

Crystal structure of minamiite, a new mineral of the alunite group

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Abstract

Minamiite, $(\text{Na}_{0.36}\text{K}_{0.1}\text{Ca}_{0.27}\square_{0.27})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$, a new mineral of alunite group, is trigonal with $a = 6.981(2)$, $c = 33.490(14)\text{\AA}$; $R\bar{3}m$ and $Z = 6$. The structure has been determined from three-dimensional X-ray diffractometer data and refined by the least-squares method to an R value of 0.045 for 389 observed reflections. The structure is composed of Al octahedra, S tetrahedra and M coordination polyhedra, and is analogous to that of alunite. Minamiite shows superlattice reflections doubling the c axis compared with that of alunite and probably caused by the partial ordering of the cations located in the M sites. The populations of M(1) and M(2) sites are determined to be $\text{Na}_{0.44(3)}\text{K}_{0.2}\square_{0.36}$ and $\text{Na}_{0.28}\text{Ca}_{0.54}\square_{0.18}$ respectively.

Introduction

The compounds of the alunite type can be represented by the formula $\text{MR}_3(\text{XO}_4)_2(\text{OH})_6$ (M: K, Na, H_3O , Ag, NH_4 , Ca, Sr, Pb, Ba, Ce; R: Al, Fe, Cu; X: S, P, As). About twenty kinds of minerals have been reported to be alunite type by many workers. The crystal structures of alunite, jarosite (Menchetti and Sabelli, 1976), plumbojarosite (Kato, 1979), woodhouseite (Kato, 1977), svanbergite (Kato and Miura, 1977), crandallite (Blount, 1974) and goyazite (Kato, 1971) have been described.

Ossaka (1972) reported an unknown mineral from Kusatsu-Shirane volcano, in Gumma Prefecture, Japan which has similar chemical composition to alunite but has superlattice reflections doubling the c axis compared to alunite. However, no investigations of this mineral were made. Investigation was undertaken not only to elucidate the details of this structure but to further elucidate the crystal chemistry of the alunite group.

This new mineral is named minamiite, in honor of

the late Dr. A. E. Minami (1899-1977), who made detailed geochemical studies on the hot springs around Kusatsu-Shirane Volcano. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA. Type specimens will be deposited at the National Science Museum, Hyakunin-cho, Shinjuku-ku, Tokyo 160, Japan.

Occurrence

Minamiite was found at Okumanza which is situated in the western foot hills of Mt. Shirane and at the source of the Okumanza River in Gumma Prefecture Japan as reported by Ossaka (1972). This area has been attacked by complicated hydrothermal actions along Okumanza fault. The mineral was found in a hydrothermally altered quartz bearing augite-hypersthene labradorite andesite of Neogene to Pleistocene age (Ota, 1957) exposed at this area. Minamiite, alunite and quartz were identified by X-ray powder diffraction. Unfortunately, the inclusions of alunite and quartz cannot be completely removed. Wet chemical analysis of the sample which contained minor inclusions is given in Table 1. Major components of the sample were Al_2O_3 , SO_3 , H_2O , Na_2O , K_2O and CaO . No jarosite,

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Observed and calculated structure factors (x100)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
1	1	0	17863	17108	1	9	4	5003	5143	5	1	10	8123	7921
4	1	0	11482	11212	0	1	5	1017	978	8	1	10	4398	3737
7	1	0	9636	9744	9	0	6	7794	7305	6	2	10	14357	13729
8	2	0	9943	10036	6	0	6	7799	7443	3	2	10	7731	7335
5	2	0	4674	4810	3	0	6	46236	41574	0	2	10	8848	7115
2	2	0	41078	40295	0	0	6	7262	6617	1	3	10	11258	10616
3	0	0	1643	517	1	1	6	29741	28767	4	3	10	5759	5569
3	3	0	25954	25449	4	1	6	13835	13334	5	4	10	2322	2572
7	4	0	5029	4807	7	1	6	8733	8497	2	4	10	18442	18153
4	4	0	14132	14516	5	2	6	15426	15421	0	5	10	6307	6069
5	5	0	9349	9847	2	2	6	3501	3191	3	5	10	7763	8063
6	0	0	15165	15152	0	3	6	5472	5595	6	5	10	5306	4534
9	0	0	10684	10765	3	3	6	12270	12132	4	6	10	7643	7703
0	2	1	1649	1528	6	3	6	13872	13803	3	8	10	4335	4012
1	0	1	1549	1834	7	4	6	4977	5067	0	8	10	13590	13605
8	0	2	6140	5988	1	4	6	18301	18541	0	4	11	1920	2072
5	0	2	1946	2197	2	5	6	10882	11322	1	2	11	1518	1630
2	0	2	24921	27712	5	5	6	4695	4639	2	0	11	1826	1503
0	1	2	5227	5085	3	6	6	3887	4366	6	0	12	13814	12950
3	1	2	2671	2174	0	6	6	7361	7764	3	0	12	3370	2896
7	2	2	2671	2988	1	7	6	5879	6384	0	0	12	22490	22246
4	2	2	11488	11234	4	7	6	8373	8088	4	1	12	2697	2758
2	3	2	5546	5801	2	8	6	3949	3731	8	2	12	8060	7976
6	4	2	7857	8010	0	9	6	6766	6887	2	2	12	20398	19896
0	4	2	14832	14503	2	1	7	2332	1815	0	3	12	1857	1735
1	5	2	2191	2489	1	0	7	1586	1625	4	4	12	10084	10578
2	6	2	10961	10680	4	0	7	1628	1309	2	5	12	2113	2591
0	10	2	8780	8765	8	0	8	4200	4417	0	6	12	13574	14125
0	0	3	2556	2573	5	0	8	3667	4305	2	8	12	4560	4623
2	2	3	1508	1211	2	0	8	8284	9196	0	2	13	1435	1637
1	1	3	1153	1238	0	1	8	3876	390	8	0	14	5921	5867
10	0	4	4158	4306	3	1	8	11044	10270	5	0	14	3015	3036
7	0	4	6792	7638	6	1	8	2269	2004	2	0	14	11884	11743
4	0	4	12734	14449	7	2	8	2692	2347	0	1	14	34969	34195
1	0	4	20789	21322	4	2	8	12338	12582	3	1	14	12719	12382
2	1	4	11253	10044	1	2	8	3276	2893	6	1	14	4700	4682
5	1	4	9239	10019	2	3	8	5535	5588	9	1	14	4502	4815
8	1	4	6912	8314	5	3	8	4993	4714	7	2	14	4993	5199
9	2	4	4836	4936	6	4	8	3188	3358	4	2	14	1836	2368
6	2	4	10116	11166	0	4	8	16271	16629	1	2	14	3662	4100
3	2	4	15317	15417	1	5	8	5467	5326	2	3	14	23471	23826
1	3	4	13538	12814	5	6	8	2786	2375	5	3	14	3584	3228
4	3	4	6046	6196	2	6	8	11039	11231	3	4	14	9896	10493
7	3	4	4977	5373	0	7	8	6052	6316	0	4	14	11242	11288
2	4	4	2515	2378	0	10	8	7204	7174	1	5	14	5660	6066
0	5	4	5864	6078	3	0	9	1831	1774	4	5	14	4367	4287
3	5	4	9677	9673	10	0	10	9886	9508	5	6	14	9776	9774
6	5	4	7366	7102	4	0	10	13736	13001	2	6	14	6135	6045
1	6	4	3709	3485	1	0	10	13167	13103	0	7	14	9980	9949
2	7	4	5342	5125	2	1	10	3250	3019	1	8	14	9531	9489

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
2	2	15	1685	1713	3	4	20	4523	4703	5	3	26	8102	7763
1	1	15	1909	1408	0	4	20	20163	20766	3	4	26	9109	9266
0	0	15	3094	3350	1	5	20	12813	13502	0	4	26	1800	1995
7	0	16	3334	3133	2	6	20	9046	9498	1	5	26	10110	10814
1	0	16	1080	1611	0	7	20	5274	5640	4	5	26	9531	9640
2	1	16	14571	14368	3	7	20	4539	5135	2	6	26	3568	3465
5	1	16	7575	7228	1	8	20	3662	3181	0	7	26	9761	10240
8	1	16	3542	3525	0	6	21	1857	2032	3	7	26	4914	5054
3	2	16	1549	1920	1	4	21	2400	2166	1	8	26	5102	4751
0	2	16	8076	8187	1	1	21	2316	2126	0	3	27	3177	3504
1	3	16	5519	5592	0	0	21	1315	1558	2	2	27	1680	1774
4	3	16	5332	5338	3	0	21	3954	4145	1	1	27	2478	2173
7	3	16	7836	8153	7	0	22	4095	3999	6	0	27	2149	2610
5	4	16	7356	6945	4	0	22	15468	14900	4	0	28	3829	3393
2	4	16	6485	6774	2	1	22	4095	3863	2	1	28	8545	9025
0	5	16	10627	11011	6	2	22	11503	10835	5	1	28	8253	7967
3	5	16	7768	8022	3	2	22	2567	2736	3	2	28	2368	2140
4	6	16	4507	4099	0	2	22	13778	13985	0	2	28	2426	1637
1	6	16	9046	9360	5	4	22	4111	3893	1	3	28	7178	7405
2	7	16	3667	3486	2	4	22	11341	11543	4	3	28	2958	3283
3	8	16	6219	6177	0	5	22	2994	3065	7	3	28	3991	3878
0	8	16	6192	6515	4	6	22	8806	8823	5	4	28	4080	3751
1	9	16	4873	5069	1	6	22	2864	2828	2	4	28	8368	8268
2	3	17	1424	1808	0	8	22	10074	9745	0	5	28	7935	7902
0	1	17	2718	2777	2	0	23	2384	2323	3	5	28	7351	7219
2	0	17	1915	1737	9	0	24	6328	5675	4	6	28	2843	2745
6	0	18	9328	8797	6	0	24	14492	14031	1	6	28	5071	4820
3	0	18	16830	17000	3	0	24	12953	13227	2	7	28	4711	4878
0	0	18	29006	28467	1	1	24	4267	4671	0	8	28	7804	7924
1	1	18	4721	4716	7	1	24	6151	5549	6	0	30	9150	8771
8	2	18	7768	7112	8	2	24	6156	5930	3	0	30	6077	6298
5	2	18	6010	6148	5	2	24	5191	5365	2	2	30	8371	8810
2	2	18	11957	12031	2	2	24	6719	6591	3	3	30	6119	6130
3	3	18	3224	3173	0	3	24	10439	10670	6	3	30	4194	4532
6	3	18	5222	5426	3	3	24	9834	9551	4	4	30	8644	8703
4	4	18	5639	5554	6	3	24	5707	5697	2	5	30	2989	2589
1	4	18	5389	5737	4	4	24	5243	5572	0	6	30	12406	12728
8	0	20	8895	8917	1	4	24	7032	7362	2	1	31	2483	1839
5	0	20	2488	2096	5	5	24	4805	4628	1	0	31	1393	592
2	0	20	42351	41596	3	6	24	2942	2737	8	0	32	6693	6021
0	1	20	6516	6176	1	7	24	4554	3595	5	0	32	2311	2107
3	1	20	14732	15038	0	9	24	4288	4719	2	0	32	18822	19110
6	1	20	3902	4163	5	0	26	14957	14710	3	1	32	4523	4756
9	1	20	4022	3289	2	0	26	1701	1226	6	1	32	4492	4406
7	2	20	7048	7081	0	1	26	14915	14555	4	2	32	9521	10042
4	2	20	15979	16329	3	1	26	14378	14816	1	2	32	3965	4340
1	2	20	4695	4438	6	1	26	10611	10155	5	3	32	5217	5504
2	3	20	3647	3553	7	2	26	8639	8264	0	4	32	14983	15471
5	3	20	12573	12312	1	2	26	17643	18295	1	5	32	4998	4643
6	4	20	10971	10642	2	3	26	10778	10913	2	6	32	7658	8118

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
1	0	34	4215	3747	6	1	38	4450	4261	4	2	44	6881	6818
2	1	34	10475	10556	4	2	38	3229	3910	1	2	44	2979	3547
0	2	34	9975	10384	1	2	38	9396	9401	2	3	44	2937	2877
4	3	34	4481	4127	2	3	38	2264	1693	0	4	44	3980	3422
5	4	34	4367	4481	3	4	38	4382	4299	1	5	44	3417	3743
2	4	34	4706	4945	7	0	40	3214	3365	1	0	46	8337	7866
0	5	34	9928	10259	4	0	40	12281	11944	2	1	46	8660	8649
1	6	34	4460	4405	2	1	40	4424	4179	5	1	46	7324	6716
0	8	34	5024	5558	5	1	40	4643	4433	3	2	46	6380	6002
2	0	35	2301	2452	6	2	40	7533	6808	1	3	46	8530	8209
3	0	36	5264	5447	0	2	40	15129	15077	4	3	46	6104	6012
0	0	36	5415	5250	1	3	40	5238	5058	0	5	46	7752	7717
1	1	36	5347	5533	2	4	40	7366	7163	4	2	47	2567	2300
4	1	36	5034	4734	3	5	40	4747	4892	0	1	47	2577	2433
7	1	36	5039	4670	1	6	40	3678	3887	0	0	48	3047	2735
5	2	36	4419	3953	5	0	41	2708	2716	1	1	48	4293	4736
2	2	36	2572	2169	6	0	42	10084	9986	4	1	48	5029	5421
0	3	36	6344	6786	3	0	42	3198	2853	0	3	48	7272	7611
3	3	36	3521	3784	0	0	42	4930	5310	3	3	48	6537	6649
6	3	36	3777	3216	1	1	42	3177	3090	2	0	50	3094	3675
1	4	36	4982	5145	5	2	42	3177	3387	0	4	50	5608	5404
2	5	36	2948	3284	2	2	42	7721	7902	0	3	51	2405	2114
3	6	36	4502	4781	0	3	42	5885	6434	4	0	52	7538	7063
1	7	36	4356	4833	4	4	42	7199	7691	1	0	52	2687	2507
0	2	37	2400	2459	0	6	42	6938	7334	0	2	52	11973	11627
5	0	38	9552	9518	5	0	44	3631	3453	1	3	52	4972	4687
2	0	38	8248	8737	2	0	44	3281	2787	0	0	54	8540	7882
0	1	38	4351	4133	0	1	44	2003	1829	0	3	54	4215	3617