring are listed in Table 12. In each ring, lithium is exactly coplanar with the three Si,Al atoms and almost coplanar with the four bridging oxygen atoms. It seems that the forming of such 4-membered rings may help to stabilize the lithium position.

Two additional tetrahedral sites were found for lithium in 6-fold positions. One is in $6h$, $x0\frac{1}{2}$; $x = 0.1415$, and the other in $6e$, $00z$; $z = 0.3649$. The details of the lithium tetrahedron at these two sites, together with that at the present lithium site, are listed for comparison in Table 13. The 6-fold site in $6e$ is very close and similar to the present 3-fold lithium site in $3a$. Yet, both lithium sites in 6-fold positions, $6e$ and $6h$, were found to be less favorable because the lithium tetrahedra were more distorted and the Li—O distances were longer. The chemical composition of $LiAlSi_2O_6$ III may also be represented as $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ and its solid solution as $Li_2O \cdot Al_2O_3 \cdot nSiO_2$. As n decreased from 4 to 2, the number of lithium atoms per unit cell increases from 1 to 1.5. Based on the following reasons, it seems that lithium would occupy the $6h$ position when n is less than 4: (1) More lithium atoms have to be accommodated. (2) Evans (1964) reported a diagram of a and c vs. n. According to this diagram, a changes gradually with n, but c changes rapidly with n when n is less than 4, and slowly with n when n is greater than 4. This seems to indicate that for n less than 4, there is an empty space along the c axis so that the c axis may fluctuate more rapidly. If this is the case, lithium atoms would certainly be favored to occupy the $6h$ site.

Thermal-expansion behavior

$LiAlSi_2O_6$ III is known to have low thermal expansion. This behavior may be explained in terms of the repulsion existing between Si,Al and Li atoms. As mentioned earlier, each Li tetrahedron shares two edges with two Si,Al tetrahedra. All the four atoms involved in each edge sharing, i.e., Si,Al, the neighboring Li, and two edge-sharing oxygen atoms, were found to be exactly coplanar. The exceptionally short distance between Si,Al and Li, i.e., 2.609 Å, indicates the presence of a strong repulsive force between them. Upon heating, thermal energy is used to reduce the strong repulsive force by increasing the Si,Al—Li distance which, in turn, decreases the shared edge, and likely the Li—O distance. As mentioned earlier, the Li—O distance would be longer when Si,Al—Li becomes shorter. On the other hand, the Li—O distance may become shorter if the Si,Al—Li distance increases. In this structure, a and b axes are functions of the Si,Al—Li distance alone, i.e., $a = b = 2$ (Si,Al—Li), and the c axis is a function of shared edge and the Li—O distance as is illustrated in Fig. 3. Hence

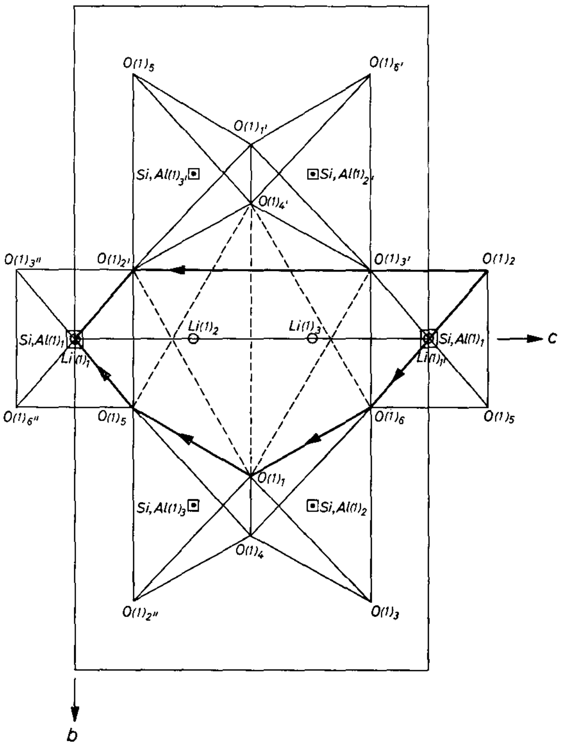

Fig. 3. Thermal expansion behavior of c axis.

$$\vec{c} = \overrightarrow{O(1)_2 - O(1)_2'} =$$

$$\overrightarrow{O(1)_2 - O(1)_6} + \overrightarrow{O(1)_6 - O(1)_1} + \overrightarrow{O(1)_1 - O(1)_5} + \overrightarrow{O(1)_5 - Li(1)_1} + \overrightarrow{Li(1)_1 - O(1)_2'}$$

where $O(1)_2 - O(1)_6$, $O(1)_6 - O(1)_1$, and $O(1)_1 - O(1)_5$ are shared edges

upon heating, the a and b axes may be expected to expand and the c axis may be expected to contract. As a result of this kind of anisotropic thermal expansion, the overall volume may remain almost unchanged. It is very likely that the bond lengths and angles within each Si,Al tetrahedron may change very little and the only significant changes may occur in the angles between the neighboring tetrahedra.

According to Winkler (1948), the high-temperature form of $LiAlSiO_4$ was also a stuffed derivative of high quartz. In this compound, Gillery and Bush (1959) found that upon heating, the *c* axis contracted and both *a* and *b* axes expanded up to 817 °C. This observation may provide some indirect evidence for the explanation just described.

A similar situation exists for $LiAlSi_2O_6$ II (Li and Peacor, 1968). Thus, the same explanation of the thermal-expansion behavior may also be used as an alternative one for $LiAlSi_2O_6$ II. In $LiAlSi_2O_6$ II the *a* and *b* axes are functions of the shared edge while the *c* axis is a function of the Si,Al—Li distance. Hence upon heating, the *a* and *b* axes contract and the *c* axis expands.

Density versus bond distance

It is also interesting to follow the change in density along with crystallization of the glass and the transformation from $LiAlSi_2O_6$ III to II. The $LiAlSi_2O_6$ glass has a density of 2.374 g/cm^3. As this structure is being crystallized from the glass, the density increases from 2.374 to 2.395 g/cm^3. This may indicate that the atoms start to rearrange in a much more regular and compact fashion. When $LiAlSi_2O_6$ III transforms into II, the density decreases from 2.395 to 2.365 g/cm^3. This is reflected in the general increase of the bond distances in $LiAlSi_2O_6$ II, e.g. Si,Al—O from 1.641 to 1.643 Å, Li—O from 2.068 to 2.081 Å, O—O from 2.679 to 2.682 Å for Si,Al tetrahedra and from 3.337 to 3.339 Å for Li tetrahedra, and Si,Al—Li from 2.609 to 2.628 and 2.710 Å. This difference in density between $LiAlSi_2O_6$ III and II may explain why high pressure is needed to transform $LiAlSi_2O_6$ II to III, as demonstrated by Munoz (1966). One way to prepare $LiAlSi_2O_6$II is by heating at high temperature the $LiAlSi_2O_6$ I (the mineral spodumene) which is known to have a density of 3.16 g/cm^3. From the density difference and the transformation between $LiAlSi_2O_6$ III and II, it is suspected that, under controlled heating, $LiAlSi_2O_6$ I will first transform into $LiAlSi_2O_6$ III and then transform into $LiAlSi_2O_6$ II.

Thermal ellipsoids

The thermal ellipsoid data were found to be very similar to those of high quartz. Values are listed for comparison in Table 6. It may be worthwhile to point out that the maximum and minimum vibration axes for all independent atoms are as follows: for Si,Al: along shortest

Si,Al—Li distance and the *c* axis; for Li: along the *c* axis and shortest Si,Al—Li direction; for oxygen: perpendicular to the Si,Al—O—Si,Al plane and along the Si,Al—Si,Al direction.

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