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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 structual 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).

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In a previous report (Bosmans & Andries, 1990), two types of transformations were proposed: (i) the $R180$ transformation rotates neighbouring hexagonal sheets by 180° parallel to (001) (the hexagonal xy plane) and (ii) the $T2/3R$ transformation replaces all T_{2m} units (denoting two T atoms on a trigonal axis, connected across a mirror plane, with a T–O–T bond angle of 180°) by single three-membered rings ($S3R$). The same concepts and notations will be used here. Unless otherwise stated, net numbers refer to nets described in that paper. In the third report (Andries, 1990) of a series of three successive papers of which the present is the second, a compilation is given of all enumerated nets and of all definitions, abbreviations and notations used.

Firstly, two novel types of transformations that are specifically applicable to nets of the tridymite group will be described: the tridymite group-extended tridymite group (TET) transformation and the tridymite group-$2T$ orthorhombic (TO) transformation. Furthermore, the $2T$ orthorhombic-extended orthorhombic (OEO) transformation is based on the same principles as the TET transformation. We will apply then the TET, TO, $T2/3R$ and $R180$ transformations (or combinations thereof) to structures of the tridymite group. Finally, some properties of the resulting nets will be discussed. A complete systematic and crystallographic description of all theoretically possible (4; 2)-connected 3D nets is beyond the scope of this study but will be published in the future.

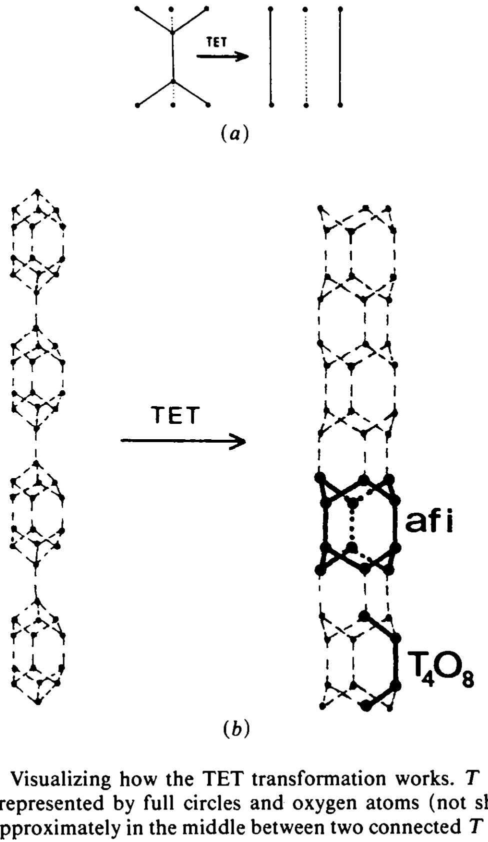
Geometrical transformations used for deriving novel framework topologies from nets of the tridymite group

1. *The extended tridymite group and the tridymite group-extended tridymite group (TET) transformation*

This transformation removes all T_{2m} units connecting neighbouring $2T$ trigonal cages (denoting polyhedral cages with threefold symmetry and two on-axis oppositely oriented T nodes) along the trigonal axes and extends the cage (becoming an infinite trigonal column) by an infinite repetition of the horizontal stack sequence of the cage. The sequence 3-1(m)1-3 [1(m)1 is used to denote the T_{2m} unit] is hereby reduced to 3(S)3 (denoting two three-membered horizontal stacks with an 'eclipsed' or '*cis*' configuration). This transformation is visualized in Fig. 1(a), where the T_{2m} unit with its associated three-membered stacks (3MS) is converted into a pair of S-connected 3MS's. The conversion into a trigonal column for a chain of $2T$ trigonal CSC cages [*afo* cage (Smith, 1988); the notation CSC is a shorthand notation for cage 1-3(C)3(S)3(C)3-1; C denotes a 'staggered' or '*trans*' configuration] connected along the trigonal axis by forming T_{2m} units is represented in Fig. 1(b). The column now has an infinite repetition of the 3(C)3(S) stack sequence (or CS).

In this way net 4 is converted into a net of the extended tridymite group, designated structure type 28 [Figs. 6(a1), (a2)] and enumerated by Bennett & Smith (1985) as their net 82a. Nets 3b, 4, 6b and 8 are all converted into net 28 by the TET transformation. As such, nets of the extended tridymite group can be derived from group 1 3D nets, as well as from group 2 3D nets of the tridymite group (the former are constructed from $2T$ trigonal cages symmetry-related by mirror planes parallel to the hexagonal c axis, the latter from $2T$ trigonal cages symmetry related by threefold axes). It should be noted that the trigonal columns in frameworks of the extended tridymite group are laterally connected in the same way as are the $2T$ trigonal cages in the respective nets of the tridymite group from which they have been derived (T_{2m} units do not participate in lateral linkages).

This transformation converts the $(4^3)_1(4^2.12)_3(4^3.12)_3$ (3, 4)-connected 2D net of net 4 [Fig. 14 of Bosmans & Andries (1990)] into the (4.6.12) 3-connected 2D net of net 28 (Fig. 2) by removing the on-axis T atoms [the notation $(A^b.C^d)_e(F^g.H^i)_j\ldots$ is a net symbol denoting the



(a)

(b)

Fig. 1. Visualizing how the TET transformation works. T atoms are represented by full circles and oxygen atoms (not shown) lie approximately in the middle between two connected T atoms or are not 2-connected. In (b) the TET-transformed column is constructed by connecting *afi* units (bold lines), which themselves are constructed by linking T_4O_8 units (bold lines) across a trigonal axis.

geometry of a 2D net: each T atom in the net is part of b A-membered rings, d C-membered rings,...; if $A^b.C^d\ldots = X$ and $F^g.H^i\ldots = Y$, then X_eY_j means that the ratio of the number of type X T nodes to the number of type Y T nodes in the net is e/j; all letters represent integral values]. The TET transformation preserves the hexagonal a parameter, while the c repeat is reduced and TET-transformed 3D nets have an integral multiple of three T atoms in their unit cell: no T atoms on trigonal axes occur.

Most extended nets have no channels of appreciable dimension perpendicular to the hexagonal c axis, because channel system A or B (formed between neighbouring hexagonal sheets in all frameworks of the tridymite group made of isolated $2T$ trigonal cages) vanishes as a consequence of eliminating the T_{2m} units. The TET transformation does not affect the aperture of the channels along the hexagonal c axis; on the contrary, in some cases a supplementary channel system along the symmetry axis is created [compare nets 19 [Fig. 15(*b*) of Bosmans & Andries (1990)] and 31 [Fig. 6(*b*3)]}.

2. *The 2T orthorhombic group and the tridymite group–2T orthorhombic (TO) transformation*

In all group 1 3D nets of the tridymite group, each $2T$ trigonal cage is linked to three adjacent cages to form a hexagonal sheet; two neighbouring cages are symmetry related by a mirror plane. This mode of connecting cages is visualized for the *CSC* cage in Fig. 3(*a*): the letters a, b and c refer to coplanar T atoms in planes parallel to the mirror planes between neighbouring cages. As represented in Fig. 3(*a*), the *CSC* cage is linked to five other *CSC* cages (a to e: three in the sheet, one above and one below) to form a net of the tridymite group (simple net 4).

Definition: An alternative orthorhombic way for connecting this type of cage is represented in Fig. 3(*b*). The letters a and b define planes 2 and 1 parallel to the respective mirror planes between neighbouring cages. This leaves c and d available for connections in the other direction to form an orthorhombic sheet. A new set of mirror planes is thus formed in this net, *i.e.* perpendicular to planes 1 and 2 and parallel to edge d–d. A schematic drawing of the projection onto (001) (the orthorhombic xy plane; the orthorhombic c axis runs parallel to the trigonal axis of the $2T$ trigonal cages) for this type of sheet is given in Fig. 4. Notice that the density of bonds in the y direction is higher than in the x direction. In Fig. 4, we denote the c–c and d–d distances (of Fig. 3*b*) by F (far) and N (near), respectively.

A 3D net is then constructed by connecting the sheets along **z** through the remaining e and f nodes. In this case, neighbouring sheets are symmetry related by translation along **z**: a simple orthorhombic 3D net is formed. In this particular 3D net, designated type 47 (and in every $2T$ orthorhombic net in general), each $2T$ trigonal cage is linked to six others: four in the sheet, one above and one below. The bond density between neighbouring sheets is lower than in the x direction and comparable with the bond density between sheets in the corresponding nets of the tridymite group. The orthorhombic and hexagonal unit-cell parameters are related as follows (subscripts o and h denote orthorhombic and hexagonal parameters respectively) (a_o along **x**, b_o along **y**):

$$\begin{cases} a_o \text{ is (slightly) higher than } 2b_o \\ b_o = a_h/(2\cos 30°) \\ c_o = c_h. \end{cases}$$

Notice that the 2D net in Fig. 4 is designated the $(4^3.8)_4(4.8^2)_2(4^3)_1$ (3, 4)-connected 2D net. Besides

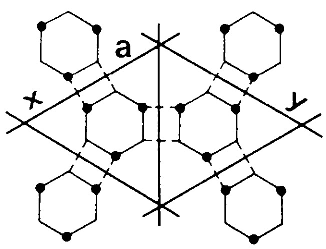
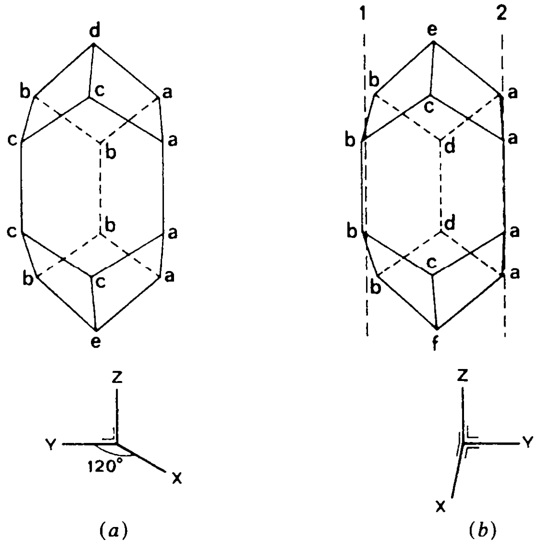


Fig. 2. The lateral connection of *CS*-type trigonal columns in net 28. View along the hexagonal c axis. Colums are represented with full lines and their connections with dashed lines. T nodes are up (circle) or down (no circle). Oxygen atoms (not shown) lie approximately in the middle between two connected T atoms or not 2-connected. Note the hexagonal unit cell bounded by mirror planes and the position of the trigonal columns at $x = 2/3$, $y = 1/3$ and at $x = 1/3$, $y = 2/3$.



(*a*) (*b*)

Fig. 3. Connecting *CSC* cages to form (*a*) group 1 nets of the tridymite group and (*b*) $2T$ orthorhombic nets. T nodes lie at the intersections of lines and oxygen atoms (not shown) lie approximately in the middle between two connected T atoms or are not 2-connected.

the T nodes on the (original) trigonal axes, the 4-connected nodes also are part of three four-membered rings (in net 47, 71·4% of the T nodes are part of three $S4R$'s; compare with 100% in net 4). The type 47 structure can be made from the above type of 2D net connected across mirror planes.

Related nets: Other $2T$ trigonal cages, belonging to the $C(SC)_r$ series (r is zero or a positive integer), can also be assembled into $2T$ orthorhombic nets. Nets made of C ($r=0$), $CSCSC$ ($r=2$) and $CSCSCSC$ ($r=3$) cages are designated structure types 46, 48 and 49 respectively [Figs. 4 and 7($b1$)]. Nets constructed from cages with $r=$ odd all have the same projection onto the xy plane as in Fig. 4 (this type of cage has a mirror plane perpendicular to the trigonal axis, while cages with $r=0$ or even have an inversion centre).

The notations N and F (Fig. 4) do not always refer to 'near' and 'far', such as in cases where NN and FF linkages are symmetrically equivalent (*e.g.* in $2T$ orthorhombic nets made of $C(SC)_r$-type cages with $r=0$ or even). In the latter case, the $R180$ transformation can be applied in a straightforward way, such as to framework types 46 and 48. The respective non-simple nets are designated structure types 46b and 48b.

Because lateral bonds in the y direction are not symmetrically equivalent to those in the x direction, the constituent sheets of nets 46 to 49 probably cannot be rotated by $(90\times f)°$ (where f is 1 or 3) to form a 3D net. *DLS* refinements (Baerlocher, Hepp & Meier, 1977) of the resulting non-simple nets were not performed.

Neighbouring orthorhombic sheets are symmetry related by a mirror plane in structure types 46b, 47, 48b and 49 and by inversion in nets 46 and 48. In all structure types 46 to 49, channels along the x and the z axes occur with a maximum aperture of eight-rings (the channel system along **x** is equivalent to channel system A present in all group 1 nets of the tridymite group constructed from isolated $2T$ trigonal cages; see Fig. 4 for the channel system along **z**). In nets 46 and 48, the apertures along **y** are ten-rings, in types 47 and 49 twelve-rings. In all types, the channel system intersects and is three-dimensional. The TO transformation lowers the number of the largest channels in the net (*i.e.* channels along the y axis). In some cases, the transformation lowers the maximum channel aperture also {*e.g.* compare structure types 3 and 6 [$S12R$, Fig. 15($a3$) of Bosmans & Andries (1990)] with nets 46 and 48 ($S10R$)}.

Application of the TO transformation to simple nets of the tridymite group results in simple $2T$ orthorhombic nets. It is furthermore obvious that non-simple nets can be constructed by stacking different sheet types onto each other along [001].

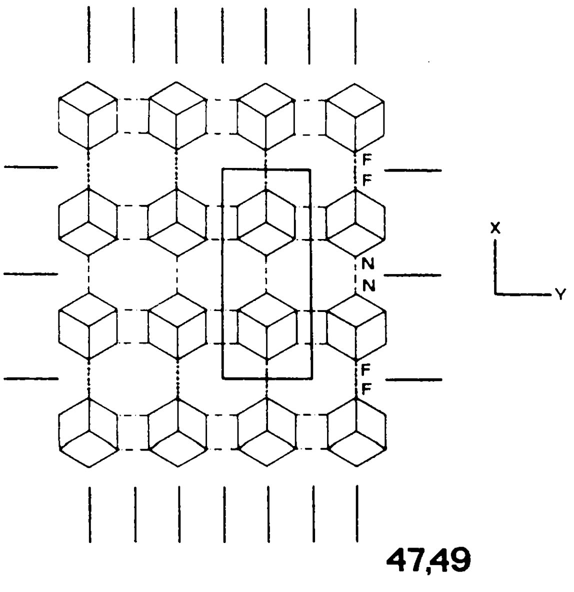


Fig. 4. The $2T$ orthorhombic sheet made of CSC $2T$ trigonal cages. Cages are represented with full lines and different types of lines have been used for the symmetrically non-equivalent bonds connecting them. T atoms lie at the intersections of lines and oxygen atoms (not shown) lie approximately in the middle between two connected T atoms or are not 2-connected. Mirror planes and the orthorhombic unit cell are indicated. Figures are net numbers.

3. *The extended orthorhombic group and the $2T$ orthorhombic-extended orthorhombic (OEO) transformation*

In some $2T$ orthorhombic nets, the T_{2m} units along **z** can be removed whereby the cages are converted into trigonal columns, in exactly the same way as was described for nets of the extended tridymite group. A schematic representation of the projection of these structures onto the xy plane is as in Fig. 4, with the on-axis T nodes removed.

This transformation converts the 2D net represented in Fig. 4 into the $(4.6.8)_2(6.8^2)_1$ 3-connected 2D net [Fig. 7($b6$)]. Structures derived from this type of net are $AlPO_4$-21 [ATF (Bennett, Cohen, Artioli, Pluth & Smith, 1985)] and $AlPO_4$-EN3 (Bennett, Dytrych, Pluth, Richardson & Smith, 1986). A systematic enumeration of structures made from this type of 2D net with the orientation of the T nodes being either up or down has not yet been done. A limited number of 3D nets built up with this type of 2D net were described by Smith (1979).

The OEO transformation does not affect the orthorhombic a or b dimension but the c repeat is reduced. Nets of the extended orthorhombic group exhibit the lowest bond density in the x direction.

The OEO transformation applied to nets 46b, 47, 48b and 49 results in one and the same net, designated structure type 52 [Fig. 7($b6$)].

Because the TO transformation is only concerned with lateral linkages of the trigonal units and does not in any way affect the stack sequence of the trigonal columns, it can be applied to structures of the extended tridymite group, just as well as to structures of the tridymite group. In this way, net 52 can be derived from net 28 by the TO transformation.

The maximum channel dimension is lower for extended orthorhombic nets than for the corresponding frameworks in the extended tridymite group {*e.g.* compare nets 28 (*S*12*R*) and 35 [*S*18*R*, Fig. 6(*b*5)] with nets 52 (*S*8*R*) and 53 [*S*12*R*, Fig. 7(*b*7)] respectively}.

The systematic enumeration of 3D nets derived from structures of the tridymite group by applying geometrical transformations

Novel nets can be derived systematically by the application of the following transformations to nets of the tridymite group: (i) *R*180, (ii) *T*2/3*R*, (iii) TET and (iv) TO. The OEO transformation is applicable to 2*T* orthorhombic nets only and the resulting nets can be regarded as being derived from structures of the tridymite group by the application of the TET and the TO transformations. Net numbers are compiled in Table 1.

Some supplementary nets, besides those in Table 1, were derived (schematic drawings of these nets are given in Figs. 6 and 7):

(i) Net 34 can be obtained by alternating unit cells of nets 31 and 32 in the [001] direction.

(ii) Nets 35 to 37 belong to the extended (group 1) tridymite group and are made of trigonal columns 3(*LH*)6(*H*)3(*S*), 3(*H*)6(*LH*)6(*L*)6(*H*)3(*S*) and 3(*H*)6(*L*)6(*LH*)6(*L*)6(*L*)6(*H*)3(*S*) respectively [see Bosmans & Andries (1990) for notation]. The corresponding group 1 nets of the tridymite group from which they are derived are constructed from group *B* 2*T* trigonal cages (denoting 2*T* trigonal cages constructed from 3MS's and 6MS's without any *S*3*R* perpendicular to the trigonal axis) with an *S*6*R* perpendicular to the trigonal axis. The latter nets were mentioned in the paper of Bosmans & Andries (1990), but no *DLS* refinements were performed.

(iii) Nets 38 and 39 are derived from nets 36 and 37 respectively by replacing the *S*6*R*'s perpendicular to the trigonal axes by *D*6*R*'s (by a $\sigma_{(002)}$ transformation).

(iv) Net 53 is derived from net 35 by the TO transformation.

Table 1. *The systematic derivation of hypothetical* 3*D nets from structures of the tridymite group by applying geometrical transformations*

Figures are net numbers. Columns 2 to 5 are derived from column 1 (Bosmans & Andries, 1990) and columns 6 and 7 from column 5. Nets in column 6 can also be derived from column 3, and those in column 7 from column 4 by the TO transformation. Slashes denote impossible transformations.

(1) Net number	(2) *R*180	(3) *T*2/3*R*	(4) TET	(5) TO	(6) *T*2/3*R*	(7) OEO
Group 1						
1	/	40	/	/	/	/
2	/	41	/	/	/	/
3	3*b*	/	/	46	/	/
3*b*	3	42	28	46*b*	54	52
4	4*b*	43	28	47	18	52
5	/	66	29	/	/	/
6	6*b*	/	/	48	/	/
6*b*	6	65	28	48*b*	72	52
7	/	67	30	/	/	/
8	8*b*	64	28	49	69	52
11	/	40	41	/	/	/
12	12*b*	42	43	50	54	18
13	13*b*	43	64	51	18	69
19	/	44	31	/	/	/
20	/	45	32	/	/	/
21	/	68	31	/	/	/
22	/	70	32	/	/	/
23	/	62	/	/	/	/
24	/	63	/	/	/	/
25	/	71	33	/	/	/
Group 2						
55	55b	17	/	/	/	/
60	60b	17	/	/	/	/

(v) The net obtained from structure type 52 by applying σ^{-1} transformations at the mirror planes perpendicular to the *y* axis between neighbouring trigonal colums is designated structure type 61. This net was not enumerated previously (Smith, 1977); using the terminology of the author, it is constructed from 6^3 (simple hexagonal) 2D nets with sequences *CCCCCC* and *CCSCCS* in the hexagons [Fig. 7(*b*8)]. When the mirror planes perpendicular to x in structure type 61 are replaced by *c* glides, the tridymite net (Gibbs, 1926) is obtained.

Some remarks concerning the enumerated 3D nets should be made (see Figs. 6 and 7 for representations):

(i) AlPO$_4$-5 (AFI) (Bennett, Cohen, Flanigen, Pluth & Smith, 1983) and nets 28 and 52 can all be made of the *afi* unit [Fig. 1(*b*), 6≡6, 6^5 (Smith, 1988)], which itself can be derived from the *afo* unit (Smith, 1988) ($T_{14}O_{28}$ *CSC* 2*T* trigonal cage) by removing the *T* atoms on the trigonal axis (the notation 6≡6 denotes two parallel *S*6*R*'s interlinked with three bonds around the threefold axis; the notation 6^5 is a face symbol denoting a polyhedral cage bounded by five six-rings).

(ii) Nets derived from structures of the tridymite group by the *T*2/3*R* transformation all have the same schematic projection onto the hexagonal (001) plane as their respective analogues in the tridymite group, with T_{2m} units being replaced by *S*3*R*'s; their unit cell *a* parameter is almost identical, but their *c* repeat is smaller. This reduction can be very striking if the respective net of the tridymite group is constructed from group *C* 2*T* trigonal cages [*e.g.* net 13 (Bosmans & Andries, 1990) *versus* net 43]. The number of *T* atoms per unit cell is an integral multiple of three for this type of $T2/3R$-transformed nets.

(iii) A similar line of thought as under (ii) can be made for nets that are derived from $2T$ orthorhombic structures by the $T2/3R$ transformation. The reduction of the c repeat is striking by comparing for example structure types 51 and 18.

(iv) All hexagonal nets made of $[(S)3(C)3]_p(LH)3$-type trigonal columns (p is a positive integer) can be derived from nets of the tridymite group by the $T2/3R$ transformation and/or the TET transformation (nets 42, 43, 65 and 64 have $p = 1$ to 4 respectively). Similarly, all orthorhombic nets constructed from the same type of trigonal column can be derived from $2T$ orthorhombic nets by the $T2/3R$ and/or the OEO transformation (nets 54, 18, 72 and 69 have $p = 1$ to 4 respectively).

(v) No hypothetical nets of the extended tridymite group, derived from group 2 nets of the tridymite group, have been identified so far.

Some topological relations between several nets derived are given in Fig. 5. From this figure it is obvious that a simple relation exists between the topology of Linde Q of Breck & Acara (1961) [net 4: Andries, Bosmans & Grobet (1990); structure-type code BPH (Harvey & Meier (1989)] and the tridymite structure (Gibbs, 1926): indeed, the 3-connected 2D net in net 28 (derived from net 4 by the TET transformation, Fig. 2) converts into the 6^3 3-connected 2D net present in tridymite (simple hexagonal 2D net with alternately up and down tetrahedra) by applying σ^{-1} transformations at the mirror planes symmetry-relating neighbouring hexagons.

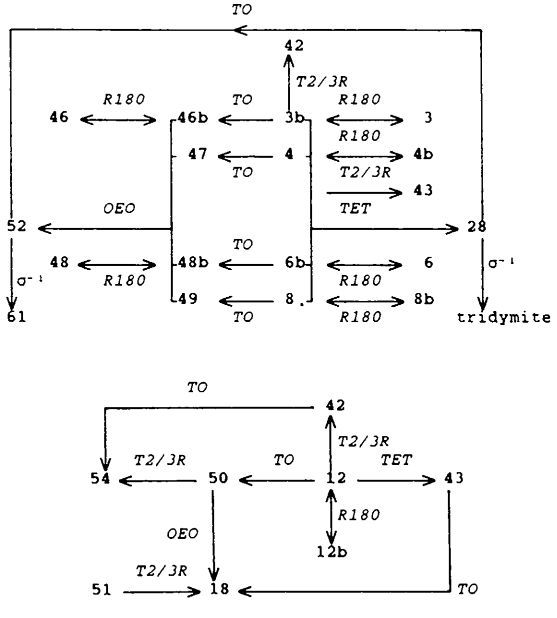


Fig. 5. Some topological relations between nets derived from 3D nets of the tridymite group. Figures are net numbers.

Table 2. *Secondary building units for the 3D nets derived from structures of the tridymite group by applying the transformations of Table* 1

In those cases where more than one structural subunit is given, no attempt was made to characterize one single SBU [according to the original definition by Meier (1968)]. The notation 'i' (i integer) designates a single i-membered ring; see Bosmans & Andries (1990) for the other designations.

SBU	Net numbers
3	17
4	28, 30, 31, 32, 33, 34, 39, 52
$1\equiv 3$	46*b*
$3+4$	18, 35, 41, 42, 43, 44, 45, 53, 62, 64, 65, 67, 68, 69, 70, 71, 72
$1\equiv 6$	47
$3+6$	40, 54, 63, 66
$4+6$	29, 36, 37, 38
$1\equiv 6\equiv 3$	48*b*
$1\equiv 6+3$	50
$1\equiv 6\equiv 6$	49
$1\equiv 6\equiv 6+3$	51

The secondary building units for all nets derived from structures of the tridymite group by applying the transformations of Table 1 are compiled in Table 2. Net 61 can be built from the 4 (*i.e.* the $S4R$) and T_4O_8 SBU's; the latter unit is the repetitivity unit of the single crankshaft chain (Fig. 1*b*).

Schematic representations for nets 28, 29, 31, 32, 35 and 44 are given in Fig. 6 and important crystallographic data for structure types 28 to 32, 35, 44 and 47 are given in Table 3. Refinement of the unit-cell parameters and the atomic positions was done with *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 factor was lowered by permitting the T–O distances to vary between the values for pure Si–O and Al–O bonds. Space groups $P\bar{6}2m$ (net 28), $Pmmm$ (net 47) and $P321$ (other nets) were assumed.

Schematic projections onto the hexagonal or orthorhombic (001) plane for all nets enumerated can be found in Figs. 4, 6 and 7. Structural characteristics for all nets [repetition sequence of the trigonal columns and reference to a schematic representation of the projection onto (001)] can be found in Table 4.

Some specific properties

Framework structures of the extended tridymite group: All differences in properties for frameworks of the extended tridymite group and their analogues of the tridymite group will be related to the effect of removing the T_2 units on the trigonal axes. Because structures of the extended tridymite group do not exhibit a sheet-like character, their (framework) density is consistently higher than that of their corresponding

Table 3. *Crystallographic data for some 3D nets derived from group 1 nets of the tridymite group*

MSG = maximum space-group symmetry; TUC = number of tetrahedral atoms in the unit cell; IT = number of non-equivalent tetrahedral atoms for MSG; FD = framework density (number of tetrahedral atoms per unit volume of 1000 Å^3); V_f = void fraction (g cm^{-3}), calculated according to the experimentally derived relation (Breck, 1973); $V_f = (-0{\cdot}0375\text{FD}) + 0{\cdot}975$; RF = established materials with the framework structure described; REF = reference to the first description of the net topology; N designates the sequence 3(C)3(S)3(C)3.

Net number	Repetition sequence	MSG	TUC	IT	a	b (Å)	c	FD	V_f	RF	REF
28	CS	$P6_3/mcm$	24	1	14·04		9·50	14·8	0·42	/	(1)
29	$SSCSC$	$P\bar{6}2m$	30	3	12·52		11·41	19·4	0·25	/	/
30	$SSSCSC$	$P\bar{6}2m$	36	3	13·20		13·85	17·2	0·33	/	/
31	3(H)6(H)3	$P6/mmm$	24	2	16·12		7·39	14·4	0·43	/	/
32	3(H)6(L)6(H)3	$P6/mmm$	36	2	16·68		9·94	15·0	0·41	/	/
35	3(LH)6(H)3	$P6_3/mcm$	48	2	17·01		13·85	13·8	0·46	/	/
44	3(H)6(H)3(LH)3	$P6/mmm$	30	3	15·52		9·37	15·3	0·40	/	/
47	1-N-1(m)	$Pmmm$	28	5	17·43	7·19	12·89	17·3	0·32	/	/

Reference: (1) Bennett & Smith (1985).

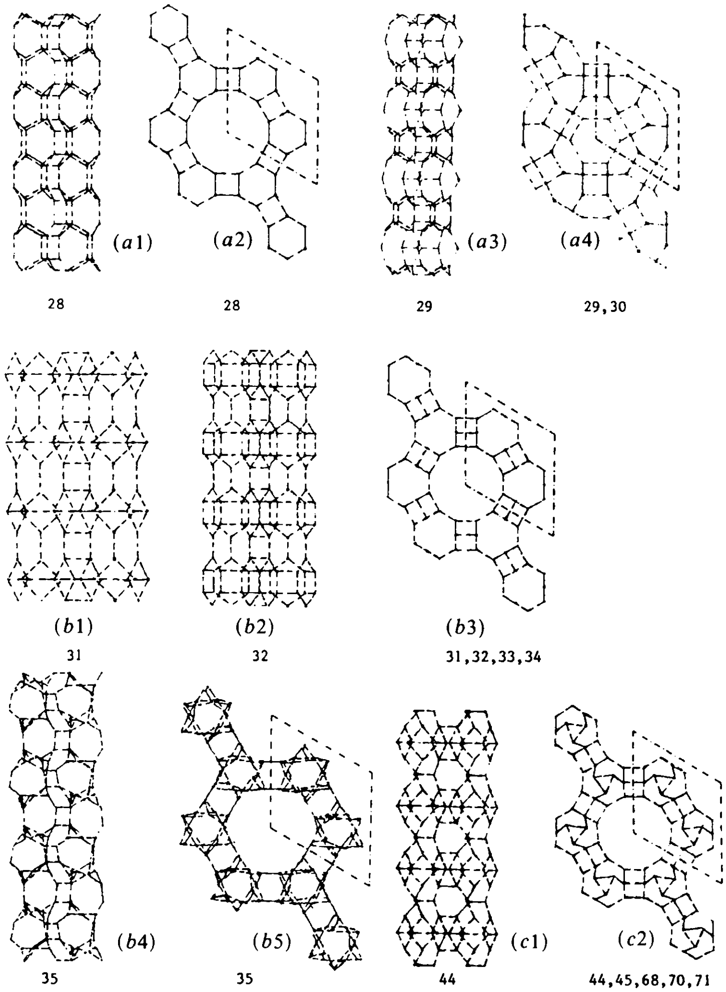


Fig. 6. Schematic representations for some nets derived from nets of the tridymite group by applying geometrical transformations. Each time, two laterally connected trigonal columns and the projection of the net onto the hexagonal (001) plane have been drawn: (*a*1 to *a*4) nets derived by the TET transformation from group 1 nets of the tridymite group made of group *A* 2*T* trigonal cages; (*b*1 to *b*5) nets derived by the TET transformation from group 1 nets of the tridymite group made of group *B* 2*T* trigonal cages and (*c*1 and *c*2) net 44. Figures are net numbers. *T* atoms are represented by squares whose size is proportional to the distance from the eye; oxygen atoms (not shown) lie approximately in the middle between two interconnected *T* atoms or are not 2-connected. (Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.)

analogues in the tridymite group. On the other hand, since they do not contain the inflexible 1-1 units, they exhibit a higher thermal stability.

2T orthorhombic framework structures: 2*T* orthorhombic framework structures exhibit a higher framework density than their corresponding analogues in the tridymite group. The thermal stability of 2*T* orthorhombic framework structures will be similar to (or will be slightly better than) that of their analogues in the tridymite group because of their higher framework density. Because of the lower symmetry of the T_2 unit in the 2*T* orthorhombic nets, the ^{29}Si NMR and the IR spectra might not be as distinct as for frameworks of the tridymite group (Bosmans & Andries, 1990). 2*T* orthorhombic nets will also exhibit a sheet-like character.

Extended orthorhombic framework structures: Nets belonging to the extended orthorhombic group also have a higher framework density than the corresponding structures in the extended tridymite group.

The TET, TO and OEO transformations will increase the framework density [approximate values (g cm^{-3}) in brackets after net numbers]:

$$\begin{tikzcd}
3b, 4, 6b, 8\ (12\cdot7\text{–}14\cdot3) \arrow[r, "\text{TET}"] \arrow[d, "\text{TO}"] & 28\ (14\cdot8) \arrow[d, "\text{TO}"] \\
46b, 47, 48b, 49\ (14\cdot0\text{–}17\cdot0) \arrow[r, "\text{OEO}"] & 52\ (>17\cdot0).
\end{tikzcd}$$

Discussion

Novel framework topologies can be enumerated by the application of three classes of transformations to 3D nets constructed from trigonal columns:

(i) transformations that change the stack sequence of the trigonal columns in the net but that do not alter the nature of their lateral connections: the symmetry of the net is preserved;

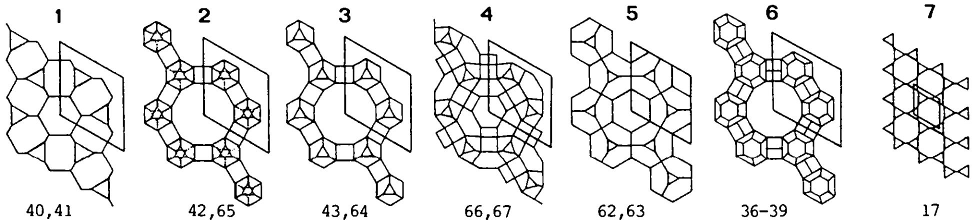
(ii) transformations that do not alter the stack sequence of the trigonal columns in the net but that do change the nature of their lateral connections; in the most general case, the symmetry of the net is not preserved, unless in those cases where the transformation in itself preserves the symmetry [*e.g.* (*a*) the transformation of net 82*a* of Bennett & Smith (1985) into the tridymite net (Gibbs, 1926); (*b*) some novel hypothetical nets can be derived from structures of the tridymite group by inserting an *S*4*R* between every two adjacent 2*T* trigonal cages in the same hexagonal sheet];

(iii) transformations that alter the stack sequence of the trigonal columns as well as their lateral connections; in the most general case, the symmetry of the net is not preserved.

The TET and OEO transformations belong to class (i) and the TO transformation belongs to class (ii).

At this time, no materials with framework structures belonging to the extended tridymite group, the 2*T* orthorhombic group or the extended orthorhombic group have been established.

(*a*) Hexagonal nets



(*b*) Orthorhombic nets

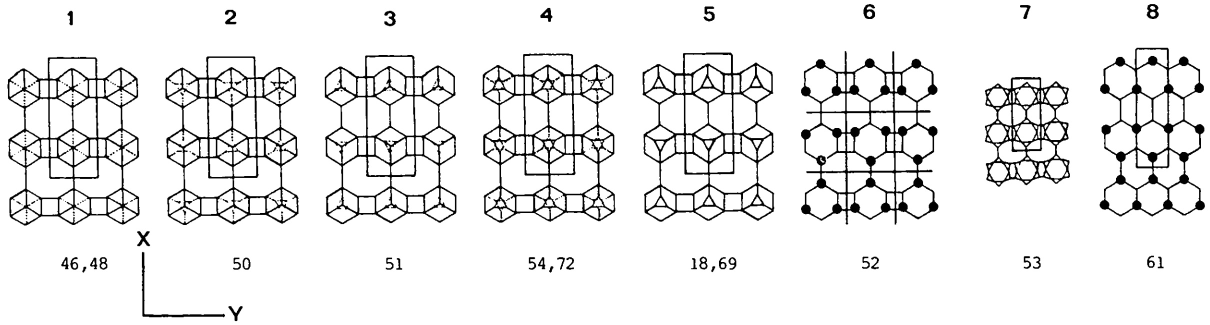


Fig. 7. Schematic projections onto the hexagonal (*a*) or the orthorhombic (*b*) (001) plane for all hypothetical nets that were not represented in Figs. 4 or 6. Small figures are net numbers. Unit cells are indicated. In (*b*6) mirror planes are represented. In (*b*6) and (*b*8) up (circle) and down (no circle) tetrahedra are indicated. See Table 4 for supplementary information on the individual nets.

Table 4. *Structural information on all nets derived*

Neighbouring trigonal columns are symmetry related by mirror planes parallel to the column axis, except in net 17 where they are symmetry related by trigonal axes. Nets that cannot be constructed from isolated trigonal columns (neighbouring columns share faces and/or edges) are indicated by *.

Net number	Repetition sequence	Projection onto (001)
17	$3(LH)3(S)$	Fig. 7(a7)
18	$3(C)3(S)3(C)3(LH)3(S)$	Fig. 7(*b*5)
28	$3(C)3(S)$	Fig. 6(*a*2)
29	$3(C)3(S)3(S)3(C)3(S)$	Fig. 6(*a*4)
30	$3(C)3(S)3(S)3(S)3(C)3(S)$	Fig. 6(*a*4)
31	$3(H)6(H)3(S)$	Fig. 6(*b*3)
32	$3(H)6(L)6(H)3(S)$	Fig. 6(*b*3)
33	$3(H)6(H)3(S)3(H)6(L)6(H)3(S)$	Fig. 6(*b*3)
34	$[3(H)6(H)3(S)]_2 3(H)6(L)6(H)3(S)$	Fig. 6(*b*3)
35	$3(LH)6(H)3(S)$	Fig. 6(*b*5)
36	$3(H)6(LH)6(L)6(H)3(S)$	Fig. 7(*a*6)
37	$3(H)6(L)6(LH)6(L)6(L)6(H)3(S)$	Fig. 7(*a*6)
38	$3(H)6(LH)6(LH)6(L)6(H)3(S)$	Fig. 7(*a*6)
39	$3(H)6(L)6(LH)6(LH)6(L)6(L)6(H)3(S)$	Fig. 7(*a*6)
40	$3(LH)3(S)$	Fig. 7(*a*1)
41	$3(S)3(LH)3(S)$	Fig. 7(*a*1)
42	$3(C)3(LH)3(S)$	Fig. 7(*a*2)
43	$3(C)3(S)3(C)3(LH)3(S)$	Fig. 7(*a*3)
44	$3(H)6(H)3(LH)3(S)$	Fig. 6(*c*2)
45	$3(H)6(L)6(H)3(LH)3(S)$	Fig. 6(*c*2)
46	$1\text{-}3(C)3\text{-}1$	Fig. 7(*b*1)
46*b*	$1\text{-}3(C)3\text{-}1(m)1\text{-}3(C)3\text{-}1$	Fig. 7(*b*1)
47	$1\text{-}3(C)3(S)3(C)3\text{-}1$	Fig. 4
48	$1\text{-}[3(C)3(S)]_2 3(C)3\text{-}1$	Fig. 7(*b*1)
48*b*	$1\text{-}[3(C)3(S)]_2 3(C)3\text{-}1(m)1$ $\text{-}[3(C)3(S)]_2 3(C)3\text{-}1$	Fig. 7(*b*1)
49	$1\text{-}[3(C)3(S)]_3 3(C)3\text{-}1$	Fig. 4
50	$1\text{-}3(C)3(LH)3(S)3(C)3\text{-}1$	Fig. 7(*b*2)
51	$1\text{-}3(C)3(S)3(C)3(LH)3(S)3(C)3(S)3(C)3\text{-}1$	Fig. 7(*b*3)
52	$3(C)3(S)$	Fig. 7(*b*6)
53	$3(LH)6(H)3(S)$	Fig. 7(*b*7)
54	$3(C)3(LH)3(S)$	Fig. 7(*b*4)
61*	$3(C)3(S)$	Fig. 7(*b*8)
62*	$3(H)6(H)3(LH)3(S)$	Fig. 7(*a*5)
63*	$3(H)6(L)6(H)3(LH)3(S)$	Fig. 7(*a*5)
64	$[3(C)3]_4(LH)3(S)$	Fig. 7(*a*3)
65	$[3(C)3]_3(LH)3(S)$	Fig. 7(*a*2)
66	$3(C)3(S)3(S)3(C)3(LH)3(S)$	Fig. 7(*a*4)
67	$3(C)3(S)3(S)3(S)3(C)3(LH)3(S)$	Fig. 7(*a*4)
68	$3(H)6(H)3(S)3(H)6(H)3(LH)3(S)$	Fig. 6(*c*2)
69	$[3(C)3]_4(LH)3(S)$	Fig. 7(*b*5)
70	$3(H)6(L)6(H)3(S)3(H)6(L)6(H)3(LH)3(S)$	Fig. 6(*c*2)
71	$3(H)6(H)3(S)3(H)6(L)6(H)3(LH)3(S)$	Fig. 6(*c*2)
72	$[3(C)3]_3(LH)2(S)$	Fig. 7(*b*4)

All hexagonal 3D nets are constructed from trigonal columns and a systematic enumeration and classification of such nets has been carried out (Andries, 1990).

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Towards a General Description of Hexagonal Three-Dimensional Framework Structures: the Lateral Connection of Trigonal Columns (LCTC) Group

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Abstract

Hexagonal three-dimensional framework structures are constructed from trigonal columns. When two types of trigonal column are distinguished, all hexagonal 3D framework structures known to date can be classified in the lateral connection of trigonal columns (LCTC) group. Also, orthorhombic 3D nets

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