pound Nb_3Sn which has the highest known superconducting transition temperature (Matthias *et al.*, 1954) one might try to make $Mo_3Sn_2Zr_3$ or $Sr_3Sn_2Ru_3$ or $Rb_3Sn_2Rh_3$.

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The crystal structure of xanthophyllite.

By Y. Takéuchi and R. Sadanaga, *Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo, Japan*

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In spite of the numerous reports on the polymorphism in micas, little is known of the detailed structures of the individual members of this group of minerals. Since it is believed that the differences in configurations of the mica sheet are responsible for the generation of various polymorphs, the accurate analyses are desirable to elucidate the mutual relationship of the structures. The purpose of the present paper is, as a part of our research program of silicate sheet structures, to present the results of our study of xanthophyllite, the member of the simplest structure in the brittle mica group. The structure analysis of this mineral is of special advantage for the investigation of the general nature of structural change in the micas due to isomorphous replacement, because potassium atoms in the ordinary micas are fully replaced by smaller calcium atoms in the species under consideration.

The crystals used for the present X-ray analysis were from Chichibu mine, Japan. They are well developed and of pale green color. A chemical analysis made by H. Minato, gave the chemical formula as

$$Ca_{1\cdot10}Mg_{2\cdot18}Al_{0\cdot72}(Al_{2\cdot95}Si_{1\cdot05})O_{10}(OH)_2\ .$$

The cell dimensions were determined using precession photographs (Cu *K*, $\lambda = 1{\cdot}5418$ Å) and they are listed in Table 1 together with those of other brittle micas. The lattice constants of xanthophyllite give the axial ratio, $a:b:c = 0{\cdot}577:1:1{\cdot}082$. There are two formula units in the cell, giving the calculated density of 3·11 g.cm.$^{-3}$ which compares well with the measured value of 3·06 g.cm.$^{-3}$. By the missing rule of spectra and the test of piezo effect the most probable space group is shown to be *C*2/*m*. These data agree with those of the materials from other localities (Sanero, 1940; Forman, 1951) and suggest the single-layer mica structure. In the X-ray photographs, however, diffuse streaks are observed along the reciprocal lattice rows with $k \neq 3n$ in addition to sharp Laue–Bragg reflections, indicating the presence of mozaic blocks in which mistakes of layer stackings occur.

Intensity data were obtained by the multiple-film technique using Cu *K* radiation and absorption corrections for platy crystal habits (Takéuchi, 1958) were applied because it was not possible to obtain the specimens with ideal cross sections. Since, as shown in the above chemical formula, xanthophyllite contains Ca instead of K as in micas, it is expected that, if mica sheets are present in the structure, they are considerably deformed from hexagonal symmetry in such a way as to make cationic niches between the sheets shrunk. An approximate structure was derived by assuming such a deformed mica sheet and it was found to be correct in the electron-density projections

Table 1. *Crystal data for xanthophyllite, margarite and seybertite*

	a (Å)	*b* (Å)	*c* (Å)	β	$d_{(001)}$	Space group	Cell content
Xanthophyllite (Chichibu)	5·19	9·00	9·74	100·1°	9·59 Å	*C*2/*m*	$2\ Ca\ Mg_2\ Al\ (Al_3Si)\ O_{10}(OH)_2$
Margarite* (Chester, Mass.)	5·13	8·89	19·40	99·5°	9·56 × 2	*C*2/*c*	$4\ Ca\ Al_2\ (Al_2Si_2)O_{10}(OH)_2$
Seybertite† (Amity, N.Y. USNM 125425)	5·19	8·99	28·76		9·59 × 3	$P3_112$ or $P3_212$	$6\ Ca\ (Mg, Al, Fe)_3\ (Al,Si)_4O_{10}(OH)_2$

Accuracy: ±0·01 Å for lattice constants and ±0·2° for β angles.

* Lattice constants for margarite from the same locality have also been given by Mauguin (1930).

† Orthohexagonal cell is given for comparison with others. Chemical formula of seybertite has not been exactly established but is close to that of xanthophyllite.

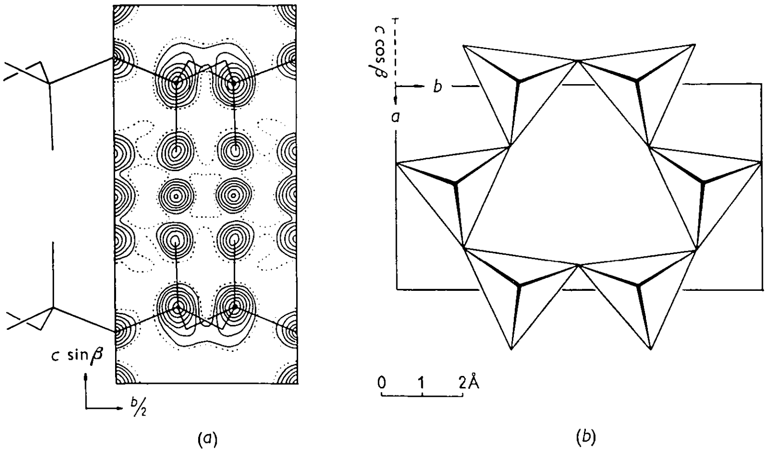

Fig. 1. (*a*) Electron-density projection along the *a*-axis. Contours are drawn at intervals of 2 e.Å^{-2} for oxygen atoms and 4 e.Å^{-2} for the other atoms, the dotted contour being two-electron line. (*b*) The sheet of xanthophyllite projected on (001). Compare with that of single-layer phlogopite (Pabst, 1955).

along the *a*- and the *b*-axis. The atomic co-ordinates were refined in the two projections by successive $F_o - F_c$ syntheses and the *R*-factor for (0*kl*) and (*h*0*l*) reflections have been reduced to 18% and 21% respectively. The co-ordinates of atoms are listed in Table 2.

Table 2. *Co-ordinates of atoms*

Atom	*x*	*y*	*z*
OH	0·632	½	0·398
O_1	0·419	0	0·140
O_2	0·841	0·185	0·140
O_3	0·602	0·161	0·383
Al	0	½	½
Al, Si	0·556	0·172	0·205
Mg	½	0·328	½
Ca	½	½	0

The deformed (aluminum, silicon)–oxygen sheets in xanthophyllite have trigonal symmetry. So that the oxygen atoms shared by neighboring tetrahedra in a sheet form, with those of the adjacent sheet, trigonal antiprisms instead of hexagonal prisms like in micas. Calcium atoms are at the centers of these polyhedra and co-ordinated by six oxygen atoms with the average distance of 2·38 Å. An interesting feature is the Al:Si ratio which amounts approximately to Al:Si = 3:1. This is a much greater substitution of aluminum for silicon than is normally observed in silicates. These atoms are distributed in the sheets at random, giving $(Al_{\frac{3}{4}}Si_{\frac{1}{4}})$–O distances 1·77, 1·71, 1·71, and 1·75 Å. The mean value of them, 1·74 Å, is very close to the value which has been empirically derived for the $(Al_{\frac{3}{4}}Si_{\frac{1}{4}})$–O distances (Smith, 1954). Four Mg and two Al atoms in the cell are located in the octahedral positions formed by unshared oxygen atoms of the sheets and hydroxyl groups. Calculation of atomic distances suggests that these atoms are not distributed over the octahedral positions at random but occupy the discrete positions as shown in Table 2, the average of Al–O and that of Mg–O distances being 1·98 and 2·11 Å, respectively. The fixed positions of these atoms may be the cause for the invariance of chemical composition of xanthophyllite (Forman, 1951).

Intensity distributions of (*h*0*l*) reflections for margarite and seybertite are similar to each other and essentially identical with that of xanthophyllite after index transformations. This suggests that the configurations of (aluminum, silicon)–oxygen sheets in these brittle micas are also deformed and of trigonal symmetry. A marked difference is observed, however, between the diffraction patterns of these two minerals as far as their general (*hkl*) reflections are concerned; namely, those with $k \neq 3n$ of seybertite are all drawn out, while the corresponding reflections from margarite are sharp and no traces of diffuse streaks are observed. This situation seems to reveal an extremely interesting point on the polymorphism of the brittle micas. The chemical formula of margarite corresponds to that of the heptaphyllite mica and the crystal gives sharp (*hkl*) reflections. On the other hand, the structures of xanthophyllite and seybertite, which are octophyllite micas, are different from each other. These results are in good agreement with Hendricks' hypothesis on the mica polymorphism (Hendricks, 1939) that muscovite (heptaphyllite) has a unique structure, while biotites (octophyllites) have variable structures.

The results of further refinement of the structure of xanthophyllite will be reported at a later date.

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