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The crystal structure of katayamalite

Toshio KATO and Nobuhide MURAKAMI

Institute of Earth Sciences, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, Japan

Abstract

The crystal structure of katayamalite has been determined by Patterson method and refined by the least-squares method using single crystal diffractometer data, giving R = 0.057 for 5785 reflections. Formula: $(K,Na)Li_3Ca_7(Ti,Fe^{3+},Mn)_2[Si_6O_{18}]_2(OH,F)_2$. Cell dimensions: a 9.721(2), b 16.923(3), c 19.942(3)Å, α 91.43(10)°, β 104.15(11)°, γ 89.94(10)°, space group $C\bar{1}$, $Z = 4$; or a 9.763(2), b 9.721(2), c 19.942(3)Å, α 104.15(11)°, β 81.76(9)°, γ 119.92(10)°, space group $P\bar{1}$, $Z = 2$. Katayamalite is a ring silicate with two-layered structure parallel to (001), and consists of Si_6O_{18} rings connected with Ca–(O,OH) octahedral sheets, and with Ti–O octahedra, Li–O tetrahedra, and 12-fold K polyhedra. The crystal structure of katayamalite is very similar to that of baratovite. However, the distortion in the katayamalite structure results in the lower symmetry of triclinic system. Half of the motifs of the katayamalite structure and the baratovite structure are similar to that of cordierite, and we can propose the following structure series; beryl → cordierite → katayamalite and baratovite.

Introduction

Katayamalite is a new Ca–Li–Ti silicate mineral found as an accessory mineral in the aegirine syenite from Iwagi Islet, Ehime Prefecture, Southwest Japan. The mineral was described by Murakami *et al.* (1983), who gave crystal and chemical data, optical and physical properties. These data lead to an idealized formula $(K,Na)Li_3Ca_7(Ti,Fe^{3+},Mn)_2[Si_6O_{18}]_2(OH,F)_2$. One of the unique features of this mineral is to give a brilliant bluish white color to the ultraviolet ray of a short wave. We have determined the crystal structure of this mineral and confirmed that katayamalite is a ring silicate very similar to baratovite. This paper describes the details of our results.

Experimental

A colorless crystal, 0.027 x 0.020 x 0.013 cm in size, was selected for our work. Cell dimensions were determined using 25 high-angle reflections measured on a Philips PW-1100 single crystal diffractometer. Crystal data are given in Table 1. Intensity data were collected on the same computer-controlled diffractometer with graphite-monochromated Mo$k\alpha$ radiation ($\lambda = 0.71069$Å) and the $\theta - 2\theta$ scan mode. The scan range was $1^\circ < \theta < 30^\circ$. The reflections of $I > 3\sigma(I)$ were considered to be observed.

Absorption was negligibly small. 5785 reflections were used in the structure determination and refinements.

TABLE 1. Crystal data

Formula:	$(K_{0.89}Na_{0.11})Li_3(Ca_{6.96}Mn_{0.04})_7(Ti_{1.95}Fe_{0.05})_2[Si_6O_{18}]_2(OH_{1.76}F_{0.24})_2$				
Cell dimensions:	a	9.721(2)Å		9.763(2)Å	
	b	16.923(3)		9.721(2)	
	c	19.942(3)		19.942(3)	, where
			or		
	α	91.43(10)°		104.15(11)°	$a_c = b_p$
	β	104.15(11)		81.76(9)	$b_c = -2a_p - b_p$
	γ	89.94(10)		119.92(10)	$c_c = c_p$
Space group		$C\bar{1}$		$P\bar{1}$	
Z		4		2	
$D_{meas.}$			2.91		
$D_{calc.}$			2.899		

Standard deviations are given in parentheses.

Structure determination and refinement

The structure was solved by interpreting Patterson maps. Patterson sections of (*uv1/4*) and (*uv3/4*) gave the image of Ca octahedral sheets, and Si_6O_{18} rings could be located by the restriction given by these two sections. The positions of K and Ti atoms were determined by Patterson sections of (*uv0*) and (*uv1/2*). The positions of Li and OH were determined by referring to those of Al in the cordierite structure and those of F in the baratovite structure, respectively.

The ideal formula $(K_{0.89}Na_{0.11})Li_3Ca_7(Ti_{1.95}Fe_{0.05})[Si_6O_{18}]_2(OH_{1.76}F_{0.24})_2$ was adopted in calculation. Atomic scattering factors used in calculation were taken from the *International Tables for X-ray Crystallography IV* (1974). At first, non-centrosymmetric space group *C1* was assumed. The coordinates of one of K atoms determined by Patterson section (*uv0*) were fixed. The refinement was carried out using a block diagonal matrix least-squares program, HBLS, written by Ashida after modification (Sakurai, 1967). The final R and R2 were 0.050 and 0.062, respectively. Based on these results, the previous paper by Murakami *et al.* (1983) described the space group as *C1*.

Later, however, it was found that the structure was nearly centrosymmetric if we chose one of Ca atoms as origin. So we adopted centrosymmetric space group

TABLE 2. Atomic parameters

Atom	x	y	z	B(Å^2)
Ca(1)	.0	.0	.0	0.74(3)
Ca(2)	.25	.25	.5	0.66(3)
Ca(3)	.434(2)	.286(2)	.013(2)	0.67(2)
Ca(4)	.139(2)	.428(2)	.000(2)	0.66(2)
Ca(5)	.213(2)	.642(2)	−.007(2)	0.70(2)
Ca(6)	.171(2)	.464(2)	.487(2)	0.68(2)
Ca(7)	.470(2)	.608(2)	.507(2)	0.72(2)
Ca(8)	.111(2)	.678(2)	.500(2)	0.60(2)
K	.446(3)	.375(3)	.750(3)	1.95(4)
Ti(1)	.445(1)	.709(1)	.748(1)	0.41(2)
Ti(2)	.446(1)	.041(1)	.752(1)	0.37(2)
Li(1)	.192(17)	.627(17)	.750(18)	1.18(24)
Li(2)	.693(16)	.621(15)	.753(17)	0.90(22)
Li(3)	.458(16)	.875(16)	.749(17)	0.90(22)
Si(1)	.253(2)	.499(2)	.860(2)	0.39(3)
Si(2)	.564(2)	.561(2)	.859(2)	0.43(3)
Si(3)	.810(2)	.439(2)	.860(2)	0.36(3)
Si(4)	.745(2)	.256(2)	.859(2)	0.42(3)
Si(5)	.439(2)	.192(2)	.862(2)	0.30(3)
Si(6)	.195(2)	.316(2)	.860(2)	0.38(3)
Si(7)	.300(2)	.689(2)	.360(2)	0.32(3)
Si(8)	.544(2)	.811(2)	.359(2)	0.38(3)
Si(9)	.856(2)	.749(2)	.360(2)	0.44(3)
Si(10)	−.085(2)	.566(2)	.360(2)	0.43(3)
Si(11)	.673(2)	.442(2)	.362(2)	0.44(3)
Si(12)	.364(2)	.506(2)	.359(2)	0.45(3)
O(1)	.230(7)	.405(6)	.841(7)	1.00(10)
O(2)	.141(6)	.550(6)	.806(6)	0.69(9)
O(3)	.253(7)	.517(6)	.939(7)	0.90(10)
O(4)	.413(7)	.515(7)	.851(7)	1.23(10)
O(5)	.555(6)	.628(6)	.804(7)	0.84(9)
O(6)	.621(6)	.591(6)	.938(7)	0.85(9)
O(7)	.670(7)	.494(6)	.841(7)	0.92(10)
O(8)	.909(6)	.456(6)	.809(6)	0.74(9)
O(9)	.891(6)	.449(6)	.942(6)	0.78(9)
O(10)	.744(7)	.350(6)	.845(7)	1.03(10)
O(11)	.809(6)	.207(6)	.804(6)	0.73(9)
O(12)	.824(6)	.241(6)	.938(7)	0.82(9)
O(13)	.580(7)	.230(6)	.845(7)	1.00(10)
O(14)	.381(6)	.119(6)	.810(7)	0.83(9)
O(15)	.469(6)	.171(6)	.942(6)	0.70(9)
O(16)	.326(7)	.264(6)	.845(7)	1.02(10)
O(17)	.047(6)	.291(6)	.808(6)	0.70(9)
O(18)	.195(6)	.311(6)	.941(6)	0.76(9)
O(19)	.353(7)	.600(6)	.345(7)	1.07(10)
O(20)	.150(6)	.706(6)	.309(6)	0.74(9)
O(21)	.301(6)	.700(6)	.441(6)	0.72(9)

O(22)	.422(7)	.743(6)	.340(7)	0.91(9)
O(23)	.499(6)	.879(6)	.304(6)	0.79(9)
O(24)	.568(6)	.840(6)	.438(7)	0.87(9)
O(25)	.687(7)	.765(7)	.350(7)	1.13(10)
O(26)	.913(6)	.799(6)	.306(6)	0.77(9)
O(27)	−.063(6)	.768(6)	.439(7)	0.86(9)
O(28)	.860(6)	.655(6)	.340(6)	0.80(9)
O(29)	.010(6)	.542(6)	.308(6)	0.66(9)
O(30)	−.002(6)	.562(6)	.441(6)	0.69(9)
O(31)	.769(7)	.514(6)	.345(7)	1.08(10)
O(32)	.679(6)	.370(6)	.310(6)	0.74(9)
O(33)	.722(6)	.420(6)	.442(6)	0.74(9)
O(34)	.515(7)	.480(6)	.345(7)	1.04(10)
O(35)	.245(7)	.457(6)	.304(7)	0.94(10)
O(36)	.365(6)	.491(6)	.438(7)	0.82(9)
OH(1)	.453(6)	.623(6)	.043(6)	0.69(9)
OH(2)	.340(6)	.372(6)	.543(6)	0.69(9)

$C\bar{1}$ and repeated the refinement. In this case, the final R and R2 were 0.056 and 0.067, respectively. The obtained values of coordinates, temperature factors, and bond distances are more reasonable, so we judge that the most probable space group of katayamalite is $C\bar{1}$. Final atomic and isotropic thermal parameters are given in Table 2, while bond distances and angles are listed in Table 3.

Discussion

Katayamalite is a ring silicate of two-layered structure parallel to (001). The structure scheme is very simple in spite of the lower symmetry. Fig. 1 shows a partial view of the structure on (001). Pairs of Si_6O_{18} rings are superimposed along the c^*-axis, and the rotation angle between these two rings is about 22°. Note that the motif in Fig. 1 is similar to that of cordierite if K atoms are excluded and the replacement of cations takes place. In this sense, we can propose the following structure series; beryl → cordierite → katayamalite and baratovite.

Fig. 2 represents a projection along the *a*-axis. Ca atoms lie nearly at z = 0 and 1/2, Ti, Li and K atoms nearly at z = 1/4 and 3/4, and Si atoms nearly at z = 2/14, 5/14, 9/14 and 12/14. Perpendicular to (001), Si_6O_{18} rings are connected with Ca octahedral sheets on one side and with Ti octahedra, Li tetrahedra, and 12-fold K polyhedra on the other side.

The structure of katayamalite is very similar to that of baratovite. Baratovite was described by Dusmatov *et al.* (1975) and its crystal structure was determined by Sandomirskii *et al.* (1976), and Menchetti and Sabelli (1979). Its formula: KLi_3

TABLE 3. Interatomic distances(Å) and angles(°)

K Polyhdron

K	– O(1)	3.13(12)
	– O(4)	3.14(14)
	– O(7)	3.15(10)
	– O(10)	3.08(8)
	– O(13)	3.22(12)
	– O(16)	3.12(13)
	– O(19)'	3.07(13)
	– O(22)'	3.14(13)
	– O(25)'	3.14(12)
	– O(28)'	3.12(10)
	– O(31)'	3.12(8)
	– O(34)'	3.21(13)
Mean		3.14

Ca Octahedra

Ca(1)	– OH(1)	x2	2.31(10)
	– O(3)	x2	2.43(7)
	– O(6)	x2	2.46(7)
Mean			2.40

Ca(2)	– OH(2)	x2	2.31(10)
	– O(24)	x2	2.45(9)
	– O(27)	x2	2.44(10)
Mean			2.40

Ca(3)	– OH(1)'	2.35(11)
	– O(6)'	2.39(11)
	– O(12)'	2.36(7)
	– O(15)	2.46(11)
	– O(18)	2.46(17)
	– O(18)'	2.41(17)
Mean		2.41

Ca(4)	– O(3)	2.39(12)
	– O(6)'	2.39(7)
	– O(9)	2.44(7)
	– O(9)'	2.42(11)
	– O(15)'	2.43(11)
	– O(18)	2.40(13)
Mean		2.41

Ca(5)	– OH(1)	2.33(6)
	– O(3)	2.42(14)
	– O(9)'	2.42(12)
	– O(12)	2.41(11)
	– O(12)'	2.46(12)
	– O(15)	2.39(7)
Mean		2.41

Ca(6)	– OH(2)	2.35(10)
	– O(24)	2.39(11)
	– O(30)	2.40(11)
	– O(30)'	2.48(10)
	– O(33)'	2.43(11)
	– O(36)	2.37(10)
Mean		2.40

Ca(7)	– OH(2)'	2.33(10)
	– O(21)	2.42(9)
	– O(27)'	2.40(11)
	– O(33)'	2.38(10)
	– O(36)	2.46(11)
	– O(36)'	2.41(10)
Mean		2.40

Ca(8)	– O(21)	2.45(11)
	– O(21)'	2.41(10)
	– O(24)'	2.34(11)
	– O(27)	2.40(9)
	– O(30)	2.39(10)
	– O(33)'	2.43(9)
Mean		2.40

Ti Octahedra

Ti(1)	– O(5)	1.94(10)
	– O(11)	1.92(11)
	– O(17)	1.93(10)
	– O(20)'	1.95(10)
	– O(26)'	1.95(11)
	– O(32)'	1.95(9)
Mean		1.94

Ti(2)	– O(2)	1.94(7)
	– O(8)	1.95(11)
	– O(14)	1.94(12)
	– O(23)'	1.92(12)
	– O(29)'	1.97(11)
	– O(35)'	1.92(7)
Mean		1.94

TABLE 3. (Continued)

Li Tetrahedra

						around Li
Li(1)	– O(2)	1.87(21)	O(2)	– O(11)	3.12(13)	111.9(6.0)
	– O(11)	1.90(17)		– O(23)′	2.59(15)	86.5(2.2)
	– O(23)′	1.91(13)		– O(32)′	3.51(16)	134.5(2.2)
	– O(32)′	1.93(30)	O(11)	– O(23)′	3.52(11)	135.3(1.8)
Mean		1.90		– O(32)′	2.61(17)	85.7(2.4)
			O(23)′	– O(32)′	3.16(10)	110.6(6.8)
			Mean		3.08	110.8
Li(2)	– O(5)	1.89(29)	O(5)	– O(14)	3.16(10)	112.4(6.8)
	– O(14)	1.91(19)		– O(26)′	2.63(18)	86.9(3.4)
	– O(26)′	1.94(27)		– O(35)′	3.53(16)	136.8(5.4)
	– O(35)′	1.91(31)	O(14)	– O(26)′	3.52(12)	132.4(5.2)
Mean		1.91		– O(35)′	2.61(16)	86.6(3.4)
			O(26)′	– O(35)′	3.13(14)	109.0(6.8)
			Mean		3.10	110.7
Li(3)	– O(8)	1.92(31)	O(8)	– O(17)	3.09(14)	106.2(6.4)
	– O(17)	1.94(28)		– O(20)′	3.50(15)	132.6(4.0)
	– O(20)′	1.91(28)		– O(29)′	2.64(18)	87.2(4.6)
	– O(29)′	1.90(26)	O(17)	– O(20)′	2.63(14)	86.3(4.6)
Mean		1.92		– O(29)′	3.66(16)	142.2(4.0)
			O(20)′	– O(29)′	3.13(13)	109.5(6.3)
			Mean		3.11	110.7

$Ca_7(Ti_{0.87}Zr_{0.13})_2[Si_6O_{18}]_2F_2$ and cell dimensions: *a* 16.941, *b* 9.746, *c* 20.907Å, β 112.50°, space group *C2/c*, and $Z = 4$.

There is a relationship between the cells of katayamalite and baratovite as follows:

$$a_{\text{kat.}} = b_{\text{bar.}}$$
$$b_{\text{kat.}} = -a_{\text{bar.}}$$
$$c_{\text{kat.}} = 1/2a_{\text{bar.}} - 1/2b_{\text{bar.}} + c_{\text{bar.}}$$

We inspected carefully both structures and found the reason for the triclinic symmetry of katayamalite. In the baratovite structure, the upper (nearly z = 1/2) and the lower (nearly z = 0) Ca octahedral sheets are restricted by the symmetry condition of *C2/c*. However, those in the katayamalite structure are distorted slightly and some atoms show deviation of maximum 0.1Å and do not obey this restriction. Some oxygen atoms in the Si_6O_{18} rings also show similar deviation. Thus, the distortion of the structure in such sense is the main reason for the triclinic symmetry of katayamalite.

These two minerals have similar cell volume and layer thickness; the cell volume

TABLE 3. (Continued)

Si Tetrahedra

						around Si
Si(1)	– O(1)	1.63(11)	O(1)	– O(2)	2.65(11)	110.1(2.2)
	– O(2)	1.60(10)		– O(3)	2.66(17)	110.5(2.6)
	– O(3)	1.61(14)		– O(4)	2.56(13)	103.1(2.2)
	– O(4)	1.63(9)	O(2)	– O(3)	2.70(17)	114.5(2.4)
Mean		1.62		– O(4)	2.65(9)	109.8(2.2)
			O(3)	– O(4)	2.63(17)	108.3(2.0)
			Mean		2.64	109.4
Si(2)	– O(4)	1.63(9)	O(4)	– O(5)	2.67(16)	111.9(2.0)
	– O(5)	1.59(13)		– O(6)	2.63(13)	108.7(2.6)
	– O(6)	1.60(13)		– O(7)	2.58(11)	104.8(2.2)
	– O(7)	1.63(8)	O(5)	– O(6)	2.68(18)	114.2(2.4)
Mean		1.61		– O(7)	2.58(14)	106.8(2.4)
			O(6)	– O(7)	2.65(17)	110.0(2.0)
			Mean		2.63	109.4
Si(3)	– O(7)	1.62(8)	O(7)	– O(8)	2.64(12)	109.7(2.4)
	– O(8)	1.61(12)		– O(9)	2.68(12)	111.5(2.4)
	– O(9)	1.62(12)		– O(10)	2.53(14)	102.2(1.6)
	– O(10)	1.63(11)	O(8)	– O(9)	2.71(18)	113.9(1.6)
Mean		1.62		– O(10)	2.64(14)	109.3(2.4)
			O(9)	– O(10)	2.66(14)	109.5(2.6)
			Mean		2.64	109.4
Si(4)	– O(10)	1.63(12)	O(10)	– O(11)	2.67(12)	111.2(2.8)
	– O(11)	1.61(12)		– O(12)	2.64(12)	109.0(2.4)
	– O(12)	1.61(12)		– O(13)	2.58(12)	105.4(2.0)
	– O(13)	1.62(7)	O(11)	– O(12)	2.70(12)	114.6(2.0)
Mean		1.62		– O(13)	2.58(12)	106.4(2.2)
			O(12)	– O(13)	2.64(10)	109.9(2.4)
			Mean		2.64	109.4
Si(5)	– O(13)	1.62(10)	O(13)	– O(14)	2.64(12)	110.1(2.4)
	– O(14)	1.60(15)		– O(15)	2.65(17)	110.7(2.0)
	– O(15)	1.60(15)		– O(16)	2.54(11)	102.6(2.2)
	– O(16)	1.63(15)	O(14)	– O(15)	2.69(17)	113.7(2.4)
Mean		1.61		– O(16)	2.62(15)	108.6(2.0)
			O(15)	– O(16)	2.66(15)	110.6(2.6)
			Mean		2.63	109.4
Si(6)	– O(1)	1.62(12)	O(1)	– O(16)	2.55(15)	103.4(2.2)
	– O(16)	1.63(10)		– O(17)	2.58(12)	106.2(2.2)
	– O(17)	1.63(10)		– O(18)	2.66(18)	111.3(2.4)
	– O(18)	1.61(14)	O(16)	– O(17)	2.67(9)	111.1(2.2)
Mean		1.62		– O(18)	2.65(17)	109.9(2.2)
			O(17)	– O(18)	2.70(16)	114.3(2.2)
			Mean		2.63	109.4

TABLE 3. (Continued)

Si(7)	– O(19)	1.64(11)	O(19)	– O(20)	2.64(12)	109.4(2.2)
	– O(20)	1.60(8)		– O(21)	2.66(17)	109.9(2.6)
	– O(21)	1.62(14)		– O(22)	2.53(15)	101.5(2.2)
	– O(22)	1.63(17)	O(20)	– O(21)	2.70(16)	114.2(2.2)
Mean		1.62		– O(22)	2.63(9)	109.4(2.2)
			O(21)	– O(22)	2.69(17)	111.7(2.2)
			Mean		2.64	109.4
Si(8)	– O(22)	1.62(9)	O(22)	– O(23)	2.59(15)	106.8(2.0)
	– O(23)	1.61(12)		– O(24)	2.65(15)	110.8(2.4)
	– O(24)	1.60(14)		– O(25)	2.57(10)	104.3(2.2)
	– O(25)	1.63(9)	O(23)	– O(24)	2.67(18)	114.5(2.4)
Mean		1.62		– O(25)	2.67(13)	111.2(2.4)
			O(24)	– O(25)	2.63(17)	108.7(2.2)
			Mean		2.63	109.4
Si(9)	– O(25)	1.63(7)	O(25)	– O(26)	2.63(14)	109.6(2.2)
	– O(26)	1.58(13)		– O(27)	2.63(11)	108.7(2.4)
	– O(27)	1.60(12)		– O(28)	2.54(13)	102.7(2.0)
	– O(28)	1.62(11)	O(26)	– O(27)	2.67(18)	113.9(2.2)
Mean		1.61		– O(28)	2.62(15)	109.6(2.6)
			O(27)	– O(28)	2.67(16)	111.9(2.2)
			Mean		2.63	109.4
Si(10)	– O(28)	1.63(11)	O(28)	– O(29)	2.58(14)	105.7(2.4)
	– O(29)	1.60(12)		– O(30)	2.68(15)	111.6(2.2)
	– O(30)	1.61(12)		– O(31)	2.56(15)	103.8(2.4)
	– O(31)	1.62(9)	O(29)	– O(30)	2.68(18)	113.4(2.2)
Mean		1.62		– O(31)	2.66(13)	111.3(1.8)
			O(30)	– O(31)	2.66(12)	110.6(1.8)
			Mean		2.64	109.4
Si(11)	– O(31)	1.63(11)	O(31)	– O(32)	2.62(14)	108.4(2.6)
	– O(32)	1.60(12)		– O(33)	2.66(18)	111.1(2.2)
	– O(33)	1.60(13)		– O(34)	2.54(11)	102.7(2.2)
	– O(34)	1.63(8)	O(32)	– O(33)	2.68(17)	113.9(2.2)
Mean		1.61		– O(34)	2.64(12)	109.9(2.0)
			O(33)	– O(34)	2.65(13)	110.3(2.4)
			Mean		2.63	109.4
Si(12)	– O(19)	1.63(12)	O(19)	– O(34)	2.57(14)	104.6(2.0)
	– O(34)	1.62(9)		– O(35)	2.67(14)	111.6(2.2)
	– O(35)	1.60(10)		– O(36)	2.64(17)	109.3(2.6)
	– O(36)	1.61(14)	O(34)	– O(35)	2.58(9)	106.6(2.2)
Mean		1.61		– O(36)	2.64(17)	109.8(2.2)
			O(35)	– O(36)	2.70(17)	114.5(2.4)
			Mean		2.63	109.4

TABLE 3. (Continued)

Si–Si distances

Si(1)	– Si(2)	3.20(4)
Si(2)	– Si(3)	3.15(4)
Si(3)	– Si(4)	3.17(5)
Si(4)	– Si(5)	3.17(4)
Si(5)	– Si(6)	3.16(4)
Si(6)	– Si(1)	3.15(4)
Si(7)	– Si(8)	3.15(4)
Si(8)	– Si(9)	3.20(4)
Si(9)	– Si(10)	3.15(5)
Si(10)	– Si(11)	3.15(4)
Si(11)	– Si(12)	3.18(4)
Si(12)	– Si(7)	3.17(4)
Mean		3.16_6

Si–O–Si angles

Si(1)	– O(1)	– Si(6)	151.3(3.1)
Si(1)	– O(4)	– Si(2)	158.3(2.9)
Si(2)	– O(7)	– Si(3)	152.5(2.9)
Si(3)	– O(10)	– Si(4)	152.6(2.0)
Si(4)	– O(13)	– Si(5)	156.8(2.9)
Si(5)	– O(16)	– Si(6)	151.5(3.1)
Si(7)	– O(19)	– Si(12)	151.9(3.1)
Si(7)	– O(22)	– Si(8)	151.1(3.1)
Si(8)	– O(25)	– Si(9)	158.0(2.6)
Si(9)	– O(28)	– Si(10)	150.3(2.6)
Si(10)	– O(31)	– Si(11)	151.8(2.6)
Si(11)	– O(34)	– Si(12)	156.6(3.3)
Mean			153.5_6

of katayamalite is 3180.0Å^3, that of baratovite is 3189.1Å^3, and $d_{(001)}$ of katayamalite is 19.331Å, and that of baratovite is 19.315Å.

In general, mean bond lengths of katayamalite agree well with those of baratovite. In the order of katayamalite and baratovite, K – O are 3.13_6 and 3.140Å, Li – O are 1.91_0 and 1.908Å, Ti – O are 1.93_5 and 1.945Å, Si – O are 1.61_6 and 1.618Å, Ca – (O,OH) or Ca – (O,F) are 2.40_4 and 2.403Å, respectively.

Menchetti and Sabelli (1979) inspected the Si–O bond lengths and angles in the baratovite structure and noticed several features among them. Similar results were obtained in the katayamalite structure, too, though the precision of our results is inferior.

These features are as follows:

(1) The Si–O(br) bridging bond lengths are greater than the Si–O(nbr) bond lengths. The mean values are 1.62_6 and 1.60_5Å, respectively, and correspond to those of baratovite, 1.628 and 1.607Å, respectively. This satisfies the prediction

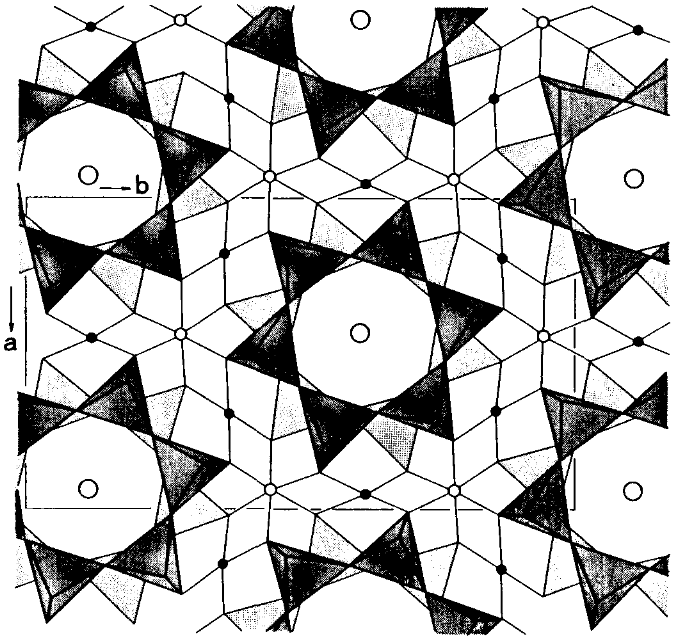

FIG. 1. A partial view of the structure at z = 1/4, projected on (001), showing Si_6O_{18} rings, Ti (middle open circles) and Li (small solid circles) polyhedra, and K atoms (large open circles). Note that this motif is similar to that of cordierite if K atoms are excluded and the replacement of cations occurs.

derived from Cruickshank's *d–p π* model for the crystals contain TO_4^{n-} groups (Cruickshank, 1961 and Brown *et al.*, 1969). The overall Si–O mean bond length is 1.61_6 Å and comparable with 1.618Å in baratovite.

(2) The mean Si–Si bond length is 3.16_6 Å and in agreement with 3.151Å in baratovite. Recently O'Keefe and Hyde (1978) represented a histogram showing the distribution of 141 nearest-neighbors Si–Si in various silicates and silicas. It has a pronounced peak at 3.06Å and ranges from 2.94 to 3.27Å. Thus, the value found in katayamalite fall on the greater side of the histogram.

(3) The twelve independent Si tetrahedra show O–Si–O angles ranging from 101.5° to 114.5°. These values are in good agreement with those 101.8° and 114.6°, respectively, in baratovite. Among these angles, the smallest angle in each tetrahedron is the one involving two bridging oxygen atoms which are shared with the K polyhedron.

(4) The relationship between Si–O(br) bond lengths and Si–O(br)–Si angles was not clearly oserved. Brown *et al.* (1969) predicted that the Si–O(br) bond lengths

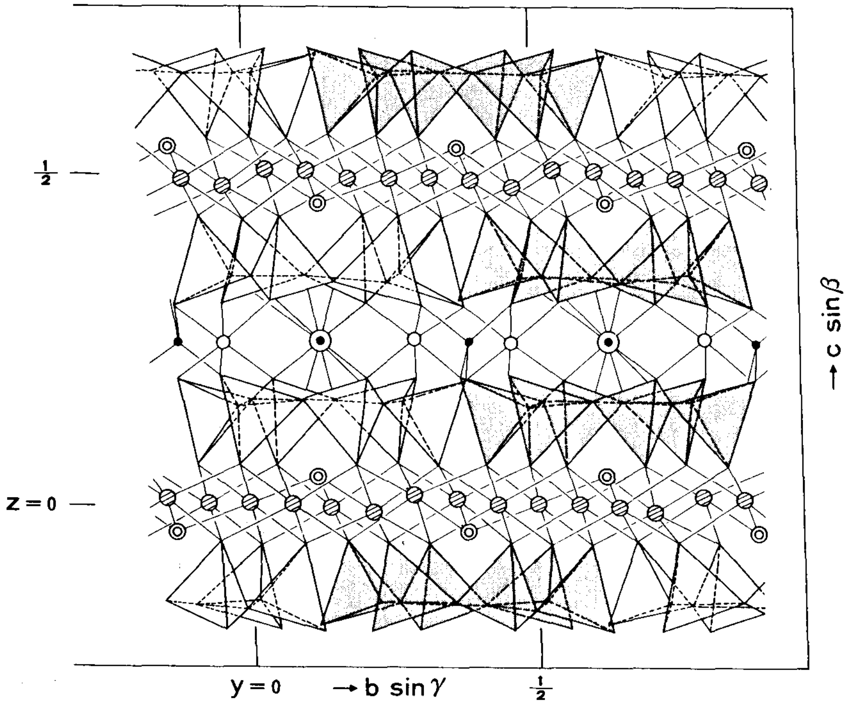

FIG. 2. A partial projection of the structure along the *a*-axis. At z = 1/4, Ti (small open circles), Li (small solid circles) and K (large open circles) polyhedra lie. At z = 0 and 1/2, Ca (shaded circles) octahedral sheets are represented. Double open circles are OH.

and its π-bond order should vary directly with the Si–O(br)–Si angle. On the other hand, O'Keefe and Hyde (1978) have described that Si–O(br) bond lengths do not depend on the Si–O(br)–Si angle when this angle is greater than 145°. Baur (1977) also found that there was only very weak correlation between the Si–O(br) bond length and the Si–O(br)–Si angle. In the case of katayamalite, a clear correlation was not observed, and also Si–O(br)–Si angles ranged from 151.1° to 158.3° and all exceed the value of 145°. Thus the results agree with those obtained by O'Keefe and Hyde (1978) and Baur (1977).

(5) Brown *et al.* (1969) also predicted that the O–Si–O angles should decrease in the order of O(nbr)–Si–O(nbr), O(br)–Si–O(nbr) and O(br)–Si–O(br). The obtained results of katayamalite satisfy this prediction.

(6) A similar relationship to baratovite was observed between the Si–O bond length and $(O\text{–}Si\text{–}O)_3$ angle [the mean of three O–Si–O angles common to the bond]. The experimental points split into two groups: one of them is related to the bridging oxygen atoms and make a cluster around 1.63Å and 107.5°, and the other

is related to the non-bridging oxygen atoms and makes a cluster around 1.61Å and 111°. Therefore the correlation of the Si–O bond length with $(O\text{–}Si\text{–}O)_3$ is not clear.

Thus the features of six membered Si rings of katayamalite are very similar to those of baratovite.

We have also found another monoclinic polymorph with a large cell: *a* 3 x 9.721, *b* 2 x 16.923, *c* 19.942Å, *β* 104.15°. Diffraction aspect is *P**/*. The study of this polymorph will be published in a separate paper.

There is an experimental technique to judge a crystal structure is centric or acentric; second harmonic generation (SHG). We are going to ask some laboratories for obtaining such facilities. Notice, however, that the results of SHG are sometimes not decisive.

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