

MgSiO₃ (ilmenite-type): single crystal X-ray diffraction study

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A structure refinement of MgSiO₃ with the ilmenite-type structure has been carried out with single crystal X-ray diffraction techniques. Magnesium and silicon atoms are completely ordered in the structure. The magnesium silicates with higher transition pressures have smaller MgO₆ and larger SiO₆ octahedra than those with lower transition pressures, resulting in more compact arrangements of oxygen atoms in the higher-pressure phases. Cation-oxygen distances of ilmenite-type structures systematically change depending on the ionic radii of cations, and this relation is followed for Mg-O and Si-O distances of ilmenite-type MgSiO₃. The degree of distortion of cation octahedra in the ilmenite-type structures is independent of the kinds of cations but the shifts of cations from the centers of octahedra systematically change as a function of ionic radius.

Introduction

A "hexagonal" modification of MgSiO₃ was first synthesized by Kawai *et al.* (1974) at ultra-high-pressure. Detailed investigations by Ito and Matsui (1974) revealed that it is trigonal (space group $R\bar{3}$) with the ilmenite-type structure.

In a series of high-pressure phase transformations in MgSiO₃, it has been established that the ilmenite-type structure is stabilized in the pressure range approximately from 210 to 250 kbar at 1100°C (Ito and Yamada, 1981), suggesting that the ilmenite structure with octahedrally coordinated Si is one of the important constituents of the deep mantle. It has also been observed that the solid solution of Fe for Mg in the ilmenite-type phase is limited to only 10 mole percent (Ito and Yamada, 1981), whereas that of 2Al for Mg plus Si is more extensive, resulting in the pyrope composition of 3MgSiO₃·Al₂O₃ (Liu, 1977). In this context, the details of the structure of ilmenite-type MgSiO₃ are basic to an understanding of the stability of silicate ilmenite and to mantle mineralogy.

There are only a few structure determinations for high-pressure compounds in which Si atoms are octahedrally coordinated; *e.g.*, SiO₂ stishovite

(Baur and Khan, 1971, and Sinclair and Ringwood, 1978) and perovskite-type MgSiO₃ (Ito and Matsui, 1978, and Yagi *et al.*, 1978); all of these studies except that of Sinclair and Ringwood (1978) were performed by powder X-ray diffraction. Structure analysis of ilmenite-type MgSiO₃ is thus basic to an understanding of the SiO₆ octahedral configuration. In the case of ilmenite-type structures, however, single crystal analysis is indispensable because many crystallographically non-equivalent reflections with the same Bragg angles are superposed in the powder diffraction pattern. In the present study the crystal structure of ilmenite-type MgSiO₃ was therefore refined by single-crystal X-ray diffraction techniques.

Experimental

The specimen used in this work was synthesized at approximately 220 kbar pressure and 1550°C with the run time of 20 minutes, using a uniaxial split-sphere-type high-pressure apparatus (Kawai *et al.*, 1973) with synthetic clinoenstatite as starting material. The single crystal specimen which was used in the crystal structure analysis is platy in shape parallel to (001), approximately 40 μm in thickness and 90 μm in diameter. It is transparent

Table 4

Observed and calculated structure factors for ilmenite-type $MgSiO_3$ ($\times 10$).

*-marked reflections have been eliminated in the least squares refinement.

H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C
-6	0	0	423	401	4	-7	2	280	-287	6	-10	4	174	-168
-3	0	0	1191	1236	7	-7	2	141	-142	1	-9	4	162	-139
-8	1	0	160	150	2	-6	2	24*	-32	4	-9	4	111	-103
-5	1	0	391	395	5	-6	2	71*	-44	7	-9	4	70*	-19
-2	1	0	557	609	8	-6	2	79*	-57	2	-8	4	184	-183
-7	2	0	344	328	3	-5	2	69*	-59	5	-8	4	223	-207
-4	2	0	521	546	6	-5	2	135	-124	8	-8	4	183	-174
-9	3	0	144	172	9	-5	2	134	-105	3	-7	4	296	-279
-6	3	0	527	548	1	-4	2	458	-479	6	-7	4	328	-325
-8	4	0	189	196	4	-4	2	312	-326	9	-7	4	246	-235
-5	4	0	418	430	7	-4	2	102	-91	1	-6	4	270	-254
-10	5	0	190	207	10	-4	2	0*	0	4	-6	4	175	-153
-7	5	0	298	284	2	-3	2	90	-92	7	-6	4	0*	-13
-9	6	0	196	174	5	-3	2	24*	-48	10	-6	4	0*	21
-8	7	0	254	226	8	-3	2	0*	-16	2	-5	4	518	-507
6	-10	1	40*	54	3	-2	2	360	-360	5	-5	4	423	-411
1	-9	1	20*	17	6	-2	2	289	-285	8	-5	4	231	-236
4	-9	1	32*	40	9	-2	2	173	-168	3	-4	4	622	-619
7	-9	1	26*	36	1	-1	2	511	-508	6	-4	4	465	-468
2	-8	1	0*	20	4	-1	2	161	-160	9	-4	4	225	-236
5	-8	1	104	-77	7	-1	2	27*	-19	1	-3	4	522	-502
8	-8	1	111*	-117	2	0	2	89	-96	4	-3	4	268	-253
3	-7	1	97	102	5	0	2	0*	1	7	-3	4	77	-66
6	-7	1	169	170	8	0	2	18*	31	2	-2	4	836	-843
9	-7	1	178	153	5	-10	3	35*	-61	5	-2	4	454	-447
1	-6	1	24*	-42	3	-9	3	0*	-34	8	-2	4	232	-207
4	-6	1	0*	18	6	-9	3	25*	17	3	-1	4	860	-844
7	-6	1	27*	38	1	-8	3	37*	-46	6	-1	4	393	-390
10	-6	1	42*	23	4	-8	3	72*	-61	9	-1	4	154	-135
2	-5	1	69*	-34	7	-8	3	96*	-78	1	0	4	784	-797
5	-5	1	167	-171	2	-7	3	125	-124	4	0	4	363	-350
8	-5	1	129	-147	5	-7	3	147	-155	7	0	4	146	-121
3	-4	1	221	229	8	-7	3	0*	-77	2	-9	5	104*	-109
6	-4	1	218	223	3	-6	3	89	-88	5	-9	5	0*	-88
9	-4	1	130	142	6	-6	3	17*	-61	8	-9	5	0*	-16
1	-3	1	147	-147	9	-6	3	90*	-69	3	-8	5	204	188
4	-3	1	0*	32	1	-5	3	55*	62	6	-8	5	114	132
7	-3	1	30*	44	4	-5	3	53*	48	9	-8	5	0*	29
2	-2	1	257	-246	7	-5	3	19*	-26	1	-7	5	146	125
5	-2	1	186	-185	10	-5	3	32*	-46	4	-7	5	128	126
8	-2	1	83	-80	2	-4	3	348	-366	7	-7	5	100*	77
3	-1	1	163	168	5	-4	3	229	-240	2	-6	5	114*	-114
6	-1	1	138	131	8	-4	3	24*	-56	5	-6	5	0*	-28
9	-1	1	17*	72	3	-3	3	166	-164	8	-6	5	83*	53
1	0	1	129	125	6	-3	3	163	-147	3	-5	5	307	296
4	0	1	97	106	9	-3	3	119	-120	6	-5	5	178	164
7	0	1	23*	28	1	-2	3	661	657	9	-5	5	0*	44
4	-10	2	180	-181	4	-2	3	202	207	1	-4	5	251	236
2	-9	2	32*	9	7	-2	3	0*	-9	4	-4	5	127	116
5	-9	2	32*	-6	2	-1	3	766	-722	7	-4	5	24*	5
8	-9	2	80*	-47	5	-1	3	207	-215	2	-3	5	0*	15
3	-8	2	28*	36	8	-1	3	78*	-20	5	-3	5	168	151
6	-8	2	78*	1	0	0	3	390	-377	8	-3	5	154	137
9	-8	2	20*	-22	3	0	3	182	-188	3	-2	5	385	363
1	-7	2	286	-290	6	0	3	104	-131	6	-2	5	186	164

Table 4 (continued)

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC
9	-2	5	35*	64	4	-3	7	90	-78	8	-4	9	142	-135
1	-1	5	213	218	7	-3	7	71*	-43	3	-3	9	136	-133
4	-1	5	0*	-40	2	-2	7	163	157	6	-3	9	92	-95
7	-1	5	88	-93	5	-2	7	190	217	9	-3	9	24*	-29
2	0	5	366	372	8	-2	7	101*	134	1	-2	9	774	-799
5	0	5	262	255	3	-1	7	69	-82	4	-2	9	508	-500
8	0	5	126	148	6	-1	7	24*	-29	7	-2	9	169	-181
3	-9	6	137	137	9	-1	7	0*	-25	2	-1	9	105	-95
6	-9	6	37*	123	1	0	7	164	-148	5	-1	9	166	-152
1	-8	6	120*	126	4	0	7	80	-84	8	-1	9	169	-140
4	-8	6	237	229	7	0	7	19*	1	0	0	9	41*	-50
7	-8	6	188	209	2	-9	8	93*	25	3	0	9	130	-118
2	-7	6	265	262	5	-9	8	26*	32	6	0	9	42*	-80
5	-7	6	230	230	3	-8	8	46*	-97	4	-9	10	185	-163
8	-7	6	155	138	6	-8	8	0*	-47	7	-9	10	237	-205
3	-6	6	189	189	1	-7	8	233	224	2	-8	10	139	-155
6	-6	6	172	170	4	-7	8	205	220	5	-8	10	174	-186
9	-6	6	140	149	7	-7	8	73*	103	8	-8	10	161	-142
1	-5	6	387	382	2	-6	8	81	69	3	-7	10	165	-174
4	-5	6	416	419	5	-6	8	84	51	6	-7	10	89*	-61
7	-5	6	236	227	8	-6	8	93*	33	9	-7	10	0*	1
2	-4	6	720	695	3	-5	8	57*	-24	1	-6	10	317	-303
5	-4	6	463	482	6	-5	8	24*	60	4	-6	10	382	-403
8	-4	6	239	230	9	-5	8	31*	80	7	-6	10	332	-346
3	-3	6	213	188	1	-4	8	346	345	2	-5	10	312	-306
6	-3	6	196	208	4	-4	8	234	258	5	-5	10	298	-306
9	-3	6	175	167	7	-4	8	94	81	8	-5	10	175	-183
1	-2	6	824	787	2	-3	8	129	134	3	-4	10	312	-306
4	-2	6	497	517	5	-3	8	0*	10	6	-4	10	94	-105
7	-2	6	184	180	8	-3	8	0*	-32	9	-4	10	34*	-26
2	-1	6	1167	1164	3	-2	8	225	225	1	-3	10	642	-635
5	-1	6	508	506	6	-2	8	229	205	4	-3	10	586	-594
8	-1	6	212	193	9	-2	8	132*	132	7	-3	10	363	-357
0	0	6	134	-79	1	-1	8	344	354	2	-2	10	568	-570
3	0	6	215	195	4	-1	8	161	175	5	-2	10	385	-387
6	0	6	194	192	7	-1	8	100*	47	8	-2	10	155	-166
1	-9	7	0*	26	2	0	8	59*	64	3	-1	10	388	-376
4	-9	7	30*	-10	5	0	8	76	-75	6	-1	10	186	-149
7	-9	7	0*	-32	8	0	8	0*	-81	1	0	10	683	-673
2	-8	7	37*	33	3	-9	9	45*	-99	4	0	10	448	-443
5	-8	7	131	130	6	-9	9	140	-142	7	0	10	210	-220
8	-8	7	160	164	1	-8	9	104*	-95	5	-9	11	169	170
3	-7	7	24*	-28	4	-8	9	143	-129	3	-8	11	22*	-6
6	-7	7	86	-69	7	-8	9	88	-91	6	-8	11	90*	18
9	-7	7	86*	-70	2	-7	9	110	-104	1	-7	11	0*	-34
1	-6	7	76	84	5	-7	9	88*	-66	4	-7	11	0*	-9
4	-6	7	0*	-11	8	-7	9	81*	-71	7	-7	11	0*	26
7	-6	7	28*	-47	3	-6	9	147	-141	2	-6	11	291	290
2	-5	7	99	105	6	-6	9	144	-135	5	-6	11	214	206
5	-5	7	221	231	9	-6	9	25*	-71	8	-6	11	82*	64
8	-5	7	204	204	1	-5	9	342	-346	3	-5	11	77*	47
3	-4	7	136	-130	4	-5	9	346	-344	6	-5	11	20*	36
6	-4	7	89	-96	7	-5	9	188	-180	9	-5	11	25*	35
9	-4	7	24*	-61	2	-4	9	106	-121	1	-4	11	55*	57
1	-3	7	50*	55	5	-4	9	128	-123	4	-4	11	122	136

Table 4 (continued)

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC
7	-4	11	155	139	1	-3	13	183	164	8	-1	15	87*	-54
2	-3	11	354	351	4	-3	13	277	266	0	0	15	603	-628
5	-3	11	156	153	7	-3	13	201	196	3	0	15	466	-450
8	-3	11	0*	18	2	-2	13	95	77	6	0	15	212	-208
3	-2	11	108	104	5	-2	13	0*	-6	2	-8	16	95	-92
6	-2	11	0*	10	8	-2	13	23*	-21	5	-8	16	31*	-57
1	-1	11	267	285	3	-1	13	182	180	3	-7	16	180	-168
4	-1	11	304	309	6	-1	13	119	120	6	-7	16	239	-228
7	-1	11	200	213	1	0	13	247	254	1	-6	16	96*	-85
2	0	11	209	204	4	0	13	231	237	4	-6	16	93*	-63
5	0	11	79*	43	7	0	13	112	110	7	-6	16	24*	-15
8	0	11	22*	-9	3	-8	14	234	237	2	-5	16	172	-183
3	-9	12	0*	52	6	-8	14	192	179	5	-5	16	92	-96
6	-9	12	37*	78	1	-7	14	83*	-4	8	-5	16	0*	-39
1	-8	12	105*	79	4	-7	14	0*	15	3	-4	16	314	-303
4	-8	12	84	30	7	-7	14	108*	55	6	-4	16	251	-294
7	-8	12	0*	5	2	-6	14	25*	101	1	-3	16	142	-149
2	-7	12	20*	31	5	-6	14	101	123	4	-3	16	94	-108
5	-7	12	0*	47	8	-6	14	96*	95	7	-3	16	73*	-40
8	-7	12	97*	59	3	-5	14	320	319	2	-2	16	204	-221
3	-6	12	178	179	6	-5	14	179	168	5	-2	16	111*	-104
6	-6	12	140	136	1	-4	14	123	108	8	-2	16	37*	-59
9	-6	12	24*	33	4	-4	14	112	108	3	-1	16	320	-322
1	-5	12	123	135	7	-4	14	26*	85	6	-1	16	230	-223
4	-5	12	119	106	2	-3	14	262	264	1	0	16	278	-266
7	-5	12	84*	87	5	-3	14	273	260	4	0	16	177	-170
2	-4	12	75*	-61	8	-3	14	147	174	7	0	16	56*	-67
5	-4	12	0*	-13	3	-2	14	283	274	3	-8	17	0*	14
8	-4	12	0*	29	6	-2	14	33*	76	1	-7	17	129	123
3	-3	12	327	327	1	-1	14	278	277	4	-7	17	120	102
6	-3	12	143	150	4	-1	14	158	157	7	-7	17	50*	43
9	-3	12	0*	4	7	-1	14	90*	66	2	-6	17	118	-126
1	-2	12	220	214	2	0	14	391	395	5	-6	17	85*	-79
4	-2	12	187	176	5	0	14	318	312	3	-5	17	22*	38
7	-2	12	146	128	1	-8	15	102*	-107	6	-5	17	38*	42
2	-1	12	191	-172	4	-8	15	78*	-92	1	-4	17	121	128
5	-1	12	0*	-24	7	-8	15	34*	-88	4	-4	17	48*	51
8	-1	12	30*	32	2	-7	15	147	-150	7	-4	17	24*	-30
0	0	12	475	495	5	-7	15	187	-186	2	-3	17	20*	-68
3	0	12	309	319	8	-7	15	112	-121	5	-3	17	31*	-24
6	0	12	94	101	3	-6	15	261	-235	8	-3	17	37*	12
4	-9	13	103	99	6	-6	15	169	-173	3	-2	17	71	92
2	-8	13	34*	60	1	-5	15	142	-106	6	-2	17	88	101
5	-8	13	0*	-11	4	-5	15	93	-99	1	-1	17	16*	42
3	-7	13	140	125	7	-5	15	39*	-106	4	-1	17	83*	-68
6	-7	13	115	123	2	-4	15	314	-304	7	-1	17	105	-100
1	-6	13	96*	73	5	-4	15	242	-233	2	0	17	32*	23
4	-6	13	190	183	8	-4	15	99	-86	5	0	17	17*	15
7	-6	13	186	195	3	-3	15	461	-442	4	-8	18	0*	7
2	-5	13	22*	55	6	-3	15	314	-264	2	-7	18	0*	25
5	-5	13	77*	-45	1	-2	15	81	-96	5	-7	18	84*	22
8	-5	13	90*	-75	4	-2	15	114	-107	3	-6	18	32*	-66
3	-4	13	224	220	7	-2	15	144	-117	6	-6	18	27*	-51
6	-4	13	175	161	2	-1	15	370	-396	1	-5	18	103*	-74
9	-4	13	111*	98	5	-1	15	213	-208	4	-5	18	0*	-54

Table 4 (continued)

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	F
7	-5	18	0*	-34	3	-2	20	103	110	3	-2	23	103*	-146
2	-4	18	103	119	6	-2	20	112*	114	6	-2	23	168	-148
5	-4	18	89	78	1	-1	20	191	189	1	-1	23	141	-134
8	-4	18	0*	7	4	-1	20	201	189	4	-1	23	0*	-52
3	-3	18	72*	-119	2	0	20	33*	81	2	0	23	49*	-89
6	-3	18	23*	-35	5	0	20	0*	-27	5	0	23	0*	-44
1	-2	18	153	-149	3	-6	21	25*	-51	1	-5	24	24*	34
4	-2	18	118	-109	6	-6	21	49*	-62	4	-5	24	26*	23
7	-2	18	25*	-63	1	-5	21	159	-182	2	-4	24	48*	-129
2	-1	18	184	175	4	-5	21	198	-193	5	-4	24	86*	-91
5	-1	18	97*	79	2	-4	21	177	-162	3	-3	24	0*	-7
0	0	18	170	-173	5	-4	21	130	-133	1	-2	24	24*	79
3	0	18	104*	-111	3	-3	21	0*	-23	4	-2	24	43*	56
6	0	18	0*	-12	6	-3	21	27*	-39	2	-1	24	173	-176
3	-7	19	107*	125	1	-2	21	324	-317	5	-1	24	97*	-87
6	-7	19	146	128	4	-2	21	237	-236	0	0	24	33*	-8
1	-6	19	49*	160	2	-1	21	229	-210	3	0	24	0*	-14
4	-6	19	32*	79	5	-1	21	152	-153	2	-5	25	84*	105
7	-6	19	0*	6	0	0	21	0*	-3	3	-4	25	120	153
2	-5	19	248	254	3	0	21	20*	-19	1	-3	25	189	208
5	-5	19	240	279	6	0	21	17*	-46	4	-3	25	221	250
3	-4	19	197	200	1	-6	22	23*	-74	2	-2	25	142	159
6	-4	19	192	166	4	-6	22	0*	-72	5	-2	25	105	107
1	-3	19	237	236	2	-5	22	0*	-52	3	-1	25	168	149
4	-3	19	103	110	5	-5	22	122	-112	1	0	25	211	226
7	-3	19	0*	30	3	-4	22	23*	34	4	0	25	209	205
2	-2	19	334	336	6	-4	22	105	75	1	-4	26	24*	28
5	-2	19	262	277	1	-3	22	102	-102	4	-4	26	27*	5
3	-1	19	262	275	4	-3	22	39*	-80	2	-3	26	0*	3
6	-1	19	202	166	2	-2	22	98	-90	3	-2	26	98*	69
1	0	19	254	258	5	-2	22	129	-117	1	-1	26	0*	26
4	0	19	124	131	3	-1	22	0*	7	4	-1	26	27*	-25
4	-7	20	145	124	6	-1	22	0*	27	2	0	26	19*	80
2	-6	20	165	163	1	0	22	0*	-48	3	-3	27	127	-119
5	-6	20	104	119	4	0	22	21*	-33	1	-2	27	88*	40
3	-5	20	32*	-3	2	-6	23	0*	7	2	-1	27	36*	40
6	-5	20	32*	47	3	-5	23	33*	-71	0	0	27	157	-162
1	-4	20	164	168	1	-4	23	183	-188	3	0	27	117*	-120
4	-4	20	154	169	4	-4	23	131	-132	2	-2	28	0*	15
7	-4	20	96	112	2	-3	23	95*	-47	1	0	28	51*	-31
2	-3	20	170	163	5	-3	23	79*	-42	1	-1	29	139	-126
5	-3	20	27*	60										