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Al,Si ORDER AND THE INTERNAL TEXTURE OF PREHNITE

MIZUHIKO AKIZUKI

Institute of Mineralogy, Petrology, and Economic Geology, Faculty of Science, Tohoku University, Sendai 980, Japan

ABSTRACT

Prehnite crystals from Glasgow, Scotland, were observed by high-resolution transmission-electron microscopy, scanning-electron microscopy and optical microscopy. Three polymorphs, *Pncm, P2cm* and *P2/n*, were observed in the (100) thin foils produced by ion thinning. The *P2/n* polymorph consists of extremely fine polysynthetic twins parallel to (001) plane, and the *Pncm* polymorph has fine lamellae consisting of the *P2/n* structure, whereas the *P2cm* polymorph is more or less homogeneous. The three polymorphs are metastably produced by a charge-balance effect on the crystal surface during growth. Furthermore, the *Pncm* crystal, which consists of Al,Si disordered structure, transforms into the ordered *P2/n* crystal with fine twins. The *P2cm* structure may be maintained as it appears after growth, because of its homogeneous texture.

Keywords: prehnite, polymorphs, Al,Si ordering, crystal growth, optics, high-resolution transmission-electron microscopy, scanning-electron microscopy.

SOMMAIRE

Des cristaux de prehnite provenant de Glasgow, en Ecosse, ont fait l'objet d'une étude par microscopie électronique par transmission à haute résolution, microscopie électronique à balayage et microscopie optique. On peut trouver les trois polymorphes *Pncm, P2cm* et *P2/n* dans de minces feuillets (100) préparés par amincissement en faisceau ionique. Le polymorphe *P2/n* est fait de macles polysynthétiques extrêmement minces parallèles à (001): le polymorphe *Pncm* possède de fines lamelles de la structure *P2/n* , tandis que le polymorphe *P2cm* est plus ou moins homogène. Les trois polymorphes sont métastables, et dus à une satisfaction locale des charges sur la surface du cristal pendant sa croissance. De plus, le cristal *Pncm*, à agencement Al,Si désordonné, se transforme en forme ordonnée *P2/n* à macles fines. La structure *P2cm* peut persister après la croissance, à cause de sa texture homogène.

(Traduit par la Rédaction)

Mots-clés: prehnite, polymorphes, mise en ordre Al–Si, croissance cristalline, propriétés optiques, microscopie électronique par transmission à haute résolution, microscopie électronique à balayage.

INTRODUCTION

In 1931, Gossner & Mussgnug suggested that the space group of prehnite is either *P2cm* or *Pncm*. Nuffield (1943) proposed that because of its pyroelectric character, the *Pncm* structure of prehnite consists of finely twinned domains having the *P2cm* structure. Peng *et al.* (1959) analyzed the structure of prehnite having *Pncm* symmetry. Preisinger (1965) refined the structure in the space group *P2cm*. Papike & Zoltai (1967) concluded that although prehnite has an average structure with a symmetry very nearly described in space group *Pncm,* most crystals have an ordered distribution of tetrahedrally co-ordinated aluminum, leading to space group *P2cm* or *P2/n.* Aumento (1968) found by X-ray analysis and electron microscopy that the *P2cm* structure is predominant in the specimens he examined, and suggested that submicroscopic polysynthetic twinning of this structure simulates the space group *Pncm.*

Based on studies of the relationship between surface features and internal textures of many minerals such as feldspars, topaz, garnet and zeolites (Akizuki & Sunagawa 1978, Akisuki *et al.* 1979, Akizuki 1981a, b, c, 1984, 1985a, b, 1986, 1987a, Akizuki & Konno 1985), Akizuki (1987b) suggested a general mechanism for formation of the structural growth-sectors: a crystal has some growth hillocks with fine steps on its growth surface when the solution is low in supersaturation. Ions are adsorbed on side faces of the steps, and the crystal grows. Therefore, a three-dimensional crystal structure of a growth hillock is produced by a piling up of a two-dimensional atomic arrangement. According to Pauling's second rule, local charge-balance must be maintained in a three-dimensional structure. Thus tetrahedra that are directly co-ordinated by alkali ions are preferentially occupied by aluminum in aluminosilicates because of local charge-balance. The electrostatic charge on the growth surface, however, is not balanced in the direction perpendicular to the surface; therefore, an ionic crystal can grow continuously. The balance of charges should be maintained along the two-dimensional structure exposed on the growth surface as well as within the crystal.

The two-dimensional atomic arrangements exposed on the surface of a growth step of a silicate differ among different kinds of surfaces. If the tetrahedron is produced after an alkali ion is adsorbed on the side face of a growth step, the aluminum ion will preferentially occupy the tetrahedron, whereas if the tetrahedron is produced prior to lodging of the cation, the silicon ion will occupy the site. Thus the degree of the Al,Si order may differ from sector to sector. If the vicinal surface is normal to a mirror or glide plane, the two symmetrical sites will be

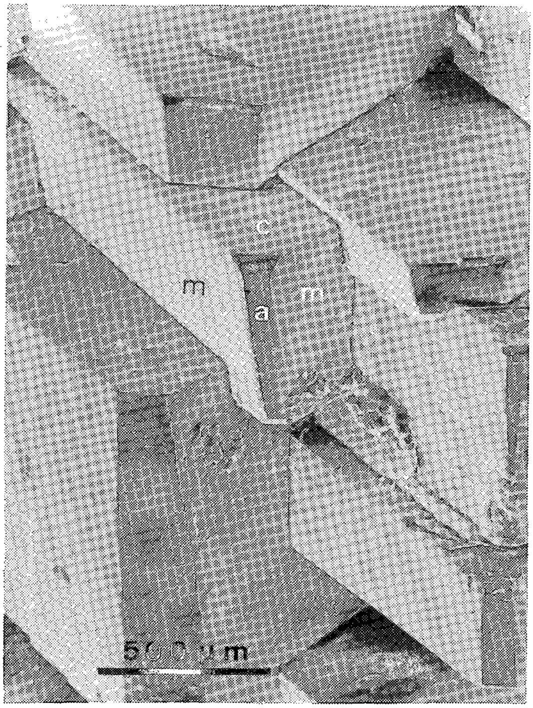

FIG. 1. Crystal form of prehnite from Glasgow. Crystal faces *c*(001), *a*(100) and *m*(110) are observed. SEM.

equivalent on the step surface, resulting in disordered arrangements. Conversely, if the vicinal surface is inclined to the mirror or the glide plane, the two symmetrical sites in a crystal will not be equivalent on the surface, and thus ordering will occur, and the symmetry of the crystal will be reduced. The morphological mirror plane changes into a twin plane owing to the symmetrically ordered arrangements.

OBSERVATIONS

Prehnite crystals from Glasgow, Scotland, were studied by high-resolution transmission-electron microscopy (JEM 1000) (TEM), scanning-electron microscopy (SEM) and polarized-light optical microscopy. In order to illustrate the relationship among the three symmetries, the *X* axis has been taken as the two-fold axis of rotation in the *P*2/*n* prehnite structure.

The crystal forms consist of *a*(100), *c*(001) and *m*(110) faces, with a small (101) face (Fig. 1). The (100) and (001) surfaces are finely irregular, with no visible growth-steps. However, the (110) face is composed of small rectangular sectors parallel to the [1$\bar{1}$0] and *Z* axes whose surfaces are finely irregular (Fig. 2). Figure 3 shows the internal texture in a thin section parallel to the (001) face. This thin section shows two {110} and one {100} growth sectors between crossed polars. The {110} sectors have lamellae crossing growth bands parallel to the (110)

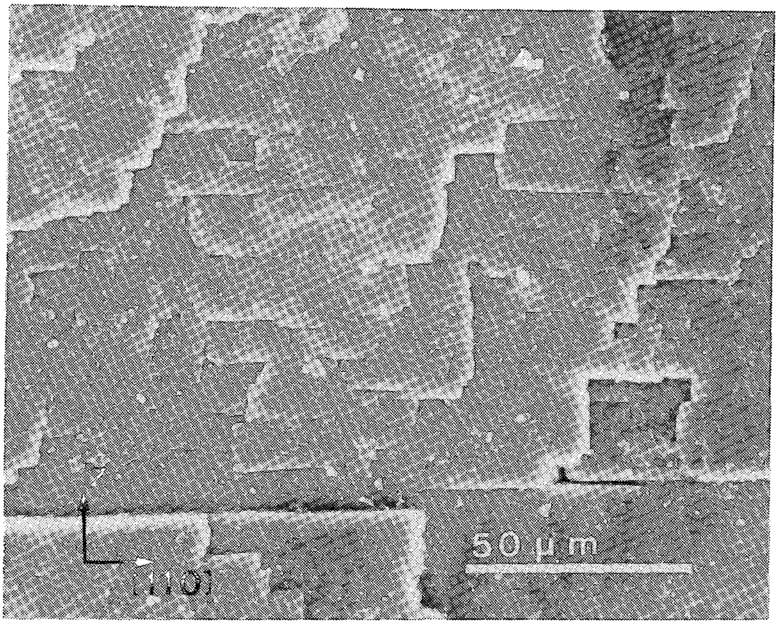

FIG. 2. Rectangular growth-pattern on the (110) face. The *Z* axis is in the vertical direction. SEM.

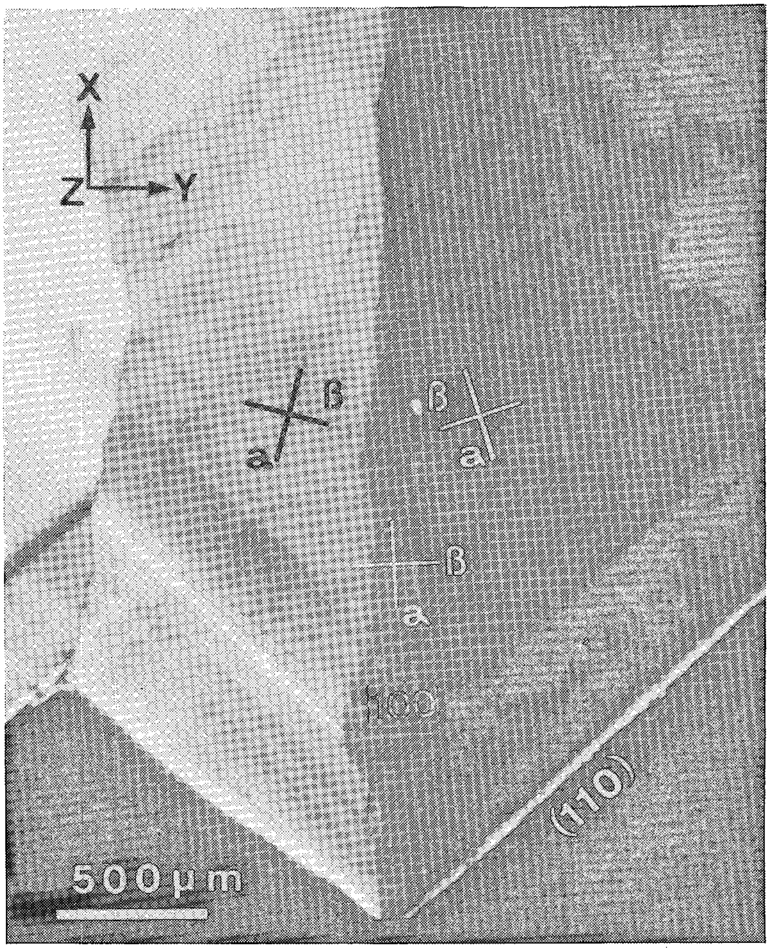

FIG. 3. The (001) thin section observed between crossed polars. Two {110} and one {100} sectors are observed. Lamellae corresponding to the growth feature on the (110) surface, which cross growth bands parallel to the surface, are observed in the {110} sectors. The *X* axis, which is in the vertical direction, is oriented in the direction parallel to the two-fold rotation axis in prehnite. Optical vibration directions α,β, which are approximately parallel to the sheet of paper, are shown. See text for details.

crystal face, which correspond to the rectangular growth-patterns on the surface. The directions of optical vibration are symmetrically inclined to the *X* axis (two-fold axis in the monoclinic *P*2/*n* structure), suggesting triclinic symmetry and twinning. In the {100} sector, however, the vibration directions are parallel to the crystal axes of an orthorhombic prehnite crystal through the sector, suggesting orthorhombic symmetry.

The (100) thin sections of prehnite crystals were ion-thinned, and observed by TEM at 1000 kV. Figure 4 shows a lamellar structure parallel to the (001), though a homogeneous area is observed as well. Figure 5 shows the electron-diffraction pattern of prehnite. The diffraction spots indicated by arrows are due to the *P*2*cm* structure, and the split spots represent twins of the *P*2/*n* structure.

Figure 6 shows the lattice images of the prehnite structure in the (100) thin foil (Fig. 4), accompanied by optical-diffraction patterns produced from the negatives using a He–Ne gas laser beam. The optical-diffraction patterns indicate that the *P*2*cm* and *Pncm* structures both occur. Although the crystal with space group *P*2*cm* is more or less homogeneous, as

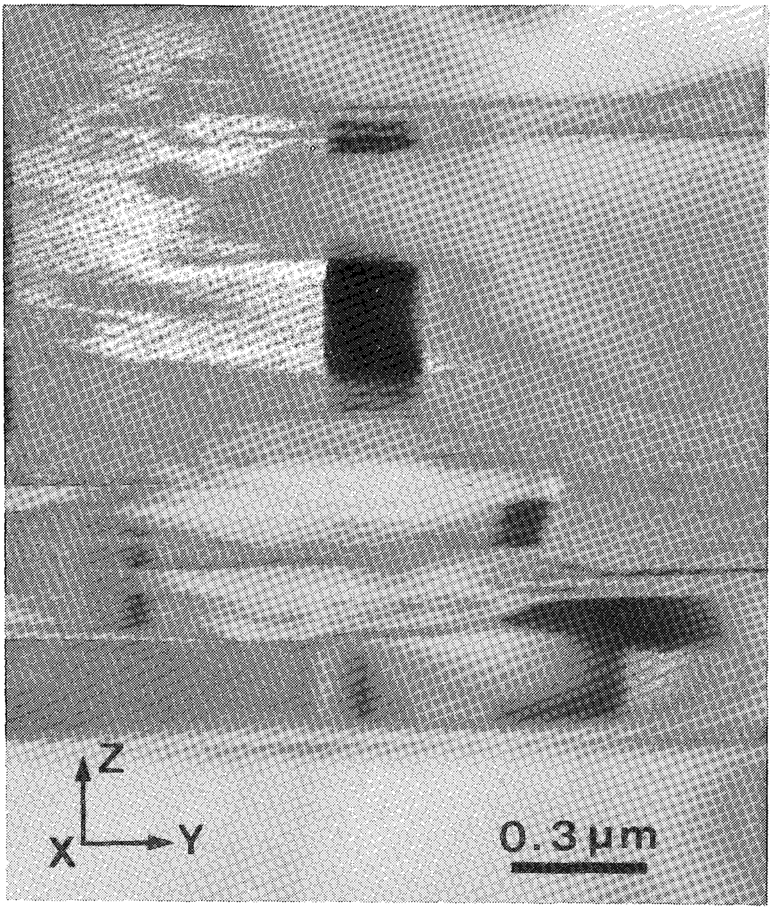

FIG. 4. Fine lamellae parallel to the (001) in the (100) thin foil of prehnite.

Aumento (1968) suggested, the crystal with space group *Pncm* is accompanied by lamellar lattice-patterns (*P*2/*n*) parallel to the (001). Figure 7 shows the lattice image of an extremely fine lamellar pattern. The electron-diffraction pattern consists of strong streaks elongated to the *Z* axis, with split spots. The optical-diffraction pattern (Fig. 7) represents a twinned structure of the monoclinic *P*2/*n* crystals. A few *P*2/*n* crystals, however, are homogeneous and show sharp diffraction-spots. No important differences are observed between the {100} and {110} sectors.

Although the lattice image is regularly oriented through the thick crystal foil (about 1000 Å in thickness), it rotates irregularly, but very slightly, in an extremely thin area such as the crystal edge in the ion-thinned crystal, and therefore, it is very difficult to take photographs of the high-resolution lattice image.

DISCUSSION

The *P*2*cm* crystals are homogeneous, whereas the *Pncm* crystals contain twin lamellae of *P*2/*n*. It is assumed that the two polymorphs, *P*2*cm* and *Pncm*, were produced metastably during crystal growth, but that the *P*2/*n* polymorph was formed by a phase transition from the Al,Si disordered structure with space group *Pncm*. The *P*2*cm* structure, however, may be maintained as it appears, after crystal growth. This phenomenon may correlate with a relationship in which space group *Pncm* is a supergroup of *P*2/*n*, whereas the *P*2*cm* is not.

Figure 8 represents crystal structures of the two polymorphs *P*2*cm* and *P*2/*n* projected onto the (010) plane. Figure 9 shows a partial representation of the crystal structure projected on the (001) plane of prehnite. Only *T*(Si,Al) and Ca sites are drawn. The two Al atoms are confined to the T_2 tetrahedra because

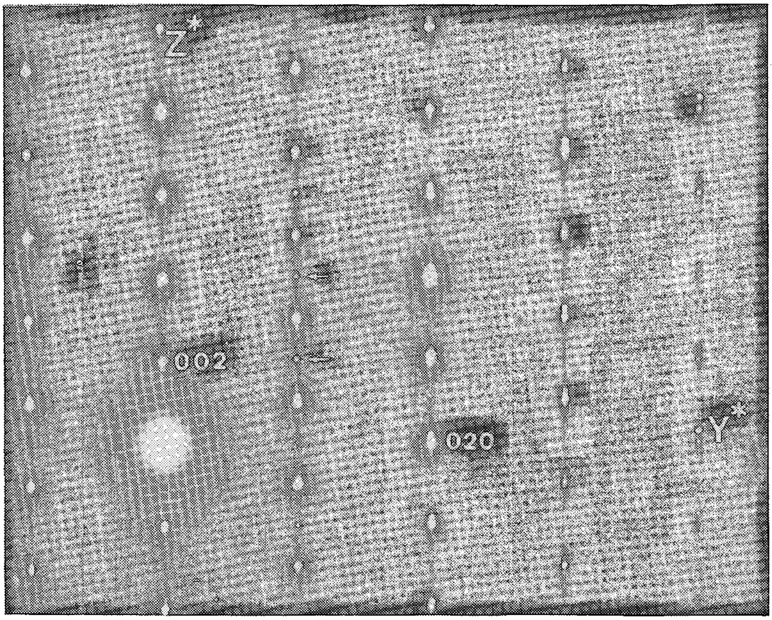

FIG. 5. Electron-diffraction pattern of prehnite. Arrows indicate *P*2*cm* spots.

of an avoidance rule forbidding the Al–O–Al bond. Two oxygen atoms of each T_2 tetrahedron coordinate directly to the nearest Ca ion. If growth steps move in the direction shown by thin arrows on the (001) and the (110) faces, T_2(b) and T_2(d) sites will be produced after the Ca ion on the side face of growth steps and, therefore, the two sites will be preferentially occupied with Al atoms because of the charge-balance effect. On the other hand, T_2(a) and T_2(c) sites are produced before the Ca ion, and the two sites will be occupied with Si atoms, resulting in the *P*2*cm* structure. If the step moves in the direction along the *Y* axis on the (001) surface, as indicated by the thick arrow, all the T_2 sites will be equivalent with each other with respect to Ca ions on the side face of growth step and, therefore, the disordered structure *Pncm* will be produced in the crystal.

Figure 10 shows a partial crystal-structure of prehnite projected onto the (100) plane. If the steps move in the direction of [01$\bar{1}$] on the (011) face as shown by arrows, the T_2(b) and T_2(c) sites will be preferentially occupied by Al atoms, and the T_2(a) and T_2(d) sites by Si atoms, because of the charge balance between T_2 sites and Ca ions, resulting in monoclinic *P*2/*n* structure shown in Figure 8. The crystal consists of a finely irregular surface and, therefore, the three kinds of polymorphs are produced in one sector during growth.

The monoclinic polymorph (*P*2/*n*) will be stable at a low temperature, because the crystal is produced during the phase transition, though a few *P*2/*n* crystals are produced during growth. The two orthorhombic polymorphs, however, may be metastable phases, which grow at a high growth-rate. At a higher growth-rate, the more disordered structure (*Pncm*) will form. Furthermore, the volume of the *P*2/*n* structure increases during transition relative to that of the *Pncm* structure. Thus various proportions of the three polymorphs are observed in all sectors under TEM. Also, this mechanism suggests that the proportions may be different in the specimens from different localities, being consistent with the observation by Aumento (1968). The *Pncm* crystal of prehnite is explained in terms of an (Al,Si)-disordered structure rather than by fine twins of the ordered structures (*P*2*cm* and *P*2/*n*).

A growth band parallel to the crystal face is attributed to chemical or structural variations due to a change in growth rate. Also, the degree of Al,Si order is correlated to the growth pattern on crystal surface, which develops continuously during growth, resulting in lamellae approximately normal to the crystal face. Therefore, the growth bands and the lamellae cross each other in the {110} sector, as observed in Figure 3.

Since the crystal consists of the two orthorhombic and one monoclinic polymorphs and since the monoclinic polymorph is finely twinned, the crystal should be optically orthorhombic. The {110} sectors,

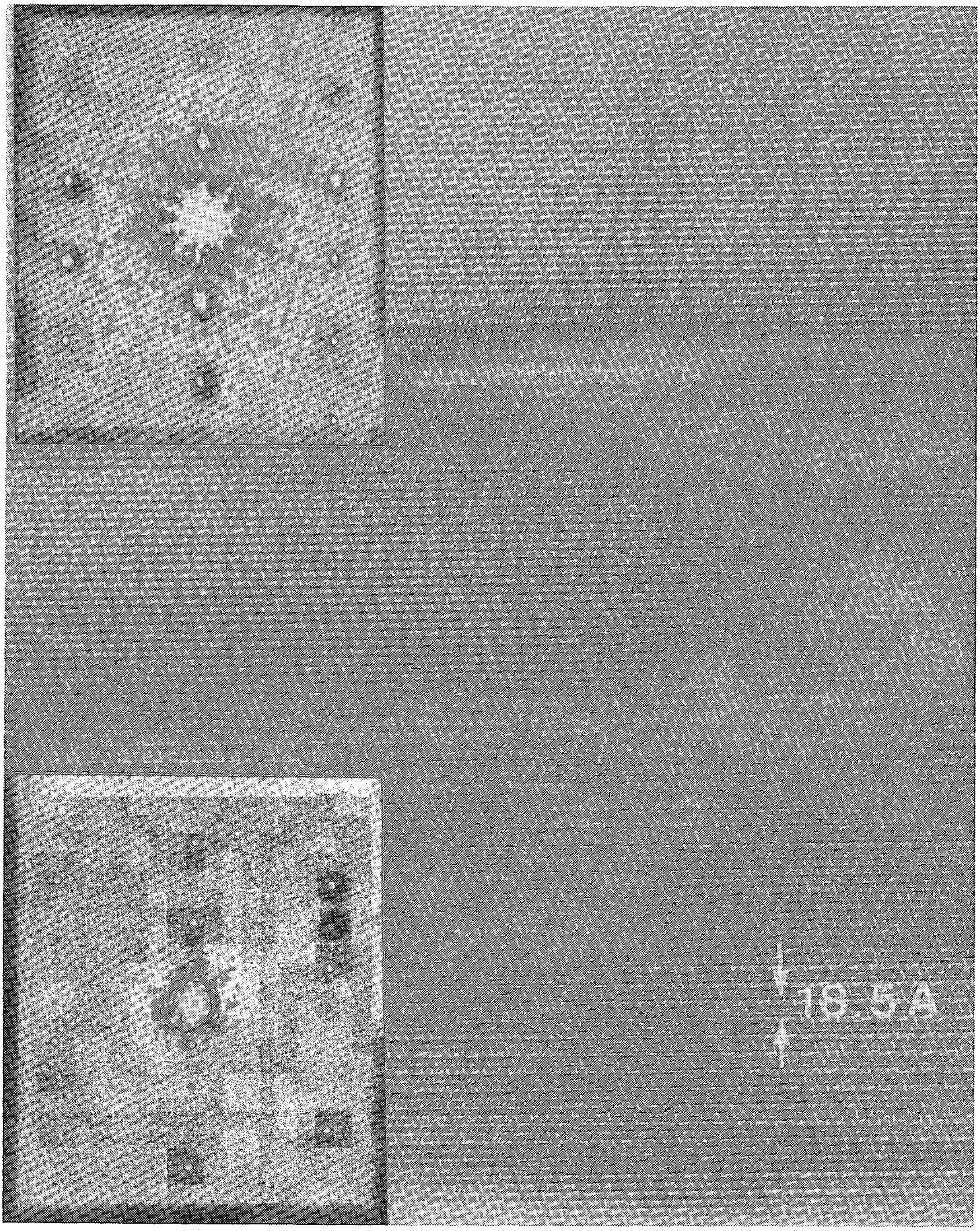

FIG. 6. Lattice image of the *Pncm* and *P2cm* prehnite structures, accompanied with optical-diffraction patterns. The upper part consists of the *Pncm* structure (c = 9.3 Å), and the bottom the *P2cm* structure (c = 18.5 Å). The Z axis is in the vertical direction.

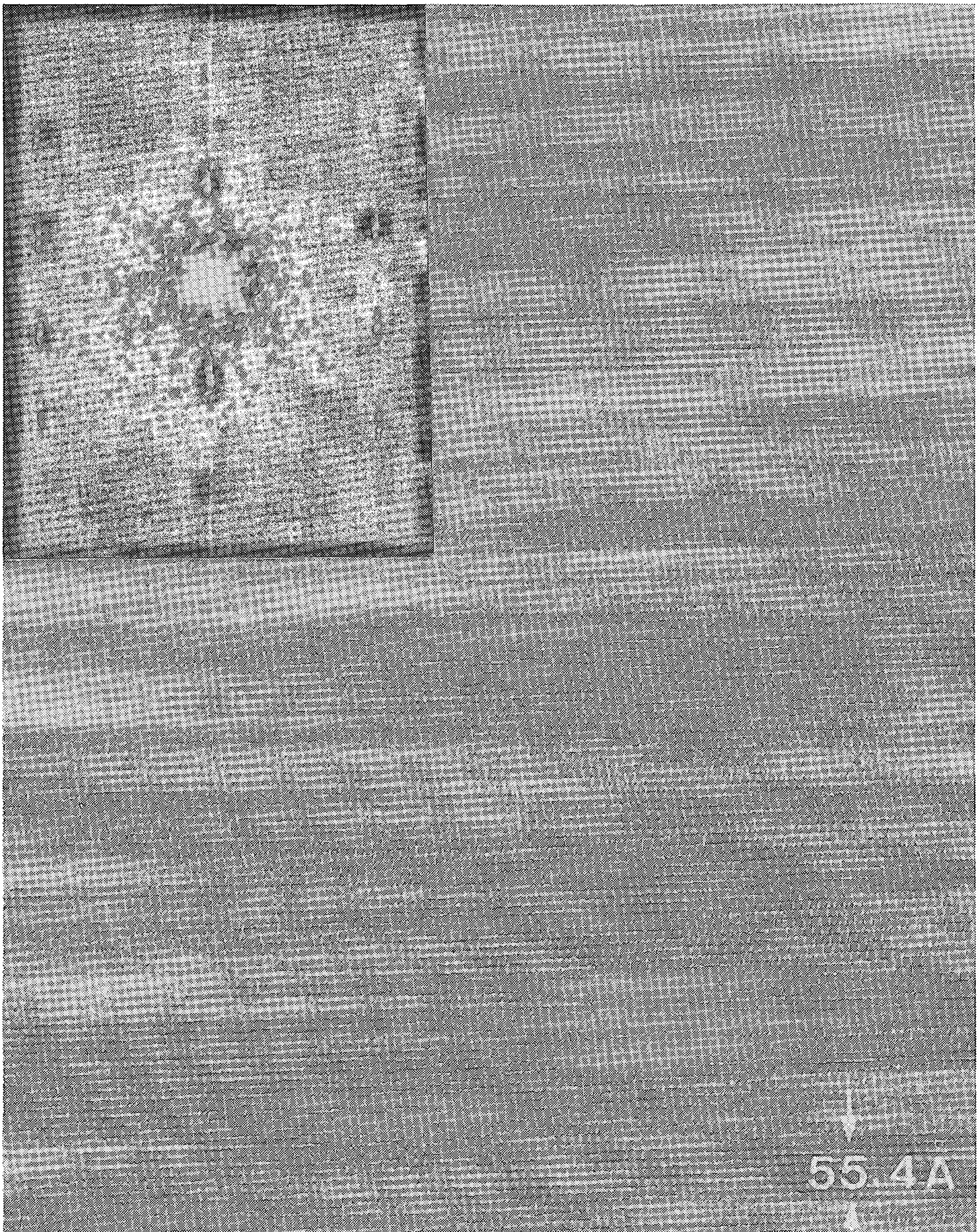

FIG. 7. Lattice image and optical-diffraction pattern of the polysynthetically twinned $P2/n$ prehnite structure. The length of $6c$ is equal to 55.4 Å. The Z axis is in the vertical direction.

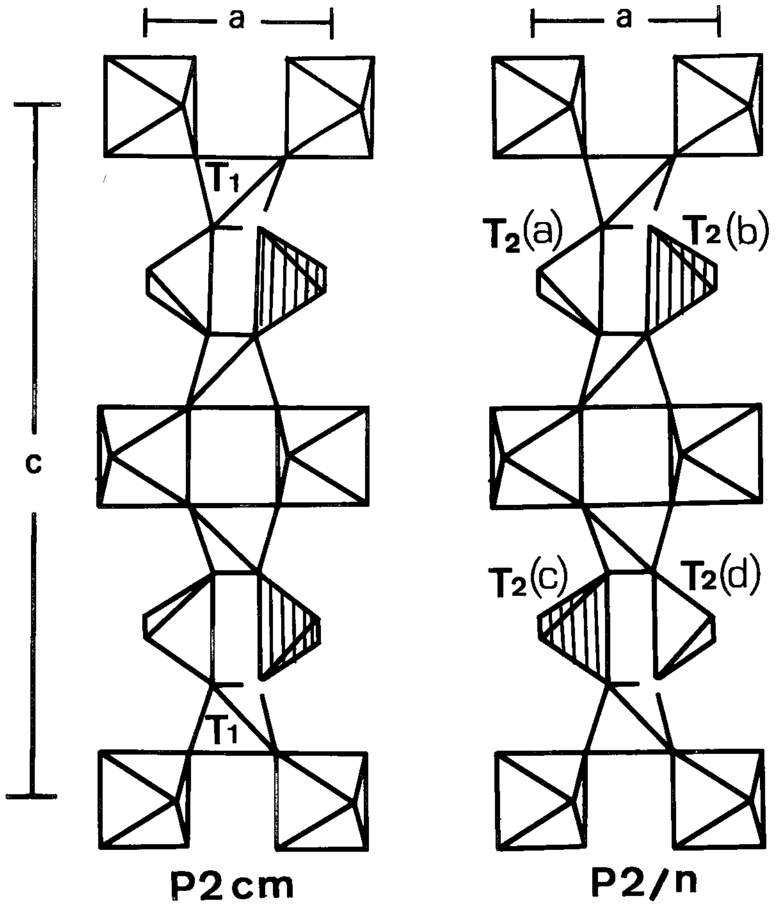

FIG. 8. Two ordering schemes of the prehnite polymorphs, *P2cm* and *P2/n*. The crystals consist of octahedra and tetrahedra (T_1 and T_2). Al atoms occupy shaded T_2 sites. The *Pncm* structure is disordered with respect to Al, Si atoms. Ca atoms are omitted. Modified from Papike & Zoltai (1967).

however, are optically triclinic. The cell dimensions vary according to the pattern of atomic ordering, which differs from growth domain to growth domain. Therefore, strain occurs along the domain boundaries. Because the two (110) and ($1\bar{1}0$) faces are symmetrically inclined to the *X* axis, the strain, which is induced during growth, changes the orthorhombic symmetry into optically triclinic symmetry in the {110} sectors and, therefore, their optical orientations are symmetrical with respect to the *X* axis. Owing to the strain, the crystal begins to split during its growth, forming a sheaf or a spherulite (Grigor'ev 1965). This is the origin of so-called splitting growth in prehnite crystal. The (100) face, however, is normal to the crystal axis; therefore, right and left inclinations of the crystal structures due to growth strain occur in the same proportion with each other in the {100} sector. Thus the {100} sector is optically orthorhombic. The strain, which is maintained in the thick crystal, is released in an extremely thin crystal, such as at the edge of the ion-thinned sample. As a result, the lattice orientations rotate slightly from place to place along the edge of the crystal during ion thinning.

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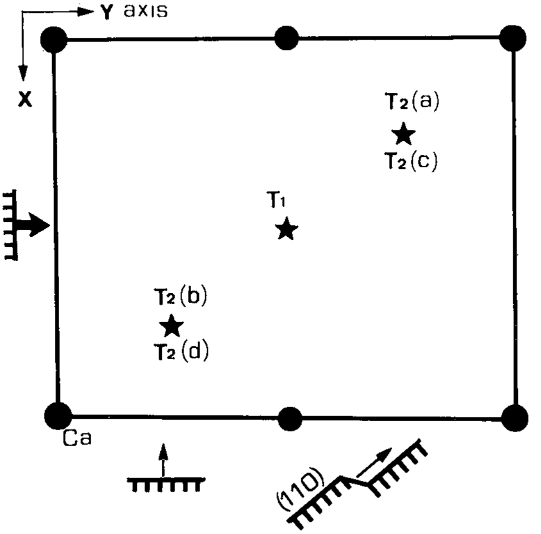

FIG. 9. Repesentation of part of the crystal structure of prehnite projected on the (001) plane. Only the T(Si,Al) and Ca sites are shown. Growth directions are shown by arrows on the steps. See text for details.

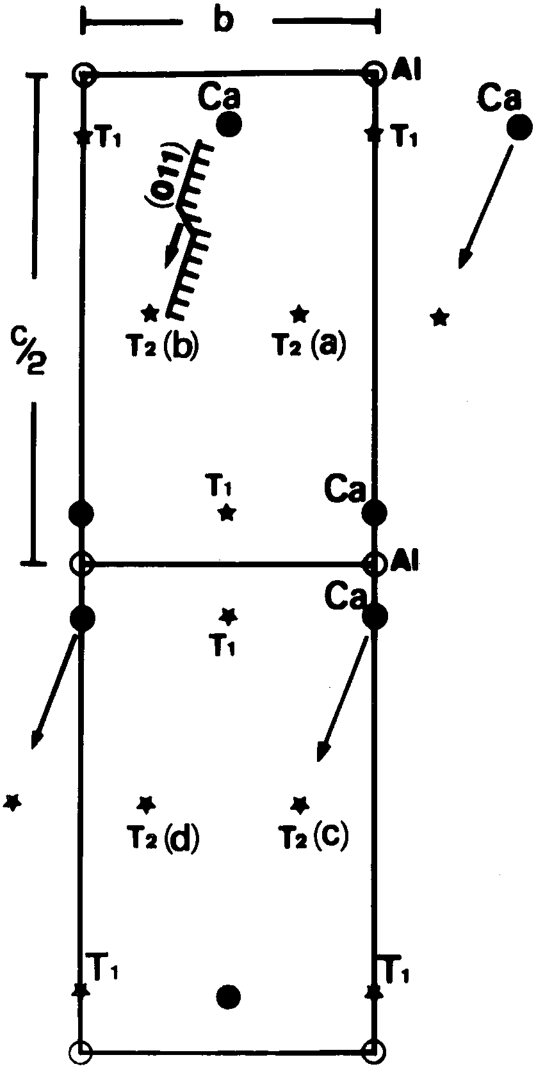

FIG. 10. Representation of part of the crystal structure of prehnite projected on the (100) plane. The growth step moves in the direction shown by the short arrow on the (011) face, normal to the sheet of paper. Long arrows are directed from Ca atoms toward T_2 sites. See text for details.

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