

High-pressure and high-temperature crystallographic study of the gillespite I-II phase transition

ROBERT M. HAZEN AND LARRY W. FINGER

*Geophysical Laboratory, Carnegie Institution of Washington
Washington, D.C. 20008*

Abstract

Crystal structures of gillespite, $\text{BaFeSi}_4\text{O}_{10}$, which has a reversible first-order phase transition at 18 kbar, were refined from data collected at 1 bar and 9, 21, and 45 kbar. Silicate-layer topology is constant through the transition, but coordination of barium increases from 8 to 10. The almost perfect square-planar coordination group of iron in gillespite I ($\text{Fe-O} = 1.98\text{\AA}$) changes to a flattened tetrahedron with two additional long Fe-O bonds ($\sim 3\text{\AA}$) in gillespite II. The volume discontinuity at the gillespite I-II transition is best described as a consequence of the increased coordination of barium and iron.

Unit-cell parameters of gillespite were measured under nine high-pressure and fourteen combined high-pressure, high-temperature (PT) conditions. The Clausius-Clapeyron slope of the transition is $27 \pm 9 \text{ bar/}^\circ\text{C}$, which is similar to the slope of gillespite-I isochores. On the basis of these observations, the behavior of the gillespite I-II transition is consistent with a geometrically controlled phase transformation, in which the size of the barium site is the critical dimensional factor.

Introduction

The barium-iron silicate gillespite ($\text{BaFeSi}_4\text{O}_{10}$), though a rare mineral, has been the subject of much research, due to both an unusual square-planar coordination of ferrous iron and to a high-pressure phase transition, the latter characterized by a striking red-to-blue color change. Strens (1966) first described the transition, which was subsequently examined by absorption spectroscopy (Abu-Eid *et al.*, 1973) and Mössbauer spectroscopy (Huggins *et al.*, 1975, 1976). Hazen and Burnham (1974, 1975) and Hazen (1977), employing high-pressure, single-crystal X-ray diffraction techniques, were successful in identifying a change from tetragonal to orthorhombic symmetry at the phase transition and an associated distortion of the iron site from ideal square-planar coordination. Hazen (1977) also discussed mechanisms of the first-order transition ($\Delta V = 1\%$) and modes of twinning induced by the reduction of symmetry at high pressure.

Gillespite I is tetragonal, $P4/ncc$, $a = 7.516$, $c = 16.076\text{\AA}$, $Z = 4$. The structure (Fig. 1) has an 8\AA subcell parallel to c , but alternate left- and right-handed rotations of four-membered silicate tetrahedral rings cause the c -dimension to be doubled to 16\AA (Hazen and Burnham, 1974). Four nonbridging oxygen (O3) atoms surround each ferrous iron in almost perfect square-planar coordination. The layers of tetrahedrally coordinated silicon are linked by barium atoms in eight-fold distorted cubic coordination.

"Gillespite II" is orthorhombic, $P2_12_12$, $a \cong b \cong 7.4\text{\AA}$, $c \cong 7.9\text{\AA}$, $Z = 2$, and differs from the room-pressure phase in that all four-membered rings in adjacent silicate layers have the same rotational sense. One consequence of the change in relative layer orientation is that the coordination polyhedra of both iron and barium are altered. Details of these changes were poorly resolved in the previous study of the structure at high pressure, due to the low precision of the refinement.

Several questions regarding the gillespite I-II transition remain unresolved. Hazen and Burnham's single high-pressure refinement of gillespite II, which was the first silicate structure to be determined from single-crystal, high-pressure data, is inadequate both in precision and in the number of pressures studied for calculation of polyhedral distortions and compressibilities. The pressure of the natural gillespite transition was uncertain, because internal pressure standards were not available to them. All previous experiments were performed at room temperature; thus the Clausius-Clapeyron slope of the gillespite I-II transition is also unknown. Other unresolved aspects of gillespite at high pressure are the origin of an extra absorption doublet in Mössbauer spectra of synthetic

¹ "Gillespite II," the high-pressure form of $\text{BaFeSi}_4\text{O}_{10}$, has not been observed in nature and thus is not a proper mineral name. This name has been used for convenience only.

STRUCTURE FACTORS FOR GILLESPIE I AT 1 BAR AND 23 C

FACTOR =

10.00

Table with columns: L OBS CALC, L OBS CALC, L OBS CALC, L OBS CALC, L OBS CALC, L OBS CALC, L OBS CALC. Rows contain numerical data and labels like '0 0 L', '1 1 L', '2 2 L', etc.

STRUCTURE FACTORS FOR GILLESPIE II AT 21 KBAR AND 25 C.

FACTOR = 10.00

K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC
0	0	8720	4	323	328	4	306	297	0	684	694	9	442	455	8	114	101
2	133	134	5	76	44	5	599	565	1	173	176	10	228	207	7	114	101
4	1540	1639	7	181	180	6	411	412	2	611	620	3	130	113	3	114	101
8	563	581	9	218	228	8	185	189	3	130	113	2	130	113	7	114	101
10	353	361	6	K	0	9	424	400	4	543	515	5	208	201	1	490	499
1	K	0	0	829	845	10	212	197	5	524	527	3	405	406	2	442	448
1	455	393	1	324	327	2	K	1	6	324	327	4	542	578	3	573	574
2	553	527	2	644	655	1	538	524	5	368	363	4	368	363	4	316	282
3	488	494	3	66	24	0	803	773	7	97	77	7	158	130	5	390	372
4	515	540	4	912	900	8	290	277	8	279	287	8	279	287	6	122	107
5	243	259	5	218	195	0	570	595	9	177	168	3	K	2	8	K	2
7	243	251	6	324	303	1	401	397	0	89	90	0	160	166	0	160	166
8	103	125	7	291	200	2	135	123	1	776	808	1	106	103	1	106	103
9	172	188	8	599	623	3	475	475	2	716	727	2	599	573	2	599	573
10	291	278	9	K	0	4	444	420	3	444	420	3	277	243	3	277	243
2	K	0	7	474	488	4	261	259	4	375	393	4	375	393	4	375	393
0	168	177	1	135	137	5	248	219	5	495	464	5	495	464	5	495	464
1	206	210	2	85	86	6	347	372	6	328	324	6	328	324	6	328	324
2	162	1629	4	445	435	7	101	176	7	101	176	7	101	176	7	101	176
3	317	303	5	160	152	8	437	451	8	255	260	8	255	260	8	255	260
4	884	894	6	176	182	9	507	499	9	298	302	9	298	302	9	298	302
5	340	352	7	K	0	0	683	702	0	136	155	0	344	347	0	344	347
6	531	542	8	K	0	1	642	676	1	437	451	1	304	298	1	142	136
7	275	286	9	514	509	2	483	491	2	372	399	2	367	376	2	367	376
8	627	637	0	188	197	3	665	619	3	308	313	3	308	313	3	308	313
9	154	154	4	404	391	4	647	611	4	424	292	4	424	292	4	424	292
10	444	448	5	247	237	5	435	431	5	290	293	5	290	293	5	290	293
3	K	0	6	597	585	6	338	324	6	222	208	6	222	208	6	222	208
1	804	798	9	K	0	9	K	1	7	226	236	7	226	236	7	226	236
2	539	516	0	663	646	8	231	259	8	168	147	8	168	147	8	168	147
3	75	29	1	96	69	9	361	359	9	152	149	9	152	149	9	152	149
4	535	528	2	1015	935	10	K	1	0	860	870	10	860	870	10	860	870
5	700	687	3	362	362	0	317	332	0	916	909	0	916	909	0	916	909
6	195	192	10	K	0	3	218	196	1	138	138	1	138	138	1	138	138
9	227	230	0	595	620	2	479	482	2	760	706	2	760	706	2	760	706
4	K	0	1	309	299	3	697	644	3	448	411	3	448	411	3	448	411
1	125	124	2	326	349	4	677	644	4	716	664	4	716	664	4	716	664
2	862	862	3	121	117	5	527	494	5	338	341	5	338	341	5	338	341
3	232	226	0	K	1	6	159	126	6	171	185	6	171	185	6	171	185
4	838	814	2	1287	1399	3	348	347	3	106	103	3	106	103	3	106	103
5	537	537	4	669	671	4	135	154	4	544	531	4	544	531	4	544	531
6	911	927	5	609	601	4	154	154	4	277	243	4	277	243	4	277	243
7	289	282	6	124	121	5	796	757	5	495	479	5	495	479	5	495	479
8	364	362	7	542	537	6	442	421	6	491	479	6	491	479	6	491	479
9	286	308	8	111	139	7	121	104	7	171	185	7	171	185	7	171	185
5	K	0	10	282	288	8	282	272	8	237	226	8	237	226	8	237	226
1	95	82	9	282	288	9	384	380	9	160	166	9	160	166	9	160	166
2	211	215	1	K	1	920	977	920	1	110	112	1	110	112	1	110	112
3	532	525	2	791	785	3	544	531	3	277	243	3	277	243	3	277	243
			3	743	754	4	827	868	4	189	175	4	189	175	4	189	175
			3	634	634	5	629	608	5	380	380	5	380	380	5	380	380
						6	629	608	6	380	380	6	380	380	6	380	380
						7	629	608	7	380	380	7	380	380	7	380	380
						8	629	608	8	380	380	8	380	380	8	380	380
						9	629	608	9	380	380	9	380	380	9	380	380
						10	629	608	10	380	380	10	380	380	10	380	380

