Am-82-243

American Mineralogist, Volume 69, pages 783–787, 1984

The crystal structure of davreuxite, $MnAl_6Si_4O_{17}(OH)_2$

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Abstract

The structure of davreuxite, $MnAl_6Si_4O_{17}(OH)_2$, (space group $P2_1/m$; a = 9. 8(6), b = 5.753(2), c = 12.04(1)Å, β = 108.00(5)°; Z = 2) was determined using diffract .eter data (1079 unique observed reflections, R = 0.06). Davreuxite contains $[SiO_4]$ and $[Si_2O_6(OH)]$ groups and is related to the sorosilicates. The structure consists of double and single chains of alternating vertex-sharing SiO_4 and AlO_4 tetrahedra aligned parallel to [010]. These chains share vertices with parallel chains of vertex-sharing AlO_6 and $AlO_5(OH)$ octahedra. The $Si_2O_6(OH)$ groups and manganese ions (with distorted six-fold coordination) occupy channels between the chains.

Introduction

Davreuxite occurs in the Stavelot Massif, Belgium. It has recently been characterized by Fransolet and Bourguignon (1976), and Fransolet et al. (1984). The crystal structure analysis discussed here was necessary to establish the chemical formula and the structure type.

Experimental and data reduction

Preliminary X-ray investigations with photographic methods showed that davreuxite crystallizes in the monoclinic space group $P2_1/m$ (or $P2_1$) and that crystals are generally of very poor quality. A single crystal was selected for intensity measurements from a fibrous sample obtained from the Institut Royal des Sciences Naturelles (Brussels). It had an irregular lath shape with approximate dimensions 340 × 50 × 8 μm parallel to b, c, and a respectively.

The crystal was oriented on a Syntex-R$\bar{3}$ four-circle diffractometer (Mo$K\alpha$ radiation, graphite monochromator). Lattice constants were determined from the angular positions of 20 reflections by least-squares refinement: a = 9.518(6), b = 5.753(2), c = 12.04(1)Å, β = 108.00(5)°. The intensities of 4920 reflections to θ_{max} = 30° (sin θ/λ = 0.7Å^{-1}) were measured with variable speed ω-scans and scaled by comparison with repeatedly measured standard reflections. After applying Lp and absorption corrections (the latter based on distances between indexed faces), averaging equivalents (merging R-value 0.04) gave 1231 unique reflections, of which 1079 with $F > 4\sigma(F)$ were considered to be observed.

Structure determination and refinement

All calculations were performed with the program system SHELXTL written by G. M. Sheldrick.

The structure was solved in $P2_1/m$ by multisolution direct methods. The best E-map showed the positions of all cations; at this stage, it was not possible to differentiate between Al and Si. After refinement, a difference synthesis showed all the oxygen atoms. Al and Si sites were distinguished by the different M–O bond lengths, and by the temperature factors obtained using neutral Al scattering factors for all the cations. Refinement with anisotropic temperature factors for Al and Si caused all the U_{22} values to become close to zero, presumably due to anisotropic extinction caused by fibrous crystals or residual absorption errors. Refinement (with isotropic temperature factors for the oxygen atoms) proceeded to R = 0.06 and R_w = 0.06 for all 1079 observed reflections.[1] The final positional and thermal parameters of the metal and oxygen atoms are listed in Table 1.

Determinations of (OH)-groups

The structure determination shows that the cell contains $Mn_2Al_{12}Si_8O_{38}$. Four hydrogen atoms are thus needed for charge balance. Since it was not possible to find the positions of the hydrogen atoms by difference syntheses, the method of Donnay and Allmann (1970) was used to identify O^{2-}, OH^- and H_2O. The structure contains no H_2O but O(5) and O(10) correspond to (OH)-groups. The

[1] To receive a copy of the list of observed and calculated structure amplitudes, order Document AM-84-243 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfiche.

0003–004X/84/0708–0783$02.00

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DAVREUXIT

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	14	-16	5	3	0	21	-20	2	0	1	19	-21	1	2	1	90	-79	1	4	1	12	12
2	0	0	54	52	6	3	0	9	9	3	0	1	15	13	2	2	1	100	93	2	4	1	16	-14
3	0	0	48	51	8	3	0	16	-15	4	0	1	7	-2	3	2	1	34	33	3	4	1	8	10
4	0	0	33	-37	9	3	0	18	18	5	0	1	106	-106	4	2	1	22	21	4	4	1	8	5
5	0	0	66	-66	0	4	0	400	295	6	0	1	24	-24	5	2	1	101	104	5	4	1	66	-64
6	0	0	48	49	1	4	0	9	-9	7	0	1	138	140	6	2	1	8	4	6	4	1	16	-17
7	0	0	83	-83	2	4	0	33	28	8	0	1	32	-31	7	2	1	51	-51	7	4	1	105	105
8	0	0	52	-51	3	4	0	35	35	9	0	1	48	47	8	2	1	11	10	8	4	1	22	-24
9	0	0	46	-46	4	4	0	34	-34	10	0	1	34	35	9	2	1	28	-27	-7	5	1	8	-1
10	0	0	23	21	5	4	0	44	-43	-10	1	1	24	-25	10	2	1	25	-24	-5	5	1	13	11
2	1	0	63	61	6	4	0	27	27	-9	1	1	11	-8	-9	3	1	9	7	-4	5	1	51	-51
3	1	0	23	-23	7	4	0	60	-61	-8	1	1	11	12	-8	3	1	14	-14	-3	5	1	18	16
4	1	0	29	-29	8	4	0	38	-38	-6	1	1	8	3	-7	3	1	8	-6	-2	5	1	20	17
5	1	0	18	19	1	5	0	8	4	-5	1	1	18	18	-6	3	1	12	-12	-1	5	1	10	7
6	1	0	10	-9	2	5	0	38	35	-4	1	1	63	-62	-5	3	1	19	-18	0	5	1	8	6
7	1	0	9	10	3	5	0	18	-17	-3	1	1	16	16	-4	3	1	38	37	1	5	1	15	13
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9	1	0	24	-24	7	5	0	10	10	0	1	1	11	14	-1	3	1	22	18	3	5	1	45	42
10	1	0	9	9	0	6	0	71	-59	1	1	1	12	7	0	3	1	16	-14	4	5	1	8	2
0	2	0	172	-116	1	6	0	13	12	2	1	1	59	-59	1	3	1	16	14	6	5	1	11	-10
1	2	0	24	21	2	6	0	33	29	3	1	1	59	59	2	3	1	45	43	7	5	1	9	-7
2	2	0	62	53	5	6	0	39	41	7	1	1	11	-10	3	3	1	32	-33	-4	6	1	45	-43
3	2	0	21	-21	-10	0	1	37	37	9	1	1	41	40	4	3	1	11	10	-2	6	1	63	-62
4	2	0	9	10	-9	0	1	20	22	10	1	1	8	-7	5	3	1	8	6	-1	6	1	19	-17
5	2	0	57	59	-8	0	1	11	9	-10	2	1	11	7	6	3	1	12	-11	0	6	1	9	7
6	2	0	75	-75	-7	0	1	15	-15	-9	2	1	8	-4	7	3	1	12	9	1	6	1	48	-47
7	2	0	26	26	-6	0	1	52	-53	-8	2	1	19	19	9	3	1	37	-37	2	6	1	63	61
8	2	0	18	-18	-5	0	1	11	12	-7	2	1	10	-8	-8	4	1	10	8	3	6	1	11	8
9	2	0	45	-47	-4	0	1	24	21	-6	2	1	17	18	-7	4	1	13	-14	4	6	1	19	19
10	2	0	9	-6	-3	0	1	111	101	-4	2	1	103	-95	-6	4	1	41	-42	-10	0	2	11	-12
1	3	0	20	17	-2	0	1	11	-7	-3	2	1	50	42	-4	4	1	14	-18	-9	0	2	18	19
2	3	0	48	-43	-1	0	1	40	-40	-2	2	1	123	-107	-3	4	1	71	62	-8	0	2	12	11
3	3	0	17	16	0	0	1	10	9	-1	2	1	41	-31	-1	4	1	28	-24	-7	0	2	55	-57
4	3	0	28	28	1	0	1	14	19	0	2	1	14	10	0	4	1	11	7	-6	0	2	116	116

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DAVREUXIT

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	0	2	15	13	9	1	2	19	-20	3	3	2	37	38	-5	6	2	14	14	-4	1	3	26	-25
-3	0	2	114	113	10	1	2	21	20	4	3	2	18	-19	-4	6	2	13	-10	-3	1	3	40	44
-2	0	2	38	-42	-9	2	2	9	0	5	3	2	15	12	-3	6	2	8	7	-2	1	3	24	-27
-1	0	2	39	43	-8	2	2	60	61	6	3	2	12	-11	-2	6	2	42	-37	-1	1	3	63	60
0	0	2	18	-20	-7	2	2	95	95	7	3	2	23	-23	-1	6	2	9	3	0	1	3	29	-24
1	0	2	103	-107	-6	2	2	45	43	8	3	2	10	-J	0	6	2	42	-39	1	1	3	38	-42
2	0	2	104	-100	-5	2	2	28	27	9	3	2	12	13	1	6	2	20	-17	3	1	3	29	30
3	0	2	18	-22	-4	2	2	30	-31	-9	4	2	15	14	2	6	2	12	-7	4	1	3	21	-21
4	0	2	18	-16	-3	2	2	24	21	-7	4	2	44	-44	3	6	2	31	-29	5	1	3	41	41
5	0	2	15	16	-2	2	2	88	-73	-6	4	2	85	85	-11	0	3	26	-26	6	1	3	20	-21
6	0	2	8	9	-1	2	2	16	11	-5	4	2	12	12	-10	0	3	66	-65	7	1	3	11	-7
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-10	1	2	28	28	5	2	2	44	-44	1	4	2	72	-66	-3	0	3	94	95	-5	2	3	101	-100
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2	1	2	36	35	-4	3	2	39	-38	-1	5	2	24	-21	8	0	3	14	-14	7	2	3	31	-31
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5	1	2	17	-17	-1	3	2	15	12	3	5	2	47	-47	-8	1	3	18	-20	-9	3	3	14	-15
6	1	2	16	16	0	3	2	18	17	4	5	2	18	19	-7	1	3	20	21	-8	3	3	23	23
7	1	2	29	28	1	3	2	19	-17	5	5	2	13	-14	-6	1	3	13	12	-7	3	3	15	-17
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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-1	3	3	68	-59	2	5	3	9	-6	-11	1	4	17	16	6	2	4	48	49	-7	5	4	22	-24
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5	3	3	46	-45	-4	6	3	27	28	-5	1	4	43	45	-7	3	4	36	37	-1	5	4	31	-30
6	3	3	15	15	-3	6	3	31	-28	-4	1	4	32	-34	-5	3	4	28	-27	0	5	4	11	10
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-8	4	3	15	15	-1	6	3	46	52	-2	1	4	18	20	-3	3	4	8	7	2	5	4	25	-25
-7	4	3	72	-73	0	6	3	38	32	-1	1	4	58	-61	-2	3	4	20	-19	-5	6	4	101	-103
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-4	4	3	31	29	3	6	3	16	-15	2	1	4	36	-38	1	3	4	19	-19	0	6	4	49	48
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-2	4	3	85	76	-10	0	4	30	-30	4	1	4	8	6	3	3	4	9	-5	2	6	4	29	29
-1	4	3	18	-17	-9	0	4	28	28	6	1	4	43	44	4	3	4	9	-4	3	6	4	52	53
0	4	3	38	-32	-8	0	4	22	-21	7	1	4	9	7	5	3	4	13	14	-11	0	5	16	-13
1	4	3	34	32	-7	0	4	44	43	8	1	4	13	-14	6	3	4	42	-43	-10	0	5	10	-8
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5	4	3	54	-55	-2	0	4	9	10	-7	2	4	51	-52	-5	4	4	24	23	-6	0	5	34	37
6	4	3	20	20	-1	0	4	9	-9	-6	2	4	42	-41	-4	4	4	63	-59	-5	0	5	28	29
7	4	3	11	9	0	0	4	123	-126	-5	2	4	185	-184	-3	4	4	72	-71	-4	0	5	11	11
-7	5	3	14	16	1	0	4	121	124	-4	2	4	24	22	-1	4	4	8	-5	-3	0	5	18	-19
-6	5	3	8	9	2	0	4	78	-80	-3	2	4	7	7	0	4	4	94	-90	-2	0	5	39	-44
-5	5	3	9	-9	3	0	4	55	54	-2	2	4	9	-10	1	4	4	88	86	-1	0	5	32	-31
-4	5	3	16	-15	4	0	4	129	132	-1	2	4	12	-11	2	4	4	50	-50	0	0	5	12	11
-3	5	3	33	31	5	0	4	85	87	0	2	4	92	92	3	4	4	34	32	1	0	5	81	81
-2	5	3	8	-8	6	0	4	30	31	1	2	4	20	-21	4	4	4	92	93	2	0	5	33	36

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR DAVREUXIT

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
3	0	5	7	2	3	2	5	40	40	-5	5	5	25	-25	-7	1	6	22	-21	-8	3	6	15	1
4	0	5	9	-7	4	2	5	62	-63	-4	5	5	12	13	-6	1	6	8	6	-7	3	6	17	1
5	0	5	46	48	5	2	5	23	-26	-3	5	5	21	-23	-5	1	6	28	30	-6	3	6	9	-
7	0	5	12	-12	6	2	5	31	33	-1	5	5	17	16	-4	1	6	21	-20	-5	3	6	26	-2
9	0	5	49	46	7	2	5	26	26	0	5	5	25	-25	-3	1	6	42	45	-4	3	6	13	1
-11	1	5	15	-15	8	2	5	25	-25	2	5	5	31	32	-2	1	6	39	-41	-3	3	6	37	-3
-10	1	5	8	4	-9	3	5	12	11	3	5	5	8	-8	-1	1	6	22	-23	-2	3	6	50	5
-9	1	5	12	-11	-8	3	5	26	27	4	5	5	30	32	0	1	6	39	41	-1	3	6	17	1
-8	1	5	26	-27	-7	3	5	40	-42	5	5	5	10	10	1	1	6	8	9	0	3	6	31	-3
-7	1	5	34	34	-5	3	5	26	27	-2	6	5	19	20	2	1	6	7	-8	1	3	6	11	-1
-6	1	5	11	-11	-4	3	5	21	-23	-1	6	5	10	-11	3	1	6	25	26	2	3	6	8	
-5	1	5	36	-37	-3	3	5	12	12	1	6	5	9	-8	4	1	6	36	-35	3	3	6	28	-2
-4	1	5	26	26	-1	3	5	50	-50	2	6	5	97	-100	5	1	6	12	12	4	3	6	39	4
-3	1	5	26	-28	0	3	5	30	30	-10	0	6	8	9	7	1	6	12	-11	5	3	6	13	-1
-1	1	5	44	45	1	3	5	10	10	-9	0	6	21	-19	-10	2	6	10	-11	6	3	6	13	-1
0	1	5	37	-38	2	3	5	25	-25	-8	0	6	29	29	-9	2	6	13	-14	-8	4	6	20	2
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