Epistilbite: Symmetry and twinning

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Abstract

Two kinds of sectoral twinning are observed in epistilbite: one is that of a structure with topologic symmetry $C2/m$, and the other is due to (Al,Si) ordering. Two-dimensional atomic arrangements are similar on the (001) and (10$\bar{1}$) surfaces of epistilbite. Of the two kinds of atomic arrangements, the one that is presumably more stable will develop on both crystal surfaces; precession photographs have confirmed that this is the (10$\bar{1}$) arrangement. The (10$\bar{1}$) face is normal to the (010) mirror plane in $C2/m$ symmetry, and therefore the two symmetry sites are equivalent on the (10$\bar{1}$) growth surface, resulting in an (Al,Si)-disordered, monoclinic structure in the {10$\bar{1}$} sectors. Since the (110) faces are inclined to the mirror plane, the two symmetry sites in the crystal are not equivalent on the surface, resulting in an (Al,Si)-ordered, triclinic structure in the four {110} sectors, which are related by both the (100) and (010) sectoral twin planes.

Introduction

Epistilbite, $Ca_{2.5}(Na,K)(Al_6Si_{18}O_{48}) \cdot 16H_2O$, is a zeolite that is found in cavities of volcanic rock. The composition of the framework is nearly constant, and the ratio Ca: (Na + K) ranges from 9 to 2 (Gottardi and Galli, 1985). The most common habit of epistilbite crystals possesses the simple combination of {110}, {001}, and {011} with small {010}. (100) twinning is common in the crystal.

The epistilbite structure is related to that of mordenite. Kerr (1964) suggested a pseudo-orthorhombic structural model for the epistilbite framework from X-ray powder data. Perrotta (1967) refined the structure in the space group $C2/m$. The tetrahedra that are coordinated by the (Ca,Na) atoms on the mirror plane are preferentially occupied by Al atoms. Slaughter and Kane (1969) and Alberti et al. (1985) explained the epistilbite structure as noncentrosymmetric with space group $C2$. Galli and Rinaldi (1974) described chemical compositions, crystallographic data, and densities of 13 epistilbite crystals.

On the basis of studies of the relationship between surface features and internal textures of some zeolites and other minerals, Akizuki (1981a, 1981b, 1984, 1985, 1986, 1987a, 1987b, 1987c), Akizuki and Sunagawa (1978), Akizuki and Konno (1985) and Akizuki et al. (1979) interpreted their optical properties and sectoral twinnings as being produced by atomic ordering on side faces of growth steps, which are inclined to the crystal face. Furthermore, Akizuki (1987b) suggested a general mechanism for the formation of growth sectors. These concepts are applied in this paper to epistilbite.

Optical observations

Epistilbite crystals from two localities (Fossarfell, Berufjord, Iceland; Kuroiwa, Niigata Prefecture, Japan) were observed under reflection interference and transmission polarized optical microscopes. Crystal forms of epistilbite are similar in the specimens from the two localities (Fig. 1). A (100) twin is indicated by the labeled dashed line on the crystal form, which looks like a single (i.e., untwinned) crystal; that is, the (100) twin plane is coincident with the boundary between the two (10$\bar{1}$) faces. Specimens studied consist of (10$\bar{1}$), (110), (010), and (011) faces, and corresponding growth sectors are observed between crossed polars. Crystal faces, especially (10$\bar{1}$) and (110) faces, consist of small parallel-grown crystals, and the corresponding domains are observed between crossed polars as well. The optical orientation of each sector was determined within 1° by the crystal morphology, (010) cleavage plane, and the (100) and (010) twins in the sections, with some exceptions. The optic axial angle was measured within 1° by both conoscopic and orthoscopic methods on a universal stage, though the error may be slightly larger than 1° in some sectors showing diffuse extinction.

Epistilbite from Fossarfell, Iceland

The {10$\bar{1}$} sector. Figures 2a and 2b show growth patterns on the (10$\bar{1}$) face and growth sectors and domains in the section normal to the c axis. The (10$\bar{1}$) face consists of small parallel-grown crystals with circular-growth hillocks, which are separated from each other by straight steps. The {10$\bar{1}$} sector consists of small domains. Al-
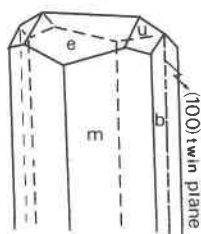
Fig. 1. General crystal form of epistilbite. The crystal shows (100) twinning between crossed polars without exception, though the form is single. $b(010)$, $e(10\bar{1})$, $m(110)$, $u(011)$

though the growth pattern on the surface suggests that each domain has the same crystallographic orientation, each domain shows wavy optical extinction, that is, the optical vibration direction Y is not always parallel to the b axis, suggesting a small deviation from monoclinic symmetry. Figure 3 shows a composition plane of a (100) twin that corresponds to the boundary between the two $\{10\bar{1}\}$ sectors. The composition plane, which is inclined to the (100) plane, is a fine comblike plane. Except for this comblike twin plane, no twins are observed within the $\{10\bar{1}\}$ sectors. The extinction directions with respect to the c axis are different between the two $\{10\bar{1}\}$ sectors, though their crystal orientations are related by the (100) twinning: one is about 10°, and the other is less than 5°. The (010) sections, which were variously inclined, as is clearly seen on a universal stage, show lamellae approximately normal to the $(10\bar{1})$ face, and ends of the lamellae correspond to the parallel-grown crystals. The optic axial angle, which was measured in the (100) section, is $2V_X = 46°$.

The $\{110\}$ sector. The $\{110\}$ sector has small domains, some of which are related by the (100) twinning (Fig. 2b). Fine growth bands parallel to the (110) face develop through the domains in the thin section normal to the c axis. The Y vibration directions are approximately symmetrically inclined about 2° to the b axis in the $\{110\}$ and $\{1\bar{1}0\}$ sectors, though they vary slightly from place to place, suggesting triclinic symmetry. Therefore, the (010) "mirror plane" is really a twin plane. Thus, the four triclinic $\{110\}$ sectors are related by the (100) and (010) twins (Fig. 2b).

Figures 4a and 4b show the growth pattern on the (110) face and the corresponding growth domains in the $\{110\}$ sector, which are observed in the (110) section. The (110) face consists of curved growth steps and parallel-grown epistilbite crystals with vicinal faces. Figure 4b shows domains corresponding to the vicinal faces of one parallel-grown crystal. The optic orientations of the three small domains (A, B, and C) are shown by stereographic projections in Figure 5. The thin section was cut in the direction parallel to the (110) face, and the crystal orientation was confirmed by the (010) cleavage. The optical orientation of each sector, however, varies within about 3° because of the diffuse extinction. The A sector corresponds to the growth face parallel to the (110) face. The
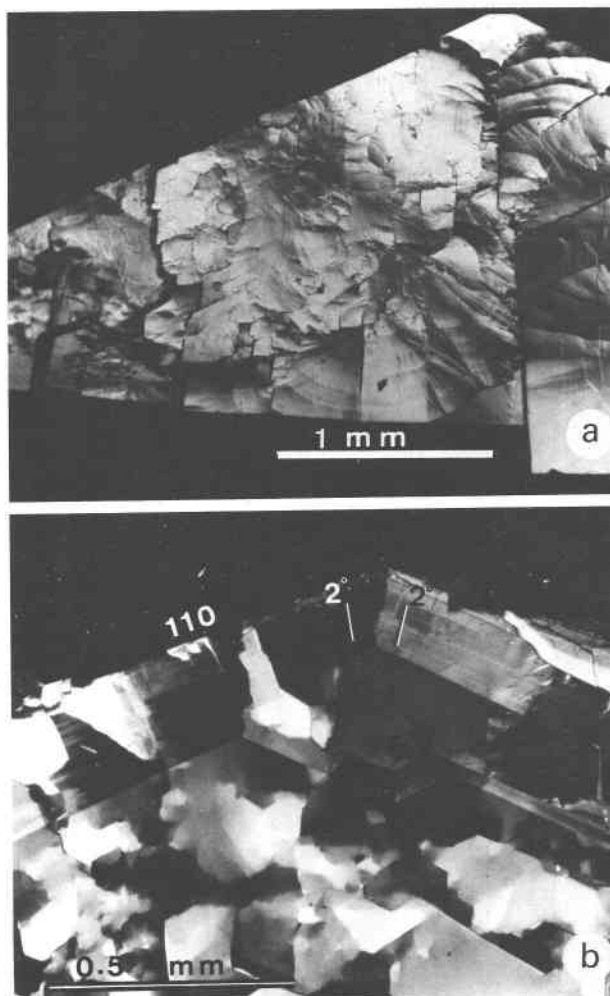

Fig. 2. Interference reflection optical photomicrograph of growth features on the $(10\bar{1})$ face (**a**), and cross-polarized photomicrograph of the thin section cut normal to the c axis (**b**). The section consists of the $\{10\bar{1}\}$ (central and lower portions) and $\{110\}$ (upper portion) sectors. The $\{10\bar{1}\}$ sector is divided into small sectors, and the $\{110\}$ sectors have growth bands parallel to the (110) face. The extinction directions of the $\{110\}$ sectors are inclined about 2° to the (010) plane. The b axis is horizontal. Epistilbite from Fossarfell, Iceland.

B sector corresponds to the $(hk0)$ face, and the C sector to the $(10\bar{1})$ face. Both the A and B sectors may be triclinic, and the C sector may be monoclinic.

The $\{010\}$ sector. The (010) face consists of fine striations parallel to the c axis. The thin section normal to the c axis shows fine polysynthetic twinning parallel to the b axis in the $\{010\}$ sector, which is correlated to the striations on the (010) face. The symmetry is reduced slightly from the monoclinic orientation.

Epistilbite from Kuroiwa, Japan

The $\{10\bar{1}\}$ sector. The $(10\bar{1})$ surface consists of many parallel-grown crystals, whose surface is flat with some simple steps. In the $(10\bar{1})$ and (010) sections between

Fig. 3. Cross-polarized photomicrograph of {10$\bar{1}$} sectors in the (010) thin section. The crystal has two (10$\bar{1}$) faces and two corresponding {10$\bar{1}$} sectors, which are related by the (100) twinning with comblike composition plane. The c axis is vertical. Epistilbite from Fossarfell, Iceland.

TABLE 1. Chemical analyses and unit-cell parameters of epistilbite crystals

	Fossarfell (wt%)	Kuroiwa (wt%)
SiO_2	57.79	58.22
Al_2O_3	17.62	17.35
Fe_2O_3	0.02	0.02
MgO	0.02	0.01
CaO	8.21	8.46
Na_2O	1.39	0.59
K_2O	0.06	0.03
$H_2O(+)$	12.21	11.92
$H_2O(-)$	3.10	3.68
Total	100.42	100.28
B.E.*	+1.8%	+5.8%
Cations on the basis of 48 oxygens		
Si	17.67	17.82
Al	6.35	6.26
Fe	0.00	0.00
Mg	0.01	0.00
Ca	2.69	2.77
Na	0.82	0.35
K	0.02	0.01
$H_2O(+)$	12.45	12.17
$H_2O(-)$	3.16	3.76
a (Å)	9.089(2)	9.099(2)
b (Å)	17.769(4)	17.765(3)
c (Å)	10.237(2)	10.239(2)
β (°)	124.57(2)	124.58(2)
V (Å³)	1361(1)	1363(1)

Note: Numbers in parentheses are esd's in the last decimal place.
* Balance error.

crossed polars, the {10$\bar{1}$} sector is seen to consist of the domains corresponding to the parallel-grown crystals on the surface. The optical extinction is sharp, and the Y direction is parallel to the b axis, suggesting monoclinic symmetry. The comblike twin plane is observed between the two {10$\bar{1}$} sectors as well.

The {110} sector. The (110) section shows a texture similar to that of the crystal from Fossarfell. The optical vibration direction Y is inclined about 2° to the b axis, suggesting triclinic symmetry as well.

The {010} sector. Growth features on the (010) face and internal textures in the {010} sector are similar to those of the crystal from Fossarfell.

CHEMICAL AND X-RAY ANALYSES

Wet-chemical analyses and unit-cell parameters of the specimens used for the study are indicated in Table 1. No differences in chemical composition were observed between growth sectors by electron-microprobe analysis. The unit-cell parameters were derived by least-squares refinement of powder-diffraction data corrected by using synthetic fluorophlogopite (N13S 675) as an internal standard. Also, both the specimens from the two locali-

ties are similar in the unit-cell parameters, though the a cell edge is slightly longer in the Kuroiwa specimen than in the Fossarfell specimens. In powder-diffraction profiles, no splitting of peaks was observed in either specimen; that is, no deviations from monoclinic symmetry were found in the crystals in the present X-ray analyses.

Because of pseudo-orthorhombic symmetry, atomic arrangements along both the (001) and (10$\bar{1}$) faces are similar. It is not clear from morphological observation which face appears on the surface of the (100) twinned crystal. A single crystal with a natural face [either (001) or (10$\bar{1}$)] at the crystal edge, which was obtained from the thick (010) section, was observed by a precession camera. This observation shows that (10$\bar{1}$) faces, not (001) faces, appear on the surface in the structural setting.

DISCUSSION

Low symmetry in minerals showing so-called optical anomalies had not been detected by X-ray analysis for many years, and therefore its origin was attributed to crystal strain. The low symmetries, however, have been observed by recent X-ray and neutron analyses of some minerals with optical anomalies such as garnet (Takéuchi et al., 1982), topaz (Akizuki et al., 1979; Parise et al., 1980), analcime (Mazzi and Galli, 1978), stilbite (Galli, 1971; Akizuki and Konno, 1985), chabazite (Mazzi and Galli, 1983), and edingtonite (Akizuki, 1986). Their internal textures, which are observed between crossed polars, are correlated with the surface growth features. However, yugawaralite (Akizuki, 1987b), brewsterite (Artioli
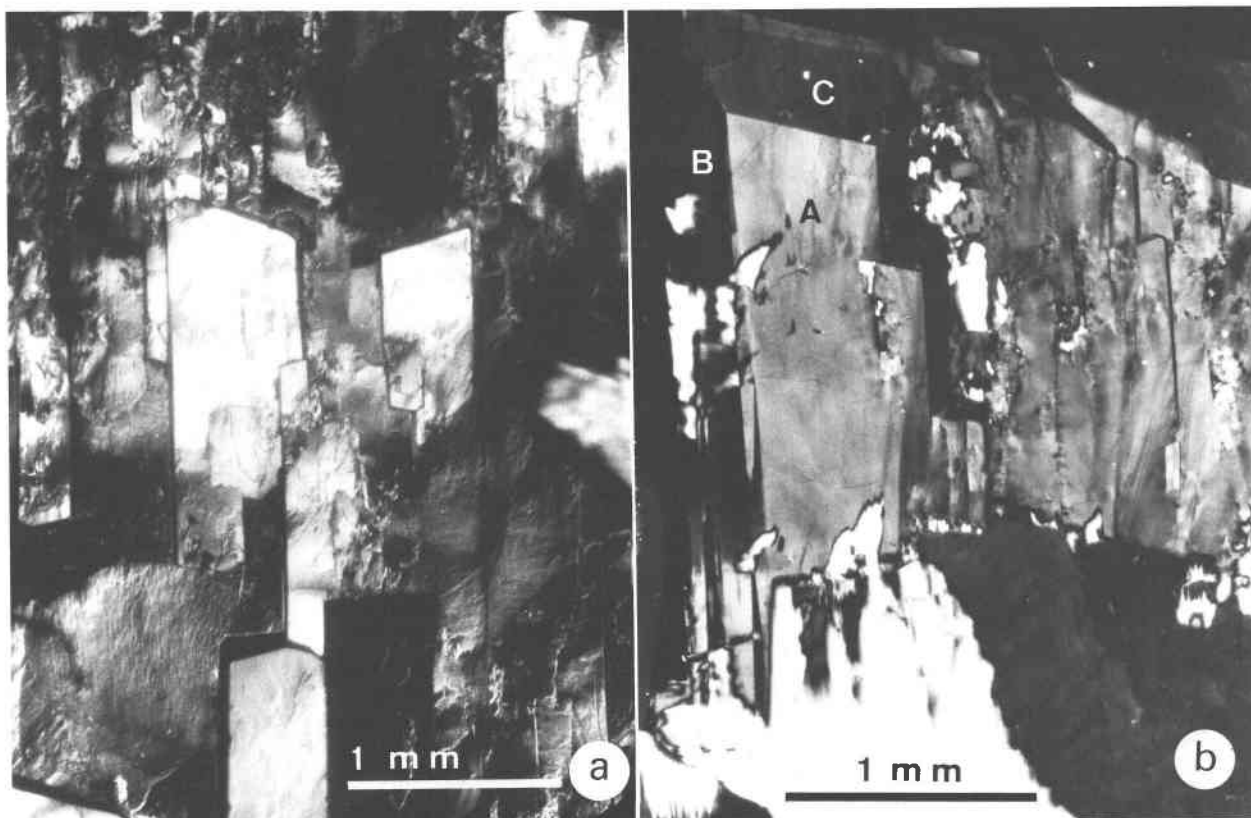
Fig. 4. Interference reflection optical photomicrograph of growth features on the (110) face (a), and cross-polarized photomicrograph of the thin section parallel to the (110) face (b). The c axis is vertical. Three small sectors (A, B, C), which may correspond to the three vicinal faces, (110), ($hk0$), and (10$\bar{1}$), are represented. Epistilbite from Fossarfell, Iceland.

et al., 1985; Akizuki, 1987a), and harmotome (Akizuki, 1985), which show clearly lower symmetries between crossed polars, show no evidence of the lower symmetry by X-ray diffraction. Also, the second group of the minerals shows the internal textures that are correlated to the surface growth features, and therefore, their internal textures and optical properties were explained according to Akizuki's theory of sectoral twinning. The atomic ordering, which reduces the symmetry in X-ray analysis, may be too little in such minerals for detection by X-ray diffraction. Although epistilbite crystals used for the study do not show low symmetry by X-ray analysis, they have optical characteristics similar to those of garnet, topaz, and other zeolites. Therefore, the symmetry and twinning of epistilbite seemed explicable by Akizuki's theory as well. Although very fine growth sectors with different atomic orderings were observed in adularia and prehnite with electron microscopy (Akizuki and Sunagawa, 1978; Akizuki, 1987c), epistilbite is homogeneous under a low-magnification electron microscope. Two kinds of sectoral twins are observed in epistilbite: one is that of structure with symmetry $C2/m$, and the other is due to the (Al,Si) ordering.

The twinning of structure with symmetry $C2/m$

Figure 6 shows a partial crystal structure projected along the b axis of epistilbite. If the composition plane between the {10$\bar{1}$} sectors is inclined to the (100) plane, strain will occur along the boundary. However, the inclination of the comblike composition plane is small, reducing the strain. Some domains in the {110} sectors are related by the (100) twinning. The two-dimensional atomic arrangements are similar on the (110) and ($\bar{1}$10) faces, because of the pseudo-orthorhombic symmetry. If the ($\bar{1}$10) face of the parallel-grown crystal is produced on the (110) face of the host, the (100) twin will result. Such a relation does not occur in the {10$\bar{1}$} sector, and therefore no twins are observed between the domains in the {10$\bar{1}$} sector.

The twinning due to (Al,Si) ordering

The tetrahedral sites that are directly coordinated with cations such as Ca and Na are preferentially occupied with Al atoms. The crystal symmetry is attributed to charge balance between Al or Si atoms and the cations on crystal faces. If the tetrahedra are produced after the cations on the growth step, the tetrahedra will be pref-
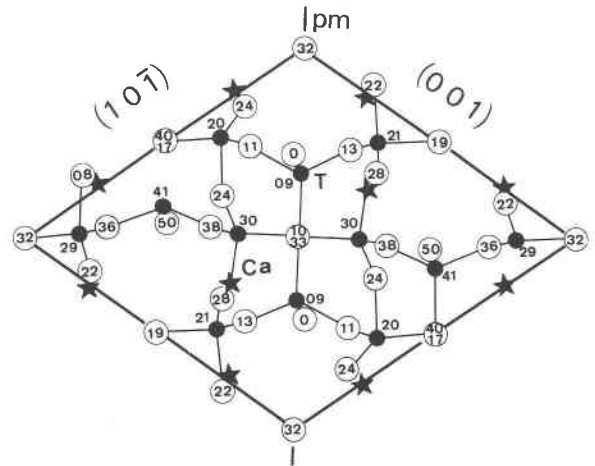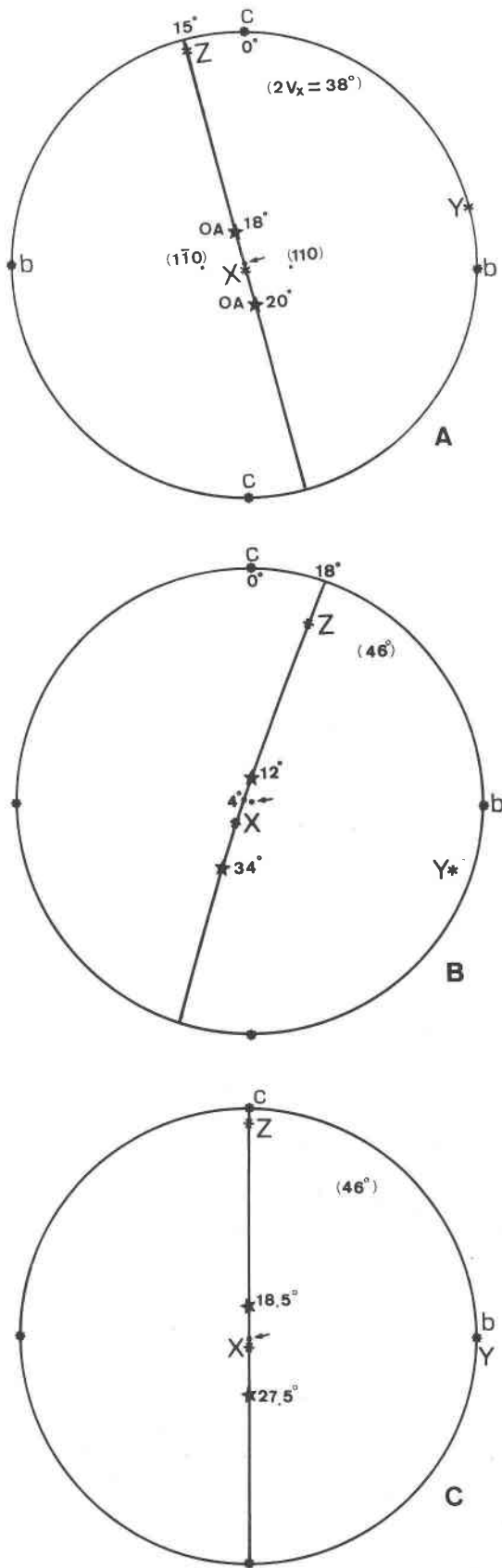
Fig. 6. A partial crystal structure of epistilbite projected onto the (010) plane. Pseudomirror plane (pm) is vertical in the pseudo-orthorhombic structure. T(Al,Si) sites (solid circles), oxygen atoms (open circles), and Ca atoms (stars) are represented. Numbers give the heights of the atoms in thousandths of a cell edge. Water molecules are omitted. (Modified from Slaughter and Kane, 1969).

erentially occupied by Al ions. On the other hand, if the tetrahedra form prior to the addition of cations during growth, the tetrahedra will be occupied by Si ions. If the growth step is normal to a mirror plane, the two symmetric sites will be equivalent on the step surface, and the mirror plane will be maintained, resulting in a disordered structure. Conversely, if the step inclines to the mirror plane, the two symmetric sites in a crystal will not be equivalent on the step surface, and therefore ordering will occur and the symmetry will be reduced. In this case, the mirror plane will change into a twin plane. Thus, the (Al,Si) ordering may differ from sector to sector (Akizuki, 1987b).

The optical properties of the epistilbite crystals can be explained by this concept. Figure 7 is a partial crystal structure projected onto the plane normal to the *a* axis. According to Perrotta (1967) and Slaughter and Kane (1969), the TA sites, which are directly coordinated by Ca and minor Na ions, are preferentially occupied with Al atoms, rather than the TB and TC sites. If the crystal grows on the (10$\bar{1}$) face, normal to the (010) mirror plane, the mirror plane will be maintained, and the twofold axis will disappear during growth; that is, the TA-1 and TA-2 sites and the T'A-1 and T'A-2 sites will be equivalent with each other with respect to the Ca ion on the surface, whereas the TA-1 and T'A-1 sites will not be equivalent with each other. This result means that in the Kuroiwa

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Fig. 5. Stereographic projections of the optical orientations of A, B, and C domains shown in Fig. 4b. Optic vibration directions (*X, Y, Z*), optic axes (stars), and a center of the projection (arrow) are shown.
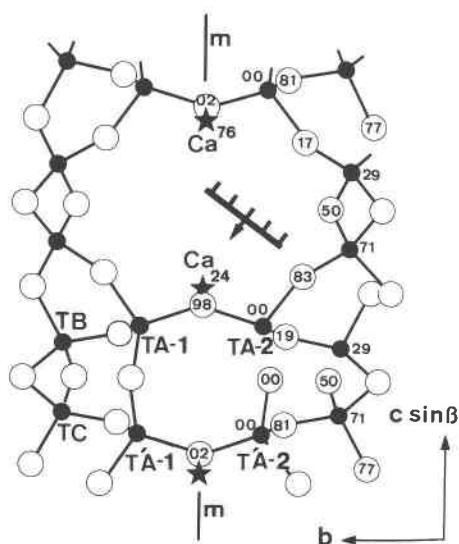
Fig. 7. Crystal structure of epistilbite projected along the *a* axis. Mirror plane (m) is vertical. Side face of growth step, which is inclined to the *b* axis, moves in the direction of the arrow. T(Al,Si) sites (solid circles), oxygen atoms (open circles), and Ca atoms (stars) are represented. Numbers give the heights of the atoms in thousandths of a cell edge. Water molecules are omitted. (Modified from Perrotta, 1967.)

specimen with the flat domains on the (10$\bar{1}$) face, the {10$\bar{1}$} sector consists of the monoclinic structure with space group *Cm*. Two morphologically symmetric {10$\bar{1}$} sectors show different 2*V* values, suggesting that the degree of (Al,Si) ordering is different between the two.

If the growth surface or step, which is inclined to the mirror plane, moves in the direction shown by arrow in Figure 7, the four TA-1, TA-2, T'A-1 and T'A-2 sites will not be equivalent with respect to the Ca ion on the surface; that is, both the mirror plane and twofold axis will disappear in the crystal, resulting in an (Al,Si)-disordered structure. This reasoning suggests that the space group is the noncentrosymmetric, triclinic *C*1 in the {110} sectors. Thus, the (010) mirror and the [010] twofold axis in the monoclinic structure change into a twin plane and twin axis in the epistilbite crystal, respectively: the {110} and {1$\bar{1}$0} sectors and the {$\bar{1}$10} and {$\bar{1}\bar{1}$0} sectors are related by the (100) twin, and the {110} and {$\bar{1}$10} sectors and the {1$\bar{1}$0} and {$\bar{1}\bar{1}$0} sectors are related by the (010) twin. Differences in the optical orientations of the A, B, and C sectors, which are shown in Figure 4b, may suggest the differences of (Al,Si) ordering among the sectors.

If the crystal grows on the (010) face, the mirror plane will disappear in the crystal, and the twofold axis will be maintained, resulting in a structure with the space group *C*2. Such a {010} sector consists of polysynthetic sectoral twinnings of the {110} and {$\bar{1}$10} sectors, suggesting *C*1 symmetry. Some (010) faces have fine striations parallel to the *c* axis, which may be due to a repetition of the (110) and ($\bar{1}$10) faces. In the epistilbite crystal from Fossarfell, the growth steps on the (10$\bar{1}$) face are circular, and

therefore the (Al,Si) ordering varies along the steps, showing a wavy extinction in the {10$\bar{1}$} sector; that is, the structure deviates slightly from the monoclinic symmetry. Thus, epistilbite consists of crystal structures with the space groups *C*1, *C*2, and *Cm*, all of which are consistent with the piezoelectric effect observed in this mineral (Bond, 1943; Ventriglia, 1953).

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