

## The crystal structures of helvite group minerals, (Mn,Fe,Zn)<sub>8</sub>(Be<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>)S<sub>2</sub>

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### Abstract

The structures of six members of the helvite-genthelvite series (Mn,Fe,Zn)<sub>8</sub>(Be<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>)S<sub>2</sub> have been refined in the space group  $P4_3n$  to  $R$  factors between 0.024 and 0.029 for observed reflections measured on an automated single-crystal 4-circle X-ray diffractometer using MoK $\alpha$  radiation. The 1:1 BeO<sub>4</sub> and SiO<sub>4</sub> tetrahedra are completely ordered. The Be-O, Si-O and O-O distances of the two distinct tetrahedra are constant throughout the compositional series, indicating that the interframework cations have no effect on the dimensions of the framework tetrahedra. Thus the geometrical sodalite model of Hassan and Grundy (1984) is applicable to the helvite group minerals and is used for a thorough analysis of the variations in crystal parameters. The results also indicate that pure danalite is probably stable and that complete miscibility should exist between the Mn, Fe and Zn end-members.

### Introduction

The chemical composition of the helvite group minerals can be expressed as C<sub>8</sub>(Be<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>)S<sub>2</sub>, with C = Mn (helvite), Fe<sup>2+</sup> (danalite) and Zn (genthelvite). The helvite group minerals are isotypic with cubic sodalite, Na<sub>8</sub>(Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>)Cl<sub>2</sub> and their structures are characterized by four-membered rings of BeO<sub>4</sub> and SiO<sub>4</sub> tetrahedra in each of the faces of the unit cell; these rings are linked together, forming six-membered rings about each of the cell corners. The Al atoms in sodalite correspond to Be atoms in the helvite group minerals, the Na atoms to Mn, Fe<sup>2+</sup> or Zn atoms and the Cl atoms to S atoms (see Fig. 1 of Hassan and Grundy, 1984).

Barth (1926) and Gottfried (1927) reported that helvite has space group  $P4_3n$  and Pauling (1930) determined the structure of a helvite from Schwarzenberg, Saxony by making full use of the isotypic relationship with sodalite. A sample of helvite from the same locality was refined to an  $R$ -factor of 0.04 by Holloway et al. (1972).

Dunn (1976) analyzed seventy-five members of the helvite group from world-wide localities and also used fifty seven analyses from the literature, and concluded that the chemical analyses indicate complete miscibility between the Fe- and Mn-members and between the Fe- and Zn-members but not between the Mn- and Zn-members. Essentially pure helvite and genthelvite occur naturally but the nearest approach to pure danalite is a

sample with 86% of the Fe end-member. Danalite was the only end-member of the helvite group that could not be synthesized by Mel'nikov, Latvia and Fedosova (1968). This would suggest that pure danalite is unstable. Structural analyses and the sodalite model of Hassan and Grundy (1984) may be useful in considering the existence of pure danalite and the absence of miscibility between the Mn- and Zn-members of the Helvite group.

Hassan and Grundy (1984) have developed a geometrical model for structures based on the sodalite framework topology. In this model, they assumed that the interframework ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, H<sub>2</sub>O, SO<sub>4</sub><sup>2-</sup>, etc.) have no effect on the Si-O and Al-O distances. The helvite group minerals provide an ideal opportunity to examine the isolated effect of the interframework cations on analogous Be-O and Si-O distances, together with the application of the sodalite model to variations of crystal parameters and thermal expansion behavior.

The sodalite structure has also been modelled by Taylor (1968, 1972), Taylor and Henderson (1978), Dempsey and Taylor (1980) and Beagley, Henderson and Taylor (1982). These models, including that of Hassan and Grundy (1984) have been used to analyze the thermal expansion behavior of aluminosilicate-sodalites; using thermal expansion data of Taylor (1968, 1972) and Henderson and Taylor (1978). The sodalite-type framework topology is usually in a partially collapsed state due to the relatively small interframework ions (Pauling, 1930). Heating (or substitution) causes the framework tetrahedra to rotate. This rotational mechanism is described in terms of  $\psi_{Si}$  and  $\psi_{Al}$ , the angles through which the distinct framework tetrahedra are rotated relative to their position

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# HELVITE (M30349)

0	1,0,L	0	0	2	703	702	5	2	167	167	3	8,8,L	10,4,L
0	40*	0	0	3	0*	0	0	4	257	256	0	0	0
0	1,1,L	0	0	0	5,4,L	0	0	0	7,5,L	0	0	0	0
1	0*	29	500	0	11*	3	500	0	174	169	0	0	0
0	0*	0	0	1	796	795	194	0	37*	11	177	0	0
0	2,0,L	0	0	2	216	208	3	0	40*	384	201	0	0
0	326	309	500	3	325	313	57	0	0*	33	182	0	0
0	2,1,L	0	0	4	0*	0	0	0	416	399	203	0	0
0	325	339	0	0	5,5,L	0	0	0	7,6,L	0	0	0	0
1	1320	1270	818	0	220	230	0	0	146	147	500	0	0
0	2,2,L	0	0	1	0*	0	0	0	249	248	910	0	0
0	364	368	0	2	165	172	881	0	24*	5	201	0	0
2	79*	702	950	3	507	495	771	0	58*	70	935	0	0
0	3,0,L	0	0	4	0*	0	0	0	138	136	995	0	0
0	0*	0	0	0	6,0,L	0	0	0	377	371	43	0	0
0	3,1,L	0	0	1	1311	1325	0	0	0*	0	0	0	0
1	609	620	500	0	6,1,L	0	0	0	374	375	0	0	0
0	19*	0	0	1	20*	220	0	0	0*	0	0	0	0
0	3,2,L	0	0	0	279	297	14	0	468	450	812	0	0
0	273	285	500	0	453	460	500	0	27*	502	836	0	0
2	642	626	951	1	0*	0	506	0	497	0	0	0	0
0	19*	0	0	2	416	406	208	0	0*	0	0	0	0
0	3,3,L	0	0	0	6,3,L	0	0	0	230	215	954	0	0
0	1533	1535	0	0	202	210	0	0	20*	0	0	0	0
3	289	290	158	1	208	199	186	0	145	156	0	0	0
0	4,0,L	0	0	2	946	945	24	0	0*	0	0	0	0
0	625	598	500	3	57*	36	500	0	31*	0	0	0	0
0	4,1,L	0	0	0	194	196	3	0	650	661	178	0	0
0	20*	3	500	1	198	192	36	0	0*	0	0	0	0
1	1200	1213	230	2	183	178	33	0	545	563	0	0	0
0	4,2,L	0	0	3	183	178	33	0	168	172	1	0	0
0	575	590	0	0	315	310	991	0	364	362	170	0	0
2	252	258	998	0	6,4,L	0	0	0	8,0,L	0	0	0	0
2	831	818	772	1	181	185	0	0	8,1,L	0	0	0	0
0	4,3,L	0	0	0	580	581	20	0	8,2,L	0	0	0	0
0	147*	150	160	1	301	304	21	0	545	563	0	0	0
2	237	242	999	2	157	155	996	0	168	172	1	0	0
3	574	557	959	3	440	437	538	0	364	362	170	0	0
0	4,4,L	0	0	0	6,5,L	0	0	0	8,3,L	0	0	0	0
0	1283	1314	0	0	181	185	0	0	25*	4	500	0	0
2	0*	0	0	1	580	581	20	0	339	335	945	0	0
3	895	874	803	2	301	304	21	0	164	158	3	0	0
4	861	808	193	3	157	155	996	0	514	514	35	0	0
0	5,0,L	0	0	0	440	437	538	0	8,4,L	0	0	0	0
0	0*	0	0	0	6,6,L	0	0	0	565	577	0	0	0
0	5,1,L	0	0	0	546	543	0	0	469	458	915	0	0
0	474	493	0	1	576	560	98	0	0*	2	172	0	0
1	0*	0	0	2	201	180	914	0	569	576	861	0	0
0	5,2,L	0	0	3	207	193	3	0	8,5,L	0	0	0	0
0	223	237	500	0	7,0,L	0	0	0	0*	7	500	0	0
2	506	489	218	0	21*	0	0	0	414	412	770	0	0
0	5,3,L	0	0	0	177	181	0	0	143	140	998	0	0
0	767	781	500	1	33*	0	0	0	151	167	83	0	0
1	0*	2	43	0	7,1,L	0	0	0	0*	3	886	0	0
0	7,0,L	0	0	0	177	181	0	0	320	325	148	0	0
0	7,1,L	0	0	0	33*	0	0	0	8,6,L	0	0	0	0
0	7,2,L	0	0	0	187	194	500	0	251	255	500	0	0
0	5,1,L	0	0	1	545	571	828	0	136	132	998	0	0
0	5,2,L	0	0	2	0*	0	0	0	224	231	981	0	0
0	5,3,L	0	0	3	554	569	500	0	136	129	996	0	0
0	223	237	500	0	187	194	500	0	410	388	991	0	0
2	506	489	218	1	545	571	828	0	119	117	3	0	0
0	5,3,L	0	0	2	0*	0	0	0	394	395	26	0	0
0	767	781	500	0	7,3,L	0	0	0	0*	0	0	0	0
1	0*	2	43	0	554	569	500	0	317	309	186	0	0
0	7,4,L	0	0	1	12*	2	217	0	127	121	990	0	0
0	533	530	773	0	360	357	41	0	192	98	83	0	0
0	7,4,L	0	0	1	29*	0	0	0	10*	3	73	0	0
0	533	530	773	0	226	218	767	0	226	218	767	0	0
1	0*	1	0	0	101*	94	14	0	101*	94	14	0	0
0	9,0,L	0	0	0	9,0,L	0	0	0	9,0,L	0	0	0	0
0	9,1,L	0	0	0	9,1,L	0	0	0	9,1,L	0	0	0	0
0	9,2,L	0	0	0	9,2,L	0	0	0	9,2,L	0	0	0	0
0	9,3,L	0	0	0	9,3,L	0	0	0	9,3,L	0	0	0	0
0	9,4,L	0	0	0	9,4,L	0	0	0	9,4,L	0	0	0	0
0	9,5,L	0	0	0	9,5,L	0	0	0	9,5,L	0	0	0	0
0	9,6,L	0	0	0	9,6,L	0	0	0	9,6,L	0	0	0	0
0	9,7,L	0	0	0	9,7,L	0	0	0	9,7,L	0	0	0	0
0	9,8,L	0	0	0	9,8,L	0	0	0	9,8,L	0	0	0	0
0	10,0,L	0	0	0	10,0,L	0	0	0	10,0,L	0	0	0	0
0	10,1,L	0	0	0	10,1,L	0	0	0	10,1,L	0	0	0	0
0	10,2,L	0	0	0	10,2,L	0	0	0	10,2,L	0	0	0	0
0	10,3,L	0	0	0	10,3,L	0	0	0	10,3,L	0	0	0	0
0	10,4,L	0	0	0	10,4,L	0	0	0	10,4,L	0	0	0	0









### GENTHELVITE (M32727)

0	36*	0	0
0	140	146	0
1	23*	0	0
0	497	492	500
0	344	340	0
1	1480	1548	794
0	456	452	0
1	792	693	15
0	53*	0	0
0	872	847	500
1	30*	0	0
0	294	288	500
1	814	775	947
0	0*	0	0
0	1778	1834	0
1	406	418	102
0	1060	1019	500
0	0*	2	500
1	1398	1367	246
0	770	756	0
1	225	261	494
2	1117	1033	77*
0	28*	2	0
1	294	297	93
2	255	244	109
3	822	733	914
0	1596	1633	0
1	1003	996	781
4	868	858	235
0	30*	0	0
0	586	583	0
1	43*	0	0
0	244	242	500
1	903	870	234

0	895*	889	500
1	47*	745	795
2	755*	737	16
3	0*	0	0
0	30*	2	500
1	1045	1040	196
2	230	215	956
3	437	421	2
4	33*	0	0
0	182	184	0
1	0*	0	0
2	52*	542	798
3	40*	0	0
4	762	752	760
5	0*	0	0
0	1646	1687	0
0	227	226	0
1	460	460	37
0	623	637	500
1	39*	2	215
2	457	435	234
0	214	215	0
1	252	208	850
2	182*	3	192
3	1282	1281	20
0	264	260	500
1	205	202	1
2	221	221	973
3	193	188	1
4	480	467	12
0	184	192	0
1	654	653	0
2	46*	1	850
3	367	377	445
4	194	167	946
5	426	415	961
0	454	871	0
1	45*	0	0
2	765*	745	958
3	29*	0	0
4	367	364	373
5	35*	0	0
6	482	458	567
0	39*	0	0
0	314	315	0
1	0*	0	0
0	207	203	500
1	543	669	796
2	35*	0	0
0	762	761	500

0	46*	1	83
1	439	490	31
2	54*	0	0
0	29*	0	0
1	648	640	798
2	191	174	2
3	372	362	478
4	0*	0	0
0	290	274	0
1	500*	0	58
2	500*	537	224
3	500*	1	48
4	500*	530	198
5	0*	0	0
0	160	158	500
1	359	348	953
2	34*	2	770
3	115	120	106
4	194	147	998
5	468	472	25
6	18*	0	0
0	454	450	0
1	0*	0	0
2	536	560	790
3	24*	0	0
4	562	584	836
5	0*	0	0
6	304	287	11
0	275	270	0
0	47*	5	0
1	892	899	196
0	552	559	0
1	176	180	1
2	641	641	211
0	0*	1	500
1	380	362	932
2	164	169	1
3	521	529	37
0	541	542	0
1	34*	1	929
2	674*	653	227
3	0*	2	26
4	722	752	359
0	675	679	753
1	155	151	998
2	161	165	136
3	0*	1	361
4	577	580	196
0	244	250	500
1	129	143	499
2	229	222	16
3	132	134	378
4	442	430	480
5	124	127	1
6	396	394	19

0	425	420	194
1	137	132	996
2	135	137	66
3	1*	0	759
4	345	335	763
5	133*	104	5
0	614	607	0
1	47*	0	0
2	499	516	786
3	0*	0	0
4	542	515	177
0	63*	0	0
0	509	515	500
1	71*	0	0
0	153	163	500
1	455*	480	43
2	37*	0	0
0	895	901	0
1	0*	1	816
2	203	214	0
3	50*	0	0
0	0*	1	0
1	235	242	33
2	142	144	998
3	457	444	975
4	22*	0	0
0	370	381	500
1	42*	1	169
2	459	446	915
3	0*	1	823
4	153	146	567
5	0*	0	0
0	122	124	500
1	167	191	35
2	0*	0	0
3	971	883	5
4	113*	123	2
5	206	193	881
0	397	369	500
1	0*	1	750
2	347	347	24
3	27*	1	317
4	134	188	953
0	155	124	500
1	193*	110	909
0	236	229	500
0	145	144	0
1	527	491	161

0	149	136	0
1	9*	64	843
2	627	658	825
0	125*	137	0
1	279	272	931
2	0*	3	784
3	44*	105	201
0	401	388	0
1	132	130	999
2	410	414	226
3	136	124	999
4	439	413	218
0	109*	122	0
1	366	386	755
2	69*	2	174
3	435	435	29
4	104	116	1
5	421	406	191
0	241	239	500
1	0*	2	250
2	103	75	61
3	31*	3	125
0	103*	110	0
1	503	493	190
0	0*	0	0
0	104*	112	0
1	29*	0	0
0	122	125	500
1	428	415	226
2	0*	0	0
0	184	181	500
1	0*	1	76
2	365	365	0
3	75*	0	0
0	404	406	231
1	113	116	998
2	31*	16	989
0	137	142	0
1	0*	1	966
2	333	367	794
0	899	914	0
0	0*	2	500
1	257	257	83
0	178	164	500
1	97*	106	2