# Masutomilite, manganese analogue of zinnwaldite, with special reference to masutomilite–lepidolite–zinnwaldite series

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## ABSTRACT

A new mineral with the following formula is described: $(K_{1.788}Na_{0.148}$ $Rb_{0.141})(Li_{2.536}Mn^{2+}_{0.985}Fe^{2+}_{0.183}Fe^{3+}_{0.061}Al_{1.958}Ti_{0.012})(Si_{6.646}Al_{1.354}) \cdot O_{19.634}(F_{3.159}$ $(OH)_{1.202}) = (K, Na, Rb)_{2.077}(Li, Mn, Fe^{2+}, Fe^{3+}, Al, Ti)_{5.735}(Si, Al)_{8.000} \cdot O_{19.639}$ $(F, OH)_{4.361}$ as $OH+O+F=24$. It corresponds to manganese analogue of zinnwaldite and is expressed by a $K_2(Mn^{2+}_{2-1}Li_{2-3}Al_2)(Al_{2-1}Si_{6-7}O_{20})(F_{2-3}$ $(OH)_{1-2})$. The name masutomilite is proposed for the material with $Mn^{2+} >$ $Fe^{2+}$ in honor of Dr. Kazunosuke Masutomi for his contribution to minerals of Japan.

X-ray powder diffraction and optical data indicate the mineral to be monoclinic, space group $Cm$ or $C2/m$ with $a$ 5.253(8) Å, $b$ 9.085(4) Å, $c$ 10.108 (8) Å, $\beta$ 100.15(0.03)°, $V$ 474.84(0.56) Å$^3$ and $Z=1$. The precession method verified the space group. The strongest lines in the X-ray powder pattern are 10.10(72)(001), 3.64(43)($\bar{1}$12), 3.32(100)(003), 3.09(58)(112), 2.903(35)($\bar{1}$13, 031), 2.589(17)(200, $\bar{1}$31), 1.989(46)(005), 1.653(23)(204, $\bar{1}$35). It is pale purplish pink. Transparent. Cleavage {001} perfect. Hardness (Mohs) 2.5.

Sp. Gr. (meas.) 2.94 and 2.96 (calc.). Optically biaxial negative with $\alpha$ 1.534, $\beta$ 1.569, $\gamma$ 1.570, $(-)2V$ 29°–31°, $r>v$ very weak, X, Z colorless to pale purple, Y purple, absorption X<Z<Y. Optical orientation $b=$Y, X nearly perpendicular to (001), $a \wedge Z$ 3°.

The mineral occupies core part of a zoned single mica crystal up to 10 cm across and 1 cm thick found in a druse of granite pegmatite at Tanakamiyama, Ōtsu, Shiga Prefecture, Japan. The outer part of the crystal is a brown manganoan zinnwaldite. The associated minerals are topaz, schorl, albite and quartz.

For comparison of a high manganese zinnwaldite with masutomilite, a mica from Tawara, Naégi district, Hirukawa-mura, Gifu Prefecture, Japan is also described.

A complete solid solubility does exist for the masutomilite-lepidolite-zinnwaldite series. The relationship between chemical composition, unit-cell dimensions $a$ or $b$, and optical properties for the masutomilite-lepidolite series is figured out.

## Introduction

Zinnwaldites and lepidolites rich in manganese have been known to occur in pegmatites in Japan. A manganese analogue of zinnwaldite ranging up to 7% manganese from Tanakamiyama, Shiga Prefecture, Japan was chemically analyzed by Yasuda (1908), though no physical, optical and X-ray data were given. Shibata (1939) reported a manganoan zinnwaldite containing 2.66% MnO from Hirukawa-mura, Gifu Prefecture, together with its optical data. Ukai, Nishimura and Hashimoto (1956) described a manganoan zinnwaldite containing 3.86% MnO and 4.58% FeO from Minagi, Shōwa-chō, Kibi-gun, Okayama Prefecture, together with its optical data. Nagashima *et al.* (1974), in their work on the chemical data of some manganoan lepidolites and manganoan zinnwaldites from several localities in Japan, discussed the origin of manganese in the Japanese lithium micas. The material from Tanakamiyama containing 8.12% MnO, 1.53% FeO and 0.38% $Fe_2O_3$ (Nagashima *et al.*, 1974) is also a manganese analogue of zinnwaldite as previously been described by Yasuda (1908). Unit-cell dimensions, polymorphic types, refractive indices and 2V for the

seven lithium micas described by Nagashima *et al.* (1974) are redetermined accurately together with a new analysis of ferroan masutomilite from Tawara, Hirukawa-mura, Gifu Prefecture. These eight lithium micas are plotted in a $Fe^{2+}$-$Mn^{2+}$-($Fe^{3+}$, Al, Li) diagram to show their octahedral occupancies (Fig. 1).

This paper gives these results and deals with chemical, physical and optical properties of Japanese manganoan lepidolites in general. A new mineral name masutomilite is proposed for the manganese analogue of zinnwaldite, and the relationship between chemical and physical properties for lepidolite-masutomilite series is described.
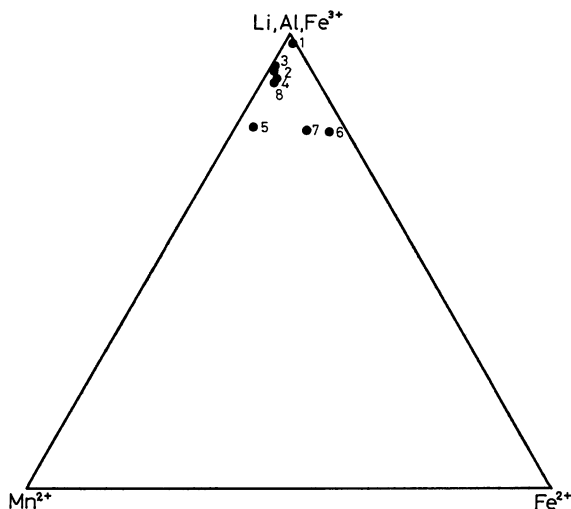


Fig. 1.  The octahedral occupancy in the diagram (Li, Al, $Fe^{3+}$)-$Fe^{2+}$-$Mn^{2+}$.  Numbers correspond to those in Table 1.
Note:  The data are from Nagashima *et al.* (1974) and a new analysis of high manganese zinnwaldite is added.  The analyses of Nos. 6 and 7 are natural two phase lithium micas of $1M+2M_1$ polytypes, which are similar to the data given by Munoz (1960) and further noticed by Bailey (1972).

## Experimental

The chemical data have been reported previously (Nagashima *et al.*, 1974). A new chemical analysis was made by the following procedures. Determination of most components was done by the normal wet methods, except for $Li_2O$ and $Rb_2O$ determined by atomic absorption spectrometry, and $K_2O$ and $Na_2O$ by flame-photometry. $SiO_2$ was determined on a separate portion after removing fluorine to minimize the loss of this constituents during evaporation after main fusion as suggested by Chaudhry and Howie (1973). Fluorine was determined by the usual titrimetric method after the separation of this elements by the steam-distillation (Kolthoff and Sandell, 1952). The positive bias in the flame-photometric determination of $K_2O$ due to interference of $Rb_2O$ was corrected by the interference curves as suggested by Chaudhry and Howie (1973). Refractive indices were determined with a Leitz 4-axis universal stage. Refractive index $\alpha$ could not be obtained for some specimens. Specific gravity was determined with a pycnometer. X-ray powder diffraction patterns were recorded with a diffractometer and the cell dimensions were obtained from them through a least-squares unit-cell refinement program. Silicon metal was used as an internal standard. By making use of the refined cell dimensions the powder data for the micas have successfully been indexed. The refractive indices, 2V, unit-cell dimensions and polymorphic types for the studied specimens are summarized in Table 1.

## Masutomilite

A pale purplish pink mica has been collected and deposited by Mr. Minoru Nakatsukasa in Tanakami Museum at Ōtsu, Shiga Prefecture. The pale purplish pink crystal of mica occupies the core part of a zoned single crystal of zinnwaldite, 10 cm across and 1 cm thick, found in a druse of granite pegmatite at Tanakamiyama. The

Table 1.    Unit-cell dimensions and optical properties for eight Japanese lithium micas.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| $\alpha$ (±0.002) | 1.529 | — | 1.536 | — | 1.534 | 1.551 | — | 1.536 |
| $\beta$ (±0.001) | 1.549 | 1.567 | 1.550 | 1.551 | 1.569 | 1.577 | 1.573 | 1.570 |
| $\gamma$ (±0.0005) | 1.552 | 1.569 | 1.553 | 1.554 | 1.570 | 1.578 | 1.576 | 1.571 |
| $\gamma-\alpha$ | 0.023 | — | 0.017 | — | 0.036 | 0.027 | — | 0.035 |
| (−)2V | 39° | 29°-32° | 25°-28° | 30°-35° | 29°-31° | 2°-3° | 32° | 28° |
| $a$(Å) | 5.197( 5) | 5.218( 5) | 5.21 ( 1) | 5.215( 5) | 5.253( 8) | 5.23 ( 1) | 5.22 ( 1) | 5.248(10) |
| $b$(Å) | 8.994( 5) | 9.030( 8) | 9.010( 7) | 9.020( 5) | 9.085( 4) | 9.065( 8) | 9.066( 3) | 9.087( 6) |
| $c$(Å) | 10.040(10) | 10.071( 5) | 10.065(10) | 10.052( 5) | 10.107( 8) | 10.126(10) | 10.090(10) | 10.090(10) |
| $\beta$(°) | 100.65 (45) | 100.74 (76) | 100.71 (76) | 100.67 (64) | 100.15(0.03) | 100.65 (76) | 100.81 (30) | 100.10(0.3) |
| P.T.* | 1M+2M$_1$ | 1M+2M$_1$ | 1M | 1M | 1M | 1M | 1M | 1M |

* Polymorphic type

Note: 1) Minagi: $(K_{0.880}Na_{0.079}Ca_{0.065}Rb_{0.059})(Li_{1.503}Mg_{0.001}Mn_{0.015}Fe_{0.037}Al_{1.175})(Si_{3.594}Al_{0.406})\cdot O_{10}(F_{1.892}OH_{0.519})$.

2) Nagatare: $(K_{0.916}Na_{0.056}Rb_{0.045}Ca_{0.006})(Li_{1.011}Mg_{0.142}Mn_{0.180}Fe_{0.025}Ti_{0.002}Al_{1.327})(Si_{3.288}Al_{0.712})\cdot O_{10}(F_{1.012}OH_{1.016})$.

3) Sakihama: $(K_{0.919}Rb_{0.068}Na_{0.037}Ca_{0.012})(Li_{1.720}Mg_{0.001}Mn_{0.200}Fe_{0.014}Ti_{0.002}Al_{1.128})(Si_{3.600}Al_{0.400})\cdot O_{10}(F_{1.772}OH_{0.430})$.

4) Suisawa: $(K_{0.872}Rb_{0.066}Na_{0.053})(Li_{1.536}Mg_{0.002}Mn_{0.226}Fe_{0.067}Al_{1.125})(Si_{3.471}Al_{0.529})\cdot O_{10}(F_{1.614}OH_{0.431})$.

5) Tanakamiyama: structural formula (see Text).

6) Nairi: $(K_{0.860}Rb_{0.086}Na_{0.055})(Li_{0.756}Mg_{0.007}Mn_{0.087}Fe_{0.471}Ti_{0.011}Al_{1.297})(Si_{2.848}Al_{1.152})\cdot O_{10}(F_{1.006}OH_{1.133})$.

7) Tawara (brown): $(K_{0.860}Rb_{0.057}Na_{0.053})(Li_{1.281}Mg_{0.005}Mn_{0.207}Fe_{0.387}Al_{0.950})(Si_{3.198}Al_{0.802})\cdot O_{10}(F_{1.489}OH_{0.531})$.

8) Tawara (pink): structural formula (see Text).

Analyst: 1, 2, 3, 4, 6, 7—Kozo Nagashima, Mariko Honda and Junko Iino; 5—Kozo Nagashima; 8—Kazuo Harada and Satoshi Kanisawa.

outer part of the crystal is a brown manganoan zinnwaldite. The boundary between brown zinnwaldite and pink mica is sharp. The cleavage surface of the mica is smooth and no fractures or translation gliding inclined to (001) as frequently found in biotite, phlogopite and hendricksite is found. The associated minerals are topaz, schorl, albite and quartz. The pale purplish pink material carefully hand picked under a handlens was chemically analyzed and its optical, physical and X-ray properties have been determined (Tables 1, 2 and 3).

The structural formula of this mineral is calculated on the basis of $OH+F+O=24$:

$$(K_{1.788}Na_{0.148}Rb_{0.141})(Li_{2.536}Mn^{2+}_{0.985}Fe^{2+}_{0.183}Fe^{3+}_{0.061}Al_{1.958}Ti_{0.012})(Si_{6.646}Al_{1.354})\cdot O_{19.639}(F_{3.159}(OH)_{1.202})=(K, Na, Rb)_{2.077}(Li, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al, Ti)_{5.735}(Si, Al)_{8.000}\cdot O_{19.639}(F, OH)_{4.369}.$$

High manganese content is noted. It is pale purplish pink and transparent even in thick flake, and nearly colorless in thin flake. The crystal is homogeneous and not zoned. The cleavage flake of the mica is somewhat plastic rather than elastic as compared to biotite or phlogopite.

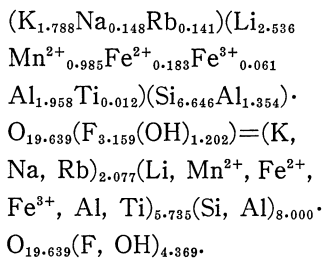Table 2. Chemical composition of masutomilite from Tanakamiyama, and high manganese zinnwaldite from Tawara.

|  | 1 | 2 |
|---|---|---|
| $SiO_2$ | 46.85 | 47.67 |
| $Al_2O_3$ | 19.81 | 22.17 |
| $TiO_2$ | 0.13 | 0.09 |
| $Fe_2O_3$ | 0.38 | 0.35 |
| FeO | 1.53 | 1.12 |
| MnO | 8.12 | 4.27 |
| MgO | 0.00 | 0.02 |
| $Li_2O$ | 4.45 | 5.78 |
| CaO | 0.00 | 0.08 |
| $K_2O$ | 9.88 | 9.78 |
| $Na_2O$ | 0.54 | 0.61 |
| $Rb_2O$ | 1.54 | 1.20 |
| F | 7.04 | 6.84 |
| $H_2O+$ | 1.27 | 1.95 |
| $H_2O-$ | 1.36 | 0.45 |
| Total | 102.90 | 102.38 |
| $-F_2=O$ | 2.96 | 2.88 |
| Total | 99.94 | 99.50 |

Analyst: 1—Kozo Nagashima, 2—Kazuo Harada and Satoshi Kanisawa

1. $(K_{1.788}Na_{0.148}Rb_{0.141})(Li_{2.536}Mn^{2+}_{0.985}Fe^{2+}_{0.183}Fe^{3+}_{0.061}Al_{1.958}Ti_{0.012})(Si_{6.646}Al_{1.354})O_{19.639}(F_{3.159}(OH)_{1.202})$

2. $(K_{1.702}Na_{0.161}Rb_{0.105}Ca_{0.011})(Li_{3.171}Mg_{0.004}Mn^{2+}_{0.494}Fe^{2+}_{0.128}Fe^{3+}_{0.036}Al_{2.070}Ti_{0.009})(Si_{6.505}Al_{1.495})O_{19.272}(F_{2.952}(OH)_{1.776})$

Hardness (Mohs) is 2.5. The observed specific gravity is 2.94, in agreement with the calculated value of 2.96. Optically biaxial negative with $\alpha$ 1.534, $\beta$ 1.569, $\gamma$ 1.570, $\gamma-\alpha$ 0.036, $(-)2V$ $29°-31°$, dispersion $r>v$ very weak. X, Z colorless to pale pink, Y purple and absorption $X<Z<Y$. Optical orientation $b=Y$, X nearly perpendicular to (001), $a\wedge Z$ 3°, and sign of elongation positive. These physical properties accord with what are expected for zinnwaldite.

The X-ray powder diffraction data indicate it to be monoclinic, 1M polytype, probable space group $Cm$ or $C2/m$ with $a$ 5.253(8)Å, $b$ 9.085(4)Å, $c$ 10.107(8)Å, $\beta$ 100.15(0.03)°, $V$ 474.84Å, and $Z=1$. The precession method (Ross, Takeda and Wones, 1966) has further verified the space group. Indexed powder data are shown in Table 3.

In spite of these normal physical properties the higher MnO content of the present specimen is remarkable when compared with zinnwaldite, $K_2(Fe^{2+}_{2-1}Li_{2-3}Al_2)(Al_{2-1}Si_{6-7}O_{20})(F_{3-2}(OH)_{1-2})$ (Foster, 1960; Deer, Howie and Zussman, 1962). Thus, the mica under study is considered to represent its manganese analogue with the general formula $K_2(Mn^{2+}_{2-1}Li_{2-3}Al_2)(Al_{2-1}Si_{6-7}O_{20})(F_{3-2}(OH)_{1-2})$. The name masutomilite is proposed for the material with $Mn^{2+}>Fe^{2+}$, and has been approved by the Commision on New Minerals and Mineral Names, I. M. A.

The type material is preserved in Department of Earth Sciences, Kanazawa University.

### Ferroan masutomilite

In order to find masutomilite from other localities, a specimen of purple lithium mica with similar appearance to masutomilite was examined. The specimen was collected by Dr. Kazunosuke Masutomi from Tawara, Hirukawa-mura, Gifu Prefecture, which is a part of the Naégi district known by Japanese mineralogists. In this area brown zinnwaldite has been well known to occur and was chemically analyzed by Nagashima *et al.* (1974) (Table 1). The present sample is a

　Masutomilite, manganese analogue of zinnwaldite

Table 3. X-ray powder diffraction data of masutomilite.

| $d$(obs.) | $d$(calc.) | $I$ | $hkl$ |
|-----------|-----------|-----|-------|
| 10.10 | 9.952 | 72 | 001 |
| 4.99 | 4.976 | 30 | 002 |
| 4.54 | 4.540 | 25 | 020 |
| 4.37 | 4.364 | 14 | 012 |
| 4.13 | 4.130 | 7 | 021 |
| 3.86 | 3.877 | 12 | 111 |
| 3.64 | 3.621 | 43 | $\bar{1}12$ |
| 3.35 | 3.354 | 65 | 022 |
| 3.32 | 3.317 | 100 | 003 |
| 3.09 | 3.106 | 58 | 112 |
| 2.903 | 2.896 ⎫ 2.888 ⎭ | 35 | 031 $\bar{1}13$ |
| 2.679 | 2.678 | 22 | 023 |
| 2.607 | 2.616 | 20 | $\bar{2}01$ |
| 2.589 | 2.584 ⎫ 2.583 ⎭ | 46 | 200 $\bar{1}31$ |
| 2.484 | 2.479 ⎫ 2.473 ⎭ | 17 | $\bar{2}02$ 131 |
| 2.401 | 2.402 | 26 | $\bar{1}32$ |
| 2.270 | 2.270 | 10 | 040 |
| 2.144 | 2.147 ⎫ 2.144 ⎭ | 19 | $\bar{1}35$ $\bar{2}02$ |
| 1.989 | 1.990 | 46 | 005 |
| 1.964 | 1.969 | 12 | 133 |
| 1.737 | 1.740 ⎫ 1.731 ⎭ | 5 | 223 $\bar{2}05$ |
| 1.717 | 1.718 ⎫ 1.714 ⎭ | 6 | $\bar{3}11$ $\bar{2}41$ |
| 1.653 | 1.656 ⎫ 1.653 ⎭ | 23 | 135 204 |
| 1.646 | 1.649 | 18 | 241 |
| 1.592 | 1.594 ⎫ 1.592 ⎭ | 5 | $\bar{2}43$ 152 |
| 1.552 | 1.558 | 4 | 026 |
| 1.512 | 1.519 ⎫ 1.513 ⎭ | 6 | 135 060 |
| 1.480 | 1.484 | 1 | 116 |
| 1.419 | 1.422 ⎫ 1.419 ⎭ | 2 | 007 $\bar{1}17$ |
| 1.371 | 1.377 | 1 | 063, $\bar{3}34$ |
| 1.353 | 1.350 | 2 | $\bar{2}07$ |
| 1.341 | 1.347 ⎫ 1.339 ⎭ | 2 | 136 046 |
| 1.297 | 1.296 ⎫ 1.293 ⎭ | 1 | $\bar{3}35$ 064 |

CuK$\alpha$—Ni filter.　1M polytype.
$a$ 5.253(8)Å, $b$ 9.085(4)Å, $c$ 10.108(8)Å, $\beta$ 100.15(0.03)° and $V$ 474.84(56)Å$^3$.

pseudohexagonal crystal, 3 cm across and 1 cm thick, and is slightly deeper in color than the type masutomilite. The associated minerals are cassiterite, topaz, schorl, albite and quartz. It is purple and translucent in thick flake and transparent in thin flake. The crystal is not zoned. The mica is not so elastic as compared to the masutomilite but is rather plastic to brittle. The cleavage surface is smooth and no fractures or translation gliding is found. Hardness (Mohs) is 2.5-3. The material was carefully hand picked and chemically analyzed. The optical, physical and X-ray properties have also been determined (Tables 1 and 2).

The structural formula of this specimen is calculated on the basis of $O+OH+F=24$ : $(K_{1.702} Na_{0.161}Rb_{0.105}Ca_{0.011}) (Mn^{2+}_{0.494}Fe^{2+}_{0.128}Fe^{3+}_{0.036} Al_{2.070}Li_{3.171}Ti_{0.009})(Si_{6.505}Al_{1.495}) \cdot O_{19.272}(F_{2.952}(OH)_{1.776}) = (K, Na, Rb, Ca)_{1.979} (Mn^{2+}, Fe^{2+}, Fe^{3+}, Al, Li, Ti)_{5.908}(Si, Al)_{8.000} \cdot O_{19.272}(F, (OH))_{4.728}$.

This mineral is in general agreement with the structural formula of zinnwaldite, however manganese content is the highest among the zinnwaldite analyses ever reported (Foster, 1960; Deer, Howie and Zussman, 1962; Rieder, 1970; Chaudhry and Howie, 1973; Brock, 1974). This mica would be correctly termed as ferroan masutomilite owing to the high iron content.

Optically biaxial negative with $\alpha$ 1.536, $\beta$ 1.570, $\gamma$ 1.571, $(-)2V$ 28°, dispersion $r>v$ very weak. X, Z colorless to pale purple and absorption $X<Z<Y$. Optical orientation $b=Y$, X nearly perpendicular to {001}, $a \wedge Z$ 2°-4° and sign of elongation positive. These data are in agreement with masutomilite and zinnwaldite. The observed specific gravity is 2.90, which agrees well with the calculated value of 2.85.

The X-ray powder diffraction data indicate it to be monoclinic, 1M polytype, probable space group $Cm$ or $C2/m$. $a$ 5.248(10)Å, $b$ 9.087(6)Å, $c$ 10.090(8)Å, $\beta$ 100.10(0.03)°. $V$ 473.12(74)Å$^3$ and $Z=1$. This specimen is deposited in the Department of Earth Science at Tōhoku University, Kawaúchi.

*Masutomilite-lepidolite series*

The unit-cell dimensions $a$ or $b$, and refractive indices for lepidolites, manganoan lepidolites, zinnwaldites and masutomilite described in the present paper are plotted against $A'$ value proposed by Rieder *et al.* (1970, 1971) (Figs. 2, 3 and 4). These data clearly indicate that the complete solid solubility does exist in the masutomilite-zinnwaldite-lepidolite series.

The refractive indices with similar $A'$ value for the different specimens shown in Fig. 2 are found to have considerable ranges. A similar trend was also noticed in the results of Rieder *et al.* (1971) and Chaudhry and Howie (1973). This may probably be due to complex ionic substitutions such as octahedral Li and Al for Fe, Mn and Mg substitutions, tetrahedral Si for Al substitution, OH for F substitution, interlayer K for Cs and Rb substitutions observed in the lepidolite, zinnwaldite and masutomilite series. Heinrich (1946) has shown that the refractivity of $Mn^{2+}$ is less than that of $Fe^{2+}$ in the phlogopite-biotite series. The masutomilite with similar $A'$ value to the zinnwaldite shows slightly lower $\beta$ and $\gamma$ refractive indices than those of the normal zinnwaldite (Fig. 2).

The X-ray and chemical data given by Takeda and Burnham (1969), Rieder *et al.* (1971) and Sartori, Franzini and Merlino (1973) are also plotted in Figs. 3 and 4. The result indicates that the masutomilite-lepidolite series represents a continuous solid solution, which follows the Vegard's rule in a roughly linear manner as shown by lines B in Figs. 3 and 4. However, the lines in Figs. 3 and 4 are slightly but substantially deviated from the lines for annite-lepidolite series given by Rieder *et al.* (1971), which are added as lines A in the figures. 1M masutomilite or 1M manganoan lepidolites has slightly but substantially larger cell dimensions $a$ and $b$ than 1M zinnwaldite or 1M lepidolite of similar composition has, since the ionic radii of $Mn^{2+}(0.80\text{Å})$ is slightly larger than that of $Fe^{2+}(0.76\text{-}0.78\text{Å})$.
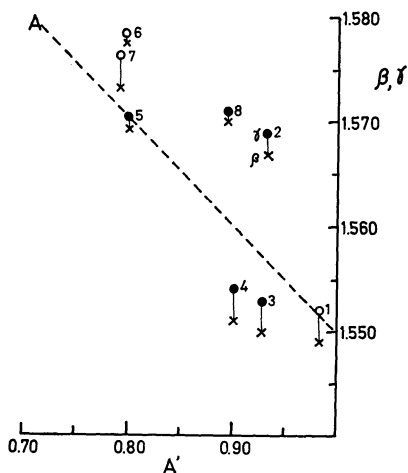
Fig. 2. Diagram showing the relation of refractive indices $\beta$, $\gamma$ to $A'$ value (Rieder et al., 1971). Numbers correspond to those in Table 1. A: The line for lepidolite-zinnwaldite-annite series given by Rieder et al. (1971). Solid circle of $\gamma$: 1M masutomilite-1M lepidolite series with $Mn^{2+} > Fe^{2+}$. Open circle of $\gamma$: 1M zinnwaldite-1M lepidolite series with $Mn^{2+} < Fe^{2+}$.
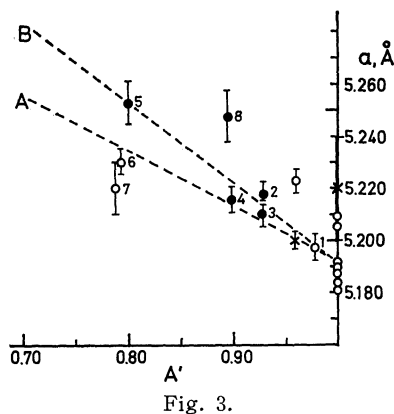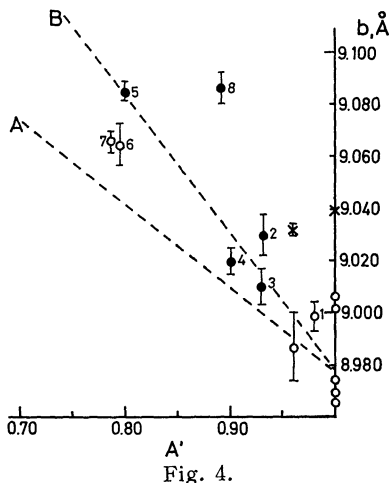
Fig. 3. Diagram showing the relation of unit-cell dimension $a$ to $A'$ value. Numbers correspond to those in Table 1. The data from Rieder et al. (1971), Takeda and Burnham (1969) and Sartori et al. (1971) are also plotted.

Note: Solid circle: 1M masutomilite-1M lepidolite series with $Mn^{2+} > Fe^{2+}$. Open circle: 1M zinnwaldite-1M lepidolite series with $Mn^{2+} < Fe^{2+}$. Cross: Zinnwaldite or lepidolite with $2M_2$ structure. A: The line for lepidolite-zinnwaldite-annite series (Rieder et al., 1971). B: The line for lepidolite-masutomilite-Mn mica series (The present work and Frondel and Ito, 1966).

Fig. 4. Diagram showing the relation of unit-cell dimension $b$ to $A'$ value. The legend is the same as shown in Fig. 3.

A Mn mica with end composition $KMn_3(OH)_2AlSi_3O_{10}$ synthesized from tephroite (Frondel and Ito, 1966; Harzen and Wones, 1972) has slightly larger $b$ than an iron analogue of annite (Eugster and Wones, 1962; Hazen and Wones, 1972) has, i. e., 9.394 against 9.348.

The model of the ordered structure of one small and two large octahedra in the octahedral sheets of the zinnwaldite structure has been proposed by Rieder (1968). The model of the ordered structure requires smaller cell dimensions $a$ and $b$ than those for disordered micas (Rieder $et\ al.$, 1971). The regression curves for cell dimensions $a$ and $b$ for ordered structure calculated by Rieder $et\ al.$ (1971) are shown in Figs. 3 and 4 as lines A. The masutomilite–lepidolite series follows almost completely the regression curves A in the octahedral Al- and Li-rich portions, which shows that the series may also have octahedral ordering of one small and two large octahedra as advocated in the zinnwaldite structure by Rieder (1968) and recognized in the xanthophyllite structure by Takéuchi and Sadanaga (1966) and in the synthetic ferri-annite structure by Donnay $et\ al.$ (1964). From similar size and nature of $Fe^{2+}$ and $Mn^{2+}$ ions the above consideration may also be predicted.

For polylithionite whose tetrahedral sheets contain only $SiO_4$ tetrahedra, Takeda and Burnham (1969) showed that the mean of the three basal Si–O distances is 1.638Å, which is much larger than the apical Si–O distance (1.564Å). This value results in that the surface oxygen ring is almost hexagonal and that the tetrahedral rotation angle $\alpha$ is only 3°. The tetrahedral sheets of masutomilite contain some polylithionite molecules and tetrahedral Si: Al is 3.32: 0.68 instead of 3: 1 in muscovite, suggesting that its tetrahedral rotation angle $\alpha$ may also be small. A $2M_2$ lepidotite whose tetrahedral Si: Al ratio is 3.39: 0.61 has tetrahedral rotation angle $\alpha$ of 5.3° (Takeda, Haga and Sadanaga, 1971). Hazen and Wones (1972) pointed out that cations with radii greater than 0.78Å are too large for the octahedral sites in trioctahedral micas; they also note an inverse relation between

$\alpha$ and $R^{2+}$ radius in stable trioctahedral micas. If the correlation between $\alpha$ and $R^{2+}$ can be extrapolated to the dioctahedral micas, then the octahedral sites in lepidolite (transitional between dioctahedral and trioctahedral) must be somewhat larger than the corresponding 6-fold sites in the normal muscovite, whose tetrahedral rotation angle $\alpha$ is nearly 13° (Radoslovich, 1960). Thus $Mn^{2+}$ may more easily be substituted in lepidolite or masutomilite than in muscovite or biotite. In fact Brock (1974) has shown that the $Mn^{2+}$ is characteristically concentrated in the lepidolite coexisting with muscovite, and he pointed out that the characteristic concentration of $Mn^{2+}$ in the lepidolite would also reflect a larger octahedral sites and smaller tetrahedral rotation angle $\alpha$ of lepidolite. The similar assumption may correctly be applied to masutomilite; the more manganese-rich mica.

The refinement of the crystal structures of zinnwaldite and masutomilite is necessary to confirm the above assumption.

### Origin of Mn in masutomilite

As suggested by Nagashima et al. (1974), the Japanese zinnwaldites and lepidolites contain considerable amounts of Mn, which was regarded to have been derived from Palaeozoic to Mesozoic sedimentary rocks intruded by the lepidolite- or zinnwaldite-bearing Mesozoic to Tertiary granite (Ichikawa et al., 1968). The product of the latest stage of consolidation of the Tanakamiyama pegmatite contains some manganese-bearing minerals such as manganese-bearing montmorillonite (takizōlite), manganese-bearing hydromuscovite (Sekino et al., 1973), manganoan zinnwaldite and masutomilite. The basement of the area is Palaeozoic sedimentary rocks with some stratiformed manganese ore bodies of the workable grade, which is cut by the Tanakamiyama granite of the Mesozoic age (Yoshizawa et al., 1965). In the Naégi district, where manganoan zinnwaldite is found (Shibata, 1939) a similar geologic relation, i. e., Tertiary to Cretaceous granite and Palaeozoic basement is recognized (Shibata, 1939).

## REFERENCES

BAILEY, S. W. (1972)  *Proc. Internat. Clay Conf., Madrid, 1973*, 1, 3.
BROCK, K. J. (1974)  *Amer. Miner.*, **59**, 1242.
CHAUDHRY, M. N. & HOWIE, R. A. (1973)  *Miner. Mag.*, **39**, 289.
DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1962)  *Rock-forming minerals, 3, Sheet silicate.* Longmans, London.
DONNAY, G., MORIMOTO, N., TAKEDA, H. & DONNAY, J. D. H. (1964)  *Acta Cryst.*, **B17**, 1369.
EUGSTER, H. P. & WONES, D. R. (1962)  *Journ. Petrol.*, **3**, 82.
FOSTER, M. D. (1960)  *U. S. Geol. Surv. Prof. Paper*, **354–E**, 115.
FRONDEL, C. & ITO, J. (1966)  *Amer. Miner.*, **51**, 1107.
HAZEN, R. M. & WONES, D. R. (1972)  *Amer. Miner.*, **57**, 103.
HEINRICH, E. W. (1946)  *Amer. Journ. Sci.*, **244**, 836.
ICHIKAWA, K., MURAKAMI, N., HASE, A. & WADATSUMI, K. (1968)  *Pacific Geol.*, **1**, 97.
KOLTHOFF, I. M. & SANDELL, E. B. (1952)  *A textbook of quantitative inorganic analysis*, 3rd ed. *New York.*
NAGASHIMA, K., HARADA, K., HONDA, M. & IINO, J. (1974)  *Proc. I. M. A. meeting, Berlin, 1974* (in press).

Munoz, T. L. (1968)   *Amer. Miner.*, **53**, 1490.

Radoslovich, E. W. (1960)   *Acta Cryst.*, **13**, 919.

Rieder, M. (1968)   *Science*, **160**, 1338.

Rieder, M., Huka, M., Kučherová, D., Minařík, L., Obermajer, J. & Povondra, P. (1970)   *Contr. Miner. Petrol.*, **27**, 131.

Rieder, M., Pichova, A., Fassova, M., Fediukova, E. & Černý, P. (1971)   *Miner. Mag.*, **38**, 190.

Ross, M., Takeda, H. & Wones, D. R. (1966)   *Science*, **151**, 191.

Sartori, F., Franzini, M. & Merlino, S. (1973)   *Acta Cryst.*, **B29**, 573.

Sekino, H., Nagashima, K. & Harada, K. (1973)   *Neues Jahrb Miner., Monatsh.*, **1973-H5**, 189.

Shibata, H. (1939)   *Journ. Geol. Soc. Japan*, **46**, 69.

Takeda, H. & Burnham, C. W. (1969)   *Miner. Journ.*, **6**, 102.

Takeda, H., Haga, N. & Sadanaga, R. (1961)   *Miner. Journ.*, **6**, 203.

Takéuchi, Y. & Sadanaga, R. (1966)   *Miner. Journ.*, **4**, 424.

Ukai, Y., Nishimura, S. & Hashimoto, Y. (1956)   *Miner. Journ.*, **2**, 27.

Yasuda, W. (1908)   *Journ. Geol. Soc. Tokyo*, **15**, 386.

Yoshizawa, H., Ishizaka, K., Kaneko, K. & Kawahara, M. (1965)   *Mem. Coll. Sci. Univ. Kyoto, ser. B*, **31**, 279.