

Framework Structures Derived from a Novel Type of Trigonal Secondary Building Unit with on-axis T atoms: the Tridymite Group

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Abstract

An infinite series of secondary building units generated around a trigonal axis, with the top and/or bottom T atom coinciding with the symmetry axis allows the systematic enumeration of a novel class of (4; 2)-connected 3D framework structures. Known members of this group are the framework topologies of tridymite, cristobalite, MAPSO-46 (AFS), CoAPO-50 (AFY) and beryllophosphate-H (BPH). Adjacent T atoms on a trigonal axis with a T -O- T bond angle of 180° (T_2 unit) present in all structures confer some specific properties on this class of compounds.

Introduction

The systematic enumeration of (4; 2)-connected 3D nets (this notation denotes framework structures extended in three-dimensional space with every framework T atom being tetrahedrally coordinated by oxygen atoms, while every oxygen atom itself is connected to two T atoms) has proven to be a valuable tool in the structural classification of zeolites and molecular sieves (Alberti, 1979; Kerr, 1963; Sato, 1979; Smith, 1977, 1978, 1979; Smith & Bennett, 1981, 1984; Barrer & Villiger, 1969; Bennett & Smith, 1985). At the same time it predicts the existence of as yet unknown phases of potential importance. There are several ways of performing such an enumeration: by using (i) secondary building units (SBU's) (Meier, 1968), (ii) various configurations of chains and/or sheets (e.g. Barrer, 1984), (iii) polyhedral cages (e.g. Smith & Bennett, 1981; Liebau, Gies, Gunawardane & Marler, 1986), (iv) various operators (e.g. Barrer, 1984) such as the sigma (σ) transformation (Shoemaker, Robson & Broussard, 1973), (v) coordination sequences and radial distribution functions (Meier & Moeck, 1973, 1979), (vi) coordination networks (Sato, 1983; Sato & Ogura, 1981), (vii) slipping schemes (Sato & Gottardi, 1982) and (viii) the enumeration of 2D nets extended to 3D nets by the use of supplementary linkages (e.g. Smith, 1977, 1979). Detailed structural information on zeolite frameworks can be found in the recently revised *Atlas of Zeolite Structure Types* (Meier & Olson, 1987) and in a comprehensive review (Smith, 1988).

The theoretical derivation of open nets is of much interest to the zeolite structural chemist (Barrer & Villiger, 1969; Brunner, 1979; Meier, 1986; Smith & Dytrych, 1984).

During the search for an adequate structure model for zeolite Linde Q (Breck & Acara, 1961), it soon became apparent that the conventional way of proceeding (by using hexagonal rings) never could lead to a solution for this hexagonal framework (Andries, Bosmans & Grobet, 1990). The structure model appeared to belong to a novel group of framework structures whose systematic enumeration is presented here. The present report is the first in a series of three papers dealing with framework structures of the tridymite group (this report), topologically related frameworks (Andries & Bosmans, 1990) and a general classification scheme for three-dimensional nets constructed from trigonal columns (Andries, 1990). In the third paper a compilation is given of all enumerated nets and of all definitions, notations and abbreviations used throughout.

Firstly, a new set of cages will be enumerated: a non-integral multiple of three T atoms in a hexagonal net is only possible if at least one node is coinciding with the trigonal symmetry axis. These cages can then be connected laterally in two ways to form sheets with hexagonal symmetry. Finally, the resulting sheets can be joined vertically into 3D nets.

Establishing the crystallographic basis for the topology of (4; 2)-connected 3D nets constructed from $2T$ trigonal cages

The only way by which hexagonal nets can be constructed with a non-integral multiple of three T atoms per unit cell is by placing one or more tetrahedra on a trigonal axis, *i.e.* point positions of type $00z$, $1/3\ 2/3\ z$ and $2/3\ 1/3\ z$. The present enumeration focuses on 3D nets that can be constructed from cages between two oppositely oriented tetrahedra on a trigonal axis in such a way that the top T atom points upwards and the bottom T node points downwards (Fig. 1). An infinite number of cages can be thought of with any number of off-axis tetrahedra inserted between these two. These off-axis T atoms are

necessarily coplanar in planes perpendicular to the trigonal axis. In our systematic enumeration n denotes the number of horizontal stacks between these top and bottom T atoms. We are not limited to only three off-axis T atoms in the same horizontal plane: each stack can contain $(3 \times m)$ T atoms, where m is a positive integer. The present enumeration has been restricted to a maximum value of $m = 2$. The various ways by which adjacent horizontal stacks can be connected to form cages can be described by building all possible sequences starting from the top T atom on the trigonal axis and extending the sequence downwards. Two types of cages will be enumerated: (i) cages without any single three-membered ring ($S3R$) perpendicular to the trigonal axis and (ii) cages with such (a) ring(s).

1. Cages without three-membered ring(s) perpendicular to the trigonal axis

First stack: We fix the orientation of the top T atom (up), such that it can be linked to three T atoms in the first horizontal stack (Fig. 2). Characterizing a horizontal stack by its number of trigonally related T atoms ($3 \times m$), this first sequence is denoted by 1-3.

The possible designations for any horizontal stack are 1, 3 or 6 because of the restriction to $m = 2$ made above. The first horizontal stack can only be 3; 1 and 6 are excluded for obvious reasons: the former possibility is not plausible, the latter is not possible because all atoms of a particular stack are coplanar and each of them has to be connected to at least one atom of the previous layer.

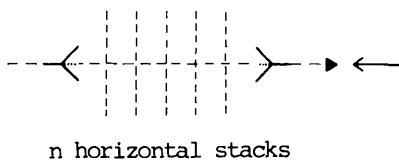


Fig. 1. The construction of a $2T$ trigonal cage. The arrow indicates the view direction for Figs. 4 to 8.

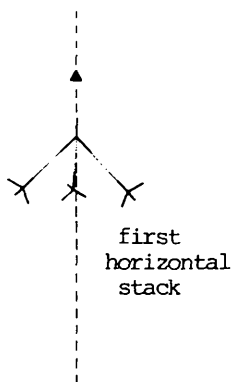


Fig. 2. The sequence represented is denoted by 1-3.

Second stack: The second horizontal stack is denoted by 1, 3 or 6, as well as by a letter describing the particular way by which it is linked to the previous layer. There are several ways for doing this: in our notation this letter (placed between brackets) will be indicated between subsequent stack symbols. This letter will only be used if there is more than one possibility for connecting subsequent stacks. The rules governing the ways of linking subsequent layers are represented in Fig. 3.

A second one-membered stack (1MS) closes the cage (1-3-1, simplest trigonal cage).

A three-membered second stack can be linked to the first one in two distinct ways, denoted by S and C in Fig. 4 to form 1-3(S)3 or 1-3(C)3. Figs. 4 to 8 are schematic representations of the connectivities down the trigonal axis (indicated by the arrow in Fig. 1) and are no actual projections in order to avoid overlap between subsequent stacks. Returning to Fig. 4, the symbol S indicates that the connected T atoms are situated in the same (S for same) vertical planes through the trigonal axis and C indicates the other possibility (C for changed). In other words, S and C denote an 'eclipsed' and a 'staggered' configuration respectively.

Furthermore, an important difference in connectivity can be noted between S - and C -connected

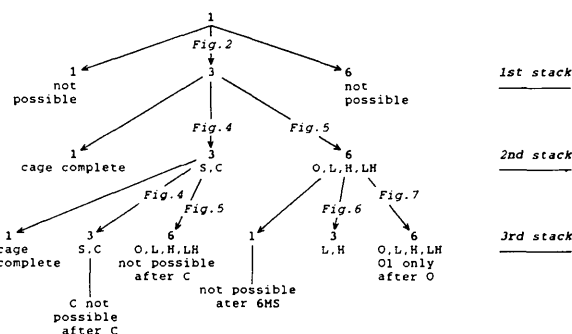


Fig. 3. Schematic representation of all possible stack sequences, starting from the top on-axis tetrahedron in Fig. 1, up to the third horizontal stack. Figures represent numbers of tetrahedra in a horizontal layer. Letters refer to modes of linking (with the previous layer) illustrated in Figs. 4 to 8. Avoidance rules are indicated.

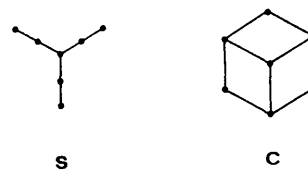


Fig. 4. The two possibilities for connecting a second 3MS to the previous 1-3 sequence are denoted (a) 1-3(S)3 (eclipsed or *cis*) and (b) 1-3(C)3 (staggered or *trans*). T atoms are represented by circles; oxygen atoms (not shown) lie approximately in the middle between two connected T atoms or are not 2-connected.

3MS's: the *T* atoms of an *S*-connected 3MS have only one bond with the previous stack while the *T* atoms of a *C*-connected 3MS have two, leaving three and two free bonds, respectively.

The second stack can also be six membered and there are four distinct ways in which such a stack can be connected to the previous 3MS as represented in Fig. 5.

The *T* atoms of this 6MS can be connected in the same layer in three different ways: (i) none of them is connected to a *T* atom of the same stack (Fig. 5*a*, *O* for open); (ii) the *T* atoms of this 6MS are interconnected in pairs. In that case there are two options, designated *L* (Fig. 5*b*, *L* for low-membered rings, actually *S3R*'s) and *H* (Fig. 5*c*, *H* for high-membered rings, actually *S5R*'s); (iii) all *T* atoms of the 6MS form a single six-ring, designated *LH* [Fig. 5(*d*), *LH* for low- and high-membered rings, actually *S3R*'s and *S5R*'s].

Third stack: No two (or more) *C*-connected 3MS's can follow each other because a *C*-connected 3MS has only three free bonds down while it has six bonds with the previous 3MS.

The rules for a 3-6 connection were described above (*i.e.* *O*, *L*, *H*, *LH*). However, because a 6MS needs six bonds at least with a previous stack as well as with a subsequent layer, a 6MS cannot succeed a *C*-connected 3MS. A 1MS cannot succeed a 6MS for obvious reasons. A 3MS can be linked to a 6MS in two distinct ways as visualized in Fig. 6.

Because there are four possible 1-3-6 configurations, eight possible 1-3-6-3 sequences result. If the 6MS is not an *S6R*, lowest-membered rings [Figs. 6(*a*), (*c*), (*e*): *L*] or highest-membered rings [Figs. 6(*b*), (*d*), (*f*): *H*] are formed. If the 6MS is an *S6R*, the sequence of rings (starting from the *T* atoms of the last 3MS and moving to the central *T* atom) is used to assign the designations *L* [Fig. 6(*g*), actually *S3R*+*S3R*] or *H* [Fig. 6(*h*), actually *S3R*+*S5R*].

Two subsequent 6MS's can be connected in four different ways as represented in Fig. 7. The *T* atoms of the last 6MS can be connected in the same layer in three different ways: (i) none of them is connected to a *T* atom of the same stack [Figs. 7(*a*), (*f*), (*j*), (*n*): *O*]; (ii) the *T* atoms of this 6MS are connected

in pairs. Criteria similar to those in Fig. 6 were used for assigning the designations *L* [Figs. 7(*b*), (*g*), (*k*), (*o*)] or *H* [Figs. 7(*c*), (*h*), (*l*), (*p*)]. (iii) All *T* atoms of the last 6MS form an *S6R* [Figs. 7(*d*), (*i*), (*m*), (*q*): *LH*]. Finally, the last 6MS can be *O1*-connected to a previous *O*-connected 6MS (Fig. 7*e*). As can be

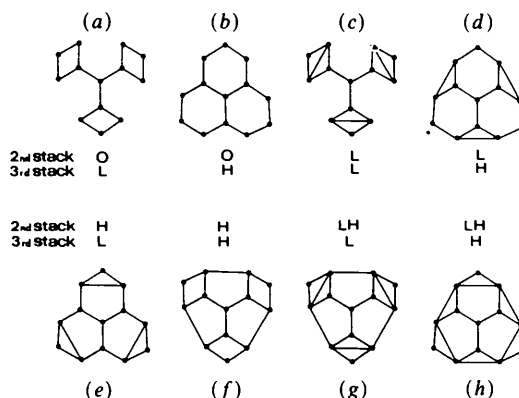


Fig. 6. There are eight possible 1-3-6-3 sequences. See Fig. 4 for explanation on representations. Sequence designations: (a) 1-3(*O*)6(*L*)3; (b) 1-3(*O*)6(*H*)3; (c) 1-3(*L*)6(*L*)3; (d) 1-3(*L*)6(*H*)3; (e) 1-3(*H*)6(*L*)3; (f) 1-3(*H*)6(*H*)3; (g) 1-3(*LH*)6(*L*)3; (h) 1-3(*LH*)6(*H*)3.

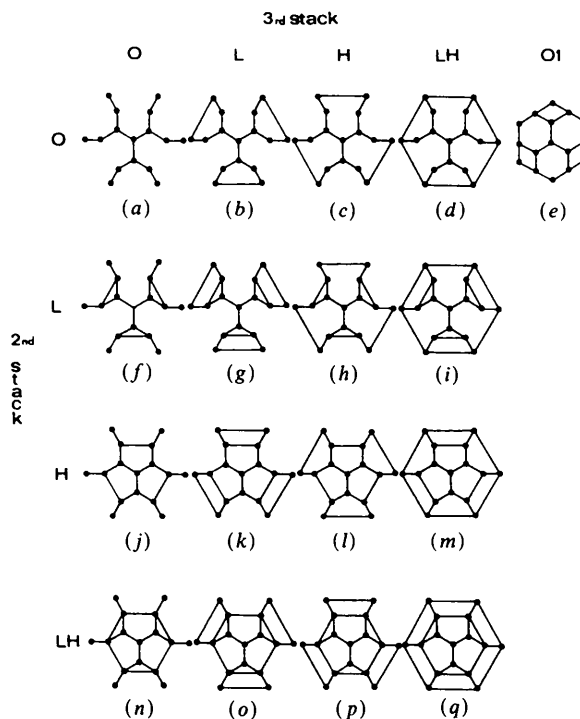


Fig. 7. There are seventeen 1-3-6-6 sequences possible. See Fig. 4 for explanation on representations. Sequence designations: (a) 1-3(*O*)6(*O*)6; (b) 1-3(*O*)6(*L*)6; (c) 1-3(*O*)6(*H*)6; (d) 1-3(*O*)6(*LH*)6; (e) 1-3(*O*)6(*O1*)6; (f) 1-3(*L*)6(*O*)6; (g) 1-3(*L*)6(*L*)6; (h) 1-3(*L*)6(*H*)6; (i) 1-3(*L*)6(*LH*)6; (j) 1-3(*H*)6(*O*)6; (k) 1-3(*H*)6(*L*)6; (l) 1-3(*H*)6(*H*)6; (m) 1-3(*H*)6(*LH*)6; (n) 1-3(*LH*)6(*O*)6; (o) 1-3(*LH*)6(*L*)6; (p) 1-3(*LH*)6(*H*)6; (q) 1-3(*LH*)6(*LH*)6.

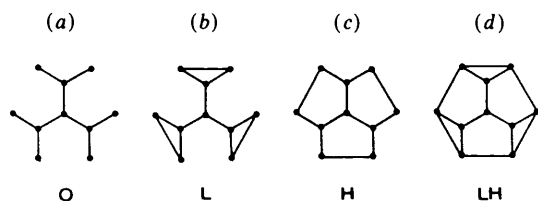


Fig. 5. The four possibilities for connecting a second 6MS to the previous 1-3 sequence are denoted (a) 1-3(*O*)6, (b) 1-3(*L*)6, (c) 1-3(*H*)6 and (d) 1-3(*LH*)6. See Fig. 4 for explanation of representations.

seen in the figure, this *O*1-connected 6MS has 12 bonds up and six free bonds down. There are 17 possible 1-3-6-6 sequences.

Further possibilities: It is evident that most of the cited principles can be applied systematically when the stacking sequence is extended infinitely. From Fig. 3 it is clear that the number of possible sequences becomes very high when more than three horizontal stacks are involved. No more than two *S*6*R*'s can follow each other for geometrical reasons. A 3MS following a 6MS has only three free bonds down and thus cannot be succeeded by a 6MS nor by a *C*-connected 3MS as should be obvious from earlier considerations.

Of specific interest is the sequence 1-3(*O*)6(*O*1)6 (Fig. 7*e*) which gives rise to two enantiomorphic configurations [Figs. 8(*a*), (*b*): *A*1 and *B*1] when followed by a 3MS or to four sequences of which two again are enantiomorphic [Figs. 8(*c*) to (*f*): *O*, *A*2, *B*2, *LH*] with a subsequent 6MS.

Horizontal stacks with $m > 2$ (e.g. $m = 4$ for a 12MS) can be added following the 1-3(*O*)6 configuration represented in Fig. 5(*a*) (i.e. from the third horizontal stack on). This and other possibilities will not be treated in any further detail here. The hexagonal unit-cell *a* parameter of the resulting 3D nets to be enumerated later becomes quite high.

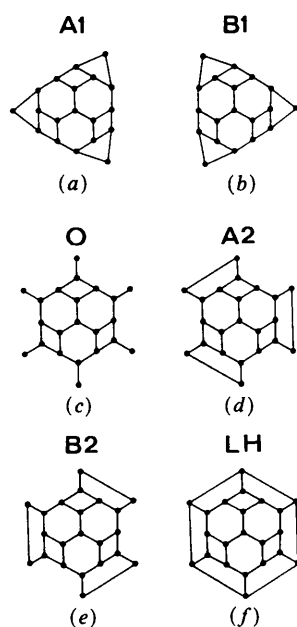


Fig. 8. Further extension of the sequence 1-3(*O*)6(*O*1)6 (Fig. 7*e*) with a fourth horizontal stack gives two enantiomorphic pairs (*a*, *b*) and (*d*, *e*). See Fig. 4 for explanation of representations. Designations: (*a*) 1-3(*O*)6(*O*1)6(*A*1)3; (*b*) 1-3(*O*)6(*O*1)6(*B*1)3; (*c*) 1-3(*O*)6(*O*1)6(*O*)6; (*d*) 1-3(*O*)6(*O*1)6(*A*2)6; (*e*) 1-3(*O*)6(*O*1)6(*B*2)6; (*f*) 1-3(*O*)6(*O*1)6(*LH*)6.

2. Cages with at least one three-membered ring perpendicular to the trigonal axis

In the preceding enumeration, the possibility of a 3MS forming an *S*3*R* was excluded. This is a special case: cages with this type of ring can be enumerated more easily starting at the *S*3*R* and moving to an on-axis *T* node, because at the other side of the *S*3*R* a different or identical sequence may occur (in the topological symmetry, the *S*3*R* may lie in a mirror plane perpendicular to the trigonal axis) (Fig. 9).

Let $n(1)'$ denote the number of horizontal stacks between the *S*3*R* and the top *T* atom and $n(1)''$ the number of stacks between the *S*3*R* and the bottom *T* atom, then $n = n(1)' + n(1)'' + 1$ in general and $n = 2n(1) + 1$ if $n(1)' = n(1)'' = n(1)$ (e.g. when the *S*3*R* lies in a mirror plane).

The systematic enumeration of all possible sequences between an *S*3*R* and an on-axis *T* atom may be represented schematically in the same way as in Fig. 3. Indeed, both the *S*3*R* and the on-axis *T* atom have three free bonds down and the same rules apply as above with the following exceptions:

(i) two sequential 3MS's can be connected *S*, *C* (Fig. 4) or *LH* (designating an *S*3*R* in analogy with an *LH*-connected 6MS);

(ii) the sequence *S*3*R*-1 [or 1(*LH*)3, 3^4] (3^4 is a face symbol, denoting a polyhedral cage bounded by four three-membered rings) is not plausible and neither is the double three-membered ring [*S*3*R*(*LH*)3, *D*3*R*, 3^24^3];

(iii) an *S*3*R* has three free bonds for connecting the next stack and for that reason it cannot be followed by a *C*-connected 3MS nor by a 6MS. Thus a 3MS succeeding a 6MS can only be *L*- or *H*-connected (as in Fig. 6).

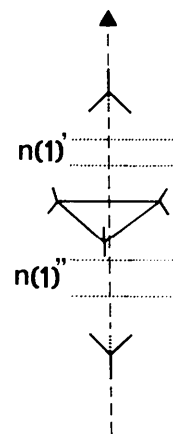


Fig. 9. The construction of a 2*T* trigonal cage by inserting horizontal stacks at both sides of an *S*3*R* perpendicular to the trigonal axis.

Table 3. Summarizing the 74 possible distinct group *D* 1*T* trigonal cages up to $n(1) = 4$, used for the subsequent enumeration of the 101 possible distinct group *C* 2*T* trigonal cages up to $n = 6$

$n(1)$	Sequence	Different cages
0	/	0
1	<i>S</i> 3 <i>R</i> -3-1	1
2	<i>S</i> 3 <i>R</i> -3-3-1	2
3	<i>S</i> 3 <i>R</i> -3-3-3-1	4
	<i>S</i> 3 <i>R</i> -3-6-3-1	8
4	<i>S</i> 3 <i>R</i> -3-3-3-3-1	9
	<i>S</i> 3 <i>R</i> -3-3-6-3-1	8
	<i>S</i> 3 <i>R</i> -3-6-3-3-1	8
	<i>S</i> 3 <i>R</i> -3-6-6-3-1	34

*S*3*R* and an on-axis *T* atom (Fig. 9) results in the total of 74 different sequences up to $n(1) = 4$. These sequences are summarized in Table 3.

In order to enumerate all possible sequences between two on-axis *T* atoms (as in Fig. 1) up to $n = 6$, each sequence derived in Table 3 (at one side of the *S*3*R*) can be combined with every sequence of the same table (at the other side of the *S*3*R*) as long as $n = n(1)' + n(1)'' + 1$ does not exceed 6. Accounting for the fact that two 'inversed' sequences lead to the same cage, the total number of different sequences adds up to 101. To illustrate this enumeration, sequence *S*3*R*-3(*LH*)3(*S*)3-1 [$n(1)' = 3$] can be combined with *S*3*R*-3(*S*)3-1 [$n(1)'' = 2$] to result in cage 1-3(*LH*)3(*S*)3(*LH*)3(*S*)3(*S*)3-1 ($n = 6$), which is identical to cage 1-3(*S*)3(*LH*)3(*S*)3(*LH*)-3(*S*)3-1. Schematic drawings for cages 1-3(*LH*)-3(*S*)3-1 and 1-3(*C*)3(*LH*)3(*S*)3(*C*)3-1 are given in Figs. 10(c1) and (c2), respectively.

Some general remarks:

(i) from the previous enumeration, the total of 218 different cages can be derived up to $n = 5$;

(ii) all group *A* cages are composed of even-membered rings only (e.g. Fig. 10a); all group *B* and group *C* cages are composed of odd- (and even-) membered rings [e.g. Figs. 10(b) and (c)];

(iii) practically all 2*T* trigonal cages enumerated have only one trigonal axis. Nevertheless, for two types of cages, all *T* atoms (in pairs) lie on a trigonal axis: firstly the 1-3(*C*)3-1 (*D*4*R*, 4⁶) cage (group *A*) and secondly the 1-3(*H*)6(*H*)6(*H*)3-1 [5^{12} , pentagondodecahedron, *rd* (Smith, 1988)] cage (group *B*);

(iv) From Fig. 10(c) it is derived that the *T* atoms of an *S*3*R* [and of any $(3 \times m)$ ring perpendicular to the trigonal axis in general] share all bonds in the cage, leaving no bonds for linking neighbouring cages laterally.

Generalized enumerations

A cage between two on-axis tetrahedra (as in Fig. 1) was called a 2*T* trigonal cage; a cage between an on-axis *T* atom and a threefold ring [as in Fig. 9: the

three-ring is in general a $(3 \times m)$ ring in the horizontal plane] is designated a 1*T* trigonal cage, and a cage between two threefold rings perpendicular to the same trigonal axis is called a 0*T* trigonal cage.

All 2*T* trigonal cages having at least one threefold ring perpendicular to the trigonal axis can be regarded as being composed of face-sharing cages, i.e. 1*T* trigonal cages (one threefold ring) or 1*T* and 0*T* trigonal cages (more than one threefold ring). Face sharing occurs at the threefold rings perpendicular to the trigonal axis.

1*T* trigonal cages between an on-axis *T* atom and an *S*3*R* belong to group *D*, those between an on-axis *T* atom and an *S*6*R* belong to group *E*. 0*T* trigonal cages between two *S*3*R*'s belong to group *F*, those between two *S*6*R*'s to group *G* and those between an *S*3*R* and an *S*6*R* belong to group *H*. It is clear that two 0*T* trigonal cages of group *H* can be regarded as a group *F* or a group *G* cage when they share *S*6*R*'s or *S*3*R*'s, respectively.

$n(1)$ is the number of horizontal stacks for cages of groups *D* and *E*, and $n(2)$ denotes the number of horizontal stacks between two threefold rings for cages of groups *F* to *H*.

Along the same lines, the foregoing enumeration can further be extended with a few simple transformations. In general, a threefold ring perpendicular to the trigonal axis may be replaced by a 0*T* trigonal cage of the appropriate group. Furthermore, an *S*3*R* may be replaced by two adjacent on-axis *T* atoms (T_2 unit). This is only so if the *T* atoms of this unit are symmetry related by a mirror plane perpendicular to the trigonal axis [designated the T_{2m} unit, Fig. 19(b1)], but not if they are symmetry related by an inversion centre [designated the T_{2i} unit, Fig. 19(b2)]. An illustrative example can be seen in Fig. 10(c1), where the 2*T* trigonal cage 1-3(*LH*)3(*S*)3-1 is represented. This cage is composed of two 1*T* trigonal cages [1-3(*LH*)3, 3^{15^3}] sharing *S*3*R*'s. The 3^{15^3} trigonal cage belongs to group *D* [$n(1) = 1$]. It can easily be derived from this figure that the *S*3*R* may be replaced by either the T_{2m} unit, converting the 3^{15^3} cage into the 4^3 cage (simplest trigonal cage), or by a 0*T* trigonal cage of group *F*.

Constructing three-dimensional lattices: from cages to 3D nets

Hexagonal sheets constructed from 2*T* trigonal cages

There are two distinct ways by which 2*T* trigonal cages can be linked laterally to form sheets with hexagonal symmetry. These two possibilities have been described systematically in the literature for the case of hexagonal frameworks constructed from 0*T* trigonal cages of group *G* (Smith & Bennett, 1981; Barrer & Villiger, 1969; Tambuyzer, 1977).

Firstly, neighbouring $2T$ trigonal cages can be symmetry related by mirror planes parallel to the trigonal axis as was described (Barrer & Villiger, 1969) for hexagonal frameworks of the *LTL* group [fourth column of Table 4 in the paper of Barrer & Villiger, Fig. 11(b)] and the *LTL*-related group [fifth column of Table 4 in the paper of Barrer & Villiger, Fig. 11(c)]. A limited number of $2T$ trigonal cages enumerated before can in this way be linked laterally with identical cages as visualized in Fig. 12(a), (b) and (c) for cages represented in Figs. 10(a), (b) and (c), respectively. Figs. 13 and 14 illustrate this for the *CSC* cage [$2T$ trigonal cage in the Linde Q topology (Andries, Bosmans & Grobet, 1990)]. It is obvious that the cage is linked to five others: three in the plane, one above and one below [characteristic for all frameworks of the tridymite group (to be described later) constructed from isolated $2T$ trigonal cages]. It can be seen from Fig. 14 that a typical hexagonal unit cell encompasses two $2T$ trigonal cages (except in cases where neighbouring cages share faces, see further). The figure is general for hexagonal sheets made of $C(SC)_r$ type cages ($r = \text{odd}$). Projections onto the hexagonal (001) plane for hexagonal sheets made in this way from cages that were visualized in Figs. 10(a), (b) and (c) are given in Figs. 15(a), (b) and (c), respectively.

A second way for connecting neighbouring $2T$ trigonal cages to form hexagonal sheets is across a threefold axis parallel to the cage's trigonal axis, as was described systematically (Smith & Bennett, 1981; Tambuyzer, 1977) for the case of hexagonal frameworks constructed from $0T$ trigonal cages of group *G* that belong to the *ABC*-6 group (chabazite group) of zeolites and related materials (Fig. 11a). Again, hexagonal sheets are formed. The projection onto the (001) plane for a hexagonal sheet made of 1-3-1 cages is represented in Fig. 16. In this type of 3D net, the $2T$ trigonal cages are connected to eight identical ones: six in the plane, one above and one below.

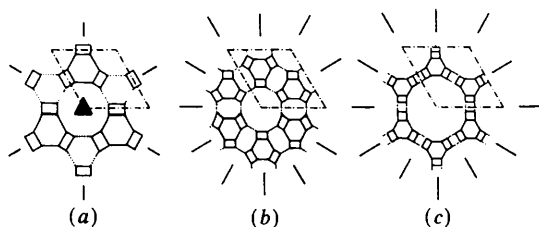


Fig. 11. Connecting trigonal columns laterally to form 3D nets. OFF columns are represented with full lines and their connections with dotted lines. Hexagonal unit cells and the main symmetry operators are indicated. (a) OFF (Gard & Tait, 1972); (b) LTL (Barrer & Villiger, 1969); (c) hypothetical LTL-related 3D net (Barrer & Villiger, 1969). In (b) high-membered rings ($S8R$) and in (c) low-membered rings ($S4R$) are formed between neighbouring columns.

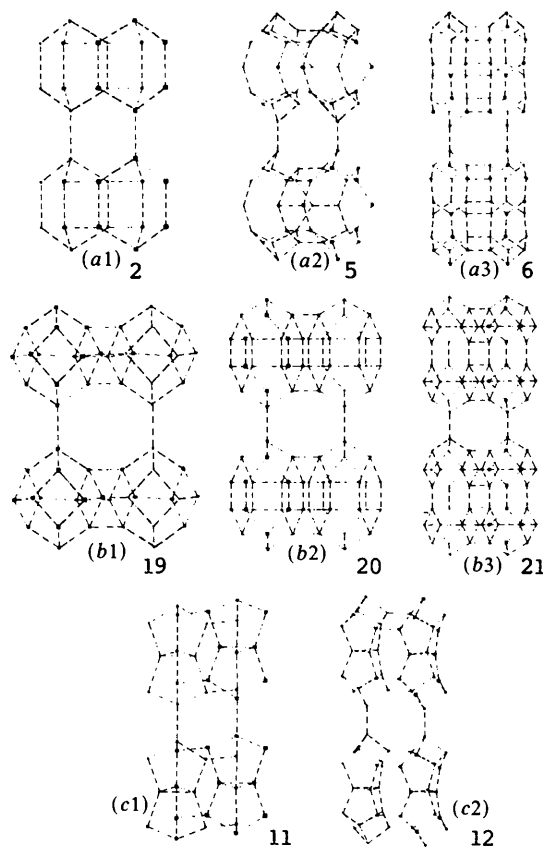


Fig. 12. The connection of $2T$ trigonal cages to form simple group 1 nets of the tridymite group. Each time, four cages have been represented in order to show their connections parallel to the trigonal axis, as well as laterally. Note the eight-ring formed between four cages (channel system A). The cages in (a), (b) and (c) correspond to the cages in Figs. 10(a), (b) and (c), respectively. Figures denote net numbers. See Fig. 10 for explanation on representations. (Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.)

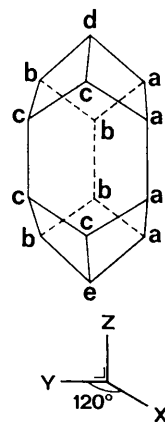


Fig. 13. Connecting *CSC* ($4^6 6^3$) cages to form a group 1 net of the tridymite group. Letters refer to other *CSC* cages.

Hexagonal 3D nets of the tridymite group

Identical hexagonal sheets can be stacked onto each other by linking the $2T$ trigonal cages *via* oxygen bridges (forming T_2 units) along their trigonal axes to form *simple nets* of the tridymite group, as represen-

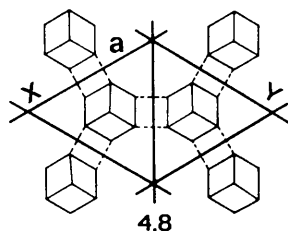


Fig. 14. The lateral connection of neighbouring $2T$ trigonal cages of the $C(SC)_r$ ($r = \text{odd}$) series to form a simple hexagonal sheet. View along the hexagonal c axis. Cages are represented with full lines and their connections with dashed lines. Note the hexagonal unit cell bounded by mirror planes and the position of the cages at $x = 2/3$, $y = 1/3$ and at $x = 1/3$, $y = 2/3$. Figures are net numbers.

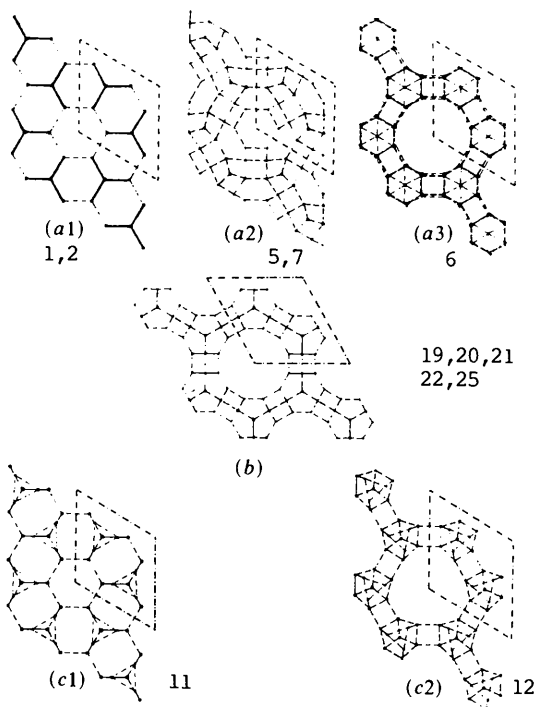


Fig. 15. Schematic drawings of the projection onto the hexagonal (001) plane for some simple group 1 nets of the tridymite group constructed from (a1 to a3) group A, (b) group B and (c1 and c2) group C $2T$ trigonal cages that were represented in Figs. 10(a), (b) and (c), respectively. Figures denote net numbers. Hexagonal unit cells are indicated. See Fig. 10 for explanation of representations. In (a1), $2T$ trigonal cages are represented with bold lines. (a3) is characteristic for nets constructed from $C(SC)_r$ ($r = \text{even}$) type cages; (b) is characteristic for nets formed from $2T$ trigonal cages that contain any combination of the $3(H)6(H)3$ and/or the $3(H)6(L)6(H)3$ sequence(s); (c2) refers to nets constructed from $1-[3(C)3]_u(LH)3[(S)3(C)3]_w - 1$ type cages. (Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.)

ted in Fig. 12: sheets are symmetry related by translation along [001] (the hexagonal c axis) and the unit-cell c parameter is equal to the sheet thickness.

Non-simple nets are characterized by at least one of the following two features:

- (i) the hexagonal sheets are not simple, *e.g.* they are made of more than one type of $2T$ trigonal cage and/or neighbouring cages are displaced along [001] (*e.g.* neighbouring cages in the same sheet are symmetry related by c glides or threefold screw axes);
- (ii) neighbouring hexagonal sheets are not symmetry related by translation along [001].

Most emphasis will be on framework structures where neighbouring $2T$ trigonal cages in the same hexagonal sheet symmetry related by mirror planes parallel to the trigonal axis (designated *group 1 frameworks of the tridymite group*). This mode of linking is most common for established materials with frameworks constructed from $2T$ trigonal cages. The second way of symmetry-relating neighbouring trigonal cages is most common for established materials with frameworks made of $0T$ trigonal (group G) cages. The designation *group 2 frameworks of the tridymite group* is used to denote nets made of $2T$ trigonal cages that are symmetry related by threefold axes. A complete systematic enumeration of all possible 3D nets is beyond the scope of this paper and a detailed crystallographic compilation will be published in the future.

Enumeration of group 1 3D nets of the tridymite group

Group 1 nets constructed from group A, B and C cages will be treated in that sequence. In each instance, some simple and related non-simple nets will be discussed.

All group 1 frameworks constructed from isolated $2T$ trigonal cages are characterized by a 2D intersecting channel system, formed by more or less distorted eight-rings along [100], [010] and [110] (called *channel system A* hereafter). If a supplementary channel

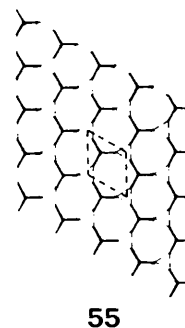


Fig. 16. Schematic drawing of the projection onto the hexagonal (001) plane for net 55. $2T$ trigonal cages are represented with bold lines. The hexagonal unit cell is indicated. See Fig. 10 for explanation on representations. (Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.)

system is present, it will be described for the specific structure.

Simple nets from group A cages: Eight simple nets were derived from group A 2*T* trigonal cages.

With $n = 1$, one possibility exists (net 1, cage 1-3-1). The 2*T* trigonal cage is identical to the T_5O_{10} SBU of the natrolite group (Meier, 1968) but with its trigonal axis parallel to the hexagonal *c* axis.

With $n = 2$, two structures were derived. The first (net 2, cage *S*) [Figs. 10(*a*1), 12(*a*1), 15(*a*1)] was previously described by Smith (1978) as his structure type 8*b*. The second structure (net 3, cage *C*) is the framework of the recently described phase CoAPO-50 (AFY) (Bennett & Marcus, 1987) which consists entirely of *D*4*R* units. It has a 1D twelve-ring channel along [001] intersecting with channel system *A*.

With $n = 3$ or $n = 7$, no simple sheets (and thus no simple nets) could be constructed.

With $n = 4$, one structure (net 4, cage *CSC*) was derived which is the framework of the synthetic zeolite Linde Q of Breck & Acara (1961) (Andries, Bosmans & Grobet, 1990). It was shown that the framework topology of beryllophosphate-H is also that of net 4, which was assigned therefore the structure type code BPH (Harvey & Meier, 1989). The hexagonal sheets are translated along [001] in the BPH structure, whereas they are rotated by 180° parallel to (001) in the (non-simple) framework of the recently described phase MAPSO-46 (AFS) (Bennett & Marcus, 1987), assigned now net 4*b*. The transformation that rotates neighbouring hexagonal sheets by 180° parallel to (001) in a 3D net will be designated the *R*180 transformation hereafter; neighbouring 2*T* trigonal cages along the trigonal axis are rotated by 60° around [001] when the *R*180 transformation is applied to simple nets, and the hexagonal *c* parameter of the resulting non-simple nets is twice the height of the constituent 2*T* trigonal cage. The 2*T* trigonal cage present in both nets 4 and 4*b* has recently been designated the *afo* unit (Smith, 1988). Both structures have a 1D twelve-ring channel along [001], intersecting with channel system *A*.

With $n = 5$, one net (net 5, cage *CSSC*) [Figs. 10(*a*2), 12(*a*2), 15(*a*2)] was constructed. It is characterized by circular 2D channels (formed by eight-rings), intersecting through windows of the same type and running parallel to, but isolated from, channel system *A*.

With $n = 6$, two new nets were derived. The first (net 6, cage *CSCSC*) [Figs. 10(*a*3), 12(*a*3), 15(*a*3)] has a 1D twelve-ring channel along [001], intersecting with channel system *A* and the second (net 7, cage *CSSSC*) is characterized by a similar channel system as present in the type 5 structure, but with the circular channels being formed by ten-rings. *D*6*R* subunits occur in the type 7 structure.

With $n = 8$, one net (net 8, cage *CSCSCSC*) was derived with a similar channel system as in nets 3, 4 and 6.

It should be noted that all cages of type *C*(*SC*), (where *r* is zero or a positive integer) can form simple frameworks. Cages of type *C*(*S*), *C* with $t > 3$ cannot form structures of the tridymite group because *D*6*R*'s are present sharing *S*6*R*'s.

Some important crystallographic data for these eight simple framework topologies are compiled in Table 4. The unit cell and atomic positional parameters were refined by *DLS* (Baerlocher, Hepp & Meier, 1977), assuming *T*-*O* distances of 1.68 Å [calculated for an Si/Al = 1.0 framework according to Ribbe & Gibbs (1969)], and *O*-*O* and *T*-*T* distances calculated according to an ideal *O*-*T*-*O* tetrahedral angle and a mean *T*-*O*-*T* angle of 140°. In some cases, the agreement *R* factor was lowered by permitting the *T*-*O* distances to vary between the values for pure Si-O and Al-O bonds. The calculations were performed assuming space group *P*31*m* for nets 1, 2 and 3, *P*3̄1*m* for net 6 and *P*321 for nets 4, 5, 7 and 8.

Non-simple nets from group A cages: Non-simple nets can be constructed from either identical but mutually rotated (*e.g.* by the *R*180 transformation) hexagonal sheets, or from different hexagonal sheet types. Application of the *R*180 transformation to the simple nets 3, 6 and 8 results in nets 3*b*, 6*b* and 8*b*, respectively. The hexagonal sheets are symmetry related by inversion in nets 3, 4*b*, 6 and 8*b*, and by a mirror plane in nets 1, 2, 3*b*, 4, 5, 6*b*, 7 and 8. It is obvious that more complex stacking variations are possible.

Other non-simple nets can be formed from different types of hexagonal sheets: sheets of nets 1 and 2 can be stacked immediately on top of each other due to their very similar *a* parameter (Table 4), giving nets with a hexagonal *c* repeat of approximately [(7.2*p*) + (9.7*q*)] Å, where the meaning of *p* and *q* is evident from Table 4. Structure types 9 ($p = 1, q = 1$) and 10 ($p = 2, q = 1$) have a *c* repeat of approximately 16.9 and 24.1 Å, respectively. Similarly, hexagonal sheets of nets 4 to 8 can be stacked.

Simple nets from group B cages: Five simple nets made of isolated group B 2*T* trigonal cages can be constructed from cages 1-3(*H*)6(*H*)3-1, 1-3(*H*)6(*L*)6(*H*)3-1, 1-3(*H*)6(*H*)3(*S*)3(*H*)6(*H*)3-1, 1-3(*H*)6(*L*)6(*H*)3(*S*)3(*H*)6(*L*)6(*H*)3-1 and 1-3(*H*)-6(*H*)3(*S*)3(*H*)6(*L*)6(*H*)3-1. They were assigned numbers 19 [Figs. 10(*b*1), 12(*b*1), 15(*b*)], 20 [Figs. 10(*b*2), 12(*b*2), 15(*b*)], 21 [Figs. 10(*b*3), 12(*b*3), 15(*b*)], 22 and 25, respectively.

Two simple frameworks can be constructed from face-sharing 2*T* trigonal cages: (i) the 4³5⁶ cage [Fig. 10(*b*1)] of the type 19 structure can share *S*4*R*'s to

Table 4. Crystallographic data for some simple nets of the tridymite group

MSG = maximum space-group symmetry; TUC = number of tetrahedral atoms in the hexagonal unit cell; IT = number of non-equivalent tetrahedral atoms for MSG; FD = framework density (number of tetrahedral atoms per unit volume of 1000 \AA^3); V_f = void fraction (g cm^{-3}), calculated according to the experimentally derived relation $V_f = (-0.0375\text{FD}) + 0.975$ (Breck, 1973); SBU = secondary building unit as defined by Meier (1968); RF = established materials with the framework topology described; REF = reference to the first description of the net topology. The letters *A*, *B*, *K* and *L* designate the sequences $3(H)6(H)3$, $3(H)6(L)6(H)3$, $3(LH)3(S)3$ and $3(C)3(LH)3(S)3(C)3$ respectively; square brackets stand for 1MS's bounding the cages.

Net	<i>n</i>	Sequence	MSG	TUC	IT	Cage	<i>a</i> (Å)	<i>c</i> (Å)	FD	V_f	SBU	RF	REF
Group 1 nets													
1	1	/	$P6/mmm$	10	2	T_5O_{10} 4^3	10.19	7.21	15.4	0.40	T_5O_{10} $1 \equiv 3 \equiv 1$	/	/
2	2	<i>S</i>	$P6/mmm$	16	2	T_8O_{16} 6^3	10.22	9.66	18.3	0.29	T_4O_8 $1 \equiv 3$	/	(1)
3	2	<i>C</i>	$P\bar{3}1m$	16	2	T_8O_{16} 4^6	12.74	8.96	12.7	0.50	T_4O_8 $1 \equiv 3$	AFY	(2)
4	4	<i>CSC</i>	$P\bar{6}2m$	28	3	$T_{14}O_{28}$ $4^6 6^3$	13.56	13.38	13.1	0.48	T_7O_{14} $1 \equiv 6$	BPH	(3, 4)
5	5	<i>CSSC</i>	$P\bar{6}2m$	34	4	$T_{17}O_{34}$ $4^6 8^3$	13.27	15.19	14.7	0.42	$T_{17}O_{34}$ $1 \equiv 6 \equiv 3 \equiv 6 \equiv 1$ $1 \equiv 6 + S6R$	/	/
6	6	<i>CSCSC</i>	$P\bar{3}1m$	40	4	$T_{20}O_{40}$ $4^6 6^6$	13.25	18.43	14.3	0.44	$T_{10}O_{20}$ $1 \equiv 6 \equiv 3$	/	/
7	6	<i>CSSSC</i>	$P\bar{6}2m$	40	4	$T_{20}O_{40}$ $4^6 10^3$	13.30	17.31	15.1	0.41	$T_{10}O_{20}$ $1 \equiv 6 \equiv 3$ $1 \equiv 6 + S6R$	/	/
8	8	<i>CSCSCSC</i>	$P\bar{6}2m$	52	5	$T_{26}O_{52}$ $4^6 6^8$	13.71	22.33	14.3	0.44	$T_{13}O_{26}$ $1 \equiv 6 \equiv 6$	/	/
11	3	[<i>K</i>]	$P6/mmm$	22	3	$T_{11}O_{22}$ 5^6	10.47	12.01	19.3	0.25	$1 \equiv 3$ +S3R	/	/
12	5	[<i>L</i>]	$P\bar{6}2m$	34	4	$T_{17}O_{34}$ $4^6 5^6$	13.52	16.10	13.3	0.47	$1 \equiv 6$ +S3R	/	/
19	3	[<i>A</i>]	$P6/mmm$	28	3	$T_{14}O_{28}$ $4^3 5^6$	15.29	11.11	12.4	0.51	$1-1$ +S4R	/	/
20	4	[<i>B</i>]	$P6/mmm$	40	3	$T_{20}O_{40}$ $4^3 5^6 6^3$	15.70	13.95	13.4	0.47	$1-1$ +S6R	/	/
21	6	[<i>A(S)A</i>]	$P6/mmm$	52	4	$T_{26}O_{52}$ $4^6 5^6 8^3$	15.47	18.51	13.6	0.47	$1-1$ +S4R	/	/
22	8	[<i>B(S)B</i>]	$P6/mmm$	76	4	$T_{38}O_{76}$ $4^6 5^6 6^6 8^3$	15.84	23.85	14.7	0.43	$1-1$ +S6R	/	/
25	7	[<i>A(S)B</i>]	$P6mm$	64	9	$T_{32}O_{64}$ $4^6 5^6 6^3 8^3$	15.64	21.06	14.3	0.44	$1-1$ +S4R +S6R	/	/
Nets constructed from face-sharing 2 <i>T</i> trigonal cages													
23	3	[<i>A</i>]	$P6/mmm$	16	3	$T_{14}O_{28}$ $4^3 5^6$	10.84	10.88	14.4	0.43	$1-1$ +S4R	/	/
24	4	[<i>B</i>]	$P6/mmm$	22	3	$T_{20}O_{40}$ $4^3 5^6 6^3$	10.63	13.87	16.2	0.37	$1-1$ +S6R	/	/
Group 2 nets													
55	1	1-3-1	$P\bar{6}m2$	5	2	T_5O_{10} 4^3	7.47	7.22	14.3	0.44	$1 \equiv 3 \equiv 1$	/	/

References: (1) Smith (1978); (2) Bennett & Marcus (1987); (3) Harvey & Meier (1989); (4) Andries, Bosmans & Grobet (1990).

form a hexagonal sheet (simple net 23), and (ii) the $4^3 5^6 6^3$ cage [Fig. 10(b2)] of the type 20 structure can share *S6R*'s to form a hexagonal sheet (simple net 24, Fig. 17).

Structures made of face-sharing trigonal cages have no appreciable channel system. The lateral connections between two isolated 2*T* trigonal cages form *D4R*'s (nets 19 and 21), *D6R*'s (nets 20 and 22) or both (net 25). In nets 20, 22 and 25, *D12R*'s restrict the dimensions of the 1D channel along [001]. In the type 24 structure, *D6R*'s occur restricting the channel

dimension along [001]. The type 23 structure can also be constructed from the $5^{12} 6^8 0T$ trigonal cage (group *G*) [designated the *dooh* cage (Smith, 1988)], also present in the structure type *DOH* (Gerke & Gies, 1984). In the type 24 structure, columns of alternating *D6R* and $5^{12} 6^8$ cages occur parallel to the hexagonal axis. The $4^3 5^6 6^3$ cage occurring as an isolated and a fundamental (Liebau, Gies, Gunawardane & Marler, 1986) cage in structure types 20 and 24, respectively, has been designated the *dooh* cage (Smith, 1988). Structure types 23 and 24 should be classified as

clathrasils. Structure type 19 can also be constructed from $4^{12}5^{12}8^6 12^2$ cages, sharing $S8R$'s parallel to (110) , $(\bar{1}\bar{2}0)$, $(\bar{1}20)$, $(2\bar{1}0)$ and $(\bar{2}\bar{1}0)$, and $S12R$'s parallel to (001) . Columns of alternating $D12R$ and $4^{12}5^{12}8^6 12^2$ cages occur in net 20. The $5^{12}6^8$ (*doh*) cage can easily be converted into the $4^{12}5^{12}8^6 12^2$ cage by the application of the same σ transformations (Shoemaker, Robson & Broussard, 1973) that convert the $S6R$ into the $S12R$. σ transformations interrelating these seven nets are represented in Fig. 18.

Some important crystallographic data for these seven simple nets are compiled in Table 4. Refinement of the unit cell and atomic positional parameters with *DLS* was done assuming space group $P31m$ for nets

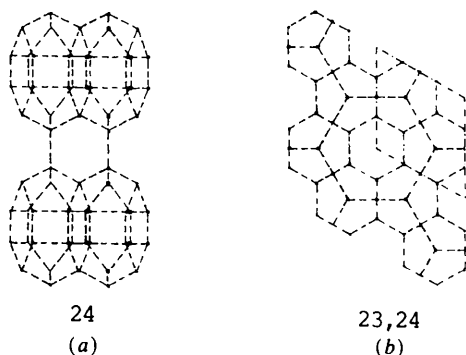


Fig. 17. Similar drawings to those in Figs. 12 and 15 for net 24. Note that the eight-rings (channel system A) in Fig. 12 are reduced to six-rings. Note also the presence of $5^{12}6^8$ cages (in *b*) that are bounded by twelve $4^3 5^6 6^3$ cages (six per hexagonal sheet). In (*b*) the hexagonal unit cell is indicated. Figures are net numbers. See Fig. 10 for explanation on representations. (Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.)

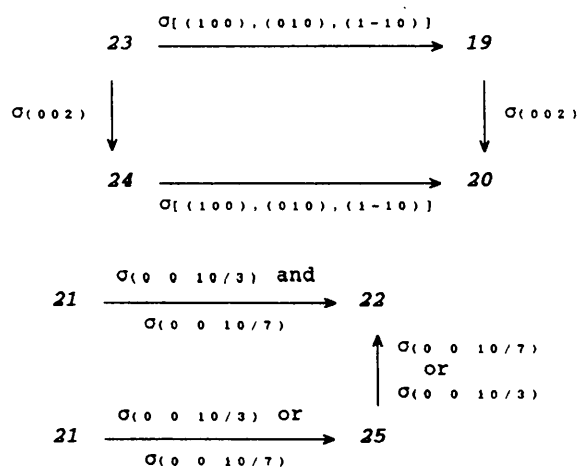


Fig. 18. σ transformations interrelating some simple group 1 nets of the tridymite group constructed from group B $2T$ trigonal cages. Figures are net numbers. The *l* Miller indices of the planes at which σ transformations interrelate nets 21, 22 and 25 represent approximate values.

19, 20 and 25, $P\bar{6}2m$ for nets 21 and 22, and $P321$ for nets 23 and 24.

It should be noted that cages of types $1- [3(H)6(H)3]_s-1$ (net 19: $s=1$; net 21: $s=2$) and $1-[3(H)6(L)6(H)3]_v-1$ (net 20: $v=1$; net 22: $v=2$) (s and v are positive integers) can all form simple frameworks. If the sequence $3(H)6(H)3$ is denoted by *A* and $3(H)6(L)6(H)3$ by *B*, then $2T$ trigonal cages can be made with all possible sequences of *A* and *B*. As an example, net 25 contains both the *A* and *B* sequences once.

Some $2T$ trigonal cages containing at least one $S6R$ perpendicular to the trigonal axis are interesting. They can all be constructed from face-sharing $0T$ and/or $1T$ trigonal cages of group *G* and *E*, respectively. Some of these $2T$ trigonal cages can form simple nets, but no *DLS* refinements were done to show whether these are possible.

An infinite number of cages exists by repeating a particular horizontal stack sequence or by combining different sequences (as was already mentioned for sequences denoted by *A* and *B*). In principle, each horizontal stack sequence beginning and ending with a $3MS$ can be repeated infinitely or be combined with other similar sequences. Furthermore, each $1T$ trigonal cage can be combined with another to give a $2T$ trigonal cage by sharing $S6R$'s. Finally, any $S6R$ can be replaced by a $0T$ trigonal cage of group *G* as for example the $D6R$ [$4^6 6^2$, $n(2)=0$], the ϵ (cancrinite) [$4^6 6^5$, $n(2)=1$] or the $3^6 6^2 8^3$ [$n(2)=2$] cage.

Non-simple nets from group B cages: Non-simple net 25*b* is made of type 25 hexagonal sheets with neighbouring sheets being symmetry related by a mirror plane. Its hexagonal *c* repeat is twice that of net 25.

Because of the structural analogy of their $2T$ trigonal cage and the comparable *a* parameter of the respective simple nets (Table 4), hexagonal sheets of nets 19, 20, 21, 22 and 25 can be stacked at random, as can the sheets of nets 23 and 24. Structure type 26 is composed of alternating type 19 and type 20 sheets, and net 27 of alternating type 23 and type 24 sheets. Both nets have a *c* repeat of approximately 25 Å.

Simple nets from group C cages: $2T$ trigonal cages of group *C* are made of at least one $S3R$ perpendicular to the trigonal axis as was explained earlier. It should be noted that nets constructed from cages with the $S3R$ lying in a mirror plane perpendicular to the trigonal axis should be examined first, because of the well accepted rule of parsimony, stating that symmetrical cages are the most promising candidates to form real framework structures. This applies to at least three group *C* cages. The first two are represented in Fig. 10(c): the $1-3(LH)3(S)3-1$ cage [Fig. 10(c1), resulting net 11] and the $1-3(C)3(LH)-3(S)3(C)3-1$ cage [Fig. 10(c2), resulting net 12].

In net 11 [Figs. 10(c1), 12(c1), 15(c1)], the chains around the trigonal axes are composed of 1*T* trigonal cages (3^15^3), alternate *S3R*'s shared and T_{2m} linkages formed [Fig. 12(c1)]. Six columns of this type surround a column made of alternating 6^8 and 6^28^6 cages sharing *S6R*'s. Channel system *A* is the widest channel system in the structure. Net 11 can be derived from net 1 by substituting all T_{2m} units [Fig. 19(b1)] in alternate layers parallel to (001) by *S3R*'s. In net 12 [Figs. 10(c2), 12(c2), 15(c2)], the chains around the trigonal axes are made of 1*T* trigonal cages ($3^14^35^3$), alternate *S3R*'s shared and T_{2m} linkages formed [Fig. 12(c2)]. Six chains of this type surround the 1D twelve-ring channel along [001]. Between two laterally linked 2*T* trigonal cages, a $4^25^46^110^1$ subunit is formed [Fig. 12(c2)]. The 1D twelve-ring channel along [001] is made up of alternating $4^18^86^612^2$ and $4^65^126^612^2$ cages, sharing non-planar *S12R*'s.

Some important crystallographic data for nets 11 and 12 are compiled in Table 4. Refinement of the unit cell and atomic positional parameters with *DLS* was done assuming space group *P321* for both structure types.

All group *C* trigonal cages of type $1-3(C)3_u(LH)3[(S)3(C)3]_w-1$ can form simple nets.

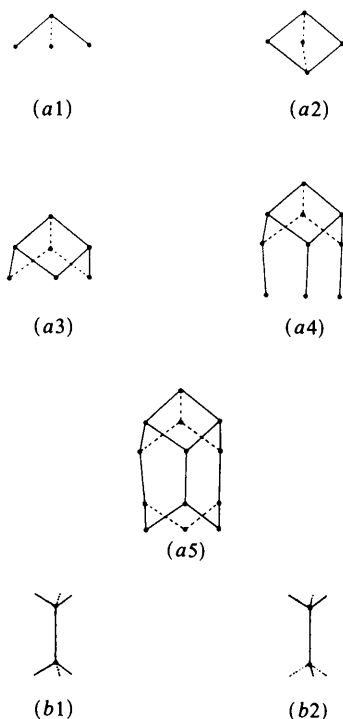


Fig. 19. Schematic drawings of some secondary building units. *T* atoms are represented by circles; oxygen atoms (not shown) lie approximately in the middle between two connected *T* atoms or are not 2-connected. Designations: (a1) $1\equiv 3$, (a2) $1\equiv 3\equiv 1$, (a3) $1\equiv 6$, (a4) $1\equiv 6\equiv 3$, (a5) $1\equiv 6\equiv 6$, (b1) T_{2m} and (b2) T_{2i} .

In this notation, *u* and *w* are positive integers with the only restriction that *u* or *w* can only take the value 1 if *w* or *u*, respectively, equals 1. All simple nets of this series can be derived from nets made of group *A* cages of type $C(SC)_r$, by substituting all T_{2m} units in alternate layers parallel to (001) by *S3R*'s. A few illustrations: (i) with $u=1$, $w=1$ the resulting simple net is structure type 12 which can be derived from net 3*b* (made of cages with $r=0$); (ii) with $u=2$, $w=2$ the resulting simple net was assigned structure type 13 and can be derived from net 4 (made of cages with $r=1$); (iii) with $u=2$, $w=3$ the resulting simple net is derived from a net with alternately identically oriented type 4 and type 6 (made of cages with $r=2$) hexagonal sheets.

Non-simple nets from group C cages: All simple nets made of type $1-3(C)3_u(LH)3[(S)3(C)3]_w-1$ 2*T* trigonal cages give rise to non-simple nets when subject to the *R180* transformation. The resulting non-simple nets, corresponding to nets 12 and 13, were assigned structure types 12*b* and 13*b*. Substitution of all *S3R*'s by T_{2m} units in the latter two structures gives nets that are made of hexagonal sheets of nets 3 and 4, respectively, with these sheets in pairs being rotated by 180° parallel to (001). It is obvious that more complex stacking variations are possible. The transformation that replaces all T_{2m} units by *S3R*'s in a 3D net will be designated the *T2/3R transformation* hereafter.

Finally, it should be mentioned that novel nets can be constructed by replacing *S3R*'s perpendicular to the trigonal axes by 0*T* trigonal cages of group *F*.

Enumeration of group 2 3D nets of the tridymite group

The 2D intersecting channel system formed between neighbouring hexagonal sheets in group 2 frameworks is similar but not identical to channel system *A* in group 1 nets: the aperture size is also the *S8R*, but the channels are not rectilinear (designated *channel system B*).

Nets 55 and 60 and related non-simple structures will be discussed.

Simple nets: Net 55 is made of 1-3-1 cages (as present in net 1). An *S3R* or an *S9R* is formed by connecting three cages at the same height. The net consists of chains of 1-3-1 cages along [001]. Three chains of this type, symmetry related by a trigonal axis, generate a column made of 3^28^3 0*T* trigonal cages sharing *S3R*'s perpendicular to [001]. Three cages of the latter type share one edge (a T_{2m} unit on the chains of the 1-3-1 cages). Channels along [001] are restricted by *S9R*'s, and by *S8R*'s (channel system *B*) perpendicular to that axis.

Net 60 is constructed from $1-3(LH)3(S)3-1$ 2*T* trigonal cages [Fig. 10(c1)], also present in net 11. It can be derived from net 55 by replacing all T_{2m} units in alternate layers parallel to (001) by *S3R*'s.

Table 5. *Structural information on the enumerated nets that were not described in Table 4*

The letters *A*, *B*, *M* and *N* designate the sequences 3(*H*)6(*H*)3, 3(*H*)6(*L*)6(*H*)3, 3(*C*)3 and 3(*C*)3(*S*)3(*C*)3, respectively; the notations 1(*m*)1 and 1(*i*)1 denote the T_{2m} and T_{2i} unit, respectively; RF=established materials with the framework topology described; REF=reference to the first description of the net topology.

Net number	Repetition sequence	RF	REF
Group 1 nets			
3b	1-M-1(m)1-M-1	/	/
4b	1-N-1(i)1-N-1	AFS	(1)
6b	1-M(S)M(S)M-1(m)1-M(S)M(S)M-1	/	/
8b	1-N(S)N-1(i)1-N(S)N-1	/	/
9	1-3-1(m)1-3(S)3-1	/	/
10	1-3-1(m)1-3-1(m)1-3(S)3-1	/	/
12b	1-M(LH)3(S)M-1(i)1-M(LH)3(S)M-1	/	/
13	1-N(LH)3(S)N-1(m)1-N(LH)3(S)N-1	/	/
13b	1-N(LH)3(S)N-1(i)1-N(LH)3(S)N-1	/	/
25b	1-A(S)B-1(m)1-B(S)A-1	/	/
26	1-A-1(m)1-B-1	/	/
Nets constructed from face-sharing 2 <i>T</i> trigonal cages			
27	1-A-1(m)1-B-1	/	/
Group 2 nets			
55b	1-3-1(i)1-3-1	/	/
60	1-3(LH)3(S)3-1(m)1-3(LH)3(S)3-1	/	/
55b	1-3(LH)3(S)3-1(i)1-3(LH)3(S)3-1	/	/

Reference: (1) Bennett & Marcus (1987).

The projection onto the (001) plane for net 55 is represented in Fig. 16. Some important crystallographic data are compiled in Table 4. Refinement of the unit cell and atomic positional parameters with *DLS* was done assuming space group *P312*.

Non-simple nets: Application of the *R180* transformation to net 55 results in a non-simple net, designated structure type 55*b*. Three chains of 1-3-1 cages that are linked by forming T_{2i} units [Fig. 19(*b2*)] generate a column formed by $3^2 4^3 8^6$ (0*T* trigonal group *F*) cages sharing *S3R*'s. Neighbouring cages are displaced $\frac{1}{2}c$ along [001]. Channel system *B* is the widest channel system in the structure.

No *DLS* refinement was done for net 60*b* derived from net 60 by the *R180* transformation.

Structural information on all of the enumerated nets that were not mentioned in Table 4, is compiled in Table 5.

Enumeration using secondary building units

Simple nets: The simplest structural unit in this group of structures is the T_2 (1-1) unit, represented in Fig. 19(*b*). A distinction has to be made between the T_{2i} [Fig. 19(*b2*)] and the T_{2m} [Fig. 19(*b1*)] units, where the *T* atoms are symmetry related by an inversion centre and a mirror plane respectively. All nets of the tridymite group contain this 1-1 type. It occurs as single SBU in all structures of the tridymite/cristobalite polytypic series, as will be discussed elsewhere (Andries, 1990). Nets 55 and 60 can be con-

structed from the T_{2m} and the *S3R* SBU's. Nets 19, 20, 21, 22 and 25 as well as nets 23 and 24 can be made of the T_{2m} SBU in combination with the *S4R* and/or the *S6R* SBU's.

More complex is the $1 \equiv 3$ unit (denoting an on-axis *T* atom, connected with three bonds to three *T* atoms in the first horizontal stack) [Fig. 19(*a1*)]. Two such units can be linked to form a cage when symmetry related by a mirror plane or an inversion centre. In the former case, the T_8O_{16} ($1 \equiv 3 \equiv 3 \equiv 1$) cage of net 2 is formed, and in the latter case the *D4R* ($1 \equiv 6 \equiv 1$) unit of net 3 results. Net 11 is constructed from the $1 \equiv 3$ and the *S3R* SBU's.

The SBU of next higher complexity is the $1 \equiv 3 \equiv 1$ SBU [Fig. 19(*a2*)] of nets 1 and 55. We prefer the notation $1 \equiv 3 \equiv 1$ instead of $4 \equiv 1$ in this structural group because it reflects the lattice symmetry; both notations are otherwise equivalent.

Next in complexity is the $1 \equiv 6$ SBU [Fig. 19(*a3*)] which can only be symmetry related by a mirror plane with a similar unit to form the $T_{14}O_{28}$ ($1 \equiv 6 \equiv 6 \equiv 1$) *afu* unit of net 4. Net 12 is generated from the $1 \equiv 6$ and the *S3R* SBU's, and both nets 5 and 7 can alternatively be made from the $1 \equiv 6$ and the *S6R* SBU's.

Next is the $1 \equiv 6 \equiv 3$ SBU [Fig. 19(*a4*)] which is symmetry related by a mirror plane in net 7, forming the $T_{20}O_{40}$ ($1 \equiv 6 \equiv 3 \equiv 3 \equiv 6 \equiv 1$) cage, and by an inversion centre in net 6 to form the $T_{20}O_{40}$ ($1 \equiv 6 \equiv 6 \equiv 6 \equiv 1$) cage.

Of similar complexity is the $1 \equiv 3(H)6$ unit which can be symmetry related by a mirror plane to generate the $T_{20}O_{40}$ cage of net 20, or by an inversion centre to form the highly symmetric 5^{12} [*rd* (Smith, 1988)] cage. Net 19 is made from the $1 \equiv 3$ and the $1 \equiv 3(H)6$ SBU's. A schematic representation of the $1 \equiv 3(H)6$ SBU viewed down its trigonal axis is identical to Fig. 5(*c*).

Next complex is the $1 \equiv 6 \equiv 6$ SBU [Fig. 19(*a5*)], which can only be symmetry related by a mirror plane, resulting in the $T_{26}O_{52}$ ($1 \equiv 6 \equiv 6 \equiv 6 \equiv 6 \equiv 1$) cage present in net 8. Net 13 is made from the $1 \equiv 6 \equiv 6$ and the *S3R* SBU's.

Of similar complexity is the $1 \equiv 3(H)6(H)3$ unit which can be symmetry related by a mirror plane to form the $T_{26}O_{52}$ cage of net 21. A schematic representation of the $1 \equiv 3(H)6(H)3$ SBU viewed down its trigonal axis is identical to Fig. 6(*f*).

The $1 \equiv 6 \equiv 3 \equiv 6 \equiv 1$ SBU of the type 5 structure is identical to its $T_{17}O_{34}$ 2*T* trigonal cage, which can be derived from the *afu* unit by edge stellation (Smith, 1988). Net 5 can alternatively be generated from the $1 \equiv 6 \equiv 3$ and the $1 \equiv 6$ SBU's.

Next in line is the $1 \equiv 3(H)6(L)6(H)3$ unit which can be symmetry related by a mirror plane to form the $T_{38}O_{76}$ cage of net 22. Structure type 25 is generated from both the $1 \equiv 3(H)6(H)3$ and the $1 \equiv 3(H)6(L)6(H)3$ SBU's.

Non-simple nets: All non-simple *b*-type nets described can be generated from the same secondary building units as their respective simple analogues, keeping in mind that the T_{2m} and T_{2i} units (if mentioned) have to be interchanged.

General group-specific properties

According to the literature, various principles can be used for the invention of open 3D nets: (i) they should be characterized by low-membered ring systems and contain *T* atoms belonging to as many such rings as possible (Brunner, 1979; Meier, 1986); (ii) it is possible to construct nets with wide 1D channels (Barrer & Villiger, 1969; Smith & Dytrych, 1984) as exemplified by Smith & Dytrych (1984) expanding their structure types 39 and 81 [zeolite VPI-5 has the 81(1) type structure (Davis, Saldarriaga, Montes, Garcés & Crowder, 1988)]; (iii) nets constructed from isolated cages in general have a low framework density such as the structure types FAU, LTA, RHO, GME, CHA and KFI (Gramlich-Meier & Meier, 1982). From this, it should be obvious that most structures of the tridymite group have a framework density of $15 \cdot 0T/1000 \text{ \AA}^3$ or lower (see Table 4). Indeed, at least two of the above-cited principles apply. Nets with the lowest framework density [nets 3(*b*), 4(*b*), 12(*b*), 19, 20 and 21] satisfy all three principles. As an example, nets 3 and 4 have a 1D twelve-ring channel along [001] and they are made of isolated 2*T* trigonal cages; net 3 contains *T* atoms that are part of three and even four *S4R*'s, while net 4 is constructed from *T* atoms that are part of three *S4R*'s. The void fractions (V_f) of these most open nets, calculated according to an experimentally derived linear relation between the framework density (FD) and V_f by Breck (1973) [$V_f = (-0.0375\text{FD}) + 0.975$] (see Table 4) are fully compatible with those of the most open zeolite frameworks (FAU, LTA).

Based on the experimental evidence of Flanigen, Khatami & Szymanski (1970), most structure types should exhibit a unique and structure specific infrared spectrum because of their openness and their high crystallographic symmetry.

Besides the low framework density, another group-specific property (less advantageous however from the technological point of view) is the low thermal stability of all phases synthesized, which is caused by the unstable *T*–*O*–*T* bridging bond of 180° . Because the cages themselves as well as their lateral connections are very rigid, the only possible framework deformation upon dehydration results in total collapse of the *T*–*O*–*T* bridges parallel to [001], which are in a crystallographically very restricted position on the trigonal axes. The low bond density in the (001) plane is responsible for the sheet-like character of these structures. In a recent paper (Alberti, 1986), *T*–*O*–*T* angles near 180° present in

the topological symmetry of some zeolites have been investigated. In all cases, the angle could be lowered by diminishing the space-group symmetry. In the higher space groups, the constrained atoms had to be assigned a high anisotropic temperature factor in order to allow for spatial displacement.

In the case of (alumino)silicates, a *T*–*O*–*T* angle strongly deviating from the normal angle of approximately 140° can often be detected by ^{29}Si HRMAS NMR spectroscopic measurements, according to empirically derived relations between *T*–*O*–*T* angles and chemical shift values (Ramdas & Klinowski, 1984; Engelhardt & Radeaglia, 1984). This is indeed the case for fully ordered structures (e.g. Fyfe, Gobbi, Kennedy, De Schutter, Murphy, Ozubko & Slack, 1984).

A comparison of crystallographic properties between the tridymite group and the chabazite group of zeolites reveals that for nets 3, 4, 5, 6, 7, 8 and 12 in Table 4, the hexagonal *a* parameter is similar to that of structures belonging to the *ABC*-6 group, being 12.7 – 13.8 \AA (Smith & Bennett, 1981). All these structures are indeed characterized by a hexagonal unit cell encompassing two more or less planar interlinked six-rings in their projection onto (001) (see Figs. 14 and 15). A close inspection of Table 4 reveals that nets made of 2*T* trigonal cages with only 3*MS*'s have a hexagonal *a* repeat of 13.2 (5) \AA if the projection onto (001) of their unit cell encompasses two six-rings [e.g. Figs. 15(*a2*), (*a3*) and (*c2*)] and $a < 13.2$ (5) \AA if the projection onto (001) of their unit cell does not encompass two six-rings [e.g. Figs. 15(*a1*), (*c1*) and 16]. Nets constructed from 2*T* trigonal cages with 6*MS*'s are characterized by a hexagonal *a* repeat of 15.5 (3) \AA if the projection onto (001) of their unit cell encompasses two nine-rings [e.g. Fig. 15(*b*)] and $a < 15.5$ (3) \AA if the projection onto (001) of their unit cell does not encompass two nine-rings [e.g. Fig. 17(*b*)].

Discussion

In addition to the nets described before, a high number of interrupted nets can be thought of under the same assumptions as for the construction of lattices of the tridymite group from cages enumerated in Tables 1 to 3. Some examples of zeolite frameworks based on interrupted (4; 2)-connected 3D nets are those of wenkite (WEN) (Wenk, 1973), roggianite (ROG) (Galli, 1980) and partheite (PAR) (Engel & Yvon, 1984). The most promising candidates for real frameworks are those with a minimum amount of interrupted nodes and hence with a sharing coefficient (Zoltai, 1960) as nearly as possible to 2.0. Examples of such hypothetical group 1 nets of the tridymite group should be constructed from cages with high *n* values, giving nets with six interrupted nodes per hexagonal unit cell.

We believe that several structures of the tridymite group could be synthesized taking into account the geometric data and the restricted list of structures discovered already with a wide range of chemical framework composition (silicate, aluminosilicate, aluminophosphate, silicoaluminophosphate, beryllophosphate).

Nets of the present tridymite group may serve as trial structure models for some microporous materials with as yet unknown structures. A potential candidate is ZSM-18 (Ciric, 1976) which is described to be open; $a = 13.2$ and $c = 15.8$ Å. The reported low thermal stability (of some samples, dependent upon synthesis conditions), the unit-cell parameters and the XRD pattern (showing the highest diffracted intensity at lowest angle) suggest a simple framework structure of the tridymite group made of group A or group C 2T trigonal cages to be highly probable.

As will be discussed (Andries, 1990), the dense nets of tridymite and cristobalite belong to the present group because they can be constructed by stacking hexagonal sheets that are made of edge-sharing 2T trigonal cages. The present group takes its name from the former mineral because its framework is built up with a simpler 2T trigonal cage than the cristobalite net is.

Novel framework topologies can be derived by the application of three classes of transformations to nets of the present group:

(i) Transformations that change the stacking sequence of the trigonal columns in the net but that do not alter the nature of their lateral connections. The resulting nets remain hexagonal;

$T2/3R$: replaces all T_{2m} units by $S3R$'s;

σ transformation(s) (Shoemaker, Robson & Broussard, 1973) at (a) plane(s) perpendicular to the trigonal axis (e.g. the transformation from net 19 into net 20);

$R180$: rotates neighbouring hexagonal sheets by 180° parallel to (001) (e.g. the transformation from net 4 into the AFS type framework).

(ii) Transformations that do not alter the stacking sequence of the trigonal columns in the net but that do change the nature of their lateral connections. The resulting frameworks are not hexagonal, unless the transformation in itself preserves the hexagonal symmetry [e.g. (a) the transformation of net 82a of Bennett & Smith (1985) into the tridymite net (Gibbs, 1926) by σ^{-1} transformations at planes parallel to the hexagonal axis; (b) some novel hypothetical nets can be derived from structures of the tridymite group by inserting $S4R$ units between adjacent 2T trigonal cages];

σ transformation(s) at (a) plane(s) not running perpendicular to the trigonal axis [e.g. the transformation from the AFI type framework into AEL (e.g. Bennett, Richardson, Pluth & Smith, 1987)];

insertion of $S4R$'s between (not every two) adjacent 2T trigonal cages in group 1 nets of the tridymite group.

(iii) Transformations that alter the stack sequence of the trigonal columns as well as their lateral connections. In the most general case, the resulting nets are not hexagonal;

any combination of transformations noted under (i) and (ii);

substitution of ring units by (trigonal) cages.

Two novel types of transformations that are specifically applicable to nets of the tridymite group were derived, one belonging to class (i) and another belonging to class (ii) (Andries & Bosmans, 1990).

Several properties characteristic for nets of the tridymite group have been observed during the structure investigation of zeolite Linde Q (Andries, De Wit, Grobet & Bosmans, 1990).

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The Systematic Enumeration of (4; 2)-Connected 3D Nets Related to the Tridymite Group

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Abstract

Forty-two hypothetical 3D nets are derived by applying four types of transformations (or combinations thereof) to the previously described tridymite group of structures. Two novel transformations are proposed, one preserving the (hexagonal or orthorhombic) symmetry and another converting the hexagonal symmetry into orthorhombic. Correspondingly, groups of hypothetical 3D framework structures are derived. The properties of frameworks belonging to these groups are compared and discussed.

Introduction

Following the enumeration of (4; 2)-connected 3D nets (this notation denotes framework structures extended in three-dimensional space with every

framework *T* atom being tetrahedrally coordinated by oxygen atoms, where every oxygen atom is shared between two *T* atoms) of the tridymite group (Bosmans & Andries, 1990), this paper describes related structure types obtained by applying geometrical transformations. Examples of such geometrical transformations applicable to (4; 2)-connected 3D nets and/or smaller structural subunits are (i) the sigma (σ) transformation (Shoemaker, Robson & Broussard, 1973), (ii) slipping schemes (Sato & Gottardi, 1982) and (iii) the stellation, the truncation and the addition (Smith, 1988).

Detailed structural information on established 3D framework structures and their secondary building units [SBU, Meier (1968)] can be found in the recently revised *Atlas of Zeolite Structure Types* (Meier & Olson, 1987) and in a comprehensive review (Smith, 1988).