

High-temperature crystal chemistry of hydrous Mg- and Fe-cordierites

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Abstract

Structural refinements have been completed for a Mg-rich cordierite using data recorded at 24°, 375°, 775° and 24°C (after heating to 775°) and for an Fe-rich cordierite at 24° and 375°C. The mean T-O bond lengths in both cordierites remain unchanged but the mean octahedral bonds (M-O) lengthen upon heating. The unusually low thermal expansion of the Mg-cordierite is the result of its relatively "rigid" tetrahedral framework and the anisotropic expansion of octahedra isolated from each other. This anisotropic expansion leads to a slight rotation of the six-membered rings, a concomitant collapse of the structure parallel to *c*, and an expansion parallel to *a* and *b*. In the Fe-cordierite, the octahedron is more flattened, resulting in *c* being smaller and *a* and *b* being larger than the cell dimensions of the Mg-cordierite. Upon heating Fe-cordierite, there is no evidence for a rotation of the rings, and *a*, *b*, and *c* increase as the M-O bonds expand.

X-ray $\Delta\rho$ maps calculated for the Mg-cordierite showed approximate positions and relative amounts of channel constituents. The peak ascribed to the alkali and other atoms that centers the six-membered rings becomes elongated parallel to *c* upon heating through 375°C. However, the peak ascribed to the oxygen associated with H₂O in the 24° and 375° maps is absent in the 775°C maps. It reappears in maps computed from the 24° (after heating) data. In both cordierites, small amounts of hematite were produced during heating (prematurely halting data collection on the Fe-cordierite), and apparently formed by combination of octahedral and channel iron with oxygen from the channel water molecules.

A re-examination of the water orientation in the channels of the Mg-cordierite using neutron and X-ray $\Delta\rho$ maps does not clearly show either type I [H-O-H in the (100) plane with the H-H vector parallel to *c*] or type II [H-O-H in the (100) plane with the H-H vector parallel to *b*] water, as previously suggested by spectroscopic studies. Instead, our $\Delta\rho$ maps indicate that the water molecule lies in a plane tilted ~29° from (100) and that the H-H vector is tilted ~19° from *c*.

Introduction

Cordierite, (Mg,Fe)₂Al₄Si₅O₁₈·*n*H₂O, has attracted the interest of mineralogists and ceramists because of

its widespread formation in moderate- to high-grade metamorphic rocks, its occurrence in a variety of structural states involving different degrees of Al/Si ordering, and its unusually low thermal expansion. Ceramists have found a number of applications for Mg-cordierite as a thermal shock resistant material.

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L	FO	FC	L	FU	FC	L	FU	FC	L	FO	FC	L	FU	FC	L	FO	FC	L	FU	FC	L	FO	FC	L	FU	FC	L	FO	FC	L	FU	FC				
4	167	147	10	546	540	1	575	-578	H= 14	K= 0	H= 15	K= 7	0	468	-470	1	67	117																		
6	110	-102	11	73	-131	2	106	-21	0		0		1	145	-144	2	761	769																		
7	201	190				3	328	-314	0	887	-934	0	114	89	2	54	42	H= 20	K= 0																	
8	70	27	H= 11	K= 3	4	576	-353	2	212	175	1	7	525	-528	3	115	-134																			
H= 9	K= 11	0	101	-128	5	479	-473	10	270	269	3	720	646	4	229	-240	0	900	899																	
0	630	623	2	162	178	6	269	235	H= 14	K= 2	5	340	-339	5	125	-129	2	105	-113																	
1	801	-789	3	1484	-1516	7	276	-288	0	687	695	H= 15	K= 4	6	63	31	4	839	843																	
2	401	-419	4	793	-804	8	225	-235	1	95	-1	0	117	113	7	116	-82	6	115	-103																
3	523	-515	5	672	-635	9	825	837	0	95	-1	H= 17	K= 7	8	593	-375	H= 20	K= 2																		
4	295	281	6	365	349	0	825	837	1	95	-1	0	238	244	1	422	423																			
H= 16	K= 0	7	109	110	1	579	588	2	473	483	0	117	113	2	238	244	4	335	-341																	
0	2808	-2713	8	196	-212	3	768	-772	4	170	174	0	660	-659	3	215	220	5	227	229																
1	144	143	9	577	-581	4	269	272	5	256	276	1	114	92	4	315	287	6	201	170																
2	538	-535	11	640	-634	5	454	436	6	603	-616	2	549	-556	5	85	-57	7	409	400																
3	527	-534	H= 11	K= 5	6	717	-711	7	127	-90	3	274	250	6	246	-248	H= 20	K= 4																		
4	527	-534	0	964	-1002	8	493	499	8	328	321	4	562	-565	7	499	482																			
5	1109	-1132	0	125	-103	9	601	591	10	698	-675	H= 16	K= 0	8	499	482	H= 17	K= 9	0	242	231															
6	361	360	1	259	224	H= 12	K= 10	H= 14	K= 4	0	208	208	0	1801	1801	1	152	-131	1	646	645															
H= 10	K= 2	2	382	-396	0	525	522	0	871	877	4	518	521	2	496	490	4	167	188																	
0	1431	1437	3	241	-245	1	202	-177	2	540	549	6	751	774	3	176	151	5	560	552																
1	138	-137	4	593	-597	2	185	-185	3	475	966	8	1065	1067	H= 16	K= 0	6	414	410																	
2	838	841	5	161	174	3	360	-357	4	84	-71	H= 16	K= 2	2	492	-444	H= 20	K= 0																		
3	1761	1772	6	127	-120	4	845	-874	5	65	-72	0	504	-521	4	232	-230																			
4	415	430	H= 11	K= 7	7	376	-361	6	162	168	7	492	485	5	271	-251	0	438	-446																	
5	56	1	0	589	-614	0	1025	-1071	8	202	200	0	271	-251	6	258	-250	1	123	-124																
6	1068	1069	1	617	-614	1	128	137	9	651	680	H= 18	K= 2	8	162	-130	2	92	92																	
7	131	135	2	617	-614	2	338	322	10	150	-151	0	66	-67	7	265	-261	3	87	90																
8	467	482	3	593	-597	3	360	-357	11	144	-154	1	801	-812	8	474	459	H= 21	K= 1																	
H= 10	K= 4	4	161	174	4	845	-874	0	244	222	H= 16	K= 4	0	403	-400	0	681	681	H= 21	K= 1																
0	771	-819	5	161	174	5	65	-72	1	275	-296	0	328	-326	1	336	-334	0	350	333																
1	317	-326	6	127	-120	6	162	168	2	275	-296	H= 16	K= 4	2	909	-934	0	733	-731																	
2	254	-262	7	376	-361	7	141	153	3	189	-192	0	403	-400	3	250	-253	1	150	-148																
3	836	853	8	382	-395	8	665	-653	4	544	540	0	328	-326	4	430	-437	2	150	-151																
4	1619	-1637	9	142	174	9	665	-653	5	203	-201	0	403	-400	5	180	-187	3	150	-151																
5	243	242	H= 11	K= 9	10	150	-151	6	638	-646	1	66	-67	6	265	-261	4	350	-346																	
6	152	132	0	608	-625	10	144	-152	7	221	-242	0	214	-242	7	265	-261	5	177	105																
7	373	-369	1	273	265	11	177	-159	8	608	-646	1	115	151	8	474	459	H= 21	K= 3																	
8	675	-672	2	123	-102	H= 13	K= 3	9	303	287	2	667	660	H= 18	K= 4	0	216	217																		
9	210	233	3	564	532	0	762	-782	3	386	399	0	430	-416	1	322	319	0	216	217																
10	354	-348	4	316	304	1	386	399	H= 14	K= 8	4	222	-247	1	341	-354	1	128	124																	
11	346	342	5	124	-87	2	499	515	0	257	222	0	222	-247	2	154	-125	2	307	317																
H= 10	K= 6	6	122	137	3	526	557	1	87	28	H= 16	K= 6	3	163	-169	3	163	-169	3	612	605															
0	811	819	H= 11	K= 11	4	378	364	2	547	550	0	1031	-1047	4	262	-244	4	467	456																	
1	112	310	5	526	557	5	526	557	3	315	-311	1	279	291	5	323	316	H= 21	K= 5																	
2	662	-656	6	378	364	6	378	364	4	472	441	2	279	291	6	323	316	0	387	-385																
3	169	-188	7	255	248	7	255	248	5	453	441	0	1031	-1047	7	323	316	0	387	-385																
4	151	-153	8	519	-522	8	519	-522	6	472	441	1	279	291	8	1524	1532	0	333	-333																
5	176	-194	9	179	257	9	179	257	7	453	441	0	1031	-1047	9	1524	1532	1	475	-464																
6	311	321	10	250	255	10	250	255	H= 14	K= 10	8	421	-424	1	229	-204	2	475	-464																	
7	320	329	H= 13	K= 5	0	105	-62	0	105	-62	0	144	-139	4	1216	1216	3	281	-286																	
8	618	-600	1	217	220	1	217	220	1	394	-395	5	144	-139	5	99	-115	4	356	-357																
H= 10	K= 8	H= 12	K= 0	2	71	-148	2	71	-148	2	345	-357	H= 16	K= 8	6	474	414	H= 18	K= 6	H= 22	K= 0															
0	628	-658	0	953	955	0	953	955	3	623	-630	0	103	-105	7	429	414	0	449	-525																
1	185	-180	1	2788	-2770	1	2788	-2770	4	429	414	1	76	58	8	115	75	2	475	456																
2	232	216	2	639	-679	2	639	-679	H= 15	K= 1	2	491	-514	2	491	-514	H= 22	K= 2																		
3	464	-456	3	1670	-16																															

L FO FC AC BC L FO FC AC BC L FO FC AC BC L FO FC AC BC L FO FC AC BC L FO FC AC BC L FO FC AC BC

Main table body with columns L, FO, FC, AC, BC and rows of numerical data. Includes sub-headers like 'M= 3 K= 7', 'M= 5 K= 11', etc., indicating different groups or parameters within the data.

M= 1 K= 11

L					L					L					L					L									
FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC	K	FO	FC	AC	BC	K					
899	855	854	-18	M	1072	1035	1034	-34	M	581	584	-585	-13	M	303	371	-316	-10	M	303	371	-316	-10	M	303	371	-316	-10	M
852	850	832	-14	M	1110	1053	1042	-34	M	587	583	-480	-70	M	307	373	-317	-10	M	307	373	-317	-10	M	307	373	-317	-10	M
830	835	815	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M
826	830	810	-70	M	1201	1126	1103	-34	M	587	583	-480	-70	M	313	379	-324	-10	M	313	379	-324	-10	M	313	379	-324	-10	M

Table with columns labeled L, FU, FC, L, FU, FC, L, FU, FC, L, FU, FC, L, FU, FC, L, FU, FC, L, FU, FC. Each column contains numerical data points and alphanumeric labels (H, K) indicating specific values or conditions for each row.

Table with columns: L, FD, FC, L, FU, FC, L, FU, FC, L, FD, FC, L, FD, FC, L, FU, FC, L, FD, FC, L, FU, FC. Rows contain numerical data for various indices (e.g., 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19).