

The crystal structure of masutomilite, Mn analogue of zinnwaldite

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Abstract

The crystal structure of masutomilite from Tanakamiyama, Ohtsu, Japan, has been refined by the X-ray single crystal method. The chemical formula is $(K_{1.79} Na_{0.15} Rb_{0.14})_{2.08} (Li_{2.54} Mn^{2+}_{0.99} Fe^{2+}_{0.18} Fe^{3+}_{0.06} Al_{1.96} Ti_{0.01})_{5.74} (Si_{6.65} Al_{1.35})_{8.00} O_{19.64} (F_{3.16} (OH)_{1.20})_{4.36}$ and the crystal data are as follows: monoclinic, $C2$, $a = 5.262(2)$, $b = 9.102(3)$, $c = 10.094(3)$ Å, $\beta = 100.83(2)^\circ$, $Z = 1$. The final R -value converged to 0.046 ($wR = 0.052$), using 519 independent reflections. The octahedral cation ordering, small Al and Fe^{3+} in the M(2) site, and the remaining large Li and Mn^{2+} in the M(1) and M(3) sites, results in the non-centrosymmetric $C2$ structure. The mean bond length of M(2)–O is 1.89 Å, and those of M(1)–O and M(3)–O are 2.13 and 2.12 Å, respectively.

Introduction

Masutomilite, a Mn analogue of zinnwaldite, found in a druse of granite pegmatite at Tanakamiyama, Ohtsu, Shiga Prefecture, Japan, was described by Harada *et al.* (1976), who gave a chemical formula (Table 1) and showed its diffraction symbol to be $2/mC-/-$.

Recently, crystal chemistry and occurrences of micas are reviewed in detail by Bailey (1984). More than twenty mica structural refinements showed characteristic octahedral cation ordering, where larger atoms occupy the M(1) site and smaller ones occupy the M(2) site. Takeda and Burnham (1969) found that the unit cell of fluoropolyolithionite with space group $C2/m$ has one large M(1) site on the mirror plane and two small symmetry-related M(2) sites. Guggenheim and Bailey (1977) refined zinnwaldite-1M, from the Sadisdorf Mine, D.D.R., as space group $C2$, where the octahedral sites are divided into three kinds of symmetrically independent sites, M(1), M(2) and M(3). M(2) in $C2/m$ is designated as M(2) and M(3) in $C2$. They found that Al completely occupies the small octahedral M(2) site, and large cations such as Fe, Li and vacancies are nearly randomly distributed over the M(1) site and the M(3) site. They anticipated that all fluorine-rich zinnwaldites and lepidolites would have a

similar ordering pattern. However, Guggenheim (1981) refined a lepidolite-1M from Radkovic and found that this crystallizes in $C2/m$. Thus, he suggested that parameters of crystallization other than fluorine content are important. Recently, in a study using the optical second harmonic generation (SHG) technique Guggenheim *et al.* (1983) predicted that masutomilite-1M crystallizes in space group $C2$. In order to more fully understand the nature of cation ordering in these fluorine-rich micas, we have refined the crystal structure of masutomilite.

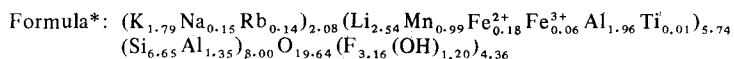
Experimental

A crystal, with dimensions of $0.28 \times 0.14 \times 0.02$ mm, from the type locality was used for the present study. Unit cell parameters (Table 1) were determined by a least-squares refinement of 25 reflections measured on a Philips PW1100 automated diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Reflections were measured by $\theta/2\theta$ scans in a quadrant of the limiting sphere from $1^\circ < \theta < 30^\circ$ in a range $-8 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 16$. 519 independent reflections, satisfying a relation $I_{\text{peak}} - 2\sqrt{I_{\text{peak}}} > I_{\text{back}}$, were observed. The intensities were corrected for L_p factors and absorption effect. The absorption corrections were made theoretically by dividing the crystal into 980 points ($\mu = 24.5 \text{ cm}^{-1}$).

For the structure refinement, scattering factors except O^{2-} were taken from the tables for full ionized atoms in the *International Tables for X-ray Crystallography*, Vol. IV, (1974). The scattering factor of O^{2-} by Tokonami (1965) was used. Weighted mean scattering factors calculated from the chemical composition for the M, T, (F, OH) sites were used in the refinement.

First, the centrosymmetric space group $C2/m$ was assumed. The atomic parameters of manganoan phlogopite-1M by Kato *et al.* (1979) were used as starting parameters. Calculations with *FLS-60*, a full-matrix least-squares program, adopting the unit-weight scheme for significant reflections and varying 53 parameters including multiplicities of the M(1) and M(2) sites and anisotropic temperature factors converged to give $R = 0.070$ ($wR = 0.081$). Next, the full-matrix least-squares calculations were

TABLE 1. Crystal data for masutomilite



Unit cell dimensions:

$$a = 5.262(2), b = 9.102(3), c = 10.094(3) \text{ \AA}, \beta = 100.83(2)^\circ$$

Space group: $C2$

Z: 1

*given by Harada *et al.* (1976)

TABLE 2. Atomic coordinates and temperature factors of masutomilite

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq.}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0	0.5	0	2.15	0.018(2)	0.0072(8)	0.0054(6)	0	0.0018(9)	0
M(1)	0	-0.0081(37)	0.5	1.09	0.007(3)	0.004(1)	0.004(1)	0	0.002(1)	0
M(2)	0	0.3190(27)	0.5	0.97	0.005(4)	0.005(1)	0.002(1)	0	0.000(1)	0
M(3)	0.5	0.1587(30)	0.5	1.00	0.009(6)	0.003(2)	0.003(2)	0	0.001(3)	0
T(1)	0.0751(15)	0.1660(20)	0.2282(11)	0.54	0.004(2)	0.002(1)	0.002(1)	-0.001(1)	0.002(1)	-0.000(1)
T(11)	0.5852(15)	0.3297(21)	0.2287(12)	0.78	0.003(3)	0.003(1)	0.002(1)	-0.002(1)	-0.000(1)	-0.001(1)
O(1)	0.0396(24)	-0.0034(42)	0.1727(12)	1.38	0.013(4)	0.004(1)	0.003(1)	-0.001(5)	0.001(2)	0.002(3)
O(2)	0.3183(46)	0.2346(37)	0.1716(30)	1.76	0.004(7)	0.008(3)	0.006(3)	-0.003(4)	0.003(4)	-0.002(3)
O(22)	0.8214(50)	0.2573(34)	0.1611(30)	1.36	0.018(8)	0.004(2)	0.002(2)	0.002(4)	0.003(3)	-0.001(2)
O(3)	0.1148(42)	0.1699(38)	0.3919(28)	1.16	0.008(6)	0.005(2)	0.002(2)	0.000(4)	0.001(3)	-0.001(2)
O(33)	0.6586(35)	0.3219(39)	0.3923(27)	0.63	0.003(5)	0.002(2)	0.002(2)	0.002(3)	0.000(2)	-0.001(2)
F, OH	0.1088(23)	0.4677(21)	0.3984(12)	0.88	0.007(4)	0.003(2)	0.003(1)	-0.001(7)	0.002(2)	0.000(1)

Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$
 $B_{eq.}$: calculated using equation, $B_{eq.} = 8\pi^2\bar{u}^2$, where \bar{u}^2 is mean square displacement of atoms.

TABLE 3. Bond distances and angles

Tetrahedron T(1)				
			around T(1)	
O(1)	1.640(41) Å	O(1) – O(2)	2.618(45) Å	106.8(1.6)°
O(2)	1.622(31)	O(2) – O(22)	2.630(47)	108.0(1.6)
O(22)	1.610(29)	O(2) – O(3)	2.686(40)	110.6(1.6)
O(3)	1.626(30)	O(2) – O(22)	2.605(37)	107.4(1.6)
		O(2) – O(3)	2.708(43)	113.0(1.6)
Mean	1.62 ₅	O(22) – O(3)	2.663(38)	110.8(1.6)
		Mean	2.65 ₂	109 ₄
Tetrahedron T(11)				
			around T(11)	
O(1)	1.622(41) Å	O(1) – O(2)	2.652(48) Å	107.9(1.1)°
O(2)	1.658(29)	O(2) – O(22)	2.649(44)	107.5(1.1)
O(22)	1.662(33)	O(2) – O(33)	2.703(39)	112.7(1.6)
O(33)	1.625(29)	O(2) – O(22)	2.677(38)	107.5(1.6)
		O(2) – O(33)	2.702(36)	110.8(1.6)
Mean	1.64 ₂	O(22) – O(33)	2.698(42)	110.3(1.1)
		Mean	2.68 ₀	109 ₅
Interlayer cation K				
O(1) x2	3.040(12) Å	O(2) x2	3.240(14) Å	
O(2) x2	3.017(32)	O(22) x2	3.248(30)	
O(22) x2	2.997(31)		3.156(29)	
Mean	3.01 ₅		3.21 ₅	
Octahedron M(1)				
O(3) x2	2.105(42) Å	O(3) – O(33) x2	3.176(50) Å	
O(33) x2	2.147(40)	F x2	3.248(32)	
F x2	2.131(12)	O(33) – F x2	3.194(27)	
Mean	2.12 ₅	Mean (unshared)	3.20 ₅	
		O(3) – O(3)	2.685(42) Å	
		F x2	2.970(33)	
		O(33) – O(33)	2.979(37)	
		F x2	2.598(31)	
		Mean (shared)	2.80 ₀	
Octahedron M(2)				
O(3) x2	1.909(37) Å	O(3) – O(33) x2	2.771(36) Å	
O(33) x2	1.917(19)	F x2	2.712(40)	
F x2	1.853(25)	O(33) – F x2	2.706(28)	
Mean	1.89 ₅	Mean (unshared)	2.73 ₀	
		O(3) – O(3)	2.685(42) Å	
		O(33) x2	2.665(40)	
		O(33) – F x2	2.598(31)	
		F – F	2.530(19)	
		Mean (shared)	2.62 ₄	
Octahedron M(3)				
O(3) x2	2.116(22) Å	O(3) – O(33) x2	3.178(35) Å	
O(33) x2	2.104(37)	F x2	3.175(32)	
F x2	2.150(29)	O(33) – F x2	3.236(41)	
Mean	2.12 ₅	Mean (unshared)	3.19 ₅	
		O(3) – O(33) x2	2.665(40) Å	
		F x2	2.970(33)	
		O(33) – O(33)	2.979(37)	
		F – F	2.530(19)	
		Mean (shared)	2.79 ₇	

attempted for the non-centrosymmetric space group $C2$. The y -coordinate of K atom was fixed at 0.5. The refinement was repeated, varying the multiplicities of M(1), M(2) and M(3), until we obtained flat difference electron density maps following the method used by Guggenheim and Bailey (1977). The R value was converged to 0.058 ($wR = 0.064$) with isotropic temperature factors. Additional least squares calculations were repeated for 92 parameters including a scale factor, atomic coordinates and anisotropic temperature factors. The final R and wR values were 0.046 and 0.052, respectively. The obtained R values and the atomic parameters (Table 2) suggest that the true space group is $C2$. The estimated standard deviations of atomic coordinates and bond lengths (Table 3) are relatively large due to the insufficient numbers of the intensity data from the thin-plate crystal used in the present work.

Computations were performed on *FACOM M-382* at the Computer Center of Kyushu University and on *ACOS 850* at the Computer Center of Yamaguchi University. We used programs in the UNICS-II system (Sakurai *et al.*, 1974), which were modified for the computer system of Kyushu University by Kawano (1980).

Discussion

The space group of masutomilite is concluded to be $C2$ as predicted by Guggenheim *et al.* (1983). The most important feature of masutomilite is the manner of octahedral ordering. The mean M–O, F values for M(1), M(2) and M(3) are 2.13, 1.89 and 2.12 Å, respectively, and the scattering powers are 8.5, 11.1 and 8.1 electrons, respectively. Thus the differences in the average M–O distances and in the scattering powers between the M(2) and M(3) sites are clear enough, though they are related with each other by the pseudo-mirror plane (Fig. 1). The M(1) and M(3) sites are nearly equal in size and scattering power. The small size but the high scattering power of the M(2) site can be attributed to the concentration of small ions, namely, Al and Fe, at this site. The remaining large octahedral cations such as Li and Mn^{2+} , and vacancies are probably distributed randomly over M(1) and M(3). The chemical formula gives 8.04 electrons for each of the M(1) and the M(3) sites, and 10.58 for the M(2) site, assuming the complete ionic valences such as Li^+ , Mn^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} and Ti^{4+} , and the equal site-preference of ions for M(1) and M(3). These values are consistent with the X-ray scattering powers obtained as mentioned above. However, this should not be considered as a unique solution. The individual ψ values (octahedral flattening angle, ideally 54.75°) (for example, Guggenheim and Bailey, 1975), for the M(1), M(2) and M(3) octahedra are 60.6° , 56.3° and 60.4° , respectively. This shows that the small M(2) octahedron is nearly regular in shape, but M(1) and M(3) octahedra are considerably flattened and distorted to accommodate large cations such as Li and Mn^{2+} (Fig. 1).

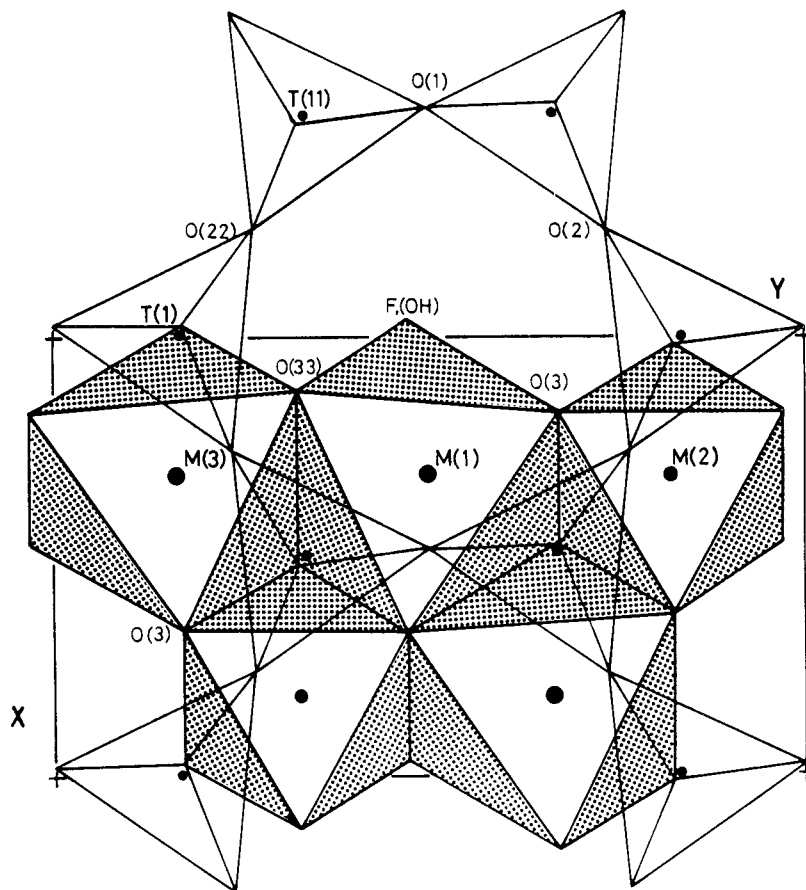


FIG. 1. View along c^* of the masutomilite structure, showing the octahedral layer and the lower Si_2O_5 ring.

We can now compare three refined structures of $1M$ -type micas with space group $C2$, zinnwaldite- $1M$ from the Sadisdorf Mine (Guggenheim and Bailey, 1977), lepidolite- $1M$ from Tanakamiyama (Guggenheim, 1981), and masutomilite in the lepidolite-zinnwaldite-masutomilite series. No systematic differences can be found among the bond-lengths of $M-(O, F)$, although there are apparent chemical differences for these sites (Table 4). Al-enrichment in the $M(2)$ site or the resultant small size of the octahedra is the most different feature of the $C2$ -micas from that of $C2/m$ -micas. Guggenheim (1981) suggested that the high fluorine content might promote the Al-ordering into either $M(2)$ or $M(3)$. But, he also pointed out that it cannot be the sole cause for the phenomenon, because a Radkovice lepidolite having the space group $C2/m$ con-

TABLE 4. Chemical constituents of tetrahedral and octahedral sites, bond lengths between metal and oxygen (fluorine) and tetrahedral rotation angles in four *C2*-micas

	Zinnwaldite-1M	Lepidolite-1M		Masutomilite	Total atoms
		Tanakamiyama	Wakefield		
Tetrahedral					
Si	6.18	7.74	6.95	6.65	} 8.00
Al(IV)	1.82	0.26	1.05	1.35	
Octahedral					
Li	1.34	2.82	3.01	2.54	} 6.00
Mg	0.02	—	0.01	—	
Mn	0.10	0.10	0.31	0.99	
Fe ²⁺	1.54	0.14	0.30	0.18	
Al(VI)	2.10	2.26	2.20	1.96	
Fe ³⁺	0.32	—	0.05	0.06	
Ti	0.02	—	0.02	0.01	
Vacancy	0.56	0.68	0.10	0.26	
Bond length					
T(1) — O	1.646 Å	1.64 Å	1.631 Å	1.62 ₅ Å	
T(11) — O	1.639	1.63	1.633	1.64 ₂	
M(1) — O, F	2.132	2.12	2.098	2.12 ₈	
M(2) — O, F	1.882	1.88	2.058	1.89 ₃	
M(3) — O, F	2.131	2.13	1.913	2.12 ₃	
Tetrahedral rotation angle					
	5.8°	3.3°	5.9°	4.3°	
	Guggenheim & Bailey (1977)	Guggenheim (1981)	Backhaus (1983)	Present work	

tains fluorine as high as that of Tanakamiyama lepidolite-1M with space group *C2*. We note, however, that the *C2/m* lepidolite from Radkovice has a high Al(VI) content of 0.433 in an octahedral site whereas the content in the three *C2* micas ranges from 0.327 to 0.377 which are calculated from Table 4. This may suggest that if the Al(VI) content exceeds a definite limit, a homogeneous distribution of Al(VI) into M(2) and M(3) sites occurs and results in the *C2/m* symmetry.

Backhaus (1983) refined the structure of another lepidolite-1M from Wakefield, Canada, and found a different scheme in octahedral ordering. He proposed two kinds of octahedral ordering in lepidolite-1M, meso-octahedral occupation type and hetero-octahedral occupation type, with space group *C2*. The one is characterized by the same chemical entity in the two octahedral sites, and the other by three different

chemical entities in the octahedral sites. Zinnwaldite and lepidolite-1M from Tanakamiyama belong to the meso-octahedral occupation type. The Wakefield lepidolite belongs to the hetero-octahedral occupation type. According to Backhaus' definition, masutomilite belongs to the meso-octahedral occupation type. The Al content of an octahedral site in the Wakefield lepidolite is calculated to be 0.367 which satisfies also the range of Al-content in C2-micas as discussed above, although the ordering scheme belongs to the hetero-octahedral type. Chemical constituents of tetrahedral and octahedral sites, bond lengths around metals and tetrahedral rotation angle of Wakefield lepidolite are also shown in Table 4.

The mean T–O bond lengths for tetrahedra T(1) and T(11) are 1.62₅Å and 1.64₂Å, respectively. From the regression analysis of Hazen and Burnham (1973) for micas, the mean T–O values correspond to tetrahedral content of 0.106 Al and 0.209 Al in T(1) and T(11), respectively. However, the standard deviation of the mean value is $\sigma_{\eta} = \sigma_{\ell}/\sqrt{\eta} = 0.02\text{Å}$ where $n = 4$ for a tetrahedron and σ_{ℓ} is the standard deviation of an individual bond length. A significant difference between two bond lengths should be over 3σ of the individual bond length at 1% level (Bailey, 1984, p42). The difference between two T–O bond lengths in masutomilite is so small that it is difficult to discuss Al–Si ordering in the tetrahedral sites. The mean Al content in T(1) and T(11) is 0.156 Al which is close to 0.169 Al given by the chemical analysis (Table 1). The tetrahedral rotation angle obtained is 4.3°.

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