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The crystal structure of synthetic chukhrovite, $Ca_4AlSi(SO_4)F_{13} \cdot 12H_2O$

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Abstract

Synthetic chukhrovite, $Ca_4AlSi(SO_4)F_{13} \cdot 12H_2O$ crystallizes in the cubic space group $Fd3$, with $a = 16.710$ (2)Å and $Z = 8$. The structure was refined to $R_w = 0.028$ and $R = 0.025$, using 481 nonzero reflections.

Al and Si are statistically distributed at the same site, M [16(d)], which is surrounded by six fluorine atoms to form the octahedral group MF_6. The remaining fluoride ion is surrounded by a tetrahedron of Ca ions [F(1)–Ca = 2.411Å] as in fluorite. The overall coordination of Ca is seven with a geometry corresponding to that of a monocapped octahedron. Each corner of the MF_6 octahedron is linked to a Ca coordination polyhedron and each Ca polyhedron shares three corners with three different MF_6 octahedra. The SO_4 ion is surrounded by 12 water molecules, all of which are hydrogen-bonded to SO_4 oxygens. The most unusual feature of this hydration is that all four faces of the SO_4 ion are linked to faces of Ca polyhedra *via* hydrogen bonding.

Introduction

The mineral chukhrovite occurs in the secondary oxidation zone of the Kara-Oba molybdenum–tungsten deposit in central Kazakhstan. These crystals have been described as face-centered cubic with $a = 16.80$Å, crystal class $T_h = m3$, and with typical octahedral habit (Ermilova *et al.*, 1960). The chemical composition was given as: $Ca_3Al_2(Y,RE)SO_4F_{13} \cdot 10H_2O$, where RE may be a mixture of rare-earth elements.

Crystals of similar composition and X-ray diffraction pattern to that of the mineral chukhrovite often occur in the filter cake during the manufacture of phosphoric acid. Lehr *et al.* (1966) and Coates and Woodard (1966) have published detailed descriptions of this mineral. Coates and Woodard suggested that these octahedral crystals are isomorphous with chukhrovite. They reported a cell parameter of 16.75(5)Å, space group $Fd3$, and gave the chemical composition as: $Ca_{4.03}Ba_{0.04}(Y,La)_{0.09}Al_{1.31}Si_{0.75}(SO_4)_{1.00}F_{13.0} \cdot 10H_2O$. Meredith (1965), in his studies of the reaction of hydrochloric acid with phosphate rock, reported a residual crystalline material with the formula $CaSO_4 \cdot 1.5CaSiF_6 \cdot AlF_3 \cdot CaF_2 \cdot 12H_2O$. The X-ray diffraction pattern and the differential thermal and thermogravimetric analysis reported by Meredith show that this material is similar to our synthetic chukhrovite. Hájek and Benda (1972) reported a synthetic material with the chemical composition $Ca_{12}Al_2Si_4(SO_4)_3F_{40} \cdot 45H_2O$ which corresponds to $Ca_4Al_{0.67}Si_{1.33}(SO_4)F_{13.3} \cdot 15H_2O$. Again, these are octahedral crystals with cubic symmetry and on the basis of the X-ray diffraction pattern appear to be quite similar to our synthetic chukhrovite.

Experimental

Our crystals of synthetic chukhrovite were prepared as part of a factorial-designed experiment to study the effect of F, Al, and Si on the precipitation of chukhrovite (Frazier *et al.*, 1977). In one of these trials exceptionally large octahedral crystals of chukhrovite were obtained (up to 200 μm along *a*) by

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Table 3.

Observed and calculated structure factors for $Ca_4(A\ell, Si)SO_4F_{13}\cdot 12\ H_2O$. The columns L, O, and C are the values of ℓ, 10 F_o and 10 F_c respectively. Reflections with $F_o < 3\sigma(F_o)$ are considered unobserved and are marked by *.

L	O	C
	1,1,L	
1	3557	3449
	2,2,L	
0	3115	-3093
2	414	-436
	3,1,L	
1	2023	-2011
	3,3,L	
1	1351	1348
3	345	347
	4,0,L	
0	4050	4196
	4,2,L	
2	1709	1651
	4,4,L	
0	1973	1942
2	755	838
4	1046	-995
	5,1,L	
1	3583	3539
3	2888	-2867
	5,3,L	
1	183	-122
3	4223	-4250
	5,5,L	
1	1067	1117
3	3008	2904
5	4179	4244
	6,0,L	
2	3057	-2994
	6,2,L	
0	3067	2944
2	450	501
4	841	-853
	6,4,L	
2	4481	-4453
4	1488	-1503
	6,6,L	
0	3926	-3938
2	2298	2240
4	1765	-1774
6	583	-532
	7,1,L	
1	2371	2451
3	505	-485
5	1068	1051
	7,3,L	
1	4938	4797
3	91*	63
5	641	598
	7,5,L	
1	418	-378
3	1401	-1380
5	1146	1181
	7,7,L	
1	306	-287
3	1351	1344
5	3195	-3202
7	1018	998
	8,0,L	
0	2064	-2012
4	2146	-2124
	8,2,L	
2	246	203
4	3237	3208
6	1436	1440
	8,4,L	
0	311	-306
2	4832	4783
4	2613	2625
6	830	-823
	8,6,L	
2	1806	1874
4	914	-879
6	51*	69
	8,8,L	
0	2928	2899
2	1892	1930
4	1106	1091
6	443	433
8	956	975
	9,1,L	
1	1473	1447
3	1549	-1596
5	1269	1241
7	653	-617
	9,3,L	
1	1944	-1951
3	3319	-3339
5	710	-667
7	805	-784
	9,5,L	
1	441	437
3	2311	2357
5	1149	1172
7	50*	-20
	9,7,L	
1	1297	-1297
3	2487	-2477
5	1002	-1011
7	934	-973
	9,9,L	
1	716	-696
3	1334	1362
5	1053	1028
7	177	62
9	494	449
	10,0,L	
2	983	-1026
6	67*	-81
	10,2,L	
0	783	766
2	2581	2590
4	774	750
6	3460	3513
8	1708	-1715
	10,4,L	
2	331	-331
4	2273	-2212
6	2389	-2381
8	137*	95
	10,6,L	
0	723	739
2	236	-202
4	1051	-1071
6	630	604
8	1187	1215
	10,8,L	
2	967	-969
4	2424	-2388
6	1294	1276
8	215	-246
	10,10,L	
0	2240	-2284
2	698	-707
4	567	531
6	740	740
8	430	457
10	2926	2997
	11,1,L	
1	229	-167
3	1920	-1965
5	208	-177
7	2537	-2574
9	660	-670
	11,3,L	
1	402	-405
3	911	903

L	O	C
	11.3.L	
5	1159	-1140
7	168	-175
9	549	518
	11.5.L	
1	684	692
3	265	-260
5	369	352
7	1741	-1784
9	363	412
	11.7.L	
1	2403	-2408
3	636	622
5	1428	-1450
7	618	-606
9	126*	72
	11.9.L	
1	297	-298
3	2198	2180
5	935	-944
7	233	-162
9	828	-801
	11.11.L	
1	908	-867
3	100*	62
5	1425	-1443
7	1118	-1142
9	966	-992
11	201	-155
	12.0.L	
0	1652	-1617
4	611	611
8	839	852
	12.2.L	
2	1744	1754
4	677	687
6	1119	1095
8	369	-354
10	1836	1871
	12.4.L	
0	1248	1263
2	800	810
4	507	525
6	169	70
8	1933	1994
10	308	-295

L	O	C
	12.6.L	
2	507	500
4	1419	-1460
6	3412	3336
8	432	-421
10	1090	1134
	12.8.L	
0	248	227
2	1406	-1477
4	2083	2128
6	212	153
8	397	-407
10	52*	15
	12.10.L	
2	766	785
4	296	-270
6	386	384
8	115*	141
10	738	740
	12.12.L	
0	2550	2606
2	139*	135
4	456	433
6	559	517
8	112*	36
10	220	146
12	793	-763
	13.1.L	
1	1690	-1695
3	1431	-1443
5	1451	-1488
7	2691	-2766
9	573	567
11	985	-970
	13.3.L	
1	88*	52
3	1417	-1401
5	1214	-1240
7	484	-496
9	202	193
11	102*	115
	13.5.L	
1	157*	-144
3	911	-929
5	455	-442
7	1219	-1226
9	726	722
11	1887	-1903

L	O	C
	13.7.L	
1	1287	-1311
3	518	-509
5	1197	-1178
7	343	347
9	752	-769
11	868	881
	13.9.L	
1	544	519
3	1527	1560
5	630	610
7	116*	107
9	814	781
11	659	-696
	13.11.L	
1	46*	41
3	219	175
5	900	-898
7	496	504
9	720	-719
11	160*	109
	13.13.L	
1	250	208
3	341	351
5	1315	1326
7	131*	136
9	573	578
11	231	-175
13	352	341
	14.0.L	
2	2388	2442
6	1572	1642
10	1261	1293
	14.2.L	
0	335	309
2	2397	2423
4	1022	-1025
6	950	920
8	66*	-65
10	801	-820
12	1224	-1209
	14.4.L	
2	244	258
4	1665	-1630
6	1517	1507
8	157*	-90
10	465	-464
12	153*	-23

L	O	C
	14.6.L	
0	690	-679
2	1105	1113
4	1098	1097
6	854	863
8	555	-557
10	285	239
12	142*	-93
	14.8.L	
2	590	581
4	1585	-1585
6	1012	-992
8	1062	-1074
10	240	-222
12	161*	-25
	14.10.L	
0	550	525
2	601	-584
4	57*	-28
6	318	323
8	653	652
10	1714	1735
12	839	-810
	14.12.L	
2	929	-946
4	308	271
6	162*	-196
8	227	-150
10	1003	-963
12	82*	15
	14.14.L	
0	614	-679
2	89*	27
4	396	417
6	247	226
8	451	-421
10	1187	1177
12	55*	27
	15.1.L	
1	376	-377
3	1078	-1069
5	409	-408
7	583	-586
9	86*	57
11	190	-141
13	671	-676
	15.3.L	
1	1662	-1672

L	O	C
	15,3,L	
3	1250	1262
5	318	-309
7	1224	1214
9	821	818
11	302	-315
13	358	344
	15,5,L	
1	99*	-54
3	310	299
5	412	435
7	189	158
9	737	-725
11	319	324
13	822	-818
	15,7,L	
1	1028	-1038
3	1809	1834
5	603	608
7	411	404
9	1149	1155
11	209	-166
13	302	-268
	15,9,L	
1	398	392
3	637	643
5	1371	-1365
7	204	-194
9	1051	-1053
11	865	-855
13	785	-741
	15,11,L	
1	343	-323
3	134*	-43
5	62*	57
7	361	367
9	1041	-1013
11	634	640
13	479	-483
	15,13,L	
1	49*	37
3	94*	53
5	504	-487
7	689	-689
9	540	-527
11	101*	-132
	15,15,L	
1	568	521
3	743	-739
5	685	-664
7	464	-469
9	964	-947
	16,0,L	
0	149*	-172
4	848	-846
8	2364	2365
12	1821	1880
	16,2,L	
2	124*	-109
4	629	-650
6	1004	1051
8	962	-956
10	474	-457
12	316	335
14	131*	-48
	16,4,L	
0	659	-691
2	1641	-1643
4	736	754
6	667	671
8	322	290
10	867	852
12	1202	1232
14	754	719
	16,6,L	
2	993	1012
4	327	307
6	290	-238
8	431	-432
10	372	326
12	240	-190
14	606	-623
	16,8,L	
0	1448	1421
2	1523	-1528
4	769	739
6	119*	-123
8	1010	1018
10	439	481
12	434	-425
14	752	754
	16,10,L	
2	410	-417
4	748	707
6	496	485
8	759	746
10	470	-446
12	181*	-132
	16,12,L	
0	543	545
2	442	435
4	1448	1460
6	202*	231
8	151*	249
10	88*	-20
12	473	445
	16,14,L	
2	260	239
4	433	445
6	276	-257
8	1004	995
	16,16,L	
0	934	926
2	778	745
4	138*	-7
6	232	248
	17,1,L	
1	1579	-1580
3	437	-420
5	975	-954
7	462	-455
9	693	722
11	957	-962
13	1088	1098
15	393	-387
	17,3,L	
1	308	-298
3	63*	-36
5	286	-273
7	86*	-67
9	848	-859
11	517	-483
13	467	-445
15	1214	-1223
	17,5,L	
1	425	445
3	678	-670
5	684	-681
7	851	-875
9	349	364
11	381	-376
13	581	571
15	154*	146
	17,7,L	
1	859	-847
3	307	-321
5	1197	-1186
7	357	357
9	242	275
11	320	303
13	145*	144
	17,9,L	
1	1137	1139
3	943	-956
5	398	374
7	59*	-11
9	300	-282
11	96*	-154
13	248	239
	17,11,L	
1	1014	-991
3	336	-316
5	808	-789
7	458	-425
9	198*	-169
11	575	531
	17,13,L	
1	838	830
3	585	-623
5	128*	59
7	152*	-106
9	193*	-152
	17,15,L	
1	567	-548
3	738	-745
5	360	-348
	18,0,L	
2	125*	-176
6	1281	1288
10	441	430
14	99*	97
	18,2,L	
0	72*	-62
2	131*	-14
4	1018	997
6	244	270
8	569	-558
10	580	582
12	335	-381
14	700	710
	18,4,L	
2	878	894
4	231	274
6	76*	-59

L	O	C
	18.4.L	
8	150*	-181
10	560	546
12	478	-454
14	275	-319
	18.6.L	
0	1904	1895
2	1565	1550
4	553	530
6	496	453
8	162*	-145
10	436	442
12	1569	-1587
	18.8.L	
2	682	-626
4	343	-313
6	312	-259
8	417	-398
10	775	-770
12	56*	-4
	18.10.L	
0	455	443
2	438	425
4	799	798
6	397	371
8	867	-830
10	499	444
	18.12.L	
2	536	-524
4	423	428
6	1531	-1512
8	177*	161
	18.14.L	
0	420	-437
2	467	467
4	588	-568
	19.1.L	
1	924	-989
3	94*	-87
5	134*	-113
7	85*	128
9	67*	-84
11	110*	26
13	191*	206

L	O	C
	19.3.L	
1	336	-333
3	819	808
5	126*	-191
7	503	489
9	253	227
11	481	469
13	304	-293
	19.5.L	
1	964	-961
3	247	-281
5	1332	-1352
7	696	685
9	583	-573
11	143*	137
	19.7.L	
1	326	328
3	96*	6
5	623	604
7	1076	1092
9	105*	-67
11	418	401
	19.9.L	
1	297	-268
3	227*	176
5	884	-889
7	153*	-185
9	1079	-1090
	19.11.L	
1	450	467
3	265	-223
5	134*	-108
7	550	537
	19.13.L	
1	777	772
3	153*	-59
	20.0.L	
0	948	979
4	1268	1291
8	238	221
12	528	517

L	O	C
	20.2.L	
2	769	764
4	954	-966
6	453	-469
8	1042	-1041
10	113*	-113
12	222	-154
	20.4.L	
0	1856	1802
2	778	-764
4	180*	87
6	192*	241
8	182*	156
10	611	616
	20.6.L	
2	347	-354
4	457	418
6	333	-319
8	296	266
10	881	-903
	20.8.L	
0	364	372
2	260	-262
4	840	816
6	222*	249
8	213*	-217
	20.10.L	
2	63*	42
4	876	843
6	816	-799
	20.12.L	
0	124*	-82
2	205*	-220
	21.1.L	
1	474	506
3	533	504
5	533	534
7	227	212
9	839	831
	21.3.L	
1	40*	30
3	502	470

L	O	C
5	1151	-1160
7	423	448
9	1055	-1088
	21.5.L	
1	169*	200
3	649	-635
5	158*	-135
7	166*	-193
9	453	-418
	21.7.L	
1	320	-282
3	349	315
5	353	-312
7	214*	-161
	21.9.L	
1	498	475
3	875	-883
5	224	-224
	22.0.L	
2	582	559
6	97*	15
	22.2.L	
0	1000	1019
2	286	-277
4	137*	-26
6	580	577
	22.4.L	
2	174*	-180
4	1106	1096
6	683	679
	22.6.L	
0	508	489
2	521	548
4	521	540
	23.1.L	
1	427	-442
3	353	-410
	23.3.L	
1	500	-519