THE SPACE GROUP OF PREHNITE

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ABSTRACT

The space groups of different constituent domains in prehnite crystals from Farmington, Conn., were identified by single crystal x-ray diffraction, transmission and replication electron microscopy, and electron diffraction.

A domain with space group $P2cm$ is predominant in both x-ray and electron diffraction patterns. Sub-microscopic interpenetrational polysynthetic twinning of this domain simulates the space group $Pncm$. The latter can be observed by x-ray diffraction of apparently single macro-crystals, and by electron diffraction on twinned micro-crystals.

A domain with space group $P2/n$ is detectable in minor proportions by x-ray diffraction of macro-crystals, but has yet to be identified by electron diffraction.

INTRODUCTION

The space group of prehnite, studied intermittently since the work of Gossner & Mussgnug (1931), has recently been re-examined by Papike & Zoltai (1967). The author presents further data to clarify some of the ambiguities arising from previous investigations.

Gossner & Mussgnug (1931) allotted prehnite either the dipyramidal space group $Pncm$ or the pyramidal $P2cm$, the latter in agreement with previous observations by Traube (1894). Traube, on examining the pyroelectric properties of prehnite, had concluded that its polar axis was the a [100] morphological axis.

Nuffield (1943), on examination of equidimensional and untwinned basal cleavage fragments from Ashcroft, B.C., suggested the space groups $Pncm$ or $Pnc2$, which contradicted the pyroelectric data of Traube (1894).

Nuffield explained the anomalous space groups by considering that, since prehnite belongs to the class $2mm$, twinning might be expected about any of the missing elements of symmetry, namely the axis b[010], c[001], or the plane a(100). He showed that a crystal of space group $P2cm$, twinned about the c[001] axis, simulated the space group $Pncm$. Such twinning would have to be interpenetrational, without optical discontinuity, to elude optical detection. Nuffield also found that powder photographs could be indexed satisfactorily according to $P2cm$. He concluded that, since both the morphology and the pyroelectric properties were in agreement with the space group of the untwinned crystals, the latter should be fairly common.

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Peng, Chou & Tang (1959) used the space group *Pncm* in their solution of the crystal structure of prehnite. Malčič & Preisinger (1960), and later Preisinger (1965) assigned the space group *P2cm* to their material.

Papike & Zoltai (1967) concluded that prehnites from different localities may be composed of intimate intergrowths of two different domains, of respective symmetries *P2cm* and *P2/n*, in varying proportions. The two symmetries arise from an "average" structure with symmetry *Pncm* in which ordering of tetrahedral aluminum occurs in two different schemes. Prehnites with a true *Pncm* symmetry were thought to be either disordered (random rotation of tetrahedral layers) or to have been mis-interpreted from *x*-ray photographs insufficiently exposed to reveal extra reflections.

After consideration of recent work on feldspars (Aberdam (1965), Laves, Nissen & Bollmann (1965), Baier & Pense (1957)) which revealed that sub-microscopic intergrown twins and exsolved lamellae can be detected by electron microscopy, the author used similar techniques to examined prehnite crystals for the possible existence of twins or intergrowths.

Method

Prehnite was collected from the Triassic basalt flows of Rattlesnake Mountain, on the east shore of the Avon River Valley, Farmington, Connecticut, where it occurs as reniform, globular linings and as barrel-shaped crystals on the walls of small veins. On optical examination, most crystals showed complex twinning and intergrowths; however, single crystal fragments were recovered for examination.

Optically "confirmed" single crystals were used for precession and Weissenberg photography and for diffractometry. The same crystals were later used for electron microscopy, using both surface replication and sample dispersion techniques. Surface replicas could only be made from (001) cleavage faces, these being the only available flat surfaces.

Results

X-ray diffraction

Single crystal photographs gave a basic orthorhombic unit cell (parameters, refined by diffractometry and least square calculations, being: $a = 4.597$ Å, $b = 5.492$ Å, $c = 18.491$ Å) for most of the crystals examined. One crystal, however, which turned out to be twinned, indicated the existence of a second minor domain of monoclinic character. The following space groups were identified:

(1) *Pncm*. Extra reflections violating the space group were completely

absent. This would be a disordered prehnite according to Papike & Zoltai (1967).

(2) $P2cm$, suggesting one type of tetrahedral aluminum ordering.

(3) $P2cm$ with minor $P2/n$ domain, resulting in an apparent space group $P222_1$, as detected by Papike & Zoltai (1967). This crystal would be composed of an intimate intergrowth of two polymorphs with different types of aluminum ordering.

It should be noted that none of the space groups identified are unique when using x-ray methods alone. However, their selection from other equally applicable space groups is justified by taking into consideration the established morphological and pyroelectric studies of the mineral by Traube, Nuffield and others.

Transmission electron microscopy and diffraction

Two characteristically different grain types were observed by transmission electron microscopy of the crystals examined above. These were (i) equidimensional grains or elongated laths showing no surface features (Fig. 1a), and (ii) rare grains showing a parallel arrangement of striations over their surfaces, producing strips of different illumination (Fig. 1c), and others showing lamellar features (Fig. 1b).

Regarding grains of type (1), their poor cleavage was insufficient to control the fall of fragments onto sample grids along major crystallographic orientations; randomly oriented particles were generally obtained. However, a number of the equidimensional flakes had settled onto their (001) cleavage plane, giving good a^*b^* nets by electron diffraction. The latter did not show systematic extinctions. The less common lath-like flakes (Fig. 1a) gave both a^*c^* and b^*c^* nets, whose systematic extinctions ($h0l: l = 2n$), combined with those of the a^*b^* nets, suggest that the featureless prehnite crystallites have the space group $P2cm$.

The lamellae of grains of the second type (Figs. 1b and 1c) exerted better control on the final orientation of the grains; this improved the orientation of the electron diffraction patterns. The lamellae (in two orders of magnitude, 0.05μ and 0.2μ) were too thin to be examined individually by the electron beam, so that composite diffraction patterns for whole grains were obtained. The systematic extinctions obtained from these grains are different from those of the featureless grains in that the b^*c^* nets give the following conditions:

$$0kl: k + l = 2n$$

$$0k0: k = 2n$$

$$00l: l = 2n \text{ indicating the space group } Pncm.$$

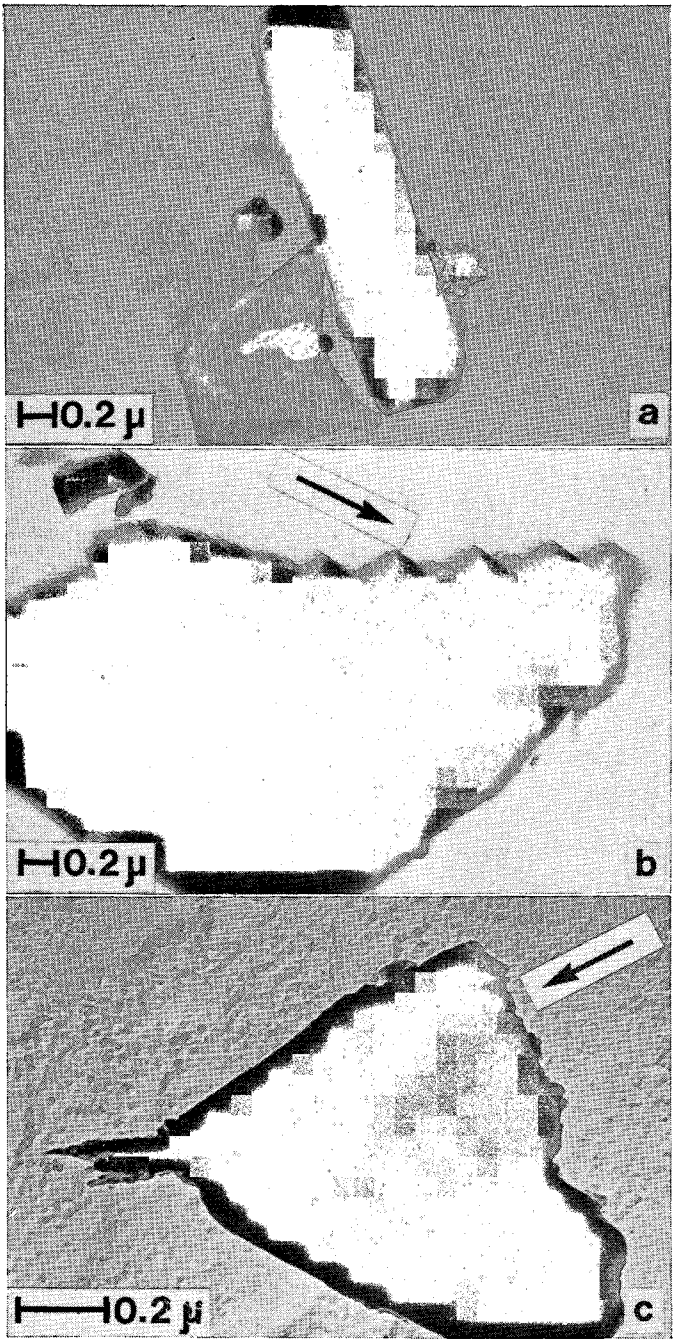

FIG. 1. Dispersed state electron micrographs of prehnite showing diverse morphologies and lamellar features.

Replication Electron Microscopy

Photomicrographs obtained with a Philips E.M. 200 electron microscope are shown in Fig. 2. The magnified (001) cleavage flakes appear to be for the most part featureless plateaus over areas of 2 × 1 mm (see Fig. 2a) interrupted, at random, by a series of linear features of different reliefs. The majority of these features lie in two distinct orientations, intersecting at approximately 48°, corresponding to the 48°20′ angle between the crystallographic directions (110) and (100). The linear features are as follows:

(a) Features parallel to (110):

(1) The most striking, running across Fig. 2b, are step-wise reliefs (note the darker shadowing of the step, and the uniform shadow of the slope), as might be expected from the "outcropping" of almost horizontal layers. These may be the outcrops of the horizontal (001) cleavage planes under control of the vertical (110) cleavage.

(2) Parallel to the above are thin, dark lines, representing thin shallow breaks perpendicular to the (001) planes. These are visible in Fig. 2b in between the main steps, and also in greater abundance in Fig. 2c. These breaks are taken to represent the vertical outcrops of the (110) cleavage planes alone, without the combined effects of the (001) cleavages.

(3) A third feature is visible in Fig. 2d and also in Fig. 2b. In this case, different shadowing effects on either sides of the lineations indicate that these are not steps, but symmetrical ridges protruding above the surface on the plateau. Figure 2d also shows that the features on either side of these ridges have reversed orientations, as though the ridges acted as mirrors. The ridges are interpreted as being either the boundaries between submicroscopic twin lamellae, or as thin intergrown lamellae themselves, in possible twin relationship with the host crystal. Twin planes may therefore exist, with orientation parallel to (110), and twin axis parallel to [001].

(b) Features parallel to (100):

(4) Short ridges, similar in appearance to those of type (3) above, are visible in Fig. 2b and Fig. 2d. These are often truncated along their length by the other features at 48° to them. They could be a second generation of intergrown twin lamellae, with the same twin axis parallel to [001] as the main set, but with twin planes parallel to (010).

(5) The remaining set of linear features, parallel to those in (4) above, are especially evident in Fig. 2c, but also occur in Fig. 2b. They consist of very fine discontinuous striations over large areas, sometimes interrupting, at other times interrupted by, all other relief features. These striations could not be accounted for.

The above mentioned features cover less than 10% of the area of any

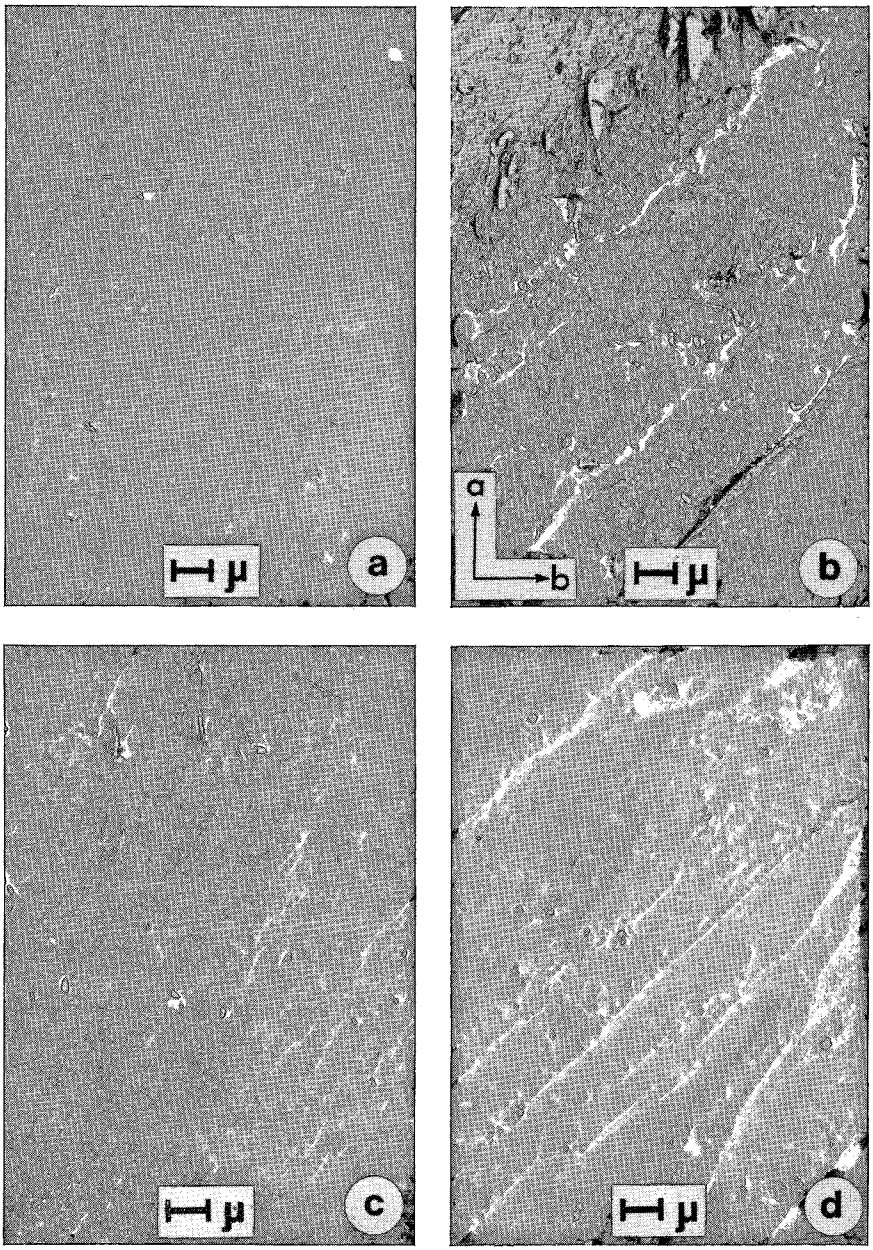

FIG. 2. Electron micrographs of replicas from the (001) cleavage surfaces of prehnite, showing featureless plateaus and lamellar features (see text).

one given cleavage flake. It was observed that the step faults caused by the imperfections on the (001) cleavage also occurred in areas of marked concentrations of twin ridges. The latter probably reduce the effectiveness of the (001) cleavage perpendicular to them, giving rise to the step breaks along (110). Traces of the (110) cleavage were also more abundant in the proximity of the twin ridges, suggesting that the twins may have assisted the formation of the weak cleavage planes parallel to themselves.

Discussion

Single crystal x-ray investigations indicate that the domains described by Papike & Zoltai (1967), namely *Pncm*, *P2cm*, and a combination of the latter with $P2/n$, occur in the Farmington prehnite. Of these, $P2/n$ is rare: when it does occur, it is only a minor component of a predominantly *P2cm* crystal. The space group $P22_12$ mentioned by Papike & Zoltai on theoretical considerations was not detected. All powder diffractograms can be indexed on the space group *P2cm* alone.

The featureless dispersed crystallites (sizes from 0.5 to 2μ) from any of the macrocrystals above give the space group *P2cm*. A domain of this symmetry must therefore make up the basic prehnite polymorph. Since crystallites showing fine lamellar structure have a *Pncm* space group, it is thought that they are made up of individual *P2cm* lamellar domains, twinned to simulate *Pncm* (as suggested by Nuffield). The twinning occurs in two scales: (i) a very fine one, with lamellae of the order of 0.05μ and (ii) a coarser twinning with 0.2μ lamellae; both result in the space group *Pncm* for even the smallest examinable crystallites in the dispersed state. Both these twin scales are discontinuous, occurring at random throughout the *P2cm* domain. The surface replica micrographs show the finer twins as features (4) in Fig. 2b and Fig. 2d, and the coarser ones as features (3) in the same plates.

Conclusions

X-ray and electron microscopic data have verified that the domain with space group *P2cm* is the major component of prehnite crystals from Farmington, Conn. A twin axis parallel to [001] produces a sub-microscopic polysynthetic twinning in two orientations; the latter are parallel to (110) and (010). The twinning occurs at random with lamellae of two distinct scales.

Both these sets of lamellae are discontinuous, can vary in proportion from both crystal to crystal and within a single crystal, and are not detectable by optical microscopic techniques. The discontinuity of the

twins explains the variations in space group found in different macrocrystals.

The domain with space group $P2/n$ has so far escaped electron microscopic identification, possibly because of its rarity in the Farmington material. Further observations may detect this domain and give an indication of its relationship to the predominant $P2cm$ domain.

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