

## Structural Relationships in Tetrahedral Frameworks: Reflections on Cristobalite

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Twinning on the unit cell level of the idealized cristobalite structure, using a mirror plane as the twin and composition plane, provides a simple relationship between 14 tetrahedral frameworks. Of these, 9 are found among the aluminosilicates with examples ranging from (stuffed) silicas to zeolites and include the framework types of nepheline hydrate I, zeolite Li-A(BW), gismondine, phillipsite, merlinoite, tridymite, paracelsian, and monoclinic  $\text{CaAl}_2\text{Si}_2\text{O}_8$ . Similar twinning relates the frameworks of natrolite, thomsonite, and edingtonite.

### Introduction

The tektosilicates have structures based on a framework of corner-sharing tetrahedra of O atoms coordinating a central Si(Al) atom. This type of tetrahedral framework can be represented by a four-connected three-dimensional net with Si(Al) at the nodes. The problem of describing a structure which is infinite in three dimensions is usually solved by dissecting it into subunits that are finite in one dimension (slabs, sheets, 2D nets) or in two dimensions (columns, chains, rods, tubes, strings) or finally in three dimensions (blocks, clusters, secondary building units, polyhedral cages). The frameworks discussed here will be described as being built from a set of parallel chains, and some early examples of this are the descriptions of natrolite, scapolite (1), and cristobalite (2).

The subunits mentioned above can also be used to systematize structures; e.g., the classification of zeolites based on secondary building units (3, 4) may be compared

with the proposed classification of tektosilicates based on chains (5). Modification and recombination of these subunits can generate new possible structures as shown, e.g., in the networks formed by combination of natrolite chains (6) and the chains, sheets, and frameworks derived from the secondary building unit 4-4-1 (7). Smith (8-10) has derived and characterized a large number of 3D nets starting from 2D nets connected by perpendicular links or simple chains.

A rather novel approach for tetrahedral frameworks is the use of the symmetry transformations, *translation*, *rotation*, and *reflection*, to describe the repetition of the subunits. *Unit cell level twinning* or *chemical twinning* was introduced by Andersson and Hyde (11) to generate complex structures from a simple parent. A general definition and a review of the numerous applications of this method based mainly on structures containing hcp and ccp arrays of atoms, are found in (12). The definition of twin plane, composition plane, and twin

axis is identical to the one for macroscopic twins with the twinning regularly repeated on the unit cell level. Throughout this discussion the twin and composition plane used is a mirror plane, except in one case. Two mirror planes at right angles generate a fourling which can be turned into a *unit cell level fourling* (13) by repeated twinning.

This work was initiated by the discovery that the close relationship between the structures of cristobalite, nepheline hydrate I (14) and the zeolite Li-A(BW) could be rationalized in terms of unit cell level twinning.

### Twinning of C9

The three most simple chains of tetrahedra and the way in which they are related by twinning are shown in Fig. 1. The twinning operation generates chains in a state of maximum expansion and also provides a simple mechanism for turning a single chain into a double chain. In this discussion, examples of structures with tetrahedral frameworks will be taken mainly from the aluminosilicate family with the name of a compound in italics to indicate a *framework type*. Theoretical framework types are designated by Smith's notation. Properties of these theoretical nets as well as literature references for the many existing structures

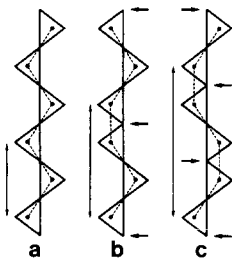


FIG. 1. The most simple single chains of tetrahedra, (a) zigzag (*Zweier*) (b) saw (*Dreier*) (c) crankshaft (*Vierer*). The tetrahedra are viewed along an edge and the dashed line connects their centers. Twin planes perpendicular to the plane are indicated by small arrows.

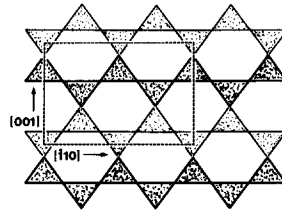


FIG. 2. The C9 structure seen along [110].

mentioned later in this text are given in (8-10).

Various cristobalites,  $\text{SiO}_2$ ; high carnegite  $\text{NaAlSiO}_4$ ; and many nonsilicates have the simple cristobalite framework (15), which when idealized to the highest possible symmetry,  $Fd3m$ , is the C9 structure shown in Fig. 2 with the O atoms occupying half the number of the positions in ccp. The C9 structure can be built from parallel zigzag chains along [110] or alternatively along  $[\bar{1}10]$ . Hereafter the chain directions will refer to the parent structure in the heading of each section. Twinning of C9, shown in Fig. 3, generates the framework type of nepheline hydrate I,  $\text{NaAlSiO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  which is composed of saw chains parallel to  $[\bar{1}10]$ . The framework type of Li-A(BW),  $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ , consisting of crankshaft chains along [110], is then produced by reducing the distance between the twin planes. This framework is also found in  $\text{CsAlSiO}_4$  and  $\text{RbAlSiO}_4$ . In *nepheline hydrate I* half of the single zigzag chains along [110] are turned into double chains, while in *Li-A(BW)* there are only

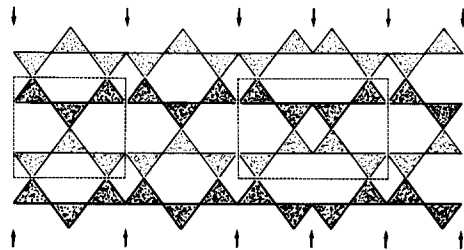


FIG. 3. *Nepheline hydrate I* (left) and *Li-A(BW)* (right).

TABLE I  
SUMMARY OF FRAMEWORK TYPES GENERATED BY  
TWINNING OF C9

Combination of chains along [110] and $\bar{1}\bar{1}0$	Framework type
zigzag-zigzag	<i>cristobalite</i>
zigzag-saw	<i>nepheline hydrate I</i>
zigzag-crankshaft	<i>Li-A(BW)</i>
saw-saw	new <sup>a</sup>
saw-crankshaft	102
crankshaft-crankshaft	<i>gismondine</i>

<sup>a</sup> A network with highest space group  $P\bar{4}m2$ , cell contents  $T_9O_{18}$  and approximate cell dimensions  $a$  and  $c = 8 \text{ \AA}$ .

double zigzag chains. Twinning of the zigzag chains parallel to [110] generates more frameworks and different combinations of twinning in the two directions generate six frameworks in all (see Table I).

### Twinning of Gismondine

The most open framework type generated so far is that of gismondine  $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 8\text{H}_2\text{O}$  which also exists in zeolite Na-Pl,  $\text{Na}_3\text{Al}_3\text{Si}_5\text{O}_{16} \cdot 6\text{H}_2\text{O}$  and in amicite  $\text{K}_2\text{Na}_2\text{Al}_4\text{Si}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$  (16). The idealized gismondine framework in the upper left part of Fig. 4 contains one set of double crankshaft chains parallel to [100] and another set to  $\bar{0}10$ .

An unlimited number of new structures including *paracelsian*, can be derived by rotating the chains along [100] by a multiple of  $\pi/2$  rad, while twinning produces two framework types, found in *phillipsite*  $\text{KCaAl}_3\text{Si}_5\text{O}_{16} \cdot 6\text{H}_2\text{O}$  or *harmotome*  $\text{BaAl}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$  and *merlinoite*  $\text{K}_5\text{Ca}_2\text{Al}_5\text{Si}_{23}\text{O}_{64} \cdot 24\text{H}_2\text{O}$  or  $\text{BaAlSi}_2\text{O}_6$  (Cl,OH). For condensed representation, Fig. 4 shows a "macroscopic" fourling of *gismondine*, with pieces of the new structures generated along the composition planes. Complete structures are generated by the familiar repeated twinning. The three

frameworks of Fig. 4 are the only structures, of those theoretically possible (9), in which all the links between two different chains consist of two tetrahedra pointing in the same direction. Only this type of link allows the crankshaft chains to expand to the typical repeat distance of  $\sim 10 \text{ \AA}$ . However the rather unexpanded chain (9.2  $\text{ \AA}$ ) of  $\text{BaAlSi}_2\text{O}_6$  (Cl,OH) should be noticed. Compounds representing new frameworks in this group will have at least slightly higher framework density than *gismondine*, *phillipsite*, and *merlinoite*, since they will contain links of tetrahedra pointing in opposite directions as in *paracelsian* (chain repeat 8.6  $\text{ \AA}$ ).

It can be noted that the first six structure types can also be represented by fourlings; thus a fourling of C9 gives *nepheline hydrate I*, *Li-A(BW)*, and *gismondine*, and a fourling of *nepheline hydrate I* gives a new framework, 102, and *gismondine*.

### Twinning of C10

If the direction of the twin planes is

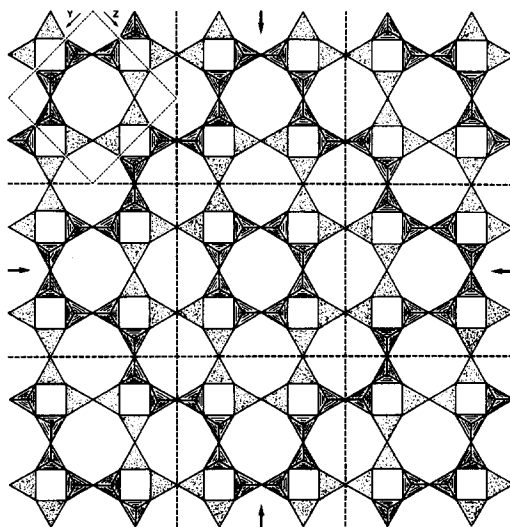


FIG. 4. Fourling of *gismondine* viewed down [100] with *phillipsite* along the twin planes and *merlinoite* in the center.

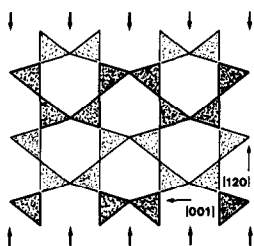


FIG. 5. The C10 structure seen along [100].

chosen as shown in Fig. 5, the idealized tridymite structure (C10) is derived from C9, and compared to the twinning in Fig. 3 this is a form of *swinging twinning* (17). The C10 structure has the maximum symmetry,  $P6_3/mmc$ , of the tridymite framework which is present in the different types of tridymite  $\text{SiO}_2$ , in stuffed derivatives like kalsilite  $\text{KAlSiO}_4$  and nepheline  $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ , as well as in several nonsilicates. It may be noted that the O atoms in C10 are in hcp positions (ccp in C9). Hcp was described some time ago as twinned ccp (18).

In the fourling of C10 (projected along [001] in Fig. 6) at least five frameworks can be recognized. The series *tridymite*, 97, and *paracelsian* is analogous to *crystalobalite*, *nepheline hydrate I*, and *Li-A(BW)* with the chains in the [010] direction as single zigzags in tridymite, single saws in 97, and single crankshafts in *paracelsian*. All three structures contain crankshafts along [001] which are closer to the real structures than the crankshaft in Fig. 1. Half the number of crankshaft chains are doubled in 97 and all of them in *paracelsian*, a framework type which exists in collapsed versions in one of the forms of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  and in a number of similar compounds containing Ca, Sr, Ba, Al, Be, Ga, Ge, P, and Si.

Twinning in the perpendicular direction introduces four-rings and gives the series *monoclinic CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>*, 99 and 46. *Monoclinic CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>* contains single four-rings, 99 single and double rings in equal proportions and 46 only double rings.

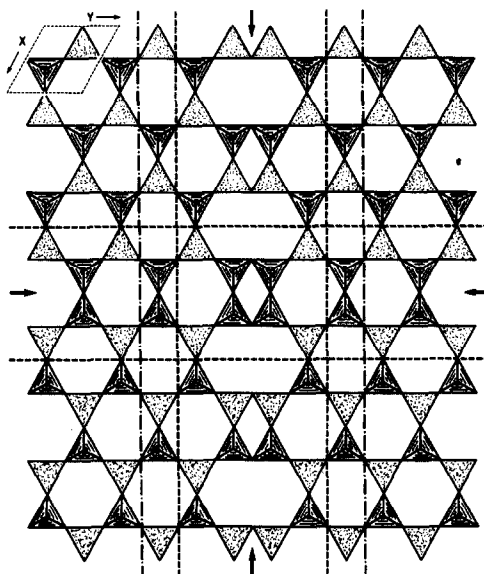


FIG. 6. Fourling of C10 viewed along [001] with *monoclinic CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>* in an east-west direction, *paracelsian* (dashed lines) and 97 (dot-dashed lines) in the north-south direction. Framework 46 (inner rectangle) and 99 (outer rectangle), can be seen in the center.

*Monoclinic CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>* is a synthetic phase with feldspar composition and 46 was proposed by Barrer for zeolite Na-Pl. The chains along [010] for the last three structure types are similar to those in *tridymite*, 97, and *paracelsian*.

Beryllonite  $\text{NaBePO}_4$ , trimerite  $\text{CaMn}_2\text{Be}_3\text{Si}_3\text{O}_{12}$ ,  $\text{NaAlSiO}_4$  and similar substances containing K, Ga, and Ge (19) have a common framework which is a unit cell level twin of C10, shown in Fig. 7. In

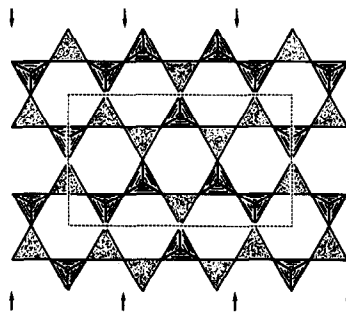


FIG. 7. The framework type of beryllonite.

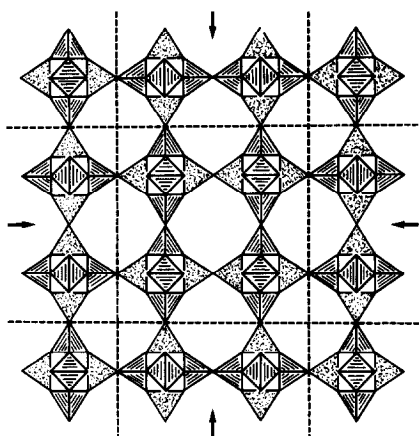


FIG. 8. Fourling of *natrolite* viewed down [001] with *thomsonite* along the twin planes and *edingtonite* in the center. The four different heights of the chains in *natrolite* are not indicated.

this case the twin operation is not a reflection but a rotation of  $\pi$  rad around a twin axis along [001] or [210]. Alternatively *beryllonite* may be derived from C10 by a slip of every second slab employing the slipvector  $(0, 0, \frac{1}{2})$ .

### Conclusion

Unit cell level twinning with a mirror plane as twin plane (and composition plane) provides a simple and visually descriptive way of showing the structural relationship of some well known tectosilicate framework types. Examples are given ranging from (stuffed) silicas to zeolites. The approach works well with a number of frameworks that can be assembled from parallel chains and a last example (Fig. 8) shows that a fourling of *natrolite* gives *thomsonite*

and *edingtonite*. Further, by varying the spacing of the mirror planes the additional five theoretical frameworks of (6) are generated.

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