

Crystal structure and thermal expansion of quartz-type aluminosilicates

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The thermal expansion of quartz-type aluminosilicates, which is very important for their usefulness in ceramics, can be negative or positive, depending on composition. The structures of these phases are generally described as being β -quartz-like, however, an analysis of T–O bond lengths and thermal parameters of the oxygen atoms indicates that in several of these aluminosilicates the local atomic arrangement is α -quartz like and that the structures derived from diffraction data are average structures only. Computer modelling of the structures strongly supports this view. In the α -quartz-like phases there are static atomic displacements from the β -quartz positions that, as in α -quartz itself, become smaller with increasing temperature. This mechanism makes a positive contribution to thermal expansion. In phases where static displacements are absent, only thermal vibrations contribute to thermal expansion. Among these, the vibrations of the oxygen atoms normal to the T–O–T bonding plane are the most important ones and make a negative contribution to thermal expansion which is dominant in β -quartz as well as in some of the aluminosilicate phases like β -eucryptite.

1. Introduction

The polymorphs of silica with quartz structure and their stuffed aluminosilicate derivatives are important constituents of many ceramics and glass ceramics. The thermal expansion of these phases can vary widely: the small or negative thermal expansion of Li–aluminosilicates is beneficial in glass ceramics. On the other side the thermal volume changes of quartz create problems in porcelain and some refractories.

For these and other reasons the thermal expansion of quartz-type phases has been studied in great detail. Various models relating thermal expansion to structural parameters have been proposed.

For the thermal expansion of α - and β -quartz and the volume change during the α to β transition Megaw [1], using the crystal structure data of Young [2], developed a model based on two contributions: the thermal changes in the tilt angle of neighbouring tetrahedra and the apparent tetrahedral bond length changes that are related to the thermal vibrations of the oxygen atoms normal to the plane of the Si–O–Si bonding. The former contribution is dominant in α -quartz and causes its positive thermal expansion whilst the latter mechanism causes the negative thermal expansion of β -quartz.

For quartz-type aluminosilicates both types of expansion behaviour have been reported: thermal expansion is negative in β -eucryptite, LiAlSiO₄, and some related phases, but positive in several others, e.g. the Mg–aluminosilicates.

Crystal structures have been determined for many quartz-type phases. Their framework is generally described as β -quartz-like, with the cations being stuffed into sites within the channels that run through the

quartz structure parallel to the c -axis. Superstructures due to Al–Si-ordering and cation ordering have been reported for some cases like β -eucryptite, Winkler [3], and MgAl₂Si₃O₁₀, [4], which, however, do not seem to have a major influence on thermal expansion. Several models have been proposed that relate crystal–chemical aspects to the thermal expansion, particularly for β -eucryptite: Li [5] suggested that thermal stress release between (Al, Si)O₄- and LiO₄-tetrahedra is the driving force for thermal contraction. Schulz and Tscherry [6] related thermal contraction in β -eucryptite to thermal site changes of the Li ions that, however, have not been confirmed in high temperature structure determinations [7, 8].

Features that are common to several quartz-type aluminosilicates are large thermal parameters, particularly of the oxygen atoms, and apparent (Al, Si)–O bond lengths which are unusually short. Unstable phases of composition HAlSi₂O₆ and Na_{0.5}H_{0.5}AlSi₂O₆ that can be prepared by ion exchange show the same phenomena [9, 10].

In this paper we will interpret the thermal parameters as being due to static disorder and relate them to the observed bond lengths. Computer modelling of the structures will be shown to support this view. A correlation between static disorder and thermal expansion is then given for the aluminosilicate phases that can be interpreted in terms of the Megaw model [1].

2. Data and computer modelling

A large number of single crystal X-ray or neutron studies on quartz and quartz-type aluminosilicates

have been published. The data and references used in this analysis are compiled in Table I. The table gives lattice constants, volume coefficients of thermal expansion, measured (Al,Si)-O distances (called T-O distances below) as compared to the distances that would be expected from average bond lengths.

For several of the aluminosilicates listed the data given apparently describe an average structure only. In one case direct evidence for ordering in α -quartz-like domains has been found by X-ray diffraction [4]. In other cases the unusually short observed T-O bond lengths also suggest that the actual framework configuration may differ from the average one derived from the diffraction data. The distance least squares (DLS) program originally developed by Maier and Villiger [11] and later modified by Baerlocher *et al.* [12] is a powerful tool for modelling idealized structures based on the known or assumed topology of the structure, expected bond lengths and measured lattice constants. Weight factors that are related to the relative stiffness of the bonds have to be assigned somewhat arbitrarily to every type of bond. In the present case, factors of 2.0 for T-O distances, 1.0 for O-O distances and 0.2 for M-O distances gave excellent agreement between the calculated model structure and the ones derived

from diffraction data if the same space group was used. These weight factors were used for all further modelling.

3. Results of modelling of quartz-type structures

The structures of all phases listed in Table I were modelled by DLS refinements both in the β -quartz (P₆22) and the α -quartz (P₃21) space groups. Table II shows the refinements in the α -quartz space group as compared to the results of the structure determinations in the β -quartz space group from X-ray diffraction data. DLS results for space group P₆22 are not listed, they generally agree within ± 0.002 with the diffraction results. Atomic positions of the P₃21 modelling, however, differ considerably from those in P₆22. Bond distance and angles calculated from the lattice constants in Table I and the two sets of atomic coordinates in Table II are listed in Table III. T-O bond distances agree very well with expected values (based on radius sums) for the P₃21 calculations, T-O-T angles are closer to the equilibrium angle of 140°, Liebau [13], and the TO₄ tetrahedra are less

TABLE I Lattice constants, thermal expansion and selected structural data of quartz and quartz-type aluminosilicates

Composition	a_0 (nm)	c_0 (nm)	α_v (10^{-6} K^{-1})	Temperature range (°C)	Reference ^b	T-O (nm)	$\Delta(\text{T-O})^a$ (nm)	Reference ^c
Zn _{0.5} AlSi ₂ O ₆	0.5220(5)	0.5460(5)	-7.0	25-800	[16]	0.1658	-0.005	[15]
LiAlSi ₂ O ₆	0.5215(3)	0.5457(3)	-4.3	25-800	[16]	0.1649(1)	0.0004	[10]
LiAlSiO ₄	1.0502(1)	1.1185(3)	-2.1	0-1100	[17]	0.1675(5)	0.0	[7]
β -quartz, 600 °C	0.4997(7)	0.5460(1)	0	600-800	[18]	0.1594(6)	0.0016	[2]
Mg _{0.5} AlSi ₂ O ₆	0.5171(5)	0.5343(5)	6.7	25-800	[16]	-	-	-
MgAl ₂ Si ₃ O ₁₀	0.5182(6)	0.5360(5)	-	-	-	0.1626(2)	0.0036	[4]
Na _{0.5} H _{0.5} AlSi ₂ O ₆	0.5161(1)	0.5452(1)	9.4	25-600	[10]	0.1620(1)	0.0033	[10]
HAlSi ₂ O ₆	0.5083(3)	0.5509(3)	15.9	25-350	[16]	0.1611(3)	0.0042	[9]
α -quartz	0.4912(1)	0.5398(8)	38.7	25-200	[18]	0.1564(2)	0.0046	[2]

^a $\Delta(\text{T-O}) = (\text{T-O})_{\text{exp}} - (\text{T-O})_{\text{obs}}$.

^b References for the lattice constants and thermal expansion.

^c References for the structural data.

TABLE II Atomic parameters, based on structure refinements from X-ray diffraction data and DLS modelling

		P ₆ 22 (X-ray)			P ₃ 21 ^a (DLS)		
		x/a	y/a	z/c	x/a	y/a	z/c
SiO ₂	Si	0.5	0.0	0.0	0.4784	0.0	0.0
	O	0.2068	0.4137	0.5	0.2530	0.4194	0.5343
HAlSi ₂ O ₆	Al, Si	0.5	0.0	0.0	0.4703	0.0	0.0
	O	0.2080	0.4160	0.5	0.2677	0.4165	0.5475
LiAlSi ₂ O ₆	Al, Si	0.5	0.0	0.0	0.4792	0.0	0.0
	O	0.2030	0.4060	0.5	0.2510	0.4205	0.5348
	Li	0.0	0.0	0.0	0.0	0.0	0.0
MgAl ₂ Si ₃ O ₁₀	Al, Si	0.5	0.0	0.0	0.4695	0.0	0.0
	O	0.2044	0.4088	0.5	0.2677	0.4161	0.5514
	Mg	0.0	0.0	0.5	0.0	0.0	0.5
Na _{0.5} H _{0.5} AlSi ₂ O ₆	Al, Si	0.5	0.0	0.0	0.4729	0.0	0.0
	O	0.2080	0.4160	0.5	0.2626	0.4188	0.5441
	Na	0.0	0.0	0.5	0.0	0.0	0.5

^a Unit cell origin in space group P₃21 is displaced by $-1/6$ in c direction for easier comparison.

TABLE III Bond distances (nm) and angles, based on structure refinements from X-ray diffraction data (space group P6₂22) and DLS modelling (space group P3₂21)

	SiO ₂		HAlSi ₂ O ₆		LiAlSi ₂ O ₆		MgAl ₂ Si ₃ O ₁₀		Na _{0.5} H _{0.5} AlSi ₂ O ₆	
	P6 ₂ 22	P3 ₂ 21	P6 ₂ 22	P3 ₂ 21	P6 ₂ 22	P3 ₂ 21	P6 ₂ 22	P3 ₂ 21	P6 ₂ 22	P3 ₂ 21
T–O(2) (nm)	0.1594	0.1610	0.1611	0.1653	0.1649	0.1654	0.1626	0.1662	0.1620	0.1656
T–O(3) (nm)	0.1594	0.1610	0.1611	0.1653	0.1649	0.1654	0.1626	0.1662	0.1620	0.1654
O(2)–O(3) (nm)	0.2559	0.2630	0.2594	0.2700	0.2587	0.2679	0.2561	0.2703	0.2599	0.2690
O(2)–O(5) (nm)	0.2615	0.2628	0.2648	0.2699	0.2748	0.2737	0.2717	0.2755	0.2682	0.2718
O(2)–O(6) (nm)	0.2634	0.2631	0.2651	0.2700	0.2737	0.2684	0.2688	0.2680	0.2657	0.2700
O(3)–O(5) (nm)	0.2634	0.2630	0.2651	0.2699	0.2737	0.2690	0.2688	0.2692	0.2657	0.2701
O(2)–T–O(3) (deg)	106.8	109.5	107.2	109.5	103.4	108.2	103.9	108.8	106.6	108.7
O(2)–T–O(5) (deg)	110.2	109.4	110.5	109.4	112.9	111.6	111.4	107.4	111.7	110.4
O(2)–T–O(6) (deg)	111.5	109.5	110.7	109.5	112.3	108.4	113.3	111.9	110.1	109.2
O(3)–T–O(5) (deg)	111.5	109.5	110.7	109.5	112.3	108.8	113.3	108.1	110.1	109.5
T–O–T (deg)	152.8	149.1	153.5	144.4	150.1	149.4	150.8	143.6	153.3	146.2
M–O(1) (nm)	–	–	–	–	–	–	0.1840	0.1913	0.1855	0.1903
M–O(2) (nm)	–	–	–	–	0.2051	0.2209	0.2565	0.2422	0.2599	0.2466
M–O(3) (nm)	–	–	–	–	0.2051	0.2046	0.2565	0.2800	0.2599	0.2802

distorted than with the P6₂22 results. Polyhedra about the cations, however, become more irregular.

4. Analysis of the thermal parameters

Table IV contains the thermal ellipsoid data (length and orientation of the principal axis) for the framework atoms T and O calculated from the thermal parameters given in the original papers. Sizes of the ellipsoids are in the normal range for ordered structures at room temperature in the case of α -quartz and β -eucryptite, but much larger for most of the other aluminosilicates listed. The ellipsoids of the oxygen atoms are considerably larger than those of the T atoms.

Table IV also contains the difference in atomic positions between the DLS refinements in space group P3₂21 and diffraction results in space group P6₂22 which we will call DLS-displacement vectors (V^*).

Fig. 1 shows the orientation of the oxygen ellipsoids relative to the crystal axes in a stereographic projection. Fig. 2 contains the direction of the normal of the plane defined by the T–O–T bonds, which is the same to within 0.7° in all quartz-type phases considered here, of the DLS-displacement vector (V^*) and of the vector describing the movement of the oxygen atoms during the α to β transition in quartz (V). Comparison of Figs 1 and 2 shows that U_3 , the longest principal axis of the thermal ellipsoids of the oxygen atoms, has nearly the same orientation as the vectors given in Fig. 2. For all phases U_3 is parallel to within 17° to the normal of the T–O–T plane, within 8° to V^* and also within 8° to V .

5. Discussion

In diffraction analysis static disorder due to atomic displacements and dynamic disorder due to atomic vibrations are generally lumped together into the thermal parameters.

Among the phases studied here α -quartz and β -eucryptite can be assumed to represent cases dominated by thermal vibrations: ellipsoid sizes are normal for ordered structures at room temperature, and become larger at higher temperature, Young [2] and Steinmann [8]. In some of the aluminosilicates, however, static displacements apparently are the main reasons for the large thermal (or, rather, pseudothermal) parameters: in MgAl₂Si₃O₁₀ this is directly evidenced by superstructure reflections and successful split-atom refinements [4]. In HAlSi₂O₆ the longest principal axis U_3 of the thermal ellipsoid derived from neutron diffraction data at 5 K actually turns out to be longer than the one at room temperature and, finally, the unusually short apparent bond lengths can also be corrected to normal values by assuming static disorder.

If, erroneously, the structure of α -quartz were derived from diffraction data obtained from a Dauphinée twin, space group P6₂22 would be the obvious choice. The result would show the features found here for the aluminosilicates: large values for the apparent thermal parameters, particularly for U_3 (containing static and vibrational parts) and T–O bond lengths much shorter than expected.

Static and/or dynamic displacements and apparent bond length shortening $\Delta(T-O)$ are related in a straightforward way [14]. From Fig. 3 it can be seen that

$$U_3 = [2(T-O)\Delta(T-O)]^{1/2} \quad (1)$$

if $2(T-O) \gg \Delta(T-O)$. In Fig. 4 this parabolic relationship between $\Delta(T-O)$ and U_3 is shown by the broken line. Ionic radii and bond distances are usually listed and discussed for room temperature. The shift of 0.0006 nm in the abscissa of Fig. 4 accounts for the difference between absolute zero and room temperature, where thermal vibration amplitudes are in the range of 0.01 to 0.015 nm in ordered structures. As can be seen, the experimental data of all phases studied

TABLE IV Thermal ellipsoid data and displacement vectors

O-position	LiAlSiO ₄	LiAlSi ₂ O ₆	β-quartz	MgAl ₂ Si ₃ O ₁₀	Na _{0.5} H _{0.5} AlSi ₂ O ₆	HAlSi ₂ O ₆	α-quartz
U ₁ (nm)	0.0101	0.0122	0.0131	0.0160	0.0192	0.0182	0.0098
a (deg)	39.2	38.4	42.9	25.9	15.4	40.5	55.6
b* (deg)	91.5	90	90	90	90	90	120.7
c (deg)	129.1	128.4	132.9	115.9	105.4	130.5	128.5
U ₂ (nm)	0.0129	0.0167	0.0229	0.0254	0.0350	0.0330	0.0052
a (deg)	85.0	90	90	90	90	90	62.8
b* (deg)	3.6	0	0	0	0	0	120.7
c (deg)	86.2	90	90	90	90	90	108.0
U ₃ (nm)	0.0154	0.0214	0.0285	0.0379	0.0350	0.0363	0.0133
a (deg)	51.3	51.6	47.1	64.1	74.6	49.5	46.7
b* (deg)	96.2	90	90	90	90	90	96.4
c (deg)	39.4	38.4	42.9	25.9	15.4	40.5	44.0
T-position							
U ₁ (nm)	0.0097	0.0108	0.0124	0.0181	0.0221	0.0177	0.0086
a	63.8	90	90	90	90	90	90
b*	107.2	90	90	90	90	90	93.8
c	32.2	0	0	0	0	0	3.8
U ₂ (nm)	0.0104	0.0099	0.0135	0.0141	0.0164	0.0176	0.0049
a	76.0	90	90	90	90	90	90
b*	18.5	0	0	0	0	0	3.8
c	78.2	90	90	90	90	90	86.2
U ₃ (nm)	0.0114	0.0107	0.0170	0.0180	0.0267	0.0196	0.0072
a	149.7	0	0	0	0	0	0
b*	83.5	90	90	90	90	90	90
c	60.6	90	90	90	90	90	90
DLS-displacement vectors V* of the O-position							
V* (nm)	—	0.0293	0.0288	0.0416	0.0366	0.0400	0.0401 ^a
a	—	43.4	41.1	41.9	41.5	40.9	41.2
b*	—	77.1	85.1	85.5	88.0	89.7	89.1
c	—	49.5	49.3	48.4	48.6	49.1	48.8

^a Displacement vector *V* of the α to β transition given in the case of α-quartz.

here fit the theoretical curve surprisingly well. α-quartz is also plotted in Fig. 4. In this case, the displacement (*V*) of the oxygen atom from α-quartz to β-quartz was used.

Fig. 5 shows the variation of the static and vibrational displacements as a function of temperature. For quartz, the static part decreases with temperature and drops to zero at the α to β transformation temperature [2]. The overall effect of static (*V*) and vibrational (*U*₃) contributions in quartz is also shown. In β-eucryptite, LiAlSiO₄, the increase of *U*₃ with temperature is very similar to the one in quartz [7, 8].

For HAlSi₂O₆ the low temperature slope is negative and comparable to the overall slope of quartz. For the remaining phases only room temperature data are known. It can be seen, however, from the size of *U*₃ that LiAlSi₂O₆ is related to LiAlSiO₄, β-eucryptite, whereas all the other aluminosilicates are closer to α-quartz.

The thermal variation of *U*₃ can, in principle, be translated into apparent thermal bond length changes via Equation 1 and thus into thermal expansion.

The positive thermal expansion of α-quartz up to the transformation temperature and the negative thermal expansion of β-quartz are immediate conse-

quences as already stated by Megaw [1]. In β-eucryptite, where static displacements are absent or at least very small and where *U*₃ has a temperature dependence similar to the one in quartz, negative thermal expansion like in β-quartz is the logical consequence.

If a larger than normal experimental value of *U*₃ is interpreted to contain a larger contribution of static displacements with a temperature dependence similar to the one in α-quartz, then a transition from negative to positive thermal expansion is to be expected.

As Fig. 6 shows, such a relationship indeed exists. Only the phases with *U*₃ < 0.03 nm have zero or negative thermal expansion, the others have positive thermal expansion. There is some uncertainty about MgAl₂Si₃O₁₀: the thermal expansion of this composition is not known, the value of a related composition, Mg_{0.5}AlSi₂O₆ has been plotted instead, which may be somewhat different. For another quartz-type aluminosilicate, Zn_{0.5}AlSi₂O₆, the thermal parameters have not been reported. The fact that it has a normal T–O bond length, Behruzi [15], is, however, fully in line with its negative thermal expansion.

It should be pointed out, finally, that the correlation shown in Fig. 6 holds only for volume expansion

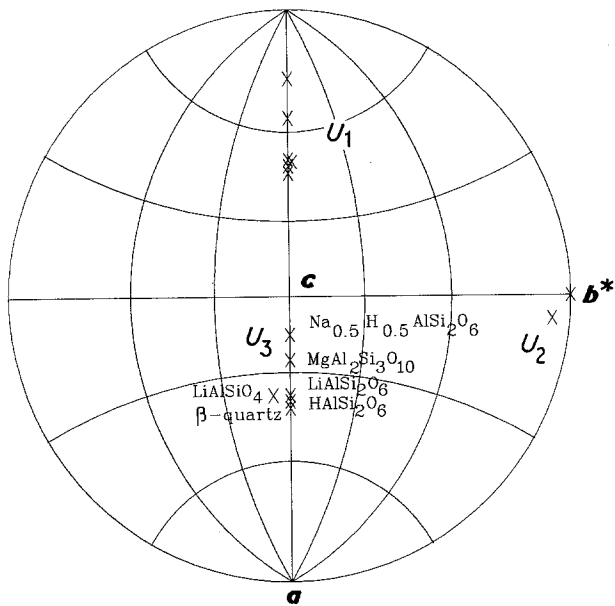


Figure 1 Orientation of the thermal ellipsoids of the oxygen atoms in quartz-type phases relative to the crystal axes, stereographic projection.

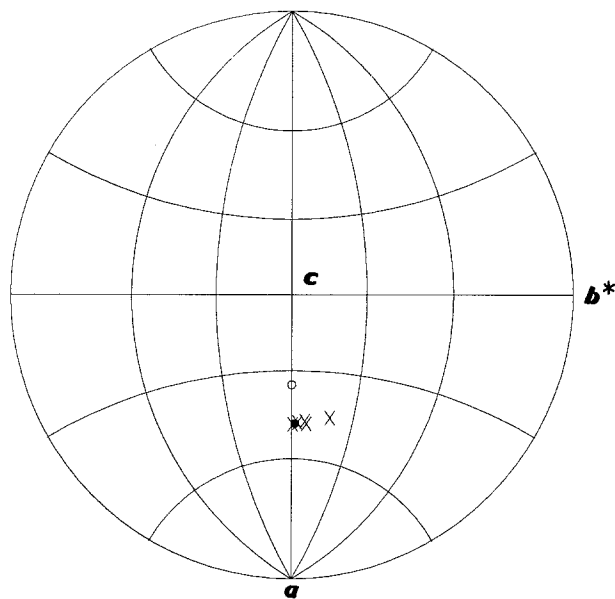


Figure 2 Direction of the DLS-displacement vectors (V^*), (\times) of the oxygen shift (V) during the α - β transformation in quartz (\bullet) and of the normal of the T-O-T bonding plane (\circ), relative to the crystal axes.

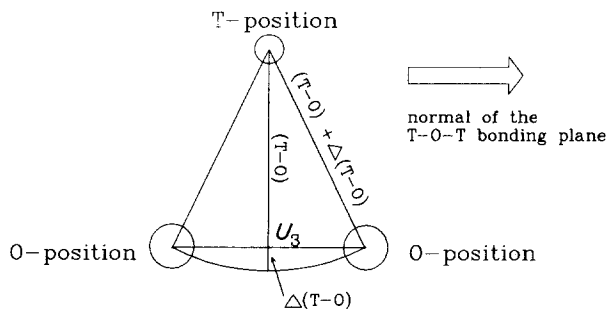


Figure 3 Geometrical relationship between the thermal ellipsoid axis U_3 of the oxygen atoms and the apparent bond length shortening $\Delta(T-O)$.

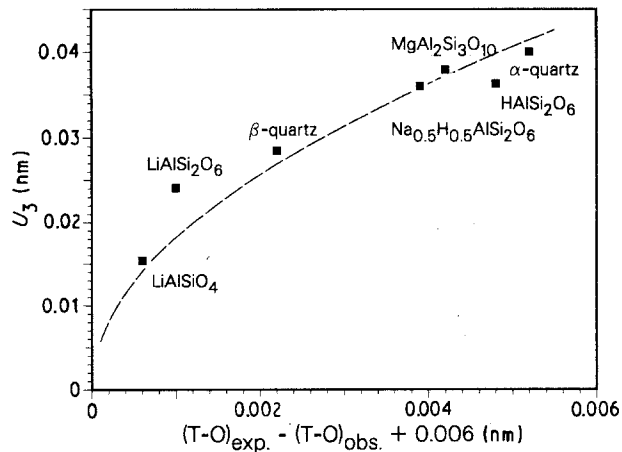


Figure 4 Correlation between thermal ellipsoid axis U_3 and apparent bond length shortening $\Delta(T-O)$. Dashed line: calculated from Equation 1. Squares: data from structure refinements. Shift of 0.0006 nm accounts for room temperature thermal vibrations.

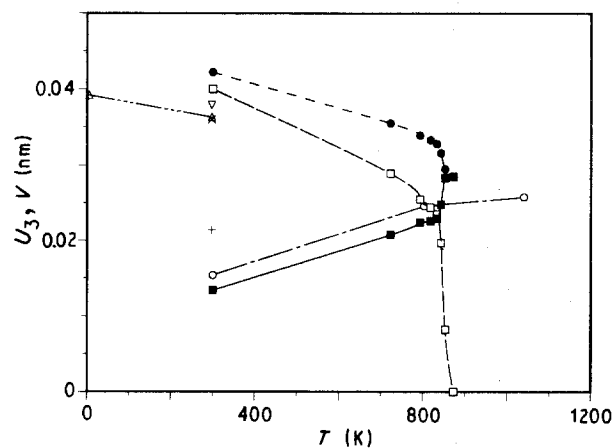


Figure 5 Static and dynamic displacements (V resp. U_3) as a function of temperature in quartz-type phases.

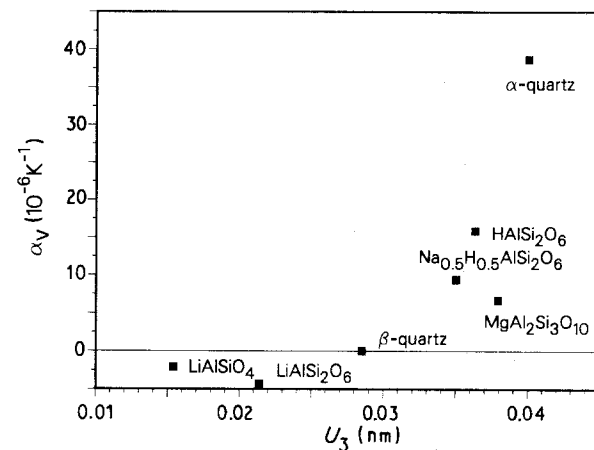


Figure 6 Thermal expansion of quartz-type phases as a function of the length of the longest oxygen thermal ellipsoid axis U_3 . (\blacksquare SiO_2 U_3 , \square SiO_2 V , \bullet SiO_2 $(V^2 + U_3^2)^{1/2}$, \circ β -eucryptite U_3 , \triangle HAlSi_2O_6 U_3 , \times $\text{Na}_{0.5}\text{H}_{0.5}\text{AlSi}_2\text{O}_6$ U_3 , ∇ $\text{MgAl}_2\text{Si}_3\text{O}_{10}$ U_3 , $+$ $\text{LiAlSi}_2\text{O}_6$ U_3)

coefficients. Axial expansion coefficients show a more complicated behaviour that seems to be related also to the type of cation polyhedron present in the aluminosilicates and, concomitantly, to the c/a ratio. The

presence of these MO_x polyhedra apparently also suppresses actual α to β phase transformations like in quartz, only smooth thermal changes with essentially constant thermal expansion coefficients are observed instead.

6. Conclusions

The volume expansion of quartz-type aluminosilicates is closely related to their thermal parameters. Large thermal parameters are accompanied by apparent T–O bond lengths shorter than expected. They indicate α -quartz like character of the actual structure that is confirmed by DLS modelling. The static displacements from the β -quartz positions, like in α -quartz itself, become smaller with increasing temperature, which creates a positive contribution to the thermal expansion. The vibrational displacements from the average positions increase with temperature thus making a negative contribution to thermal expansion. The latter contribution dominates in the Li- and Zn-aluminosilicates which explains their unusual negative thermal volume expansion. The other quartz-type aluminosilicates all have thermal ellipsoids similar in size and orientation to the static displacements in α -quartz. Consequently, they are also more related to α -quartz in their thermal expansion characteristics.

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