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(b5)
28	3(C)3(S)	Fig. 6(a2)
29	3(C)3(S)3(S)3(C)3(S)	Fig. 6(a4)
30	3(C)3(S)3(S)3(S)3(C)3(S)	Fig. 6(a4)
31	3(H)6(H)3(S)	Fig. 6(b3)
32	3(H)6(L)6(H)3(S)	Fig. 6(b3)
33	3(H)6(H)3(S)3(H)6(L)6(H)3(S)	Fig. 6(b3)
34	$[3(H)6(H)3(S)]_2$3(H)6(L)6(H)3(S)	Fig. 6(b3)
35	3(LH)6(H)3(S)	Fig. 6(b5)
36	3(H)6(LH)6(L)6(H)3(S)	Fig. 7(a6)
37	3(H)6(L)6(LH)6(L)6(L)6(H)3(S)	Fig. 7(a6)
38	3(H)6(LH)6(LH)6(L)6(H)3(S)	Fig. 7(a6)
39	3(H)6(L)6(LH)6(LH)6(L)6(L)6(H)3(S)	Fig. 7(a6)
40	3(LH)3(S)	Fig. 7(a1)
41	3(S)3(LH)3(S)	Fig. 7(a1)
42	3(C)3(LH)3(S)	Fig. 7(a2)
43	3(C)3(S)3(C)3(LH)3(S)	Fig. 7(a3)
44	3(H)6(H)3(LH)3(S)	Fig. 6(c2)
45	3(H)6(L)6(H)3(LH)3(S)	Fig. 6(c2)
46	1-3(C)3-1	Fig. 7(b1)
46b	1-3(C)3-1(m)1-3(C)3-1	Fig. 7(b1)
47	1-3(C)3(S)3(C)3-1	Fig. 4
48	1-$[3(C)3(S)]_2$3(C)3-1	Fig. 7(b1)
48b	1-$[3(C)3(S)]_2$3(C)3-1(m)1 -$[3(C)3(S)]_2$3(C)3-1	Fig. 7(b1)
49	1-$[3(C)3(S)]_3$3(C)3-1	Fig. 4
50	1-3(C)3(LH)3(S)3(C)3-1	Fig. 7(b2)
51	1-3(C)3(S)3(C)3(LH)3(S)3(C)3(S)3(C)3-1	Fig. 7(b3)
52	3(C)3(S)	Fig. 7(b6)
53	3(LH)6(H)3(S)	Fig. 7(b7)
54	3(C)3(LH)3(S)	Fig. 7(b4)
61*	3(C)3(S)	Fig. 7(b8)
62*	3(H)6(H)3(LH)3(S)	Fig. 7(a5)
63*	3(H)6(L)6(H)3(LH)3(S)	Fig. 7(a5)
64	$[3(C)3]_4$(LH)3(S)	Fig. 7(a3)
65	$[3(C)3]_3$(LH)3(S)	Fig. 7(a2)
66	3(C)3(S)3(S)3(C)3(LH)3(S)	Fig. 7(a4)
67	3(C)3(S)3(S)3(S)3(C)3(LH)3(S)	Fig. 7(a4)
68	3(H)6(H)3(S)3(H)6(H)3(LH)3(S)	Fig. 6(c2)
69	$[3(C)3]_4$(LH)3(S)	Fig. 7(b5)
70	3(H)6(L)6(H)3(S)3(H)6(L)6(H)3(LH)3(S)	Fig. 6(c2)
71	3(H)6(H)3(S)3(H)6(L)6(H)3(LH)3(S)	Fig. 6(c2)
72	$[3(C)3]_3$(LH)2(S)	Fig. 7(b4)

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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can be constructed from trigonal columns and a number of such hypothetical nets related to the hexagonal 81(i) series of Smith & Dytrych [*Nature* (*London*) (1984), **309**, 607–608] are enumerated. A systematic investigation of the several ways by which neighbouring trigonal columns can be linked and symmetry related gives rise to a large number of subgroups in the present LCTC group. A general designation for LCTC structures by means of a composite code is proposed.

Introduction

Several approaches have been used for the classification of (4; 2)-connected 3D framework structures (this notation stands to denote framework structures extended in three-dimensional space with every framework T atom being tetrahedrally coordinated by oxygen atoms, while every oxygen atom is shared between two T atoms): (i) by using the concept of secondary building unit [SBU (Meier, 1968)]; (ii) by using 1D structural subunits (chains, columns, tubes) (*e.g.* Barrer, 1984: Smith, 1989); (iii) by using 2D structural subunits (sheets or layers) (*e.g.* Barrer, 1984; Smith, 1989); (iv) by using polyhedral cages (*e.g.* Smith & Bennett, 1981; Moore & Smith, 1964; Liebau, Gies, Gunawardane & Marler, 1986; Bosmans & Andries, 1990) and (v) by using pore volumes and channel dimensions (*e.g.* Liebau, Gies, Gunawardane & Marler, 1986). In this paper we propose a classification for 3D framework structures constructed from trigonal columns (*i.e.* a 1D structural subunit).

Hexagonal three-dimensional framework structures are constructed from trigonal columns and we will systematically investigate the several ways by which such columns can be linked and symmetry related to build up (hexagonal and orthorhombic) 3D nets. A number of hexagonal 3D frameworks known to date are investigated concerning their classification in the lateral connection of trigonal columns group. The tridymite/cristobalite polytypic series is enumerated.

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

Some novel definitions and notations have been introduced in two preceding papers (Bosmans & Andries, 1990; Andries & Bosmans, 1990); we will use the same here. A table compiling all these definitions and notations used is given at the end of the present paper (Table 7, see below). Unless otherwise stated, net numbers were assigned in the two preceding papers. Table 6 (see below) compiles all nets that are described in this series of three reports. With [001] we denote the hexagonal or orthorhombic c axis running parallel to the symmetry axis of the trigonal columns building up the 3D net.

Definitions

Two different types of trigonal column can be distinguished.

1. *A type* 1 *trigonal column* is constructed from stacks of trigonally related tetrahedra lying in horizontal planes perpendicular to the trigonal axis as was described systematically by Bosmans & Andries (1990) [*e.g.* also in OFF (offretite) (Gard & Tait, 1972)]. A trigonal chain of $2T$ trigonal cages (denoting polyhedral cages with threefold symmetry and two on-axis oppositely oriented T nodes) connected by forming 1-1 (or T_2) units (denoting a group of two linked T nodes on a trigonal axis with a T–O–T bond angle of 180°) can be regarded as being a trigonal column with on-axis 1-membered stacks (1MS) and off-axis $3m$-membered stacks (m positive integer). Therefore, all type 1 trigonal columns can be generated by h-membered stacks (h is one or an integral multiple of three). From the discussion in the paper of Bosmans & Andries (1990) it should be obvious that the following h values are possible (assuming a maximum of 6): (i) 3, (ii) 6, (iii) 1 and 3, (iv) 3 and 6 or (v) 1, 3 and 6.

2. *A type* 2 *trigonal column* is constructed from T nodes that are symmetry related by a $3j$-fold screw axis (j positive integer) (*e.g.* Fig. 5). The dense net of quartz (Bragg & Gibbs, 1925) is the only (4; 2)-connected 3D net known to date that is built up with this type of trigonal column. The structure of quartz will be described in more detail later.

The group of framework structures derived from interlinked trigonal columns in general is designated the LCTC (lateral connection of trigonal columns) group. The way by which the columns are laterally connected in the 3D net defines the subgroup.

Enumerating some subgroups

Several subgroups defined so far, together with the respective criteria for the classification of framework structures, are compiled in Table 1(a) (hexagonal nets) and Table 1(b) (orthorhombic nets).

Some remarks concerning Table 1 should be made:

(i) The enumeration of subgroups is not exhaustive: it should be possible for example to build orthorhombic 3D nets from type 2 trigonal columns, as well as to define more subgroups for hexagonal 3D nets constructed from type 1 trigonal columns. A complete enumeration of all possible subgroups is being undertaken.

(ii) Subgroup 15 is generated by trigonal columns connected across mirror planes parallel to the column axis as shown in Fig. 1 for net 52 (Andries & Bosmans,

Table 1. *Criteria for classifying 3D nets in several subgroups of the hexagonal (a) and the orthorhombic (b) sets of the LCTC group*

Figures in the third column refer to hypothetical nets derived by Bosmans & Andries (1990), Andries & Bosmans (1990) or in this report, except in those cases where nets were derived elsewhere. References to structural information on established materials are found in the text and/or in Table 4. Unless otherwise stated, nets are constructed from isolated trigonal columns. Subdivisions in subgroups have only been mentioned for subgroup 7.

(*a*) Hexagonal nets

Subgroup	Symmetry relation between neighbouring trigonal columns	Examples
Nets constructed from type-1 trigonal columns		
1	Threefold rotation axis	CHA, CAN
2	Threefold screw axis	MAZ
3	Threefold rotation axis and case 1 insertion	WEN
4	Threefold screw axis and case 1 insertion	/
5	Threefold rotation axis and case 2 insertion	/
6	Threefold screw axis and case 2 insertion	/
7	(*H*, *L*) mirror plane parallel to column axis	LTL, AFS, (*a*)
8	*c* glide parallel to column axis	AFI
9	Mirror plane parallel to column axis and case 1 insertion	VPI-5
10	*c* glide parallel to column axis and case 1 insertion	81(2) (*b*)
11	Mirror plane parallel to column axis and case 2 insertion	/
12	Net constructed from face-sharing trigonal columns; in general no specific operator, but columns displaced in such a way that face sharing can occur	DDR, 23, 24, cristobalite
13	Net constructed from edge-sharing trigonal columns; in general a specific operator	Tridymite
14	Net constructed from face-sharing trigonal columns and case 2 insertion; in general a specific operator	DOH
Nets constructed from type-2 trigonal columns		
24	Net constructed from vertex-sharing trigonal columns that are symmetry related by threefold screw axes	Quartz
25	Threefold screw axis	/

References: (*a*) Barrer & Villiger (1969); (*b*) Smith & Dytrych (1984).

(*b*) Orthorhombic nets

Subgroup	Symmetry relation between neighbouring trigonal columns	Examples
Nets constructed from type-1 trigonal columns		
15	Mirror planes parallel to column axis	46,52
16	*c* glide perpendicular to **y**, mirror plane perpendicular to **x**	52*b*
17	*c* glide perpendicular to **x**, mirror plane perpendicular to **y**	52*c*
18	*c* glides perpendicular to **x** and **y**	52*d*
19	Mirror planes parallel to column axis and case 1 insertion	56, 79
20	*c* glide perpendicular to **y**, mirror plane perpendicular to **x** and case 1 insertion	57, 81
21	*c* glide perpendicular to **x**, mirror plane perpendicular to **y** and case 1 insertion	58, 74
22	*c* glides perpendicular to **x** and **y** and case 1 insertion	59, 84
23	Net constructed from trigonal columns that share edges along **y** but are isolated along **x**	61

1990). The mirror planes perpendicular to **y** between neighbouring *CS*-type trigonal columns (*CS* is a shorthand notation for the infinite repetition 3(*C*)3(*S*); *C* stands for a 'staggered' or '*trans*' configuration, while *S* denotes an 'eclipsed' or '*cis*' configuration of adjacent 3MS's) in net 52 may be substituted by *c* glides (subgroup 16, *e.g.* net 52*b*). Accordingly, the mirror planes perpendicular to **x** (subgroup 17, *e.g.* net 52*c*), or both the mirror planes perpendicular to **x** and **y** (subgroup 18, *e.g.* net 52*d*) may also be substituted by *c* glides (Fig. 1).

(iii) A group of orthorhombic framework structures can be derived from the nets represented in Fig. 1 by the insertion of one or more crankshaft chains between adjacent trigonal columns along **y**, in the same way as nets 81(1) [VPI-5 (Davis, Saldarriaga, Montes, Garces & Crowder, 1988)] and 81(2) were derived from structure types 82*a* (Bennett & Smith, 1985) and AFI ($AlPO_4$-5) (Bennett, Cohen, Flanigen, Pluth & Smith, 1983) respectively by Smith & Dytrych (1984). Furthermore, the symmetry relation between neighbouring trigonal columns along **x** provides further possibilities for the derivation of new nets. The cases for one and two crankshaft chains [Fig. 2(*c*)] inserted between *CS*-type trigonal columns are represented in Figs. 2(*a*) and (*b*), respectively. In the latter case both chains can be connected across a mirror plane to form the double crankshaft chain [*cc* (Smith, 1988)] [Fig. 2(*d*)] or across an inversion centre to form the bifurcated hexagonal-square chain [*bhs* (Smith, 1988)] [Fig. 2(*e*)]. The structural characteristics for all nets enumerated in Figs. 1, 2(*a*) and 2(*b*) are given in Table 2. It should be noted that the number of nets in this group increases considerably when more than two crankshaft chains are inserted between adjacent *CS*-type columns. Either of the hypothetical nets of this series (Table 2) can be constructed from the T_4O_8 SBU which is the repetitivity unit of the single crankshaft chain [Fig. 2(*c*)].

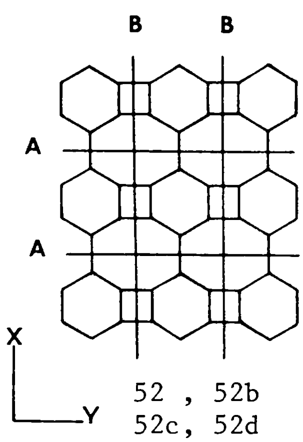


Fig. 1. Schematic projection onto the orthorhombic (001) plane for hypothetical nets 52 (Andries & Bosmans, 1990) 52*b*, 52*c* and 52*d*. The letters *A* and *B* refer to planes that can be either mirror planes or *c* glides (see Table 2); unit cells have been omitted, the size depending on the *A* and *B* symmetry operators. Hexagons are constructed from alternately up and down tetrahedra.

(iv) The insertion of extra T atoms between the trigonal columns provides still further opportunities: a *case* 1 *insertion* of T atoms between neighbouring trigonal columns enlarges the hexagonal a or the orthorhombic a and/or b unit-cell parameter {*e.g.* WEN (Wenk, 1973; see below), VPI-5, net 81(2) (Smith & Dytrych, 1984) and the hypothetical nets 56-59 and 73-86 [Figs. 2(*a*) and (*b*)]}. A *case* 2 *insertion* between neighbouring trigonal columns does not influence the hexagonal a or the orthorhombic a and/or b unit cell parameter [as in DOH (Gerke & Gies, 1984; see below). In this case, the trigonal columns are directly connected.

(v) The notation 'in general' for subgroups 12 to 14 is in no way restrictive: neighbouring trigonal columns in nets 23 and 24 (Bosmans & Andries, 1990) for example are symmetry related by mirror planes parallel to the hexagonal c axis.

(vi) Both the 3D nets of left-handed and right-handed quartz are classified in subgroup 24 as will be discussed later.

Defining subdivisions in some subgroups

For subgroups where neighbouring trigonal columns are symmetry related by mirror planes or c glides (*e.g.* subgroup 7), a distinction may be made for the case where highest-membered rings are formed between adjacent columns (subgroup 7H) and the case where lowest-membered rings are formed (subgroup 7L). An example of the former case is the LTL (Linde type L) group of Barrer & Villiger (1969) (fourth column in their Table 4), where the *NF*-type chains do not face each other [Fig. 3(*b*): H for high-membered rings]; an example of the latter case is the second - hypothetical - group of Barrer & Villiger (1969) (fifth column in their Table 4), where the *NF*-type chains face each other [Fig. 3(*c*): L for low-membered rings] (see also Table 4 below). Subgroups 12 to 14 should be included [*e.g.* DOH belongs to subgroup 14L and net 24 to subgroup 12H (see below)]. Obviously, the distinction between H- and L-connected trigonal columns needs only to be made if appropriate.

For subgroups where the trigonal columns are symmetry related by a threefold rotation or screw axis, a distinction is made whether this symmetry axis is coinciding with a mirror plane or whether it is not.

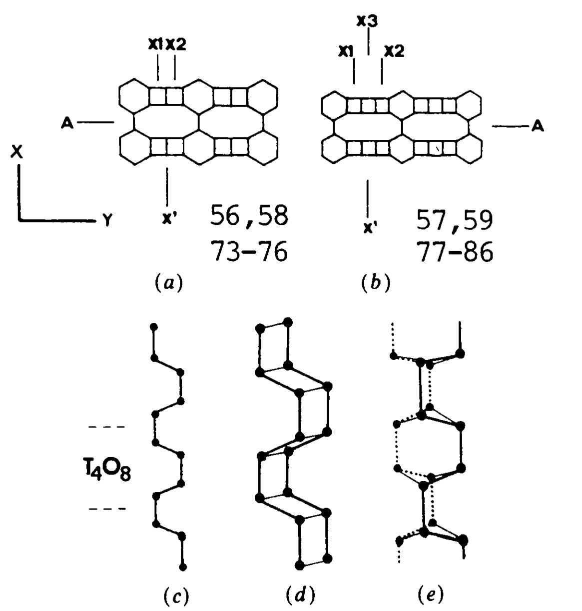


Fig. 2. The systematic derivation of orthorhombic 3D nets by the insertion of one single (*c*) or two (*d*) and (*e*) crankshaft chains between *CS*-type trigonal columns (this type of column itself is constructed by connecting crankshaft chains across a trigonal axis). In (*a*) and (*b*) $X1$, $X2$ and $X3$ stand for the characterization of the symmetry relation between neighbouring crankshaft chains [either mirror plane (*d*) or inversion (*e*)]; A and X' stand for the characterization of the symmetry relation between neighbouring trigonal columns (either mirror plane or c glide) along the orthorhombic x and y axis, respectively (see Table 2).

Table 2. *The systematic derivation of orthorhombic 3D nets by symmetry-relating neighbouring CS-type trigonal columns and/or by inserting (a) crankshaft chain(s) (cc) between neighbouring columns along the y axis*

See Fig. 1 (no *cc* inserted) and Fig. 2 [(*a*): one *cc* inserted; (*b*) two *cc*'s inserted] for representations and for the meaning of letters (denoting symmetry operations) used.

No crankshaft chain inserted (Fig. 1)

Net number	A	B
52	Mirror plane	Mirror plane
52*b*	Mirror plane	*c* glide
52*c*	*c* glide	Mirror plane
52*d*	*c* glide	*c* glide

One crankshaft chain inserted [Fig. 2(*a*)]

Net number	$X1$	$X2$	X'	A
56	Mirror plane	Mirror plane	Mirror plane	Mirror plane
58	Mirror plane	Mirror plane	Mirror plane	*c* glide
73	Inversion	Inversion	Mirror plane	Mirror plane
74	Inversion	Inversion	Mirror plane	*c* glide
75	Mirror plane	Inversion	*c* glide	Mirror plane
76	Mirror plane	Inversion	*c* glide	*c* glide

Two crankshaft chains inserted [Fig. 2(*b*)]

1. $X3$ = mirror plane (double crankshaft chain)

Net number	$X1$	$X2$	X'	A
77	Mirror plane	Mirror plane	Mirror plane	Mirror plane
78	Mirror plane	Mirror plane	Mirror plane	*c* glide
79	Inversion	Inversion	Mirror plane	Mirror plane
80	Inversion	Inversion	Mirror plane	*c* glide
81	Mirror plane	Inversion	*c* glide	Mirror plane
82	Mirror plane	Inversion	*c* glide	*c* glide

2. $X3$ = inversion centre (bifurcated hexagonal-square chain)

Net number	$X1$	$X2$	X'	A
57	Inversion	Inversion	*c* glide	Mirror plane
59	Inversion	Inversion	*c* glide	*c* glide
83	Mirror plane	Mirror plane	*c* glide	Mirror plane
84	Mirror plane	Mirror plane	*c* glide	*c* glide
85	Mirror plane	Inversion	Mirror plane	Mirror plane
86	Mirror plane	Inversion	Mirror plane	*c* glide

As an example, trigonal columns of OFF (Gard & Tait, 1972) [generated by ε (cancrinite) and $D6R$ (double six-ring) cages] also occur in the WEN structure (Wenk, 1973). In OFF [Fig. 3(*a*)] and in all structures of the *ABC*-6 group (Tambuyzer, 1977; Smith & Bennett, 1981) the trigonal axes coincide with the mirror planes parallel to the hexagonal *c* axis, while in WEN and related structures they do not [Fig. 4(*d*), see below]. A WEN-related structure can be constructed for example from the trigonal columns occurring in ERI (erionite) (Staples & Gard, 1959) by inserting interrupted *T* atoms on the trigonal axes symmetry relating the columns. The way of symmetry relating trigonal columns by threefold axes as in the *ABC*-6 group will be designated *M* (*i.e.* threefold axes coinciding with the mirror planes; *M* for mirror plane) and in the WEN-related structures *N* (*i.e.* threefold axes not coinciding with the mirror planes). The trigonal columns in MAZ (mazzite) (Rinaldi, Pluth & Smith, 1975), structure types 17 (Andries & Bosmans, 1990) and 55 (Bosmans & Andries, 1990) as well as in tridymite (Gibbs, 1926), cristobalite (Wyckoff, 1925), DOH (Gerke & Gies, 1984) and DDR (Gies, 1986) (according to the alternative way of describing these last three structures, see below) are *M* related. According to its alternative description (see below), the trigonal columns in quartz (Bragg & Gibbs, 1925) are *N* related because no mirror planes parallel to the threefold screw axes occur. In the most general case, the difference between *M* and *N* related trigonal columns may be applied to all subgroups where trigonal columns are symmetry related by $3j$-fold rotation or screw axes (j positive integer), including subgroups 12 to 14.

General rules for classifying 3D framework structures in the several subgroups of the LCTC group

Rule 1

Some ambiguity has to be resolved concerning the type of trigonal column used for classifying framework structures in the subgroups of the LCTC group: with different trigonal columns present in one and the same net, the PTC (*primary trigonal column*) used as classification criterion is the one with the lowest cross-sectional area in projection and it is generated by the simplest trigonal units.

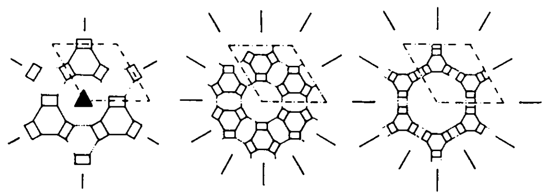


Fig. 3. Connecting trigonal columns laterally to form 3D nets. OFF columns are represented with full lines and their connections with dotted lines. Hexagonal unit cells and the main symmetry operators are indicated. (*a*) OFF (Gard & Tait, 1972); (*b*) LTL (Barrer & Villiger, 1969); (*c*) hypothetical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

The maximum number of different trigonal column types for 3D nets in the hexagonal set of the LCTC group is three (at least if we exclude nets with very large unit cells). As an example: in OFF (Gard & Tait, 1972) [Fig. 3(*a*)], three types of trigonal column can be distinguished: (i) the PTC made of ε and $D6R$ cages; (ii) the *secondary trigonal column* (STC) consisting of gmelinite cages; and (iii) the *tertiary trigonal column* (TTC) forming the $12R$ channel. In CHA (chabazite) (Smith, Rinaldi & Dent Glasser, 1963) only one type of trigonal column occurs (PTC = STC = TTC). For nets in the orthorhombic set of the LCTC group the maximum number of different trigonal column types is one (*e.g.* Figs. 1 and 2).

Furthermore, several cases concerning the number of different trigonal column types can be distinguished:

(i) the maximum number of different trigonal column types in hexagonal nets where neighbouring trigonal columns are symmetry related by mirror planes or *c* glides is two [*e.g.* Figs. 3(*b*) and (*c*)].

(ii) In hexagonal nets with *M*-related trigonal columns there are two possibilities: in frameworks where neighbouring trigonal columns are symmetry related by a threefold rotation axis, the maximum number of different trigonal column types is three [*e.g.* OFF (Gard & Tait, 1972), see above] and it is two when the trigonal columns are symmetry related by threefold screw axes [*e.g.* MAZ (Rinaldi, Pluth & Smith, 1975)].

(iii) The same number is two for nets with isolated *N*-related trigonal columns [*e.g.* WEN (Wenk, 1973), Fig. 4(*d*), see below].

(iv) The maximum number of different trigonal column types seems to be variable for hexagonal nets constructed from non-isolated trigonal columns (subgroups 12–14, 24): in frameworks where the trigonal columns share faces with six identical ones [*e.g.* DDR (Gies, 1986) and cristobalite (Wyckoff, 1925), Fig. 4(*f*) and (*c*), respectively, see below] it may be one. The same number may be two in frameworks where the trigonal columns share faces [*e.g.* DOH (Gerke & Gies, 1984), Fig. 4(*e*), see below; nets 23 and 24 (Bosmans & Andries, 1990)] or edges [*e.g.* tridymite (Gibbs, 1926), Fig. 4(*b*), see below] or vertices [*e.g.* quartz (Bragg & Gibbs, 1925), Fig. 5, see below] with three identical columns.

Rule 2

A description based on trigonal columns only is preferred over a description based on trigonal columns and inserted *T* atoms (*e.g.* DDR, see below).

Rule 3

A description based on non-interrupted trigonal columns is used instead of a description based on interrupted columns, even if the former column is more complex than the latter (*i.e.* rule 1 violated) (*e.g.* WEN, see below).

Rule 4

When a 3D net can be described using face sharing, edge sharing and/or vertex sharing trigonal columns, the following sequence should be considered ('>' stands for: is preferred over):

face sharing > edge sharing > vertex sharing > isolated.

According to this rule, tridymite, cristobalite and quartz are classified in the LCTC group (see below).

Table 3. *The systematic derivation of 3D nets constructed from parallel simple hexagonal 2D nets (T atoms alternately either up or down)*

k denotes the number of 2D net symbols in the repetitive stack sequence along the hexagonal c axis; the letters A, B and C stand for stacking positions of hexagonal layers (Fig. 4*a*); sheet designations $Z1$ and $Z2$ are explained in the text; $2T$ trigonal cage designations are found in the paper of Bosmans & Andries (1990); RF stands for established materials with the framework topology described and REF denotes reference to the first description of the net topology.

k	Stacking sequence	Sheets	$2T$ trigonal cages	RF	Net number	REF
1	*A*	*Z*1	*S*	Tridymite	14	(1)
2	/	/	/	/	/	/
3	*ABC*	*Z*2	*SCS*	Cristobalite	15	(2)
4	*AABB*	*Z*1	*SCSCS*, *S*	/	14b	/
5	*AAABC*	*Z*1, *Z*2	*SCSCSCS*, *SCS*, *S*	/	16	/
6	*AAAABB*	*Z*1	*SCSCSCSCS*, *SCSCS*, *S*	/	14*c*	/
	ABCCBA	*Z*2	*SCSCS*, *SCS*, *S*	/	15*b*	/

References: (1) Gibbs (1926); (2) Wyckoff (1925).

Detailed descriptions of some hexagonal 3D framework structures in relation to their classification in the LCTC group

1. *The tridymite/cristobalite polytypic series*

Systematic derivation: Nets constructed from simple hexagonal 2D nets with alternating up/down tetrahedra [layer A in Fig. 4(*a*)] can be enumerated systematically in the same way (A, B, C stacking) as was done for the ABC-6 group of zeolites and related materials (constructed from parallel simple hexagonal 2D nets with all T atoms identically oriented) (Tambuyzer, 1977; Smith & Bennett, 1981). All frameworks of the first type can be generated by face- and/or edge-sharing trigonal columns composed of $2T$ trigonal cages of type $S(CS)_l$ (l is zero or a positive integer; the notation SCS is shorthand for the 1-3(S)3(C)3(S)3-1 $2T$ trigonal cage]. Tridymite and cristobalite are the two simplest structures of this family [Smith (1977): structure types 2 and 1, respectively].

Polytypic structures (Verma & Krishna, 1966) with more complex stacking sequences of the 2D nets can be derived. Denoting a 2D net by a letter [either A, B or C: Fig. 4(*a*)] characterizing its stacking position, and letting k denote the number of 2D nets in the repetitive sequence of letters along the hexagonal [001] axis, the possible 3D nets up to $k = 6$, together with their net number, are compiled in Table 3. Notice that (i) sequence $AAA\ldots$ is possible, (ii) sequences ABC, BCA and CAB are identical and (iii) BAB and ABA are not possible. All structures have a hexagonal a parameter of approximately 5·05 Å and a hexagonal c repeat of approximately 4·13t Å (t denotes the number of parallel 2D nets in the unit cell). These values were derived on the basis of cell parameters for tridymite and cristobalite given by Smith (1977), assuming that all T sites are occupied by silicon.

Alternatively, all nets can be generated by chains of isolated $S(CS)_l$-type cages along the hexagonal c axis, sharing edges and/or faces with cages of adjacent chains. A sheet structure (designated type $Z1$) generated by edge-sharing S cages (one edge parallel to the hexagonal c axis shared between adjacent cages) is formed by the succession of two identical letters of parallel 2D nets (*e.g.* AA). The structure of tridymite (Table 3) can therefore also be generated by a vertical stacking of $Z1$ sheets [Fig. 4(*b*)]. The ABC sequence results in a sheet (designated type $Z2$) consisting of edge-sharing SCS cages (three coplanar edges in a mirror plane parallel to the hexagonal c axis shared between adjacent cages). The structure of cristobalite (Table 3) is constructed by stacking $Z2$ sheets [Fig. 4(*c*)]. All members of this polytypic series can be constructed from $Z1$ and/or $Z2$ hexagonal sheets, connected by forming T_2 units. In some cases, novel sheet types are formed in between; these then are composed of $S(CS)_l$-type $2T$ trigonal cages with $l < 2$ if $k < 4$ and $l > 1$ if $k > 3$ (Table 3).

Classification: The classification of tridymite (Gibbs, 1926) and cristobalite (Wyckoff, 1925) in the LCTC group still needs some explanation.

In the *tridymite* structure, two types of trigonal columns can be distinguished [Fig. 4(*b*)]: the PTC [S cages connected along [001] by forming T_{2m} units (T_{2m} stands for the T_2 unit where the T nodes are symmetry related by a mirror plane)] and the STC [repetition of 3(C)3(S)]. Using PTC's, neighbouring columns are symmetry related by a c glide parallel to the hexagonal c axis [compare with net 2 of Bosmans & Andries (1990)]: a 1-3(S)3-1 cage of one PTC is connected between two such cages of the neighbouring PTC [single six-ring ($S6R$) faces opposed].

In that way, two other S cages are formed, sharing one edge (parallel to the hexagonal c axis) with the first cage. The structure can thus be constructed from PTC's that are symmetry related by trigonal axes (the central axes of the STC's). Three trigonally related S cages share three edges and form the CS-type infinite column (a hexagon in the hexagonal 2D net).

According to rule 4, tridymite is classified in subgroup 13 instead of in subgroup 8 (Table 1a).

In accordance with its classification in the LCTC group, the net of tridymite belongs to the simple (group 2) tridymite group (containing 3D nets constructed from $2T$ trigonal cages that are symmetry related by threefold axes, whereby neighbouring hexagonal sheets are symmetry related by translation along [001]): it can be constructed by stacking hexagonal sheets made of edge-sharing S cages. According to the alternative description (in subgroup 8), the net of tridymite belongs to the non-simple (group 1) tridymite group (containing 3D nets constructed from $2T$ trigonal cages that are symmetry related by mirror planes parallel to the hexagonal c axis, whereby neighbouring hexagonal sheets are not simple (*i.e.* neighbouring cages are not identical and/or displaced along [001]) or are not symmetry related by translation along [001]): neighbouring cages in the same hexagonal sheet are displaced by the application of the c glide.

In the structure of *cristobalite* [Fig. 4(c)] only one type of trigonal column is distinguished, consisting of 1-3(S)3(C)3(S)3-1 cages. Neighbouring SCS cages form T_{2i} units (denoting the T_2 unit where the T nodes are symmetry related by inversion) along the hexagonal c axis. Each column is surrounded by six identical columns (the hexagons in the hexagonal 2D net). Neighbouring SCS cages share three edges each and are symmetry related by a mirror plane parallel to the hexagonal c axis.

Three adjacent trigonal columns symmetry related by a trigonal axis [Fig. 4(c): this axis coincides with a T node shared by three hexagons in the 2D net and runs perpendicular to the plane of the paper] build up an identical type of trigonal column (at a shorter distance in comparison with a cage that is symmetry related by a mirror plane). This column then is displaced $1/3c$ or $2/3c$ along [001]. The SCS cages of two adjacent PTC's displaced along [001] share $S6R$ faces: one column is surrounded by six identical columns that are alternately displaced $1/3c$ or $2/3c$.

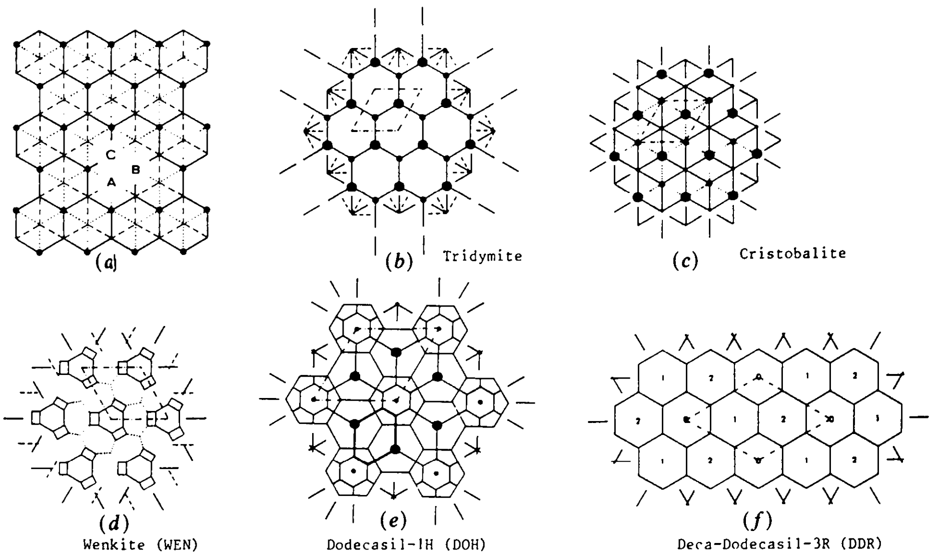


Fig. 4. Line drawings of the structures of (b) tridymite, (c) cristobalite, (d) wenkite (WEN), (e) dodecasil-1H (DOH) and (f) deca-dodecasil-3R (DDR) in a projection onto the hexagonal (001) plane, visualizing their classification in the LCTC group. Each time, mirror planes and/or c glides as well as the unit cell are indicated. In (a) the A, B and C stacking positions are shown for the simple hexagonal 2D net from which all members of the tridymite/cristobalite polytypic series are constructed. Layers A, B and C are represented with full, dashed and dotted lines respectively. In layer A only, T nodes are specified either up (circle) or down (no circle). In (b), S cages are at $z=0$ (large circles) and at $z=\frac{1}{2}$ (small circles). In (c) SCS cages are at $z=0$ (intermediate sized circles), at $z=\frac{1}{3}$ (large circles) and at $z=\frac{2}{3}$ (small circles). In (d) OFF columns are represented with full lines and their connections (by interrupted T nodes) with dotted lines; the latter lines show part of the SSS cages. In (e) the trigonal axes of the PTC's are indicated with large circles and those of the STC's with small circles; the corresponding $4^35^66^3$ and $5^{12}6^8$ cages forming these columns are clearly distinguished. One non-trigonal column made of 5^{12} cages is indicated with bold lines. In (f) $YY(m)XX$-type trigonal columns are represented by hexagons; this way of representing may be used, although it is not fully correct since the 1-1 units of the PTC's are not shown and the cross section of this type of column is not a $S6R$. 0, 1 and 2 denote PTC's at $z=0$, $z=\frac{1}{3}$ and $z=\frac{2}{3}$, respectively.

According to rule 4, cristobalite is classified in subgroup 12 instead of in subgroup 13 (Table 1*a*).

Following its description in the LCTC group, the net of cristobalite should not belong to the tridymite group because it cannot be constructed by stacking hexagonal sheets made of face-sharing *SCS* cages that are mutually displaced in the same hexagonal sheet. Nevertheless, according to the alternative description (in subgroup 13), the net of cristobalite belongs to the non-simple (group 1) tridymite group: neighbouring cages in the same hexagonal sheet share edges across a mirror plane and neighbouring sheets are rotated by 180° parallel to (001).

The structures of tridymite and cristobalite, although belonging to the same polytypic series, are not classified in the same subgroup of the LCTC group (Table 1*a*).

All nets of this series can be generated by T_2 units only (tridymite: T_{2m}, cristobalite: T_{2i}, all other nets: T_{2m} and T_{2i}).

2. *Quartz*

The PTC of quartz (Bragg & Gibbs, 1925) (Fig. 5) is a type-2 trigonal column constructed from *T* nodes that are symmetry related by a 3_2 (right-handed quartz) or a 3_1 (left-handed quartz) screw axis. One such column is connected to a second by sharing vertices, whereby both columns are symmetry related by twofold rotation around the axis through the common *T* nodes. Six vertex-sharing PTC's that are symmetry related by a 6_2 (right-handed quartz) or a 6_4 (left-handed quartz) screw axis build up the STC with six-ring cross section.

The structure can also be generated from isolated PTC's, symmetry related by 3_2 (right-handed quartz) or 3_1 (left-handed quartz) screw axes.

According to rule 4, quartz is classified in subgroup 24 instead of in subgroup 25 (Table 1*a*).

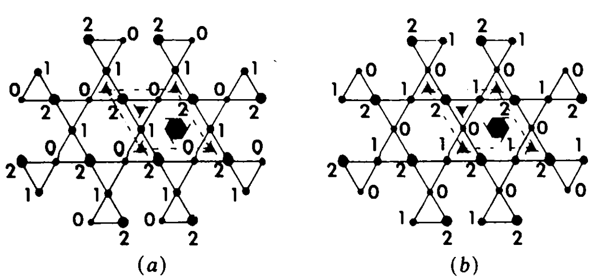


Fig. 5. Projections onto the hexagonal (001) plane for (*a*) the right-handed and (*b*) the left-handed enantiomorphs of quartz. Figures denote displacements (in thirds of the *c* repeat) from the plane of the paper (*i.e.* $z = 0$) according to Bragg, Claringbull & Taylor (1965). Unit cells with the main symmetry operators are indicated. The height of nodes around each six-turn helix is represented by the sequence 012012 [anticlockwise in (*a*), clockwise in (*b*)] (Smith, 1979).

3. *Wenkite* (*WEN*)

The framework of WEN (Wenk, 1973) can be generated in part using the trigonal OFF columns [Fig. 4(*d*)]. Neighbouring columns are not connected directly, but by means of inserted *T* atoms on the trigonal axes symmetry relating the columns. Neighbouring OFF columns are also symmetry related by glide planes parallel to the hexagonal *c* axis.

Because the inserted *T* atoms lie on trigonal axes, the structure can alternatively be described on the basis of simple hexagonal sheets made of *SSS* 2*T* trigonal cages [which are symmetry related by mirror planes parallel to the hexagonal *c* axis: compare the unit cells in Fig. 4(*d*) and in Fig. 14 of Bosmans & Andries (1990)]. When these sheets are stacked to form T_{2m} units, the resulting (group 1) simple framework is interrupted. Another way to stack these sheets is by the insertion of *S*6*R* unit layers in between them. Each *T* atom of these *S*6*R*'s then is connected to two *T* atoms of the 3MS's (closest to the 1MS's) of two *SSS* cages connected along [001]. In this case (topology of WEN), the *T* atoms of the 1MS's are not forming T_{2m} units, but are interrupted.

It is noteworthy that a case 1 insertion occurs in the first description of the WEN structure and a case 2 insertion in the second.

Obviously, the WEN framework is intermediate between both the *ABC*-6 (Tambuyzer, 1977; Smith & Bennett, 1981) and the tridymite (Bosmans & Andries, 1990) groups.

Although the OFF columns have a larger cross section and are made of more complex trigonal units than the columns made of *SSS* cages, the latter column is interrupted and is therefore not selected as PTC: according to rule 3, WEN is classified in subgroup 3 instead of in subgroup 11 (Table 1*a*).

4. *Framework structures constructed from face-sharing group B 2T trigonal cages*

Established materials with a framework belonging to this group are some clathrasils (*e.g.* Liebau, Gies, Gunawardane & Marler, 1986).

The most symmetrical 2*T* trigonal cage of group *B* (*i.e.* constructed from 3MS's and 6MS's without any *S*3*R* perpendicular to the symmetry axis) {5^{12}, pentagondodecahedron, *rd* (Smith, 1988), sequence 1-3(*H*)6(*H*)6(*H*)3-1 [see Bosmans & Andries (1990) for explanation of symbols]} can be linked with identical cages (sharing *S*5*R*'s) into a hexagonal sheet, which cannot be stacked to form a net of the tridymite group: the trigonal axes with on-axis 1-1 units disappear as a consequence of the particular mode of connecting these cages. This type of hexagonal sheet occurs in the framework types DOH (Gerke & Gies, 1984) and MTN (ZSM-39) (Gies, 1984). The 5^{12} cage also occurs in the framework-type MEP (melanophlogite) (Gies, 1983) and DDR (Gies, 1986).

Hypothetical nets related to the structure types MTN and MEP have been described by Schlenker, Dwyer, Jenkins, Rohrbaugh, Kokotailo & Meier (1981). Polytypic structures (Verma & Krishna, 1966) related to the MTN (Gies, Liebau & Gerke, 1982) and DDR (Gies, 1986) frameworks have also been described.

$1T$ trigonal cages of group E (denoting trigonal cages with one on-axis T node and an $S6R$ perpendicular to the trigonal axis) occur in the framework types DDR (see below) and MTN [$5^{12}6^4$: 1-3(H)6(O)6($O1$)6(LH)6 (Gies, 1984)]. $0T$ trigonal cages of group G (denoting trigonal cages with two $S6R$'s perpendicular to the trigonal axis) occur in the framework type DOH (see below).

Two hexagonal 3D framework structures belonging to this group will be discussed in detail: dodecasil-1H and deca-dodecasil-3R.

Dodecasil-1H (DOH)

The DOH framework (Gerke & Gies, 1984) [Fig. 4(e)] can be made of trigonal columns composed of $4^35^66^3$ cages [Fig. 10($b2$) of Bosmans & Andries (1990)], connected by forming T_{2m} units along the hexagonal c axis. Cages of neighbouring trigonal columns that are symmetry related by mirror planes share $S4R$ faces. The framework is completed by the insertion of layers of $S6R$ units, in a similar way as was described for the WEN structure (*i.e.* every T atom of an $S6R$ is connected to two T atoms of the 3MS's of two neighbouring cages along [001]).

The structure can also be described on the basis of trigonal columns that are symmetry related by trigonal axes and that are connected by supplementary T_{2m} units (case 2 insertion on the trigonal axes). These columns are made of $5^{12}6^8$ cages, sharing $S6R$'s perpendicular to [001].

A third way to describe the structure is on the basis of face-sharing non-trigonal columns made of 5^{12} cages. The parallel edges of two cages (all edges of this cage are symmetrically equivalent) are connected along [001] and form the $S4R$ shared between two $4^35^66^3$ cages. It seems surprising that the hexagonal framework of DOH can be described using only one $2T$ trigonal cage (5^{12}), while none of the trigonal axes of this highly symmetrical cage is preserved coinciding with the hexagonal c axis.

Part of the DOH framework is related to hypothetical net 24 of Bosmans & Andries (1990): both are constructed from the same PTC. In the latter net, neighbouring columns share $S6R$ faces and all T atoms are (4; 2)-connected, while in the former structure the same columns share $S4R$ faces to form an interrupted 3D net.

According to rule 1, DOH is classified in subgroup 14 instead of in subgroup 5 (Table 1a).

Deca-dodecasil-3R (DDR)

The DDR framework (Gies, 1986) is generated by trigonal columns with cage sequence $YY(m)XX$. In this notation XX denotes two $4^35^66^1$ cages, sharing $S6R$ faces perpendicular to the trigonal axis and symmetry related by an inversion centre; $1(m)1$ designates the T_{2m} unit and YY stands for two $4^35^{12}6^18^3$ cages, sharing $S6R$'s perpendicular to the trigonal axis and symmetry related by an inversion centre. The trigonal stack sequence is 1-3(H)6(L)6(O)-6($O1$)6(LH)6(O)6($O1$)6($A2$)6(L)6(H)3-1(m)1-3(H)6(LH)6(H)6(H)3-1, where the underlined sequence is represented by YY and the non-underlined sequence by XX. The geometry of the $A2$-connected 6MS is fixed by the fact that two $4^35^{12}6^18^3$ cages are symmetry related by inversion. If the height of XX along the hexagonal c axis is denoted by $2HX$ and that of YY by $2HY$, then $2HX = HY$ and $c = 2HY + 2HX = 3HY = 6HX$. One column of this type is surrounded by six identical columns [Fig. 4(l)], whereby neighbouring columns are displaced $1/3c$ or $2/3c$ along [001]. Neighbouring columns share $S4R$, $S5R$ and $S8R$ faces and (isolated) columns at the same height are symmetry related by mirror planes parallel to the hexagonal c axis.

Part of the framework can also be made of the same type of trigonal column whereby three columns are symmetry related by a trigonal axis; supplementary T atoms (case 2 insertion of T_{2m} units with associated 3MS's) have to be inserted to complete the 3D framework of DDR.

According to rule 2, DDR is classified in subgroup 12 instead of in subgroup 5 (Table 1a).

General remarks

Schematic projections onto the hexagonal (001) plane for the hypothetical nets of the tridymite/cristobalite polytypic series are not given: their two-dimensional representations would be too complicated. The repetition sequence of the PTC for nets 14b, 14c, 15b and 16 (Table 3) is 1-3(S)3-1(i), 1-3(S)3-1(m)1-3-(S)3-1(i)1-3(S)3-1(i), 1-3(S)3(C)3(S)3-1(m) and 1-3(S)3-1(m)1-3(S)3(C)3(S)3-1(i), respectively [1(i)1 denotes the T_{2i} unit].

For none of the framework structures belonging to the tridymite/cristobalite polytypic series ($k > 3$ in Table 3), nor for the structures related to DOH or belonging to the DDR polytypic series (Gies, 1986), a LCTC subgroup was assigned at present.

Hexagonal frameworks made of isolated trigonal columns belong to the subgroups 1-11 and 25 (Table 1a). Some of these have a low framework density (FD). Frameworks with lowest FD are made of trigonal columns with case 1 insertion of T atoms (subgroups 3, 4, 9 or 10) or they are generated by trigonal columns composed of horizontal stacks with

Table 4. *Detailed description of some subgroups in the LCTC group with some examples of members*

Figures in the fourth column denote net numbers assigned by Bosmans & Andries (1990) or Andries & Bosmans (1990). *h* denotes the number of *T* atoms in the horizontal stacks (1, 3 and/or 6) for type 1 trigonal columns; REF denotes reference to the first description of the net topology. Framework structures in subgroups 12 and 13 may also belong to the tridymite group.

Subgroup	h	Groups	Examples	Repetition sequence	REF
1	1+3 }	Group 2	55	1-3-1(*m*)	(1)
		tridymite	60	1-3(*LH*)3(*S*)3-1(*m*)	(1)
	1+3+6 }	group (1)			
	3		17	3(*LH*)3(*S*)	(18)
	3+6				
	6	CHA group	CAN	*LH-L*	(2)
		ABC-6S	CHA	*LH-L-L-H-H-LH*	(3)
		(16), (15)	OFF	*LH-L-LH*	(4)
			ERI	*LH-L-LH-LH-H-LH*	(5)
7	1+3 }		AFY	1-3(*C*)3-1(*i*)	(6)
		Group 1	AFS	1-3(*C*)3(*S*)3(*C*)3-1(*i*)	(6)
		tridymite	BPH	1-3(*C*)3(*S*)3(*C*)3-1(*m*)	(7, 19)
		group (1)	3*b*	1-3(*C*)3-1(*m*)	(1)
	1+3+6 }		19	1-3(*H*)6(*H*)3-1(*m*)	(1)
	3		28	3(*C*)3(*S*)	(8)
	3+6		31	3(*H*)6(*H*)3(*S*)	(18)
7H	6	LTL group (9)	LTL	*LH-L-LH*	(9)
7L	6	(9)	Hypothetical	*LH-L-LH*	(9)
8	1+3				
	1+3+6				
	3		AFI	3(*C*)3(*S*)	(10)
	3+6				
	6				
12	1+3		Cristobalite	1-3(*S*)3(*C*)3(*S*)3-1(*i*)	(11)
	1+3+6		DDR	See text	(12)
			23	1-3(*H*)6(*H*)3-1(*m*)	(1)
			24	1-3(*H*)6(*L*)6(*H*)3-1(*m*)	(1)
	3				
	3+6				
	6				
13	1+3		Tridymite	1-3(*S*)3-1(*m*)	(13)
	1+3+6				
	3				
	3+6				
	6				
14	1+3				
	1+3+6		DOH	1-3(*H*)6(*L*)6(*H*)3-1(*m*)	(14)
	3				
	3+6				
	6				
15	1+3 }	2*T*	46	1-3(*C*)3-1(*i*)	(18)
		orthorhombic	47	1-3(*C*)3(*S*)3(*C*)3-1(*m*)	(18)
	1+3+6 }	group (18)			
	3		52	3(*C*)3(*S*)	(18)
	3+6		53	3(*LH*)6(*H*)3(*S*)	(18)
	6				
24	/		Quartz (right-handed)	021	(17)
			Quartz (left-handed)	012	(17)

References: (1) Bosmans & Andries (1990); (2) Jarchow (1965); (3) Smith, Rinaldi & Dent Glasser (1963); (4) Gard & Tait (1972); (5) Staples & Gard (1959); (6) Bennett & Marcus (1987); (7) Andries (1989); (8) Bennett & Smith (1985); (9) Barrer & Villiger (1969); (10) Bennett, Cohen, Flanigen, Pluth & Smith (1983); (11) Wyckoff (1925); (12) Gies (1986); (13) Gibbs (1926); (14) Gerke & Gies (1984); (15) Smith & Bennett (1981); (16) Tambuyzer (1977); (17) Bragg & Gibbs (1925); (18) Andries & Bosmans (1990); (19) Harvey & Meier (1989).

h values exceeding 6 (*e.g.* columns with $h = 12, 24, \ldots$). It is obvious that in both cases nets with very low framework density are expected to have very large unit cells.

Hexagonal frameworks made of face-sharing trigonal columns belong to the subgroups 12 or 14 (Table 1*a*). The framework density is proportional to the number of faces shared (compare DDR with net 24) and/or to the number of *T* atoms inserted (compare DOH with net 24).

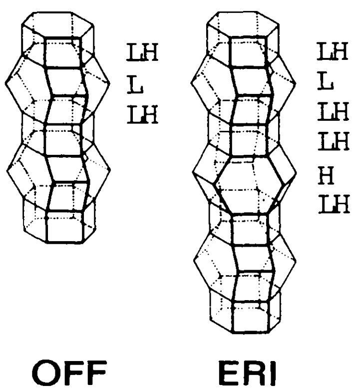
Framework structures in subgroups 1 or 7 (Table 1*a*) generated by trigonal columns with 1MS's belong to the tridymite group (Bosmans & Andries, 1990). Nets of the tridymite group made of face- and/or edge-sharing trigonal columns belong to the subgroups 12 or 13 (*e.g.* tridymite and cristobalite). Neither WEN nor DOH belongs to the tridymite group, because none of these frameworks can be made of hexagonal sheets as defined earlier by Bosmans & Andries (1990). Frameworks in the same two subgroups (1 and 7) made of trigonal columns containing *S*-connected 3MS's (no *S*3*R*'s) but without 1MS's, belong to the extended tridymite group described by Andries & Bosmans (1990). Similarly, frameworks of subgroup 15 belong to the 2*T* orthorhombic group when their trigonal columns contain 1MS's and to the extended orthorhombic group when their columns contain *S*-connected 3MS's (no *S*3*R*'s) but no 1MS's [see Andries & Bosmans (1990) for description of groups].

Table 4 gives some more detailed information on subgroups 1, 7, 8, 12, 13, 14, 24 and 15. Most established hexagonal frameworks belong to the first seven subgroups of this table.

Some explanations concerning Table 4 are necessary:

(i) the chabazite group of zeolites and related materials (Tambuyzer, 1977; Smith & Bennett, 1981) is designated the *ABC-6S group* with members being made of simple hexagonal 2D nets with identical orientation of all *T* nodes (*S* for same). The *ABC*-6*C group* designates the tridymite/cristobalite polytypic series with members being constructed from hexagonal 2D nets with alternating up and down tetrahedra (*C* for changed).

(ii) Frameworks of the *ABC*-6*S* polytypic series do not belong to the extended tridymite group (Andries & Bosmans, 1990) derived from group 2 nets of the tridymite group (Bosmans & Andries, 1990), because the extended frameworks must necessarily be made of trigonal columns with 3MS's: the TET transformation (Andries & Bosmans, 1990) removes the T_2 units only (not the associated 3MS's)



(*a*) (*b*)

Fig. 6. Line drawings showing the primary trigonal column in (*a*) OFF and (*b*) ERI. One double chain along the trigonal axis has been indicated with bold lines. Horizontal stack designations are explained in the text.

Table 5. *The designation of* (4; 2)*-connected and related hexagonal* 3*D structure types by means of a composite code and the repetition sequence of the primary trigonal column*

Figures in the first column denote net numbers assigned by Bosmans & Andries (1990). References towards structural information on established materials are found in the text and/or Table 4.

Structure type	Composite code				Repetition sequence
OFF	*H*	3(*M*)	*D*		*
CHA	*H*	3(*M*)	*D*		*
AFS	*H*	*m*(*H*)	*D*		*
BPH	*H*	*m*(*H*)	*D*		*
Quartz (right)	*H*	6_2(*N*)	*V*		*
Tridymite	*H*	3(*M*)	*E*		*
Cristobalite	*H*	*n*	*F*		*
DOH	*H*	*m*(*L*)	*F*(II)		*
DDR	*H*	*n*	*F*		*
WEN	*H*	3(*N*)	*I*	1·941	*LH-L-LH*
LTL	*H*	*m*(*H*)	*D*		*
MAZ	*H*	6_3(*M*)	*D*		*LH-L-L*
VPI-5	*H*	*m*(*H*)	*I*		*CS*
AFI	*H*	*c*(*H*)	*D*		*
55	*H*	3(*M*)	*D*		*
24	*H*	*m*(*H*)	*F*		*

* See Table 4.

and thus three-membered stacks are left in all these extended structures. Frameworks of the LTL and the LTL-related groups (Barrer & Villiger, 1969) do not belong to the extended tridymite group derived from group 1 frameworks of the tridymite group for the same reason.

(iii) The designations *L*, *H* and *LH* for describing the mode of linking adjacent 6MS's in trigonal columns generated using only 6MS's were not discussed before: *L* stands for the case where the lowest-membered ring is formed in a vertical double chain parallel to the column axis, and *H* stands for the opposite case. For example: in OFF (Gard & Tait, 1972), a double-saw chain occurs with only *S*4*R*'s along the hexagonal *c* axis [Fig. 6(*a*)]: the repetition sequence is *LH-L-LH*. In ERI (Staples & Gard, 1959) four *S*4*R*'s are separated from four others by an *S*6*R* [Fig. 6(*b*)]: the repetition sequence is denoted by *LH-H-LH-LH-L-LH*. It should be noted that in this type of trigonal column a second type of double chain can be distinguished after rotation by 60° around the column axis. The designation for this alternative double chain is identical to that of the first, with *L* and *H* interchanged. Thus the trigonal column in CHA (Smith, Rinaldi & Dent Glasser, 1963) for example is denoted by *LH-L-L-H-H-LH* or *LH-H-H-L-L-LH*.

Designating 3D LCTC framework topologies

The designation of a type 2 trigonal column [quartz and related structures (Smith, 1979)] was not discussed before: such a column may be denoted by the

Table 6. *Reference to structural information on all nets enumerated in the papers of Bosmans & Andries* (1990) (*A*: *Table* 4; *B*: *Table* 5), *Andries & Bosmans* (1990) (*C*: *Table* 3; *D*: *Table* 4) *and in this report* (*E*: *Table* 2; *F*: *Table* 3)

Figures denote net numbers.

Net	Reference	Net	Reference	Net	Reference	Net	Reference
1	*A*	18	*D*	43	*D*	62	*D*
2	*A*	19	*A*	44	*C*, *D*	63	*D*
3	*A*	20	*A*	45	*D*	64	*D*
3*b*	*B*	21	*A*	46	*D*	65	*D*
4	*A*	22	*A*	46*b*	*D*	66	*D*
4*b*	*B*	23	*A*	47	*C*, *D*	67	*D*
5	*A*	24	*A*	48	*D*	68	*D*
6	*A*	25	*A*	48*b*	*D*	69	*D*
6*b*	*B*	25*b*	*B*	49	*D*	70	*D*
7	*A*	26	*B*	50	*D*	71	*D*
8	*A*	27	*B*	51	*D*	72	*D*
8*b*	*B*	28	*C*, *D*	52	*D*, *E*	73	*E*
9	*B*	29	*C*, *D*	52*b*	*E*	74	*E*
10	*B*	30	*C*, *D*	52*c*	*E*	75	*E*
11	*A*	31	*C*, *D*	52*d*	*E*	76	*E*
12	*A*	32	*C*, *D*	53	*D*	77	*E*
12*b*	*B*	33	*D*	54	*D*	78	*E*
13	*B*	34	*D*	55	*A*	79	*E*
13*b*	*B*	35	*C*, *D*	55*b*	*B*	80	*E*
14	*F*	36	*D*	56	*E*	81	*E*
14*b*	*F*	37	*D*	57	*E*	82	*E*
14*c*	*F*	38	*D*	58	*E*	83	*E*
15	*F*	39	*D*	59	*E*	84	*E*
15*b*	*F*	40	*D*	60	*B*	85	*E*
16	*F*	41	*D*	60*b*	*B*	86	*E*
17	*D*	42	*D*	61	*D*		

sequence of the height of nodes around the threefold helix counting anticlockwise. The sequence then is composed of *y* figures (*y* represents the repetitive number of *T* nodes along the hexagonal *c* axis), whereby each figure is the fractional height of a node when divided by *y*. Doing so, the PTC's in the left- and right-handed varieties of quartz may be denoted by 012 (or 120 or 201) and 021 (or 210 or 102) respectively. The corresponding STC's may be denoted by 042042 (or 420420 or 204204) and 024024 (or 240240 or 402402) respectively (Fig. 5).

Hexagonal 3D nets are constructed from trigonal columns because the hexagonal symmetry of the 3D lattice generates from the trigonal symmetry of the trigonal columns. The following rules apply for the systematic enumeration of hexagonal 3D nets:

(i) The trigonal columns can be of two different types:

(*a*) a type 1 trigonal column has a threefold rotation axis (*e.g.* OFF);

(*b*) a type 2 trigonal column has a threefold screw axis (*e.g.* quartz).

(ii) Neighbouring trigonal columns can be symmetry related by

(*a*) a mirror plane [*e.g.* AFS (MAPSO-46) (Bennett & Marcus, 1987)] or a *c* glide (*e.g.* AFI);

(*b*) a threefold rotation (*e.g.* OFF) or screw axis (*e.g.* MAZ).

(iii) Neighbouring trigonal columns can be linked in three distinct ways:

(*a*) by direct linking (*e.g.* OFF);

(*b*) by sharing vertices (*e.g.* quartz), edges (*e.g.* tridymite) or faces (*e.g.* cristobalite);

(*c*) by inserting extra *T* atoms (case 1 insertion) between adjacent trigonal columns (*e.g.* VPI-5).

Also orthorhombic 3D nets can be constructed by linking trigonal columns: all options under (i), (ii) and (iii) are theoretically open, except option (ii*b*). Furthermore, the cases (ii*a*) and (iii) can be applied in two perpendicular directions (the orthorhombic *x* and *y* axes), giving rise to a much larger number of theoretical possibilities in comparison with the hexagonal LCTC set of structures.

Hexagonal 3D LCTC framework topologies may be characterized by means of a code which is composed of four designations, specifying (in the sequence mentioned):

(i) the crystal class (*H* for hexagonal);

(ii) the symmetry relation between neighbouring trigonal columns (*m* for a mirror plane parallel to the column axis; *c* for a *c* glide; 3*j*-fold rotation or screw axes (*j* positive integer) are indicated as such; *n* if no obvious symmetry relation exists). As was explained above, the way of symmetry relating neighbouring trigonal columns may in some cases be further specified by *L*, *H*, *M* or *N*. In such cases, this capital letter is given between brackets;

(iii) the way of linking neighbouring trigonal columns (*D* for direct linking; *V* for vertex sharing; *E* for edge sharing; *F* for face sharing; *I* to specify a case 1 insertion). If a case 2 insertion occurs, this will be indicated by giving the figure II between brackets;

(iv) the sharing coefficient (Zoltai, 1960) for interrupted frameworks. For (4; 2)-connected 3D nets it is two and will be omitted.

As such, the general composite code for a 3D hexagonal LCTC net is as follows (figures refer to the four options above):

(i) (ii){(.)} (iii){(. .)} {(iv)}

where { } denotes an optional designation.

Besides this composite code, the repetition sequence of the primary trigonal column has to be given also in order to characterize the 3D net. This sequence is given separately (not included in the code) because it would render the code too complicated. The type of trigonal column (1 or 2) needs not to be specified, a repetition sequence composed of figures only without dashes) being unambiguously characteristic for a type 2 trigonal column. Some designations are given in Table 5.

This type of 3D net designation for hexagonal LCTC structures may further be extended to characterize also orthorhombic LCTC structure types. The following extensions apply:

(1) *O* denotes the orthorhombic crystal class;

(2) the designations (ii) and (iii) above have to be specified in two perpendicular directions (x and y as in Figs. 1 and 2: the bond density along **x** is lowest) (separated by square brackets). If the code designations for both directions are identical only one needs to be specified.

As such, the general composite code for a 3D orthorhombic LCTC net is as follows (figures refer to the four extended options above):

(i) $[(\text{ii})\{(.)\}\ (\text{iii})\{(..)\}]_{\text{along } x}$ $\{[(\text{ii})\{(.)\}\ (\text{iii})\{(..)\}]_{\text{along } y}\}$ {(iv)}. In this way the composite codes for nets 61 (Andries & Bosmans, 1990), 84 [Fig. 2(*b*), Table 2] and 52 (Table 2) are $O[m(L)D][m(H)E]$, $O[c(L)D][c(H)I]$ and $O[m(L)D][m(H)D]$ respectively; for all three nets the repetition sequence of the PTC is *CS*. As was explained by Andries & Bosmans (1990), an alternative composite code for tridymite is $O[c(L)D][m(H)E]$ with repetition sequence (of the STC) *CS* (compare with the composite code of net 61 above).

It should be mentioned that many LCTC structure types are unambiguously identified by means of the composite code and the repetition sequence of their PTC. This is however not the case for some nets:

(i) those that contain inserted T atoms: the geometry of these atoms cannot be described with simple rules {an obvious solution is to describe explicitly the geometry of the inserted T atoms in the unit cell: *e.g.* one $S6R$ in DOH, two interrupted T_{2m} units in WEN, three T_4O_8 units [Fig. 2(*c*)] in VPI-5};

Table 7. *Compiling the definitions, notations and abbreviations used in the papers of Bosmans & Andries* (1990), *Andries & Bosmans* (1990) *and in this report*

Definitions, notations and abbreviations	Reference
ABC-6*C* group	*C*
ABC-6*S* group	*C*
Case 1 (or 2) insertion	*C*
c-connected trigonal column	*C*
Channel system *A* (or *B*)	*A*
Composite code for LCTC nets	*C*
I-connected trigonal column	*C*
D-connected trigonal column	*C*
DiR: double *i*-membered ring	
E-connected trigonal column	*C*
Extended orthorhombic group	*B*
Extended tridymite group	*B*
F-connected trigonal column	*C*
Group *A* (or *B* or *C*) (2*T*) trigonal cage	*A*
Group *D* (or *E*) (1*T*) trigonal cage	*A*
Group *F* (or *G* or *H*) (0*T*) trigonal cage	*A*
Group 1 (or 2) net of the tridymite group	*A*
h	*C*
H-connected trigonal column	*C*
Lateral connection of trigonal columns (LCTC) group	*C*
L-connected trigonal column	*C*
m	*A*
m-connected trigonal column	*C*
M-connected trigonal column	*C*
iMS: *i*-membered (horizontal) stack	*A*
n	*A*
n(1); *n*(2)	*A*
n-connected trigonal column	*C*
N-connected trigonal column	*C*
Primary trigonal column (PTC)	*C*
*R*180 transformation	*A*
Secondary trigonal column (STC)	*C*
Simple (or non-simple) net of the tridymite group	*A*
SiR: single *i*-membered ring	
Tertiary trigonal column (TTC)	*C*
2*T* orthorhombic-extended orthorhombic (OEO) transformation	*B*
2*T* orthorhombic group	*B*
Tridymite group	*A*
Tridymite group-extended tridymite group (TET) transformation	*B*
Tridymite group-2*T* orthorhombic (TO) transformation	*B*
*T*2/3*R* transformation	*A*
iT trigonal cage ($i=0$, 1 or 2)	*A*
T_2 (T_{2i}, T_{2m}) unit	*A*
Type 1 (or 2) trigonal column	*C*
V-connected trigonal column	*C*

References: (*A*) Bosmans & Andries (1990); (*B*) Andries & Bosmans (1990); (*C*) present paper.

(ii) those that are constructed from vertex-, edge- and/or face-sharing trigonal columns: no simple rules can be derived and an obvious possibility again is to describe explicitly the geometry of the shared structural subunit(s) in the unit cell (*e.g.* one T_{2m} unit in tridymite; three $S4R$'s in DOH; three T nodes in quartz).

Concluding remarks

In order to summarize the most important data of this paper and the preceding two papers, Table 6 compiles all structure types enumerated therein and Table 7 enumerates definitions, notations and abbreviations used throughout.

The *lateral connection of trigonal columns group* described here is flexible and amenable to change and addition: in the course of deriving new framework topologies, it will be necessary to adjust and/or extend the present classification scheme. Furthermore, the present group may serve as a mould for the further invention of novel framework topologies. It should be noted that all hexagonal (4; 2)-connected 3D and related framework structures known to date can be classified in the hexagonal LCTC set, while at this time no frameworks belonging to the orthorhombic set of the LCTC group have been established. Some nets belonging to the latter group seem however to be quite feasible. In particular, $2T$ orthorhombic structures constructed from $C(SC)_r$-type $2T$ trigonal cages are possible candidates for future synthesis.

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