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Crystal structure and Mössbauer spectrum of vonsenite, $2FeO \cdot FeBO_3$

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Abstract

The crystal structure of the mineral vonsenite has been redetermined from a synthesized specimen of composition $2FeO \cdot FeBO_3$. The unit cell dimensions are $a = 9.463(1)$Å, $b = 12.305(1)$Å, $c = 3.0727(6)$Å, $Z = 4$, space group *Pbam*. The final coordinates gave $R = 0.054$ and $\omega R = 0.029$ for 614 structure amplitudes and $R = 0.030$, $\omega R = 0.027$ for 461 amplitudes greater than $2\sigma(F)$. The crystal structure is essentially unchanged from the structure reported in 1950 but the precision of the parameters is at least an order of magnitude better. Values of valence sums, Mössbauer spectra, and the distortions present in the four crystallographically independent octahedra containing Fe1, Fe2, Fe3 and Fe4 are consistent with the presence of two pairs of physically distinct iron ions. Fe1 and Fe3 are divalent; the bond distance between Fe2 and Fe4 is 2.787Å and direct exchange occurs so that an intermediate oxidation state of +2.5 is observed. The Mössbauer spectra are complex and indicate the presence in the structure of Fe^{2+}, Fe^{3+} and $Fe^{2.5+}$. As the temperature is lowered from room temperature the Mössbauer spectra show the migration of a low velocity peak due to Fe^{3+} towards the high velocity peak due to the dinuclear complex Fe2–Fe4 in which Fe has an intermediate valence state. At room temperature charge delocalization is present over the three-dimensional structure because the next nearest Fe2–Fe2 and Fe4–Fe4 distances of 3.073Å parallel to *c* provide a path. However, as the temperature is lowered this rather large Fe–Fe distance becomes a barrier to delocalization and only the charge transfer between Fe2 and Fe4 remains.

Introduction

The mineral vonsenite is one end member of the series ludwigite-vonsenite in which the composition varies from $2MgO \cdot FeBO_3$ for the former to $2FeO \cdot FeBO_3$ for the latter. The minerals may contain varying ratios of Mg^{2+}, Mn^{2+} and Fe^{2+} in the divalent site as well as Al and Ti in the ferric ion site. The structures of ludwigite and the related minerals warwickite and pinakiolite were determined by Takéuchi *et al.* (1950) primarily from anion packing considerations. Takéuchi also later published the crystal structure of vonsenite (1956). Bertaut (1950) synthesized a series of boroferrites with the ludwigite, warwickite and pinakiolite structures, in which the divalent sites were occupied by Fe, Co, Ni, Cu and Mg, and the trivalent sites by Fe, Ti^{4+} and Mn. He determined their lattice constants and space groups. An abstract providing preliminary atomic positions and bond lengths for ludwigite was published by Carvalho da Silva *et al.* (1955) but no further work has appeared. Numerous references to these minerals and indexed powder diffraction patterns exist in the literature (Eakle, 1920; Leonard and Vlisidis, 1960, 1961; Ruiz and Salvador, 1971, Franz *et al.*, 1981).

A refinement of the ludwigite structure from a mineral specimen of composition $(Mg_{1.85}Fe^{2+}_{0.15})(Fe^{3+}_{0.60}Al_{0.40})BO_5$ described the distribution of the cations over the four crystallographically independent sites on the basis of electron density peak heights in (001) electron density projections (Mokeyeva, 1968). It was concluded that the M3 octahedral site in ludwigite was preferentially occupied by Fe^{2+}. Malisheva *et al.* (1971) discussed the results obtained from Mössbauer spectra on a series of minerals from the ludwigite-vonsenite series and also postulated that Fe^{2+}, when substituting for Mg, initially "enters first of all the most regular octahedron M3."

No recent three-dimensional crystal structure determination of the iron end member vonsenite, $2FeO \cdot FeBO_3$, with reliable bond lengths exists and we undertook to synthesize this phase, redetermine its structure and investigate its Mössbauer spectrum.

Preparation

The starting materials for the preparation of vonsenite were Fe, Fe_2O_3 and B_2O_3. The Fe and Fe_2O_3 powders (Alfa Inorganics) were nominally 99.9+% pure. An X-ray powder diffraction pattern of the B_2O_3 powder (Eastman Kodak) showed no extraneous lines. The stoichiometric mixture $4Fe:7Fe_2O_3:3B_2O_3$ was packed into a capped carbon crucible and then sealed in a vycor tube under a

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H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
*** L = -4 ***				1	10	207	200	5	9	369	353	10	0	497	494
-4	-2	777	750	1	11	130	114	5	10	129	113	10	1	139	127
-4	-1	134	113	1	12	74	13*	5	11	10	71*	10	2	221	220
-4	0	161	139	1	13	221	226	5	12	90	9*	10	3	390	401
-3	-3	118	109	2	0	186	189	6	0	177	166	10	4	940	936
-3	-2	57	17*	2	1	807	765E	6	1	780	764	10	5	410	421
-3	-1	80	95*	2	2	60	48*	6	2	602	606	10	6	48	23*
-2	-3	205	207	2	3	549	547	6	3	496	493	10	7	212	217
-2	-2	11	16*	2	4	103	97	6	4	43	44*	10	8	438	453
-2	-1	255	247	2	5	703	703	6	5	320	317	10	9	120	123
-2	0	50	61*	2	6	126	131	6	6	319	313	10	10	81	102*
-1	-4	68	38*	2	7	656	658	6	7	275	277	11	1	326	323
-1	-3	52	107*	2	8	91	80	6	8	94	16	11	2	59	89*
-1	-2	11	2*	2	9	323	311	6	9	341	328	11	3	636	643
-1	-1	107	54*	2	10	68	67*	6	10	271	280	11	4	102	97
0	-4	652	641	2	11	204	198	6	11	350	333	11	5	426	413
0	-2	208	191	2	12	10	7*	6	12	75	122*	11	6	31	56*
0	0	1065	1142	2	13	294	286	7	1	651	656	11	7	335	339
*** L = -3 ***				3	1	405	402	7	2	87	69	11	8	161	106
-3	-1	468	465	3	2	31	82*	7	3	583	573	11	9	326	349
-2	-2	336	331	3	3	324	331	7	4	88	82	11	10	62	86*
-2	-1	196	178	3	4	153	155	7	5	411	406	12	0	8	14*
-2	0	408	404	3	5	269	265	7	6	84	98	12	1	429	437
-1	-3	398	420	3	6	84	64	7	7	291	283	12	2	592	601
-1	-2	9	42*	3	7	460	460	7	8	42	66*	12	3	399	391
-1	-1	307	305	3	8	85	60	7	9	593	582	12	4	59	75*
0	-2	886	930	3	9	9	68*	7	10	62	137*	12	5	290	279
0	0	132	160	3	10	63	71*	7	11	288	290	12	6	417	418
*** L = -2 ***				3	11	277	265	7	12	100	118*	12	7	196	200
-2	-1	491	513	3	12	133	130	8	0	1568	1538	12	8	42	18*
-2	0	123	121	3	13	99	120*	8	1	491	492	12	9	292	283
-1	-1	79	89	4	0	432	427	8	2	271	266	13	1	421	428
0	-2	418	444	4	1	336	337	8	3	313	316	13	2	129	159
0	0	1774	2576E	4	2	2291	2149E	8	4	1095	1079	13	3	280	279
*** L = -1 ***				4	3	139	139	8	5	249	248	13	4	77	68*
0	0	384	374	4	4	773	759	8	6	252	233	13	5	317	312
*** L = 0 ***				4	5	247	250	8	7	335	321	13	6	151	116
0	2	682	656	4	6	1878	1876	8	8	878	875	13	7	215	231
0	4	1461	1509	4	7	275	276	8	9	230	233	13	8	11	40*
0	6	702	702	4	8	176	155	8	10	152	147	14	0	385	393
0	8	1679	1725	4	9	137	137	8	11	204	167	14	1	136	120
0	10	347	345	4	10	832	825	9	1	530	528	14	2	853	867
0	12	850	849	4	11	22	8*	9	2	178	178	14	3	175	177
1	1	141	132	4	12	406	416	9	3	550	567	14	4	116	139
1	2	22	4*	5	1	349	356	9	4	136	168	14	5	91	120*
1	3	333	330	5	2	908	855	9	5	380	378	14	6	570	577
1	4	209	193	5	3	631	616	9	6	252	247	14	7	71	62*
1	5	208	206	5	4	138	138	9	7	466	473	15	1	176	178
1	6	69	42*	5	5	596	587	9	8	191	206	15	2	10	38*
1	7	150	133	5	6	321	326	9	9	201	190	15	3	366	374
1	8	213	210	5	7	95	99	9	10	135	141	15	4	10	5*
1	9	110	35	5	8	85	74	9	11	335	342	15	5	231	244

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
15	6	87	121*	3	12	10	58*	8	2	686	690	13	3	45	9*
16	0	143	161	4	0	1057	1060	8	3	285	297	13	4	43	7*
16	1	221	199	4	1	133	156	8	4	170	158	13	5	54	70*
16	2	84	20*	4	2	100	95	8	5	233	232	13	6	109	38
16	3	379	388	4	3	283	288	8	6	517	523	13	7	15	46*
16	4	171	152	4	4	1407	1375	8	7	288	297	13	8	65	65*
16	5	387	391	4	5	266	270	8	8	199	194	14	0	570	577
17	1	78	116*	4	6	179	171	8	9	222	234	14	1	150	147
17	2	11	52*	4	7	175	161	8	10	405	401	14	2	96	91
***	L =	1	***	4	8	818	824	8	11	135	153	14	3	115	131
0	2	1645	1957E	4	9	95	117	9	1	7	9*	14	4	315	320
0	4	21	19*	4	10	10	33*	9	2	229	241	14	5	97	85*
0	6	848	869	4	11	97	77	9	3	71	36*	14	6	73	31*
0	8	92	103	4	12	467	473	9	4	48	59*	14	7	124	120
0	10	985	1003	5	1	198	202	9	5	61	94*	15	1	666	671
0	12	10	34*	5	2	191	186	9	6	48	79*	15	2	123	62
1	1	598	602	5	3	224	221	9	7	42	85*	15	3	398	408
1	2	138	134	5	4	258	252	9	8	66	6*	15	4	78	7*
1	3	852	849	5	5	199	212	9	9	93	116*	15	5	466	465
1	4	129	113	5	6	8	10*	9	10	10	7*	16	0	333	324
1	5	323	334	5	7	109	62	10	0	166	161	16	1	329	335
1	6	7	24*	5	8	203	212	10	1	184	183	16	2	127	141
1	7	482	478	5	9	247	261	10	2	207	198	16	3	188	200
1	8	171	175	5	10	10	56*	10	3	283	290	16	4	283	290
1	9	286	282	5	11	57	44*	10	4	383	382	***	L =	2	***
1	10	147	134	5	12	131	138	10	5	388	391	0	4	1113	1162
1	11	339	341	6	0	153	146	10	6	362	355	0	6	466	476
1	12	10	35*	6	1	532	541	10	7	240	230	0	8	1295	1310
2	0	754	750	6	2	712	716	10	8	217	204	0	10	272	272
2	1	128	152	6	3	616	626	10	9	147	157	1	2	15	6*
2	2	646	639	6	4	71	71*	10	10	96	118*	1	3	199	201
2	3	1102	1086	6	5	326	325	11	1	801	801	1	4	117	92
2	4	822	821	6	6	358	364	11	2	8	8*	1	5	82	117*
2	5	847	848	6	7	173	180	11	3	784	794	1	6	75	20*
2	6	428	436	6	8	122	127	11	4	76	115*	1	7	86	114*
2	7	213	213	6	9	273	269	11	5	974	979	1	8	143	148
2	8	443	440	6	10	357	383	11	6	87	104*	1	9	10	22*
2	9	273	285	6	11	425	434	11	7	660	648	1	10	143	155
2	10	234	238	6	12	116	73	11	8	39	74*	1	11	105	101
2	11	407	405	7	1	1488	1490	11	9	391	375	2	2	7	38*
2	12	272	290	7	2	105	118	12	0	269	279	2	3	408	404
3	1	799	810	7	3	785	785	12	1	548	546	2	4	55	73*
3	2	286	285	7	4	69	62*	12	2	345	355	2	5	479	485
3	3	1240	1221	7	5	620	624	12	3	202	204	2	6	44	90*
3	4	6	67*	7	6	44	49*	12	4	45	40*	2	7	467	480
3	5	1156	1149	7	7	987	985	12	5	195	204	2	8	9	62*
3	6	47	32*	7	8	9	93*	12	6	269	264	2	9	246	253
3	7	465	462	7	9	698	695	12	7	333	331	2	10	93	54*
3	8	109	93	7	10	147	140	12	8	179	184	2	11	182	169
3	9	544	544	7	11	569	561	12	9	307	305	3	1	230	239
3	10	110	136	8	0	438	435	13	1	9	30*	3	2	7	45*
3	11	367	364	8	1	438	449	13	2	28	8*	3	3	241	229

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
3	4	97	98	8	0	1109	1106	14	1	71	100*	6	3	337	342
3	5	188	171	8	1	361	355	14	2	721	715	6	4	10	52*
3	6	8	49*	8	2	190	186	14	3	141	148	6	5	208	205
3	7	342	337	8	3	243	248	14	4	100	116*	6	6	249	245
3	8	83	48*	8	4	831	829	15	1	143	146	6	7	150	134
3	9	62	47*	8	5	179	200	15	2	11	29*	6	8	49	86*
3	10		57*	8	6	170	173	***	L =	3	***	7	1	820	803
3	11		219	8	7	264	259	0	4	9	37*	7	2	9	60*
4	0	312	316	8	8	725	710	0	6	542	547	7	3	493	495
4	1	217	216	8	9	189	194	0	8	10	38*	7	4	41	38*
4	2	1436	1460	8	10	136	118	1	4	41	40*	7	5	411	397
4	3	115	113	9	1	400	398	1	5	191	194	7	6	10	36*
4	4	488	490	9	2	110	115	1	6	27	13*	7	7	664	643
4	5	176	180	9	3	426	434	1	7	298	302	8	0	265	271
4	6	1381	1367	9	4	128	119	1	8	18	102*	8	1	269	257
4	7	208	203	9	5	297	297	1	9	157	175	8	2	426	413
4	8	126	124	9	6	182	189	2	3	509	505	8	3	218	198
4	9	129	112	9	7	384	385	2	4	447	443	8	4	148	129
4	10	687	682	9	8	161	162	2	5	447	445	8	5	150	162
4	11	11	9*	9	9	141	160	2	6	265	263	8	6	333	343
5	1	278	280	10	0	404	399	2	7	142	153	8	7	222	204
5	2	465	456	10	1	122	111	2	8	266	291	9	1	10	7*
5	3	413	405	10	2	177	165	2	9	219	201	9	2	140	133
5	4	77	79*	10	3	301	304	3	2	131	111	9	3	10	28*
5	5	425	428	10	4	723	717	3	3	611	602	9	4	53	36*
5	6	212	215	10	5	345	327	3	4	84	36*	9	5	15	60*
5	7	108	85	10	6	51	21*	3	5	647	635	9	6	11	46*
5	8	80	56*	10	7	211	178	3	6	10	11*	10	0	77	124*
5	9	271	289	10	8	358	379	3	7	291	289	10	1	142	127
5	10	74	89*	11	1	249	250	3	8	85	60*	10	2	123	122
5	11	11	60*	11	2	42	68*	3	9	385	374	10	3	155	185
6	0	116	95	11	3	490	492	4	0	606	601	10	4	257	255
6	1	503	506	11	4	62	78*	4	1	107	103	10	5	270	257
6	2	418	419	11	5	320	323	4	2	115	94	11	1	541	524
6	3	339	357	11	6	85	48*	4	3	170	157	11	2	59	7*
6	4	39	26*	11	7	277	278	4	4	769	750	11	3	532	524
6	5	251	249	11	8	132	91	4	5	160	155	11	4	122	78
6	6	258	245	12	0	43	10*	4	6	121	122	12	0	191	180
6	7	233	222	12	1	363	352	4	7	100	103	12	1	385	370
6	8	50	16*	12	2	493	483	4	8	546	537	12	2	260	255
6	9	258	267	12	3	322	320	4	9	93	83*	***	L =	4	***
6	10	220	232	12	4	56	55*	5	1	133	119	2	4	104	42*
7	1	461	451	12	5	225	236	5	2	68	72*	3	4	43	48*
7	2	8	47*	12	6	338	350	5	3	111	109	4	3	11	68*
7	3	391	396	12	7	188	173	5	4	125	111	4	4	245	224
7	4	8	59*	13	1	350	349	5	5	126	133	5	1	144	161
7	5	305	312	13	2	95	123*	5	6	52	5*	5	2	212	190
7	6	91	78	13	3	230	233	5	7	10	37*	5	3	184	208
7	7	227	215	13	4	39	57*	5	8	114	131	6	0	11	42*
7	8	48	55*	13	5	274	263	6	0	124	91	6	1	276	253
7	9	469	469	13	6	124	96	6	1	304	296	6	2	192	219
7	10	143	115	14	0	318	319	6	2	402	401	0	0	0	0