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Minyulite: its atomic arrangement

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Abstract

Minyulite, $K[Al_2F(H_2O)_4(PO_4)_2]$, orthorhombic, space group $Pba2$, a 9.337(5), b 9.740(5), c 5.522(3)A, $Z = 2$, possesses rigid dimeric clusters of formula $[Al_2F(H_2O)_4(PO_4)_2(O_P)_2]$, topologically identical to the $[Fe_2^{3+}(OH)(H_2O)_4(SO_4)_2(O_S)_2]$ clusters in copiapite, where O_P and O_S correspond to the phosphate and sulfate ligands, respectively. The structure was solved by Patterson and Fourier syntheses. Hydrogen atoms were located by difference synthesis. Least-squares refinement converged to $R(hkl) = 0.022$ for 618 reflections.

The dimeric cluster consists of two Al^{3+}–O octahedra sharing one F^- vertex and two PO_4 tetrahedra, which further link the octahedra. The clusters link via shared octahedral–tetrahedral vertices to form sheets parallel to {001}. Cavities in the sheets are occupied by K^+ ions. One tetrahedral vertex is unshared and accepts four hydrogen bonds from water molecules coordinated to Al^{3+}. These hydrogen bonds provide the only linkage between the sheets.

The greater affinity of Al^{3+} for F^- than $(OH)^-$ and the violation of electrostatic valence balance when F^- bonds to more than two Al^{3+} cations are suggested as the reasons for the condensation of Al^{3+} octahedra into dimers and chains in aqueous solution, leading ultimately to the crystallization of minyulite and fluellite. The leucophosphite structure may be preferred in the absence of F^-.

Introduction

Minyulite was originally described by Simpson and LeMesurier (1933) as a new species from Minyulo Well, Western Australia, where it occurs as radiating groups of fine fibers on the surfaces of crevices in phosphatic ironstone. Using optical methods, they established orthorhombic symmetry and proposed the formula $KAl_2(OH,F)(PO_4)_2 \cdot 3.5H_2O$. Spencer *et al.* (1943) studied minyulite from Wait's quarry near Noarlunga, South Australia, where it occurs in phosphate rock as short prismatic crystals in sub-parallel growth coating apatite. From X-ray oscillation photographs, they determined the cell constants a 9.35, b 9.74, c 5.52A and the space group $Pmm2$, the hemimorphic nature of the crystals being established by etch figures. The formula $KAl_2(PO_4)_2(OH,F) \cdot 4H_2O$, $Z = 2$ was suggested.

Haseman *et al.* (1950) synthesized minyulite, as well as a number of other hydrous K^+–NH_4^+, Al^{3+}–Fe^{3+}, phosphates, including leucophosphite, $KFe_2^{3+}(OH)(PO_4)_2 \cdot 2H_2O$, and its Al^{3+} analog. They noted that minyulite and leucophosphite can be synthesized by the treatment of clays with phosphate anions at pH ranges appropriate for soil environments and at temperatures less than 95°C. They proposed that these minerals may be important in the fixation of inorganic phosphate anions in soils.

Leucophosphite bears a striking chemical similarity to minyulite, and besides their possible formation under similar conditions in the soil, the report of leucophosphite in phosphatic rock associated with iron ore at Bomi Hill and Bambuta, Liberia, by Axelrod *et al.* (1952) is further indication of similar parageneses for these two minerals. A comparison of the structures of minyulite and leucophosphite may lead to an understanding of the conditions necessary for their formation.

Also of interest for structural comparison is the mineral fluellite, $Al_2F_2(OH)(H_2O)_3(PO_4) \cdot 4H_2O$. Murray (1973) reported fluellite occurring associated with minyulite in phosphate rock near Wolffdene, Queensland, Australia, and fluellite has been verified

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MINYLLITE. OBSERVED AND CALCULATED STRUCTURE FACTORS (X10)

L= 0

K	H	FOBS	FCALC
0	2	285	283
0	4	300	288
0	6	665	664
0	8	358	361
0	10	84	74
1	1	416	405
1	2	253	242
1	3	626	625
1	4	825	786
1	6	110	104
1	7	228	232
1	9	136	131
1	10	32	24
1	11	196	195
1	12	47	45
2	0	234	227
2	1	49	57
2	2	78	79
2	3	31	8
2	4	594	601
2	5	153	153
2	7	113	111
2	8	319	326
2	9	136	137
2	10	170	170
2	11	74	74
3	1	772	757
3	2	287	285
3	3	125	130
3	4	427	419
3	5	83	82
3	6	255	256
3	7	638	644
3	8	231	224
3	9	61	58
3	10	78	81
3	11	107	93
4	0	648	621
4	1	417	425
4	2	144	156
4	3	103	107
4	4	740	732
4	5	452	452
4	6	84	83
4	7	69	70
4	8	128	136
4	9	264	268
4	10	376	378
4	11	300	300
5	1	38	40
5	2	70	80
5	3	40	33
5	4	243	240
5	5	94	98

K	H	FOBS	FCALC
11	4	34	28
11	5	39	19
11	6	284	282
12	0	65	70
12	1	54	53
12	2	280	289
12	3	87	76

L= 1

K	H	FOBS	FCALC
0	0	944	1043
0	2	332	330
0	4	207	221
0	6	648	644
0	8	363	361
0	10	49	49
0	12	106	98
1	1	121	116
1	2	710	702
1	3	582	588
1	4	165	164
1	5	196	204
1	6	219	225
1	7	97	101
1	8	204	205
1	9	73	72
1	10	66	69
1	11	257	259
2	0	588	578
2	1	639	631
2	2	357	371
2	3	153	154
2	4	170	169
2	5	399	403
2	6	410	406
2	7	77	80
2	8	294	299
2	9	198	204
2	10	190	193
2	11	158	155
3	1	618	599
3	2	331	341
3	3	317	298
3	4	147	139
3	5	112	113
3	6	183	185
3	7	632	640
3	8	99	95
3	9	92	88
3	10	145	145
3	11	45	39
4	0	312	318
4	1	310	299
4	2	348	347
4	3	390	394

K	H	FOBS	FCALC
9	4	118	117
9	5	271	275
9	6	147	143
9	7	252	249
9	8	91	90
10	0	265	263
10	1	175	183
10	2	97	105
10	3	108	108
10	4	28	25
10	5	269	271
10	6	153	156
11	1	94	102
11	2	176	188
11	3	171	167
11	4	81	77
11	5	62	59
12	0	112	110
12	1	138	138
12	2	131	122
12	3	80	81

L= 2

K	H	FOBS	FCALC
0	0	664	682
0	2	350	342
0	4	277	283
0	6	254	256
0	10	223	221
1	1	342	338
1	2	209	220
1	3	429	424
1	4	283	283
1	5	307	305
1	6	530	541
1	7	184	184
1	8	301	302
1	9	129	131
1	10	128	144
1	11	168	167
2	0	227	246
2	1	400	408
2	2	833	803
2	3	267	266
2	4	202	210
2	5	577	580
2	6	241	250
2	7	34	21
2	8	222	225
2	9	273	274
2	10	117	119
2	11	152	149
3	1	259	260
3	2	552	548
3	3	385	382

K	H	FOBS	FCALC
8	5	95	100
8	6	314	319
8	7	97	96
8	8	334	335
9	1	257	261
9	2	90	89
9	3	403	406
9	4	92	86
9	5	185	183
9	6	166	166
9	7	297	287
10	0	393	389
10	1	60	61
10	2	58	63
10	3	38	28
10	4	30	10
10	5	135	132
10	6	68	70
11	1	204	209
11	2	88	95
11	3	55	65
11	4	101	104
12	0	232	228
12	1	182	184

L= 3

K	H	FOBS	FCALC
0	2	67	60
0	4	423	420
0	6	376	379
0	8	317	320
0	10	283	278
1	1	433	430
1	2	421	414
1	3	261	265
1	4	249	245
1	5	456	458
1	6	271	272
1	7	226	227
1	8	200	196
1	9	209	209
1	10	102	103
2	0	289	297
2	1	535	539
2	2	82	79
2	3	54	52
2	4	31	28
2	5	325	325
2	6	261	267
2	8	285	287
2	9	157	148
2	10	123	120
3	1	247	252
3	2	260	258
3	3	374	372

K	H	FOBS	FCALC
8	7	61	61
9	1	61	59
9	2	33	42
9	3	270	262
9	4	108	109
9	5	157	156
9	6	135	125
10	0	133	131
10	1	177	176
10	2	33	29
10	3	127	126
10	4	104	100
10	5	230	230
11	1	202	201
11	2	224	220
11	3	161	161

L= 4

K	H	FOBS	FCALC
0	0	852	889
0	2	176	183
0	4	362	366
0	6	306	302
0	8	186	185
0	10	310	299
1	1	218	213
1	2	62	68
1	3	382	384
1	4	262	266
1	5	230	230
1	6	113	110
1	7	204	205
1	8	92	98
1	9	178	178
1	10	64	66
2	0	317	315
2	1	32	22
2	2	402	405
2	3	41	50
2	4	142	138
2	5	78	77
2	6	228	225
2	7	74	75
2	8	187	190
2	9	102	106
3	1	485	486
3	2	214	225
3	3	264	262
3	4	266	268
3	5	196	201
3	6	230	230
3	7	370	364
3	8	183	187
3	9	42	42
4	0	236	245

K	H	FOBS	FCALC
K	H	FOBS	FCALC
0	0	370	381
0	2	206	206
0	4	202	197
0	6	402	402
0	8	262	263
1	1	116	109
1	2	350	355
1	3	230	229
1	4	112	119
1	5	76	71
1	6	120	115
1	7	80	78
1	8	89	92
2	0	96	104
2	1	170	175
2	2	331	336
2	3	166	164
2	4	145	144
2	5	259	260
2	6	80	83
2	7	46	50
2	8	87	93
3	1	276	276
3	2	130	128
3	3	92	95
3	5	45	47
3	6	215	215
3	7	325	325
3	8	129	126
4	0	225	227
4	1	109	111
4	2	143	147
4	3	136	140
4	4	205	197
4	5	264	265
4	6	173	167
5	1	122	126
5	2	120	113
5	3	183	181
5	4	162	160
5	5	120	108
5	6	112	111
5	7	223	218
6	0	399	390
6	1	194	197
6	2	157	157
6	3	33	39
6	4	133	125
6	5	67	66
6	6	211	205
7	2	211	207
7	3	127	128
7	4	133	131
7	5	43	31
8	0	172	169

5	6	248	252
5	7	40	33
5	8	163	165
5	9	128	127
5	10	157	153
6	0	394	391
6	1	280	286
6	2	252	249
6	3	215	210
6	4	229	233
6	5	430	429
6	6	450	443
6	7	110	115
6	8	266	270
6	9	103	100
6	10	55	58
7	1	46	43
7	2	691	688
7	3	143	148
7	4	316	315
7	5	58	57
7	6	235	235
7	7	79	78
7	8	143	152
7	10	49	47
8	0	44	46
8	1	285	288
8	2	285	281
8	3	59	70
8	4	68	66
8	5	256	258
8	7	37	38
8	8	56	63
8	9	103	101
9	1	125	123
9	2	163	165
9	3	80	79
9	5	162	169
9	6	102	101
9	7	38	41
9	8	35	85
10	0	253	244
10	1	258	258
10	2	100	107
10	3	80	84
10	4	46	35
10	5	308	299
10	6	325	319
10	7	62	65
11	1	152	146
11	2	109	104
11	3	192	190

4	4	554	552
4	5	490	486
4	6	60	43
4	7	112	115
4	8	42	39
4	9	200	205
4	10	310	308
4	11	211	214
5	1	410	411
5	2	125	127
5	3	406	404
5	4	202	203
5	5	181	187
5	6	252	256
5	7	250	252
5	8	173	173
5	9	98	96
5	10	79	83
5	11	148	143
6	0	577	579
6	1	250	245
6	2	291	289
6	3	203	215
6	4	352	351
6	5	144	146
6	6	193	198
6	7	122	124
6	8	111	110
6	9	228	228
6	10	225	221
7	1	63	62
7	2	310	312
7	3	309	311
7	4	318	328
7	5	50	61
7	6	263	259
7	7	138	135
7	8	165	166
7	9	78	74
8	0	533	528
8	1	450	457
8	2	146	145
8	3	104	114
8	4	157	158
8	5	137	140
8	6	257	255
8	7	63	65
8	8	173	166
8	9	53	44
9	1	275	277
9	2	56	47
9	3	195	198

3	4	158	157
3	5	141	138
3	6	86	84
3	7	257	258
3	9	121	120
3	10	54	49
3	11	202	197
4	0	250	258
4	1	198	198
4	2	222	221
4	3	61	67
4	4	299	300
4	5	110	113
4	6	214	214
4	7	137	141
4	9	169	169
4	10	192	195
4	11	199	198
5	1	565	566
5	2	380	380
5	3	192	195
5	4	93	94
5	5	165	164
5	6	251	255
5	7	484	485
5	8	184	182
5	9	131	129
5	10	84	86
6	0	322	331
6	1	181	179
6	2	230	237
6	3	34	39
6	4	327	322
6	5	81	74
6	6	266	268
6	7	26	26
6	8	149	148
6	9	144	145
6	10	242	235
7	1	188	191
7	2	122	121
7	3	188	193
7	4	109	114
7	5	145	147
7	6	79	74
7	7	178	176
7	8	86	88
8	0	469	471
8	1	104	105
8	2	24	10
8	3	73	74
8	4	111	109

3	4	132	131
3	5	108	107
3	6	144	145
3	7	213	216
3	8	79	88
3	9	206	208
3	10	126	118
4	0	535	527
4	1	232	240
4	2	158	155
4	3	106	106
4	4	270	267
4	5	348	358
4	6	104	95
4	7	91	85
4	8	58	49
4	9	118	125
4	10	104	99
5	1	565	567
5	2	125	122
5	3	174	172
5	4	243	252
5	5	330	335
5	6	167	170
5	7	325	323
5	8	95	84
5	9	112	114
6	0	442	441
6	1	296	300
6	2	74	80
6	3	254	264
6	4	213	208
6	5	182	175
6	6	113	111
6	7	67	60
6	8	62	55
6	9	191	198
7	1	126	125
7	2	227	229
7	3	261	264
7	4	228	225
7	5	30	48
7	6	281	278
7	7	191	191
7	8	225	223
8	0	407	408
8	1	126	124
8	2	133	130
8	3	112	108
8	4	136	133
8	5	180	177
8	6	242	239

4	1	432	436
4	2	171	176
4	3	42	50
4	4	244	240
4	5	287	293
4	6	237	238
4	7	75	70
4	8	184	192
4	9	149	145
5	1	167	163
5	2	148	142
5	3	140	143
5	4	33	16
5	5	184	187
5	6	94	87
5	7	80	76
5	8	59	54
6	0	110	106
6	1	228	225
6	2	84	89
6	3	139	138
6	4	52	63
6	5	299	300
6	6	194	194
6	7	78	79
6	8	124	123
7	1	99	97
7	2	447	444
7	3	102	104
7	4	193	193
7	5	140	140
7	6	250	246
7	7	99	97
8	0	176	182
8	1	68	67
8	2	125	123
8	3	160	158
8	4	134	135
8	5	240	239
8	6	129	130
9	1	97	97
9	2	154	152
9	3	132	131
9	4	44	48
9	5	79	84
10	0	145	151
10	1	211	207
10	2	50	45
10	3	94	96

L= 5

8	1	204	205
8	2	88	98
8	4	243	242
9	1	169	164

L= 6

K	H	FOBS	FCALC
0	0	309	298
0	2	49	53
0	4	220	222
0	6	152	149
1	1	58	59
1	2	238	232
1	3	79	83
1	4	184	184
1	5	51	54
1	6	204	206
2	0	277	284
2	1	175	176
2	2	66	69
2	3	178	177
2	4	155	155
2	5	320	314
2	6	59	58
3	1	150	149
3	2	137	142
3	3	74	82
3	5	85	79
4	0	192	184
4	1	89	90
4	3	53	52
4	4	153	146
4	5	103	96
5	1	137	139
5	2	228	219
5	3	156	156
5	4	56	62
6	0	271	268
6	1	202	199
6	2	156	154
6	3	61	67

L= 7

K	H	FOBS	FCALC
0	0	81	72
0	2	94	100
1	1	140	132
1	2	226	220
2	0	315	310
2	1	180	170