# The structural relation between svetlozarite and dachiardite

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ABSTRACT. Svetlozarite, previously described as a new member of the mordenite group of zeolites, is re-interpreted as a multiply twinned and highly faulted dachiardite. X-ray diffraction study and transmission electron microscopy revealed (001) twins and (100) stacking faults. The former are attributed at least mainly to the insertion of a *b* glide plane between dachiardite sheets at each twin interface, which preserves the 5-ring linkages between the sheets. The latter are associated with loss of the *C* face-centring relation, and are attributed to replacement of shared 5-rings by linked 4-rings in the dachiardite sheets. Further study is needed to determine whether the structural faults in the dachiardite structures are chemically controlled.

SVETLOZARITE was reported by Maleyev (1977) as a new, high-silica zeolite that occurs as colourless or white spherulites in chalcedony veinlets cementing brecciated andesites, west of Zvezdel in eastern Rhodopes, Bulgaria. Maleyev gave a detailed description of the physical and chemical properties of the mineral, and from X-ray powder studies suggested that svetlozarite is orthorhombic, with a *c*-axis repeat of 7.5 Å. Although this repeat is characteristic of zeolites in the mordenite group, no detailed structural study was made. The present study was performed in order to obtain a clearer insight into the exact structure of svetlozarite, and was made possible through the courtesy of Professor Glauco Gottardi, who kindly provided parallelepipedal splinters of svetlozarite broken from a spherulite. Electron microprobe, powder and single crystal X-ray techniques, and transmission electron microscopy (TEM) were used.

*Observations and results.* Electron-microprobe analyses were made with an energy-dispersive system using a 15 kV accelerating voltage, a beam current of 10 nA, a spot-diameter of 20 $\mu$m, 28 000 total counts for each of seven analyses, Reed–Ware correction procedures and silicate standards. The

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range of analyses (Table I) brackets the original chemical analysis for svetlozarite (Maleyev, 1977) when normalized to 48 framework oxygens. Furthermore the analyses of svetlozarite almost fall within the known range for dachiardite, a member of the mordenite group of zeolites. In particular, svetlozarite is chemically close to a dachiardite (Table I, anal. 8) from Cape Lookout, Oregon, USA (Wise and Tschernich, 1976).

X-ray powder data were obtained with Gandolfi and Debye–Scherrer cameras (Cu–*K*α radiation, Ni filter). The strong diffraction at 9.24 Å recorded by Maleyev (1977) was not observed, but all the other lines were matched within experimental error. All lines of the new powder pattern gave *d*-spacings consistent with those recorded by Galli (1965) for a dachiardite from Elba and by Alberti (1975) for a dachiardite from Alpe di Siusi. Because of the problems of comparing qualitative estimates of intensities, a firm statement cannot be given on the relation between intensities, especially for the weak lines. Furthermore, the elongated shape of crushed material may have resulted in preferred orientation. Nevertheless it appears that the *k*-odd lines of svetlozarite are weaker than those with even *k* when compared with the Galli (1965) data; however, a closer correlation exists with the data of Alberti (1975), for which *k*-odd lines were also found to be diffuse. Interestingly, the powder data for the dachiardite most chemically similar to svetlozarite (Table I, anal. 8) is also 'essentially identical' (Wise and Tschernich, 1976) to that found by Alberti (1975). The 9.24 Å diffraction recorded by Maleyev (1977) cannot be explained in terms of an unfaulted dachiardite structure, and it is unlikely that any faults developed in dachiardite would produce diffracted intensity as strong as that reported. The 9.24 Å diffraction could not be matched positively with any likely impurity. Although it is close to a line for chabazite and one for mordenite, other stronger lines for these two zeolites could not be matched with lines in the svetlozarite pattern reported by Maleyev.

TABLE I. *Analyses of svetlozarite and dachiardite*

|  | 1 | 2 |  | 1a | 2a | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 69.58 | 64.3–65.3 (64.7) | Si | 20.19 | 20.24 | 18.81 | 18.93 | 19.61 | 20.57 | 20.67 | 20.03 | 20.48 | 19.76 |
| $Al_2O_3$ | 10.26 | 9.5–10.3 (10.0) | Al | 3.51 | 3.66 | 5.20 | 5.05 | 4.27 | 3.38 | 3.43 | 4.02 | 3.53 | 4.37 |
| $Fe_2O_3$ | 0.67 | nf | Fe | 0.15 | — | — | — | 0.11 | 0.02 | 0.02 | — | 0.01 | 0.06 |
| CaO | 3.91 | 3.3–4.2 (3.8) | Ca | 1.22 | 1.28 | 1.63 | 1.76 | 0.53 | 0.09 | 1.01 | 1.14 | 0.21 | 0.16 |
| MgO | 0.30 | 0.0–0.4 (0.2) | Mg | 0.13 | 0.09 | 0.09 | — | 0.04 | — | — | — | — | 0.01 |
| $Na_2O$ | 0.85 | 0.3–1.3 (0.6) | Na | 0.48 | 0.36 | 1.05 | 0.70 | 2.59 | 2.74 | 0.61 | 0.58 | 2.12 | 2.93 |
| $K_2O$ | 3.00 | 1.7–3.1 (2.4) | K | 1.11 | 0.95 | 0.67 | 0.73 | 0.71 | 0.60 | 0.34 | 0.91 | 0.93 | 0.36 |
| $H_2O$ | 10.94 | — | $H_2O$ | 10.59 | — | 12.68 | — | 13.43 | — | — | — | — | 12.63 |
| Sum | 99.51 | 80.5–82.4 (81.6) |  | Normalized to 48 framework oxygens |||||||||| |

1. Svetlozarite, chemical analysis (Maleyev, 1977).
2. Svetlozarite, range and mean of electron-probe analyses.

1a and 2a. Cell contents of atoms and $H_2O$ molecules normalized to 48 framework oxygens. For the electron microprobe analysis, the deviation of 81.6 % from 100 % would correspond to 13.1 $H_2O$.
3. Dachiardite, Elba, Italy (Gottardi, 1960).
4. Dachiardite, Elba, Italy (Bonardi, 1979). Also 0.02 Sr, 0.12 Cs.
5. Dachiardite, Alpe di Siusi, Italy (Alberti, 1975). Also 0.01 Ba.
6, 7. Dachiardite, Altoona, Washington, USA (Wise and Tschernich, 1976). Base and tip of cluster.
8. Dachiardite, Cape Lookout, Oregon, USA (Wise and Tschernich, 1976). Centre of cluster.
9. Dachiardite, Agate Beach, Oregon, USA (Wise and Tschernich, 1976). Centre of cluster.
10. Dachiardite, Tsugarwa, NE Japan (Yoshimura and Wakabayashi, 1977). Also 0.02 Ba.

Oscillation and Weissenberg photographs of svetlozarite showed multiple spots because of non-parallelism of crystals, even in tiny splinters for a spherulitic aggregate. In addition, the diffraction patterns showed multiple spots linked by diffuse streaks in positions consistent with irregular periodic twinning on (001) of a dachiardite-type unit cell with $a$ 18.7, $b$ 7.5, $c$ 10.3 Å, $\beta$ 108° and space group $C2/m$. This choice of cell dimensions follows Alberti (1975) and differs from that used by Gottardi and Meier (1963).

The details of the periodic twinning are complex, and vary from one crystal to the next. All oscillation photographs about the $b$-axis show strong, sharp spots and weak diffuse streaks on even layer lines. For odd layers, a few weak ill-defined spots occur in streaks extending over about 10° in $\theta$ in the layer line. Zero-level Weissenberg photographs show single sharp 00$l$ diffractions (except for the effect of disorientation of aggregated crystals) but all others are multiple (fig. 1a). The apparent $mm$ symmetry of the $a^*c^*$ plane of the reciprocal lattice results from periodic twinning. The stronger diffractions occur as pairs of sharp spots in the positions (fig. 2) for dachiardite twinning on (001). Midway between each twin pair is a weak, diffuse spot and passing through each triplet is a diffuse streak parallel to $c^*$. The central diffuse spot and the streak are interpreted to be the result of irregular spacing and high frequency of the twin planes (e.g. Smith, 1974, fig. 5-1c, d). Although the geometrical relations are correct for twinning of dachiardite, the intensities of the pairs of sharp spots do not match well with those listed in Table 1 of Gottardi and Meier (1963). There is general
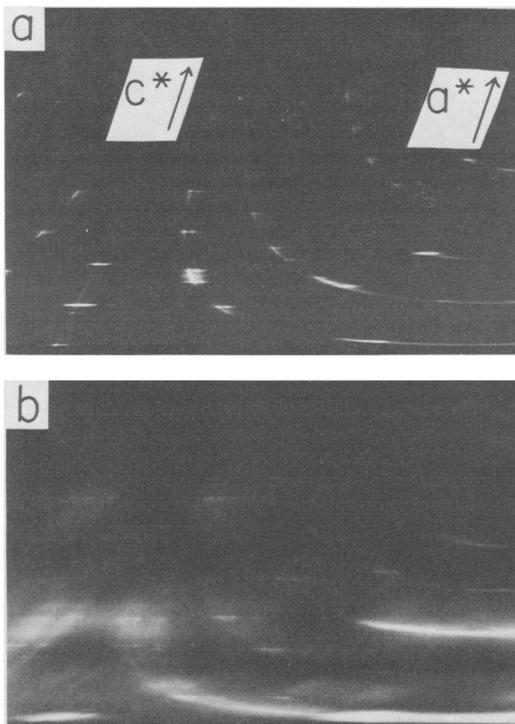


FIG. 1. $b$-axis Weissenberg photographs of a tiny near-parallel aggregate of svetlozarite crystals. (*a*) portion of zero layer showing horizontal streaking from disorientation, and triple diffractions from the periodic twinning. (*b*) corresponding portion of first layer heavily exposed to show the diffuse diffractions. Note especially the diffuse diffractions developed between the row lines forbidden in $C2/m$.
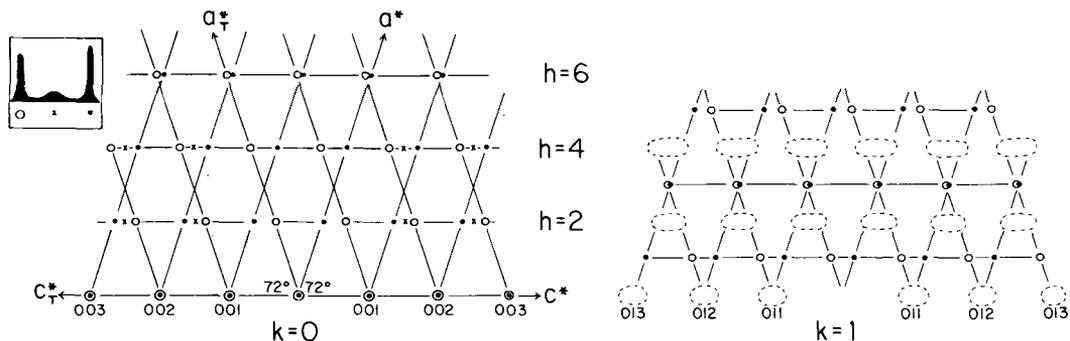
FIG. 2. Reciprocal lattice of svetlozarite. The left-hand drawing shows the positions of the lattice rows for the $k = 0$ layer of a twinned dachiardite, and the inset shows an intensity profile between the diffractions in twin positions (dot and circle) and the auxiliary maximum (cross) resulting from high frequency of the periodic twinning. In the right-hand drawing for the $k = 1$ layer, emphasis is placed on the diffuseness of the diffractions, especially those at positions forbidden by the $C$ face-centring.

agreement for the most intense diffractions, especially for $00l$, but not for the medium and weak ones. This may result from the different chemical compositions of the two specimens. The second layer is similar to the zero layer, but the first and third layers are poorly defined (fig. 1b), as is consistent with the apparent weakness of powder diffractions with $k$ odd. On these odd layers, the diffracted intensity is mostly diffuse and greatly elongated along $c^*$ and also $a^*$. In particular, there is diffuse intensity in positions forbidden by the $C$ lattice-centring of dachiardite (fig. 1b). Weak sharp diffractions are consistent with dachiardiate twinned on (001).

In an attempt to clarify further the nature of the svetlozarite structure, fragments of finely crushed svetlozarite grains were examined in a Philips EM300 TEM. Because of the extremely high sensitivity of svetlozarite to the electron beam, the samples could be observed only with relatively low beam current, and even under these conditions remained crystalline for only 1 to 2 minutes. Because virtually all the crushed grains were (001) cleavage fragments, presumably because of fracture on the twin plane, only sections containing, or lying near to, the $a$ and $b$ axes could be studied; hence detailed observations on the exact nature of the (001) twins could not be made. However, with considerable tilting, it was possible to confirm the X-ray observations that the diffraction intensities are considerably elongated or streaked parallel to $c^*$. In order for this streaking to be readily observable in the electron-diffraction patterns obtained from crushed grains, it necessarily follows that the twinning on (001) must recur every few unit cells.

In addition, electron microscopy (fig. 3a) revealed a high density of faults on (100). The faults typically occur every 40 to 100 Å within the crystal;

that is, every 2 to 5 unit cells. This high density of faulting explains the streaking along $a^*$ of diffraction spots on the X-ray photographs, and in electron-diffraction patterns (fig. 3b). The streaks are particularly prominent for diffractions in the $k$ odd layers; $h + k = 2n$ diffractions required by $C$ face-centring are weakened, and forbidden diffractions with $h + k = 2n + 1$ occur. Although it could be inferred that the $a^*$ streaking results from stacking faults on (100) and that the faults locally disrupt the $C$-face centring, the fragility of the svetlozarite prevented detailed characterization of the faults by quantitative and high-resolution electron microscopy.

*Discussion.* To explain the polysynthetic twinning and faulting of svetlozarite deduced from the diffraction properties of its reciprocal space (fig. 2), it is necessary to consider the crystal structure of dachiardite (Gottardi and Meier, 1963). Like the
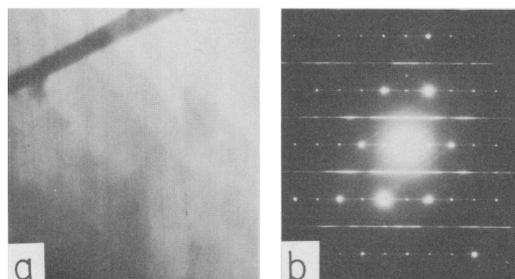


FIG. 3. (a) An electron micrograph of the (100) faults developed in svetlozarite. The faults occur every 2 to 5 unit cells in the structure. Width of field = 0.4 $\mu$m. (b) An electron diffraction pattern of an $a^*b^*$ section. Strong streaking parallel to $a^*$ occurs for $k$-odd reflections, suggesting that the $C$ face centring of the structure is partially violated. (Weak, oblique streaking originates from an adjacent crystal).

other members of the mordenite family, dachiardite contains an aluminosilicate framework based on interlinkage of 4- and 5-rings. Theoretical frameworks were enumerated by Kerr (1963), Sherman and Bennett (1973), and Merlino (1975, 1976), and postulated linkages therefrom are used in a suggested model for twinned and faulted svetlozarite (fig. 4).

The dachiardite framework can be constructed by crosslinking sheets across the (001) plane. A 4-ring at height $y = 1/2$ is linked to two tetrahedra pointing downwards (D), which in turn are linked to a tetrahedron pointing upwards (U) to generate a 5-ring. The adjacent 5-ring is composed of two U and one D, and two tetrahedra from a 4-ring, which must then lie at $y = 0$. Systematic repetition of the DDUU sequence generates the repeat of 18.7 Å along the $a$-axis, and linkage of a U to each D, and a D to each U, generates a 7.5 Å repeat along $b$. To complete the dachiardite structure, adjacent (001) sheets are cross-linked so that each D of one sheet links to a U of the next sheet to give a repeat of 10.3 Å along $c$. The pattern of 0,

$1/2$, U and D gives space group $C12/m1$, and the $\beta$-angle turns out to be 108° for the particular chemical bonds in dachiardite.

Twinning on (001) can be obtained with either a mirror operation or a $b$-glide operation. Use of a mirror operation between each (001) sheet of dachiardite type would generate an orthorhombic structure with $a$ 18.7 $b$ 7.5 $c$ 19.6 Å and space group $Ccmm$, whereas the glide operation would give another orthorhombic structure with the same cell dimensions but a different space group, $Ccma$. The latter (fig. 4, bottom) preserves the UD linkage between adjacent dachiardite sheets whereas the former generates UU and DD linkages. Furthermore the latter does not produce a displacement along $b$ whereas the former does. To obtain periodic twinning, the twin operations are used irregularly. In fig. 4, three glide operations are inserted to give one unit cell of $Ccma$ as a twin boundary between two blocks of twinned dachiardite. Because the inter-layer linkages are tilted, each twin operation causes a small change of geometry



dachiardite                    Ccma twin boundary                    dachiardite
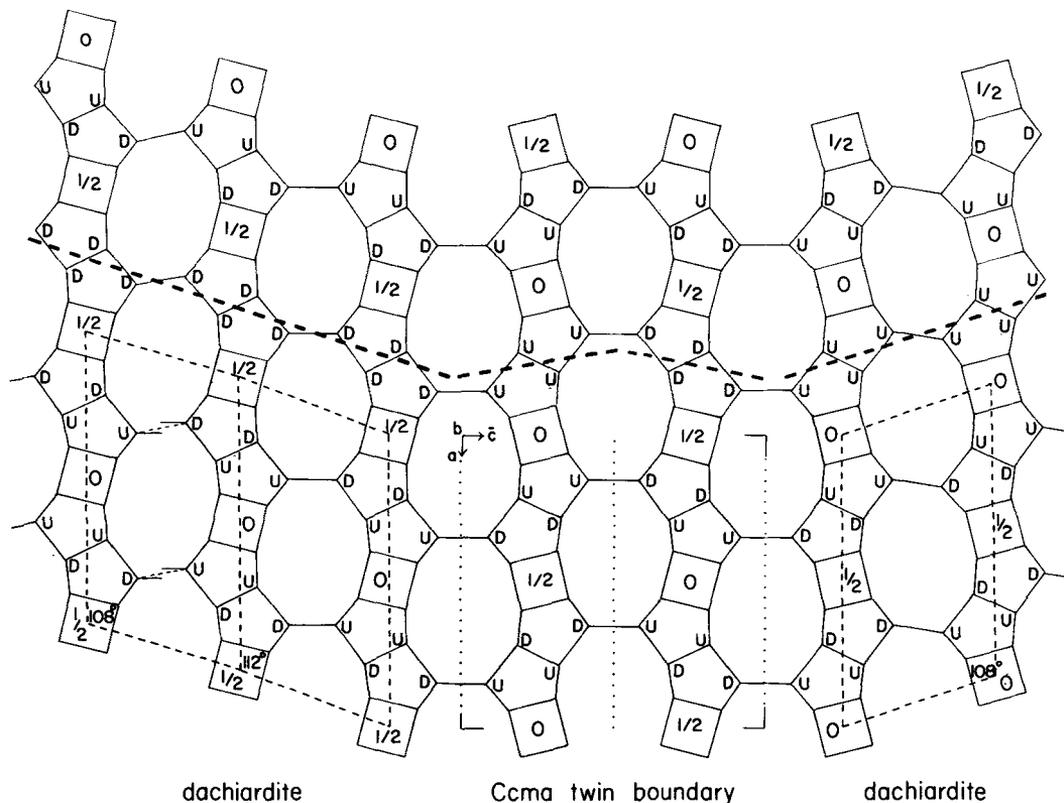
FIG. 4. Symbolic drawing of a possible twin boundary and stacking fault in dachiardite. Small dashes outline unit cells of dachiardite. Dots show the $b$ glide operations that generate the $Ccma$ twin boundary; replacement by mirror operations would give a $Ccmm$ twin boundary. Heavy dashes show the stacking fault. Note that the twin operation and the stacking fault can operate independently, and domains rather than lamellae could occur.

(cf. linkages at lower left). Because the intensities of the svetlozarite diffraction patterns were much weaker for $k$ odd than $k$ even, the $Ccma$ interface is preferred to the $Ccmm$ type, but both might actually occur. Preferred occurrence of the $Ccma$ type would be expected because the UD linkages generate a row of 5-rings along the $b$-axis whereas the UU and DD linkages generate a row of alternating 4- and 6-rings.

For a dachiardite from Alpe di Siusi (Alberti, 1975), the diffraction pattern was attributed by Merlino (1976 and pers. comm.) to a twinned intergrowth of dachiardite-type structure and a 'modified-dachiardite' structure derived by displacement by $(a + b)/2$ of alternate chains. Although such an intergrowth would undoubtedly produce disorder for $k$-odd diffractions, it would not produce the (001) twinning and (100) feature found in svetlozarite. Furthermore, use of a mirror operation to generate (100) faults through the 4-rings in the 'hypothetical structure no. 1' of Merlino (1976) is not advocated here because the frequent occurrence of such faults would be structurally incompatible with the observed high frequency of (001) twins.

A more reasonable explanation of the (100) feature is stacking faults in the $a$ direction (fig. 4 upper) so that the interface has 4-rings at the same height along $b$ instead of differing by $b/2$. Such a fault requires replacement of adjacent 5-rings by a zig-zag of 4-rings (UUUU or DDDD). The fault is structurally compatible with the (001) periodic twinning, and the boundary of the stacking fault could zig-zag in response to the twinning. Alternatively, the twin and fault operations could operate independently to produce domains instead of continuous lamellae. Chains of 4-rings were described by Sherman and Bennett (1973) in hypothetical structures related to mordenite. Although the 4-ring chains and associated 6-rings are presumably less favourable energetically than the linked 5-rings of dachiardite and mordenite, 4-ring chains are common in framework structures.

*Conclusion.* Svetlozarite is related to the ideal dachiardite structure (Gottardi and Meier, 1963) by irregular periodic twinning and faulting, and it is not a topologically distinct member of the mordenite family of zeolites. However the twin interfaces and fault boundaries are local representatives of hypothetical new frameworks not yet found in ordered materials, and it may prove convenient to use the term svetlozarite-type for the $Ccma$ framework when further study has been made of dachiardite-type materials. It will be interesting to see whether the structural features will correlate with the chemical composition (e.g. the ratios of Na, K, and Ca); perhaps svetlozarite might be used as a term for a dachiardite with one K per unit cell (cf. Table I). In the meantime, it appears to be sufficient for the name dachiardite to be used for any zeolite whose X-ray powder pattern can be indexed with a monoclinic unit cell ($a$ 18.7 $b$ 7.5 $c$ 10.3 Å, $\beta$ 108°, $C2/m$) no matter what the details of the intensities and breadths of the lines.

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