

The crystal structure of davidite

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Abstract

Davidite from the Pandora Prospect, Pima County, Arizona, crystallizes in the space group $R\bar{3}$ with lattice parameters $a = 9.190(3)\text{\AA}$, $\alpha = 68.73(1)^\circ$. Its formula, determined from microprobe analysis, is $\text{REE}_{0.91}\text{U}_{0.33}\text{Ca}_{0.50}\text{Y}_{0.23}(\text{Sr,Th,Pb})_{0.50}\text{Ti}_{12.52}\text{Fe}_{3.97}\text{Mg}_{0.24}\text{Cr}_{0.21}\text{Al}_{0.14}(\text{Mn,V,Zr,Nb,Sc})_{0.23}\text{O}_{33}$. In its natural state the mineral is metamict. The crystal structure was reconstituted by heating in air at 920°C for two hours. Davidite is isostructural with the crichtonite-group minerals, having a structure based on a close-packed anion lattice with a mixed stacking sequence (hbc ...), and with rare-earth elements (REE), M(0), occupying a site in the anion framework. The uranium atom does not substitute for REE in M(0), but occupies an octahedral site M(1) along with yttrium and small REE. The remaining small metal atoms, mainly titanium and iron, occupy a tetrahedral site, M(2), and three other octahedral sites, M(3), M(4), and M(5). A comparison is made of the site occupancies and average metal-oxygen bond lengths for five crichtonite-group minerals—senaitite, crichtonite, davidite, loweringite, and landauite. A linear correlation is observed between the unit-cell edge, a_{72} , and the M(1)-O bond length.

Introduction

The mineral davidite, an iron titanate containing a considerable amount of rare earths and uranium, was first described and named by Mawson (1906). The type material, found at Radium Hill, South Australia, occurs in an intimate intergrowth with ilmenite and rutile. Early studies were hampered by the metamict nature of the mineral, and the fact that samples reconstituted by heat treatments gave powder diffraction patterns that proved difficult to index. In a study of davidites from various localities, Pabst (1961) reconstituted samples from Norway and Arizona to single crystals and determined the space group and unit-cell parameters, rhombohedral $R\bar{3}$ or $R3$ with $a = 9.178\text{\AA}$, $\alpha = 68^\circ 48'$. Using these param-

eters, Pabst was able to completely index powder patterns of davidites from various localities and validate the mineral as a distinct species. Specific gravity data and chemical analyses were consistent with a cell content of 36 O, and Pabst proposed a general formula $\text{Y}_2\text{Z}_{15}\text{O}_{36}$, where Y = large cations: Ca, Fe^{2+} , REE, U, Pb, etc., and Z = small cations: Ti, V, Cr, Fe^{3+} .

Rouse and Peacor (1968) pointed out the close structural relationship between davidite, crichtonite, and senaitite as shown by their similar unit-cell parameters, powder patterns, and compositions. From preliminary single-crystal X-ray studies, they determined that the structures were based on a close-packed anion framework, with a nine-layer stacking

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ARIZ RADAR REFINEMENT

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	1	45	52	-2	1	3	11	5	-3	-1	4	402	397	1	3	4	13	-9	-3	-1	5	38	36
-1	1	1	14	8	-2	1	3	9	7	-2	-1	4	44	-41	3	3	4	43	40	-1	-1	5	81	-80
-2	-1	2	30	27	-1	1	3	72	70	-1	-1	4	18	12	3	3	4	79	82	0	-1	5	122	120
-1	-1	2	146	142	0	1	3	169	192	0	-1	4	30	37	-4	4	4	110	110	1	-1	5	104	-100
0	-1	2	49	-44	1	1	3	173	+171	1	-1	4	58	58	-2	4	4	106	-102	1	-1	5	110	109
1	-1	2	70	75	2	1	3	159	162	2	-1	4	154	-153	-2	4	4	153	151	3	-1	5	51	50
-2	0	2	95	92	-3	1	3	58	60	3	-1	4	164	162	0	4	4	12	-6	4	-1	5	27	27
-1	0	2	13	-10	-2	2	3	33	32	-4	0	4	15	-17	1	4	4	17	-17	-5	0	5	123	114
0	0	2	54	61	-1	2	3	198	193	-3	0	4	21	-19	2	4	4	66	93	-4	0	5	29	-26
0	0	2	54	61	-1	2	3	198	193	-3	0	4	21	-19	2	4	4	66	93	-4	0	5	29	-26
1	0	2	36	-36	0	2	3	57	55	-2	0	4	27	26	3	4	4	33	-33	-3	0	5	24	-22
-2	1	2	102	-103	1	2	3	101	105	-1	0	4	24	-25	-5	4	4	147	158	-2	0	5	17	-16
-1	1	2	16	17	2	2	3	49	50	0	0	4	41	42	-4	4	5	75	75	-1	0	5	40	-42
0	1	2	51	-52	-3	2	3	21	-23	1	0	4	191	167	-4	4	5	48	47	0	0	5	146	-139
1	1	2	13	13	-2	2	3	106	104	2	0	4	29	29	-1	4	5	96	96	1	0	5	91	90
-2	2	2	21	21	-1	2	3	17	14	2	0	4	12	-9	0	4	5	31	-32	2	0	5	35	35
-1	2	2	84	82	0	2	3	29	32	-4	1	4	12	9	1	4	5	63	63	3	0	5	12	12
0	2	2	127	127	1	2	3	16	-20	-2	1	4	97	97	1	4	5	64	62	-4	1	5	32	31
1	2	2	30	36	2	2	3	91	-96	-1	1	4	140	140	-4	4	5	33	31	-3	1	5	16	-10
-2	-2	2	13	6	-4	-2	4	47	-47	0	1	4	100	-98	-4	4	5	34	-36	0	1	5	82	79
-2	-2	2	33	35	-2	-2	4	11	5	-2	1	4	12	12	-4	4	5	34	35	-2	-2	5	152	151
-1	-2	2	79	79	-1	-2	4	126	122	-4	2	4	67	72	-1	4	5	67	67	1	2	5	284	284
0	-2	2	65	69	0	-2	4	38	-36	-4	2	4	80	87	2	4	5	57	58	3	2	5	19	20
1	-2	2	35	-37	1	-2	4	15	16	-3	2	4	76	72	4	4	5	40	-39	4	4	5	20	-1
-2	-2	2	79	-77	2	-2	4	17	-19	-2	2	4	121	121	4	4	5	91	93	-4	2	5	22	21
-3	-1	2	113	115	3	-3	4	32	32	-1	2	4	16	-13	-5	4	5	54	53	-4	2	5	20	21
0	-1	2	131	137	4	-2	4	30	31	0	2	4	32	-35	-3	4	5	45	45	-2	2	5	125	-121
1	-1	2	71	71	-3	-2	4	25	29	0	1	4	39	-42	-2	4	5	41	39	-1	2	5	122	121
2	-1	2	150	150	-2	-2	4	85	84	-1	2	4	20	-25	-1	4	5	35	39	0	2	5	11	11
-2	0	2	42	45	-1	2	4	11	-11	3	2	4	96	92	0	4	5	70	-66	1	2	5	30	-2
-2	0	2	18	-20	0	-2	4	13	17	-6	2	4	26	25	1	4	5	157	155	-2	2	5	30	34
-1	0	2	53	34	1	-2	4	17	-16	-3	3	4	85	-23	2	4	5	33	32	4	2	5	41	-41
0	0	2	67	84	2	-2	4	63	-58	-2	3	4	65	-64	3	4	5	46	51	-4	2	5	81	81
1	0	2	51	-44	3	-2	4	52	50	-1	3	4	65	66	4	4	5	31	30	4	2	5	81	81
2	0	2	152	-151	-4	-1	4	22	21	0	3	4	126	-123	-3	-1	5	30	-37	-3	3	5	82	76

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ARIZ R3BAR REFINEMENT

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
6	7	11	48	47	8	10	11	20	15	7	1	12	90	68	7	4	12	25	26	3	7	12	54	56
8	7	11	91	94	9	10	11	19	7	-1	2	12	31	31	6	4	12	76	60	5	7	12	16	-13
10	7	11	35	-37	10	10	11	19	-12	0	2	12	53	56	10	4	12	27	28	6	7	12	1	26
-1	8	11	93	92	3	11	11	32	-30	1	2	12	42	-41	-1	5	12	45	45	7	7	12	16	55
0	8	11	32	-37	4	11	11	46	46	2	2	12	41	39	2	5	12	15	-13	9	7	12	39	36
3	8	11	24	18	5	11	11	28	-24	3	2	12	29	-31	3	5	12	21	16	10	7	12	27	30
4	8	11	56	-57	6	11	11	26	25	6	2	12	35	31	4	5	12	18	-20	1	8	12	45	-41
5	8	11	71	72	7	11	11	17	19	7	2	12	32	-32	5	5	12	30	32	2	8	12	36	35
6	8	11	33	-31	8	11	11	30	30	9	2	12	35	-32	6	5	12	39	41	4	8	12	20	9
7	8	11	41	39	1	-1	12	24	24	-1	3	12	24	-32	7	5	12	22	-25	5	8	12	24	22
8	8	11	21	-13	2	-1	12	15	-11	0	3	12	31	-30	8	5	12	45	-42	6	8	12	36	34
9	8	11	55	56	3	-1	12	32	33	1	3	12	40	40	9	5	12	28	29	7	8	12	27	-22
0	9	11	50	51	4	-1	12	47	-47	2	3	12	32	-28	10	5	12	42	-43	8	8	12	31	28
1	9	11	25	-27	5	-1	12	57	57	4	3	12	57	59	1	6	12	61	-65	9	8	12	91	-93
2	9	11	42	43	-1	0	12	25	-26	6	3	12	29	-28	2	6	12	37	37	2	9	12	41	-45
3	9	11	35	35	1	0	12	18	-13	7	3	12	59	60	4	6	12	28	25	3	9	12	44	46
4	9	11	30	-43	2	0	12	40	39	8	3	12	26	-27	5	6	12	19	22	5	9	12	65	65
5	9	11	55	-57	3	0	12	18	-12	-1	4	12	27	-29	6	6	12	71	72	7	9	12	35	35
7	9	11	19	-19	6	0	12	17	11	0	4	12	64	63	7	6	12	33	-32	9	9	12	17	7
9	9	11	44	48	-1	1	12	64	63	2	4	12	16	16	8	6	12	47	44	4	10	12	69	72
10	9	11	29	30	1	1	12	22	19	3	4	12	37	-41	10	6	12	29	28	5	10	12	24	-21
2	10	11	22	26	4	1	12	19	-21	4	4	12	58	60	0	7	12	31	33	6	10	12	20	-21
5	10	11	57	55	5	1	12	52	50	5	4	12	18	-16	1	7	12	48	47	7	10	12	17	41
7	10	11	113	112	6	1	12	23	27	6	4	12	84	85	2	7	12	39	-36	6	10	12	36	33