

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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woodhouseite and crandallite were considered to exist because only trace amounts of Fe and P were found. It was noticed that the sum of Na₂O and K₂O was low compared with that of alunite, and a significant amount of CaO, which is not a constituent of alunite, was contained in the sample. Neglecting the inclusions, the chemical formula of minamiite was calculated to be (Na_{0.46}K_{0.19}Ca_{0.14}□_{0.14})_{0.93}Al_{3.11}(SO₄)₂(OH)_{5.70}. Analysis of Na, K and Ca in the crystal used for the X-ray intensity collection was performed by an EDAX microprobe. The standards used were Na₂SO₄, K₂SO₄, CaSO₄, Na_{1.2}K_{0.8}SO₄, NaKSO₄, Na_{0.8}K_{1.2}SO₄, K₂Ca₂(SO₄)₃ and Na₄Ca(SO₄)₃. The ratio of Na/S, K/S and Ca/S in this crystal were measured to be 0.18, 0.05 and 0.135 respectively, averaging 23 analysis points. Thus, the ideal chemical formula of this crystal was determined to be (Na_{0.36}K_{0.1}Ca_{0.27}□_{0.27})Al₃(SO₄)₂(OH)₆.

Experimental

From Weissenberg photographs, the crystals were found to show hexagonal Laue symmetry $\bar{3}m$. Since systematic absences were $-h + k + l \neq 3n$ for hkl and $l \neq 3n$ for $00l$, the Laue symmetry restricts the possible space groups to $R\bar{3}m$, $R32$ and $R\bar{3}m$. Cell dimensions were determined by the least-squares method using 16 reflections measured on a four-circle diffractometer. The crystal data are given in Table 2.

The crystal used for collection of intensity data is a hexagonal plate with edges of 100 μm and a thickness of 30 μm . Intensities were measured up to $2\theta = 75^\circ$ on an automated four-circle diffractometer (Philips PW 1100), with MoK α radiation reflected from a graphite monochromator, and the ω - 2θ scan technique. The scan speed was 4°min^{-1} in ω and the scan width was determined as $(1.2 + 0.3\tan\theta)^\circ$. In all, 389³ independent intensity data satisfying the condition $|F| > 3\sigma(|F|)$ were collected and used for the structure determination, where $\sigma(|F|)$ is the standard deviation due to counting statistics. The intensities were corrected for the Lorentz-polarization factor. No absorption correction was applied.

Structure analysis

Since minamiite was thought to have an alunite-type structure, the atomic parameters of alunite

³Since the intensity of 003 could not be measured using MoK α radiation by four-circle diffractometer due to the low diffraction angle, that of 003 was estimated using the intensities measured with X-ray powder diffraction pattern.

Table 1. Wet chemical analysis of minamiite

	1	2	Rem.	1	2
Na ₂ O	3.37	0.46	Fe ₂ O ₃	0.03	0.00
K ₂ O	2.17	0.19	P ₂ O ₅	0.18	0.01
CaO	1.94	0.29	SiO ₂	3.58	-
Al ₂ O ₃	37.74	3.11	TiO ₂	0.45	-
SO ₃	38.09	4	V ₂ O ₃	0.02	-
H ₂ O ⁺	12.22	5.70	MgO	-	-
Rem.	4.28	-	MnO	-	-
			H ₂ O ⁻	0.02	-
Total	99.81		Sum	4.28	

1. wt % 2. Molar numbers were calculated with SO₃=4.

reported by Menchetti and Sabelli (1976) were used for the initial parameters. The averaged structure was refined by least-squares method with omitting 38 superlattice reflections. Then, the atomic parameters of the superstructure were obtained from the difference Fourier maps phased with those of the averaged structure using all reflection data. At this stage bond lengths of M(1)-O, OH were found to be longer than those of M(2)-O, OH. Thus, we assumed that the relatively large K cation occupied the M(1) site, the relatively small Ca cation occupied the M(2) site and Na was situated in both the M(1) and M(2) sites. The populations of M(1) and M(2) were refined to be Na_{0.44(3)}K_{0.2}□_{0.36} and Na_{0.28}Ca_{0.54}□_{0.18} respectively. The atomic parameters of H atoms can be detected from the difference Fourier maps but were not refined with least-squares methods. The structure with space group $R\bar{3}m$ converged to an R value of 0.045 with anisotropic thermal parameters for all atoms except the atoms in M(1) and M(2). An R value calculated with 38 superlattice reflections was 0.109. The weighting scheme of Hughes (1941) was adopted: $w = 1.0$ if $F_o < 156.5$, and $w = (156.5/F_o)^2$ if $156.5 \leq F_o$. The F_o and F_c table has been deposited⁴. The final atomic parameters are given in Table 3. The atomic

⁴To obtain a copy of these tables, order Document AM-82-184 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W., Washington, D. C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 2. Crystal data

(Na _{0.36} K _{0.1} Ca _{0.27})Al ₃ (SO ₄) ₂ (OH) ₆	$V = 1413.5 \text{ \AA}^3$
Trigonal	$Z = 6$
Space group $R\bar{3}m$	$D_G = 2.81 \text{ gcm}^{-3}$
$a = 6.981(2) \text{ \AA}$	$M_r = 398.12$
$c = 33.490(14)$	$\mu(\text{Mo K}\alpha) = 11.4 \text{ cm}^{-1}$

Table 3a. Atomic coordinates

atom	multipl.	\bar{x}	\bar{y}	\bar{z}
M(1) $\left\{ \begin{smallmatrix} \text{Na} \\ \text{K} \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 0.036(3) \\ 0.017 \end{smallmatrix} \right\}$	0	0	0
M(2) $\left\{ \begin{smallmatrix} \text{Na} \\ \text{Ca} \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 0.024 \\ 0.045 \end{smallmatrix} \right\}$	0	0	0.5
S(1)	0.167	0	0	0.8458(1)
S(2)	0.167	0	0	0.3473(1)
Al	0.5	0.5001(7)	-0.5001	0.2496(1)
O(1)	0.167	0	0	0.8022(5)
O(2)	0.167	0	0	0.3043(4)
O(3)	0.5	0.2181(8)	-0.2181	0.0290(3)
O(4)	0.5	0.2183(9)	-0.2183	0.5274(3)
OH(1)	0.5	0.1268(9)	-0.1268	0.9294(3)
OH(2)	0.5	0.1239(9)	-0.1239	0.4321(3)
H(1)	0.5	0.180	-0.180	0.9483
H(2)	0.5	0.180	-0.180	0.4477

Estimated standard deviations are given in parentheses.

scattering factors for neutral atoms and the dispersion correction factors were taken from *International Tables for X-ray Crystallography, Vol. IV* (1974). Computations of least-squares calculations of the lattice parameters, difference Fourier synthesis, least-squares refinement of the structure, and interatomic distances were carried out using the program RSLC-3 (Sakurai, 1967), RSSFR-3 (Sakurai, 1967), LINUS (Coppens and Hamilton, 1970), and RSDA-4 (Sakurai, 1967) on an M-180 computer at the Computer Center of Tokyo Institute of Technology.

Table 3b. Anisotropic temperature factors in the form: $\exp[-2\pi^2(\sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})]$. Values are multiplied by 10^4

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B/\text{\AA}^2$
M(1)	-	-	-	-	-	-	2.4(8)
M(2)	-	-	-	-	-	-	1.9(4)
S(1)	19(21)	19	111(23)	10	0	0	0.39*
S(2)	110(28)	110	43(20)	55	0	0	0.69*
Al	53(4)	53	93(5)	29(4)	-1(2)	1	0.51*
O(1)	166(79)	166	76(49)	83	0	0	1.07*
O(2)	91(63)	91	76(49)	46	0	0	0.68*
O(3)	119(53)	119	103(27)	98(45)	10(17)	-10	0.76*
O(4)	116(59)	116	105(27)	82(51)	5(19)	-5	0.80*
OH(1)	78(42)	78	145(26)	53(41)	-23(16)	23	0.74*
OH(2)	35(35)	35	174(33)	-10(34)	-17(16)	17	0.74*
H(1)	-	-	-	-	-	-	3.0
H(2)	-	-	-	-	-	-	3.0

B: Isotropic temperature factors in the form $\exp[-B(\sin\theta/\lambda)^2]$.

: Equivalent isotropic temperature factors computed according to the relation: $4\pi^2 \sum_i \sum_j h_i h_j a_i^ a_j^* U_{ij} / 3$.

Estimated standard deviations are given in parentheses.

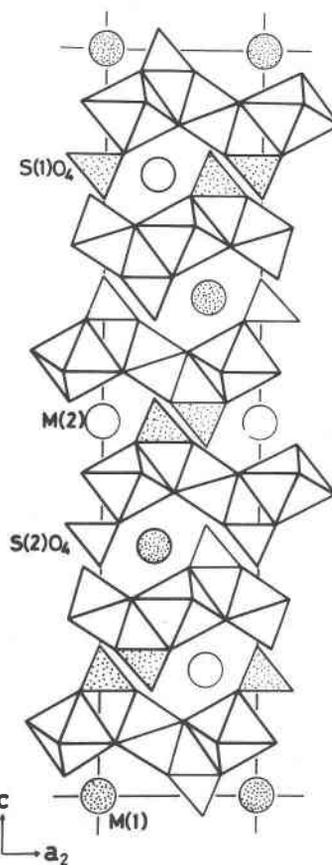


Fig. 1. Crystal structure of minamiite projected along the a_1 axis. Oxygen atoms are at the corners of tetrahedra and octahedra. Shaded and open circles represent M(1) and M(2) atoms.

Discussion

The structure of minamiite is composed of Al octahedra, two crystallographically independent S tetrahedra, and two M coordination polyhedra (Fig. 1). Each Al octahedron shares four corners with adjacent Al octahedra to form a sheet perpendicular to the c axis. Each S tetrahedron shares three corners with Al octahedra. The remaining unshared corner points towards an adjacent sheet of Al octahedra and is hydrogen bonded thereto. M(1) and M(2) are located in the large cavity between the two sheets and are surrounded by twelve O and OH atoms.

Interatomic distances and bond angles are given in Table 4. Here, the interatomic distances in the left and right columns are crystallographically equivalent in alunite and the Δ values are the differences between them in minamiite. The S-O bond lengths in tetrahedra range from 1.44(2) to 1.482(6) Å and are in good agreement with those of

Table 4. Interatomic distances (Å) and angles (degrees)

S(1) tetrahedron				S(2) tetrahedron											
	Distance	O-M-O angle		Distance	O-M-O angle	Δ									
S(1)-O(1)	1.462(17)		S(1)-O(2)	1.438(15)		0.024									
S(1)-O(4 ^{i,ii,iii})	1.478(6)		S(2)-O(3 ^{i,ii,iii})	1.482		-0.004									
mean	1.474		mean	1.471		0.003									
O(1)-O(4)	2.404(16)	109.7(4)	O(2)-O(3)	2.390(14)	109.9(4)	0.014									
O(4)-O(4)	2.410(9)	109.2(4)	O(3)-O(3)	2.414(8)	109.1(4)	-0.004									
mean	2.407		mean	2.402		0.005									
<u>Al octahedron</u>															
Al-O(4 ^v)	1.962(9)		Al-O(3 ^{iv})	1.937(10)		0.025									
Al-OH(2 ^{viii,ix})	1.882(8)		Al-OH(1 ^{vi,vii})	1.875(8)		0.007									
mean	1.902														
O(4 ^v)-OH(2 ^{viii,ix})	2.664(10)	87.7(3)	O(3 ^{iv})-OH(1 ^{vi,vii})	2.684(9)	89.5(4)	-0.020									
O(4 ^v)-OH(1 ^{vi,vii})	2.729(12)	90.7(4)	O(3 ^{iv})-OH(2 ^{viii,ix})	2.750(11)	92.1(4)	-0.021									
OH(2 ^{viii})-OH(2 ^{ix})	2.594(6)	87.1(3)	OH(1 ^{vi})-OH(1 ^{vii})	2.655(10)	90.2(4)	-0.061									
OH(2 ^{viii})-OH(1 ^{vii})	2.687(11)	91.3(3)	OH(1 ^{vi})-OH(2 ^{ix})	2.687(11)	91.3(3)	0									
<u>M(2) polyhedron</u>				<u>M(1) polyhedron</u>											
M(2)-O(4 ^{x,xi,xii,xiii,xiv,xv})	2.794(6)		M(1)-O(3 ^{x,xi,xii,xiii,xiv,xv})	2.809(5)		-0.015									
M(2)-OH(2 ^{x,xi,xii,xix,xx,xxi})	2.723(8)		M(1)-OH(1 ^{xvi,xvii,xviii,xix,xx,xxi})	2.818(9)		-0.095									
mean	2.759		mean	2.814		-0.055									
<u>Symmetry code</u>															
none	x	y	z	vi	2/3+x	-2/3+2x	-2/3+z	xii	x	2x	z	xviii	-2x	-x	-1+z
i	2/3-2x	1/3-x	1/3+z	vii	2/3-2x	-2/3-x	-2/3+z	xiii	-x	x	-z	xix	-x	x	1-z
ii	-1/3+x	1/3-x	1/3+z	viii	1/3-x	-1/3-2x	-2/3-z	xiv	-x	-2x	-z	xx	-x	-2x	1-z
iii	-1/3+x	-2/3+2x	1/3+z	ix	1/3+2x	2/3+x	2/3-z	xv	2x	x	-z	xxi	2x	x	1-z
iv	2/3-x	-2/3+x	1/3-z	x	-2x	-x	z	xvi	x	-x	-1+z				
v	1/3+x	-1/3-x	-1/3+z	xi	x	-x	z	xvii	x	2x	-1+z				

Estimated standard errors are given in parentheses and refer to last decimal place.

alunite and jarosite (Menchetti and Sabelli, 1976). The Δ values of S-O bond lengths and O-S-O bond angles are small and significant differences do not exist. The distortions of S tetrahedra are smallest among those of alunite group minerals.

The Al-O,OH bond lengths in octahedra range from 1.875(8) to 1.962(9)Å and are in good agreement with those of alunite (Menchetti and Sabelli, 1976), svanbergite (Kato and Miura, 1977), woodhouseite (Kato, 1977), and crandallite (Blount, 1974). The Δ values of Al-O,OH bond lengths are also small and significant differences do not exist. The distortion of the Al octahedron is somewhat larger than those of the S tetrahedra.

The M(1) site is statistically occupied by Na (44%), K (20%) atom and vacancy (36%) in random distribution. The M(1)-O,OH bond lengths are 2.809(5) and 2.818(9)Å. The average bond length of M(1)-O,OH(2.814Å) is a little shorter than that of alunite (2.851Å) where this site is occupied only by K atoms. On the other hand, the M(2)-O,OH bond lengths are 2.794(6) and 2.723(8)Å, and are shorter than the M(1)-O,OH bond lengths.

The M(2) site is statistically occupied by Na (28%), Ca (54%) and vacancy (18%) in random distribution. The bond length, 2.759Å is a little longer than those of woodhouseite (2.733Å) and crandallite (2.711Å) where the site is occupied by only Ca atoms. The temperature factors of M(1) and M(2) are fairly large compared with those of the other atoms. This may mean that the split Ca atom model of crandallite (Blount, 1974) might be applicable to the structure of minamiite. The OH...O distances are 2.815(9) and 2.860(10)Å and are a little shorter than that in alunite (2.925Å) reported by Menchetti and Sabelli (1976). The O-H distances are 0.86 and 0.90Å and are a little shorter than the value of 0.95-0.96Å which are estimated from the graph of Nakamoto *et al.* (1955). The O...H distances are 1.99 and 2.00Å and the O-H...O angles are 160.4 and 159.4° which are intermediate value of those reported for alunite and jarosite by Menchetti and Sabelli (1976). The IR spectra (Fig. 2) of minamiite and alunite were measured with the KBr disk method to examine the hydrogen bonds. The sample of alunite for comparison is obtained from

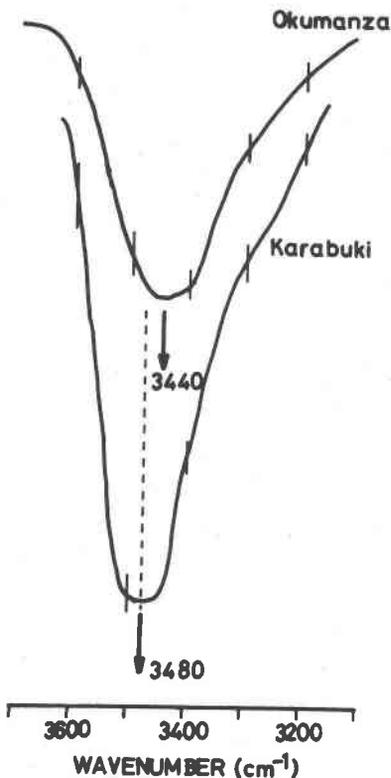


Fig. 2. The IR spectra of minamiite from Okumanza and alunite from Karabuki.

Karabuki which is about 500 m downstream from Okumanza. Absorption bands of the OH stretching vibration are observed at 3440 cm^{-1} in minamiite and at 3480 cm^{-1} in alunite. As the absorption band of minamiite is broader than that of alunite, the IR data support the presence of different OH \cdots O distances as pointed out by the structure determination. According to the graph of Nakamoto *et al.* (1955), the OH \cdots O distances are estimated to be 2.86 \AA at 3440 cm^{-1} and 2.88 \AA at 3480 cm^{-1} . These values are somewhat shorter than those obtained from structure determinations but the trend is in good agreement. However, the Δ values (Table 4) of OH(1) and OH(2), which are coordinated to M(1) and M(2) respectively, together with that of OH \cdots O are significantly greater than standard deviations.

It was concluded that the superstructure of minamiite was caused by the partial ordering of the cations in the M(1) and M(2) sites as reported in plumbojarosite (Kato, 1979). The ordering of the Pb atom is not complete in plumbojarosite, where 90 percent of Pb atoms occupy one site.

In the Weissenberg photograph, with orientation

($h0l$), some crystals show diffraction spots of minamiite ($c = 16.745 \times 2 = 33.490\text{ \AA}$) and alunite ($c = 17.278\text{ \AA}$) in almost the same orientation. This indicates the coexistences of fairly large domains of minamiite and alunite in one crystal. A scanning EPMA microprobe measurement on the (001) plane of the crystals was, therefore, performed in order to examine the existences of these domains. The distribution of Na, K and Ca in a crystal is shown in Figure 3. It is found that this crystal occurs with the K rich domain (corresponding to alunite) in 30–40 μm size and Na, Ca-rich domain (corresponding to minamiite) in almost the same size. The increase and decrease of K cation exactly corresponds to the decrease and increase of Na and Ca cations. This implies the reaction $\text{K} \rightleftharpoons \text{Na, Ca}$, *i.e.*, alunite \rightleftharpoons minamiite, occurred in the crystals. Since the Na, Ca-rich domain always appears on the edge of the crystals, minamiite may be formed by the reaction of $\text{K} \rightarrow \text{Na, Ca}$ after the alunite has crystallized. It is considered that minamiite forms under complicated hydrothermal reaction conditions.

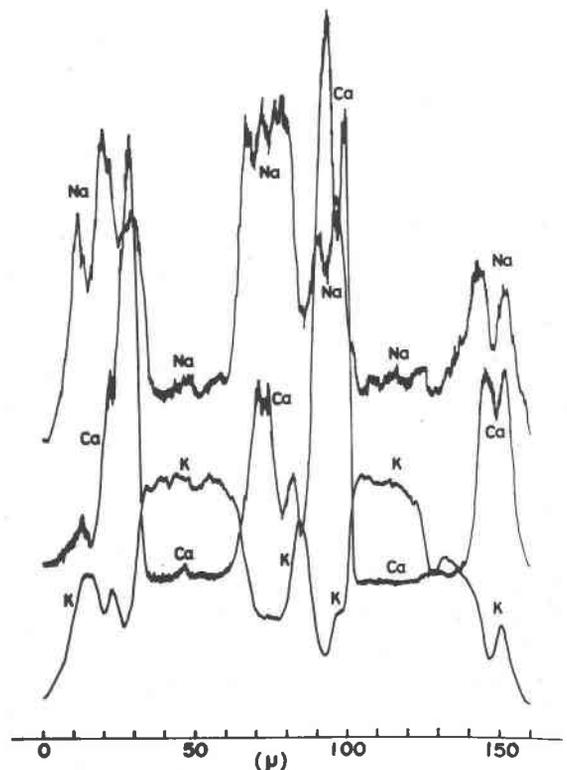


Fig. 3. A scanning EPMA microprobe analysis of a minamiite crystal from Okumanza.

Acknowledgments

We wish to thank Dr. A. Kato for constructive comments, Professor Y. Kato for four-circle diffractometer, Dr. I. Yasui for EDAX microprobe, and Mr. M. Minato for EPMA microprobe analysis.

References

- Blount, A. M. (1974) The crystal structure of crandallite. *American Mineralogist*, 59, 41–47.
- Coppens, P. and Hamilton, W. C. (1970) Anisotropic extinction corrections in the Zachariasen approximation. *Acta Crystallographica*, A26, 71–83.
- Hughes, E. W. (1941) The crystal structure of melamine. *Journal of American Chemical Society*, 63, 1737–1752.
- International Tables for X-ray Crystallography Vol. IV (1974) Kynoch Press, Birmingham.
- Kato, T. (1971) The crystal structures of goyazite and woodhouseite. *Neues Jahrbuch für Mineralogie Monatshefte*, 241–247.
- Kato, T. (1977) Further refinement of the woodhouseite structure. *Neues Jahrbuch für Mineralogie Monatshefte*, 54–58.
- Kato, T. (1979) The crystal structure of plumbojarosite (abstr.). Annual meeting abstracts of Mineralogical Society of Japan, 1979, 26.
- Kato, T. and Miura, Y. (1977) The crystal structures of jarosite and svanbergite. *Mineralogical Journal*, 8, 419–430.
- Menchetti, S. and Sabelli, C. (1976) Crystal chemistry of the alunite series: Crystal structure refinement of alunite and synthetic jarosite. *Neues Jahrbuch für Mineralogie Monatshefte*, 406–417.
- Nakamoto, K., Margoshes, M. and Rundle, R. E. (1955) Stretching frequencies as a function of distances in hydrogen bonds. *Journal of American Chemical Society*, 77, 6480–6486.
- Ossaka, J. (1972) Several formation circumstances on volcanic minerals around Kusatsu-Shirane Volcano (abstr.). Annual meeting abstracts of Mineralogical Society of Japan, 1972, 54.
- Ota, R. (1957) Geological sheet map of Kusatsu (1:50,000) and its explanatory text. Geological Survey of Japan, Tokyo.
- Sakurai, T. (1967) Universal crystallographic program system (UNICS). Crystallographic Society of Japan.

*Manuscript received, May 22, 1981;
accepted for publication, September 14, 1981.*