

Origin of low-symmetry growth sectors in edingtonite and yugawaralite, and crystal structure of the $k\{011\}$ and $v\{120\}$ sectors of yugawaralite

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ABSTRACT

Edingtonite and yugawaralite showing sectoral textures were studied by polarized optical microscopy and X-ray analysis. In edingtonite, the $m\{110\}$ sector ($2V\alpha = 22^\circ$) is optically triclinic and the $c\{001\}$ sector ($2V\alpha = 52^\circ$) is orthorhombic. In yugawaralite, the $k\{011\}$ sector is optically monoclinic, whereas the $v\{120\}$ sector is triclinic. Their crystal structures were determined. The results of refinement showed that the space groups of the $k\{011\}$ ($R_w = 4.5\%$) and $v\{120\}$ ($R_w = 5.1\%$) growth sectors are monoclinic Pc and triclinic $P1$, respectively. In the $v\{120\}$ sector, several interatomic distances, bond angles and site occupancies are different with respect to a symmetrical plane of the structure, and therefore the monoclinic c glide is extinct. Thus, the X-ray symmetry correlates with the optical one. From the relationship between the surface and internal texture, the symmetry and sector can be explained by cation (Al/Si) ordering during non-equilibrium crystal growth.

KEYWORDS: growth sectors, crystal structure, yugawaralite, zeolite.

Introduction

It was first suggested in the 19th century that optical symmetry can be lower than morphological symmetry, and similar observations have been made by X-ray study throughout the 20th century. It was thought that this lower symmetry is due to strain or phase transitions, and therefore the phenomenon was referred to as “optical anomaly” (e.g. Brauns, 1891). However, Akizuki (1981) and Akizuki *et al.* (2001) found that low optical symmetries in analcime and tourmaline could be correlated with the ordering of Al/Si and other atoms, which were produced during non-equilibrium crystal growth. Shtukenberg *et al.* (2000, 2001) and Tanaka *et al.* (2002) also showed that growth dissymmetrization and atomic ordering are important in understanding optical anomalies.

Edingtonite ($BaAl_2Si_3O_{10}\cdot 4H_2O$) is a rare Ba zeolite mineral for which Hey (1934) found two kinds of optical symmetry: one is orthorhombic ($2V\alpha = 54^\circ$), and the other is tetragonal ($2V\alpha = 15\text{--}20^\circ$). Taylor and Jackson (1933) analysed a tetragonal, disordered edingtonite (space group $P4_2/m$) from Sweden by X-ray diffraction (XRD), and Galli (1976) analysed an orthorhombic, ordered one (space group $P2_12_12$) from the same locality. Subsequently, Mazzi *et al.* (1984) described a tetragonal disordered edingtonite from Ice River, Canada, and Grice *et al.* (1984) studied an orthorhombic one from the same locality. The relationship between the two is polymorphic. However, Akizuki (1986) described a morphologically single edingtonite as consisting of both optically triclinic $m\{110\}$ and $o\{111\}$ and orthorhombic $c\{001\}$ and $p\{1\bar{1}1\}$ growth sectors.

Kerr and Williams (1969) and Leimer and Slaughter (1969) suggested, following X-ray analysis, that yugawaralite ($CaAl_2Si_6O_{16}\cdot 4H_2O$) is monoclinic. The chemical composition is similar within and between crystals (Eberlein *et*

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al., 1971), whereas the optical properties, such as the $2V$ value, vary from specimen to specimen, and from sector to sector. Sakurai and Hayashi (1952) reported that the $2V\gamma$ value ranges from 56 to 89° in a specimen from Yugawara, Japan (the type locality). However, Eberlein *et al.* (1971) suggested that the $2V\alpha$ value varies from 48 to 72° in yugawaralite from the Chena hot spring area, Alaska. Also, the $2V\alpha$ value varies from 70 to 76° in the specimens from Sardinia (Pongiluppi, 1977).

Kerr and Williams (1969) refined the crystal structure of yugawaralite and showed perfect Al/Si ordering, whereas Leimer and Slaughter (1969) suggested a partial Al/Si ordering. Alberti *et al.* (1996) refined the crystal structure of yugawaralite in order to study the dehydration and rehydration mechanisms, and showed that the space group changes from Pc to Pn at 180°C . Furthermore, Alberti *et al.* (1996) suggested that the topological symmetry $C2/m$ is reduced to Pc by Al/Si ordering.

Akizuki (1987a) observed growth sectors in yugawaralite from Toi, Shizuoka and from Takinoue in the Kakkonda hot spring area, Iwate, Japan, and found that the growth sectors show various $2V\alpha$ values and they are optically monoclinic or triclinic. Since the growth sectors correlate with the crystal faces, Akizuki (1987a) suggested that the sectors were produced during crystal growth, not by strain or phase transition. Similar textures were observed in other zeolite minerals such as analcime (Akizuki, 1981), stilbite (Akizuki and Konno, 1985), and brewsterite (Akizuki, 1987b). The crystal structures of some zeolites showing optical anomaly have been refined by X-ray methods (e.g. Smith *et al.*, 1964; Mazzi and Galli, 1978; Akizuki *et al.*, 1993, 1996), and it was found that their optical properties could be related directly to the cation (Al/Si) ordering.

The purpose of the present study is to measure the lattice parameters of each sector in edingtonite and yugawaralite and to find the structure difference between optically monoclinic $k\{011\}$ and triclinic $v\{120\}$ growth sectors in yugawaralite in order to discuss relations between the optical and X-ray symmetries.

Specimen

Edingtonite

The specimen used for the study is from Ice River, Canada, which is the same locality as that of Akizuki's sample (1986). Figure 1 shows the

crystal form consisting of $c(001)$, $p(\bar{1}\bar{1}1)$, $m(110)$ and $o(111)$ faces. The crystal size is small and varies from specimen to specimen.

The optical properties and internal textures were observed in a (001) thin-section by polarized optical microscopy (Akizuki, 1986). The $m\{110\}$ and $o\{111\}$ sectors ($2V\alpha = 22^\circ$) show greater Al/Si disorder than the $c\{001\}$ and $p\{\bar{1}\bar{1}1\}$ sectors ($2V\alpha = 52^\circ$). However, the optical symmetry is triclinic in the $m\{110\}$ and $o\{111\}$ sectors.

The chemical composition was determined by electron microprobe analysis (EPMA, JEOL-8800M) (Table 1a). Since water content cannot be measured by EPMA, the weight loss is given as H_2O wt.%.

Yugawaralite

The yugawaralite specimen is from Toi, Shizuoka Prefecture, Japan. Figure 2 shows the common crystal form of yugawaralite. The specimen is transparent and ~ 10 mm, 6 mm and 1 mm in size along the c , a and b axes, respectively. The $k\{011\}$ and $v\{120\}$ growth sectors are shown in Fig. 3, which is parallel to the (100) thin-section.

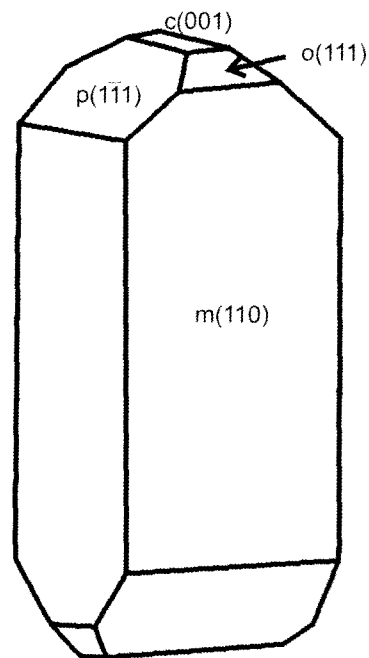


FIG. 1. Crystal form of edingtonite from Ice River, Canada.

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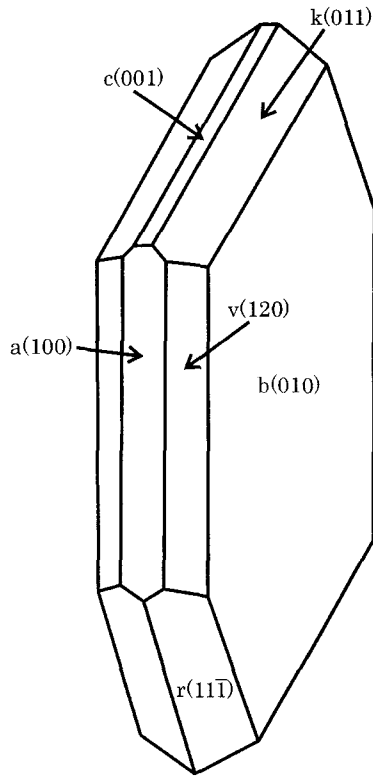


FIG. 2. Common crystal form of yugawaralite.

The $k\{011\}$ sector: several bands parallel to the $k(011)$ face are observed near the $k(011)$ surface, but they are not found in the core. The optical indicatrix X is parallel to the b axis, which is horizontal in Fig. 3, and therefore the symmetry is monoclinic.

The $v\{120\}$ sector: the optical indicatrix X is inclined at 1.5° to the b axis on the (100) thin-section, and the $v\{120\}$ and $\bar{v}\{1\bar{2}0\}$ sectors are related to each other by a reflection twinning. Therefore, the symmetry of the $v\{120\}$ sector is optically triclinic.

The chemical composition was also analysed by EPMA and shown in Table 1*b*. The weight loss is considered as H_2O wt.%.

X-ray analysis

Edingtonite

Two single crystals ($0.05 \times 0.05 \times 0.05$ mm³ in size) were handpicked from the optically homogeneous $m\{110\}$ and $c\{001\}$ sectors, showing no twin in the (001) thin-section. The lattice

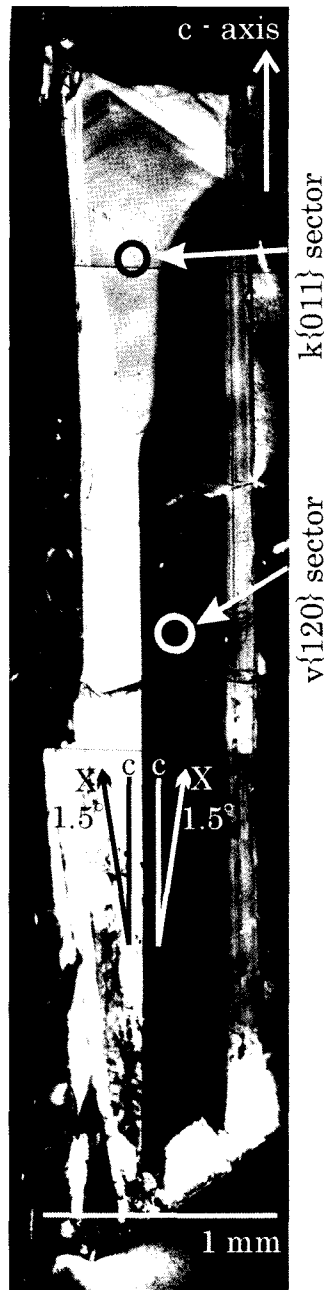


FIG. 3. Polarized optical micrograph of the (100) thin-section of yugawaralite from Toi, Japan. The core of the $k\{011\}$ sector is homogeneous and optically monoclinic, whereas the rim shows growth bands and optically triclinic symmetry. The $v\{120\}$ sector is optically triclinic. The specimens for X-ray analysis were handpicked from the areas shown by the circles. Crossed nicols.

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TABLE 1a. Chemical analyses of edingtonite determined by EPMA.

Chemical analysis (wt.%)*		Cations per unit cell	
SiO ₂	38.52	Si	5.89
Al ₂ O ₃	23.54	Al	4.24
BaO	30.54	Ba	1.83
Na ₂ O	0.12	Na	0.04
K ₂ O	0.25	K	0.05
Total**	92.97		

* The chemical analysis results are based on the average of 5 points

** The weight loss is considered as H₂O wt.% because water content cannot be estimated by EPMA.

TABLE 1b. Chemical analyses of yugawaralite determined by EPMA.

	k{011} sector Chemical analysis (wt.%)*	v{120} sector Chemical analysis (wt.%)*		k{011} sector Cations per unit cell	v{120} sector Cations per unit cell
SiO ₂	62.29	62.46	Si	12.04	12.04
Al ₂ O ₃	17.31	17.38	Al	3.94	3.95
MnO	0.03	0.05	Mn	0.01	0.01
CaO	9.50	9.58	Ca	1.97	1.98
Na ₂ O	0.12	0.09	Na	0.04	0.03
Total**	89.25	89.56			

* Results of k{011} and v{120} sectors analysis are based on the average of 5 points.

** The weight loss is considered as H₂O because water content cannot be estimated by EPMA.

parameters were measured using 25 reflections between 20 and 30°2θ by a four-circle diffractometer (Rigaku, AFC-7S) with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å).

The lattice parameters are shown in Table 2a. It is suggested that the m{110} sector is triclinic, and the c{001} sector is orthorhombic. These results correlate with optical observations.

Yugawaralite

The two single crystals which were 0.38 × 0.25 × 0.05 mm³ and 0.25 × 0.20 × 0.08 mm³ in size, respectively, were handpicked from optically homogeneous k{011} and v{120} sectors showing no twin in the (100) thin-section. The lattice parameters were measured in the same way as those of edingtonite using 25 reflections between 20 and 27°2θ (k{011} sector) and using 24 reflections between 20 and 30° (v{120} sector), respectively.

The lattice parameters shown in Table 2b suggest that the k{011} sector is monoclinic, and the v{120} sector is triclinic. These symmetries correlate with the optical observation. Although the optical symmetry is clearly triclinic in the v{120} sector, the deviation from monoclinic symmetry is small in X-ray analysis.

X-ray diffraction intensity data were measured at room temperature using the ω-2θ scan method in the range 3 to 60° in both the k{011} and v{120} sectors. Scattering factors for all atoms were taken from the *International Tables for X-ray Crystallography* (1974). After Lorentz and polarization corrections, the sets of intensity data were obtained. No absorption corrections were made because of the small sizes of the crystals and low linear absorption coefficient (~9.7/cm).

The starting atomic coordinates for the triclinic refinements were derived from the monoclinic structure by Kerr and Williams (1969). All calculations were performed using the teXsan

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TABLE 2a. Cell parameters of $m\{110\}$ and $c\{001\}$ sectors of edingtonite.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$m\{110\}$ sector	9.564(2)	9.565(2)	6.515(2)	89.95(2)	90.10(2)	89.93(2)
$c\{001\}$ sector	9.558(2)	9.572(2)	6.519(2)			
Orthorhombic (Galli, 1976)	9.550(10)	9.665(10)	6.523(5)			
Tetragonal (Mazzi <i>et al.</i> , 1984)	9.581(5)		6.526(3)			

Using 25 reflections in the range $20 < 2\theta < 30$

TABLE 2b. Cell parameters of the $k\{011\}$ and $v\{120\}$ sectors of yugawaralite.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$k\{011\}$ sector*	6.711(1)	13.969(1)	10.027(1)		111.16(1)	
$v\{120\}$ sector**	6.710(1)	13.985(2)	10.032(2)	89.96(1)	111.14(1)	90.01(1)
Alberti <i>et al.</i> (1996)	6.728(2)	14.004(2)	10.066(2)		111.13(2)	

* Using 25 reflections in the range $20 < 2\theta < 27$

** Using 24 reflections in the range $20 < 2\theta < 30$

crystallographic software package of TeXsan (1985, 1992). The results of the refinement are shown in Table 3.

The atomic coordinates and anisotropic displacement parameters of the $k\{011\}$ and $v\{120\}$ sectors are listed in Tables 4a and 4b, and Tables 5a and 5b, respectively. The a - and b -labelled sites are equivalent to each other in the monoclinic structure. The results of X-ray analysis suggest that the symmetry of $k\{011\}$ sector is monoclinic, in accord with the morphological symmetry. In the optically triclinic $v\{120\}$ sector, the $T-O$ and $Ca-O$ distances and

the $T-O-T$ angles are asymmetrical with respect to the (010) symmetrical plane (Table 6). The differences are about three times larger than the standard deviation. The average $T-O$ distances and Al occupancies of the $k\{011\}$ and $v\{120\}$ sectors are shown in Table 7. The Al contents of the tetrahedral sites were estimated from the average $T-O$ distances, by the method of Smith and Brown (1974, 1988). In the optically triclinic $v\{120\}$ sector, the average $T-O$ distances of Al(1a) and Al(1b) are slightly different, suggesting triclinic symmetry in X-ray diffraction as well.

TABLE 3. Refinement information for crystal structure of yugawaralite.

Sector	$k\{011\}$ sector	$v\{120\}$ sector
Dimension of crystal (mm)	$0.38 \times 0.25 \times 0.05$	$0.25 \times 0.20 \times 0.08$
Refinement space group	Pc	$P1$
Scan type	ω - 2θ	ω - 2θ
Unique reflections	2261	5146
Reflections used in the refinement ($I > 3\sigma_I$)	2113	4474
R value (%)*	3.3	4.4
Rw value (%)**	4.5	5.1

* $R = \sum |F_o| - |F_c| / \sum |F_o|$

** $Rw = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$

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TABLE 4a. Atomic coordinates of the $k\{011\}$ sector in yugawaralite.

Atom	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Ca	0.0429(1)	0.21606(5)	0.42458(9)	1.22(1)
Si(1)	0.3399(1)	0.14925(6)	0.98238(10)	0.56(2)
Si(2)	0.7092(2)	0.03624(6)	0.19114(10)	0.54(2)
Si(3)	0.4072(2)	0.12535(6)	0.6945(1)	0.54(1)
Si(4)	0.0246(1)	0.47569(6)	0.4384(1)	0.51(2)
Si(5)	0.3575(1)	0.37307(6)	0.9606(1)	0.61(2)
Si(6)	0.7374(1)	0.49819(6)	0.6216(1)	0.52(2)
Al(1)	0.9996(2)	0.00677(7)	0.0002(1)	0.55(2)
Al(2)	0.3917(2)	0.35535(7)	0.6524(1)	0.56(2)
O(1)	0.1106(3)	0.1063(2)	0.9525(3)	1.19(5)
O(2)	0.8521(4)	0.0454(2)	0.0966(2)	1.24(5)
O(3)	0.1896(4)	0.0770(2)	0.5923(2)	1.13(4)
O(4)	0.5085(3)	0.1091(2)	0.1334(2)	0.87(4)
O(5)	0.4320(4)	0.1225(2)	0.8593(2)	1.50(5)
O(6)	0.6151(3)	0.0714(2)	0.6846(2)	1.00(5)
O(7)	0.8455(4)	0.0648(2)	0.3537(2)	0.92(4)
O(8)	0.3355(4)	0.2634(2)	0.0001(3)	1.66(6)
O(9)	0.3980(4)	0.2322(2)	0.6357(3)	1.11(4)
O(10)	0.1626(4)	0.4289(2)	0.9870(2)	1.03(5)
O(11)	0.8333(3)	0.4830(2)	0.4975(2)	1.05(5)
O(12)	0.1646(3)	0.3820(2)	0.4992(2)	0.99(4)
O(13)	0.5768(4)	0.4113(2)	0.0814(2)	1.25(5)
O(14)	0.3551(4)	0.3896(2)	0.8059(2)	1.53(5)
O(15)	0.6240(4)	0.4026(2)	0.6389(3)	1.34(5)
O(16)	0.9290(3)	0.4704(2)	0.2667(2)	0.87(4)
O(17)	0.9825(7)	0.2536(3)	0.1731(4)	4.7(1)
O(18)	0.9049(5)	0.2323(2)	0.6251(3)	2.70(7)
O(19)	0.6924(5)	0.2895(2)	0.3346(3)	2.73(7)
O(20)	0.3407(6)	0.1488(3)	0.3603(3)	4.83(10)

Note: O(17)–O(20) are O atoms of H₂O.

Discussion**Edingtonite**

It has been thought that edingtonite consists of tetragonal and orthorhombic polymorphs. However, Akizuki (1986) suggested, after an optical study, that the disordered $m\{110\}$ sector showing a $2V\alpha$ value of 22° is triclinic, and the ordered $c\{001\}$ sector ($2V\alpha = 52^\circ$) is orthorhombic. The X-ray analysis correlates with the optical observation. Triclinic and orthorhombic sectors coexist in the morphological single crystal of edingtonite.

Atomic occupancy should be the same at the equivalent four sites around the 4-fold axis in disordered tetragonal edingtonite. However, if the atomic occupancy is slightly different among the equivalent four sites in the tetragonal edingtonite,

TABLE 4b. Atomic coordinates of the $v\{120\}$ sector in yugawaralite.

Atom	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Ca(1a)	0.041(2)	0.215(2)	0.424(2)	1.37(2)
Ca(1b)	0.041(2)	0.781(2)	0.923(2)	1.31(2)
Si(1a)	0.342(2)	0.146(2)	0.983(2)	0.61(2)
Si(1b)	0.342(2)	0.849(2)	0.483(2)	0.64(3)
Si(2a)	0.712(2)	0.033(2)	0.191(2)	0.70(3)
Si(2b)	0.712(2)	0.963(2)	0.691(2)	0.71(2)
Si(3a)	0.408(2)	0.124(2)	0.693(2)	0.65(2)
Si(3b)	0.408(2)	0.872(2)	0.194(2)	0.62(2)
Si(4a)	0.022(2)	0.474(2)	0.439(2)	0.55(2)
Si(4b)	0.022(2)	0.522(2)	0.939(2)	0.56(2)
Si(5a)	0.356(2)	0.371(2)	0.961(2)	0.64(2)
Si(5b)	0.355(2)	0.625(2)	0.461(2)	0.66(2)
Si(6a)	0.734(2)	0.496(2)	0.622(2)	0.62(2)
Si(6b)	0.736(2)	0.499(2)	0.122(2)	0.65(2)
Al(1a)	0.002(2)	0.004(2)	0.001(2)	0.59(3)
Al(1b)	0.002(2)	0.992(2)	0.500(2)	0.59(3)
Al(2a)	0.390(2)	0.353(2)	0.652(2)	0.62(3)
Al(2b)	0.390(2)	0.642(2)	0.152(2)	0.62(3)
O(1a)	0.114(2)	0.103(2)	0.955(2)	1.27(7)
O(1b)	0.113(2)	0.893(2)	0.453(2)	1.49(8)
O(2a)	0.856(2)	0.040(2)	0.097(2)	1.62(9)
O(2b)	0.858(2)	0.954(2)	0.596(2)	1.73(9)
O(3a)	0.192(2)	0.075(2)	0.591(2)	1.38(7)
O(3b)	0.194(2)	0.921(2)	0.093(2)	1.33(7)
O(4a)	0.512(2)	0.107(2)	0.132(2)	1.21(7)
O(4b)	0.512(2)	0.889(2)	0.635(2)	1.06(7)
O(5a)	0.428(2)	0.120(2)	0.858(2)	1.67(8)
O(5b)	0.429(2)	0.875(2)	0.357(2)	1.70(8)
O(6a)	0.617(2)	0.071(2)	0.683(2)	1.10(7)
O(6b)	0.617(2)	0.925(2)	0.185(2)	1.10(7)
O(7a)	0.851(2)	0.061(2)	0.356(2)	1.20(7)
O(7b)	0.852(2)	0.933(2)	0.854(2)	1.26(7)
O(8a)	0.336(2)	0.261(2)	0.000(2)	1.61(9)
O(8b)	0.334(2)	0.735(2)	0.500(2)	1.61(8)
O(9a)	0.398(2)	0.230(2)	0.636(2)	1.08(7)
O(9b)	0.400(2)	0.765(2)	0.135(2)	1.23(7)
O(10a)	0.162(2)	0.425(2)	0.988(2)	1.07(7)
O(10b)	0.163(2)	0.570(2)	0.486(2)	1.19(7)
O(11a)	0.831(2)	0.481(2)	0.497(2)	1.19(7)
O(11b)	0.831(2)	0.515(2)	0.996(2)	1.20(7)
O(12a)	0.164(2)	0.382(2)	0.500(2)	1.27(7)
O(12b)	0.164(2)	0.616(2)	0.999(2)	1.17(7)
O(13a)	0.576(2)	0.409(2)	0.082(2)	1.31(7)
O(13b)	0.575(2)	0.587(2)	0.581(2)	1.29(7)
O(14a)	0.355(2)	0.387(2)	0.807(2)	1.44(8)
O(14b)	0.355(2)	0.609(2)	0.306(2)	1.55(8)
O(15a)	0.619(2)	0.401(2)	0.639(2)	1.36(7)
O(15b)	0.620(2)	0.595(2)	0.139(2)	1.36(8)
O(16a)	0.926(2)	0.468(2)	0.266(2)	0.98(7)
O(16b)	0.927(2)	0.528(2)	0.768(2)	0.98(7)
O(17a)	0.986(3)	0.254(2)	0.173(2)	5.9(2)
O(17b)	0.986(3)	0.743(2)	0.674(2)	5.7(2)
O(18a)	0.904(2)	0.229(2)	0.626(2)	2.9(1)

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TABLE 4*b* (contd.). Atomic coordinates of the $v\{120\}$ sector in yugawaralite.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O(18b)	0.905(2)	0.766(2)	0.124(2)	3.0(1)
O(19a)	0.689(2)	0.286(2)	0.333(2)	3.5(1)
O(19b)	0.691(2)	0.709(2)	0.833(2)	3.2(1)
O(20a)	0.342(3)	0.145(2)	0.360(2)	5.8(2)
O(20b)	0.340(3)	0.851(2)	0.857(2)	5.2(2)

Note: O(17a)–O(20b) are O atoms of H₂O.

the symmetry can decrease to triclinic as a result of non-equilibrium crystal growth. This symmetry

decrease is more easily achieved in disordered structures during crystal growth. Disordered structures are more sensitive than ordered structures as regards their growth symmetries.

The four *T*-sites are equivalent in the crystal structure of the highest disordered sanidine, and the crystal symmetry is monoclinic. If the Al/Si occupancy is slightly different from one to the next, the triclinic sanidine will be produced on the crystal surface during non-equilibrium crystal growth, resulting in adularia (Akizuki and Sunagawa, 1978).

Anomalous optical symmetries and complicated growth textures are frequently observed in some minerals. Since the 19th century, this has been referred to as optical anomaly.

TABLE 5*a*. Anisotropic displacement parameters of the $k\{011\}$ sector in yugawaralite.

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ca	0.0175(3)	0.0084(3)	0.0160(3)	−0.0022(3)	0.0007(3)	0.0004(3)
Si(1)	0.0083(4)	0.0050(4)	0.0085(4)	−0.0004(3)	0.0038(3)	0.0007(3)
Si(2)	0.0072(4)	0.0063(4)	0.0075(4)	−0.0004(3)	0.0032(3)	0.0003(3)
Si(3)	0.0084(4)	0.0043(4)	0.0075(4)	−0.0003(3)	0.0026(3)	−0.0005(3)
Si(4)	0.0068(4)	0.0061(4)	0.0067(4)	−0.0002(3)	0.0026(3)	0.0005(3)
Si(5)	0.0099(4)	0.0043(4)	0.0093(4)	0.0008(3)	0.0039(3)	−0.0007(3)
Si(6)	0.0053(4)	0.0069(4)	0.0075(4)	−0.0006(3)	0.0025(3)	−0.0003(3)
Al(1)	0.0078(5)	0.0050(4)	0.0085(5)	0.0008(4)	0.0037(4)	0.0008(4)
Al(2)	0.0090(4)	0.0044(4)	0.0083(4)	−0.0002(4)	0.0039(4)	0.0006(4)
O(1)	0.0063(10)	0.014(1)	0.023(1)	−0.0045(9)	0.0040(10)	0.0037(10)
O(2)	0.012(1)	0.021(1)	0.016(1)	−0.0007(10)	0.0076(9)	0.000(1)
O(3)	0.012(1)	0.012(1)	0.015(1)	−0.0025(8)	−0.0004(9)	−0.0018(10)
O(4)	0.014(1)	0.011(1)	0.008(1)	0.0032(8)	0.0047(9)	0.0006(9)
O(5)	0.019(1)	0.027(1)	0.012(1)	0.008(1)	0.0085(10)	0.001(1)
O(6)	0.011(1)	0.010(1)	0.019(1)	0.0030(9)	0.0069(10)	−0.0008(10)
O(7)	0.018(1)	0.006(1)	0.0099(10)	−0.0006(9)	0.0047(9)	−0.0002(8)
O(8)	0.031(2)	0.004(1)	0.030(2)	−0.002(1)	0.013(1)	0.001(1)
O(9)	0.018(1)	0.0039(8)	0.020(1)	0.0024(9)	0.007(1)	0.0018(9)
O(10)	0.017(1)	0.010(1)	0.014(1)	0.0050(9)	0.0085(10)	0.0016(9)
O(11)	0.015(1)	0.017(1)	0.011(1)	−0.0023(10)	0.0085(9)	−0.0024(9)
O(12)	0.013(1)	0.010(1)	0.012(1)	−0.0005(8)	0.0010(8)	−0.0019(9)
O(13)	0.016(1)	0.016(1)	0.013(1)	−0.0055(10)	0.0013(9)	0.0028(10)
O(14)	0.030(1)	0.022(1)	0.010(1)	0.001(1)	0.012(1)	−0.001(1)
O(15)	0.014(1)	0.013(1)	0.029(1)	−0.0065(9)	0.013(1)	0.000(1)
O(16)	0.012(1)	0.011(1)	0.013(1)	0.0017(9)	0.0073(8)	0.0012(9)
O(17)	0.093(3)	0.051(2)	0.042(2)	0.025(2)	0.034(2)	0.009(2)
O(18)	0.043(2)	0.028(2)	0.045(2)	0.005(1)	0.031(2)	0.005(1)
O(19)	0.034(2)	0.025(2)	0.036(2)	0.003(1)	0.001(1)	0.007(1)
O(20)	0.062(2)	0.103(3)	0.028(2)	0.035(2)	0.028(2)	0.010(2)

Note: O(17)–O(20) are O atoms of H₂O.

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TABLE 5b. Anisotropic displacement parameters of the $v\{120\}$ sector in yugawaralite.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1a)	0.0181(6)	0.0093(5)	0.0167(5)	-0.0023(4)	-0.0031(4)	-0.0027(4)
Ca(1b)	0.0182(6)	0.0092(5)	0.0151(5)	0.0018(4)	-0.0027(4)	-0.0021(4)
Si(1a)	0.0084(6)	0.0065(6)	0.0066(6)	-0.0007(5)	0.0009(5)	-0.0008(5)
Si(1b)	0.0087(6)	0.0062(6)	0.0085(7)	0.0007(5)	0.0019(5)	-0.0031(5)
Si(2a)	0.0076(6)	0.0087(6)	0.0088(6)	-0.0010(5)	0.0012(5)	-0.0016(5)
Si(2b)	0.0085(6)	0.0084(6)	0.0082(6)	0.0008(5)	0.0007(5)	-0.0021(5)
Si(3a)	0.0077(6)	0.0063(6)	0.0088(6)	-0.0005(5)	0.0008(5)	-0.0029(5)
Si(3b)	0.0080(6)	0.0061(6)	0.0077(6)	-0.0005(5)	0.0007(5)	-0.0015(5)
Si(4a)	0.0074(6)	0.0075(6)	0.0056(6)	-0.0004(5)	0.0017(5)	-0.0015(5)
Si(4b)	0.0060(6)	0.0084(6)	0.0060(6)	0.0004(5)	0.0011(5)	-0.0026(5)
Si(5a)	0.0087(6)	0.0060(6)	0.0086(6)	0.0001(5)	0.0018(5)	-0.0026(5)
Si(5b)	0.0085(6)	0.0056(6)	0.0090(6)	-0.0001(5)	0.0005(5)	-0.0019(5)
Si(6a)	0.0066(6)	0.0079(6)	0.0076(6)	-0.0016(5)	0.0009(5)	-0.0026(5)
Si(6b)	0.0062(6)	0.0093(6)	0.0073(6)	-0.0001(5)	0.0004(5)	-0.0026(5)
Al(1a)	0.0067(7)	0.0077(7)	0.0072(7)	-0.0006(5)	0.0018(6)	-0.0019(5)
Al(1b)	0.0067(7)	0.0072(7)	0.0079(7)	0.0000(5)	0.0017(6)	-0.0025(5)
Al(2a)	0.0084(7)	0.0061(7)	0.0079(7)	-0.0011(5)	0.0015(6)	-0.0012(5)
Al(2b)	0.0086(7)	0.0056(7)	0.0079(7)	-0.0008(5)	0.0012(6)	-0.0036(5)
O(1a)	0.011(2)	0.016(2)	0.021(2)	-0.002(1)	0.005(2)	0.001(2)
O(1b)	0.012(2)	0.017(2)	0.023(2)	0.005(1)	0.002(2)	-0.011(2)
O(2a)	0.020(2)	0.023(2)	0.021(2)	-0.002(2)	0.010(2)	-0.005(2)
O(2b)	0.026(2)	0.023(2)	0.020(2)	0.002(2)	0.011(2)	-0.004(2)
O(3a)	0.010(2)	0.014(2)	0.021(2)	-0.004(1)	-0.003(1)	-0.004(2)
O(3b)	0.013(2)	0.012(2)	0.016(2)	0.003(1)	-0.006(1)	-0.002(1)
O(4a)	0.019(2)	0.011(2)	0.011(2)	0.005(1)	0.000(2)	-0.004(1)
O(4b)	0.017(2)	0.011(2)	0.009(2)	-0.005(1)	0.002(1)	-0.002(1)
O(5a)	0.021(2)	0.032(2)	0.012(2)	0.007(2)	0.007(2)	-0.001(2)
O(5b)	0.021(2)	0.033(3)	0.011(2)	-0.006(2)	0.006(2)	-0.006(2)
O(6a)	0.013(2)	0.013(2)	0.015(2)	0.003(1)	0.003(2)	-0.003(1)
O(6b)	0.008(2)	0.014(2)	0.016(2)	-0.001(1)	0.000(1)	-0.003(1)
O(7a)	0.018(2)	0.010(2)	0.012(2)	0.001(1)	-0.001(1)	-0.001(1)
O(7b)	0.019(2)	0.012(2)	0.011(2)	0.002(1)	-0.002(1)	-0.004(1)
O(8a)	0.021(2)	0.011(2)	0.024(2)	-0.001(1)	0.003(2)	-0.002(2)
O(8b)	0.023(2)	0.009(2)	0.023(2)	-0.001(1)	0.001(2)	-0.001(2)
O(9a)	0.015(2)	0.007(1)	0.018(2)	0.001(1)	0.004(2)	0.000(1)
O(9b)	0.018(2)	0.006(1)	0.023(2)	-0.002(1)	0.006(2)	-0.006(1)
O(10a)	0.018(2)	0.014(2)	0.010(2)	0.006(1)	0.007(2)	0.003(1)
O(10b)	0.016(2)	0.015(2)	0.013(2)	-0.007(1)	0.005(2)	-0.004(1)
O(11a)	0.007(2)	0.024(2)	0.013(2)	-0.003(1)	0.001(1)	-0.006(2)
O(11b)	0.008(2)	0.024(2)	0.011(2)	0.003(1)	0.001(1)	-0.003(2)
O(12a)	0.015(2)	0.014(2)	0.012(2)	0.004(1)	-0.003(1)	-0.004(1)
O(12b)	0.014(2)	0.012(2)	0.012(2)	-0.003(1)	-0.002(1)	-0.004(1)
O(13a)	0.014(2)	0.018(2)	0.012(2)	-0.006(1)	-0.001(1)	0.000(1)
O(13b)	0.015(2)	0.020(2)	0.009(2)	0.006(1)	-0.003(1)	-0.006(1)
O(14a)	0.022(2)	0.023(2)	0.011(2)	0.002(2)	0.006(2)	-0.005(1)
O(14b)	0.025(2)	0.022(2)	0.013(2)	-0.004(2)	0.009(2)	-0.002(2)
O(15a)	0.013(2)	0.015(2)	0.024(2)	-0.006(1)	0.008(2)	-0.007(2)
O(15b)	0.014(2)	0.013(2)	0.026(2)	0.006(1)	0.009(2)	-0.001(2)
O(16a)	0.013(2)	0.013(2)	0.011(2)	0.003(1)	0.003(1)	-0.002(2)
O(16b)	0.013(2)	0.014(2)	0.007(2)	-0.002(1)	0.000(1)	-0.002(2)
O(17a)	0.115(7)	0.069(5)	0.047(4)	0.041(4)	0.036(4)	0.011(3)
O(17b)	0.110(6)	0.063(5)	0.053(4)	-0.035(4)	0.039(4)	-0.026(3)
O(18a)	0.035(3)	0.030(3)	0.053(3)	0.006(2)	0.027(3)	0.001(2)
O(18b)	0.038(3)	0.032(3)	0.055(3)	-0.012(2)	0.032(3)	-0.014(2)

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TABLE 5b (contd.)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(19a)	0.041(3)	0.029(3)	0.038(3)	0.004(2)	-0.015(2)	0.002(2)
O(19b)	0.035(3)	0.030(3)	0.041(3)	0.001(2)	-0.006(2)	-0.017(2)
O(20a)	0.069(5)	0.117(6)	0.040(4)	0.032(4)	0.026(4)	-0.012(4)
O(20b)	0.064(4)	0.111(6)	0.027(3)	-0.033(4)	0.022(3)	-0.012(3)

Note: O(17a)–O(20b) are O atoms of H₂O.

Yugawaralite

Akizuki (1987a) suggested that yugawaralite consists of monoclinic and triclinic sectors. In the present study, the $k\{011\}$ sector is found to be monoclinic by X-ray diffraction, and this agrees with the optical observations. The $v\{120\}$ sector is triclinic, although the deviation from monoclinic symmetry is small.

The Ca ions are in contact with the O of AlO₄ tetrahedra in one of the main channels because of charge balance. Figure 4a,b shows the schematic crystal structures and growth directions projected on the a – b plane. If the growth step is normal to the (010) symmetrical glide plane (Fig. 4a), the Al(1a) and Al(1b) sites, and the Al(2a) and Al(2b)

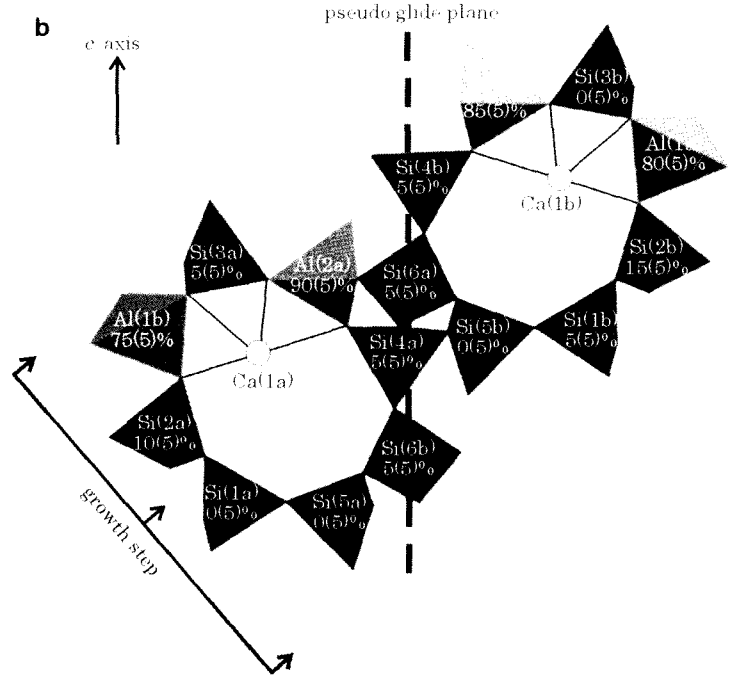
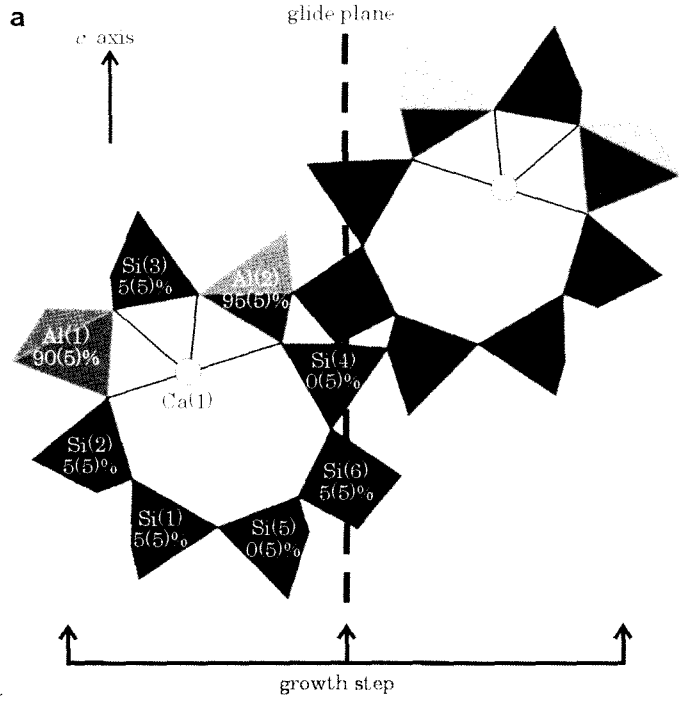
sites will be equivalent with respect to the Ca ion, respectively, resulting in monoclinic symmetry. However, since the growth step is inclined to the (010) symmetrical plane on the $v(120)$ face (Fig. 4b), these sites are non-equivalent with respect to the Ca ion. Therefore, the Al/Si ordered structure is produced along the growth steps and the symmetry is reduced to triclinic (Akizuki, 1987a). However, the homogeneous area of $k\{011\}$ sector that was produced on the rough face without growth steps is disordered, and the symmetry is monoclinic.

The monoclinic and triclinic sectors, which are correlated with the crystal faces, coexist in the morphological single crystal (Fig. 3). Therefore,

TABLE 6. Selected interatomic distances and bond angles of the $v\{120\}$ sector of yugawaralite.

Tetrahedra		Angles	
Si(1a)–O(4a)	1.616(6)	Si(2a)–O(2a)–Al(1a)	158.3(4)
Si(1b)–O(4b)	1.639(6)	Si(2b)–O(2b)–Al(1b)	157.1(4)
Si(4a)–O(12a)	1.591(6)	Si(4a)–O(12a)–Al(2a)	136.4(4)
Si(4b)–O(12b)	1.611(6)	Si(4b)–O(12b)–Al(2b)	135.0(4)
Si(5a)–O(10a)	1.612(6)	Si(1a)–O(4a)–Si(2a)	140.0(4)
Si(5b)–O(10b)	1.592(6)	Si(1b)–O(4b)–Si(2b)	138.6(4)
Si(6a)–O(16b)	1.627(6)	Si(4a)–O(10b)–Si(5b)	141.1(4)
Si(6b)–O(16a)	1.609(6)	Si(4b)–O(10a)–Si(5a)	139.6(4)
Al(1a)–O(7b)	1.755(6)		
Al(1b)–O(7a)	1.729(6)		
Cations			
Ca(1a)–O(3a)	2.537(6)		
Ca(1b)–O(3b)	2.557(6)		
Ca(1a)–O(12a)	2.508(6)		
Ca(1b)–O(12b)	2.481(6)		

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TABLE 7. Estimated Al contents (%) and averaged T -O distances in the T sites of yugawaralite.

	k{011} sector			v{120} sector				
	T -O distance	Al		T -O distance	Al		T -O distance	Al
Si(1)	1.605(5)	5	Si(1a)	1.602(6)	0	Si(5a)	1.600(6)	0
Si(2)	1.606(5)	5	Si(1b)	1.610(6)	5	Si(5b)	1.597(6)	0
Si(3)	1.605(5)	5	Si(2a)	1.618(6)	10	Si(6a)	1.609(6)	5
Si(4)	1.600(5)	0	Si(2b)	1.620(6)	15	Si(6b)	1.608(6)	5
Si(5)	1.603(5)	0	Si(3a)	1.605(6)	5	Al(1a)	1.720(6)	80
Si(6)	1.604(5)	5	Si(3b)	1.600(6)	0	Al(1b)	1.709(6)	75
Al(1)	1.732(5)	90	Si(4a)	1.605(6)	5	Al(2a)	1.735(6)	90
Al(2)	1.739(5)	95	Si(4b)	1.604(6)	5	Al(2b)	1.731(6)	85

Note: The uncertainties in Al contents are 5%, on the basis of the deviations of T -O bond length.

the structure and texture of yugawaralite are produced by a non-equilibrium crystal growth.

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Fig. 4. Crystal structure of yugawaralite. The growth step and growth direction (arrows) are shown on the figure. If the growth steps are normal to a symmetrical plane (Fig. 4a), the $T(a)$ and $T(b)$ sites (e.g. Al(1a) and Al(1b)) will be equivalent, resulting in Al/Si disordered arrangements. However, if the growth steps are inclined to a symmetrical plane (Fig. 4b), the $T(a)$ and $T(b)$ sites will be non-equivalent with respect to the symmetrical plane, resulting in an Al/Si ordered structure.

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