Understanding Zeolite Frameworks

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What are Zeolites?

History

- Zeolites have been studied by mineralogists for almost 250 years.

Zeolite	Date	Zeolite	Date
Stilbite	1756	Mordenite	1864
Natrolite	1758	Clinoptilolite	1890
Chabazite	1772	Offretite	1890
Harmotome	1775	Erionite	1890
Analcime	1784	Kehoeite	1893
Laumontite	1785	Gonnardite	1896
Thomsonite	1801	Dachiardite	1905
Scolecite	1801	Stellerite	1909
Heulandite	1801	Ferrierite	1918
Gmelinite	1807	Viseite	1942
Mesolite	1813	Yugawaralite	1952
Gismondine	1816	Wairakite	1955
Brewsterite	1822	Bikitaite	1957
Epistilbite	1823	Paulingite	1960
Phillipsite	1824	Garronite	1962
Levynite	1825	Mazzite	1972
Herschelite	1825	Barrerite	1974
Edingtonite	1825	Merlinoite	1976
Faujasite	1842		

History

- 1756: A. F. Cronstedt
  - History of zeolites starts with the discovery of Stilbite.
  - Described behavior under fast heating conditions. The mineral seemed to boil because of the fast water loss.

ζειν = zein = to boil

λιθος = lithos = stone

➔ ZEOLITE

History

- 1784: Barthelemy Faujas de Saint-Fond
  - As a French Professor in geology he formulated a nice formalism based on observations to indentify zeolites in his book ˝Mineralogie des Volcans˝.
  - In his honor, a well known zeolite is called Faujasite in 1842.

Quels font donc les caractères qui doivent diriger le Naturaliste dans la connaissance de la véritable zéolite? Je crois que ceux que je vais indiquer suffiront.

1°. La zéolite soumise à un feu vif dans un creuset, ou rougie à la lampe d'émailleur, & mieux encore, placée dans un charbon qu'on creuse & qu' on allume, & attaquée avec l' air déphlogiftiqué, jette, un instant avant sa fusion complette, un feu vif & brillant qui cesse & n' a plus le même éclat lorsque la matière parfaitement fondue roule en globules dans le creuset de charbon.

2°. La zéolite est fusible sans adition, & donne un beau verre.

3°. Réduite en poudre fine & traitée avec les acides, elle produit bientôt une gelée solide & transparente, sans faire aucune effervescence.

4°. La crystallisation réunie aux autres caractères, sert aussi à la faire reconnoître. Son origine est encore problématique.

History

- Until the early 1940's attempts to synthesize zeolites were made by mineralogists interested in the stability with other minerals.

- Union Carbide pioneered the synthetic molecular sieve zeolite business, initiating research in 1948 on adsorption for purification, separation and catalysis.
  - 1950: Synthesis of pure Zeolite A and X.
  - 1953: Patent filed for Zeolite A and X.
  - 1954: Final structure of Zeolite A and X.
  - 1956: Zeolite X with high silica/alumina ratios ➔ Zeolite Y.
  - 1956: Structure of Zeolite A published.
  - 1958: Structure of Zeolite X published.
  - 1959: Patent granted.

History

(Published 1956 in *J. Am. Chem. Soc.*)

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE LINDE AIR PRODUCTS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A

BY D. W. BRECK, W. G. EVERSOLE, R. M. MILTON, T. B. REED AND T. L. THOMAS

RECEIVED APRIL 19, 1956

The properties of a new zeolite, a hydrated crystalline sodium aluminosilicate, are described and the syntheses of 14 new zeolite species and 6 of the 35 known zeolites are announced. The new zeolite, designated type A, is represented by the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$. The structure is cubic, a_0 = 12.32 Å., space group O_h^1-Pm3m, and is characterized by a 3-dimensional network consisting of cavities 11.4 Å. in diameter separated by circular openings 4.2 Å in diameter. Removal of the crystal water leaves a stable crystalline solid containing mutually connected intracrystalline voids amounting to 45 vol. % of the zeolite. A high capacity adsorbent is produced which readily occludes molecules of a certain size and shape but excludes others. Sodium ions, accessible to the intracrystalline voids or pores, undergo cation exchange readily in aqueous solution. Replacement of sodium ions by calcium ions effectively enlarges the pore openings so straight chain hydrocarbons are readily adsorbed but branched chain hydrocarbons are excluded.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE LINDE AIR PRODUCTS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A

BY T. B. REED AND D. W. BRECK

RECEIVED APRIL 23, 1956

The new synthetic zeolite, Type A, is cubic, a_0 = 12.32 Å., and X-ray data are consistent with space group O^1-Pm3m. The unit cell composition is $Me_{12/n}[(AlO_2)_{12}(SiO_2)_{12}]\cdot NH_2O$ where Me is an exchangeable cation of charge *n*, and *N* varies from 20 to 30. The unit cell dimension varies slightly with the cation present. The aluminosilicate framework consists of 24(Si,Al)–O_4 tetrahedra which are joined to form 8-membered oxygen rings in the faces and distorted 6-membered rings on the 3-fold axes. A large cavity 11.4 Å. in diameter occupies the center of the cell and smaller 6.6 Å. cavities are located on the 3-fold axes. Probable positions of the cations in the lithium, sodium, thallium and calcium forms are indicated, and correlation of the structure with the adsorptive and ion-exchange properties of the Type A zeolite is discussed.

History

United States Patent Office

2,882,243

Patented Apr. 14, 1959

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2,882,243

MOLECULAR SIEVE ADSORBENTS

Robert M. Milton, Buffalo, N.Y., assignor to Union Carbide Corporation, a corporation of New York

No Drawing. Application December 24, 1953
Serial No. 400,388

24 Claims. (Cl. 252—455)

This invention relates to synthetic adsorbent materials and, more particularly, to a synthetic crystalline form of sodium aluminum silicate, its derivatives, and methods of making and activating these adsorbent materials.

It is the principal object of the invention to provide an adsorbent of the molecular sieve type having improved absorbing properties. A further object is to provide a novel crystalline metal aluminum silicate suitable for use as an adsorbent. Still another object of the invention is to provide a synthetic material having unique adsorptive properties and a high adsorptive capacity. Another object of the invention is to provide a convenient and efficient method of making and activating the novel adsorbent of the invention.

Naturally occurring hydrated metal aluminum silicates are called zeolites, and the synthetic materials of the invention have compositions similar to some of the natural zeolites. Accordingly, the term "zeolite" would appear to be appropriately applied to the materials of the invention. There are, however, significant differences between the synthetic and natural materials. To distinguish the one from the other the material of the invention, synthetic crystalline sodium aluminum silicate and its derivatives, will be designated hereinafter by the term "zeolite A."

Certain adsorbents, including zeolite A, which selectively adsorb molecules on the basis of the size and shape of the adsorbate molecule are referred to as molecular sieves. These molecular sieves have a sorption area available on the inside of a large number of uniformly sized pores of molecular dimensions. With such an arrangement molecules of a certain size and shape enter the pores and are adsorbed while larger or differently shaped molecules are excluded. Not all adsorbents behave in the manner of the molecular sieves. Such common adsorbents as charcoal and silica gel, for example, do not exhibit molecular sieve action.

Zeolite A consists basically of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra. The tetrahedra are cross-linked by the sharing of oxygen atoms so that the ratio of oxygen atoms to the total of the aluminum and silicon atoms is equal to two or O(Al+Si)=2. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali or alkaline earth metal ion. This balance may be expressed by the formula $Al_2/(Ca, Sr, Ba, Na_2, K_2)=1$. One cation may be exchanged for another by ion exchange techniques which are described below. The spaces between the tetrahedra are occupied by water molecules prior to dehydration.

Zeolite A may be activated by heating to effect the loss of the water of hydration. The dehydration results in crystals interlaced with channels of molecular dimensions that offer very high surface areas for the adsorption of foreign molecules. These interstitial channels will not accept molecules that have a maximum dimension of the minimum projected cross-section in excess of about 5.5 A. Factors influencing occlusion by the activated zeolite

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A crystals are the size and polarizing power of the interstitial cation, the polarizability and polarity of the occluded molecules, the dimensions and shape of the sorbed molecule relative to those of the channels, the duration and severity of dehydration and desorption, and the presence of foreign molecules in the interstitial channels. It will be understood that the refusal characteristics of zeolite A are quite as important as the adsorptive or positive adsorption characteristics. For instance, if water and another material are to be separated, it is essential that the crystals refuse the other material as it is that they adsorb the water.

A feature of the invention is the relatively simple process by which the zeolite A may be prepared. Although there are a number of cations that may be present in zeolite A it is preferred to formulate or synthesize the sodium form of the crystal since the reactants are readily available and water soluble. The sodium in the sodium form of zeolite A may be easily exchanged for other cations as will be shown below. Essentially the preferred process comprises heating a proper mixture in aqueous solution of the oxides, or of materials whose chemical compositions can be completely represented as mixtures of the oxides, Na_2O, Al_2O_3, SiO_2, and H_2O, suitably at a temperature of about 100° C. for periods of time ranging from 15 minutes to 90 hours or longer. The product which crystallizes from the hot-mixture is filtered off and washed with distilled water until the effluent wash water in equilibrium with the zeolite has a pH of from about 9 to 12. The material, after activation, is ready for use as a molecular sieve.

Zeolite A may be distinguished from other zeolites and silicates on the basis of its X-ray powder diffraction pattern. The X-ray patterns for several of the ion exchanged forms of zeolite A are described below. Other characteristics that are useful in identifying zeolite A are its composition and density.

The basic formula for all crystalline zeolites where "M" represents a metal and "n" its valence may be represented as follows:

$$M_{\frac{2}{n}}O:Al_2O_3:XSiO_2:YH_2O$$

In general a particular crystalline zeolite will have values for X and Y that fall in a definite range. The value X for a particular zeolite will vary somewhat since the aluminum atoms and the silicon atoms both occupy essentially equivalent positions in the lattice. Minor variations in the relative numbers of these atoms do not significantly alter the crystal structure or physical properties of the zeolite. For zeolite A, numerous analyses have shown that an average value for X is about 1.85. The X value falls within the range 1.85±0.5.

The value of Y likewise is not necessarily an invariant for all samples of zeolite A particularly among the various ion exchanged forms of zeolite A. This is true because various exchangeable ions are of different size, and, since there is no major change in the crystal lattice dimensions upon ion exchange, more or less space should be available in the pores of the zeolite A to accommodate water molecules. For instance, sodium zeolite A was partially exchanged with magnesium, and lithium, and the pore volume of these forms, in the activated condition, measured with the following results:

Ion exchanged form of Zeolite A	Percent Na ions replaced	Value of Y
Na	0	5.1
Mg	75	5.8
K	95	4
Ca	93	5

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used. The peak heights, I, and the positions as a function of 2θ, where θ is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities,

$$\frac{100I}{I_0}$$

where I_0 is the intensity of the strongest line or peak, and d(obs), the interplanar spacing in A., corresponding to the recorded lines were calculated.

X-ray powder diffraction data for a sodium zeolite A (Na_2A), a 95% exchanged potassium zeolite A (K_2A), a 93% exchanged calcium zeolite A (CaA), a 94% exchanged lithium zeolite A (Li_2A), a 93% exchanged strontium zeolite A (SrA), and an exchanged thallium zeolite A (TlA) are given in Table A. The table lists the 100 I/I_0 and the d values in A. for the observed line for the different forms of zeolite A. The X-ray patterns indicate a cubic unit cell of a_0 of between 12.0 and 12.4 A. In a separate column are listed the sum of the squares of the Miller indices ($h^2+k^2+l^2$) for a cubic unit cell that corresponds to the observed lines in the X-ray diffraction patterns. The a_0 values for each particular zeolite are also tabulated and in another column the estimated errors in reading the position of an X-ray peak on the spectrometer chart appear.

The relative intensities and the positions of the lines are only slightly different for these various ion exchanged forms of zeolite A. The patterns show substantially all of the same lines, and all meet the requirements of a cubic unit cell of approximately the same size. The spatial arrangement of silicon- oxygen- and aluminum atoms, i.e. the arrangement of the AlO_4 and SiO_4 tetrahedra, are essentially identical in all the forms of zeolite A. The appearance of a few minor lines and the disappearance of others from one form of zeolite A to another as well as slight changes in the intensities and positions of some of the X-ray lines can be attributed to the different sizes and numbers of cations present in the various forms since these differences effect some small expansion or contraction of the crystals.

TABLE A

($h^2+k^2+l^2$)	Na_2A		Li_2A		K_2A		Estimated error in d value, plus or minus
	d	100 I/I_0	d	100 I/I_0	d	100 I/I_0	
1	12.29	100	12.04	100	12.31	100	0.02
2	8.71	69	8.51	72	8.71	64	0.02
3	7.11	35	6.96	42	7.10	30	0.01
4	—	—	—	—	6.15	4	0.01
5	5.51	25	5.39	25	5.50	10	0.01
6	5.03	2	—	—	5.03	8	0.01
8	4.36	6	4.26	18	—	—	0.01
9	4.107	36	4.02	48	4.105	33	0.004
10	—	—	3.805	4	3.895	10	0.003
11	3.714	53	3.633	53	3.714	62	0.003
12	—	—	—	—	3.555	5	0.003
13	3.417	16	3.342	28	3.414	34	0.003
14	3.293	47	3.222	49	3.292	35	0.002
16	—	—	—	—	3.078	12	0.002
17	2.987	55	2.923	43	2.985	80	0.002
18	2.904	9	2.837	4	2.902	27	0.002
20	2.754	12	2.691	4	2.753	65	0.002
21	2.688	4	2.628	13	2.687	9	0.002
22	2.626	22	2.569	32	2.625	18	0.002
24	2.515	5	2.457	7	2.514	28	0.002
25	2.464	4	2.408	1	—	—	0.002
26	—	—	2.363	8	2.415	4	0.002
27	2.371	3	2.319	5	2.370	9	0.002
29	2.289	1	2.235	3	2.287	3	0.002
30	2.249	3	2.199	3	2.248	5	0.002
32	2.177	7	—	—	2.177	26	0.002
33	2.144	10	2.097	2	2.143	12	0.001
34	2.113	3	2.064	2	—	—	0.001
35	2.083	4	—	—	2.081	5	0.001
36	2.053	9	2.007	20	2.053	3	0.001
37	—	—	1.980	1	—	—	0.001
38	—	—	1.954	2	1.998	4	0.001
41	1.924	7	1.881	8	1.922	7	0.001
42	1.901	4	1.859	2	1.900	4	0.001
44	1.858	2	—	—	1.857	8	0.001
45	1.837	3	1.795	2	—	—	0.001
49	1.759	2	1.720	3	—	—	0.001
50	1.743	13	1.702	10	1.742	12	0.001
51	—	—	1.686	1	—	—	0.001

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TABLE A (Cont'd)

($h^2+k^2+l^2$)	Na_2A		Li_2A		K_2A		Estimated error in d value, plus or minus
	d	100 I/I_0	d	100 I/I_0	d	100 I/I_0	
53	1.692	6	1.653	8	1.691	7	0.001
54	1.676	2	—	—	—	—	0.001
57	1.632	4	1.593	3	1.631	7	0.001
59	1.604	6	1.566	3	1.603	6	0.001
61	1.577	4	1.541	5	1.576	8	0.001
62	—	—	1.529	2	—	—	0.001
65	1.528	2	1.492	3	—	—	0.001
66	1.516	1	1.481	2	—	—	0.001
67	—	—	1.470	2	—	—	0.001
68	—	—	1.459	2	1.493	7	0.001
69	1.483	3	1.449	3	—	—	0.001
70	1.473	2	1.438	1	—	—	0.001
72	—	—	1.417	4	—	—	0.001
74	1.432	3	1.399	6	—	—	0.001
75	1.422	2	—	—	—	—	0.001
77	1.404	5	—	—	1.403	4	0.001
81	1.369	2	—	—	—	—	0.001
82	1.360	8	—	—	1.359	7	0.001
a_0	12.32±0.02		12.04±0.02		12.31±0.02		

($h^2+k^2+l^2$)	CaA		SrA		Tl_2A		Estimated error in d value, plus or minus
	d	100 I/I_0	d	100 I/I_0	d	100 I/I_0	
1	12.24	100	12.36	90	12.31	13	0.02
2	8.66	39	8.72	66	8.71	8	0.02
3	7.08	32	—	—	7.11	10	0.01
4	6.12	12	—	—	6.16	24	0.01
5	5.48	20	—	—	—	—	0.01
6	5.00	4	—	—	—	—	0.01
8	—	—	—	—	4.36	100	0.01
9	4.08	35	—	—	4.11	7	0.004
10	3.875	2	—	—	—	—	0.003
11	3.696	34	3.714	60	3.717	34	0.003
12	3.539	4	3.556	15	3.558	18	0.003
13	3.398	18	3.415	21	3.418	19	0.003
14	3.276	38	3.292	68	3.294	4	0.002
16	—	—	—	—	3.081	25	0.002
17	2.972	32	2.986	100	2.990	22	0.002
18	2.888	9	2.903	38	2.906	6	0.002
19	—	—	—	—	2.828	1	0.002
20	2.741	7	2.753	49	2.757	51	0.002
21	2.676	3	—	—	—	—	0.002
22	2.614	24	2.625	49	2.630	11	0.002
24	2.502	7	—	—	2.517	55	0.002
25	2.451	7	—	—	2.466	2	0.002
26	—	—	—	—	2.416	2	0.002
27	2.359	3	—	—	—	—	0.002
29	—	—	—	—	2.291	8	0.002
30	2.238	3	—	—	—	—	0.002
32	2.166	8	—	—	2.182	19	0.002
33	2.141	8	—	—	2.144	2	0.001
34	2.103	5	—	—	2.114	2	0.001
35	2.074	2	—	—	—	—	0.001
36	2.042	4	—	—	2.057	11	0.001
40	—	—	—	—	1.951	10	0.001
41	1.914	4	—	—	1.926	3	0.001
42	1.891	3	—	—	—	—	0.001
44	—	—	—	—	1.860	14	0.001
45	—	—	—	—	1.837	2	0.001
46	—	—	—	—	1.821	2	0.001
48	—	—	—	—	1.779	3	0.001
50	1.733	11	—	—	1.743	3	0.001
52	—	—	—	—	1.710	8	0.001
53	1.683	4	—	—	1.693	3	0.001
54	1.667	2	—	—	—	—	0.001
56	—	—	—	—	1.648	9	0.001
57	1.623	2	—	—	1.633	6	0.001
58	1.608	5	—	—	—	—	0.002
61	1.569	4	—	—	1.578	3	0.002
64	—	—	—	—	1.541	2	0.002
68	—	—	—	—	1.495	11	0.002
72	1.445	2	—	—	1.453	5	0.002
74	1.425	2	—	—	1.433	2	0.002
75	1.416	1	—	—	—	—	0.002
76	—	—	—	—	1.414	4	0.002
77	1.397	3	—	—	1.406	2	0.002
82	1.353	5	—	—	—	—	0.002
84	—	—	—	—	1.346	3	0.002
a_0	12.26±0.02		12.32±0.02		12.33±0.02		

In the above table, particularly with reference to SrA, certain values have not been listed since their calculation was not necessary in the determination of the dimensions of the unit cell. The dimension of the edge of the cubic unit cell of the magnesium zeolite A was

Classical and General Definition

- Classical:
  - Aluminosilicate open network of corner-sharing $[AlO_4]^-$ and $[SiO_4]$-tetrahedra (Al, Si → T-atoms build framework).
  - Charge of the framework is compensated by mono or divalent cations or protons within the cavities or channels.
  - Exchange capability of cations.
  - Additional water molecules are present in the cavities.

- General:
  - Three-dimensional framework of tetrahedrally coordinated T-atoms with cavities or channels with the smallest opening larger than six T-atoms.
  - T-atoms: Si, Al, P, As, Ga, Ge, B, Be, etc.

Channel and Pore Opening

Aluminosilicates	:	7.4 x 7.4 Å	Faujasite
Silicates	:	8.1 x 8.2 Å	UTD-1F
Aluminophosphates	:	12.7 x 12.7 Å	VPI-5
Galliumphosphates	:	4.0 x 13.2 Å	Cloverite

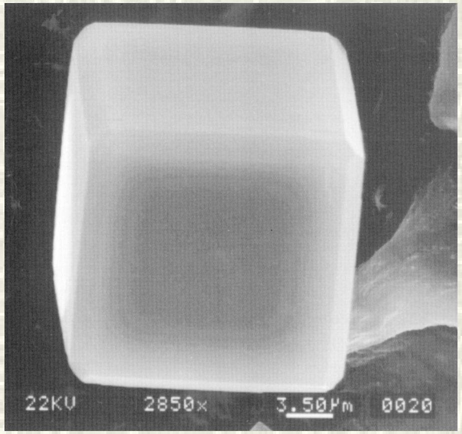
Microporous materials	:	< 20 Å
Mesoporous materials	:	20 – 500 Å
Macroporous materials	:	> 500 Å

Synthesis

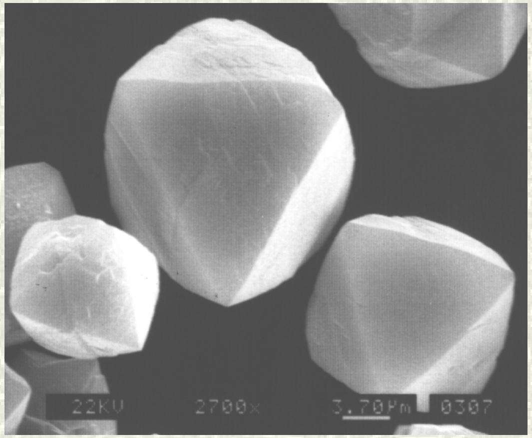
- Natural zeolites
  - Volcanic origin (hot-spring, lava, sediments).
  - Natural zeolites have been found in many different countries.
- Hydrothermal sol-gel synthesis
  - Acqueous solution under vapor pressure of the mixture.
  - Temperature range up to 300 °C.
  - Structure directing agent as template (e.g. tetramethyl-ammonium).
  - Template removal by thermal and oxidative decomposition.
- High pressure hydrothermal synthesis
  - High pressure autoclave.

Synthesis, Examples

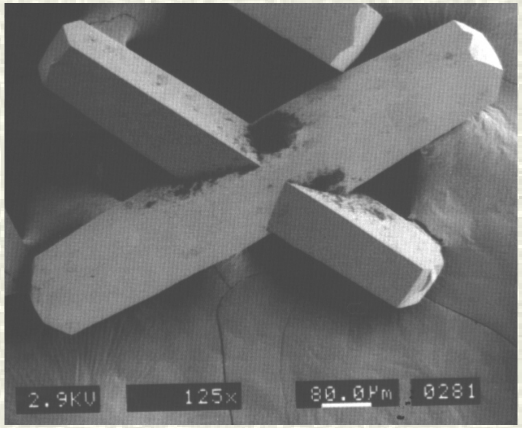
Linde Type A



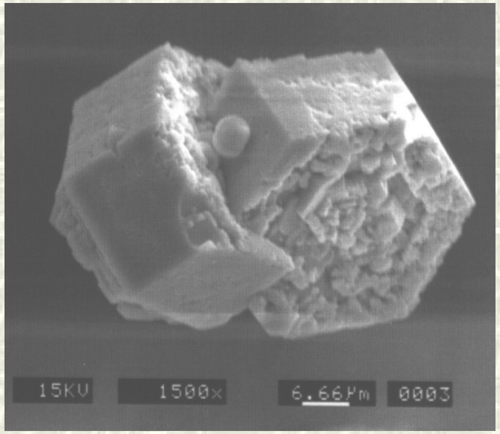
Linde X



Silicalite



AlPO-5

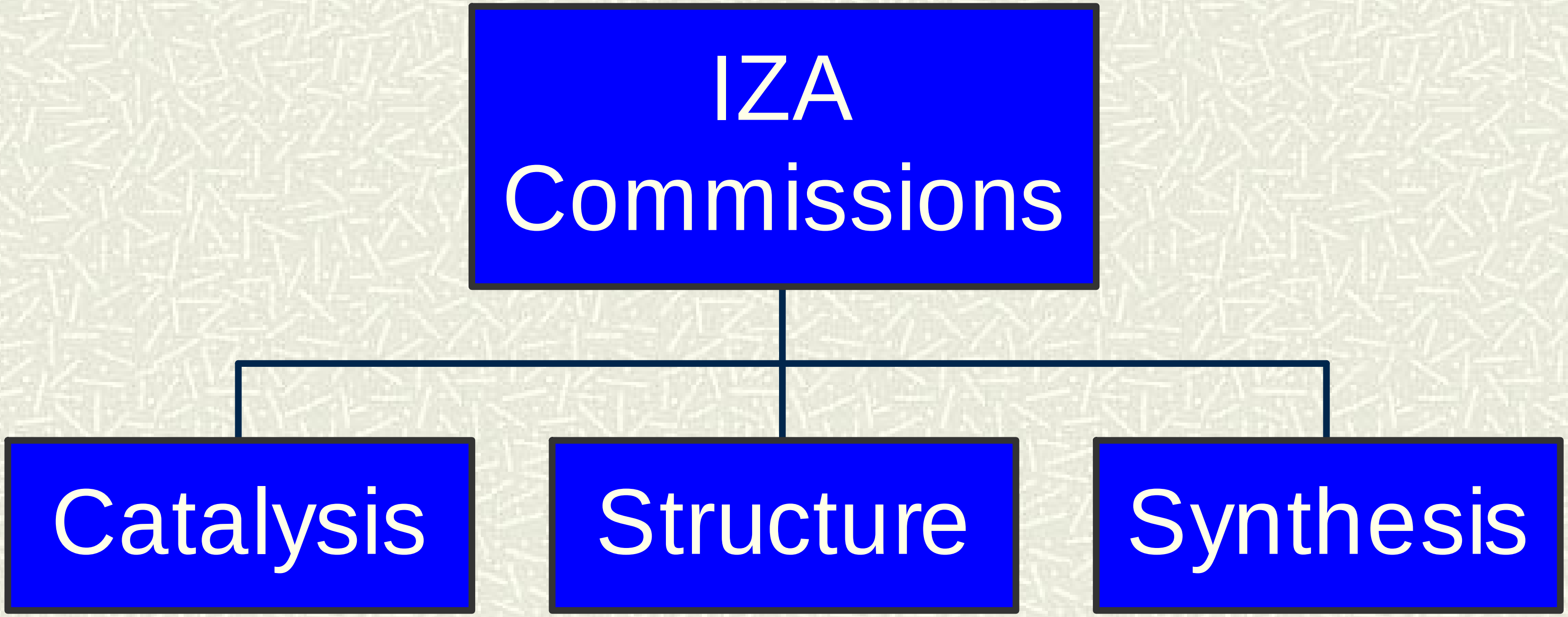


Application, Examples

- Purification of gaseous and liquid mixtures and solutions by sorption (activation by evacuation and heating).
- Reversible sorption capacity for water.
- Removal of odors and pollutants.
- Ion exchange.
- Softening of water for washing (substituted polyphospates).
- Removal of heavy metal ions in mine wastewater and radioactive fission products (Cs, Sr).
- Natural zeolites used for soil fertilizing purposes (Submit ions of potassium, ammonium, phosphate).
- Catalysis in petrochemical industries (conversion of organic molecules in liquid and gaseous phase).

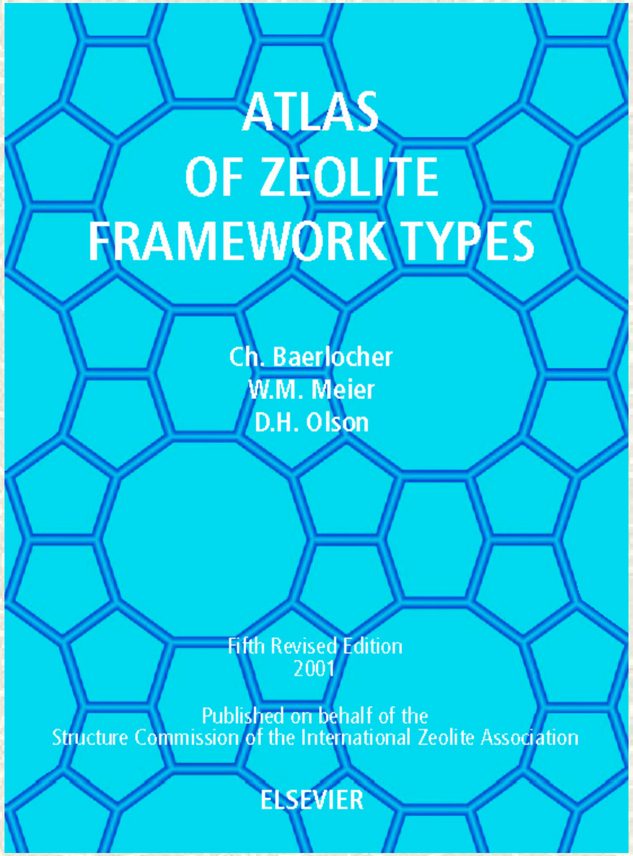
Describing Zeolite Frameworks

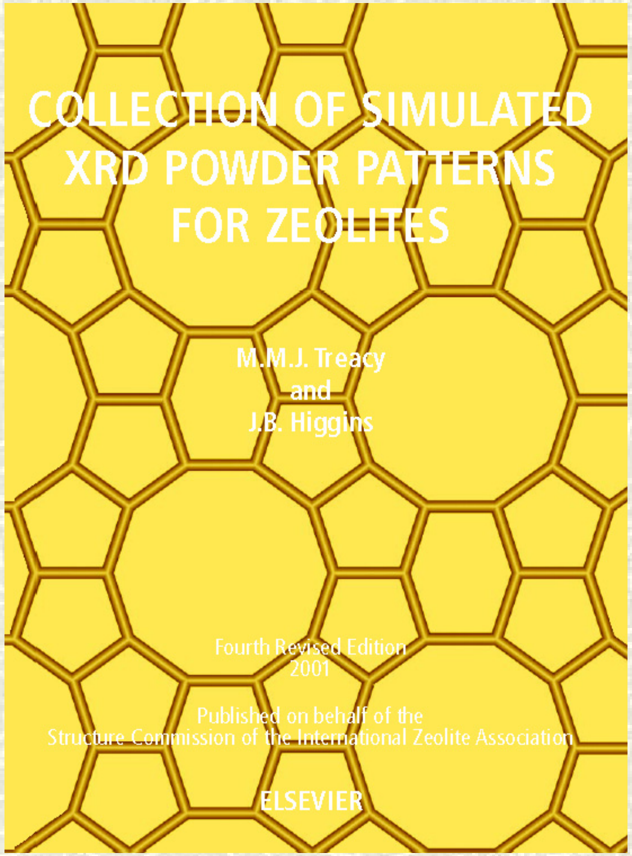
International Zeolite Association (IZA)



International Zeolite Association (IZA)

Books from the Structure Commission





Availability

- Printed Version

ELSEVIER

www.elsevier.com

- Electronic Version (pdf-Files)

IZA Structure Commission

www.iza-online.org

History of the Atlas of Zeolite Framework Types

Edition	Year	Zeolite Frameworks
1^{st}	1970	27
2^{nd}	1978	38
3^{rd}	1982	85
4^{th}	1996	98
5^{th}	2001	133
Web Edition	Dec. 2003	145

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)

Left Page

Framework Type Informations

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	

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).

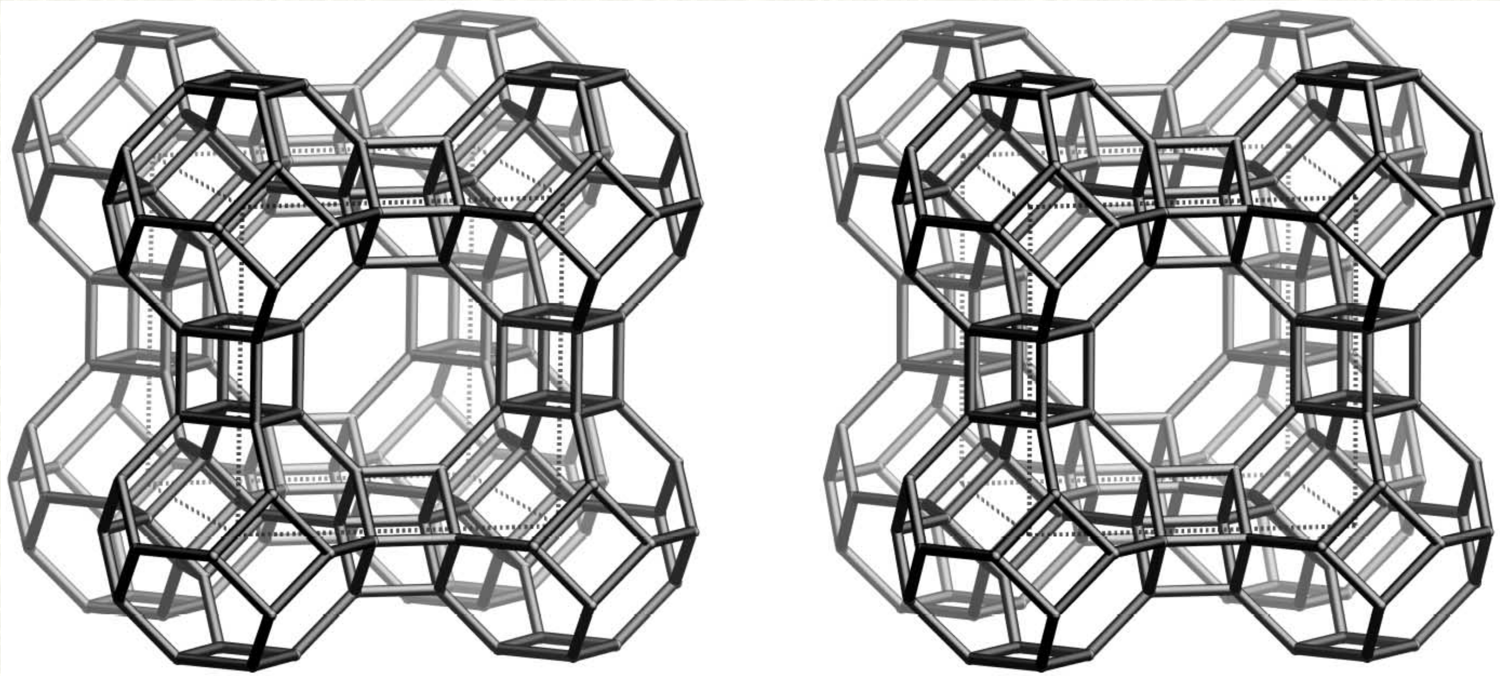
- The codes should not be confused or equated with actual materials. They only describe and define the framework.

  Not allowed:
  - NaLTA, NaLTL, NaFAU

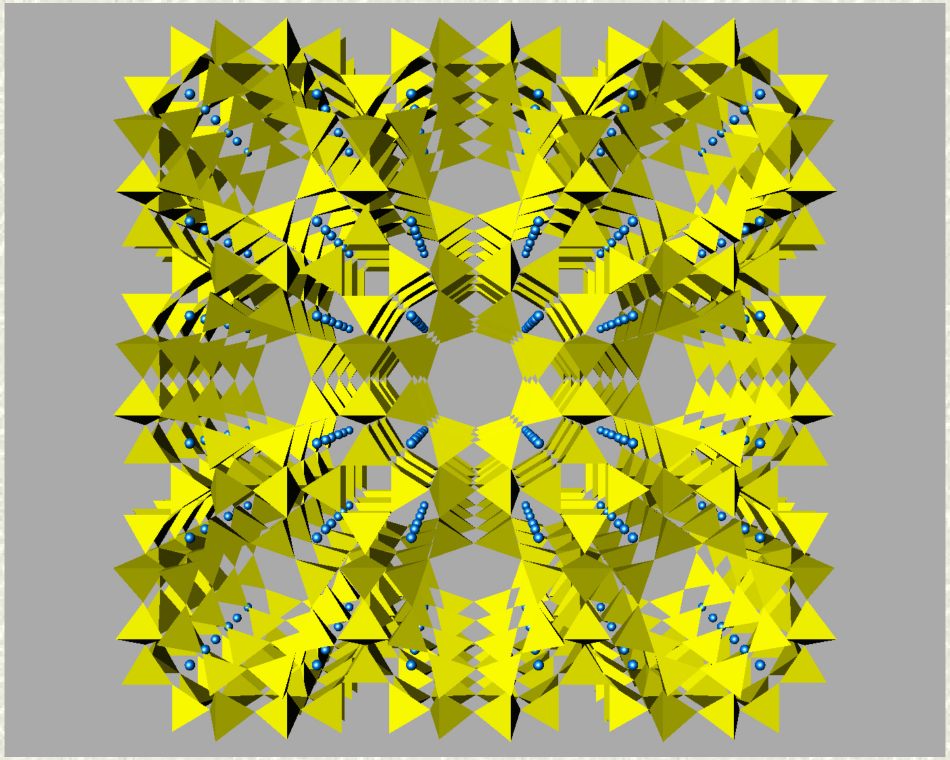
  Correct is to use: | | for guest species, [ ] for framework host
  - $|Na^+_{12}(H_2O)_{27}|_8$ $[Al_{12}Si_{12}O_{48}]_8$-LTA or |Na| [Al-Si-O]-LTA
  - $|K^+_6Na^+_3(H_2O)_{21}|$ $[Al_9Si_{27}O_{72}]$-LTL or |K-Na| [Al-Si-O]-LTL
  - $|Na_{58}|$ $[Al_{58}Si_{134}O_{384}]$-FAU or |Na| [Al-Si-O]-FAU

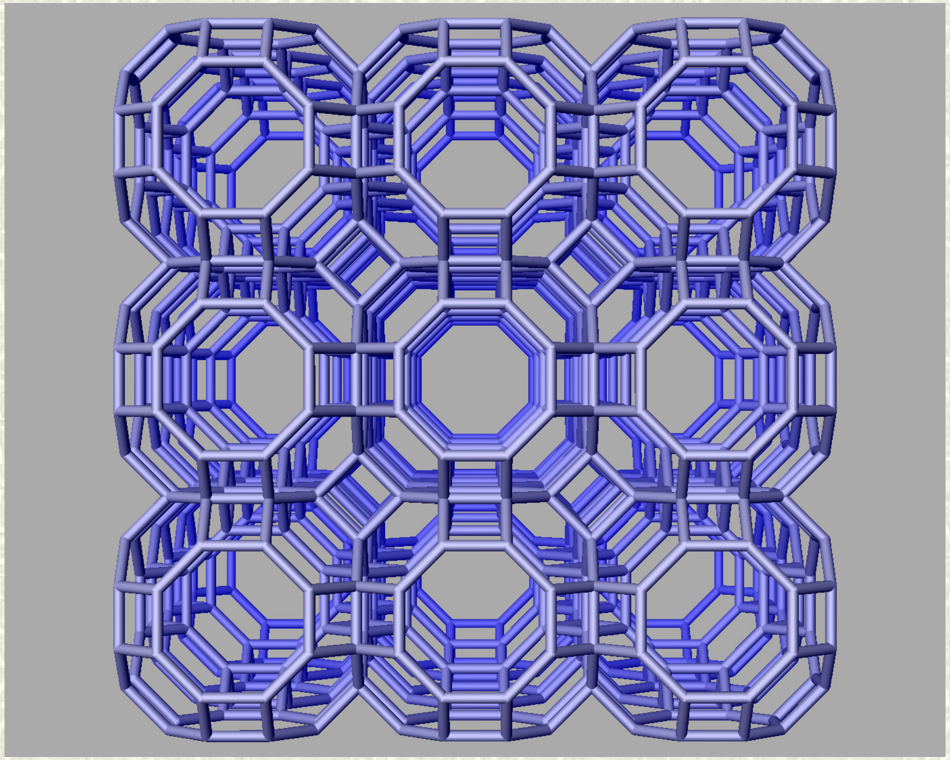
- Framework types do not depend on composition, distribution of the T-atoms, cell dimensions or symmetry (T-atoms: Si, Al, P, As, Ga, Ge, B, Be, etc.).

LTA Framework: Stereographic Figure

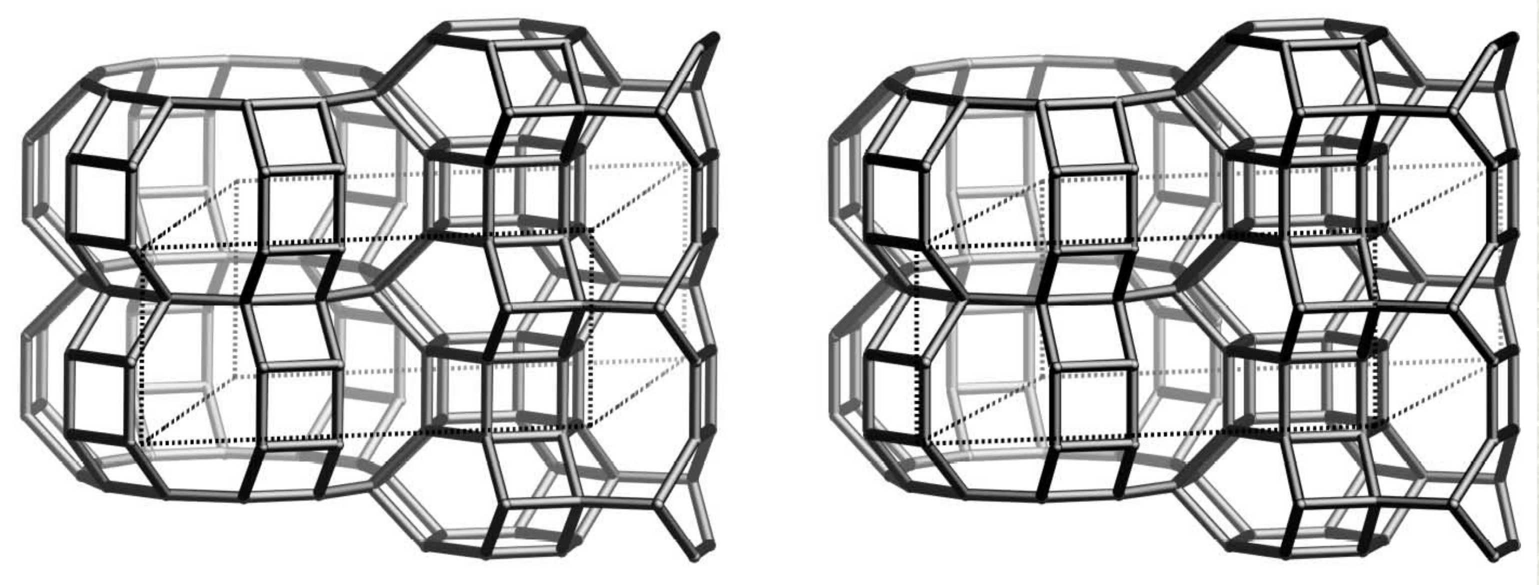


LTA: Structure and Framework Figures

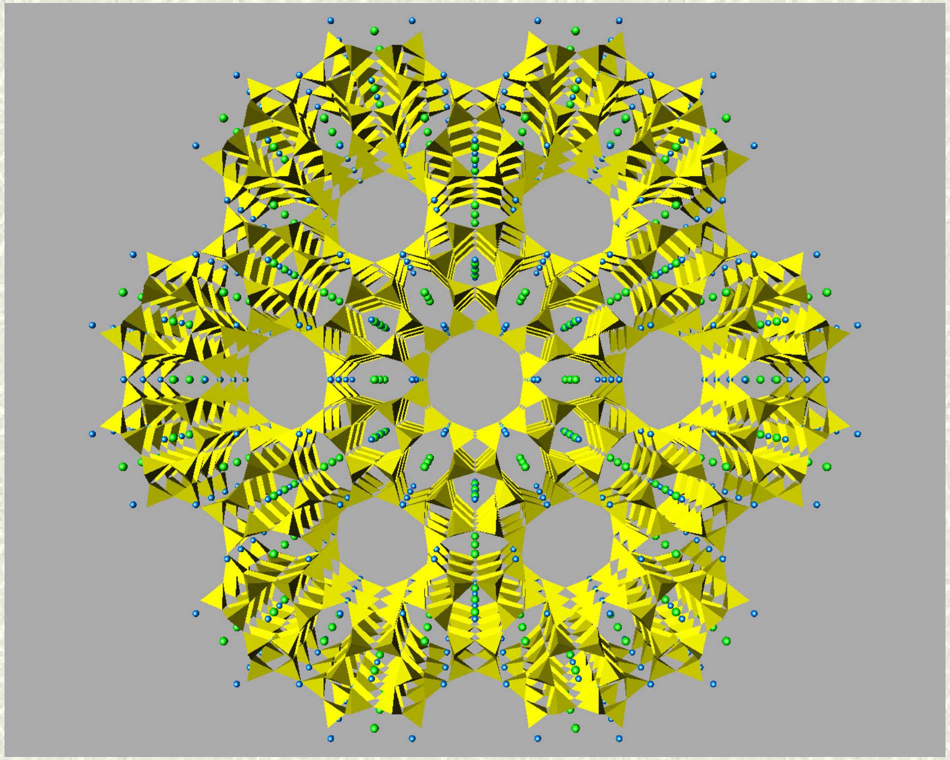


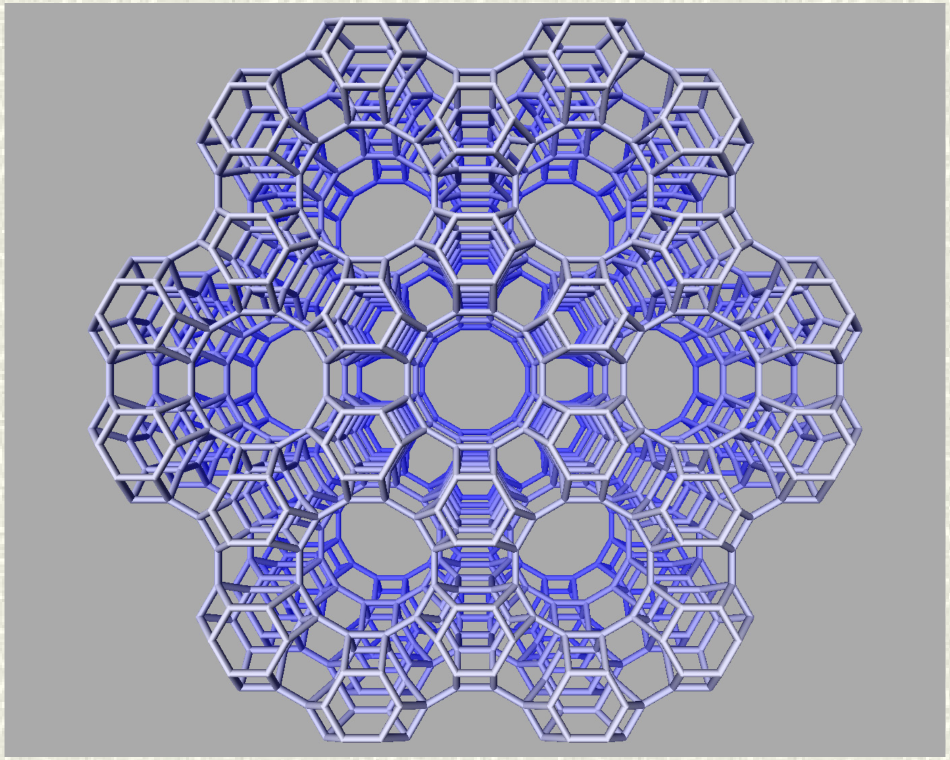


LTL Framework: Stereographic Figure



LTL: Structure and Framework Figures





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)

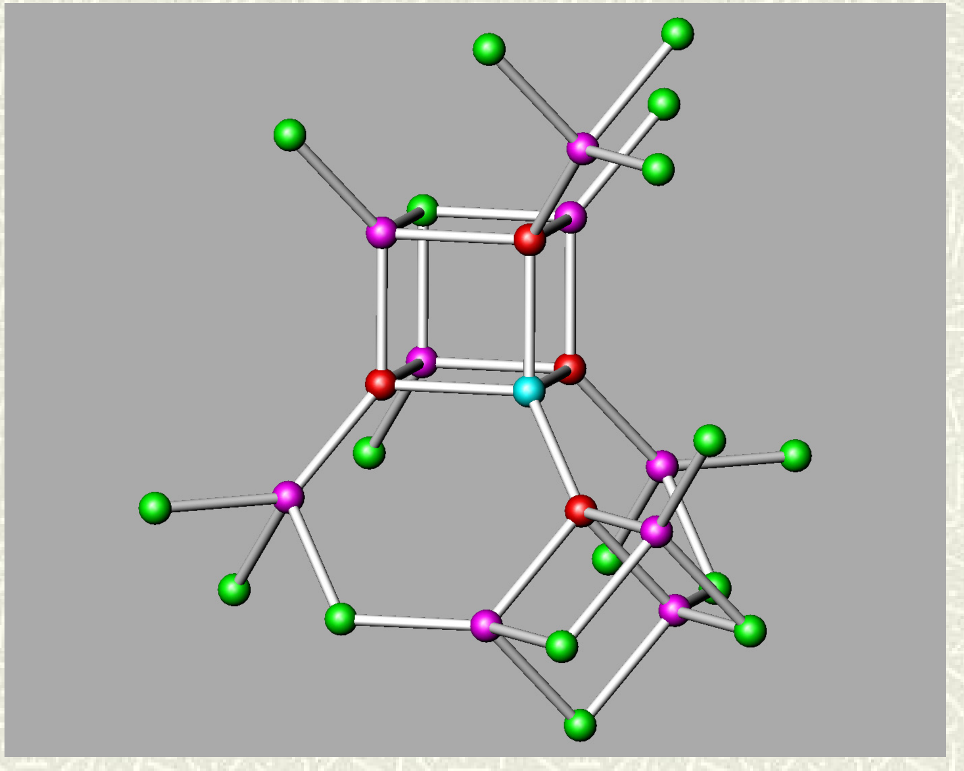
- Each T-atom is connected to $N_1 = 4$ neighboring T-atoms through oxygen bridges.
- These neighboring T-atoms are then linked in the same manner to N_2 T-atoms in the next shell.
- Each T-atom is counted only once.
- Infinite, ideal case without T-atom sharing:

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

- 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

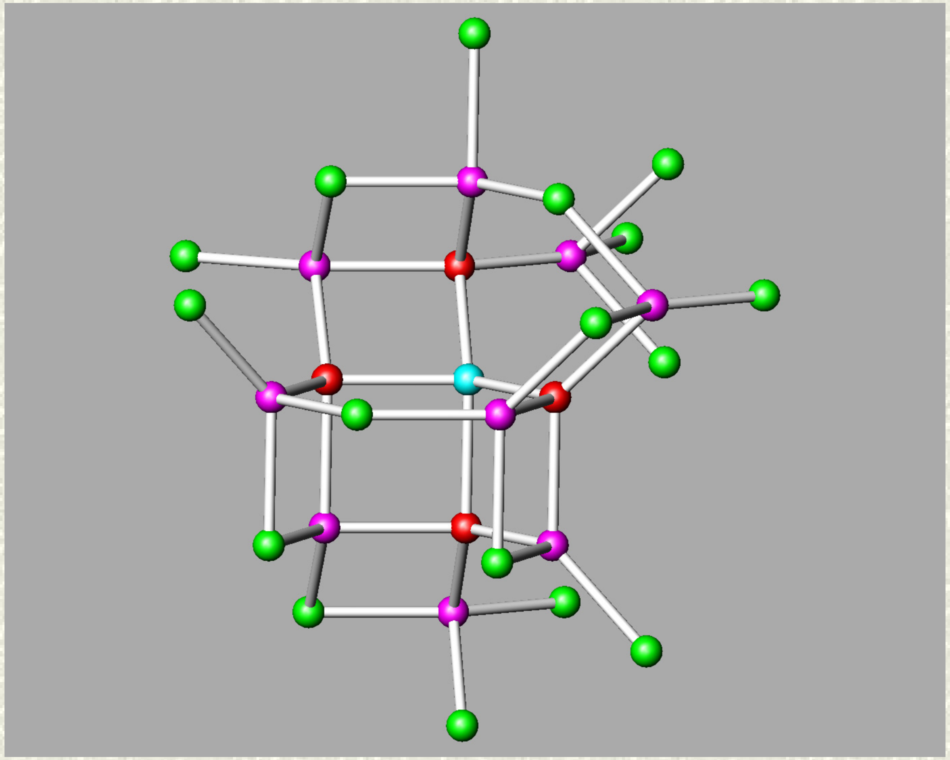
T1 (24, m) 4 9 17 28 42 60 81 105 132 162

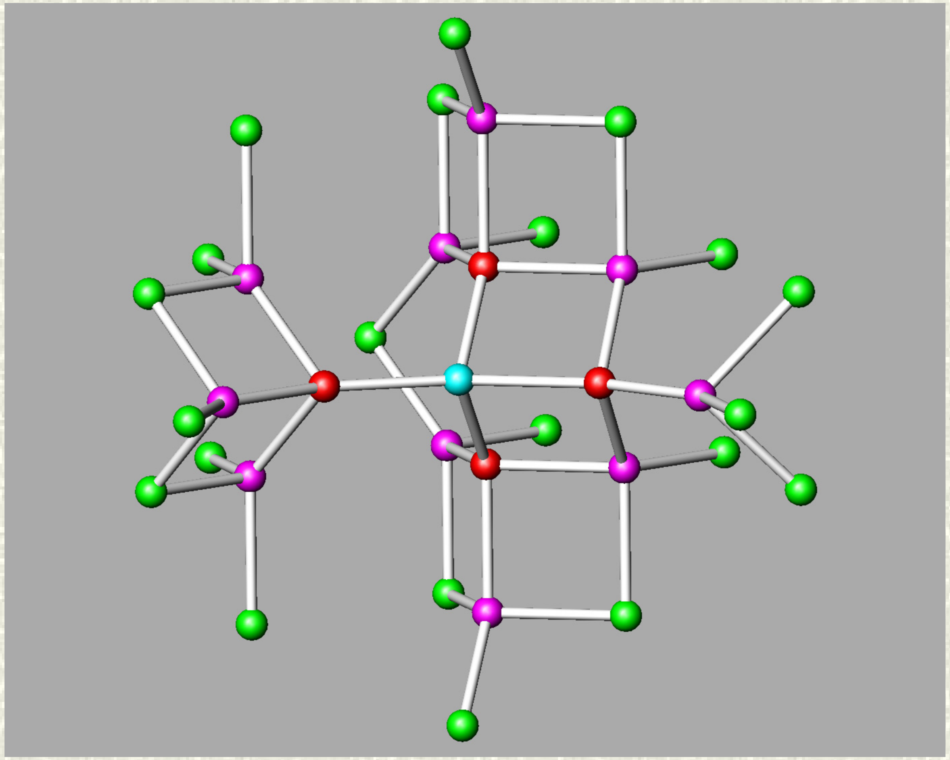


Coordination Sequences for LTL

T1 (24, 1) 4 9 17 29 46 69 …

T2 (12, m) 4 10 21 35 49 66 …





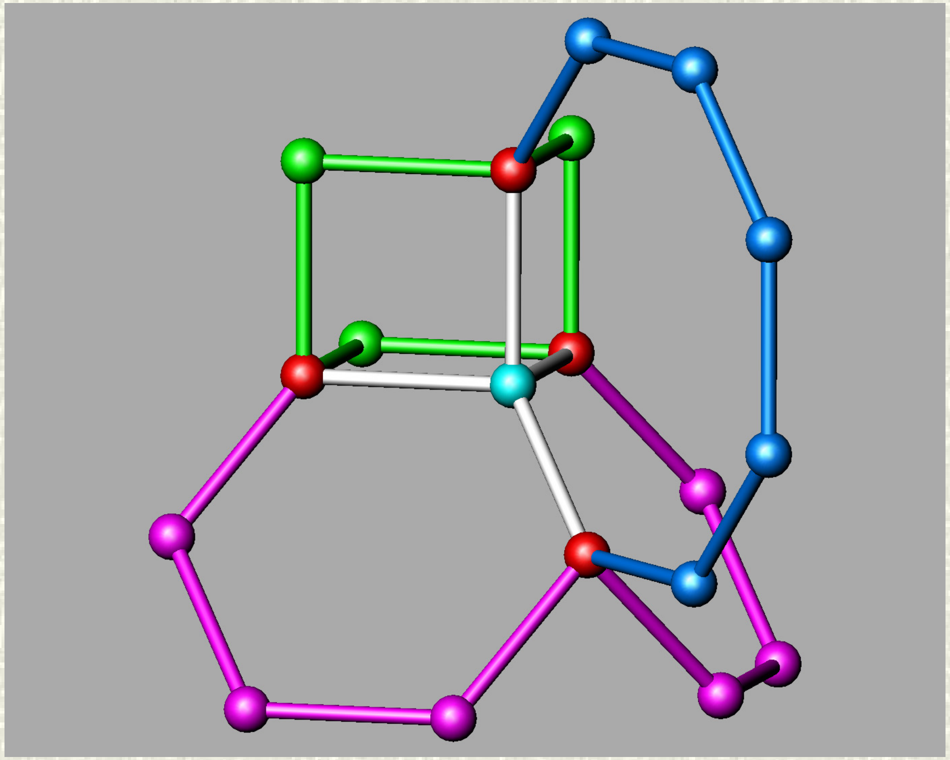
Vertex Symbols

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

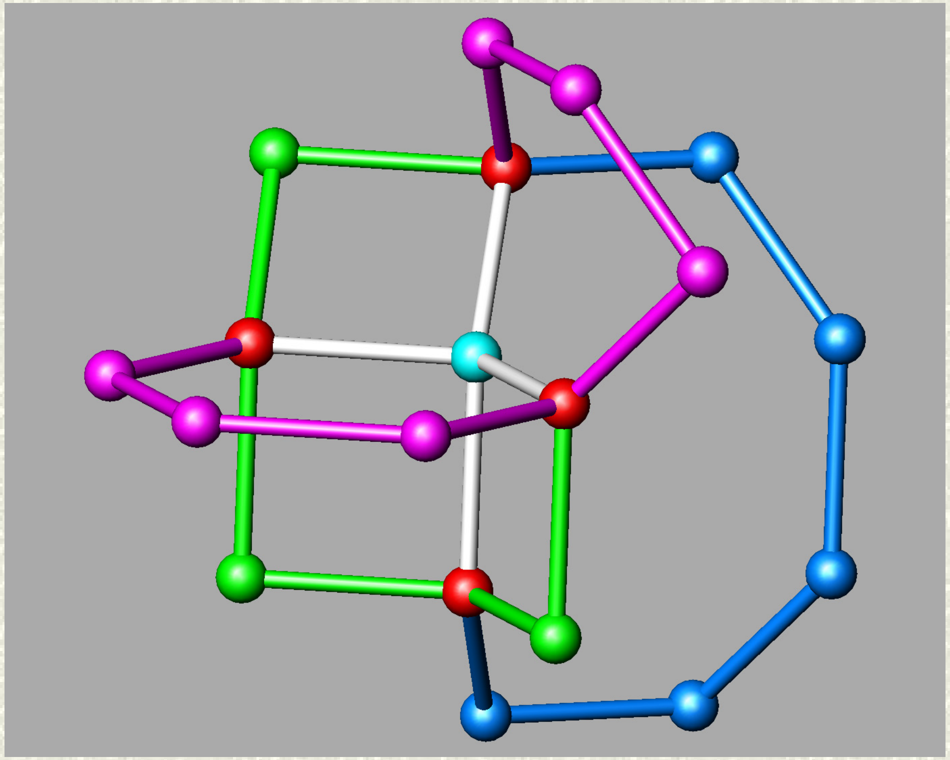
Vertex Symbol for LTA

4 . 6 . 4 . 6 . 4 . 8

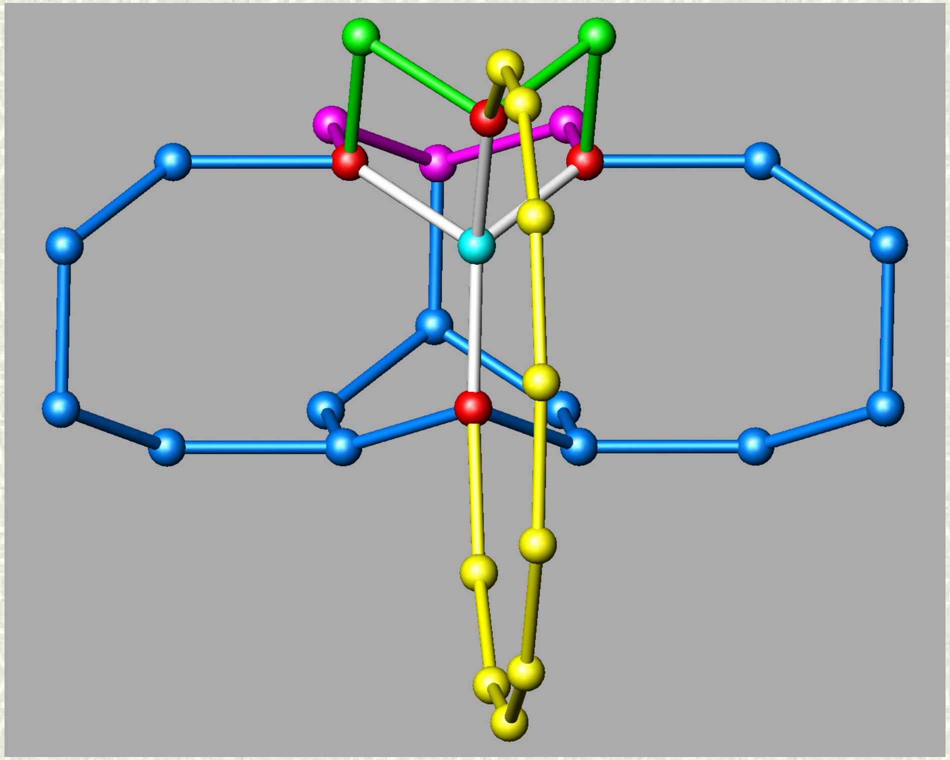


Vertex Symbols for LTL

4 . 4 . 4 . 6 . 6 . 8

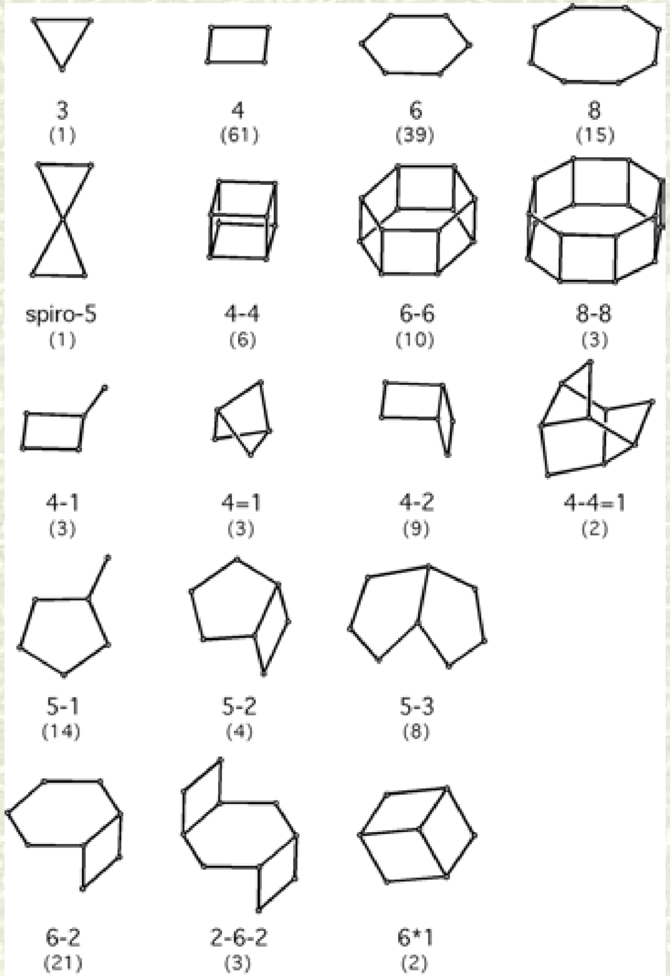


$4 . 8_3 . 4 . 8_3 . 6 . 12$



Secondary Building Units (SBU)

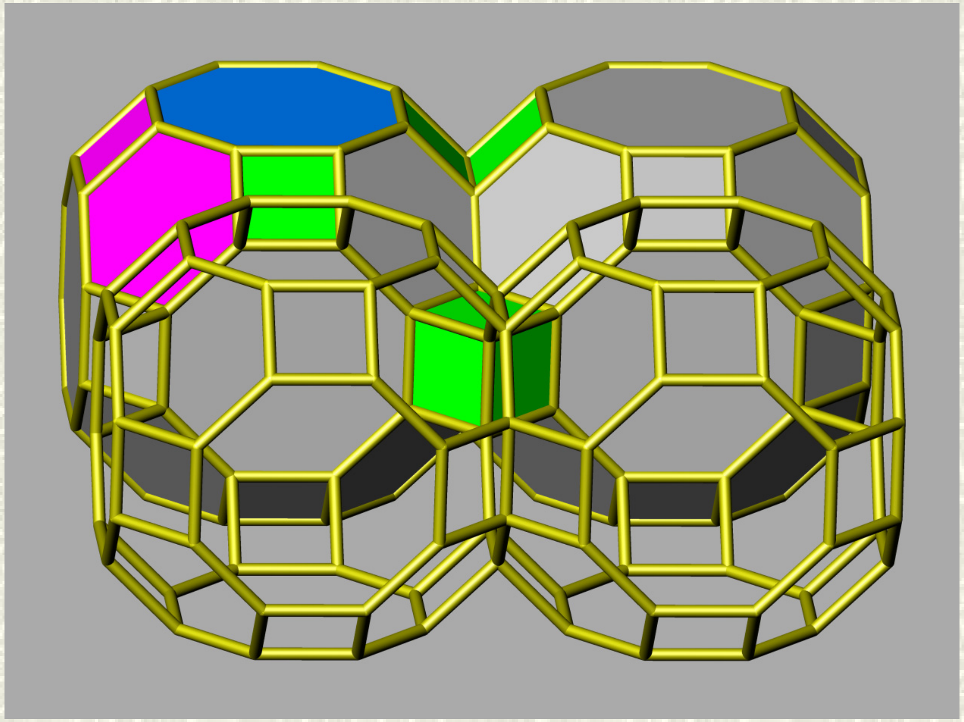
- The primary building unit is the TO_4 tetrahedra
- SBU are derived assuming that the entire framework is made up of one type of SBU only.
- Assemblage of the framework does not necessarily involve crystallographic symmetry operations.
- If more than one SBU is possible, all are listed.

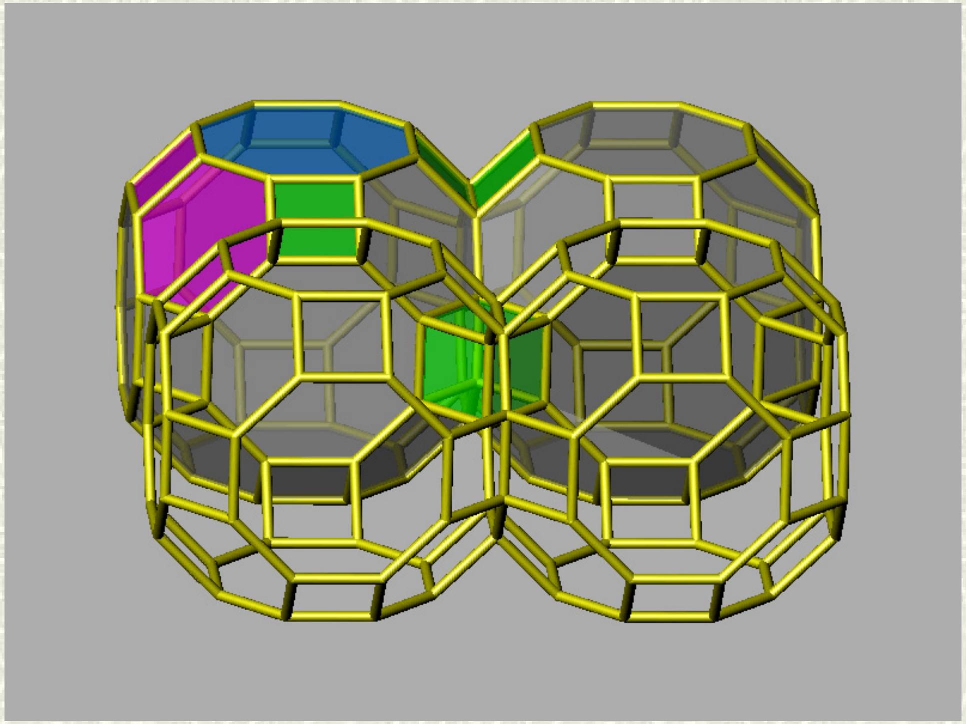


Number in ( ) = frequency of occurrence

Secondary Building Units for LTA

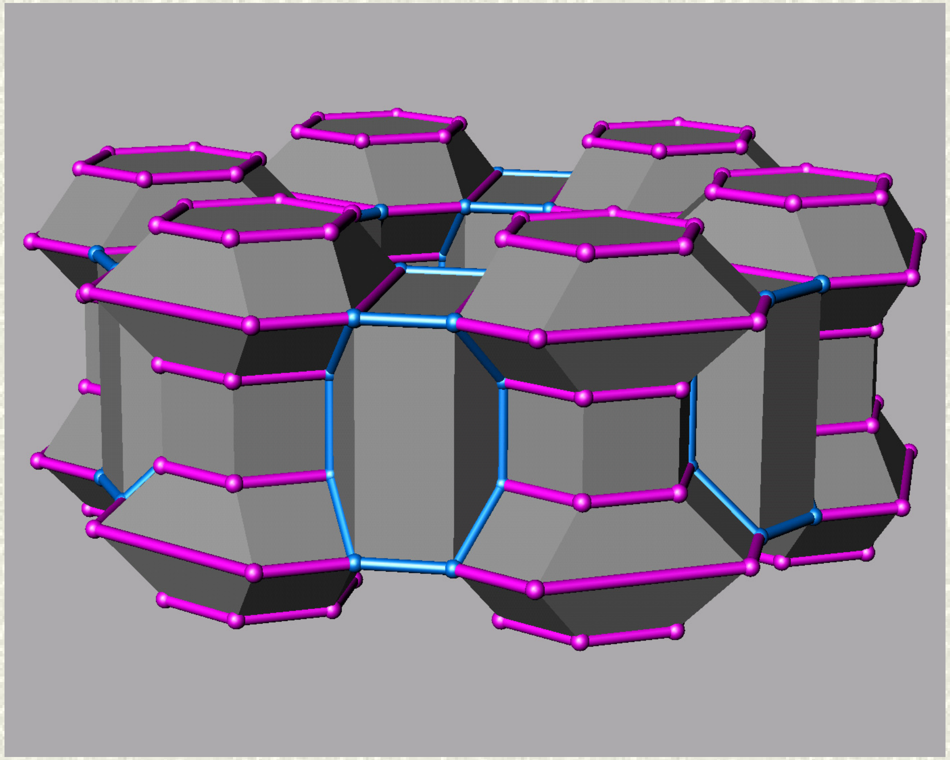
8 or 4-4 or 6-2 or 4-2 or 4

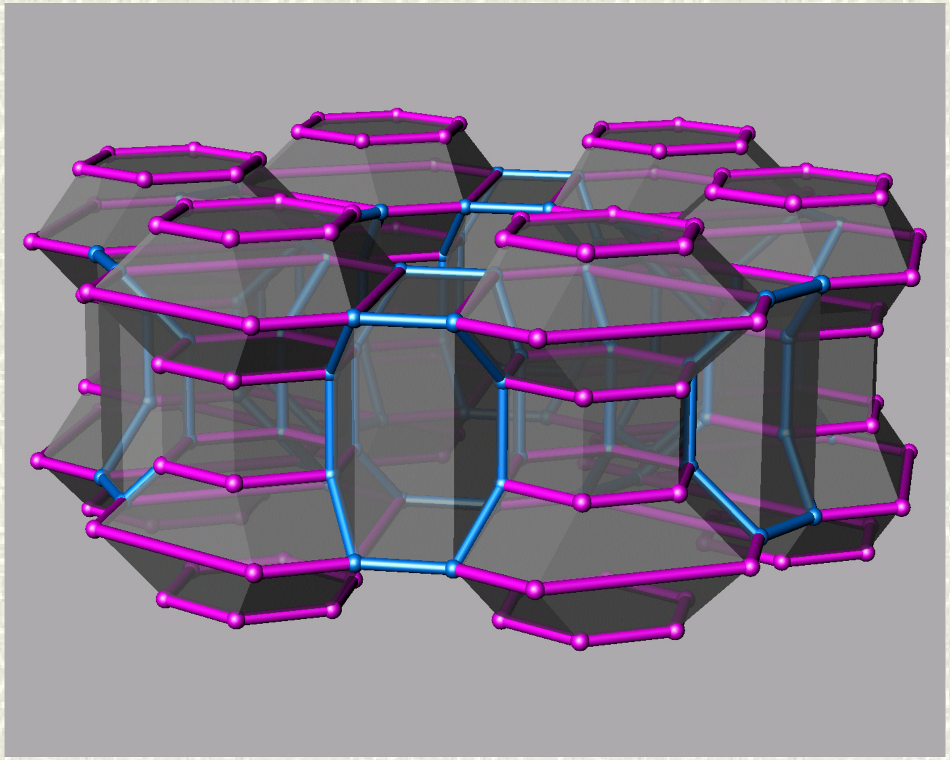




Secondary Building Units for LTL

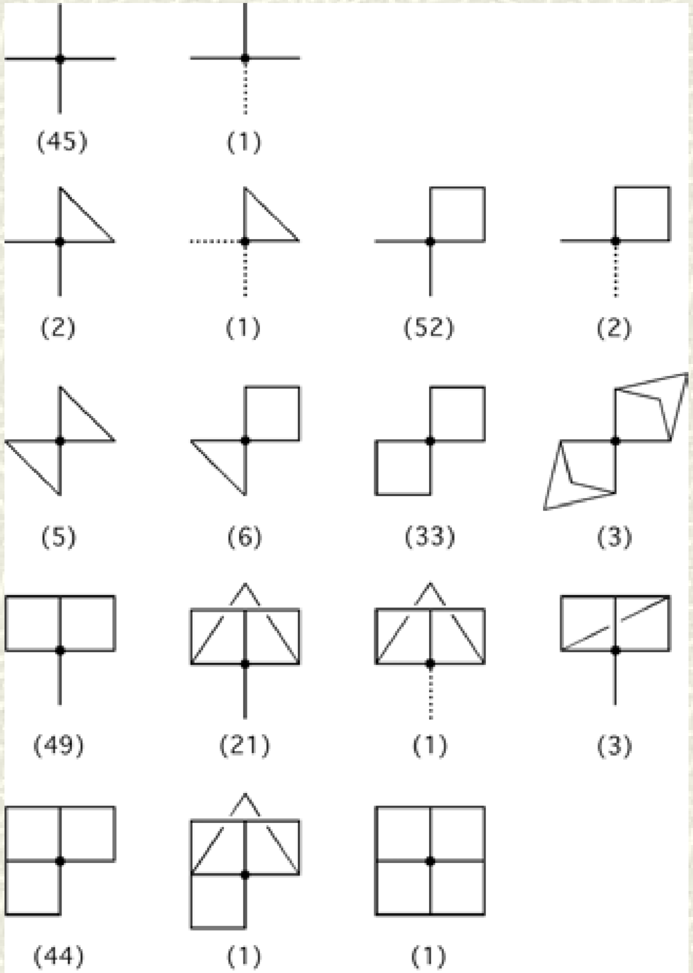
8 or 6





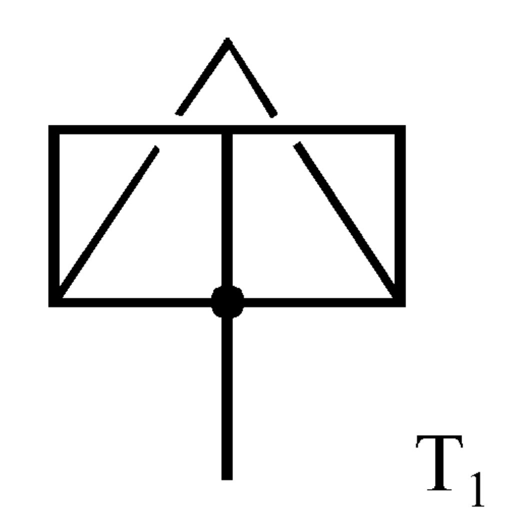
Loop Configuration of T-atoms

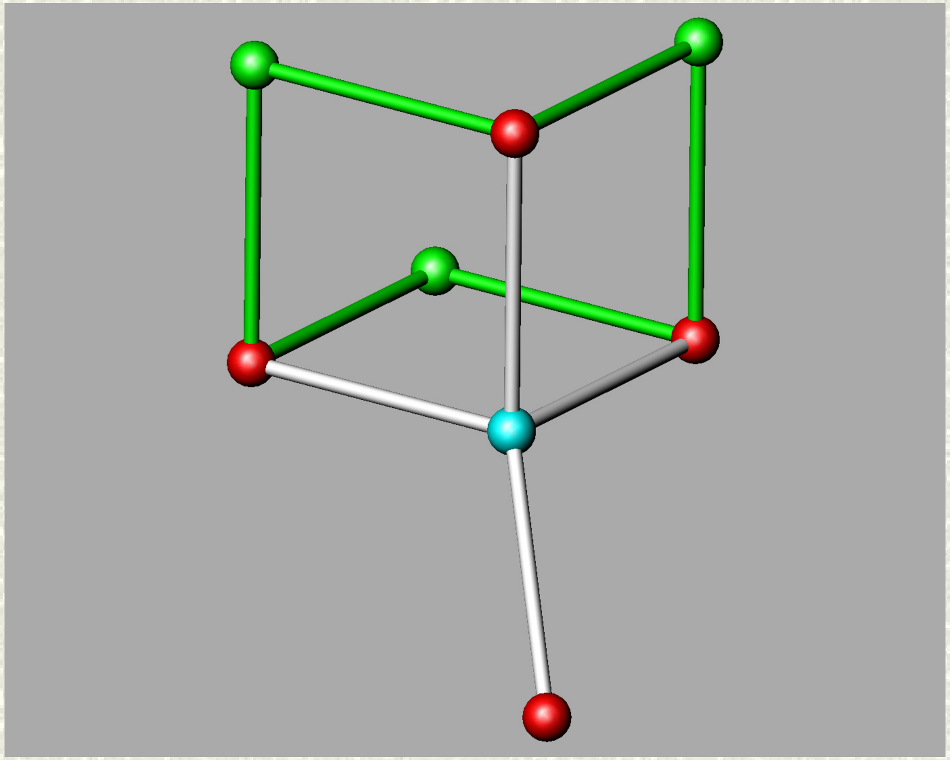
- Simple graph showing how many 3- or 4-memberd rings a given T-atom is involved in.
- Can be used for classification purposes.
- Information given is a subset of the vertex symbol.
- Solid lines: T – O – T link.
- Dotted lines: T – O bond found in interrupted frameworks.



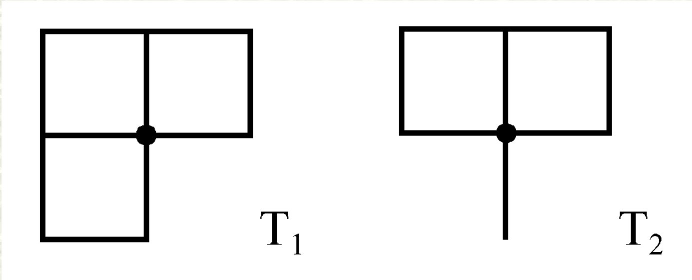
Number in ( ) = frequency of occurence

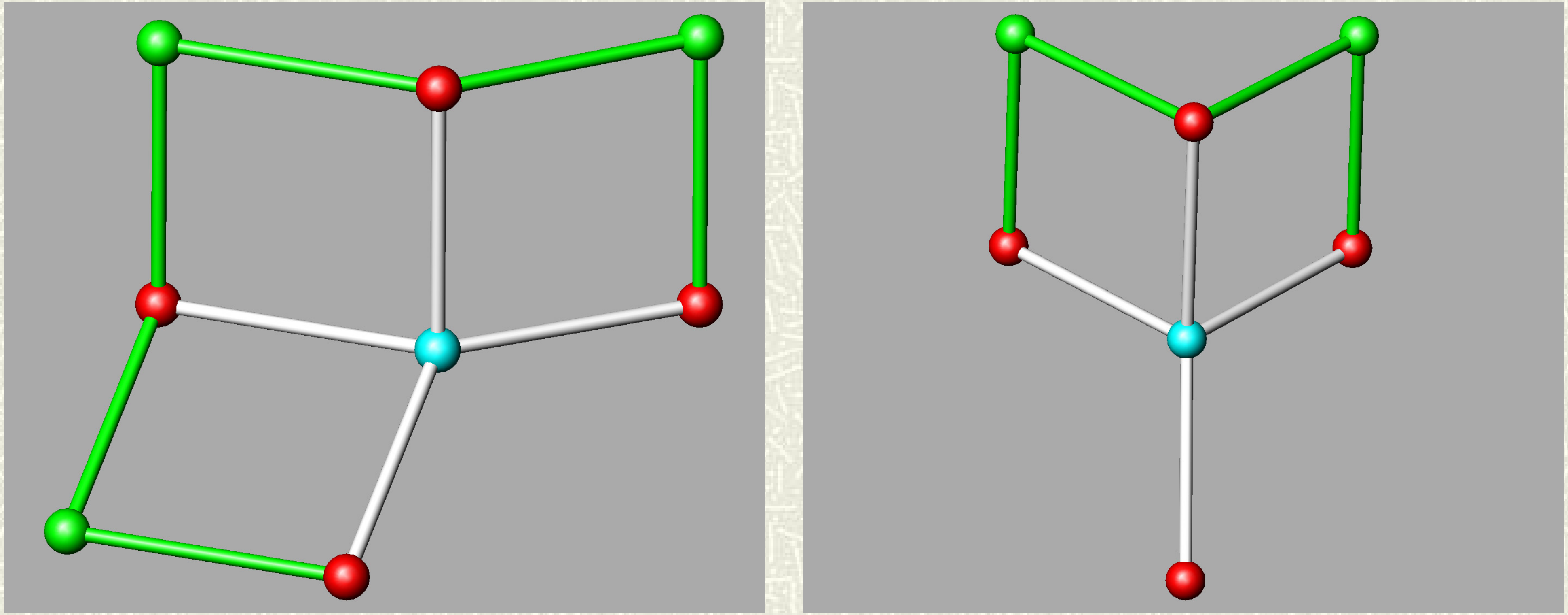
Loop Configuration of T-atom for LTA





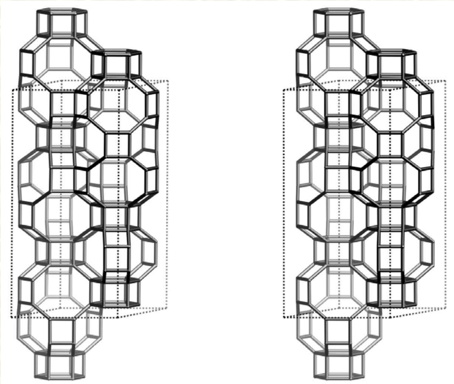
Loop Configuration of T-Atoms for LTL





Framework Description

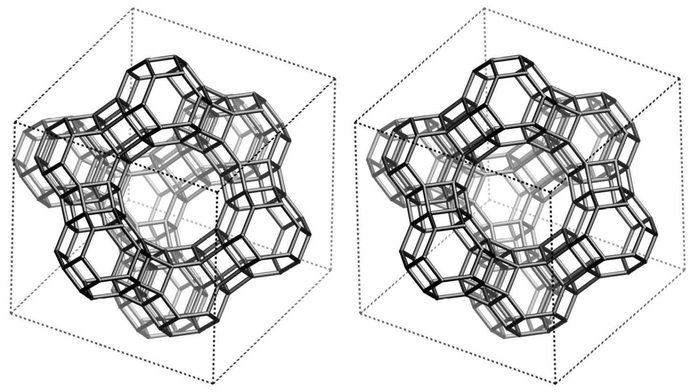
- For all 15 framework types of the so-called ABC-6-family the ABC stacking sequence is listed.



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

Isotypic Framework Structures

- The type material, the species first used to establish the framework type, is given first and marked with an asterisk.
- 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. ion exchange, dealumination) are generally not included.

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.

Right Page

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)

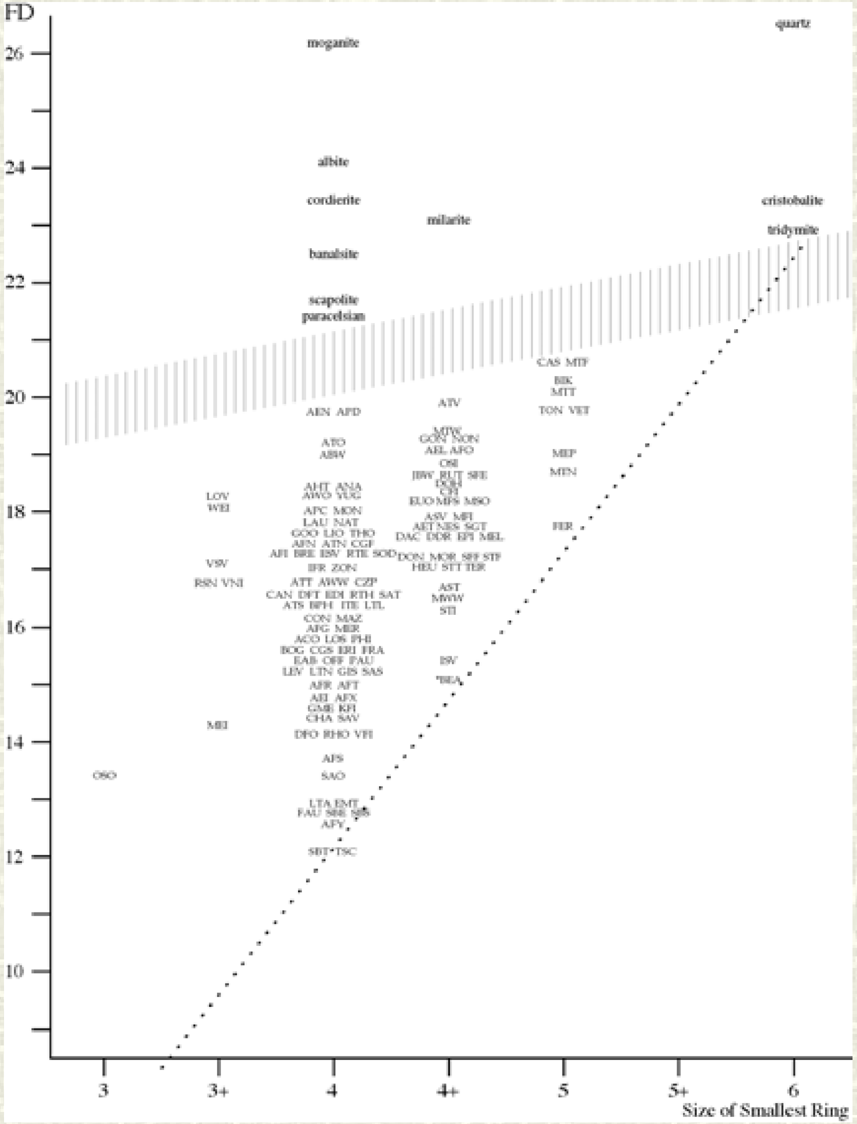
Crystal chemical data: $|K^{+}_{6}Na^{+}_{3}\ (H_2O)_{21}|\ [Al_9Si_{27}\ O_{72}]$**-LTL**
hexagonal, P6/mmm, a = 18.40Å, c = 7.52Å (2)

Framework Density (FD)

- The framework density is a simple criterion for distinguishing zeolites and zeolite-like materials from denser materials.
- Definition: $\frac{\text{Number of T-Atoms}}{1000\ \text{Å}^3}$
- Non-zeolitic, denser framework structures: FD > 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



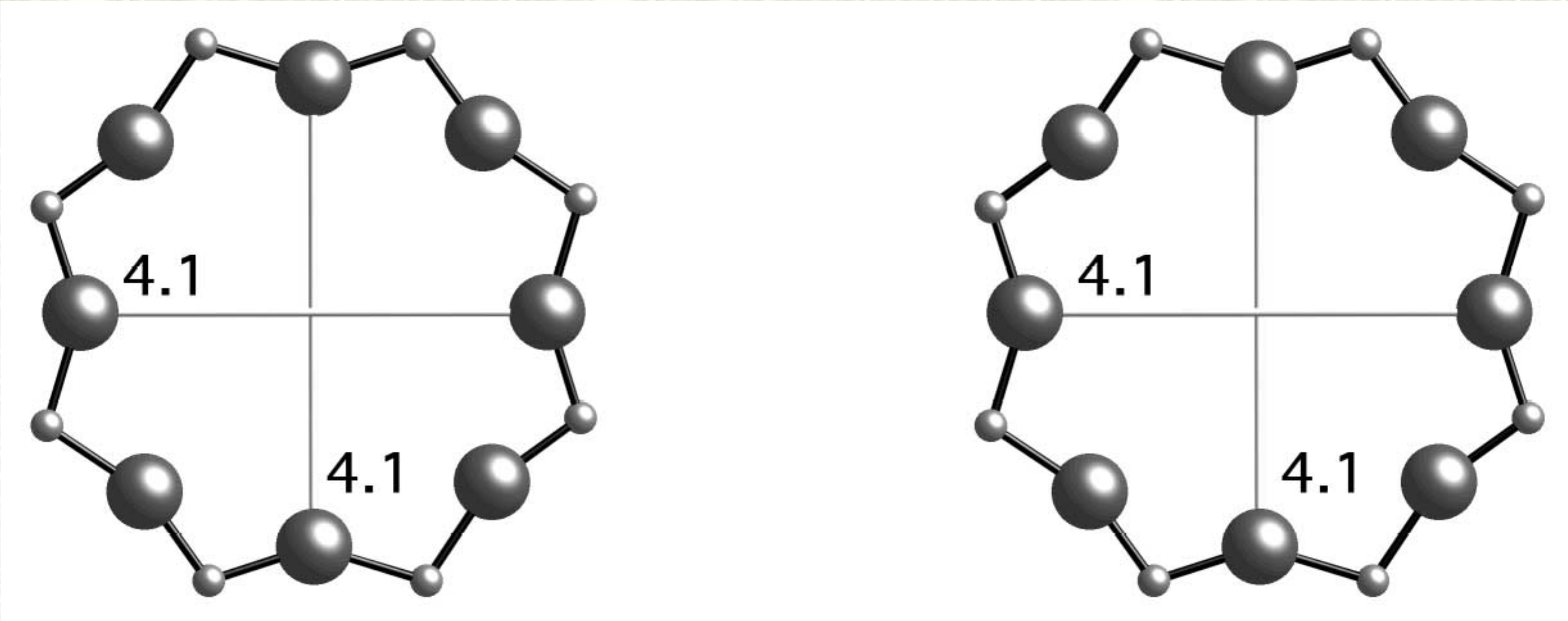
Channels

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.

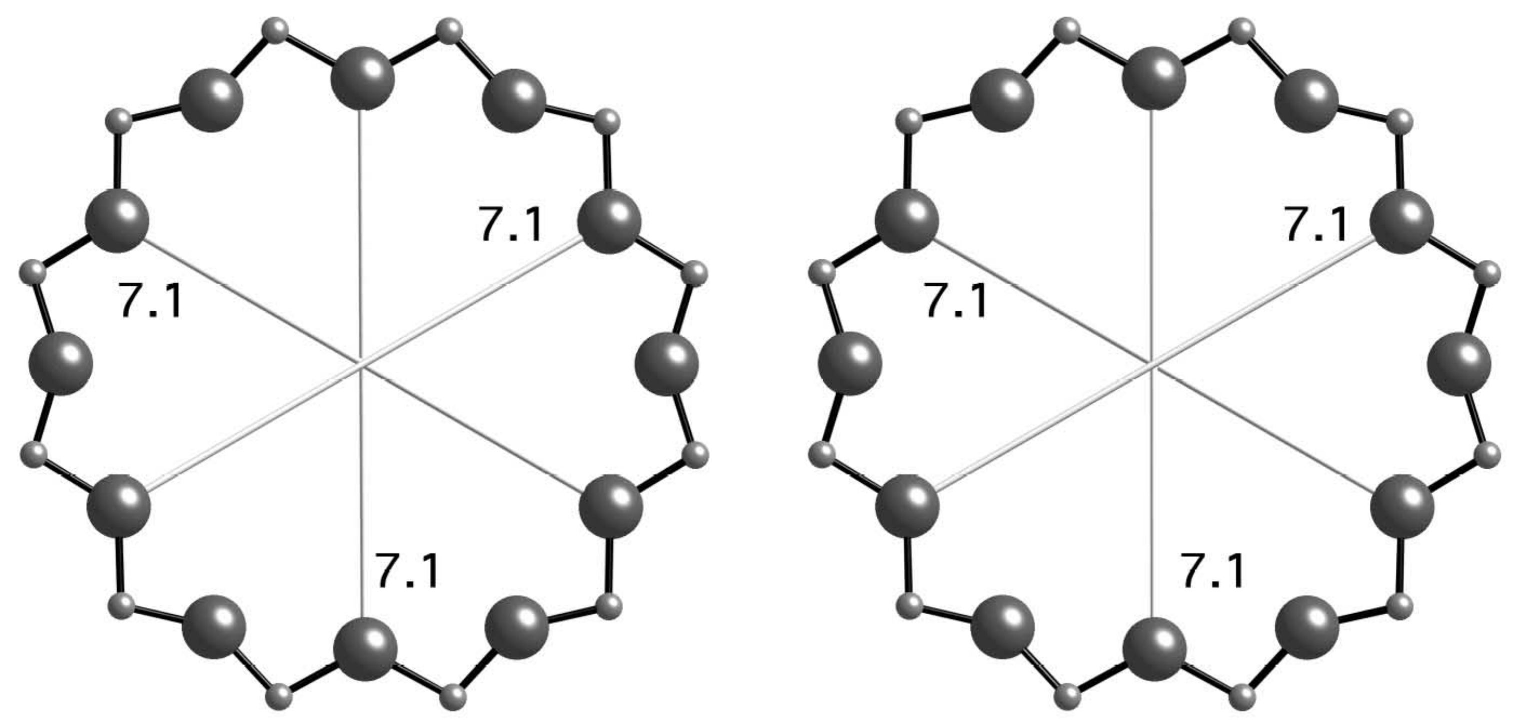
LTA: Channel

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



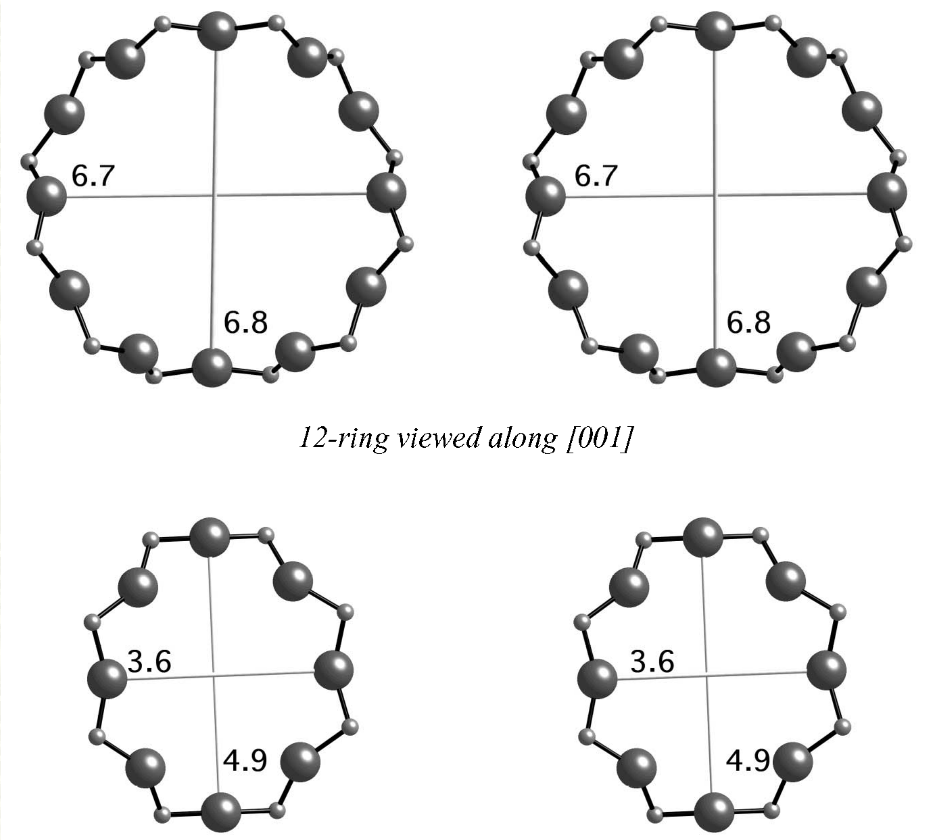
LTL: Channel

[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 **

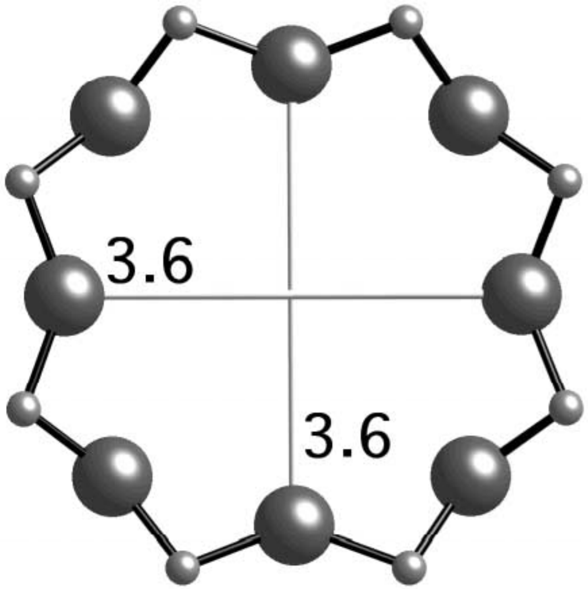


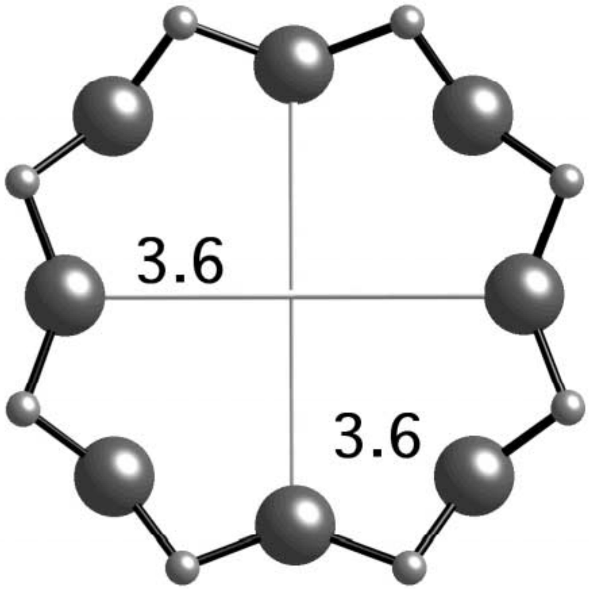
12-ring viewed along [001]

8-ring viewed normal to [001]

RHO (Zeolite Rho): Channels

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





How to Build Zeolites

Building Units

- Zeolite frameworks can be thought to consist of finite and infinite component units.

- Finite units indroduced are:
  - Secondary Building Unit (SBU)
  - Structural Sub-Unit (SSU)

- Infinite units can be build up by different finite building units:
  - Periodic Building Unit (PBU)

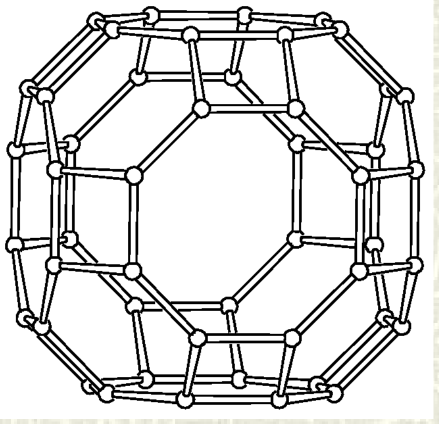
- Component units, finite or infinite, are used to build the framework using translation, rotation, or mirroring.

- Building units are common to several framework types and allow an easy description of the framework.

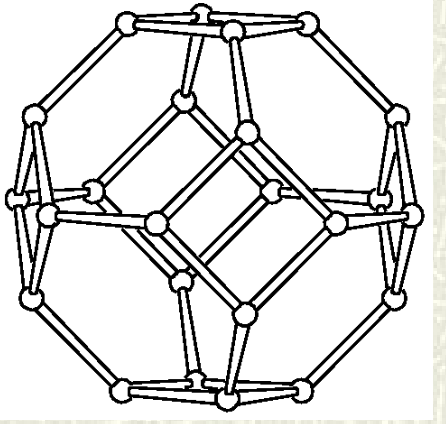
Structural Sub-Unit (SSU)

- SSU have greater complexity than SBU, e.g. polyhedral cages.

α-cage (48 T-atoms)



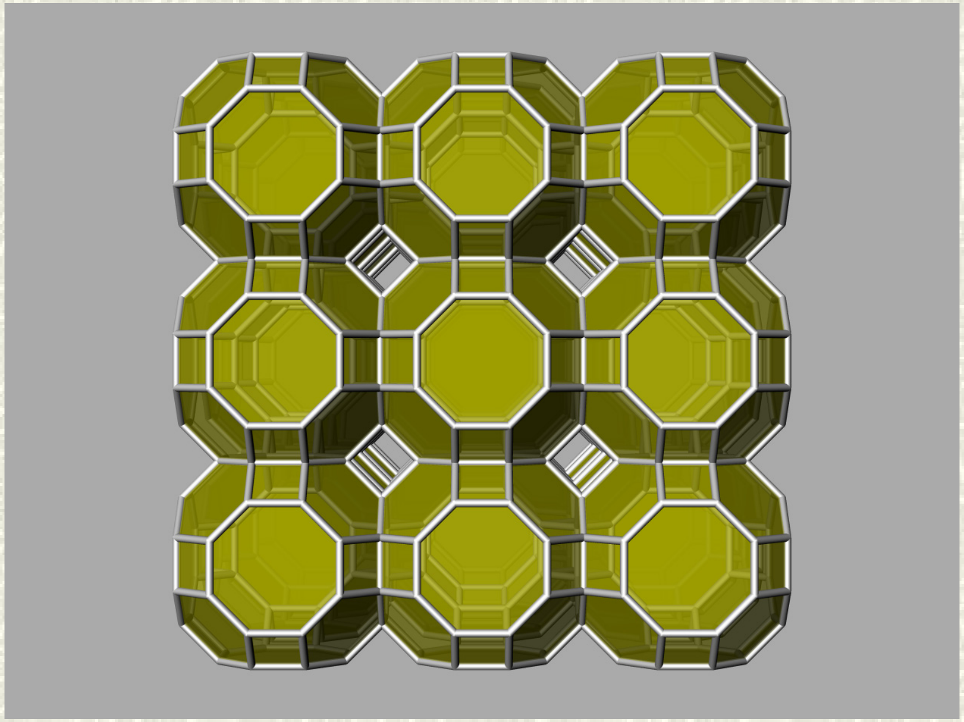
β-cage or sodalite cage (24 T-atoms)



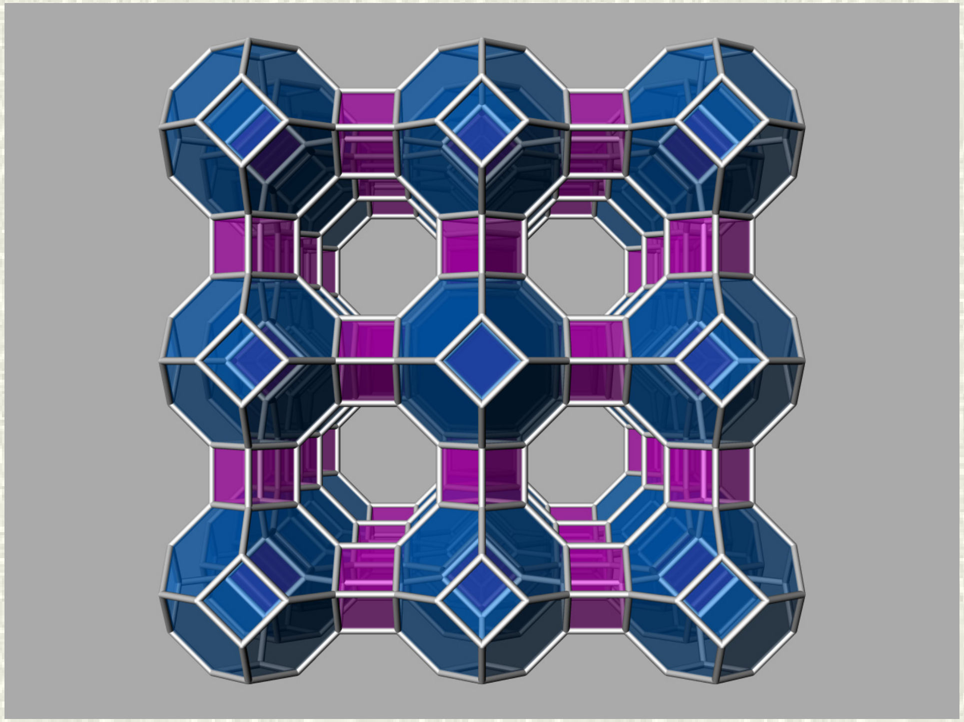
- SSU are not SBU because very often the framwork can not be constructed from SSU alone.
- Frequently, SSU need to share corners, edges or faces to complete the framework.

Structural Sub-Unit for LTA

α-cage

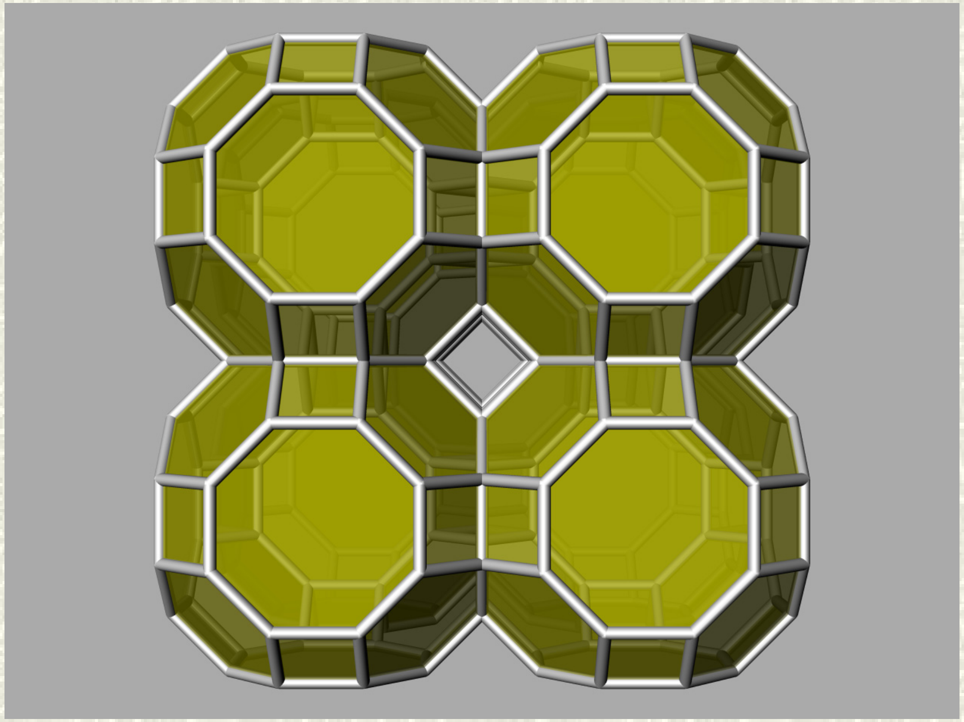


β-cage

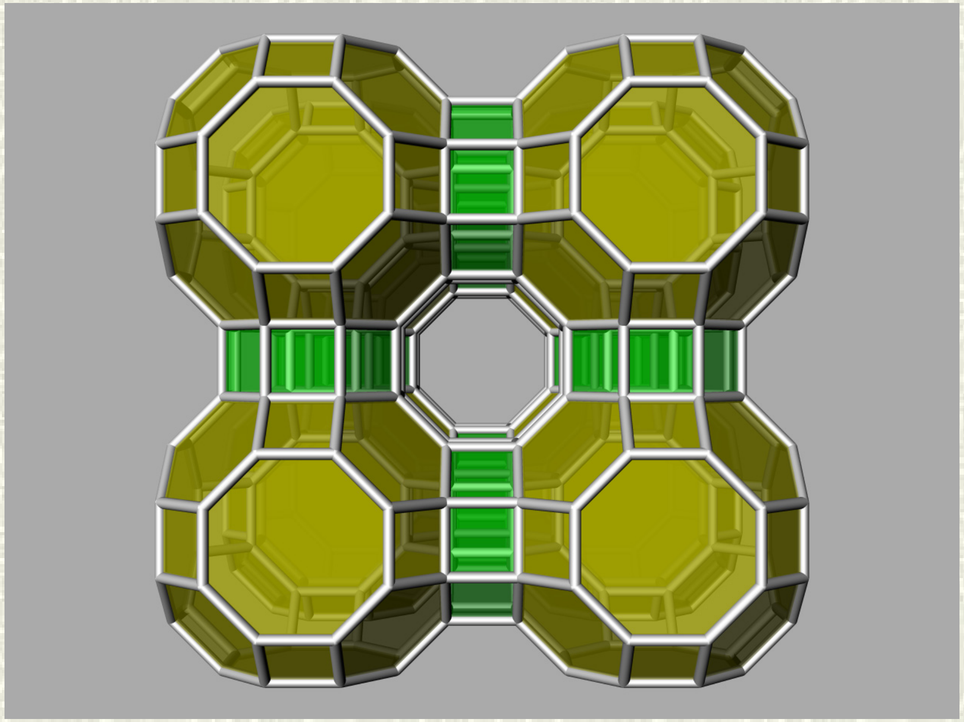


Structural Sub-Unit for LTA and RHO

LTA

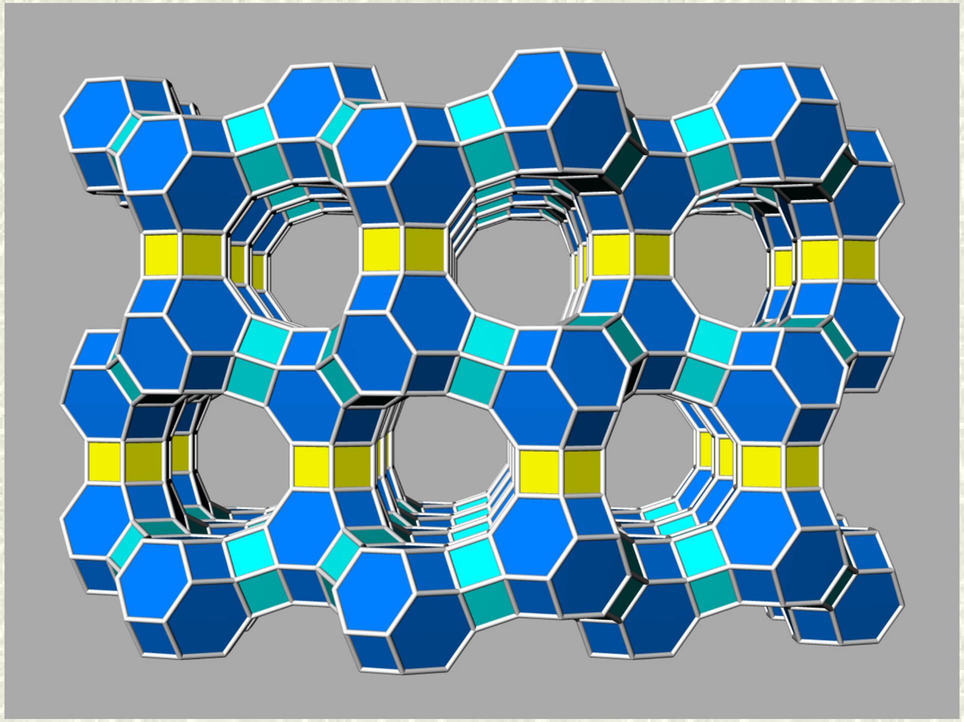


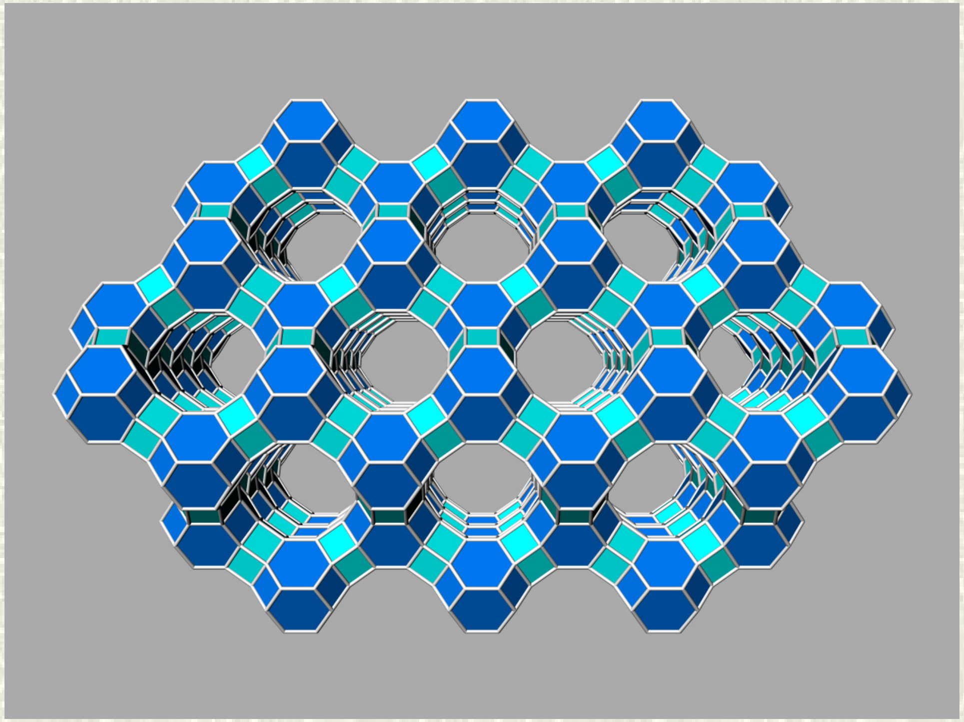
RHO



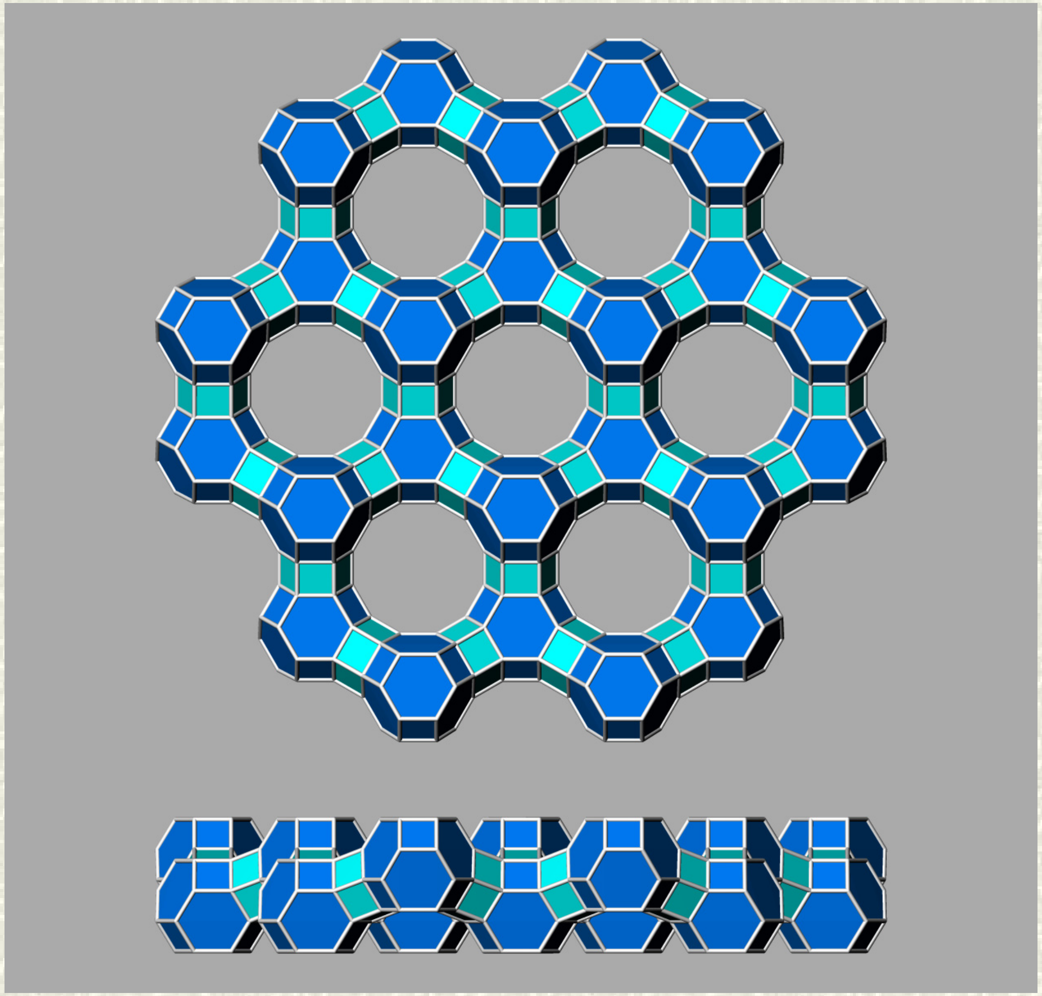
PBU: Framework of EMT and FAU

EMT View along [1 1 0] FAU



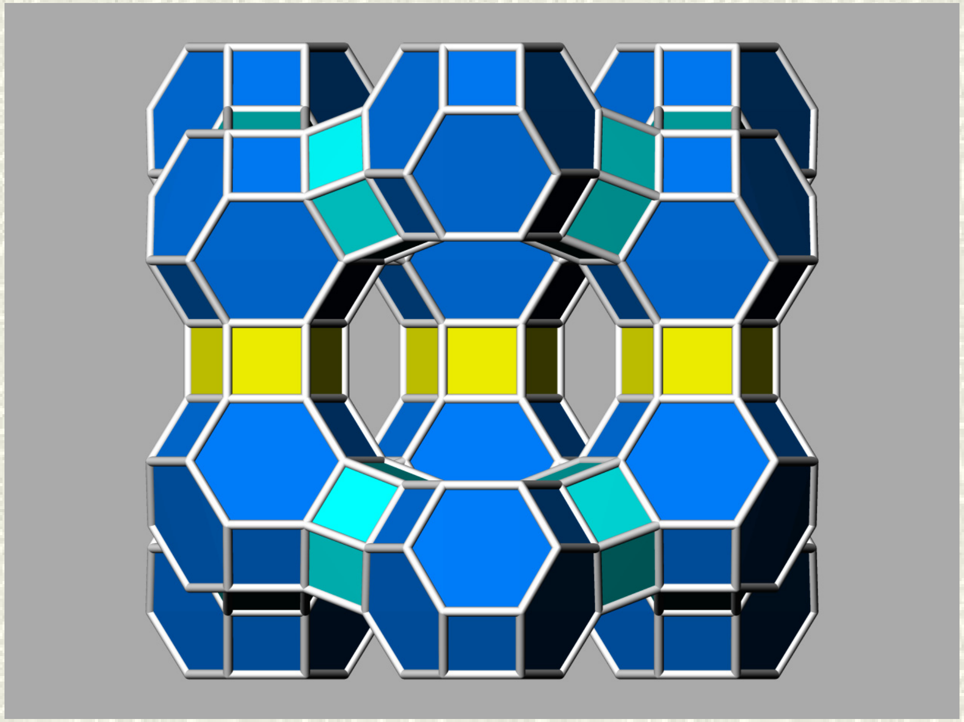


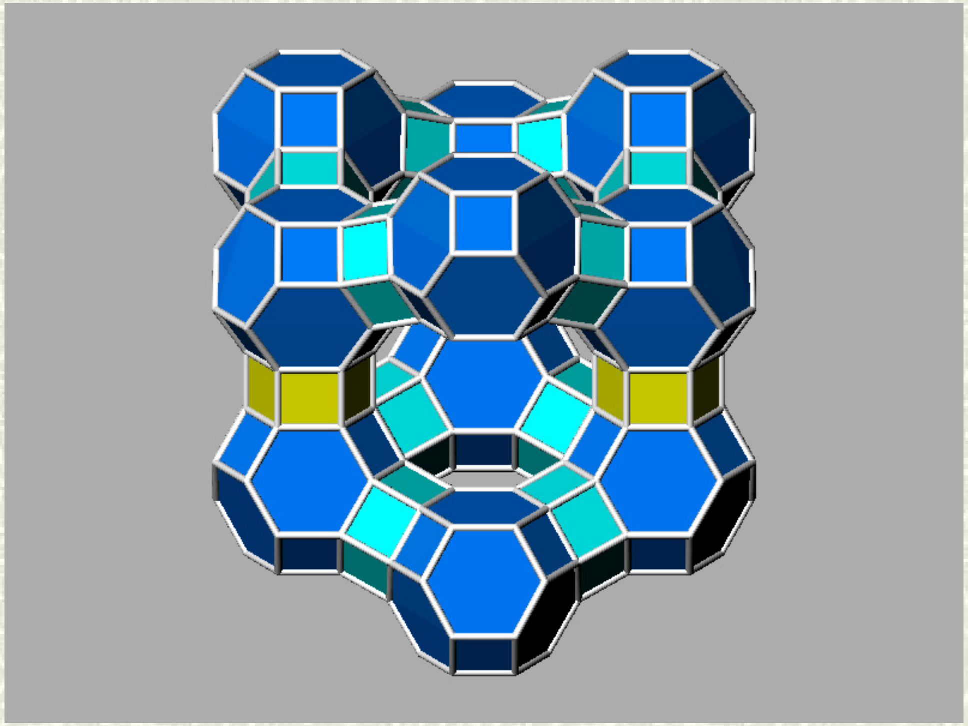
Periodic Building Unit for EMT and FAU



PBU: Framework of EMT

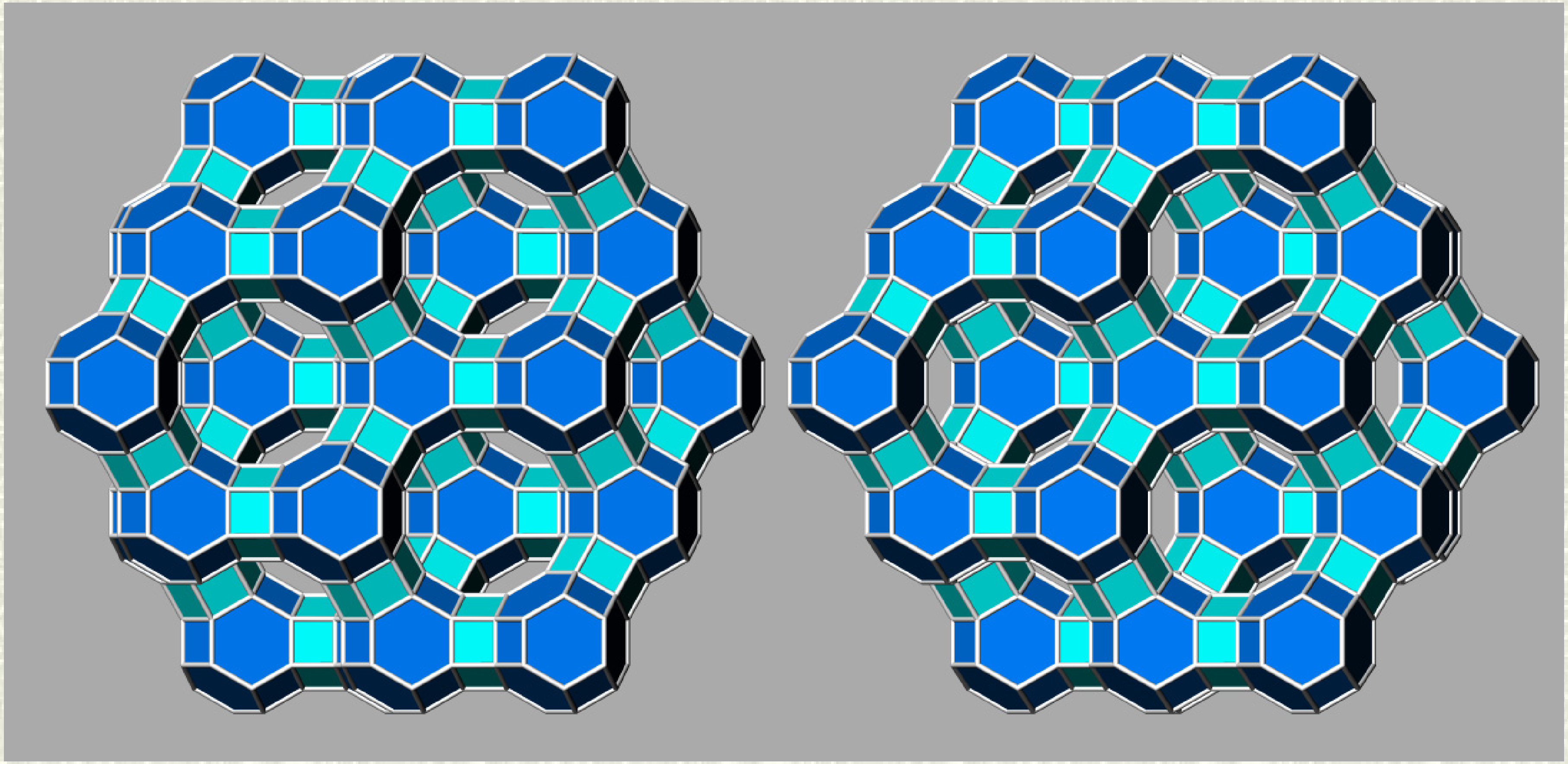
Mirror symmetry between successive layers



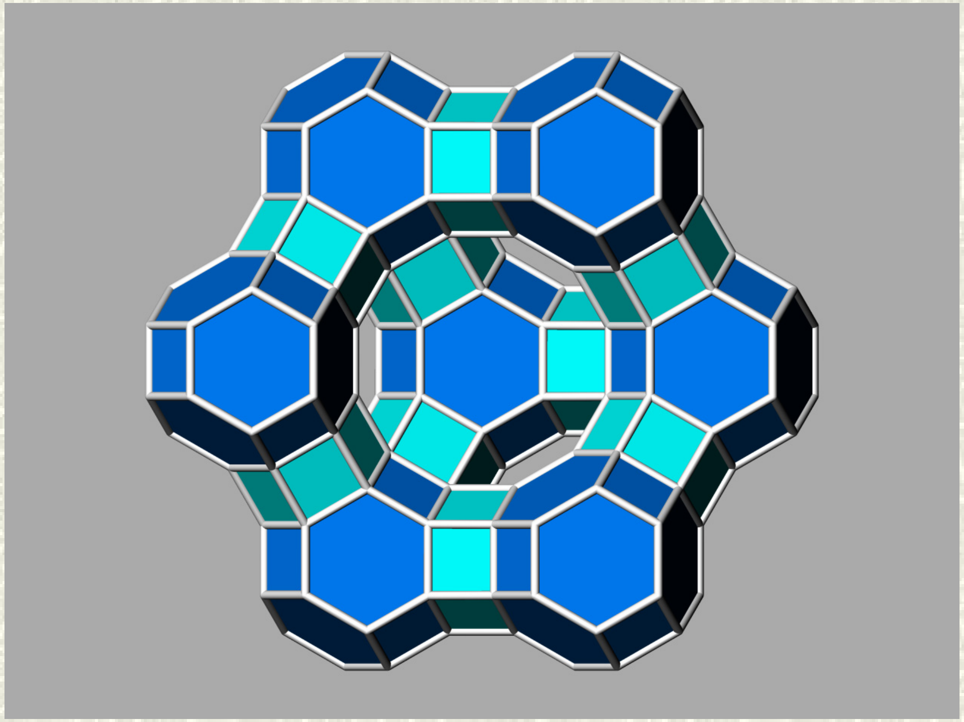


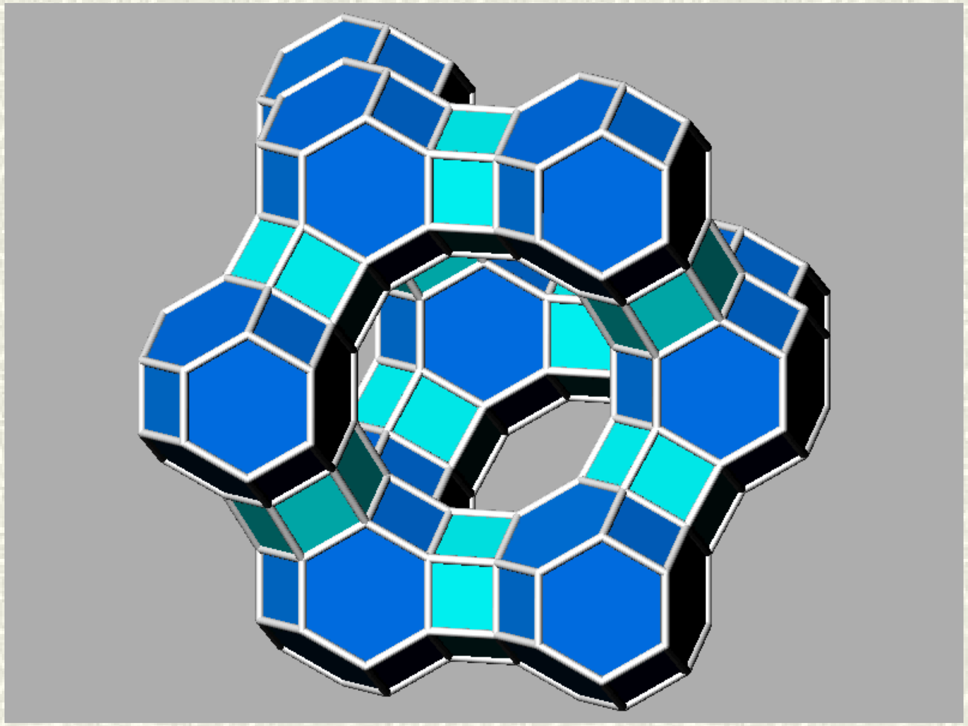
PBU: Framework of FAU

Inversion symmetry between successive layers



PBU: Super Cage of FAU





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