Atlas of Zeolite Framework Types

Fifth Revised Edition

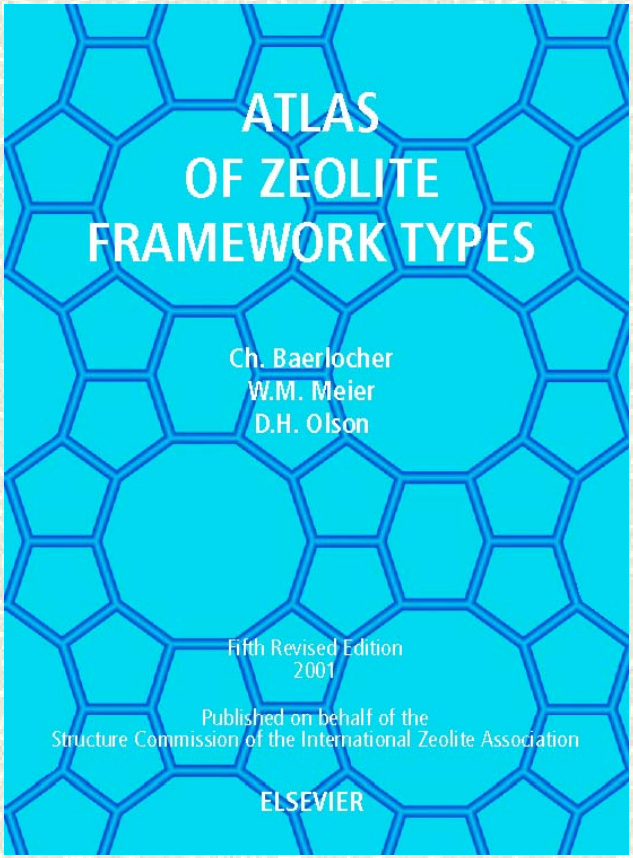
2001

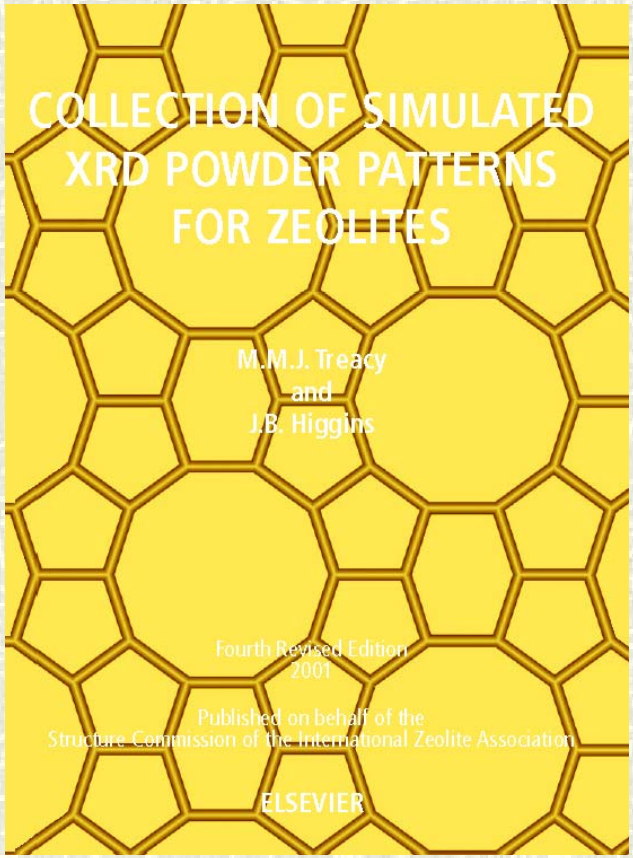
Summary

- Introduction
  - Books of the International Zeolite Association (IZA)
  - Availability
  - History of the Atlas of Zeolite Framework Types
  - Organisation of the Atlas
- Explanatory Notes from the Atlas of Zeolite Framework Types
  - Examples
    - LTA
    - LTL
    - Other framework types (if appropriate)

International Zeolite Association (IZA)

Books from the Structure Commission





Availability

- Printed Version

www.elsevier.com

- Electronic Version (pdf-Files)

www.iza-online.org

History of the Atlas of Zeolite Framework Types

Edition	Year	Zeolite Structures
1st	1970	27
2nd	1978	38
3rd	1982	85
4th	1996	98
5th	2001	133

History of the Atlas of Zeolite Framework Types

Change of name for the Atlas recommended by IUPAC in 2001

Old : Atlas of Zeolite Structure Types

New : Atlas of Zeolite Framework Types

- Structure: Implies both, the framework and extra-framework constituents

- Framework: Corner-sharing network of tetrahedreally coordinated atoms

Organisation of the Atlas

Two pages in the Atlas for each framework type code

Left page

Framework Type Informations

- Framework type code
- Stereographic figure
- Idealized cell constants
- Coordination sequences
- Vertex symbols
- Secondary building units
- Loop configurations of T-atoms
- Framework description
- Isotypic framework structures
- References

Right page

Type Material Informations

- Crystal chemical data
- Framework density
- Channels (observed rings)
- Stereographic figure (channels)

Framework Type Informations

Notes and Examples

Framework Type Code

- Previously called Structure Type Code
- Three capital letters (IUPAC Commission on Zeolite Nomenclature, 1978)
- Usually derived from the name of the type materials (Appendix D in the Atlas)
- For interrupted frameworks the 3-letter code is preceded by a hyphen (-)
- For intergrown materials, the * denotes a framework of a hypothetical end member

Code	Abbreviated Name	Full Name
LTA	Linde Type A	Zeolite A (Linde Division, Union Carbide)
LTL	Linde Type L	Zeolite L (Linde Division, Union Carbide)
FAU	Faujasite	
MFI	ZSM-5 (five)	Zeolite Socony Mobil – five
-CLO	Cloverite	Four-leafed clover shaped pore opening
*BEA	Zeolite Beta	

Notes and Examples

Framework Type Code

- Codes are only assigned to established structures that satisfy the rules of the IZA Structure Commission (Rules can be found in Appendix B)

- The codes should not be confused or equated with actual materials. They only describe and define the framework

  Not allowed:

  - NaLTA, NaLTL, NaFAU

  Correct is to use: | | for guest species, [ ] for framework host

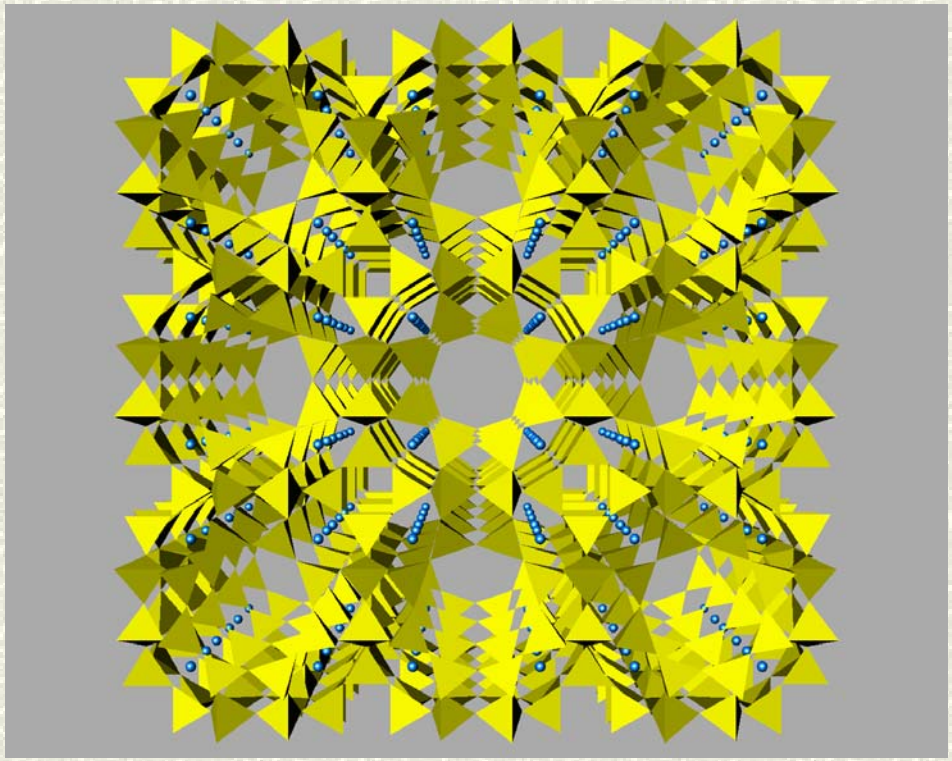
  - $|Na^{+}_{12}(H_2O)_{27}|_8\ [Al_{12}Si_{12}O_{48}]_8$-LTA or |Na| [Al-Si-O]-LTA

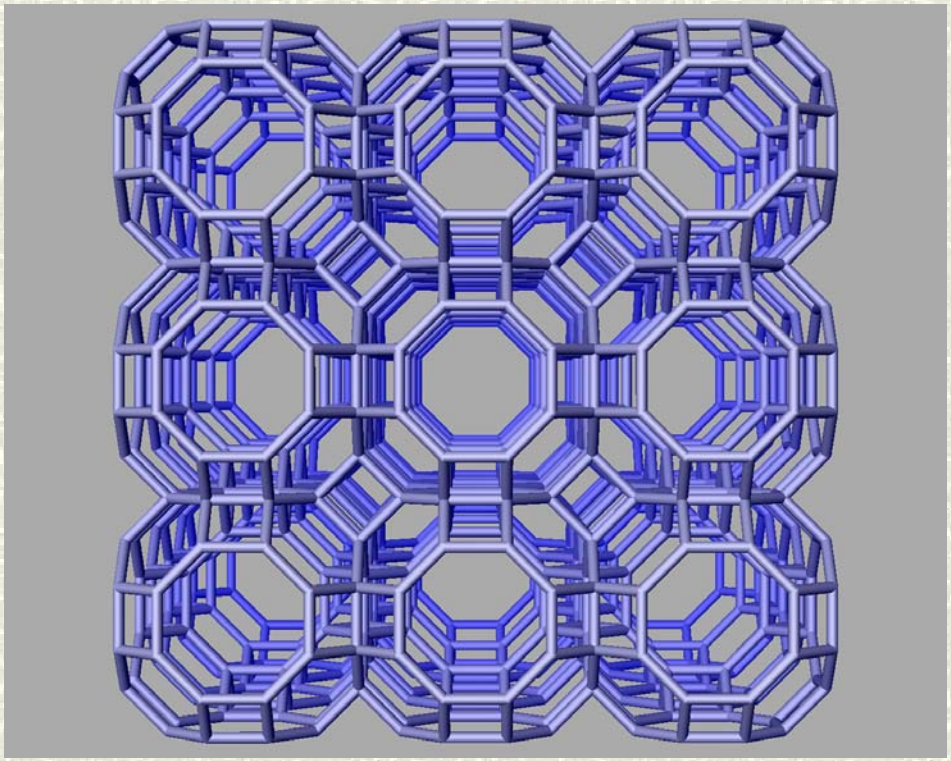
  - $|K^{+}_{6}Na^{+}_{3}(H_2O)_{21}|\ [Al_9Si_{27}O_{72}]$-LTL or |K-Na| [Al-Si-O]-LTL

  - $|Na_{58}|\ [Al_{58}Si_{134}O_{384}]$-FAU or |Na| [Al-Si-O]-FAU

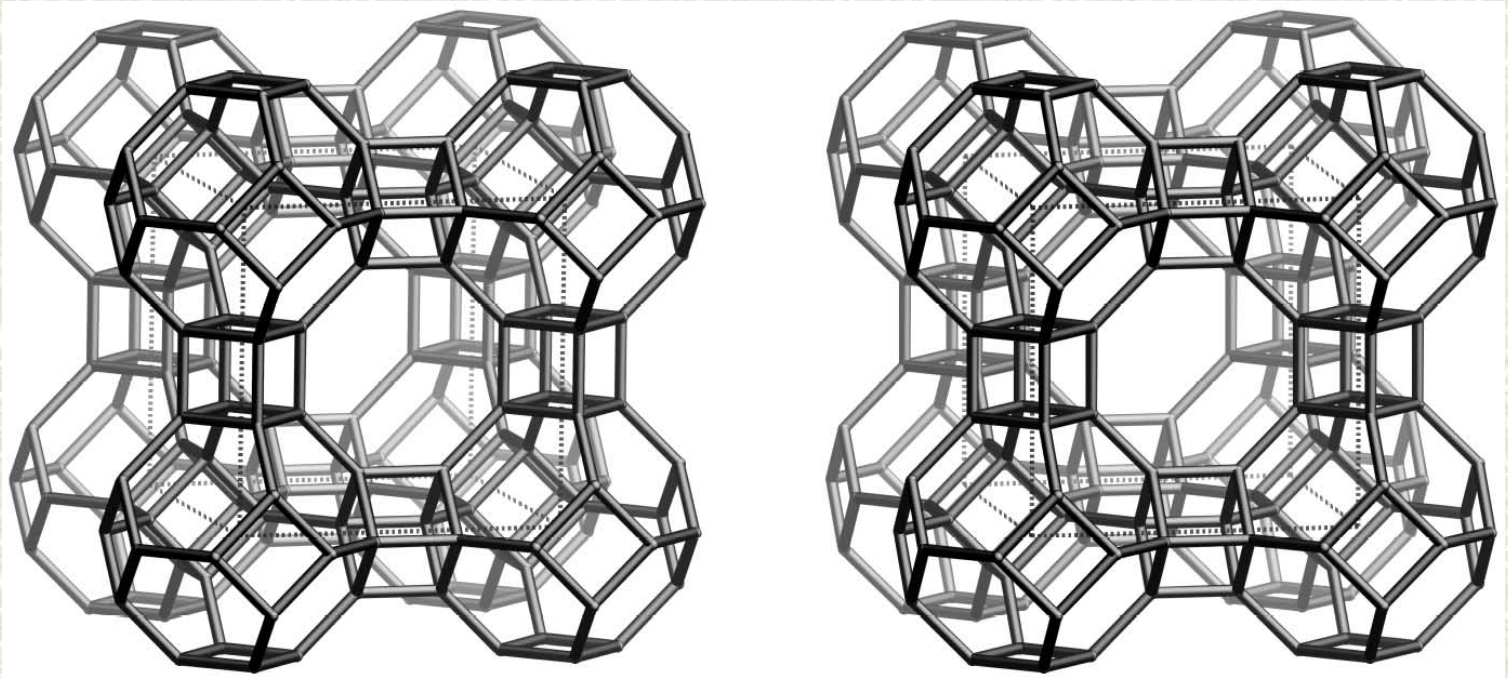
- Framework types do not depend on composition, distribution of the T-atoms, cell dimensions or symmetry (T-atoms: Si, Al, P, Ga, B, Be, etc.)

LTA: Structure and Framework Figures

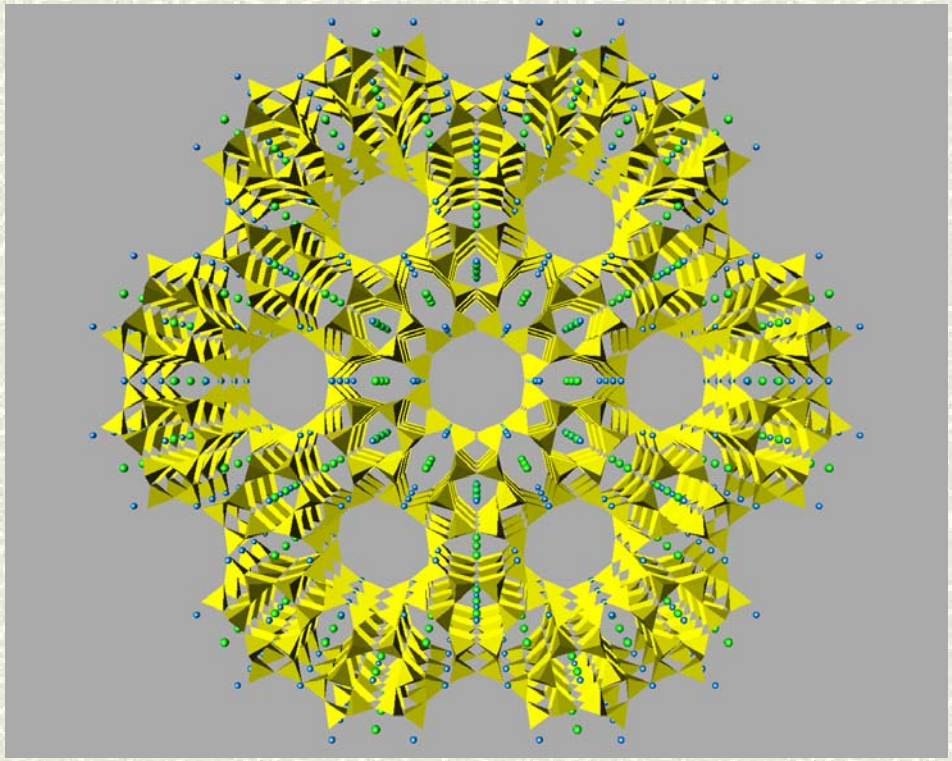


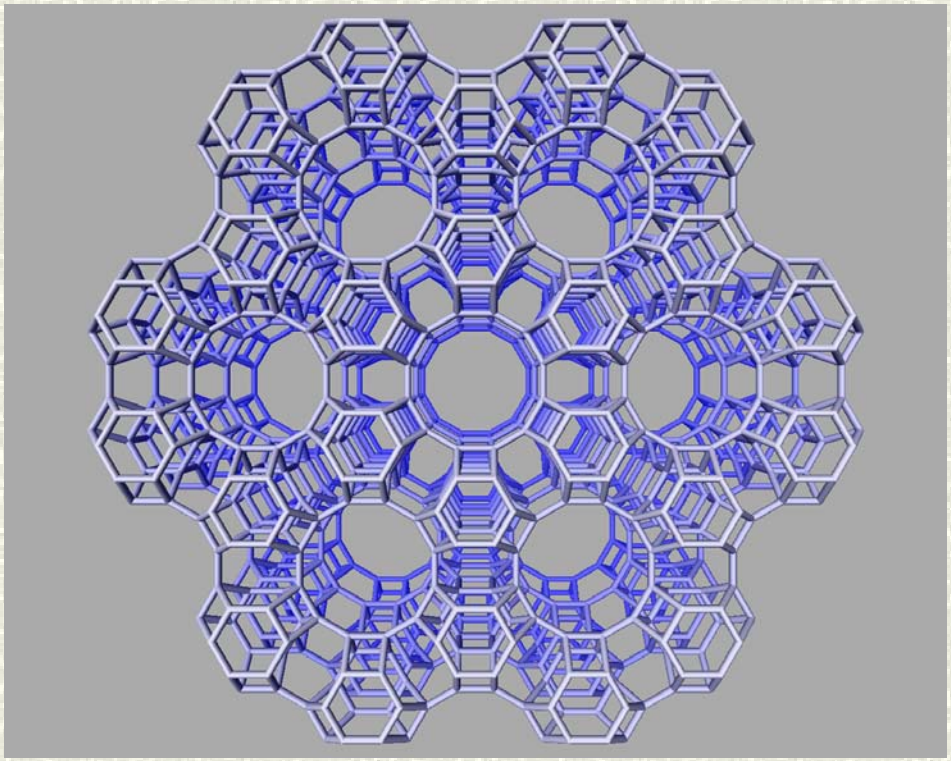


LTA Framework: Stereographic Figure

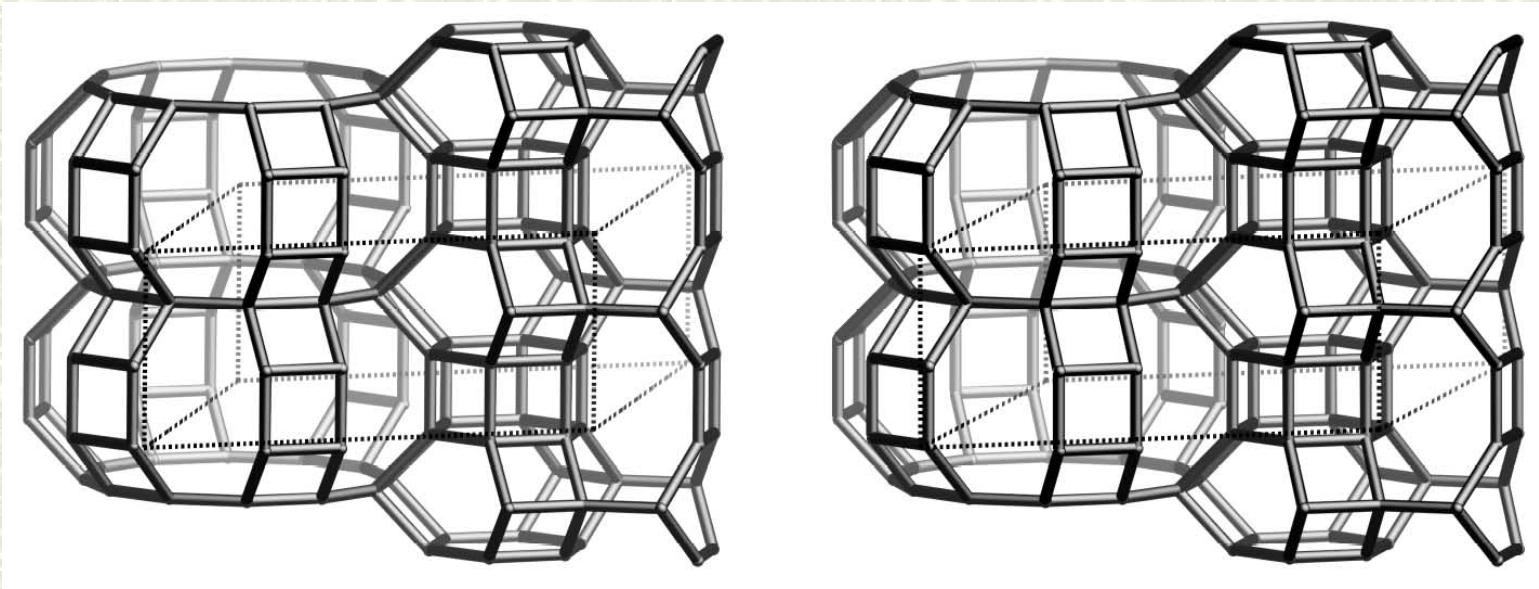


LTL: Structure and Framework Figures





LTL Framework: Stereographic Figure



Idealized Cell Parameters

- They are obtained after geometry refinement in the highest possible symmetry for the framework type

- Refinement was carried out assuming:
  - Hypothetical SiO_2 composition
  - d_{Si-O} = 1.61 Å
  - d_{O-O} = 2.629 Å
  - d_{Si-Si} = 3.07 Å

	Crystal System	Space Group	Cell Parameters
LTA	Cubic	Pm-3m	a = 11.9 Å
LTL	Hexagonal	P6/mmm	a = 18.1 Å c = 7.6 Å

Coordination Sequences (CS)

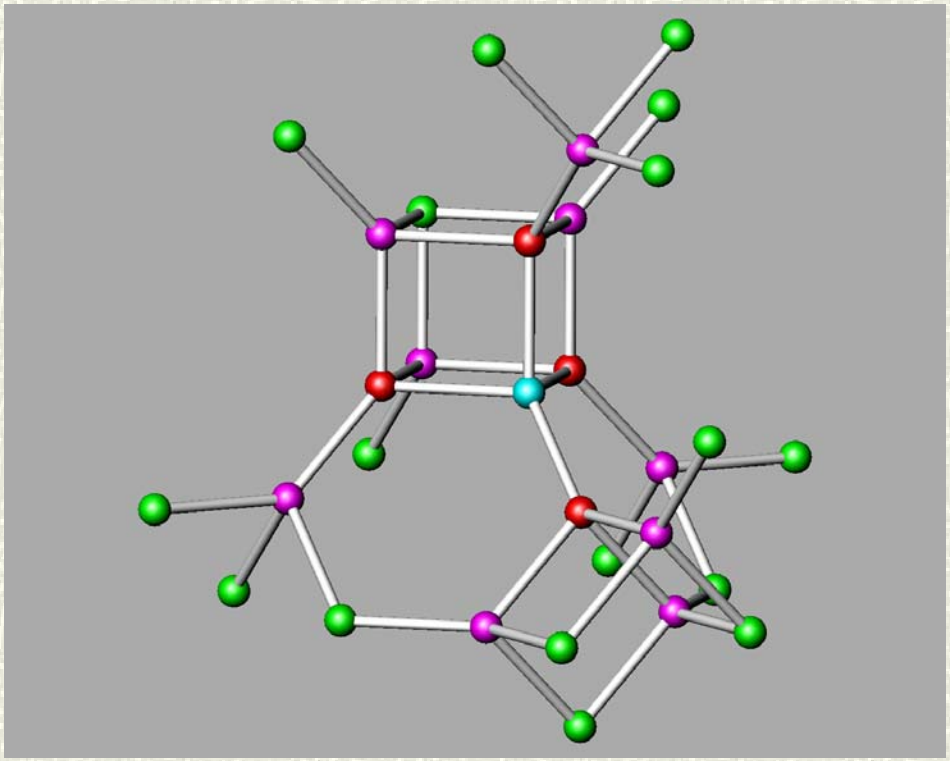
- Each T-atom is connected to $N_1 = 4$ neighboring T-atoms through oxygen bridges
- These neighboring T-atoms are then linked in the same manner to N_2 T-atoms in the next shell
- Each T-atom is counted only once
- Infinite, ideal case without T-atom sharing:

  $N_0 = 1$ $N_1 = 4$ $N_2 = 12$ $N_3 = 36$ $N_4 = 108$

- Listed in the Atlas for every T-position:
  - Multiplicity and site symmetry of the position
  - CS from N_1 up to N_{10}

Coordination Sequence for LTA

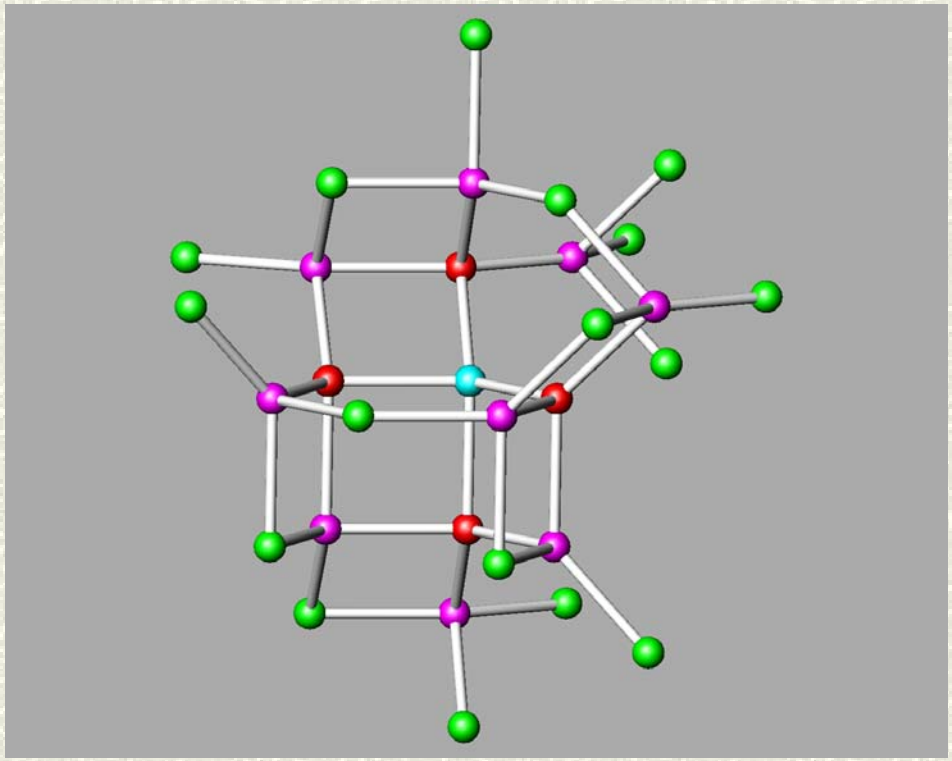
T1 (24, m) 4 9 17 28 42 60 81 105 132 162

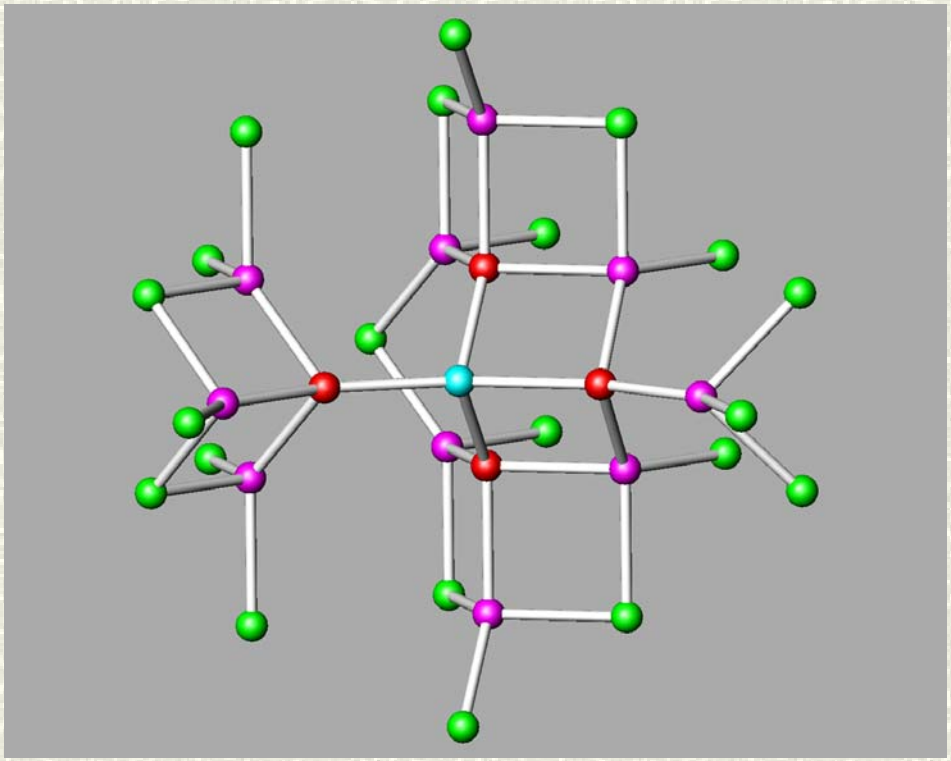


Coordination Sequences for LTL

T1 (24, 1) 4 9 17 29 46 69 …

T2 (12, m) 4 10 21 35 49 66 …





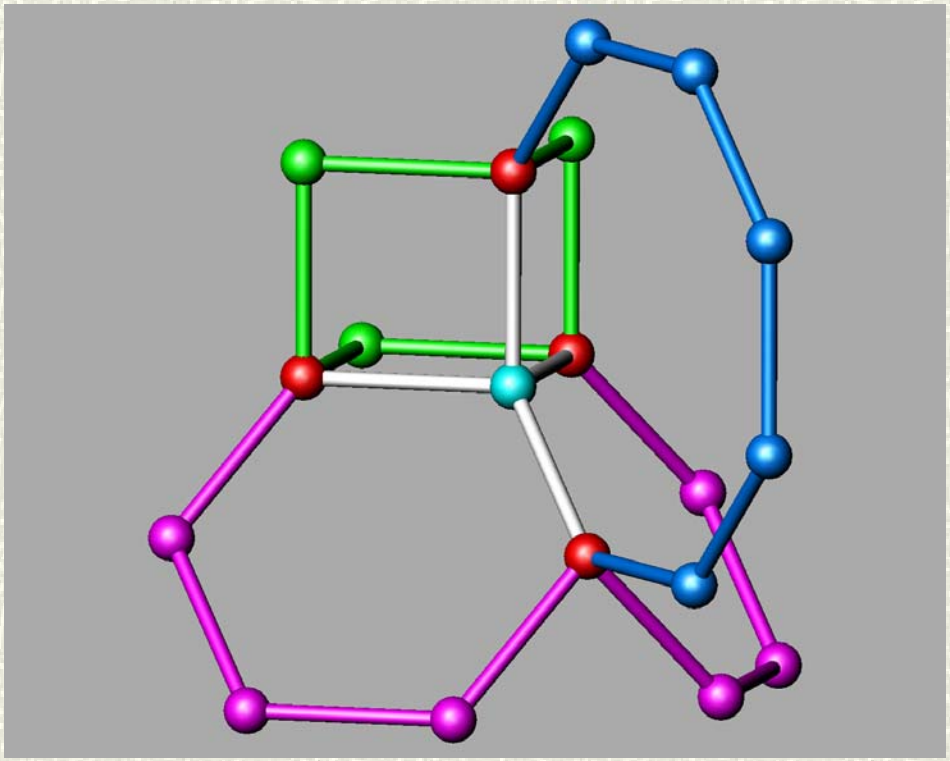
Vertex Symbols

- The vertex symbol indicates the size of the smallest ring associated with each of the 6 angles of a tetrahedron (T-atom)
- The symbols for opposite pairs of angles are grouped together
- Rings of the same size at a vertex are indicated by a subscript

LTA	T1	4 . 6 . 4 . 6 . 4 . 8
LTL	T1	4 . 4 . 4 . 6 . 6 . 8
	T2	4 . 8_3 . 4 . 8_3 . 6 . 12

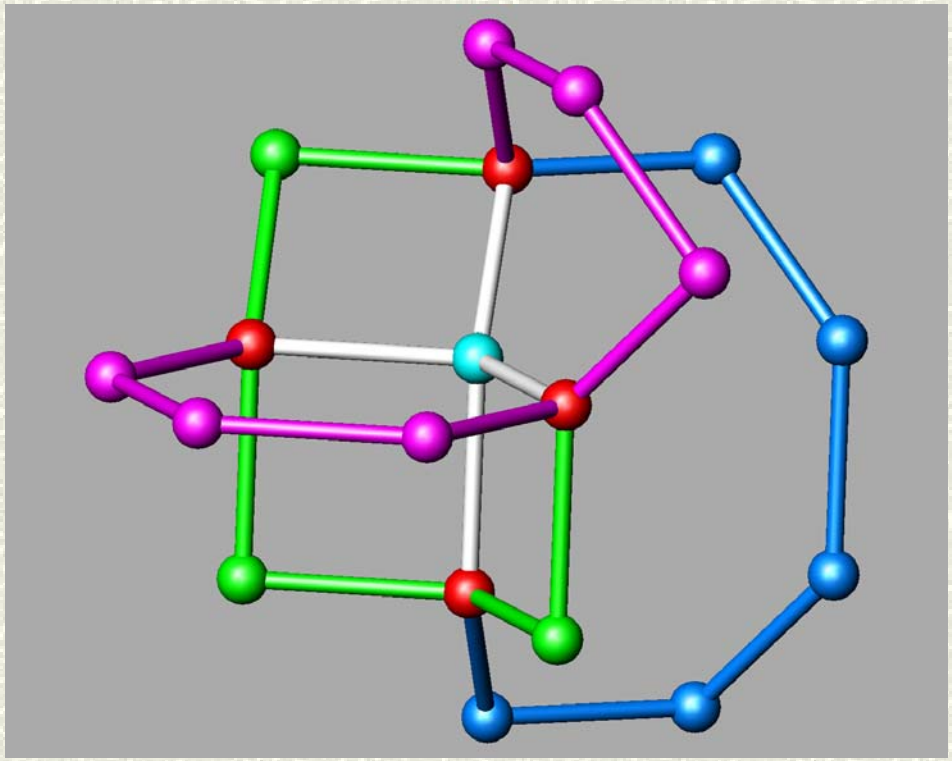
Vertex Symbol for LTA

4 . 6 . 4 . 6 . 4 . 8

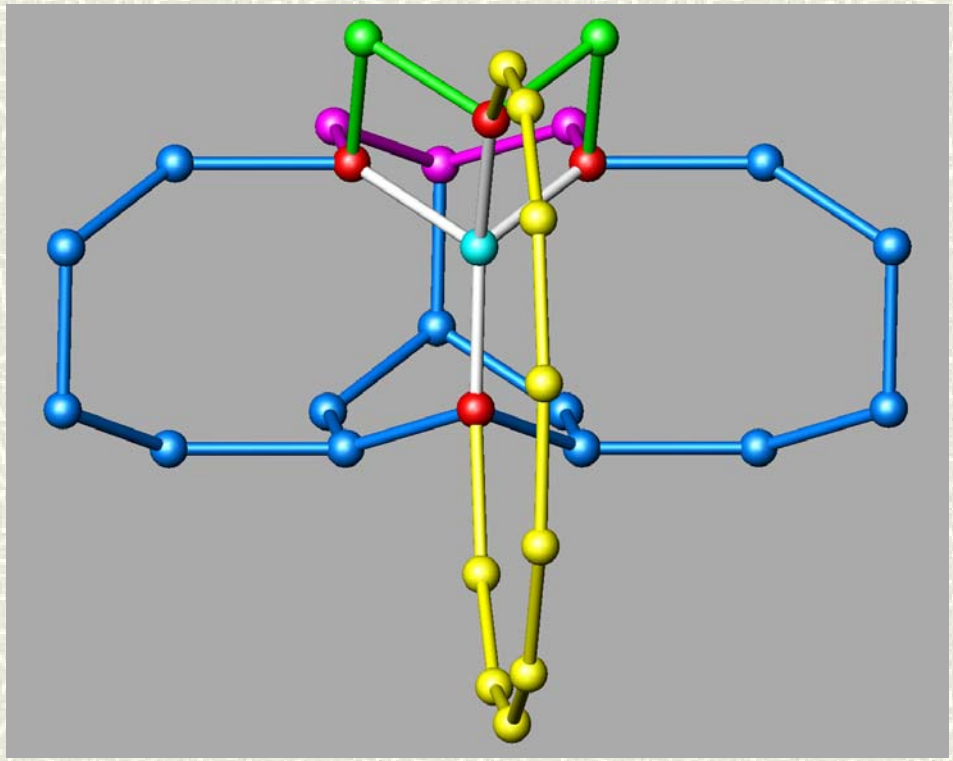


Vertex Symbols for LTL

4 . 4 . 4 . 6 . 6 . 8

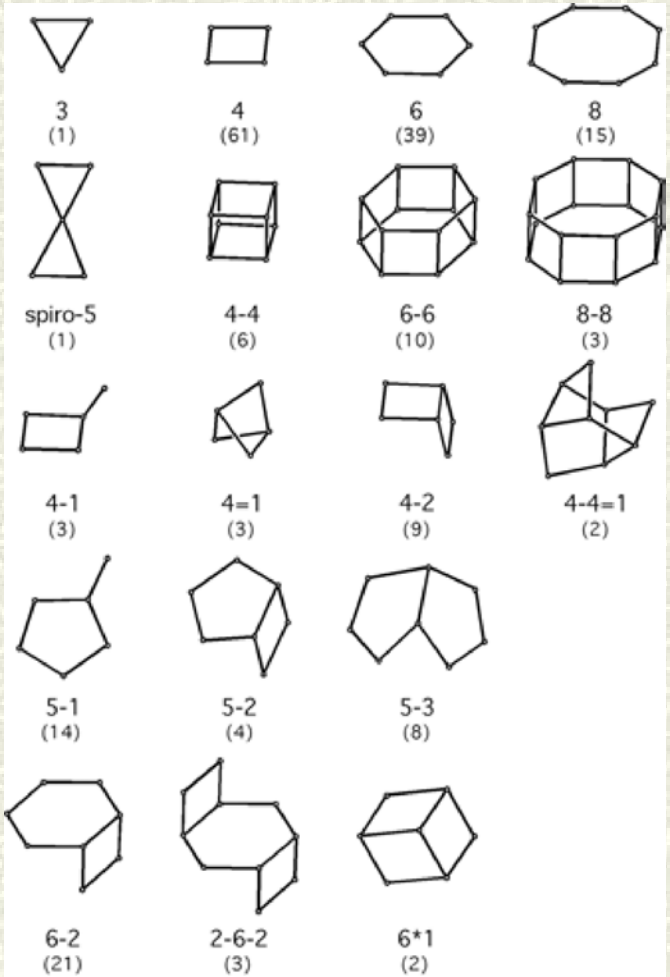


$4 . 8_3 . 4 . 8_3 . 6 . 12$



Secondary Building Units (SBU)

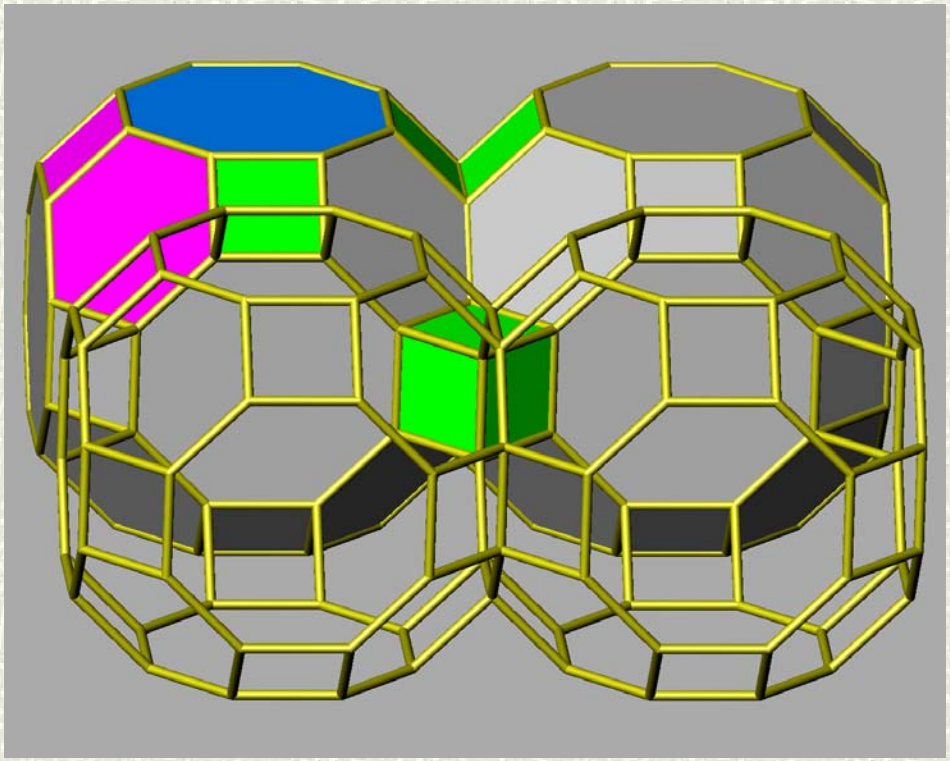
- Zeolite frameworks can be thought to consist of component units:
  - Finite (i.e. chain-like)
  - Infinite (i.e. layer-like)
- The finite units which have been found to occur in tetrahedral frameworks are called Secondary Building Units (SBU)
- The primary building units are TO_4 tetrahedra
- SBU are derived assuming that the entire framework is made up of one type of SBU only
- If more than one SBU is possible, all are listed



Number in ( ) = frequency of occurrence

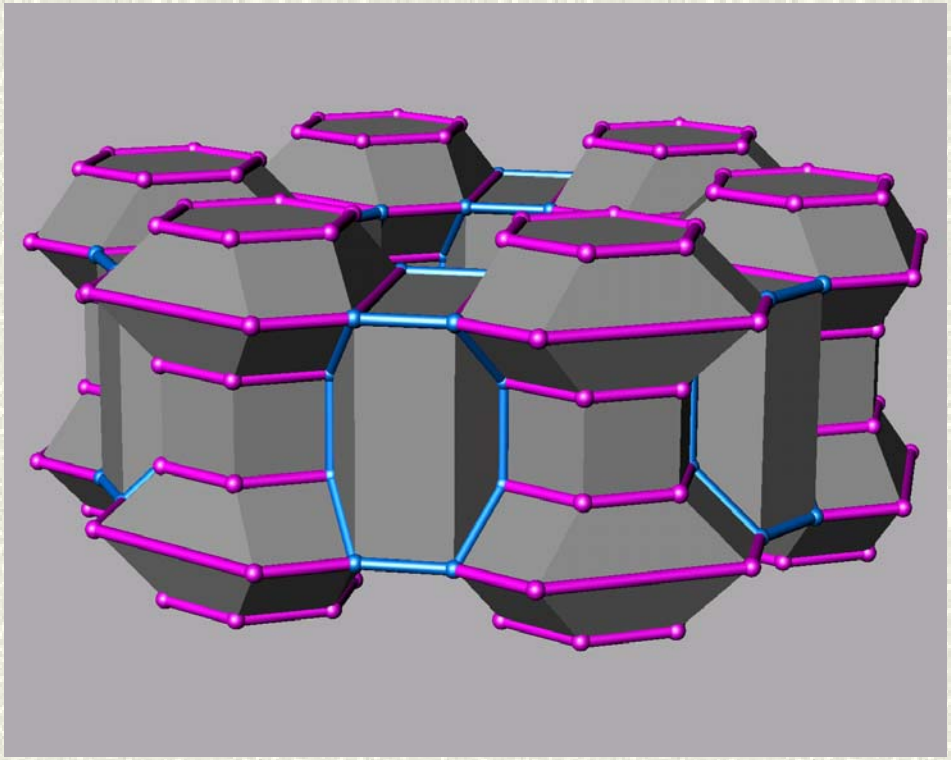
Secondary Building Units for LTA

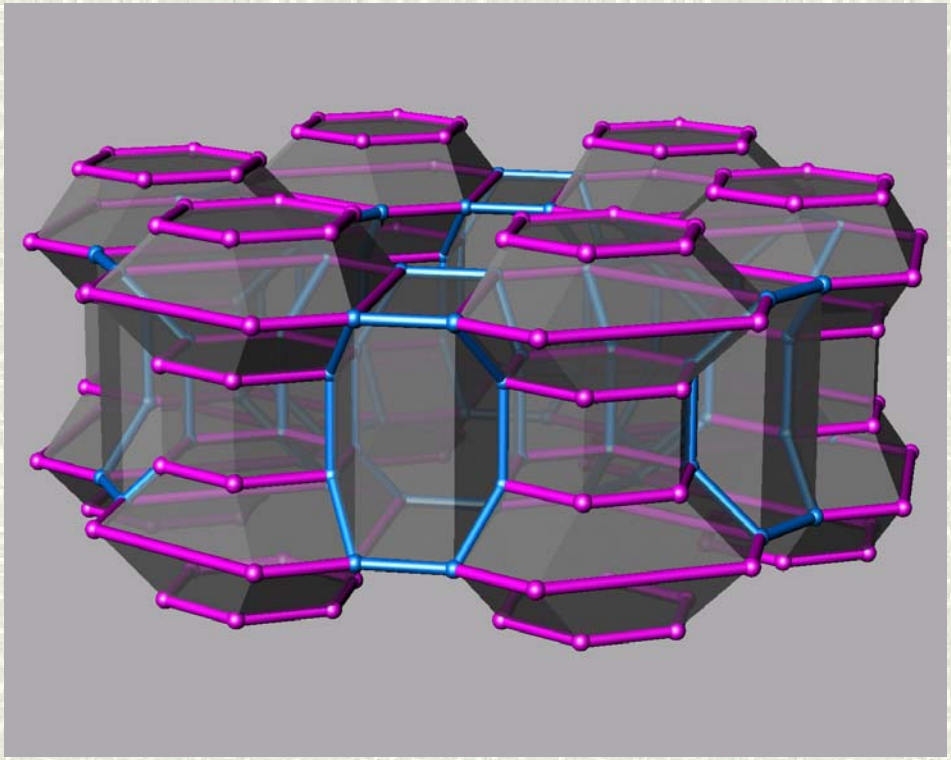
8 or 4-4 or 6-2 or 4-2 or 4



Secondary Building Units for LTL

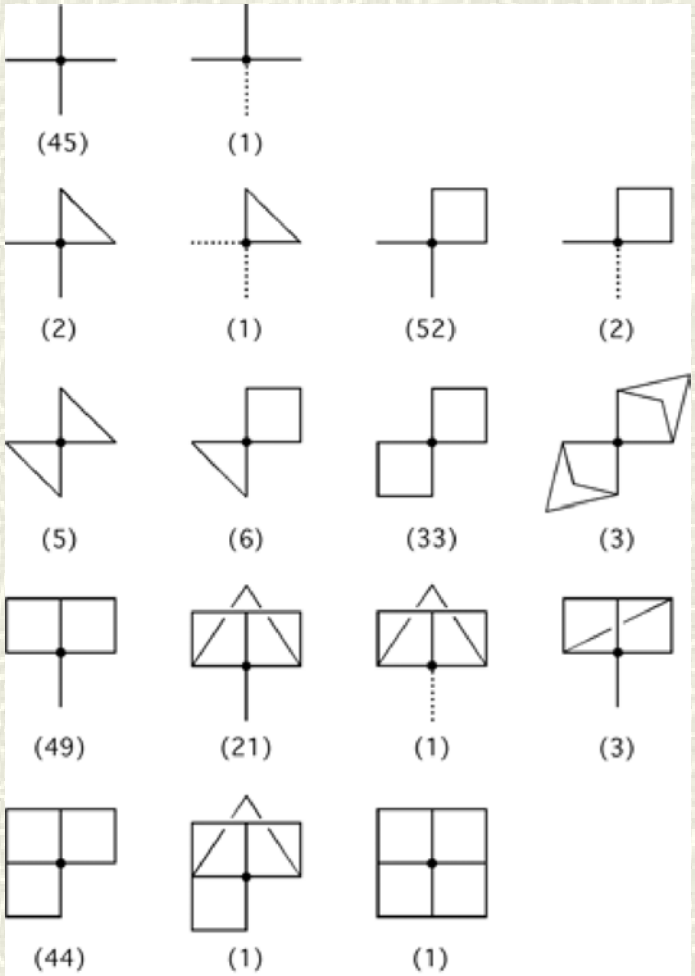
8 or 6





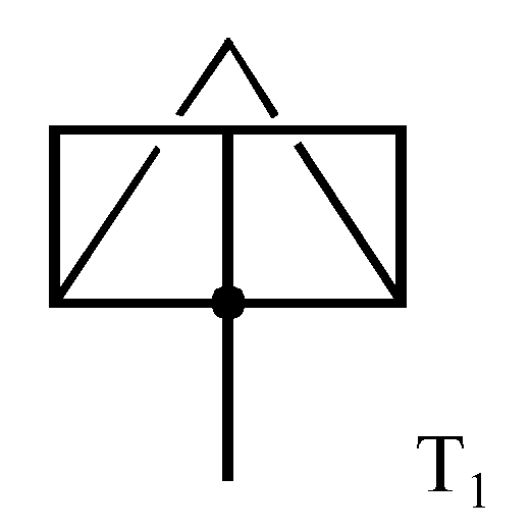
Loop Configuration of T-atoms

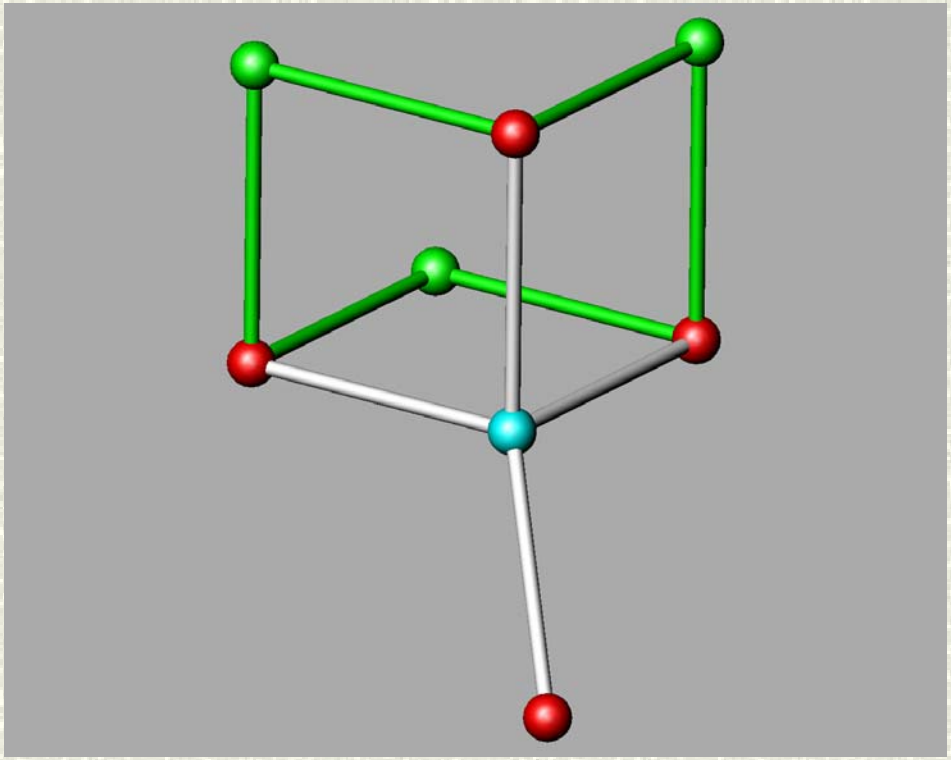
- Simple graph showing how many 3- or 4-memberd rings a given T-atom is involved in
- Can be used for classification purposes
- Information given is a subset of the vertex symbol
- Solid lines: T – O – T link
- Dotted lines: T – O bond found in interrupted frameworks



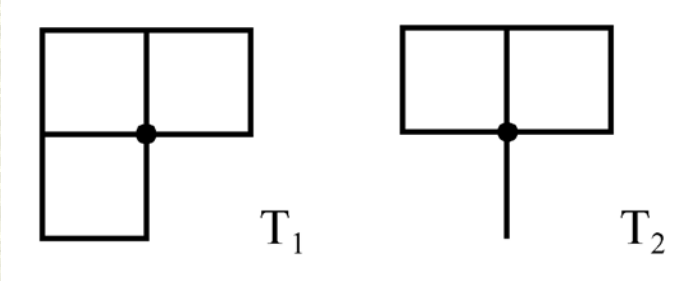
Number in ( ) = frequency of occurence

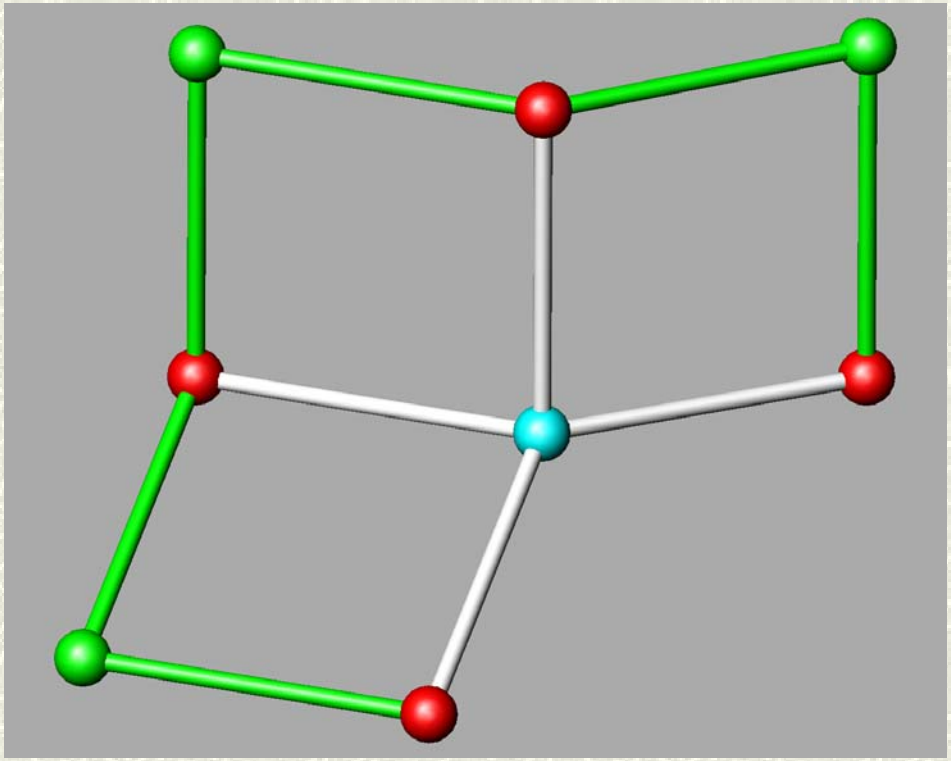
Loop Configuration of T-atom for LTA

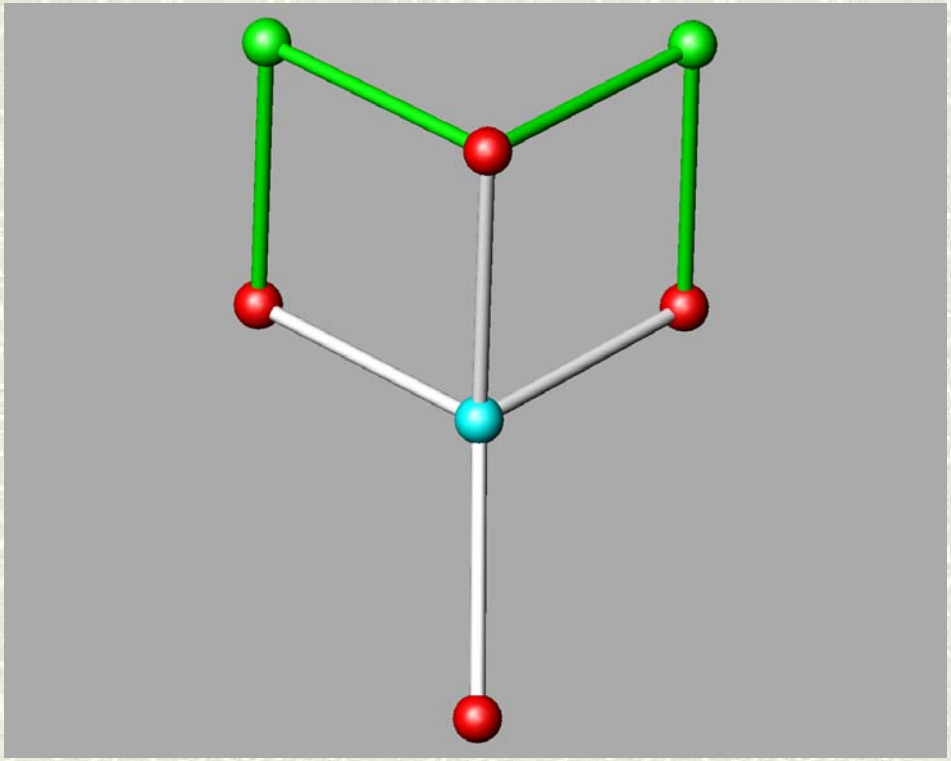




Loop Configuration of T-Atoms for LTL

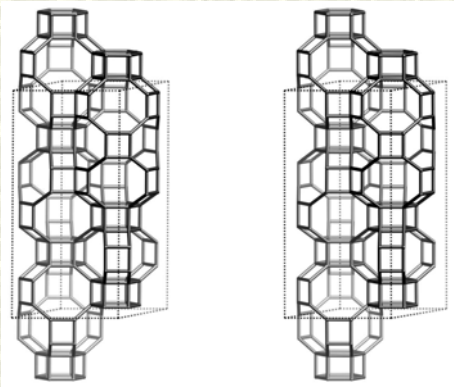






Framework Description

- For all 15 framework types of the so-called ABC-6-family the ABC stacking sequence is listed

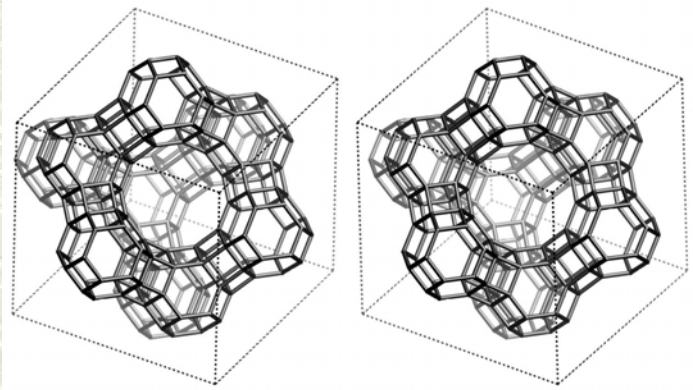


AFT

Framework description: AABBCCAACCBB sequence of 6-rings

- Listed are also some other structural relationship which are thought to be helpful

FAU



Framework description: structural derivative of diamond and cristobalite, respectively

Notes and Examples

Isotypic Framework Structures

- As-synthesized materials that have the same framework type but different chemical composition
- Materials with different laboratory code
- Materials obtained by post synthesis treatment (e.g. in exchange, dealumination) are generally not included
- The type material, the species first used to establish the framework type, is given first and marked with an asterisk

LTA

Isotypic framework structures:	*Linde Type A[1,2]	N-A[7]
	[Al-Ge-O]-LTA[3]	SAPO-42[8]
	[Ga-P-O]-LTA[4]	ZK-21[9]
	Alpha[5]	ZK-22[9]
	LZ-215[6]	ZK-4[10]

LTL

Isotypic framework structures:	*Linde Type L[1]
	(K,Ba)-G,L[2]
	Gallosilicate L[3,4]
	LZ-212[5]
	Perlialite[6,7]

Zeolite Type Categories and Framework Type Groups

- Zeolite type categories
  - Silicates
  - Phosphates
- Framework type groups
  - Silicates
  - Phosphates
  - Both, silicates and phosphates

Silicates[a]			Both Silicates and Phosphates	Phosphates[b]	
AFG	IFR	OFF	ABW	ACO	SAO
ASV	ISV	OSO	AET	AEI	SAS
*BEA	ITE	-PAR	AFI	AEL	SAT
BIK	JBW	PAU	AFX	AEN	SAV
BOG	KFI	-RON	ANA	AFN	SBE
BRE	LIO	RSN	AST	AFO	SBS
CAS	LOV	RTE	BPH	AFR	SBT
CFI	LTN	RTH	CAN	AFS	VFI
-CHI	MAZ	RUT	CGS	AFT	WEI
CON	MEI	SFE	CHA	AFY	ZON
DAC	MEL	SFF	DFT	AHT	
DDR	MEP	SGT	EDI	APC	
DOH	MFI	STF	ERI	APD	
DON	MFS	STI	FAU	ATN	
EAB	MON	STT	GIS	ATO	
EMT	MOR	TER	LAU	ATS	
EPI	MSO	TON	LEV	ATT	
ESV	MTF	TSC	LOS	ATV	
EUO	MTN	VET	LTA	AWO	
FER	MTT	VNI	LTL	AWW	
FRA	MTW	VSV	MER	CGF	
GME	MWW	-WEN	PHI	-CLO	
GON	NAT	YUG	RHO	CZP	
GOO	NES		SOD	DFO	
HEU	NON		THO	OSI	

[a] including germanates
[b] including arsenates

References

- Is not a complete list
- As general rule, references are given to:
  - Work to type of materials first establishing that framework type
  - Subsequent work adding significant information regarding the framework topology
- References to isotypes are limited to the work in which sufficient data are provided to establish the identity

Type Material Informations

Crystal Chemical Data

- Composition, expressed in terms of cell contents (New IUPAC rules are used)
- Crystal system, space group and cell parameters
- Relationship of the unit cell orientation with respect to the framework type, if the space group setting of the type material differs from that of the framework type

Crystal chemical data: $|Na^{+}_{12}\ (H_2O)_{27}|_8\ [Al_{12}Si_{12}\ O_{48}]_8$ **-LTA**
cubic, $Fm\bar{3}c$, a = 24.61Å [2]
(Relationship to unit cell of Framework Type: a' = b' = c' = 2a)

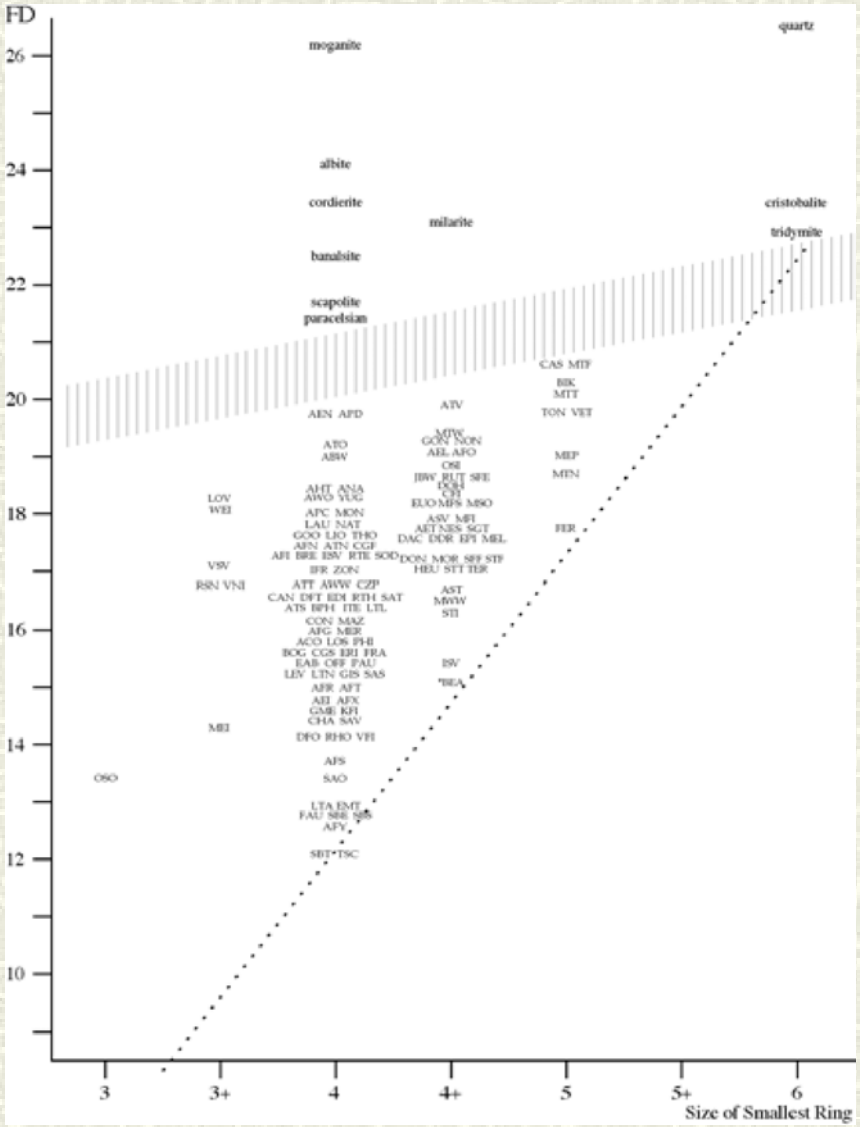
Crystal chemical data: $|K^{+}_{6}Na^{+}_{3}\ (H_2O)_{21}|\ [Al_9Si_{27}\ O_{72}]$**-LTL**
hexagonal, P6/mmm, a = 18.40Å, c = 7.52Å [2]

Framework Density (FD)

- The framework density is a simple criterion for distinguishing zeolites and zeolite-like materials from denser materials
- Definition: $\frac{\text{Number of T - Atoms}}{1000\ \text{Å}^3}$
- The figures given refer to the type materials
- Non-zeolitic framework structures: FD = 20 – 21
- Zeolite with fully crosslinked frameworks: FD = 12.1 – 20.6
- FD's less than 12 have only been encountered for the interrupted framework of cloverite (-CLO)
- The FD is obviously related to the pore volume but does not reflect the size of the pore openings

FD vs. Smallest Ring in Loop Configuration

- The + sign indicates that there are some T-positions associated with only larger rings
- LTA
  - Smallest ring size: 4
  - FD = 12.9
- LTL
  - Smallest ring size: 4
  - FD = 16.3
- MFI
  - Smallest ring size: 4+
  - FD = 17.9



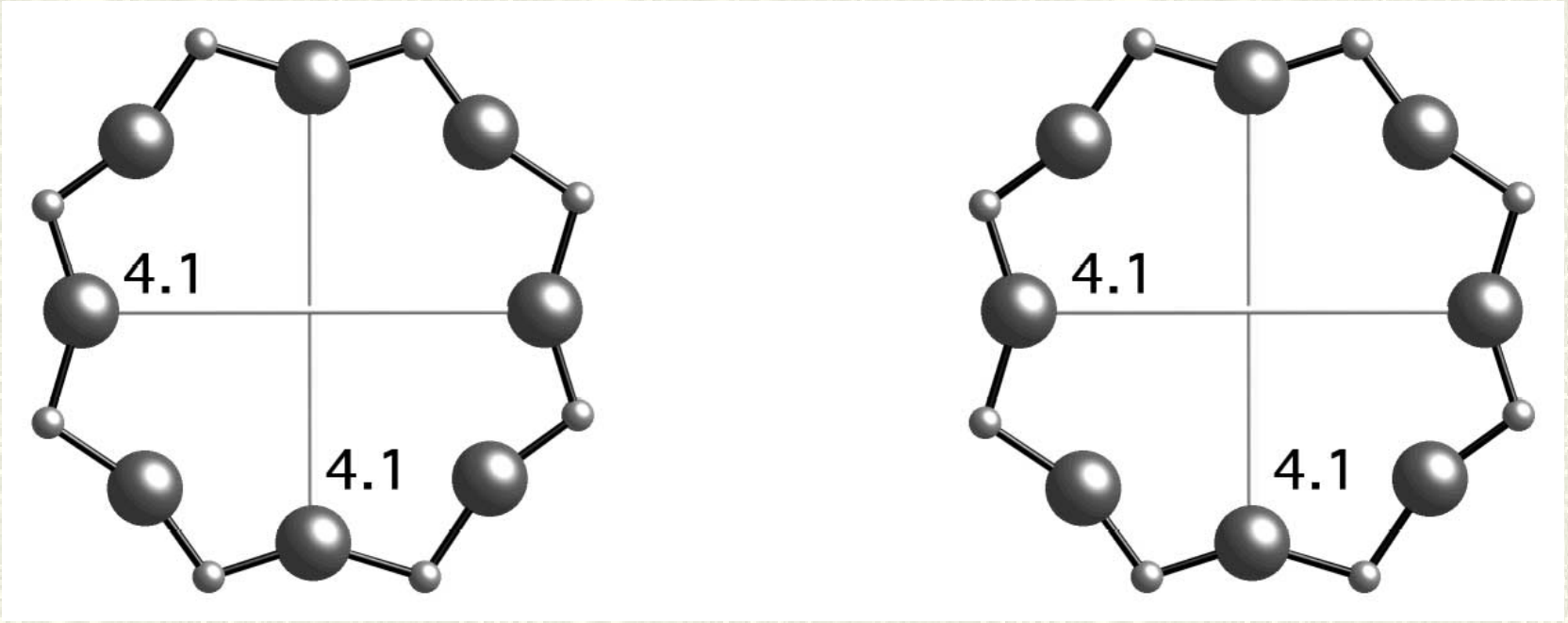
Channels

Short notation for description of channels

- Channel direction, relative to the axis of the type material structure
  - <. . .> : All symmetry related directions
  - [. . .] : Only given direction
  - ⊥[. . .] : Channel direction is at right angle to the given direction
- Number of T-atoms forming the ring (in bold type)
- Free diameters of the channels in Å
- Number of asterisks (*): Channel is one- two- or three-dimensional
- Double arrow (↔): Interconnecting channel systems
- A vertical bar (|): No direct access frome one channel system to the other

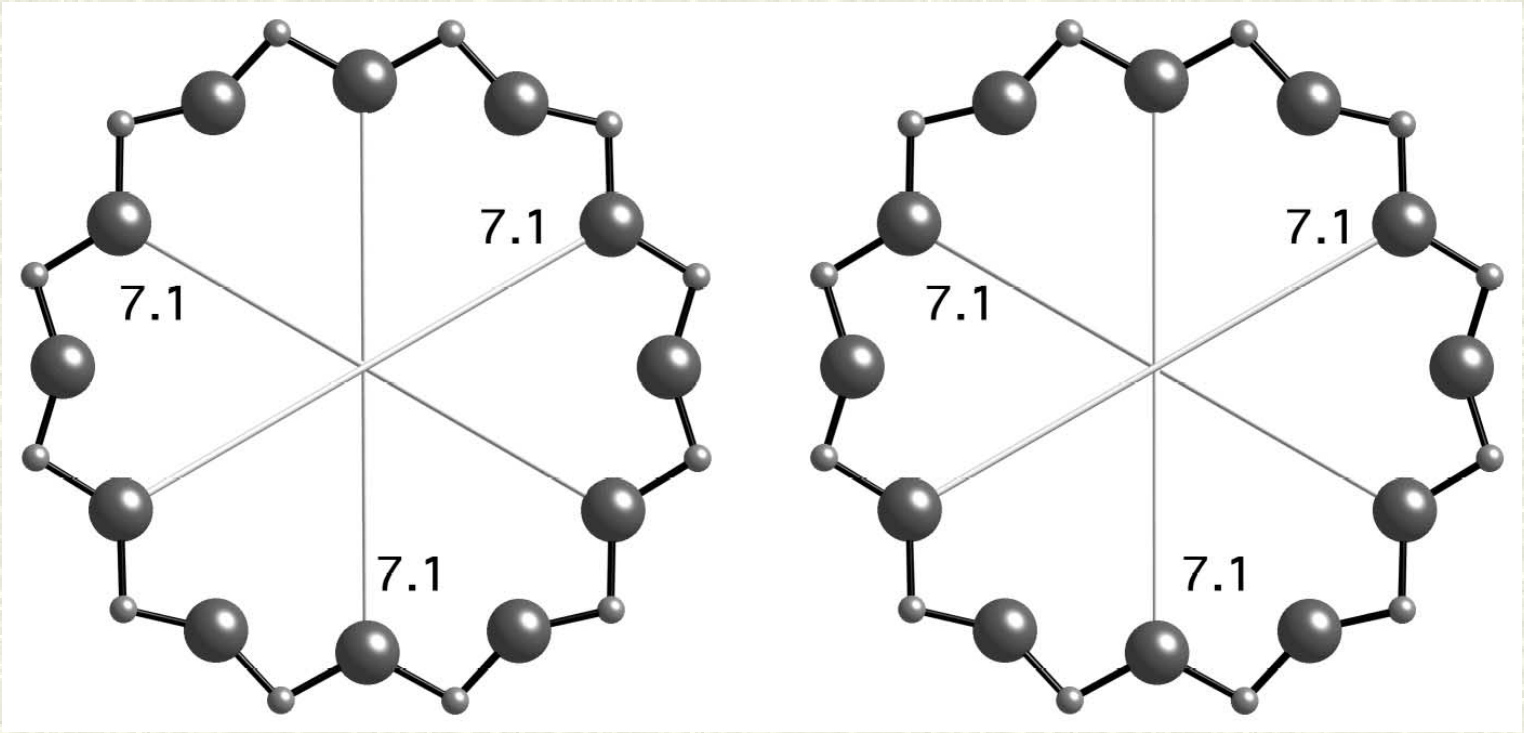
LTA: Channel

<1 0 0> **8** 4.1 x 4.1 ***



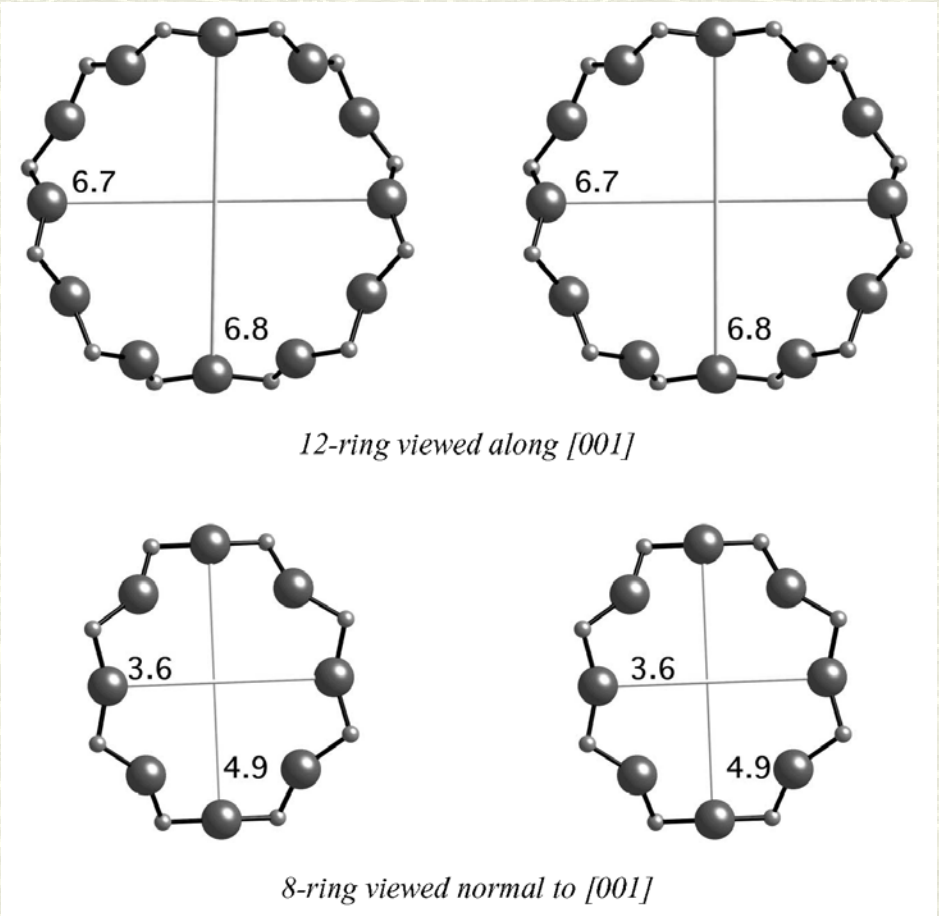
LTL: Channel

[0 0 1] **12** 7.1 x 7.1 *



OFF (Offretite): Channels

[0 0 1] **12** 6.7 x 6.8 * ↔ ⊥[0 0 1] **8** 3.6 x 4.9 **



RHO (Zeolite Rho): Channels

<1 0 0> **8** 3.6 x 3.6 *** | <1 0 0> **8** 3.6 x 3.6 ***