

Crystal structure refinement and thermal expansion of a Li, Na, Be-cordierite between 100 and 550 K

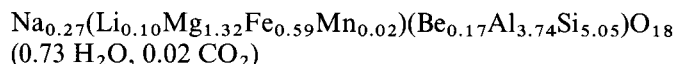
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Cordierite | Crystal structure | Crystal chemistry | Thermal expansion

Abstract. A low-cordierite (*Cccm*) with the composition



was investigated. Single-crystal X-ray structure refinements are reported for 100, 300 and 500 ± 10 K. As temperature increases the oblate six-membered rings of oxygen atoms centered about Na become slightly more circular and the (Mg,Fe)–O bond lengths increase. A preferred H₂O orientation within the structural cavity can not be determined, but the observed electron density is in agreement with static and dynamic disorder models in previous single-crystal IR and NMR studies. Temperature dependent lattice dimensions were measured between 110 and 548 K. As the temperature increases, *a* increases, *b* decreases slightly, *c* remains invariant, and the distortion index Δ [$\Delta = 1.094 \cdot (a - b \cdot \sqrt{3})$] increases from 0.148 (110 K) to 0.181 (548 K).

Introduction

Cordierite, whose simplified formula is (Mg, Fe)₂^{VI}(Al₄Si₅)^{IV}O₁₈¹, is interesting not only as a mineral but also as a ceramic material because of its unique low thermal expansion properties.

In the present study the effect of temperature on a low-cordierite (*Cccm*, *Z* = 4) is investigated. Temperature dependent studies on natural cor-

¹ Roman superscripts denote coordination numbers

dierites are restricted to a limited temperature range in which the chemistry of the sample remains unaltered. At elevated temperature volatiles trapped in the structural channels may escape and the oxidation state of iron may change. Hochella et al. (1979) studied the temperature dependence of White Well and Dolni Bory cordierites. They noticed a difference in the color of the crystals and at the same time observed changes in the electron density within structural channels before and after the heating excursion. Questions remained about which structural changes are associated with temperature variation and which with change in composition.

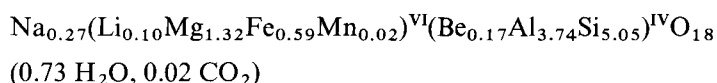
The role of Na in the structure of low-cordierite has been subject of a recent crystal structure study (Armbruster, 1986). Two models for Na incorporation into channel sites could be distinguished on the basis of X-ray structure refinements and chemical analyses

- a) $\text{Na} + \text{Be}^{\text{IV}} \rightarrow \text{Al}^{\text{IV}}$
- b) $\text{Na} + \text{Li}^{\text{VI}} \rightarrow (\text{Mg}, \text{Fe}, \text{Mn})^{\text{VI}}$.

These substitutions were also confirmed by Gordillo et al. (1985) who applied statistical tests on chemical analyses of cordierites.

Experimental

A room temperature structure refinement of the same Haddam cordierite crystal



used in the present study has already been described (Armbruster, 1986). These results are designated 'Haddam 300 K'. The crystal contains Na due to both substitution reactions described above. The chemical composition of the framework was determined by electron microprobe analyses and wet chemical analyses for Li and Be (Armbruster and Irouschek, 1983). All X-ray intensity measurements were performed on an Enraf Nonius CAD4 diffractometer up to $\theta = 40^\circ$ (graphite monochromated MoK α radiation). The unit-cell parameters were refined from the positions of 22 reflections between 19° and $37^\circ \theta$. Reflection intensities at 110 ± 10 K (designated 'Haddam 100 K') were collected using an Enraf Nonius liquid nitrogen cooling device and at 500 ± 10 K using a self-constructed hot air blower. The actual temperature during data collection was monitored with a thermocouple mounted close to the crystal. The reliability of the heating and cooling devices was determined before and after the experiment with a thermocouple mounted on a goniometer head at the crystal position. The crystal was glued to a long silica glass fiber using a high-temperature

Table 1. Cell dimensions [\AA] and details of data collection

Crystal	Haddam 100 K	Haddam 300 K	Haddam 500 K
Number of observations	2485	2528	2532
Number of contributions ^a	2341	2367	2363
R, R_w [%]	1.9, 2.6	2.0, 2.7	2.0, 2.7
Extinction ^b	1.5	2.7	3.1
a [\AA]	17.049(2)	17.054(1)	17.066(1)
b [\AA]	9.766(2)	9.759(2)	9.760(1)
c [\AA]	9.324(1)	9.324(1)	9.327(1)
V [\AA^3]	1552.5	1551.8	1553.5
Δ^c [\AA]	0.146	0.165	0.176

^a Reflections for which $F(\text{obs}) < 6 \sigma F(\text{obs})$ and $F(\text{calc}) > F(\text{obs})$ were rejected

^b Isotropic extinction coefficient ($\cdot 10^3$). The X-ray program (Stewart et al. 1976) uses the extinction method proposed by Larson (1967)

^c $\Delta = 1.094 \cdot (a - b \cdot \sqrt{3})$

epoxy (Epoxy Technology Inc.: EPO-TEK 353 ND)² to obtain mechanical stability of the crystal in the center of the X-ray beam at high and low temperature. 500 K is about the maximum temperature at which oxidation ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) and loss of volatiles can be neglected during one week of data collection. Additional details about data collection and structure refinement with the 'X-ray System of Crystallographic Programs' (Stewart et al., 1976) have already been described (Armbruster, 1986). Conventional R -values and isotropic extinction coefficients are given in Table 1. Fractional coordinates and conventional anisotropic temperature factors (U_{ij}) are summarized in Table 2.

Atom sites are labelled using the nomenclature of Cohen et al. (1977). All site occupancies were fixed according to the analytical results. Li, Mg, Fe, and Mn were assigned to the six-fold coordinated M-site, while Be partially occupies the Al-tetrahedron T₁1.

Unit-cell expansion

Cell parameters for the Haddam cordierite at 19 temperatures between 110 and 548 K are presented in Table 3. The a -axis increases linearly with temperature, whereas the b -axis decreases (Fig. 1). The c -axis remains essentially constant in the temperature range studied. The cell-length changes have little effect on the cell volume but give a highly significant increase of Δ [defined by Selkregg and Bloss (1980) as: $\Delta = 1.094 \cdot (a - b \cdot \sqrt{3})$] with temperature (Table 3).

² Available from: Polyscience AG, Schwerstr. 12, CH-6300 Zug, Switzerland

Table 2. Fractional coordinates and temperature factors U_{ij} ($\cdot 10^2$) for the Haddam cordierite at various temperatures. Standard deviations are in parentheses. $B_{\text{eq}} = \frac{1}{3} \sum_k \beta_{ik} (a_i \cdot a_k)$ where $\beta_{ik} = U_{ik} \cdot 2 \pi^2 \cdot a_i^* \cdot a_k^*$

	HAD 100 K	HAD 300 K	HAD 500 K		HAD 100 K	HAD 300 K	HAD 500 K
O_{11}				T_{11} (Al, Be)			
x	0.24622(4)	0.24592(4)	0.24571(4)	x	1/4	1/4	1/4
y	-0.10431(6)	-0.10438(8)	-0.10444(7)	y	1/4	1/4	1/4
z	0.35822(7)	0.35850(8)	0.35861(8)	z	0.25023(5)	0.25011(6)	0.25003(5)
U_{11}	0.78(2)	1.20(3)	1.65(3)	U_{11}	0.40(1)	0.76(2)	1.09(2)
U_{22}	0.50(2)	0.80(3)	1.20(3)	U_{22}	0.31(2)	0.61(2)	0.89(2)
U_{33}	0.52(2)	0.83(3)	1.21(3)	U_{33}	0.33(2)	0.61(2)	0.96(2)
U_{12}	0.03(2)	-0.04(2)	-0.07(2)	U_{12}	0.03(1)	0.10(1)	0.19(1)
U_{13}	0.21(2)	0.35(2)	0.52(2)	B_{eq}	0.27	0.52	0.77
U_{23}	0.01(2)	-0.07(2)	-0.13(2)				
B_{eq}	0.47	0.74	1.07	T_{16} (Si)			
O_{16}				x	0	0	0
x	0.06198(3)	0.06187(4)	0.06173(4)	y	1/2	1/2	1/2
y	-0.41571(6)	-0.41574(7)	-0.41575(7)	z	1/4	1/4	1/4
z	0.34889(7)	0.34885(8)	0.34899(7)	U_{11}	0.37(2)	0.60(2)	0.80(2)
U_{11}	0.51(2)	0.83(3)	1.10(2)	U_{22}	0.32(2)	0.66(2)	0.99(2)
U_{22}	0.55(2)	1.02(3)	1.56(3)	U_{33}	0.28(2)	0.48(2)	0.76(2)
U_{33}	0.46(2)	0.81(3)	1.17(3)	B_{eq}	0.26	0.45	0.67
U_{12}	-0.11(2)	-0.14(2)	-0.23(2)	T_{21} (Si)			
U_{13}	0.02(2)	0.03(2)	0.06(2)	x	0.19207(2)	0.19179(2)	0.19147(2)
U_{23}	-0.17(2)	-0.32(2)	-0.52(2)	y	0.07857(4)	0.07870(4)	0.07883(3)
B_{eq}	0.40	0.70	1.01	z	0	0	0
O_{13}				U_{11}	0.31(1)	0.55(1)	0.76(1)
x	-0.17315(4)	-0.17331(4)	-0.17341(4)	U_{22}	0.26(1)	0.45(1)	0.64(1)
y	-0.30869(6)	-0.30849(7)	-0.30809(7)	U_{33}	0.36(1)	0.61(2)	0.87(1)
z	0.35812(7)	0.35792(9)	0.35818(8)	U_{12}	0.01(1)	0.02(1)	0.03(1)
U_{11}	0.56(2)	0.94(3)	1.33(3)	B_{eq}	0.24	0.42	0.60
U_{22}	0.53(2)	1.02(3)	1.48(3)	T_{23} (Si)			
U_{33}	0.51(2)	0.86(3)	1.16(3)	x	-0.13565(2)	-0.13563(2)	-0.13563(2)
U_{12}	0.03(2)	0.11(2)	0.21(2)	y	0.23639(3)	0.23636(4)	0.23616(4)
U_{13}	-0.08(2)	-0.17(2)	-0.31(2)	z	0	0	0
U_{23}	-0.19(2)	-0.28(3)	-0.40(2)	U_{11}	0.28(1)	0.51(1)	0.70(1)
B_{eq}	0.42	0.74	1.04	U_{22}	0.28(1)	0.52(1)	0.76(1)
				U_{33}	0.39(1)	0.63(2)	0.90(1)
				U_{12}	-0.04(1)	-0.06(1)	-0.11(1)
					0.25	0.44	0.62

O ₂ 6			
x	0.04279(5)	0.04315(6)	0.04318(6)
y	-0.24373(9)	-0.24496(12)	-0.24552(11)
z	0	0	0
U ₁₁	0.36(3)	0.62(4)	0.75(4)
U ₂₂	0.84(3)	1.43(5)	2.35(5)
U ₃₃	1.21(4)	1.90(6)	2.54(5)
U ₁₂	-0.10(3)	-0.16(3)	-0.26(3)
B _{eq}	0.63	1.04	1.48

O ₂ 1			
x	0.11991(5)	0.11975(7)	0.11967(6)
y	0.18170(9)	0.18176(11)	0.18226(11)
z	0	0	0
U ₁₁	0.80(3)	1.21(5)	1.62(4)
U ₂₂	0.68(3)	1.14(5)	1.57(5)
U ₃₃	0.99(4)	1.81(6)	2.69(6)
U ₁₂	0.41(3)	0.61(4)	0.86(4)
B _{eq}	0.65	1.09	1.55

O ₂ 3			
x	0.16393(6)	0.16350(7)	0.16307(6)
y	-0.07867(9)	-0.07847(11)	-0.07811(10)
z	0	0	0
U ₁₁	0.80(3)	1.44(5)	2.07(5)
U ₂₂	0.35(3)	0.59(4)	0.83(4)
U ₃₃	1.07(4)	1.85(6)	2.76(6)
U ₁₂	-0.19(3)	-0.35(4)	-0.53(3)
B _{eq}	0.58	1.02	1.49

T ₂ 6 (Al)			
x	0.05073(2) ^{M, R}	0.05052(3)	0.05030(2)
y	0.30856(4)	0.30856(4)	0.30841(4)
z	0	0	0
U ₁₁	0.30(1)	0.51(2)	0.68(1)
U ₂₂	0.30(1)	0.58(2)	0.85(1)
U ₃₃	0.30(1)	0.57(2)	0.86(1)
U ₁₂	0.02(1)	0.06(1)	0.09(1)
B _{eq}	0.24	0.44	0.63

M (Mg, Fe, Mn, Li)			
x	0.33617(4)	0.33622(6)	0.33627(4)
y	0	0	0
z	1/4	1/4	1/4
U ₁₁	0.38(2)	0.67(3)	0.96(3)
U ₂₂	0.61(3)	0.93(3)	1.31(3)
U ₃₃	0.43(3)	0.85(3)	1.39(3)
U ₂₃	0.01(2)	0.00(3)	0.00(3)
B _{eq}	0.37	0.64	0.96

Ch0 (Na)			
x	0	0	0
y	0	0	0
z	0	0	0
U ₁₁	1.2(1)	2.1(2)	3.4(2)
U ₂₂	0.5(1)	1.1(2)	2.1(2)
U ₃₃	1.8(2)	4.1(3)	5.9(5)
U ₁₂	0.0(1)	0.1(2)	0.0(2)
B _{eq}	0.92	2.0	3.0

Ch1/4 (O)			
x	0	0	0
y	0	0	0
z	1/4	1/4	1/4
U ₁₁	7.7(3)	12.8(5)	15.2(5)
U ₂₂	3.0(2)	6.6(3)	9.5(4)
U ₃₃	2.5(2)	4.9(3)	7.3(4)
B _{eq}	3.5	6.4	8.4

Table 3. Cell dimensions, cell volume and calculated distortion index (Δ) versus various temperatures for the Haddam cordierite

Temperature [K]	a [Å]	b	c	V [Å ³]	Δ
110	17.047(3)	9.764(2)	9.323(1)	1551.8	0.148
133	17.047(3)	9.764(1)	9.323(1)	1551.8	0.148
148	17.048(2)	9.764(1)	9.323(1)	1551.9	0.149
158	17.048(3)	9.763(1)	9.323(1)	1551.7	0.151
173	17.047(3)	9.763(1)	9.323(1)	1551.6	0.150
188	17.049(3)	9.762(1)	9.324(1)	1551.8	0.152
206	17.050(2)	9.762(1)	9.323(1)	1551.7	0.155
220	17.049(2)	9.762(1)	9.323(1)	1551.6	0.154
238	17.051(2)	9.762(1)	9.323(1)	1551.8	0.156
255	17.051(2)	9.761(1)	9.323(1)	1551.7	0.158
268	17.052(2)	9.760(1)	9.323(1)	1551.6	0.161
298	17.053(2)	9.760(1)	9.323(1)	1551.7	0.162
313	17.054(1)	9.759(2)	9.324(1)	1551.8	0.165
343	17.057(1)	9.759(2)	9.325(1)	1552.2	0.168
373	17.060(1)	9.760(2)	9.325(1)	1552.7	0.170
403	17.062(1)	9.759(2)	9.325(1)	1552.7	0.174
468	17.062(1)	9.759(2)	9.325(1)	1552.7	0.174
493	17.066(1)	9.760(1)	9.327(1)	1553.5	0.176
548	17.070(2)	9.760(5)	9.327(2)	1553.9	0.181

The numbers in parentheses represent the estimated standard error (1 σ) of the last decimal quoted

In most previous studies (Hochella et al., 1979, Mirwald, 1981) a decrease of the c -axis with temperature is reported, which is different from what is found in this investigation. In addition, the previous studies describe an increase of the b -axis with temperature, whereas in this study the b -axis decreases. These discrepancies indicate that the temperature range and the chemical composition of the cordierite, especially the channel occupants, have a strong bearing on the nature of the thermal expansion.

Bond length and angle variation

Variation of the distortion index Δ [$\Delta = 1.094 (a-b \cdot \sqrt{3})$] is connected with a distortion of the six-membered ring (Armbruster, 1986), induced by variable Na–O₂ interaction. Indeed, the shortest Ch0–O distance, Na–O₂₆, increases with temperature (Table 4). The longest distance, Na–O₂₃, becomes significantly shorter while Na–O₂₁ changes only slightly and unsystematically. The tetrahedral bond lengths (T–O) and angles (O–T–O) around T₂₁ and T₂₃ remain the same within 3 σ . Only the ring tetrahedron around T₂₆ distorts with increasing temperature. The tetrahedral angle O₂₁–T₂₆–O₂₆ expands and the bond T₂₆–O₂₆

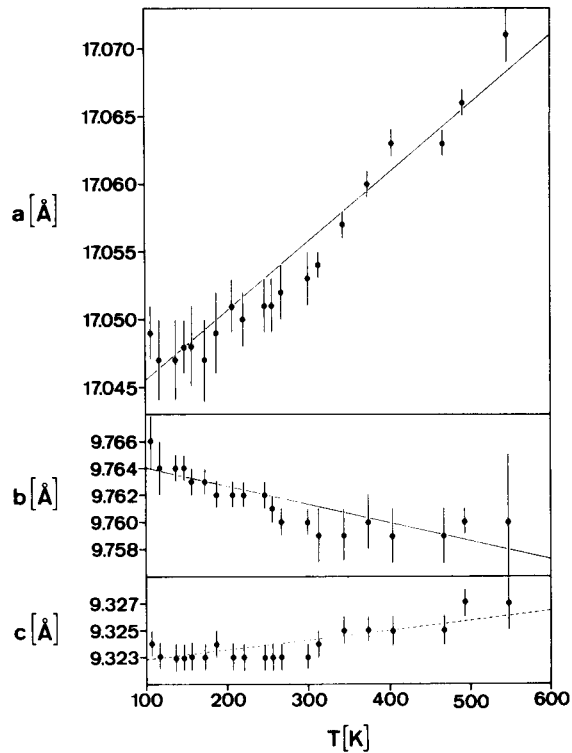


Fig. 1. Variation of cell dimensions of the Haddam cordierite with temperature between 110 and 550 K. Error bars indicate 2 standard deviations. Solid lines result from linear regression analyses and are statistically significant (Armbruster, 1983) on the basis of a chi-square-test (95% probability level). The dashed contour does not satisfy the statistical test but illustrates a trend

decreases. As O_{26} moves away from Ch_0 the concave angle $T_{23}-O_{26}-T_{26}$ (Fig. 2) has to increase. In agreement with previous work (Hochella et al., 1979) all other tetrahedral bond lengths remain essentially invariant (within 3σ) and only the M octahedron expands. Both Wallace and Wenk (1980) and Hochella et al. (1979) came to the conclusion that an expansion of the M octahedron, either caused by rising temperature or by substitution of larger cations at M, is responsible for a slight opposite rotation of the six-membered rings of tetrahedra. This twisting is associated with a change in certain T-O-M and T-O-T angles and is also observed in the present study.

Temperature factors

If the isotropic equivalents (B_{eq}) of individual temperature factors for positions occupied by only one chemical species are plotted against the

Table 4. Selected bond lengths [Å], T–O–T, O–T–O, and T–O–M angles [°] for the Haddam cordierite at various temperatures. Standard deviations given in parentheses for Haddam 500 K refer also to the Haddam 100 and 300 K data

Dist./angl.	Mult.	Haddam 100 K	Haddam 300 K	Haddam 500 K	Dist./angl.	Mult.	Haddam 100 K	Haddam 300 K	Haddam 500 K
T ₁ 1–O ₁ 1	(2)	1.747	1.746	1.746(1)	T ₂ 6–O ₁ 6	(2)	1.765	1.766	1.766(1)
–O ₁ 3'	(2)	1.748	1.746	1.745(1)	–O ₂ 1	(1)	1.710	1.710	1.708(1)
Mean		1.7475	1.7460	1.7455	–O ₂ 6	(1)	1.716	1.714	1.709(1)
O ₁ 3''–T ₁ 1–O ₁ 3'	(1)	109.80	109.67	109.40(3)	Mean		1.7390	1.7390	1.7373
O ₁ 1–T ₁ 1–O ₁ 3''	(2)	95.36	95.61	95.88(4)	O ₁ 6–T ₂ 6–O ₁ 6m	(1)	105.90	105.91	105.78(5)
–O ₁ 3'	(2)	124.91	124.77	124.61(4)	–O ₂ 6	(2)	108.64	108.48	108.45(4)
–O ₁ 1'	(1)	109.26	109.12	109.08(4)	–O ₂ 1	(2)	110.76	110.66	110.54(4)
Mean		109.93	109.93	109.91	O ₂ 1–T ₂ 6–O ₂ 6	(1)	111.94	112.40	112.84(1)
T ₁ 6–O ₁ 6	(4)	1.626	1.624	1.624(1)	Mean		109.44	109.43	109.43
O ₁ 6–T ₁ 6–O ₁ 6'	(2)	119.17	119.18	119.17(4)	T ₂ 1–O ₂ 1–T ₂ 6	(2)	172.91	172.96	173.40(12)
–O ₁ 6'''	(2)	110.92	110.87	110.72(4)	T ₂ 1–O ₂ 3–T ₂ 3	(2)	180.00	179.68	179.33(10)
–O ₁ 6'	(2)	98.95	98.99	99.13(3)	T ₂ 3–O ₂ 6–T ₂ 6	(2)	160.94	161.78	162.44(8)
Mean		109.68	109.67	109.67	Mean		171.28	171.47	171.72
T ₂ 1–O ₁ 1	(2)	1.632	1.630	1.631(1)	T ₂ 1–O ₁ 1–T ₁ 1	(2)	127.98	128.11	128.15(5)
–O ₂ 3'	(1)	1.608	1.608	1.607(1)	T ₂ 6–O ₁ 6–T ₁ 6	(2)	133.00	132.96	132.99(5)
–O ₂ 1	(1)	1.590	1.588	1.588(1)	T ₂ 3–O ₁ 3–T ₁ 1	(2)	128.23	128.42	128.69(5)
Mean		1.6156	1.6148	1.6143	Mean		129.77	129.83	129.94
O ₁ 1–T ₂ 1–O ₁ 1m	(1)	108.21	108.12	107.96(4)	T ₁ 1–O ₁ 1–M	(2)	95.17	94.93	94.80(4)
–O ₂ 1	(2)	109.88	109.93	109.91(4)	T ₁ 1–O ₁ 3–M	(2)	94.11	94.13	94.00(4)
–O ₂ 3'	(2)	108.41	108.46	108.51(4)	T ₁ 6–O ₁ 6–M	(2)	95.07	95.10	95.05(4)
O ₂ 1–T ₂ 1–O ₂ 3'	(1)	111.95	111.85	111.96(6)	T ₂ 1–O ₁ 1–M	(2)	136.73	136.80	136.88(5)
Mean		109.46	109.46	109.46	T ₂ 3–O ₁ 3–M	(2)	137.28	137.08	136.96(5)
T ₂ 3–O ₁ 3	(2)	1.631	1.632	1.630(1)	T ₂ 6–O ₁ 6–M	(2)	131.48	131.52	131.56(4)
–O ₂ 3	(1)	1.615	1.612	1.612(1)	Mean		114.97	114.93	114.88
–O ₂ 6	(1)	1.585	1.579	1.580(1)	M–O ₁ 6	(2)	2.131	2.133	2.135(1)
Mean		1.6155	1.6138	1.6130	–O ₁ 1'	(2)	2.099	2.105	2.110(1)
O ₁ 3–T ₂ 3–O ₁ 3m	(1)	108.54	108.54	108.43(5)	–O ₁ 3'	(2)	2.128	2.132	2.135(1)
–O ₂ 6	(2)	111.84	111.74	111.71(4)	Mean		2.1193	2.1233	2.1267
–O ₂ 3	(2)	107.23	107.23	107.29(4)	Na–Ch1/4	(2)	2.3309	2.3309	2.3320(5)
O ₂ 6–T ₂ 3–O ₂ 3	(1)	109.96	110.17	110.20(7)	Na–O ₂ 6	(2)	2.490	2.501	2.507(1)
Mean		109.44	109.44	109.44	Na–O ₂ 3	(2)	2.898	2.891	2.885(1)
					Na–O ₂ 1	(2)	2.707	2.705	2.709(1)
					Mean		2.6067	2.6080	2.6085

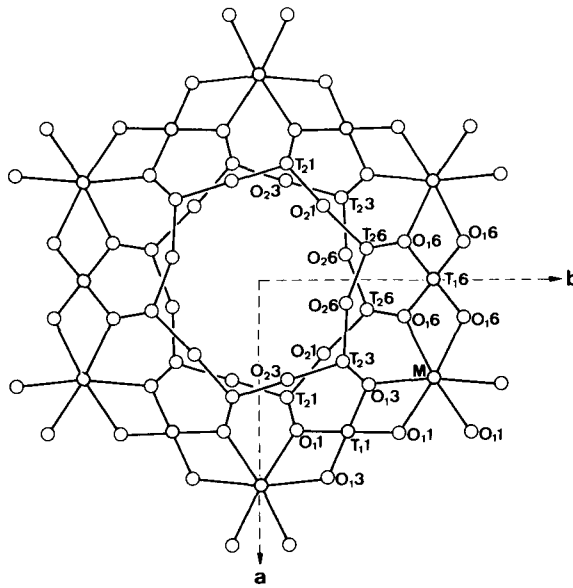


Fig. 2. Portion of the cordierite structure viewed down *c* along a structural channel. Atom positions are labelled according to the nomenclature of Cohen et al. (1977). Na centers the six-membered ring of tetrahedra at the height $z = 0$ (Ch0). Water molecules are positioned at the structural cavities with $z = 1/4$ (Ch1/4)

temperature, three groups of curves can be distinguished (Fig. 3): a) Thermal vibrations of tetrahedrally coordinated cations increase the least, and extrapolation to 0 K yields a mean value of $B_{\text{eq}} = 0.18 \text{ \AA}^2$. There is no significant difference between Si ($T_{1,6}$, $T_{2,1}$ and $T_{2,3}$) and Al ($T_{2,6}$). b) Oxygen atoms of the type O_1 linking two tetrahedra to an octahedron show an intermediate slope with temperature, and extrapolation to 0 K yields a mean value of $B_{\text{eq}} = 0.28 \text{ \AA}^2$. c) Oxygen atoms of the type O_2 within the six-membered ring show the largest increase with temperature and B_{eq} at 0 K tends to a mean value of 0.4 \AA^2 .

The temperature factors in the White Well cordierite (Hochella et al., 1979) for which refinements at 297, 648 and 1048 K are available, show the same trend. The mean square vibrational amplitude ($\overline{u^2} = B_{\text{eq}}/8 \cdot \pi^2$) at temperatures above the Debye temperature can be calculated (Willis and Pryor, 1975) according to

$$\overline{u^2} = (3 \cdot \hbar^2 \cdot T) / (m \cdot k_b \cdot T_D^2), \quad (1)$$

where \hbar is the Planck constant divided by 2π ($1.05 \cdot 10^{-34} \text{ Js}$), k_b is the Boltzmann constant ($1.38 \cdot 10^{-23} \text{ J/K}$), m is the mean atomic mass and T_D is the Debye temperature. At absolute zero Eq. (1) reduces (Willis and Pryor, 1975) to

$$\overline{u^2} = (3 \cdot \hbar^2) / (4 \cdot m \cdot k_b \cdot T_D) = (3.60 \cdot 10^{-22}) / (MG \cdot T_D) \quad (2)$$

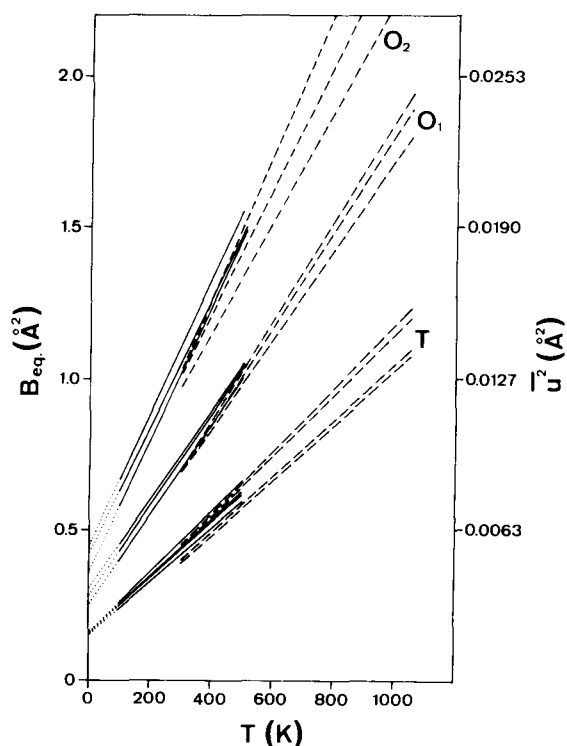


Fig. 3. Isotropic equivalent temperature factors (B_{eq}) for the Haddam cordierite (solid lines), and the natural White Well cordierite of Hochella et al. (1979) (dashed lines) plotted as function of temperature. Dotted lines are extrapolated to 0 K. Only temperature factors of positions which are occupied by only one chemical species are displayed

and for a Mg-cordierite with a mean molar weight per atom (MG) of 0.0193 kg Eq. (2) becomes

$$\overline{u^2} (\text{\AA}^2) = 1.87/T_D.$$

T_D for cordierite, however, is unknown but judging from other substances (e.g. Herrmann and Preppernau, 1979) the Debye temperature of cordierite ranges between 500 and 1500 K and is probably closer to 1500 K, leading to a zero point motion between 0.0012 and 0.0037 \AA^2 . The mean extrapolated value for $\overline{u^2}$ (Fig. 3) of about 0.003 \AA^2 is rather high. A disorder model accounts at least partly for this discrepancy. Statistical occupancy of Ch0 by Na and of Ch1/4 by H_2O in the Haddam cordierite leads to distortions, which are cooperative and involve the whole framework. The same is true for the M position which is randomly filled by Mg, Fe and Li and the T_11 site which hosts Al and Be. Thermal vibration

parameters extrapolated to 0 K reflect this positional disorder. Therefore, the expression 'displacement vectors' seems to be a more appropriate term than vibrational amplitudes. In addition, the influence of an improper extinction model on the displacement vectors is still uncertain, particularly if the extinction coefficient is highly temperature dependent as in the present study (Table 1). It is also puzzling why the White Well data (Hochella et al., 1979) extrapolate to similar $\overline{u^2}$ values even though this cordierite is almost a Mg-end member and alkali-poor. The natural White Well crystal, however, contained volatiles which were partly released during the experiment causing a significant change of some fractional coordinates and cell dimensions before and after the heating cycle. In addition, Hochella et al. (1979) neglected scattering from Ch1/4, thus the observed high values of $\overline{u^2}$ versus temperature might be an artifact.

The isotropic temperature factor of T₁₁, partially occupied by Al and Be, shows a significantly steeper slope when plotted against the temperature than the ones of other T-positions, a phenomenon also observed for the essentially Be-free White Well and Dolni Bory cordierites (Hochella et al., 1979). Similarly, all of the B_{eq} for the M site in the Haddam, White Well, and Dolni Bory specimens are between those of T₁₁ and O₁, and show no dependence on Fe → Mg substitution. It is suggested that these effects are related to the strong angular distortions around M and around the tetrahedron T₁₁, which shares edges with the M octahedron. The second edge-linked tetrahedron T₁₆(Si) is significantly less distorted and consequently possesses a lower B_{eq} .

All individual anisotropic temperature factors increase fairly linear with temperature, except U_{11} and U_{22} of O₂₆, U_{22} of Ch0(Na) and U_{11} of Ch1/4(H₂O). The latter exception will not be further discussed because the occupation and orientation of H₂O and other volatiles is only poorly defined (Goldman et al., 1977, Carson et al., 1982). The longest axis of the thermal O₂₆ ellipse in (001) is oriented towards Na. Compared to the increase between 100 and 300 K, the O₂₆ vibration in the direction of Na, primarily reflected in the term U_{22} , increases at a greater rate than expected between 300 and 500 K. Simultaneously O₂₆ vibrates less parallel to the T–O bonds. U_{22} of Na is also directed towards O₂₆ and increases at a greater rate between 300–500 K than between 100 and 300 K. As a matter of fact, these atoms are also involved in the largest changes of bond lengths and angles (Table 4).

Channel occupants in Ch1/4

Difference Fourier maps (Fig. 4) were obtained from structure factor calculations without considering channel constituents at the sites Ch0 and Ch1/4. The oxygen of the water molecule in Ch1/4 exhibits an almost circular electron distribution in the (100) sections. In (010) projections the

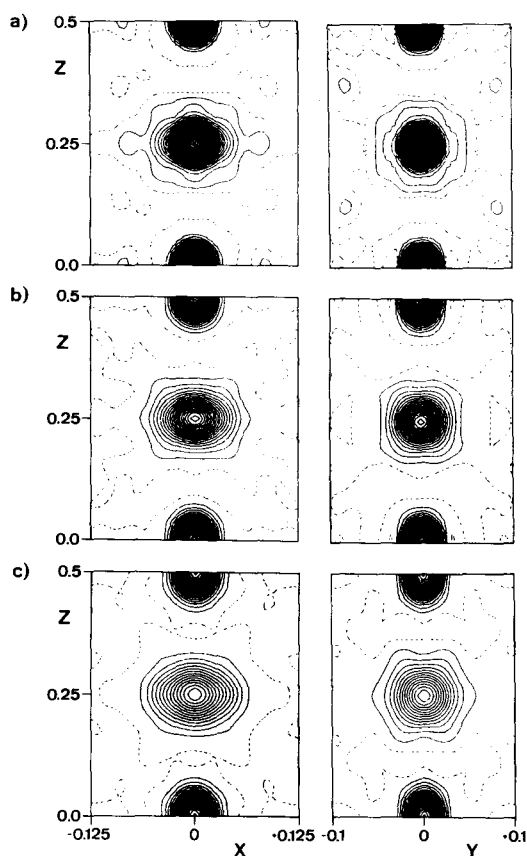


Fig. 4. Difference Fourier maps of the Haddam cordierite calculated without considering channel occupants at Ch0 and Ch1/4. All sections are through the center of the cavity. Negative contours are omitted, dashed contours indicate $0 \text{ e}/\text{\AA}^3$, solid contours are positive with an interval of $0.5 \text{ e}/\text{\AA}^3$. The following maximum electron densities are observed within the structural channels: a) 100 K, at Ch0: $12.6 \text{ e}/\text{\AA}^3$, at Ch1/4: $11.5 \text{ e}/\text{\AA}^3$; b) 300 K, at Ch0: $9.7 \text{ e}/\text{\AA}^3$, at Ch1/4: $6.5 \text{ e}/\text{\AA}^3$; c) 500 K, at Ch0: $7.2 \text{ e}/\text{\AA}^3$, at Ch1/4: $4.6 \text{ e}/\text{\AA}^3$. Left: projection along the *b*-axis, right: projection along the *a*-axis

density becomes elongated parallel to **a**. With increasing temperature the electron densities at Ch0 and Ch1/4 become less compact (Fig. 4).

Goldman et al. (1977) distinguish two water orientations. 'type I water' with the H–H vector parallel to **c** and 'type II water' characteristic of Narich cordierites where the H–H vector is parallel to **b**. Assuming that each Na in Ch0 is coordinated by two water molecules of 'type II' in Ch1/4 at $z = 1/4$ and $z = -1/4$, respectively, then the Haddam cordierite possesses predominantly water of 'type II' and only minor amounts of 'type I' water. This is in agreement with the single-crystal IR-results of Goldman et al.

(1977). Some readers may be tempted to discuss the dent visible in the 500 K (100) difference Fourier section of the Haddam cordierite, but according to the detailed single-crystal IR-work of Aines et al. (1984) 'random motion of gas-like water molecules predominates at high temperature and is already significant at 500 K.

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