

The crystal structures and the phase transformation of Zn-Li silicates

SHU-CHENG YU¹, DEANE K. SMITH

Department of Geosciences, The Pennsylvania State University
University Park, Pennsylvania 16802

AND STANLEY B. AUSTERMAN

Electronic Operations, Rockwell International
Anaheim, California 92803

Abstract

The room-temperature form (α) of colorless transparent synthetic $\text{Zn}(\text{Zn}_{0.1}\text{Li}_{0.6}\text{Si}_{0.3})\text{SiO}_4$ has monoclinic symmetry with $a = 6.340(1)$, $b = 10.516(2)$, $c = 5.011(1)\text{Å}$, $\beta = 90.50(2)^\circ$, space group $P2_1/n$, and $Z = 4$. It transforms at about 400°C to a high-temperature form (β) which is orthorhombic with $a = 6.406(3)$, $b = 10.520(8)$, $c = 5.043(2)\text{Å}$, space group $Pmnb$, and $Z = 4$. The crystal structures for both forms were determined by 3-dimensional Patterson analysis from X-ray intensity data collected at room temperature and at 450°C . The structures were refined by the least-squares methods to a final weighted $R = 0.068$ (unweighted $R = 0.068$) and 0.064 (unweighted $R = 0.070$) for the room-temperature and the high-temperature form respectively.

The high-temperature structure is a tetrahedral framework structure with a sharing coefficient of 3. There are two different tetrahedral sites: T1, an 8-fold site, and T2, a 4-fold site. The T1 site contains all Zn and Li and some Si; the T2 site is all Si. The T1 tetrahedra form puckered layers parallel to (010) and are composed of corner-shared tetrahedral chains. These chains are parallel to [100]. Unlike pyroxenes, all tetrahedra lie on the same side of the chain axis. The layers stack in antiparallel arrangement and are cross-linked by the T2 tetrahedra to constitute the framework structure.

Below the transition temperature, the 8-fold T1 site splits into two symmetry-independent 4-fold positions T1(o) and T1(m) sites, and the symmetry degenerates from $Pmnb$ to $P2_1/n$. Zn atoms are completely ordered on T1(o). At the transition, Zn atoms may concentrate in either of the two T1 positions. This option results in a domain structure with the two related by reflection across (100). The order-disorder transformation also produces twin (α') structure which has monoclinic symmetry with space group $B2_1$ and $a = 13.01$, $b = 10.41$, $c = 10.07\text{Å}$, and $\beta \approx 90^\circ$.

Introduction

During exploratory studies of willemite crystal growth from a polymolybdate flux with methods previously developed for BeO (Austerman, 1964), a new non-hexagonal crystal form was obtained. The crystal-growth experiments were made with Li_2MoO_4 - MoO_3 as the flux composition, over the range of 10 percent to 35 percent MoO_3 by weight, at temper-

atures between 900° and 1100°C . At all flux compositions with greater than 20 ± 1 percent MoO_3 , willemite invariably formed. However, with the MoO_3 component ≤ 20 percent, only the new type of crystal, with good crystal faces, was grown. The flux composition boundary between the willemite and the new structure regions was found to be independent of temperature within a range of ± 1 percent MoO_3 . In some experiments Mn was added in small amounts, but this Mn did not appear to influence the formation of the new type of crystal.

The preliminary electron microprobe chemical

¹ Present address: Laboratory for High Pressure Science, Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742.

Table 1. Space groups and unit-cell constants of Zn-Li silicates at different temperatures

Space Group	Second room temp. phase (α)*	Room temp. form (α)*	High temp. form (β)*
	$B2_1$	$P2_1/n$	$Pmnb$
a(A)	13.01	6.340(1)**	6.406(3)**
b(A)	10.41	10.516(2)**	10.520(8)**
c(A)	10.07	5.011(1)**	5.043(2)**
β (°)	≈ 90	90.50(2)**	

* α is an ordered structure; β is a disordered structure; second room temperature phase is a twinned form of α .
 ** Refined by 12 reflections on Picker automated single crystal diffractometer.

analyses² suggested that a previously unknown crystal of composition $ZnSiO_3$ had been grown. A search of the pertinent literature on powder patterns and unit-cell data yielded no match with any known structure.

Because of the apparent pyroxene-like composition, a detailed structure analysis was initiated to determine whether or not this compound did indeed have a pyroxene-like structure.

Experimental studies

Crystal morphology and phase transition

Crystals of this synthetic Zn-Li silicate are transparent and colorless. From the X-ray and interfacial angle data, a preliminary evaluation of lattice parameters was made. The crystal appears to be orthorhombic with $a = 12.77$, $b = 10.45$, $c = 10.05A$.

Petrographic observations indicate that the sample contains fine lamellae, about $2 \mu m$ thick, oriented in two perpendicular directions. Since the lamellae might be an exsolved second phase, experiments were performed under a petrographic microscope with a heating stage. Very thin (010) tabular crystals, about $75 \mu m$ thick, were selected for examination because this is the best orientation to observe the lamellae. With increasing temperature, the lamellae became indistinct and gradually disappeared.

Preliminary X-ray precession photographs of the sample showed that there are two phases in the apparent single crystals. Heating experiments were also carried out on a Buerger precession camera, with a high-temperature heater of the design of Brown *et al.* (1973). The crystal was mounted on a pyrex-glass fiber with high-temperature quartz cement. The

sample was heated slowly at atmospheric pressure. Above $400^\circ C$ only one sharp diffraction pattern was observed. This pattern was orthorhombic with $a = 6.406(3)$, $b = 10.520(8)$, $c = 5.043(2)A$, with extinction conditions corresponding to space group $Pmnb$ or $P2_1nb$, and was designated as the high-temperature or β form. When the sample is cooled to room temperature, two phases reappear in the precession patterns, although intensities of one pattern are weaker than in the original patterns.

In the search for a single crystal of the room-temperature form, Zn-Li silicate samples were heated at $700^\circ C$ and atmospheric pressure for about 100 hours in a 75Ag-25Pd container. All samples, whether slowly cooled or quenched to room temperature, still contained observable lamellae. One crystal containing a large region with no visible lamellae under the polarizing microscope was successfully cut into a single-crystal fragment measuring $125 \times 30 \times 30 \mu m$. X-ray precession photographs of this fragment indicate that this crystal was indeed single with monoclinic symmetry and $a = 6.340(1)$, $b = 10.516(2)$, $c = 5.011(1)A$, $\beta = 90.50(2)^\circ$, space group $P2_1/n$. The lattice was pseudo-orthorhombic. This phase was designated as the room-temperature or α form. Subtracting the α phase from the precession patterns with two phases, the space group and the unit-cell constants of the second phase were determined to be $B2_1$ and $a = 13.01$, $b = 10.41$, $c = 10.07A$, $\beta \approx 90^\circ$, as listed in Table 1. This cell is close to the one determined morphologically.

Table 2 gives the powder pattern, taken at room temperature, of unheated powder samples, which could only be indexed on the basis of the lattice parameters of the α form. Hayashi *et al.* (1965) reported the formation of two forms of $ZnSiO_3$ at high pressure (42 kbar) and high temperature (600° and

Table 2. X-ray powder pattern for the synthetic Zn-Li silicate

d(obs)	d(calc)*	hkl*	I/I ₀
5.45 A	5.43 A	(110)	10
4.23	4.52	(011)	10
4.07	4.05	(120)	50
3.97	3.92	(101)	20
3.09	3.07	(130)	40
2.711	2.715	(220)	30
2.658	2.629	(040)	30
2.632	2.611	(131)	30
2.521	2.506	(002)	100
2.452	2.437	(012)	30
1.6282	1.6118	(103)	20
1.5429	1.5338	(260)	40
1.5179	1.5175	(420)	25
1.3720	1.3721	(342)	25

* Based on the unit cell parameters of the room temperature form.

² Atomics International, Autonetics Divisions of Rockwell International and the National Bureau of Standards.

900°C). The diffraction pattern of neither form matches the one given in Table 2. Syono *et al.* (1971) gave data for five forms of Zn_2SiO_4 and two forms of $ZnSiO_3$ whose patterns also did not match this compound.

A density of 3.53 g/cm³ was measured at room temperature with a Berman microbalance (calibrated with a quartz standard) and toluene as the immersion liquid. Based on this observed density and the assumed stoichiometric composition of $ZnSiO_3$, the calculated Z value was 5.01. Because the density measurement is relatively reliable (it is reproducible with less than 3 percent uncertainty), the deviation of the Z from a more plausible value of 4 suggested an incorrect chemical composition. Consequently, the composition was redetermined by electron microprobe analysis conducted by John Hunt at the Mineral Constitution Laboratory of The Pennsylvania State University. Wavelength scans were carried out before the detailed quantitative measurements were made. The result was essentially the same as the preliminary analyses except that we found less than 2 percent (by weight) Mn in the crystal. No detectable Mo was found. However, the total composition was only 93 percent. Emission spectroscopic analysis for Li was then performed at the same laboratory by Professor Norman H. Suhr, and 10 percent Li (by weight) was detected. Because of much higher uncertainty in Li analysis and more reliable electron microprobe result, 7 percent Li (by weight) was assigned to the compound in order to bring total chemical composition to 100 percent. Accordingly, the structure formula was calculated to be $Zn(Zn_{0.1}Li_{0.6}Si_{0.3})SiO_4$.

X-ray intensity data collection

The single-crystal α form isolated during the heating experiments was mounted for X-ray intensity measurement on a Picker FACS-1 computer-controlled four-circle diffractometer using Zr-filtered Mo radiation. There were 1198 observed reflections in two octants of reciprocal space, which were collected to $\sin \theta/\lambda = 1.28$ employing 2θ scans. The observed intensities were corrected for Lorentz, polarization, and absorption ($\mu = 85.47 \text{ cm}^{-1}$) effects using the ACAC program written by C. T. Prewitt (see Wuensch and Prewitt, 1965). The intensity-data collection for the β form was carried out at 450°C in the same way as that for the α form. The sample was ground into a sphere of 150 μm in diameter, and 667 reflections in one octant of the reciprocal space to $\sin \theta/\lambda = 1.28$ were measured. Table 3 gives the summary of crystal-structure data.

Table 3. Summary of crystal-structure data

	Room temperature	At 450°C
Structural formula	$Zn(Zn_{0.1}Li_{0.6}Si_{0.3})SiO_4$	$(Zn_{1.1}Li_{0.6}Si_{0.3})SiO_4$
Space group	$P2_1/n$	Pmnb
Size of crystal (mm)	0.12x0.03x0.03	0.15 (diameter)
Measured density (g/cm ³)	3.53	----
Calculated density (g/cm ³)	3.51	3.45
Number of formula unit Z	4	4
Linear absorption coefficient for MoK α (cm ⁻¹)	85.47	84.01
Residual factors R^*	0.068	0.070
$R(\text{wtd})^*$	0.068	0.064

$$* R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad R(\text{wtd}) = \left(\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right)^{1/2} \text{ and unit weight assumed}$$

Structure determinations and refinements

The α form

The structure was solved by analyzing a three-dimensional Patterson map which revealed the Zn atoms. Silicon and oxygen atoms were located by subsequent Fourier syntheses with phases determined by the Zn atoms. The peak in the Fourier map with an electron density lower than that of Zn but higher than that of Si was assigned to be occupied by a mixture of $Zn_{0.1}Li_{0.6}Si_{0.3}$. This selection resulted in an unambiguous resolution of the full structure. Full-matrix, least-squares refinements were carried out with the use of a modified ORFLS program (Busing *et al.*, 1962) and scattering factors of Zn^{2+} , Si^{4+} from Cromer and Mann (1968) and O^{2-} from Suzuki (1960). After three cycles the residual factors, $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, dropped to 0.075 with anisotropic temperature factors for 1198 independent reflections. Six reflections apparently affected by extinction were deleted from the least-squares calculations in the further refinements, which gave $R = 0.068$. Anomalous dispersion corrections for Zn and Si from Cromer (1965) were included in the last refinement; they did not improve the R factor significantly.

The β form

In view of the close resemblance in their diffraction patterns, unit-cell parameters, and the intensities of the corresponding reflections on their precession photographs between the high-temperature form and the

Table 4a. Final atomic positional parameters for the synthetic Zn-Li silicates*

Room temperature	Site	X	Y	Z	B(eq)**
T1(o) (Zn)	4e	0.0015(1)	0.1630(1)	0.1882(1)	0.80
T1(m) (ZnLiSi)	4e	0.5031(11)	0.1553(7)	0.1797(13)	1.45
T2(Si)	4e	0.2524(2)	0.4112(1)	0.1852(3)	0.67
O1	4e	0.2544(6)	0.4050(4)	-0.1381(7)	0.76
O2	4e	0.2523(7)	0.0568(4)	0.2117(9)	1.18
O3(o)	4e	0.0449(7)	0.3396(4)	0.2948(8)	1.09
O3(m)	4e	0.4637(7)	0.3395(4)	0.2949(8)	1.32
At 450°C					
T1 (ZnLiSi)	8d	0.0004(2)	0.1607(1)	0.1860(2)	1.66
T2(Si)	4c	0.25	0.4107(2)	0.1834(4)	0.92
O1	4c	0.25	0.4021(5)	-0.1374(10)	1.53
O2	4c	0.25	0.0575(5)	0.2201(15)	2.30
O3	8d	0.04337(7)	0.3406(4)	0.2954(8)	2.02

* Parenthesized figures represent the estimated standard deviation in terms of least units cited for the value to their immediate left.

** B(eq)=equivalent isotropic temperature factor computed from anisotropic temperature factors, β_{ij} , according to B(eq)= $4/3\sum\beta_{ij}a_ia_j$ (Hamilton, 1965).

low-temperature form, one would speculate that their crystal structures would be similar if not identical. Both possible space groups, $Pmnb$ or $P2_1nb$, of the β form require that the T1(o) and T1(m) 4-fold independent sites in space group $P2_1/n$ of the room-temperature form become a symmetry-related equivalent 8-fold site T1. This symmetry condition requires all Zn and Li and some Si to be randomly distributed on the T1 site in the β form. With this occupancy for T1, and with the Si and oxygen atomic coordinates from the low-temperature form as the initial values, full-matrix least-squares refinement with anisotropic temperature factors and $Pmnb$ space group led to weighted R factor, $R_{wtd} = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2} = 0.068$ for the high-temperature form. In the later stage of least-squares refinement, 14 reflections with intensity below the minimum observed level and 2 reflections, (200) and (400), apparently subject to extinction were omitted from the calculations. The final weighted R factor was 0.064 (unweighted $R = 0.070$) for 651 independent reflections. Throughout the entire refinement process, unit weights for all reflections were assumed. The structure refinement verified the space group $Pmnb$. The atomic positional parameters with anisotropic temperature factors are listed in Table 4a and 4b. Bond lengths and bond angles for both the α form and the β form are listed in

Table 5a and 5b. Calculated and observed structure factors are given in Table 6a and 6b.³

Discussion

Structure descriptions

Both forms have a framework structure. In the β form there are two different tetrahedral sites. T1 is an 8-fold site containing $Zn_{1.1}Li_{0.6}Si_{0.3}$ while T2 is a 4-fold site containing only Si. Each oxygen atom is shared by two T1 tetrahedra and one T2 tetrahedron. The T1 tetrahedra are all corner-shared to form puckered layers parallel to (010). Within the layer one can identify a distinct chain linkage with one tetrahedral edge forming the chain axis. Unlike the

³ To obtain a copy of this table, order document AM-78-081 from the Business Office, Mineralogical Society of America, LL1000, 1909 K Street, N.W., Washington, D. C. 20006. Please remit \$1.00 in advance for the microfiche.

Table 4b. Atomic anisotropic temperature factors in the expression $\exp(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}2hk + \beta_{23}2kl + \beta_{13}2hl)^*$

Room temperature		At 450°C	
T1(o) (Zn)		T1 (ZnLiSi)	
β_{11}	0.0056(1)	β_{11}	0.0097(3)
β_{22}	0.0018(1)	β_{22}	0.0035(1)
β_{33}	0.0060(2)	β_{33}	0.0162(4)
β_{12}	-0.0002(1)	β_{12}	-0.0002(1)
β_{13}	0.0008(1)	β_{13}	0.0010(3)
β_{23}	-0.0001(1)	β_{23}	0.0001(1)
T1(m) (ZnLiSi)			
β_{11}	0.0105(14)		
β_{22}	0.0027(6)		
β_{33}	0.0147(19)		
β_{12}	0.0001(7)		
β_{13}	-0.0003(13)		
β_{23}	0.0001(9)		
T2(Si)		T2(Si)	
β_{11}	0.0065(3)	β_{11}	0.0072(4)
β_{22}	0.0012(1)	β_{22}	0.0017(1)
β_{33}	0.0032(4)	β_{33}	0.0079(6)
β_{12}	-0.0001(1)	β_{12}	0.0
β_{13}	0.0004(3)	β_{13}	0.0
β_{23}	0.0002(2)	β_{23}	0.0002(2)
O1		O1	
β_{11}	0.0053(8)	β_{11}	0.0099(11)
β_{22}	0.0027(3)	β_{22}	0.0049(5)
β_{33}	0.0028(10)	β_{33}	0.0081(16)
β_{12}	-0.0004(40)	β_{12}	0.0
β_{13}	0.0003(7)	β_{13}	0.0
β_{23}	0.0000(4)	β_{23}	-0.0002(7)
O2		O2	
β_{11}	0.0085(9)	β_{11}	0.0088(11)
β_{22}	0.0015(3)	β_{22}	0.0022(4)
β_{33}	0.0131(15)	β_{33}	0.0389(30)
β_{12}	0.0003(4)	β_{12}	0.0
β_{13}	0.0003(9)	β_{13}	0.0
β_{23}	0.0003(5)	β_{23}	0.0039(9)
O3(o)		O3	
β_{11}	0.0097(9)	β_{11}	0.0154(10)
β_{22}	0.0020(3)	β_{22}	0.0038(3)
β_{33}	0.0070(13)	β_{33}	0.0175(14)
β_{12}	-0.0009(4)	β_{12}	-0.0026(5)
β_{13}	0.0021(9)	β_{13}	0.0043(10)
β_{23}	-0.0006(5)	β_{23}	-0.0012(5)
O3(m)			
β_{11}	0.0106(10)		
β_{22}	0.0025(3)		
β_{33}	0.0081(13)		
β_{12}	0.0017(5)		
β_{13}	-0.0005(9)		
β_{23}	-0.0001(5)		

*Parenthesized figures represent the estimated standard deviation refers to the last digit.

Table 5a. Interatomic distances for Zn-Li silicate at room temperature and 450°C*

Room temperature		At 450°C	
T1(o)(Zn)-O1	1.936(4)	T1(ZnLiSi)-O1	1.950(3)
T1(o)(Zn)-O2	1.946(4)	T1(ZnLiSi)-O2	1.940(3)
T1(o)(Zn)-O3(o)	1.951(4)	T1(ZnLiSi)-O3	1.990(4)
T1(o)(Zn)-O3(m)	1.984(4)	T1(ZnLiSi)-O3	1.990(4)
Mean of 4	1.954	Mean of 4	1.968
T1(m)(ZnLiSi)-O1	1.936(8)		
T1(m)(ZnLiSi)-O2	1.905(8)		
T1(m)(ZnLiSi)-O3(o)	1.950(8)		
T1(m)(ZnLiSi)-O3(m)	2.037(9)		
Mean of 4	1.957		
Mean of 8	1.956		
T2(Si)-O1	1.622(4)	T2(Si)-O1	1.620(5)
T2(Si)-O2	1.617(4)	T2(Si)-O2	1.618(5)
T2(Si)-O3(o)	1.616(5)	T2(Si)-O3	1.617(6)
T2(Si)-O3(m)	1.628(5)	T2(Si)-O3	1.617(5)
Mean of 4	1.621	Mean of 4	1.618

* Parenthesized figures represent the estimated standard deviation refers to the last digit.

pyroxene chain, all tetrahedra within a chain lie on the same side of the chain axis. The layers stack in antiparallel arrangement and are cross-linked by the T2 tetrahedra to constitute the three-dimensional framework structure shown in Figure 1.

Below the transition temperature, the 8-fold T1 site splits into two symmetry-independent 4-fold positions T1(o) and T1(m) sites, and the symmetry degenerates from $Pmnb$ to $P2_1/n$. Zn atoms completely fill T1(o) site and $Zn_{0.1}Li_{0.8}Si_{0.3}$ occupy T1(m). In both Zn-Li silicate structures and in pyroxene, the tetrahedra repeat with every second tetrahedron along the chain direction. The chains in Zn-Li silicate are composed of the tetrahedra of the larger cations; in pyroxene the chains are composed of smaller SiO_4 tetra-

Table 5b. Bond angles for Zn-Li silicate at room temperature and 450°C*

Room temperature		At 450°C	
O1-T1(o)-O2	115.1(2)	O1-T1-O2	116.6(2)
O1-T1(o)-O3(o)	110.0(2)	O1-T1-O3	108.0(2)
O1-T1(o)-O3(m)	110.5(2)	O1-T1-O3	109.5(2)
O2-T1(o)-O3(o)	114.6(2)	O2-T1-O3	113.2(2)
O2-T1(o)-O3(m)	98.3(2)	O2-T1-O3	101.5(3)
O3(o)-T1(o)-O3(m)	107.5(2)	O3-T1-O3	107.5(2)
O1-T1(m)-O2	117.8(4)		
O1-T1(m)-O3(o)	110.9(4)		
O1-T1(m)-O3(m)	106.3(4)		
O2-T1(m)-O3(o)	102.7(4)		
O2-T1(m)-O3(m)	112.8(4)		
O3(o)-T1(m)-O3(m)	105.8(4)		
O1-T2-O2	111.0(2)	O1-T2-O2	110.7(3)
O1-T2-O3(o)	109.5(2)	O1-T2-O3	108.9(2)
O1-T2-O3(m)	107.8(2)	O1-T2-O3	108.9(2)
O2-T2-O3(o)	108.4(2)	O2-T2-O3	109.3(2)
O2-T2-O3(m)	110.4(2)	O2-T2-O3	109.3(2)
O3(o)-T2-O3(m)	109.8(2)	O3-T2-O3	109.9(3)

*Parenthesized figures represent the estimated standard deviation refers to the last digit.

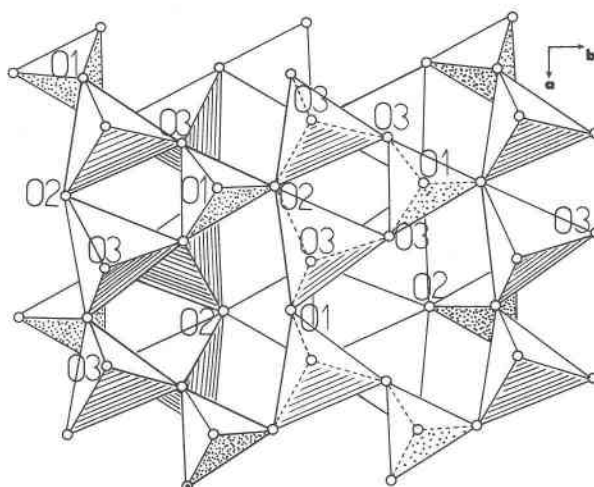
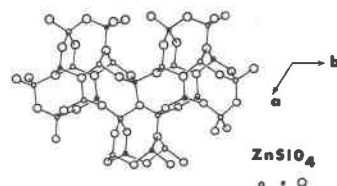


Fig. 1. The crystal structure of Zn-Li silicate at 450°C in comparison with that of willemite. Shaded tetrahedra are T1O₄, and dotted ones are T2O₄ (SiO₄).

hedra. This difference results in a longer dimension of the a axis (chain direction) in the Zn-Li silicates (6.4Å) than of the c axis (chain direction) in pyroxene (5.2Å).

Both Zn-Li silicates and willemite have a framework structure which gives a sharing coefficient of 3 (Zoltai, 1969). The structures, however, show little similarity. One of the common structure features in both willemite and Zn-Li silicate is the ring composed of corner-shared tetrahedra. The 3-tetrahedra rings in the Zn-Li silicates are isolated one with respect to another (see Fig. 1). In the willemite structure, the three bonds pointing to each oxygen from two Zn and one Si atoms are in the same plane and nearly 120° apart. But in the Zn-Li silicate structure no 3 coplanar bonds around an oxygen atom are found, although O2 has 3 bonds nearly aligned in a plane.

Hemimorphite has a structure even more different from the Zn-Li silicate than willemite. The hemimorphite structure contains Si_2O_7 groups, composed of

Table 7. Displacements of the 4-fold site in the α form with respect to the β form

Site	Δa (Å)	Δb (Å)	Δc (Å)
T1(o)	0.007	0.024	0.011
T1(m)	0.022	-0.057	-0.032
O1	0.028	0.031	-0.004
O2	0.015	-0.007	-0.042
O3(o)	0.010	-0.011	-0.003
O3(m)	0.044	-0.012	-0.003

two SiO_4 tetrahedra with a common corner, which gives a sharing coefficient of 2.75.

T1 tetrahedra

The tetrahedral angles of the TlO_4 tetrahedra for the β form range from 101.5° to 116.6° . They are less distorted from the ideal tetrahedron than either the T1(o)O_4 or T1(m)O_4 in the α form. If the mean T1-O distance is simply a weighted linear combination of the bond lengths for the various ions present in the T1 site, a predicted T1-O interatomic distance can be calculated. Taking Zn-O = 1.94Å, Si-O = 1.621Å from this study and Li-O = 2.00Å, the calculated value is 1.918Å, in comparison with the observed value, 1.968Å.

The T1(o)O_4 and T1(m)O_4 tetrahedral angles for the α form are significantly distorted, ranging from 98.3° to 115.1° and 102.7° to 117.8° respectively. Employing the same assumption as used in the β form, the mean T1(m)-O distance was calculated to be 1.882Å in contrast to the measured value 1.957Å.

T2 tetrahedra (Si tetrahedra)

Both forms have very regular SiO_4 tetrahedra with angles ranging from 111.0° to 107.8° for the α form and 110.7° to 108.9° for the β form. The mean Si-O interatomic distance, 1.621Å at room temperature, is insignificantly longer than 1.618Å at 450°C . Such an insignificant change in Si-O bond length with temperature has been reported by many authors in some high-temperature crystal-structure studies of silicates. Smyth and Hazen (1973) in olivines, Cameron *et al.* (1973) in pyroxenes, Sueno *et al.* (1973) in amphibole, Foit and Peacor (1973) in feldspar, and others have reported that the small increase in mean Si-O interatomic distances with increasing temperature is not statistically significant. On the other hand, Smyth (1973) and Peacor (1973) have found a slight decrease

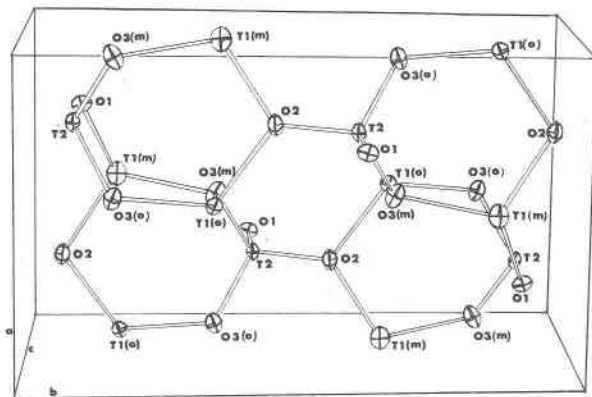


Fig. 2. Atomic thermal vibration ellipsoids for the α form of Zn-Li silicate. Drawing produced by ORTEP (Johnson, 1965).

in mean Si-O distances for orthopyroxene and natrolite with increasing temperature. Because the difference in Si-O distances in α and β structures is within experimental error, no final conclusions can be drawn as to whether or not the average Si-O interatomic distances truly exhibit any thermal change with increasing temperature.

Temperature factors

Ohashi *et al.* (1975) found the relatively large isotropic temperature factor for the M2 site at the middle of the hedenbergite-ferrosilite solid solution series resulting from the multiple occupancy of Ca and Fe atoms in the M2 site. The very similar markedly large isotropic temperature factors for the T1(m) site at room temperature and the T1 site at 450°C were also detected in this study. The O1, O2, and O3 oxygen atoms also exhibit large apparent temperature factors in the β form. According to Ohashi *et al.*

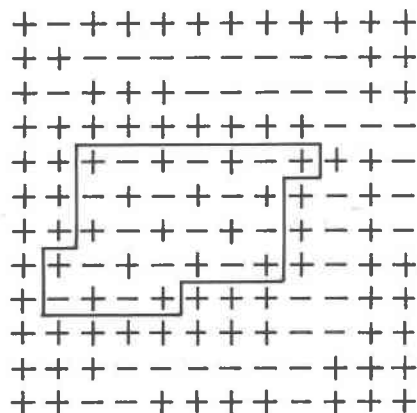


Fig. 3. Domain and twin structures of Zn-Li silicate projected on (010), showing that the twin has a B-centered lattice and its a and c double those of the untwinned single crystal.

(1975), abnormally large temperature factors are explained by the effect of significant positional disorder due to multiple occupancy of these tetrahedral sites. Because both the T1(m) site for the α form and the T1 site for the β form are occupied by atoms of Zn, Li, and Si in a completely disordered manner, and because their ionic radii are substantially different from each other [the effective ionic radii are Zn(IV) = 0.60, Li(IV) = 0.59, and Si(IV) = 0.26Å, see Shannon and Prewitt, 1969], there should be a variation of the atomic position among different unit cells of the crystal. The displacement of each individual 4-fold site in the α form, as shown in Table 7, can be correlated with the orientation of corresponding thermal vibration ellipsoids. It turned out that, except for T1(m), all 4-fold sites have the thermal vibration ellipsoids with their longest axes matching the displacement vectors in the α structure (compare Fig. 2 and Table 7).

Phase transition mechanisms and domain structures

At 450°C, Zn, Li, and some Si appear fully disordered on the T1 site. Below the transition temperature, ordering occurs as Zn atoms move to the preferred site and destroy the mirror plane at $a/4$. The loss of the mirror plane causes the splitting of the higher-temperature 8-fold T1 site into the two symmetry non-equivalent 4-fold positions at room temperature designated as T1(o) and T1(m) sites. The

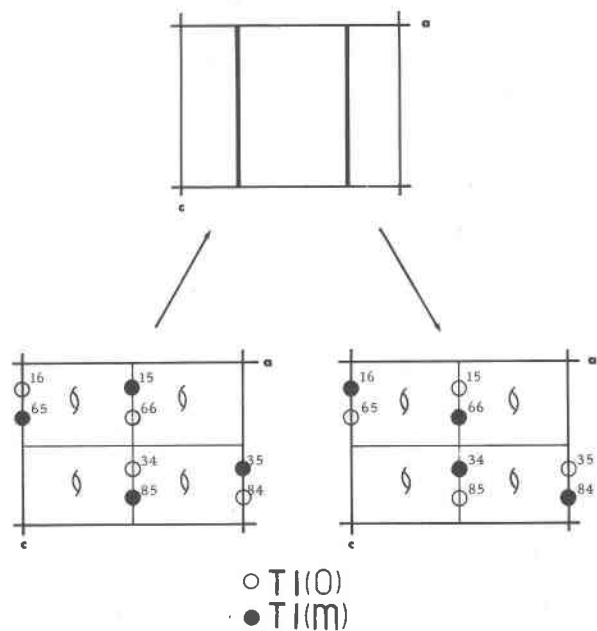


Fig. 4. Schematic diagrams showing the domain relation with reflection across (100) plane.

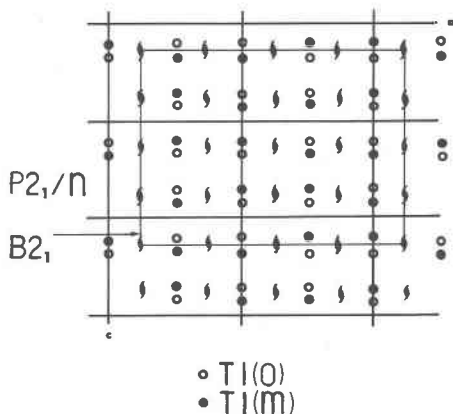


Fig. 5. Diagram showing the symmetry of space group $B2_1$ of twinned crystal.

T1(o) site is designated as the one fully occupied by Zn atoms. The T1(m) site is filled with a mixture of Zn, Li, and Si. Although the α form exhibits the true monoclinic symmetry created by the ordering of the Zn atoms at T1(o) site over T1(m) site, it displays strong pseudo-orthorhombic symmetry, due to the basic crystal structure which does not deviate significantly from that of the orthorhombic β form. The T1(o) and T1(m) tetrahedral sites alternate along the a direction (the tetrahedral chain direction) below the transformation temperature. However, when the transition takes place ordering occurs, and the Zn atoms may concentrate in either of the two 4-fold positions as T1(o) site. The T1(o) site at one part of the crystal might be different from the T1(o) site at another part of the crystal, which gives rise to a twinned domain structure (Fig. 3). Each domain is identical to the surrounding ones but out of phase by reflection across the (100) plane, as shown in Figure 4. Figure 3 depicts schematically the domain relation, with plus and minus signs representing two different domains on a unit-cell scale.

Twinning

The existence of the second room-temperature phase can be interpreted as the result of a portion of a crystal being twinned on the unit-cell scale. With the same axial direction for reference, the twin has a B -centered lattice with its a and c unit translations double and b equal to the corresponding vectors in the true single crystal as indicated in Figure 3. Figure 5 demonstrates that the twin structure has a $B2_1$ space group. The twinned fraction of a given crystal usually changes each time the crystal is cycled through the reversible order-disorder phase transition, and may

also change as the temperature is lowered. This explains why the X-ray intensities for the second room-temperature phase became weaker when the crystal was cooled from 450°C to room temperature.

Acknowledgments

The authors acknowledge the financial support of NSF grant G-25665. One of the authors (S.C.Y.) is grateful for the Kraus Crystallographic Research Fund Award of the Mineralogical Society of America.

References

- Austerman, S. B. (1964) Growth and properties of beryllium oxide crystals. *J. Nucl. Mater.*, **14**, 225.
- Brown, G. E., S. Sueno and C. T. Prewitt (1973) A new single-crystal heater for the precession camera and four-circle diffractometer. *Am. Mineral.*, **58**, 698-704.
- Busing, W. R., K. O. Martin and H. A. Levy (1962) ORFLS, a Fortran crystallographic least-squares program. *U. S. Natl. Tech. Inf. Serv. ORNL-TM-305*.
- Cameron, M., S. Sueno, C. T. Prewitt and J. J. Papike (1973) High-temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene and ureyite. *Am. Mineral.*, **58**, 594-618.
- Cromer, D. T. (1965) Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. *Acta Crystallogr.*, **18**, 17-23.
- and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.*, **24**, 321-324.
- Foit, F. F., Jr. and D. R. Peacor (1973) The anorthite crystal structure at 410 and 830°C. *Am. Mineral.*, **58**, 665-675.
- Hamilton, W. C. (1965) On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.*, **12**, 609-610.
- Hayashi, H., N. Nakayama, K. Hasegawa, S. Mizukusa, M. Mizuno and S. Ogiso (1965) Phase transition under high pressure (V). Transition of Zn_2SiO_4 . *Nagoya Kogyo Gijyutsu Shikensho Hokoku*, **14**, 384.
- Johnson, C. K. (1965) ORTEP, A Fortran thermal ellipsoid plot program for crystal structure illustrations. *U. S. Natl. Tech. Inf. Serv. ORNL-3794*.
- Ohashi, Y., C. W. Burnham and L. W. Finger (1975) The effect of Ca-Fe substitution on the clinopyroxene crystal structure. *Am. Mineral.*, **60**, 423-434.
- Peacor, D. R. (1973) High-temperature single crystal X-ray study of natrolite. *Am. Mineral.*, **58**, 676-680.
- Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, **25B**, 925-946.
- Smyth, J. R. (1973) An orthopyroxene structure up to 850°C. *Am. Mineral.*, **58**, 636-648.
- and R. M. Hazen (1973) The crystal structures of forsterite and hortonolite at several temperatures up to 900°C. *Am. Mineral.*, **58**, 588-593.
- Sueno, S., M. Cameron, J. J. Papike and C. T. Prewitt (1973) The high temperature crystal chemistry of tremolite. *Am. Mineral.*, **58**, 649-664.
- Suzuki, T. (1960) Atomic scattering factor for O^{2-} . *Acta Crystallogr.*, **13**, 279.
- Syono, Y., S. I. Akimoto and Y. Matsui (1971) High pressure transformations in zinc silicates. *J. Solid State Chem.*, **3**, 369-380.
- Wuensch, B. J. and C. T. Prewitt (1965) Corrections for X-ray absorption by a crystal of arbitrary shape. *Z. Kristallogr.*, **122**, 24-59.
- Zoltai, T. (1960) Classification of silicates and other minerals with tetrahedral structures. *Am. Mineral.*, **45**, 960-973.

Manuscript received, May 16, 1977; accepted for publication, April 7, 1978.