CHEM 548: MATERIALS CHEMISTRY

LECTURE 6: NETWORKS, SILICATES, AND MICROPOROUS SOLIDS

Mon 09/14/2026

Network topology, silicates, and microporous solids

Core structural motif: $\mathrm{SiO_4}$ tetrahedra

Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry* Ch. 1 §§1.4.3–1.4.4, §§1.5.4–1.5.5; Ch. 14 §14.4

LEARNING OBJECTIVES FOR NETWORKS

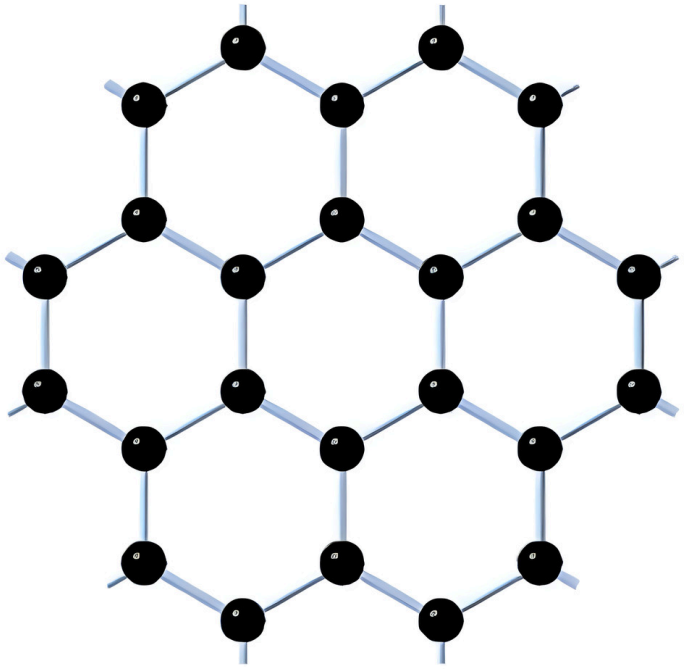
Coordination to topology	understand how coordination numbers lead to network topologies in crystal structures
Vertex and linker	a **vertex** is a linking point; a **linker**, or edge, is the connection between two vertices
Linker kinds	recognize a linker as a bond, an atom (O in a zeolite), or a polyatomic group (CN^- in Prussian blue, dicarboxylates in MOFs)
Uninodal, binodal, regular	all vertices equivalent; two kinds of vertex; all vertices, edges, and angles equivalent
Binary compounds and frameworks	apply network ideas to simple binary compounds and to zeolites and MOFs alike
Read a real structure	relate TiO_2 to its underlying topology as a (6,3) binodal net

NETWORK VOCABULARY

Vertex	a linking point — generally an atom, though in some cases a cluster of atoms
Linker	connects vertices: a bond, as in diamond; an atom, such as the oxygen in a zeolite; or a molecule, such as a dicarboxylic acid in a MOF
Uninodal net	all vertices are the same
Binodal net	two types of vertex, written as an (N,M)-connected net — TiO_2 is a (6,3) net
Regular net	all vertices, edges, and angles are equivalent by symmetry

See: M. O'Keeffe, M. Eddauodi, H. Li, T. Reinke & O.M. Yaghi, *J. Solid State Chem.* **152**, 3-20 (2000).

UNINODAL 3-CONNECTED NETS

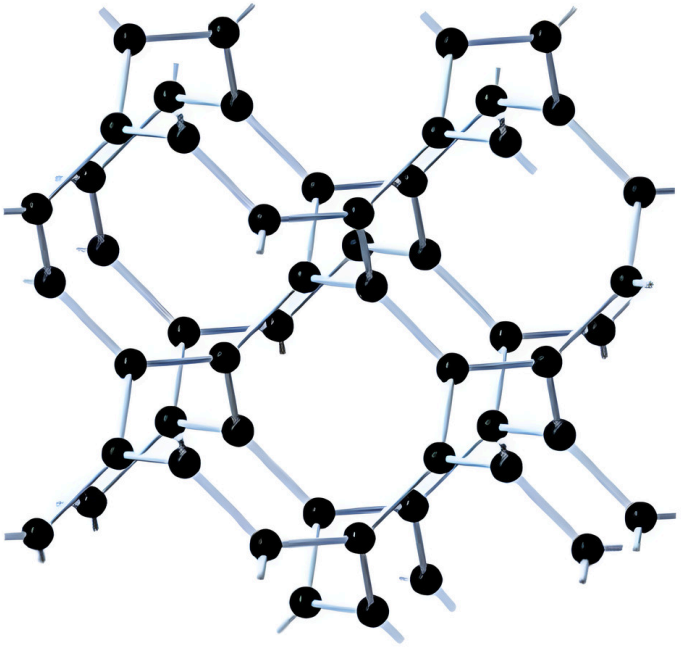


Graphite (2D Net)

Space Group = $P6_3mc$

Site symmetry = $3m$ (C_{3v})

Regular network

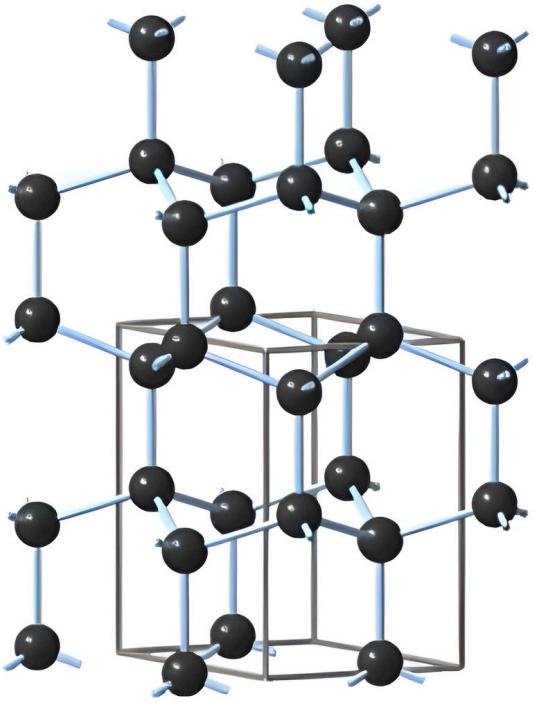


$SrSi_2$ (Silicon network)

Space Group = $I4_132$

Site symmetry = 32 (D_3)

UNINODAL 4-CONNECTED NETS

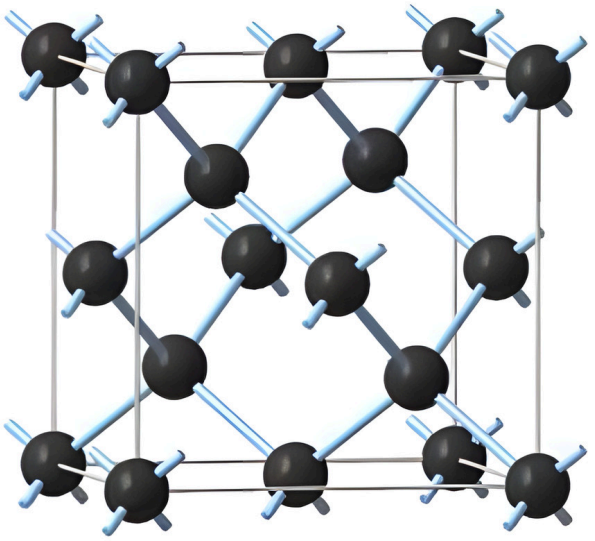


Lonsdaleite

Space Group = $P6_3/mmc$

Site symmetry = $3m$ (C_{3v})

Regular network

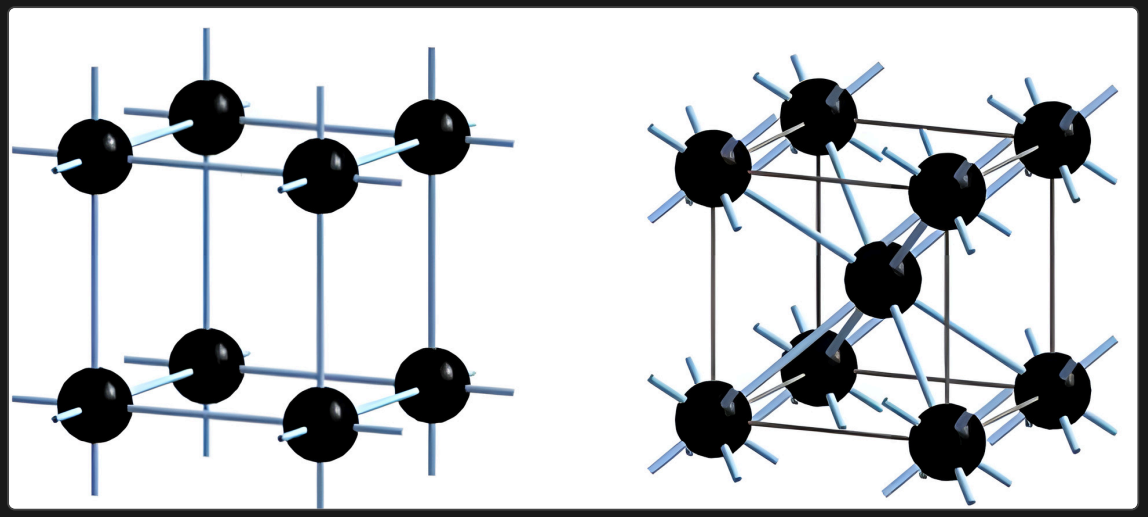


Diamond

Space Group = $Fd\bar{3}m$

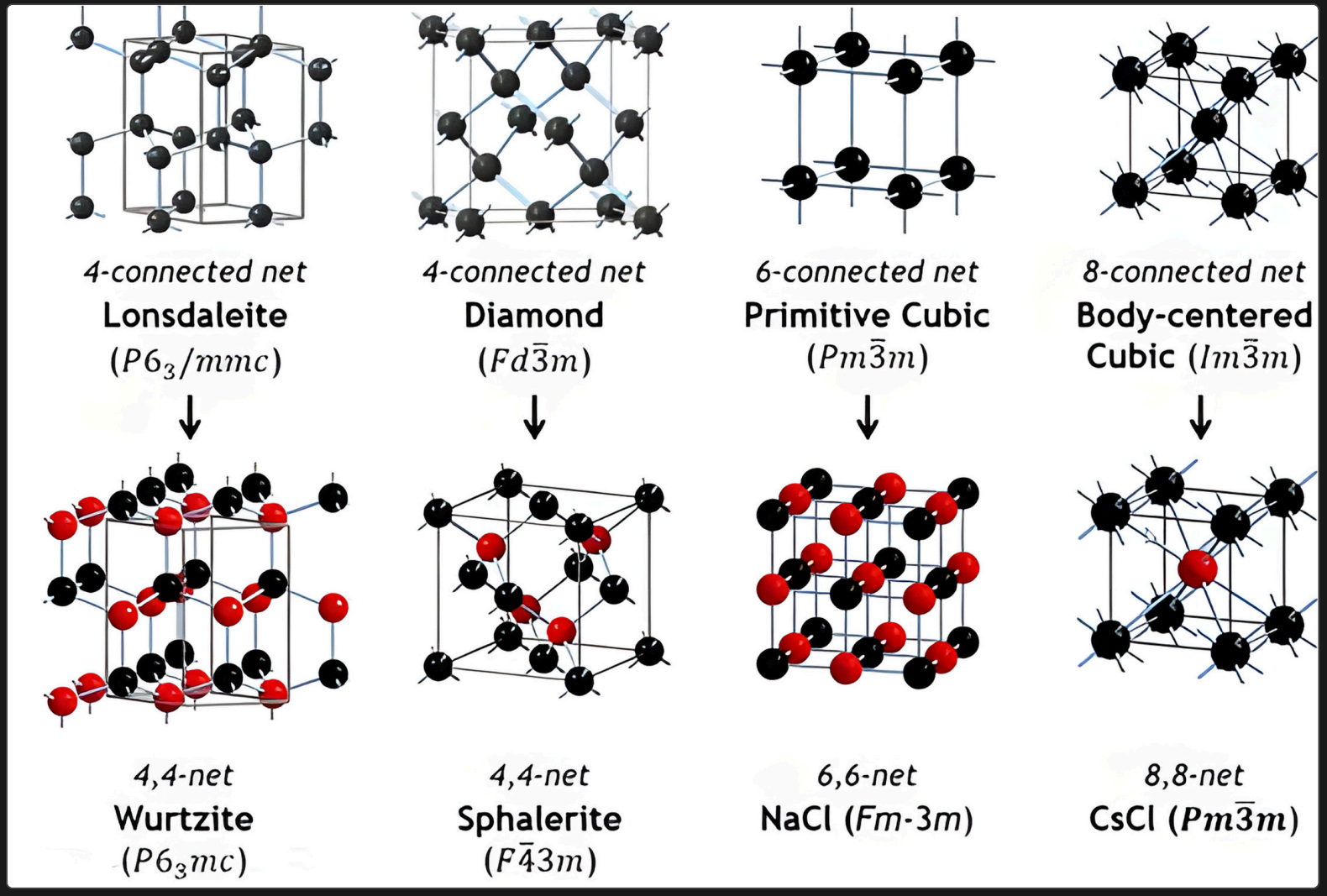
Site symmetry = $\bar{4}3m$ (T_d)

UNINODAL 6- AND 8-CONNECTED NETS

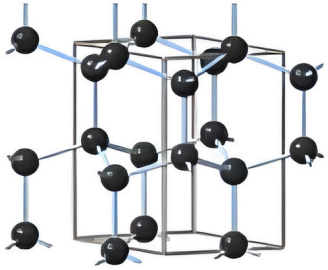


Regular network	Regular network
Primitive cubic (Po)	**Body-centered cubic (Fe)**
Space Group = $Pm\bar{3}m$	Space Group = $Im\bar{3}m$
Site symmetry = $m\bar{3}m$ (O_h)	Site symmetry = $m\bar{3}m$ (O_h)

SITE ORDERED HOMEOTYPES



NETWORK EXPANSION

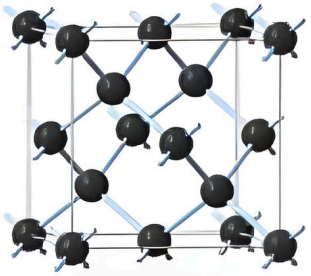


4-connected net

Lonsdaleite

$(P6_3/mmc)$

Si(4f)

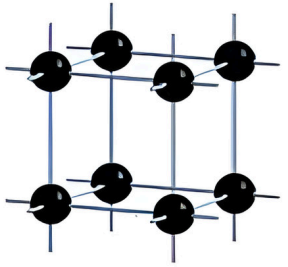


4-connected net

Diamond

$(Fd\bar{3}m)$

Si(8a)

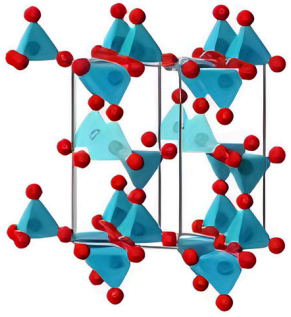


6-connected net

Primitive Cubic

$(Pm3m)$

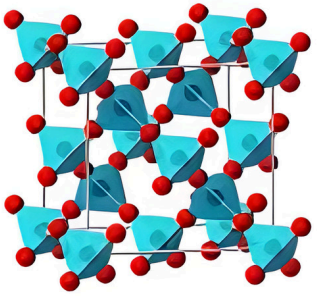
Po(1a)



Tridymite

$(P6_3/mmc)$

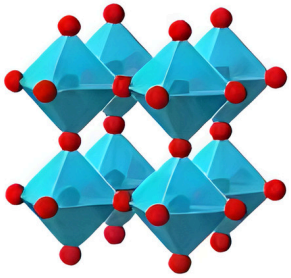
Si(4f), O(2c), O(6g)



Cristobalite

$(F43m)$

Si(8a), O(16c)



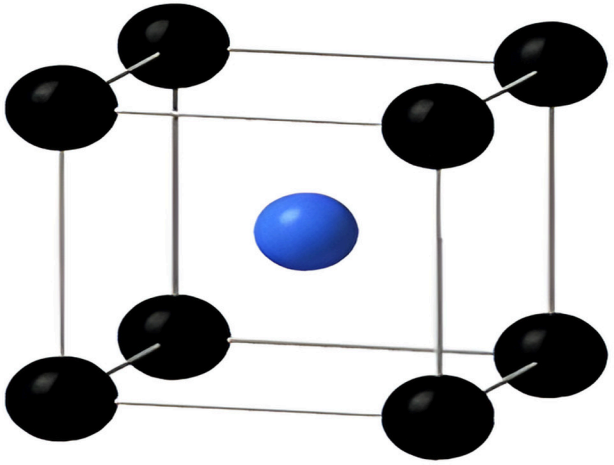
ReO_3

$(Pm3m)$

Re(1a), O(3d)

O: the linker Si, Po: parent-net vertices SiO_4, ReO_6 polyhedra: Si or Re at the centre

DECORATION: CATE AND CAB_6



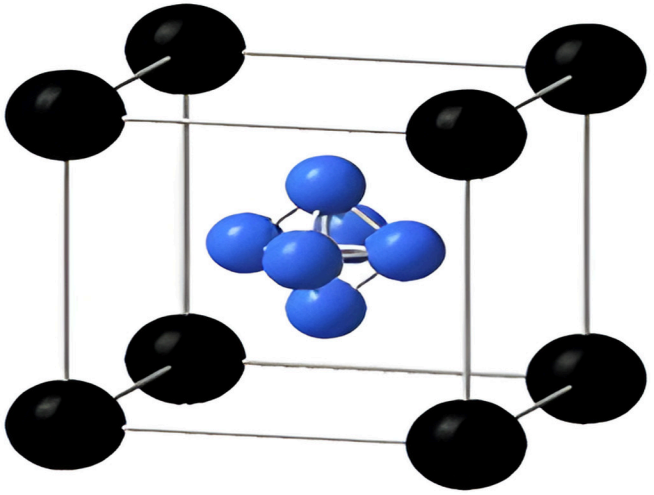
CaTe (CsCl structure type)

Space Group = $Pm\bar{3}m$

a = 3.387 Å

Ca (1a) 0 0 0

Te (1b) ½ ½ ½



CaB_6

Space Group = $Pm\bar{3}m$

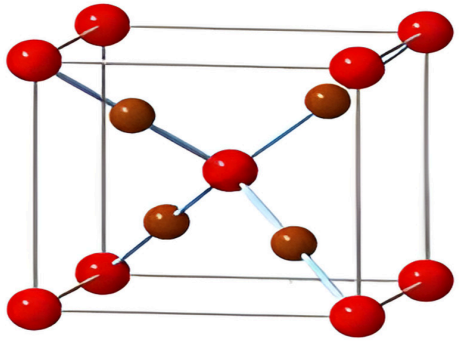
a = 4.15 Å

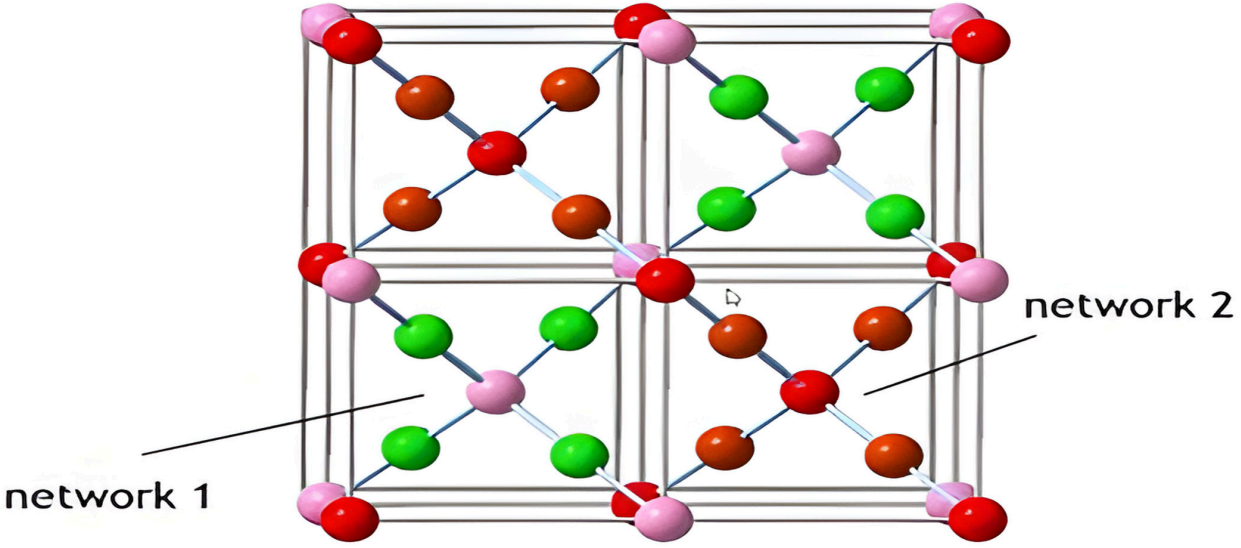
Ca (1a) 0 0 0

B (6f) ½ ½ 0.20

INTERPENETRATION: CU_2O

Unit cell view





$Cu_2^{[2]}O^{[4]}$

Space Group: $Pn\bar{3}m$

a 4.257 Å

Cu (2a) 0 0 0

O (4b) ¼ ¼ ¼

False colors show two independent, interpenetrating cristobalite networks.

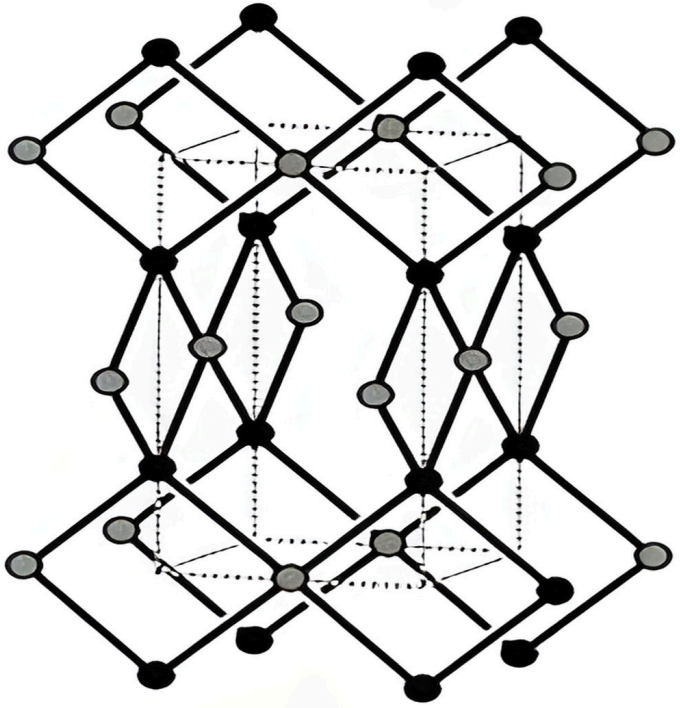
SOME IMPORTANT BINODAL NETS

(N,M)-Net	N Coordination	M Coordination	Net (Example)
4,2	Tetrahedron	Linear (bent)	SiO_2 (cristobalite, tridymite)
4,3	Tetrahedron	Triangle	Si_3N_4
4,4	Tetrahedron	Tetrahedron	ZnS (sphalerite, wurtzite)
4,3	Square	Triangle	Pt_3O_4
4,4	Square	Square	NbO
4,4	Square	Tetrahedron	Cooperite (PtS)
6,2	Octahedron	Linear	ReO_3
6,3	Octahedron	Triangle	TiO_2 (rutile, anatase)
6,4	Octahedron	Tetrahedron	Corundum (Al_2O_3)
6,6	Octahedron	Octahedron	Rock salt (NaCl)
6,6	Octahedron	Trigonal prism	NiAs
8,4	Cube	Tetrahedron	Fluorite (CaF_2)
8,8	Cube	Cube	**CsCl**

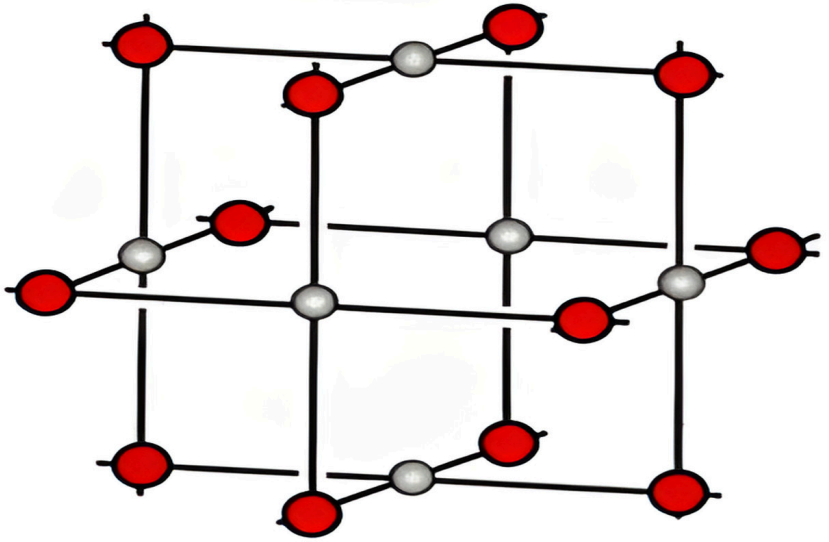
CsCl: cubic coordination at both vertices

(8,8): the numbers count neighbours; the geometry columns describe their arrangement.

(4,4) NETS: COOPERITE PTS AND NBO



Regular network



Cooperite (PtS)

Space Group = $P4_2/mmc$

a = 3.48 Å c = 6.11 Å

Pt (2c) 0 ½ 0

S (2f) ½ ½ ¼

NbO

Space Group = $Pm\bar{3}m$

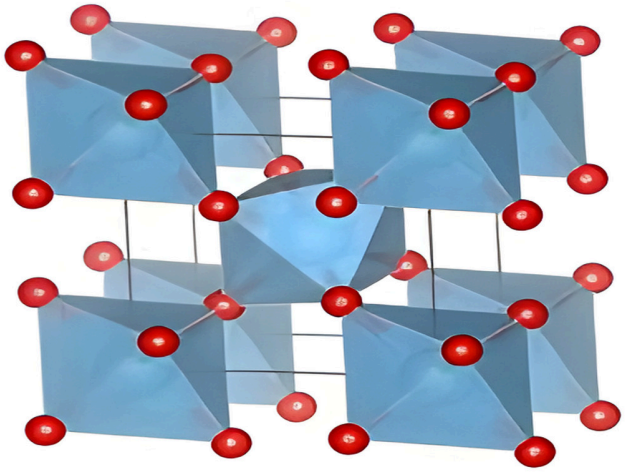
a = 4.21 Å

Nb (3c) ½ ½ 0

O (3d) ½ 0 0

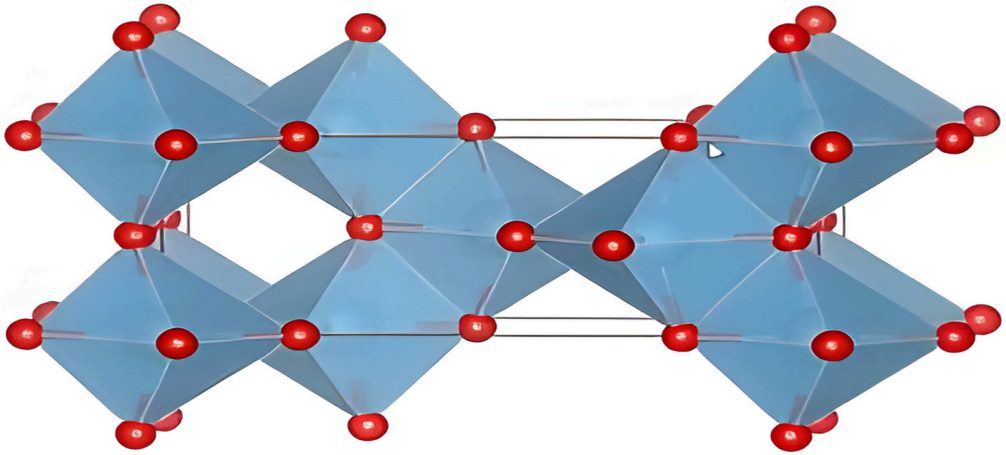
POLYMORPHS OF TiO_2: RUTILE AND ANATASE

Rutile



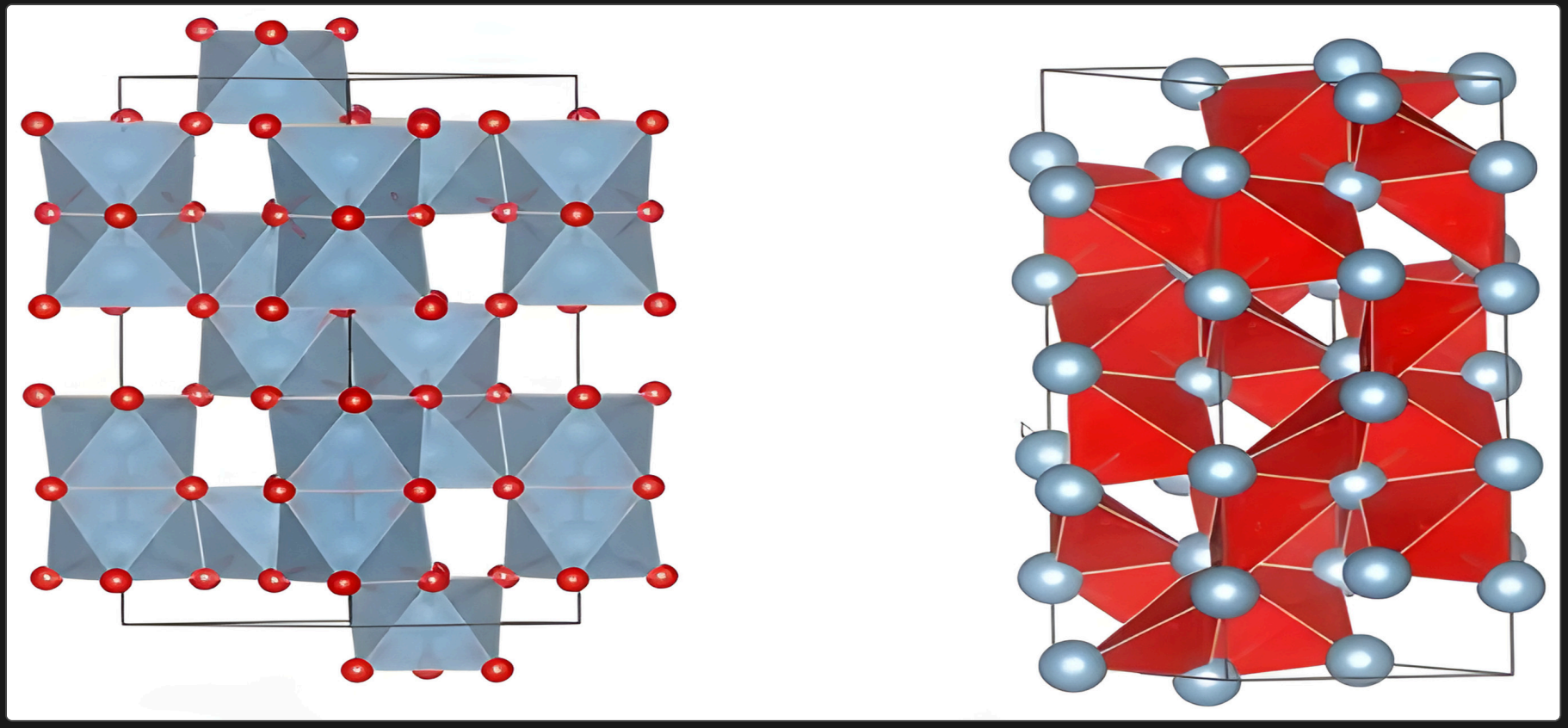
Space group: $P4_2/mnm$
Z = 2
Ti (2a) mmm
O (4f) $2mm$

Anatase



Space group: $I4_1/amd$
Z = 4
Ti (4a) $\bar{4}m2$
O (8e) $2mm$

CORUNDUM



The (6,4) network formed by two of the most common environments — octahedron and tetrahedron — does not give a regular environment for either.

SUMMARY FOR NETWORKS

A network abstracts a structure into vertices and linkers, and the coordination numbers at those vertices name the net.

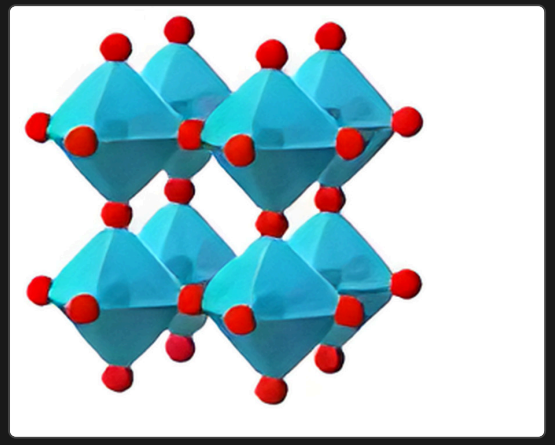
Idea	What it says	Example
Vertices and linkers	Linking points, joined by a bond, an atom, or a molecule	Diamond: C vertices, C–C bonds
Uninodal	All vertices identical	Graphite, diamond, primitive cubic, bcc
Binodal	Two vertex types with different coordination, written (N,M)	TiO_2 is a (6,3) net
Regular	All vertices, edges, and angles equivalent by symmetry	$SrSi_2$, diamond, primitive cubic, bcc, NbO
Site ordering	Order two elements onto one parent net's vertices	Diamond → sphalerite; bcc → CsCl
Expansion	Keep the vertices and insert an atom as the linker	Diamond → cristobalite; primitive cubic → ReO_3
Decoration	Replace a simple vertex with a polyatomic cluster	CaTe → CaB_6
Interpenetration	Two independent nets thread the same volume without connecting	Cu_2O

Binodal nets are the systematic link between empirical formulas, coordination numbers, and real crystal structures.

YOU TRY IT NOW: PROBLEM 1.27

Given	ReO_3 has a 3D network of octahedrally coordinated rhenium
Find	the N,M-connectivity for this binodal network

REO_3 IS A (6,2) BINODAL NET



ReO_3 ($Pm\bar{3}m$); Re(1a), O(3d)

Answer: a (6,2)-connected binodal net.

Re at the corners of a simple-cubic framework, **octahedrally coordinated** by O, so CN = 6

Both ends of every Re–O bond: $\mathrm{CN_A} \times x = \mathrm{CN_B} \times y$

Counted from Re

$$1 \times 6 = 6$$

Counted from O

$$3 \times \mathrm{CN_O} = 6$$

$$\mathrm{CN_O} = 2$$

O lies midway along a Re–Re edge, perovskite without the A cation, so every octahedron **corner is shared**, no edges or faces

Net two node types, Re and O, so it is **binodal**, with connectivities 6 and 2 → (6,2)

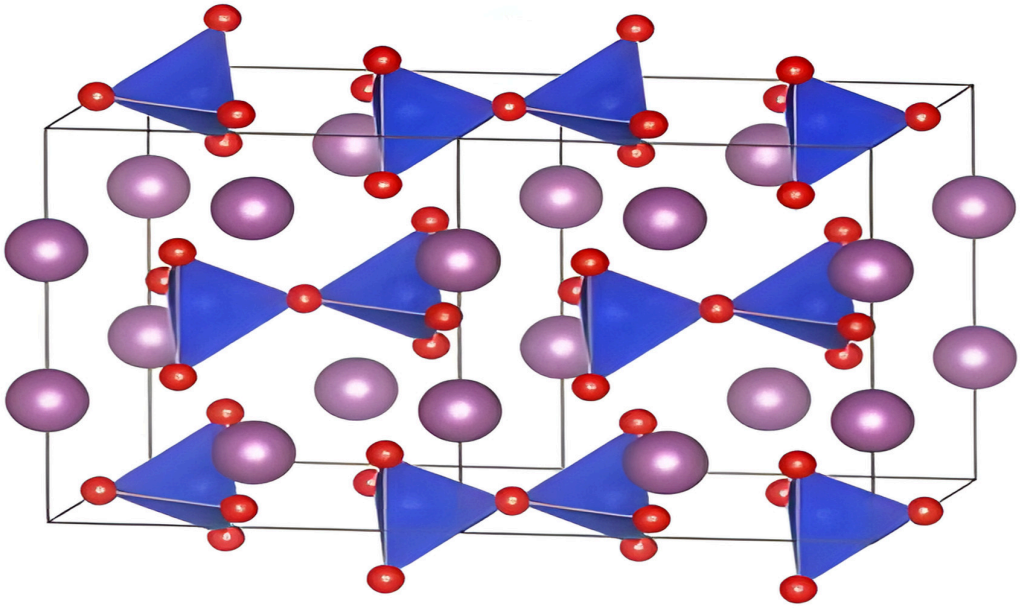
SILICATES AND MICROPOROUS SOLIDS: LEARNING OBJECTIVES

Corner sharing	explain how silicate structures are built from corner-sharing SiO_4 tetrahedra
Niggli formula	relate the oxygen-to-silicon ratio to a structural motif
Motifs	identify isolated tetrahedra, chains, rings, sheets, and frameworks from the O:Si ratio
Zeolites	describe how they form from Al and Si tetrahedra, why cations create porosity, and what makes a solid microporous (<2 nm), mesoporous (2–50 nm), or macroporous (>50 nm)
Building blocks	recognize the sodalite cage, zeolite A, and faujasite, and their pore sizes
MOFs	understand what a metal-organic framework is and how MOF-5 is built from a net

SILICATES

Abundance	the most common minerals in the Earth’s crust
Structure types	about one third of all known inorganic crystal structure types
Tetrahedral Si	silicon sits in SiO_4 tetrahedra, and connected tetrahedra share corners
O:Si ratio	sets how far the tetrahedra are connected

NIGGLI FORMULA: PYROSILICATE



$Sc_2Si_2O_7$

$Si_2O_7^{6-}$

$SiO_{3/1+1/2}$

3 oxygens belong to 1 tetrahedron

1 oxygen is shared by 2 tetrahedra

Numerators add up to the coordination number

The sum matches the empirical formula

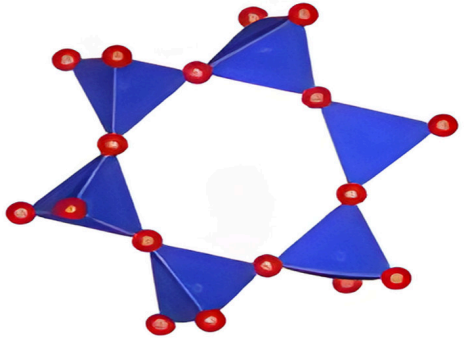
O:SI RATIO AND NIGGLI FORMULA

O:Si	Example	Niggli formula	Network connectivity
2	SiO_2	$SiO_{4/2}$	3D network of corner connected tetrahedra
2.5	$Na_2Si_2O_5$	$SiO_{1/1 + 3/2}$	2D sheets of corner connected tetrahedra
3	Na_2SiO_3	$SiO_{2/1 + 2/2}$	1D chains or rings of corner connected tetrahedra
3.5	$Sc_2Si_2O_7$	$SiO_{3/1 + 1/2}$	dimers of corner connected tetrahedra
4	$ZrSiO_4$	$SiO_{4/1}$	isolated tetrahedra

bridging oxygen · terminal oxygen

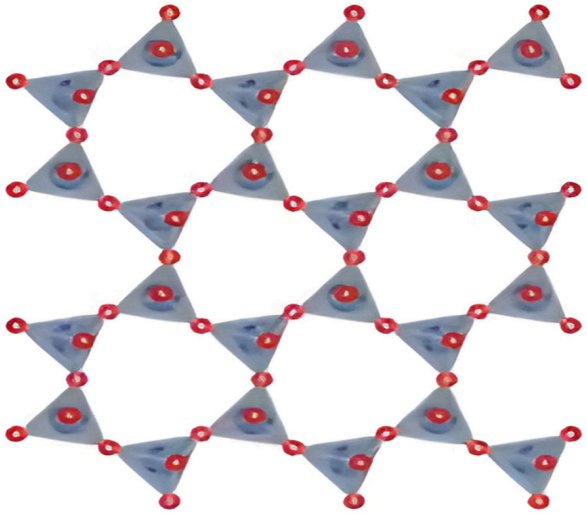
SILICATE STRUCTURES

SiO_3



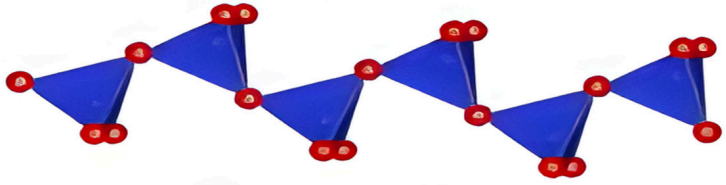
$SiO_{2/1\ 2/2}$ rings in beryl
($Al_2Be_2Si_6O_{18}$)

$SiO_{2.5}$



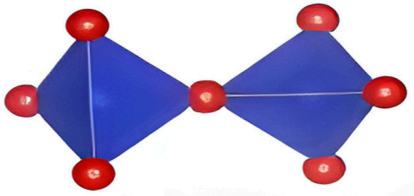
$SiO_{1/1+3/2}$ sheets in mica

SiO_3



$SiO_{2/1+2/2}$ chains in Na_2SiO_3

$SiO_{3.5}$



$SiO_{3/1+1/2}$ chains in $Sc_2Si_2O_7$

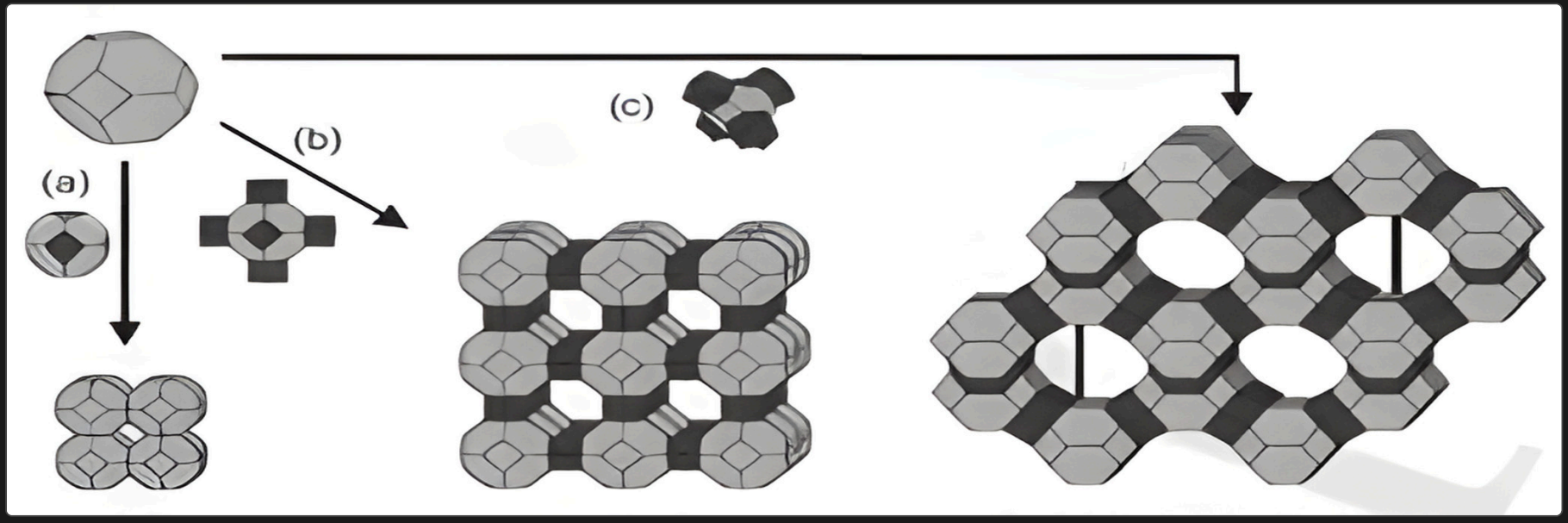
POROUS MATERIALS

Zeolites	“boiling stone”: frameworks of corner connected $SiO_{4/2}$ and $AlO_{4/2}$ tetrahedra
Zeotypes	the same frameworks with other elements on the tetrahedral sites
MOFs	porous coordination polymers: metal ions or clusters joined by multidentate polyatomic ligands
Microporous	pore size < 2 nm
Mesoporous	pore size 2–50 nm
Macroporous	pore size > 50 nm

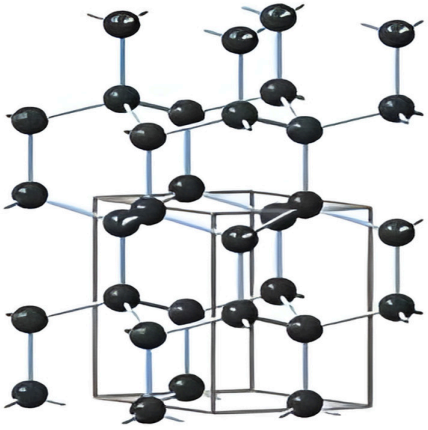
IMPORTANT ZEOLITES

Name	Framework	Ring	Accessible volume*	Channel dimensions
Sodalite	$Al_6Si_6O_{24}^{6-}$	6	0	—
Zeolite A	$Al_{12}Si_{12}O_{48}^{12-}$	8	21.4%	4.1 Å × 4.1 Å
Faujasite	$Al_{58}Si_{134}O_{384}^{58-}$	12	27.4%	7.4 Å × 7.4 Å

*Percent of volume accessible to a 2.8 Å diameter probe sphere meant to simulate a water molecule.



UNINODAL 4-CONNECTED NETS: LONSDALEITE, DIAMOND, SODALITE

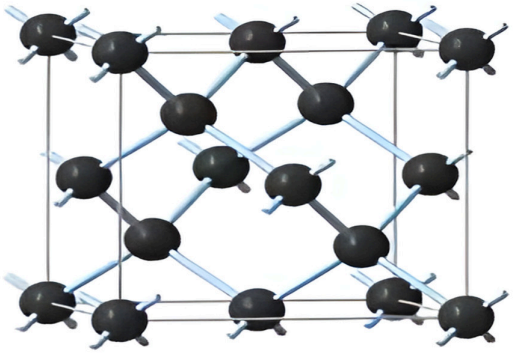


Lonsdaleite

Space Group = $P6_3/mmc$

Site symmetry = $3m$

Site symmetry C_{3v}

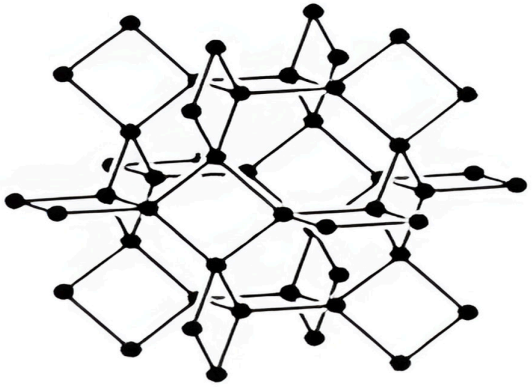


Diamond

Space Group $Fd\bar{3}m$

Site symmetry $\bar{4}3m$

Site symmetry = T_d



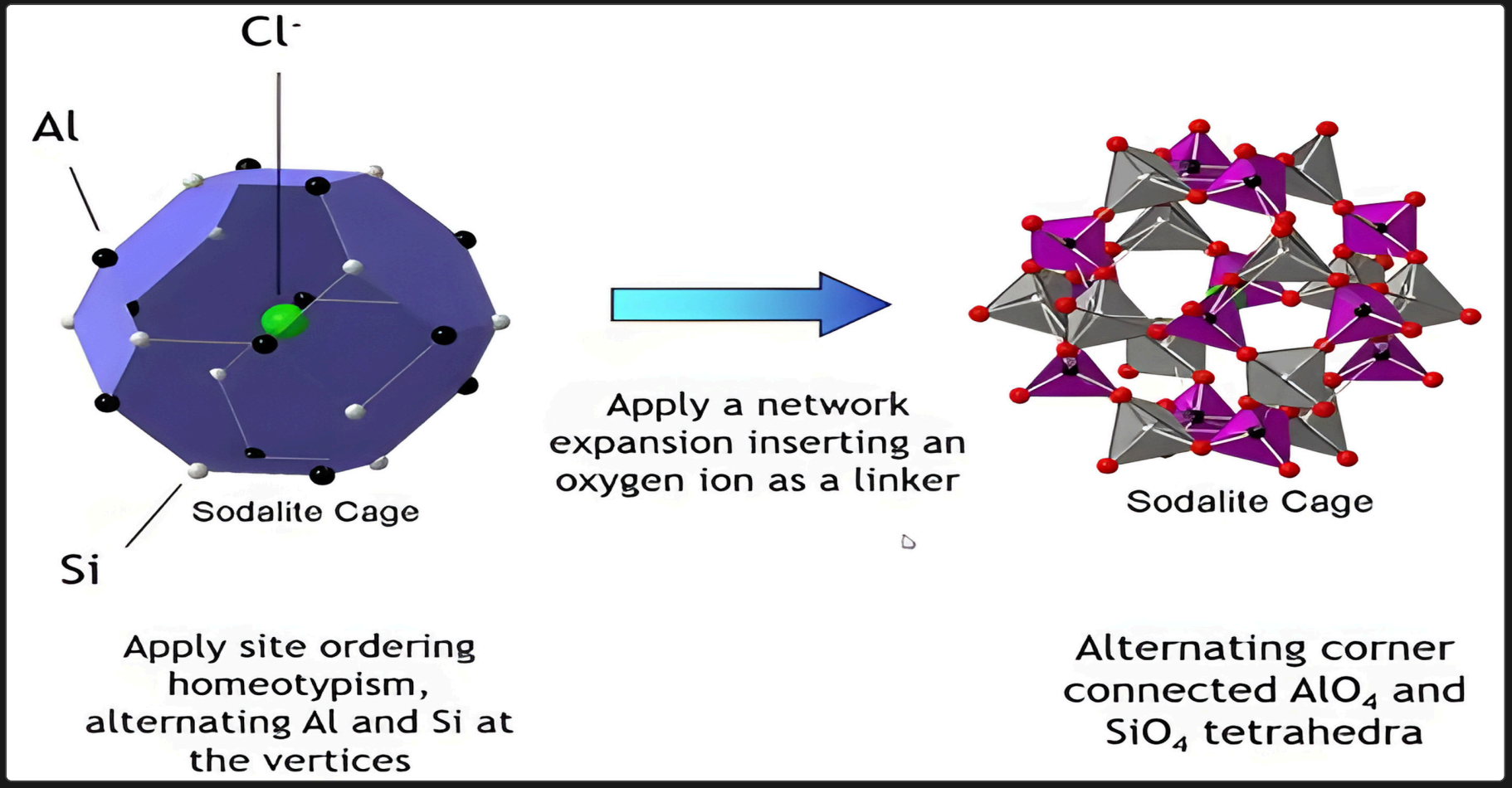
Sodalite

Space Group = $Im\bar{3}m$

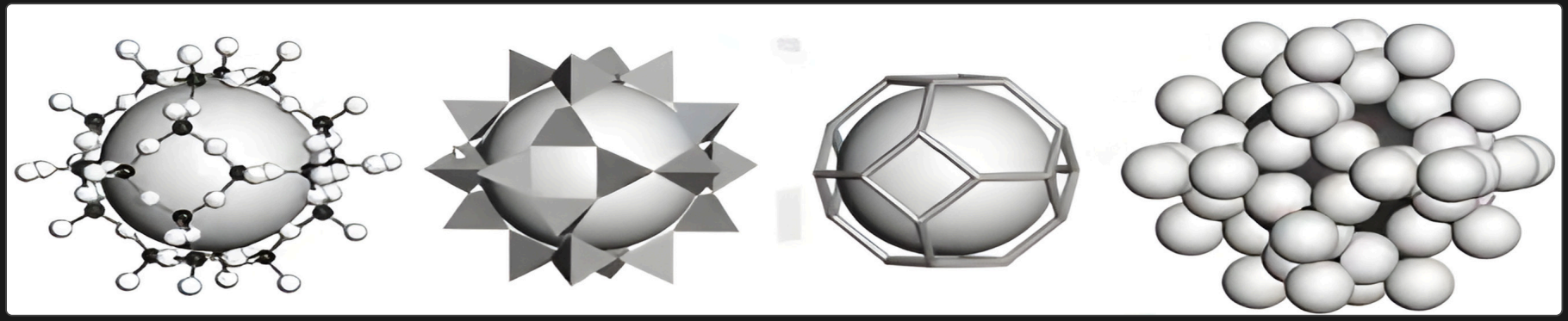
Site symmetry = $\bar{4}m2$

Site symmetry D_{2d}

SODALITE, $NA_8AL_6SI_6O_{24}CL_2$

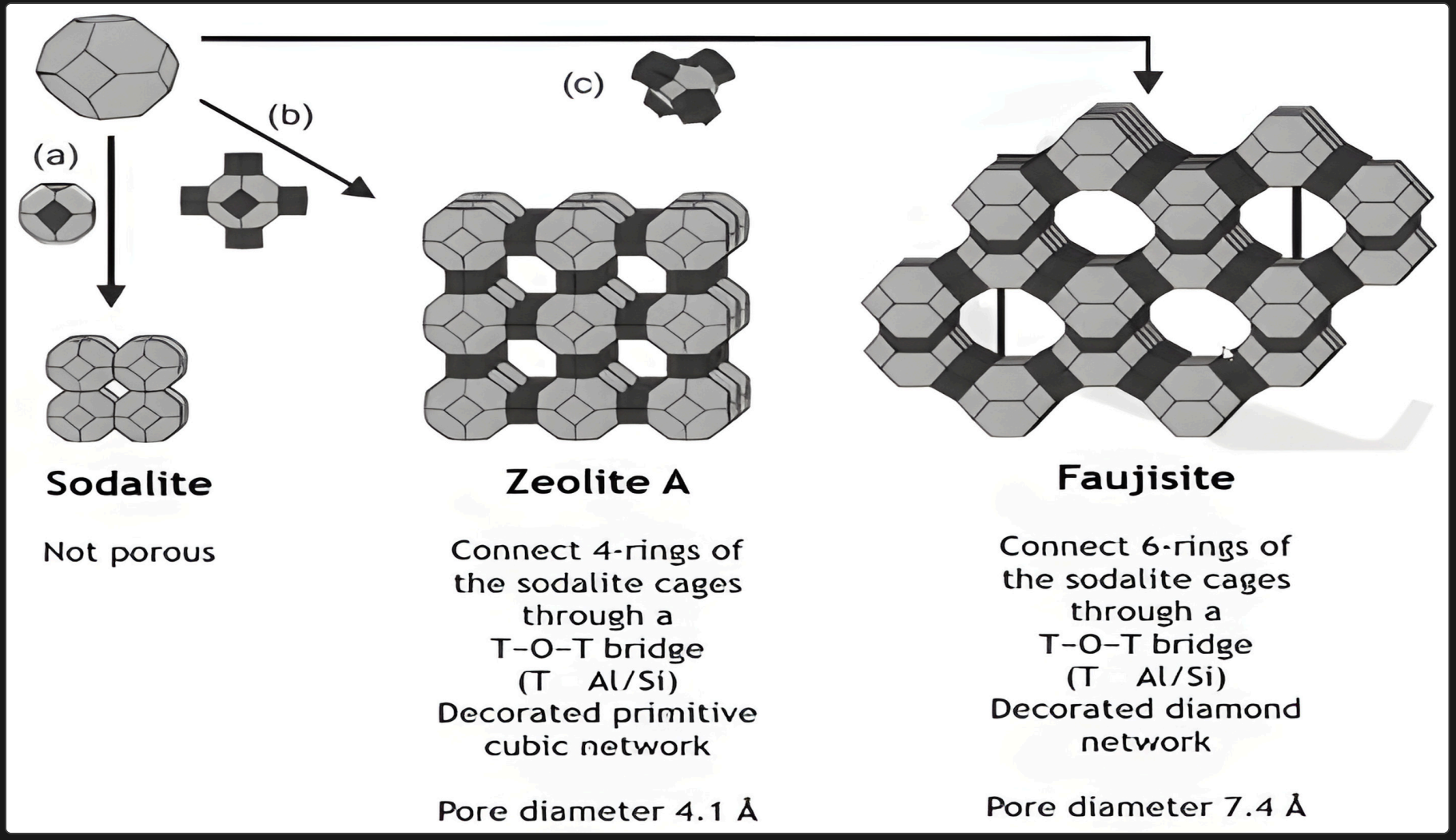


SODALITE CAGE



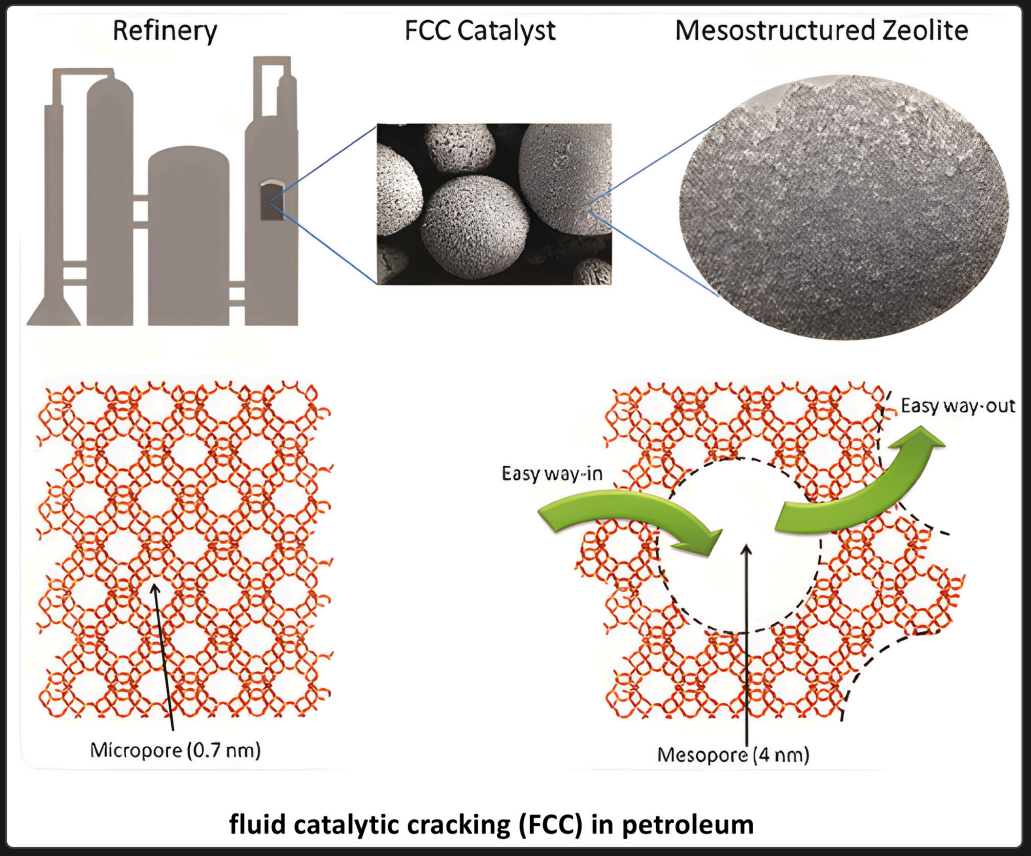
Notice the lack of porosity when oxygens are drawn with realistic radii.

FROM SODALITE TO ZEOLITE A AND FAUJASITE



HIERARCHICAL FAUJASITE CATALYST

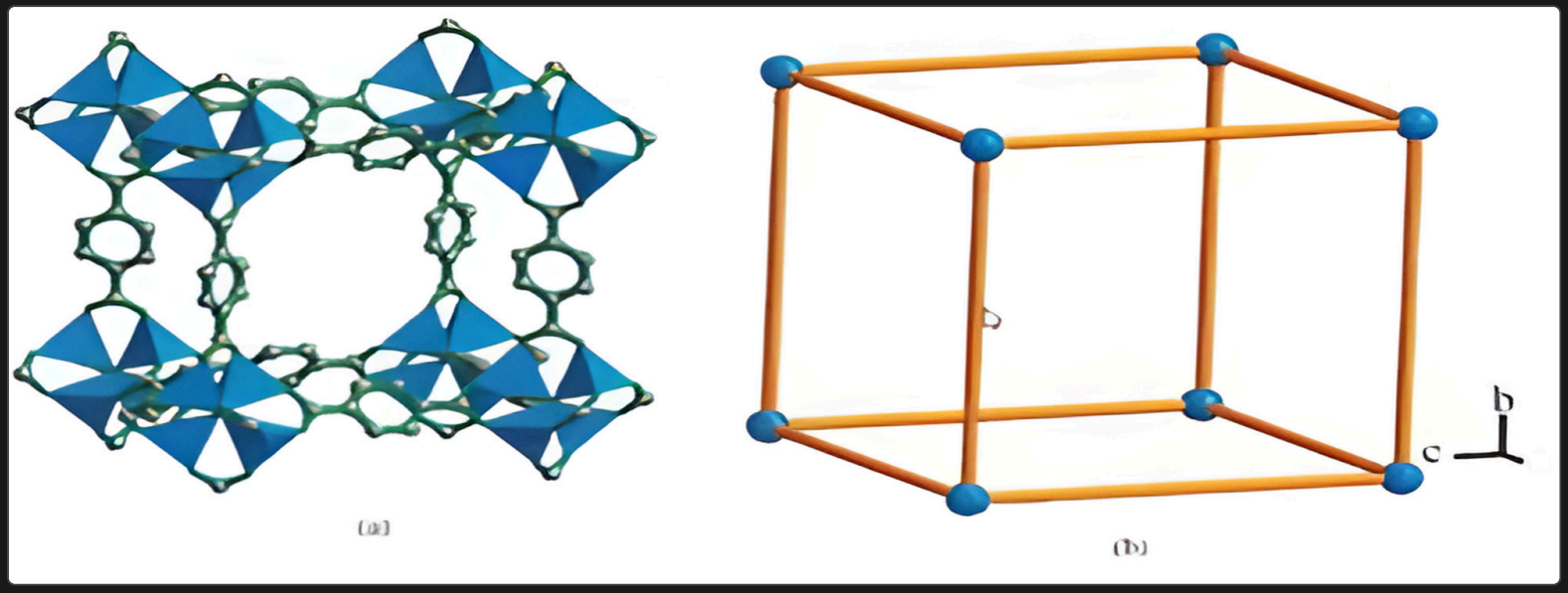
Micropores	0.7 nm pores in the zeolite framework hold the active catalytic sites
Mesopores	4 nm channels, opened by dealumination and leaching during catalyst preparation, act as diffusion paths
Effect	big feed molecules barely fit, so they **get in and stay until they crack**; the products are much smaller, diffuse out fast, and are **gone before they crack again**



fluid catalytic cracking (FCC) in petroleum

MOF-5

$Zn_4O(1,4\text{-bdc})_3(DMF)_8(C_6H_5Cl)$



Start	with the 6-connected primitive cubic net
Decorate	the vertices with OZn_4 clusters
Expand	with the 1,4-benzenedicarboxylate linker

S. Natarajan and P. Mahata, *Chem. Soc. Rev.* **2009**, *38*, 2304–2318.

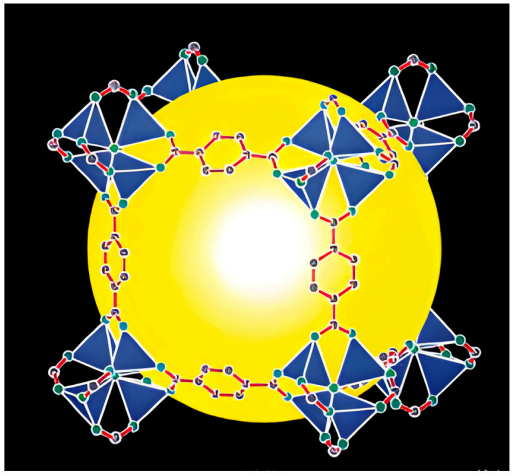
PERMANENT POROSITY: LI, EDDAOUDI, O'KEEFFE, YAGHI, *NATURE* 402, 276 (1999)

Design and synthesis of an exceptionally stable and highly porous metal-organic framework

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Open metal–organic frameworks are widely regarded as promising materials for applications[1–15] in catalysis, separation, gas storage and molecular recognition. Compared to conventionally used microporous inorganic materials such as zeolites, these organic structures have the potential for more flexible rational design, through control of the architecture and functionalization of the pores. So far, the inability of these open frameworks to support permanent porosity and to avoid collapsing in the absence of guest molecules, such as solvents, has hindered further progress in the field[14,15]. Here we report the synthesis of a metal–organic framework which remains crystalline, as evidenced by X-ray single-crystal analyses, and stable when fully desolvated and when heated up to 300 °C. This synthesis is achieved by borrowing ideas from metal carboxylate cluster chemistry, where an organic dicarboxylate linker is used in a reaction that gives supertetrahedron clusters when capped with monocarboxylates. The rigid and divergent character of the added linker allows the articulation of the clusters into a three-dimensional framework resulting in a structure with higher apparent surface area and pore volume than most porous crystalline zeolites. This simple and potentially universal design strategy is currently being pursued in the synthesis of new phases and composites, and for gas-storage applications.



THE 2025 NOBEL PRIZE IN CHEMISTRY

Robson, 1989	Linked copper ions to a four-armed molecule and got an ordered, diamond-like crystal full of cavities — fragile, and it collapsed easily
Kitagawa, 1997–1998	Built a framework crossed by open channels, showed gases flow in and out of it, and predicted that frameworks could be made flexible
Yaghi, 1999–2002	Built MOF-5, stable enough to stay open once emptied, then used rational design to grow a whole family of frameworks with larger and larger cavities

Store toxic gases — the named application behind the only commercial MOF product so far.

Royal Swedish Academy of Sciences, 8 Oct 2025: Susumu Kitagawa, Richard Robson, and Omar M. Yaghi, “for the development of metal–organic frameworks”

ION-X: THE STATUS QUO PROBLEM

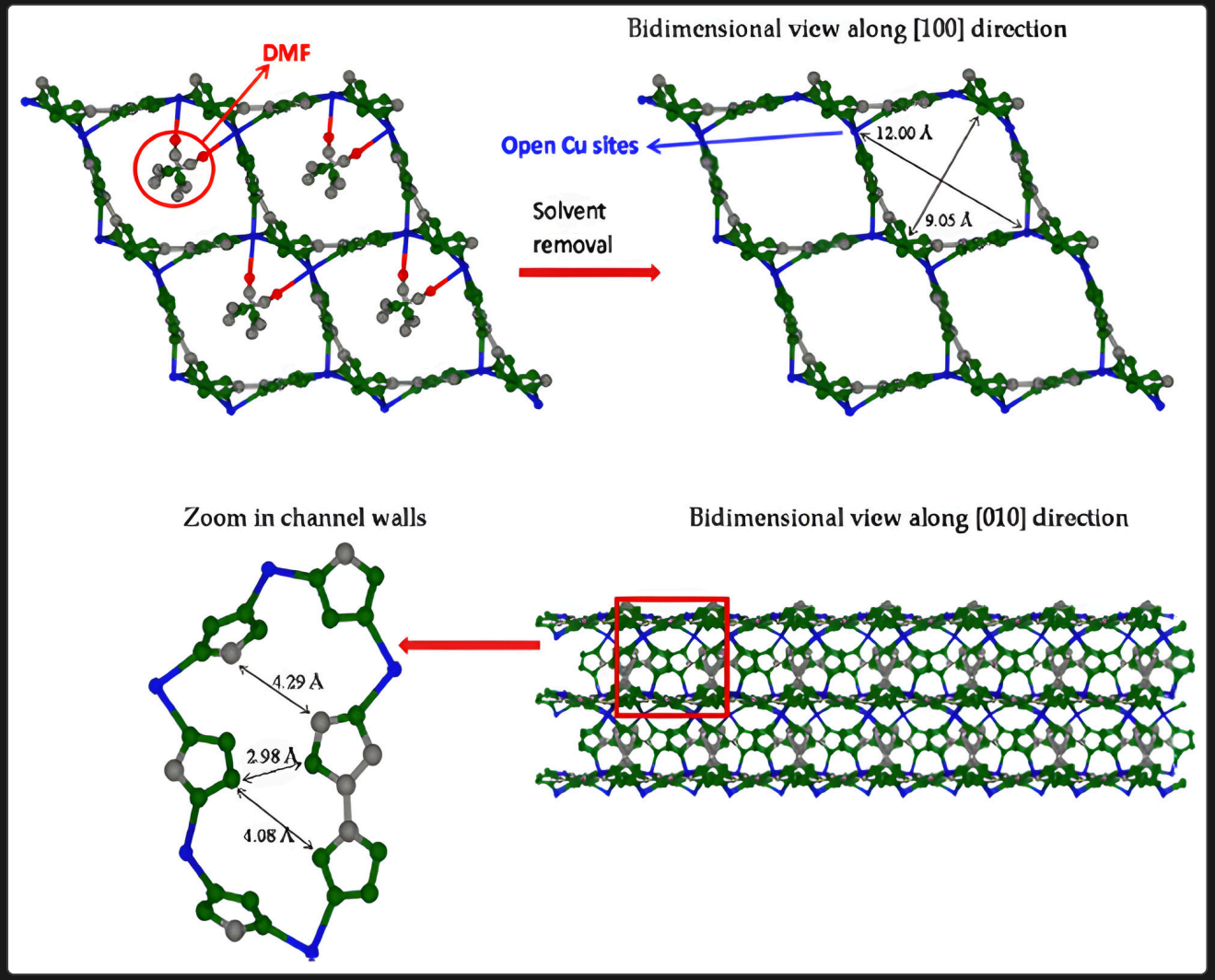
Gases	Ion-implant tools in chip fabs need toxic dopants: **arsine (AsH_3)**, **phosphine (PH_3)**, **BF_3**
Storage today	**High-pressure steel cylinders**, often above 100 psig
Leak risk	One bottle holds enough toxic gas to endanger workers and trigger a **fab-wide shutdown**
Regulatory burden	Redundant ventilation, scrubbing, and emergency protocols raise cost and insurance
Cylinder heel	Unused residual gas: waste that still poses disposal risks
What the MOF changes	The pores **adsorb and store the gas**, so the cylinder holds the same usable inventory at **sub-atmospheric pressure** (near vacuum to ~1 atm) and desorbs it to feed the tool

ION-X: WHY FABS PAY FOR IT

Safety	Breach the cylinder and no pressurized toxic gas rushes out, which cuts both the odds and the severity of a catastrophic event
Regulatory relief	A lower safety classification than high-pressure bottles: lower facility cost, easier permitting, fewer insurance penalties
Continuity	No shutdowns from leaks or alarms, which cost more than **$1M a day** in lost production
Waste	Lower heel volumes mean less toxic waste to manage and dispose of
Compatibility	ION-X cylinders plug straight into existing ion-implant tools, with no redesign

They convert a toxic-gas supply chain from a high-pressure hazard into a sub-atmospheric, fail-safe consumable, saving fabs money on risk, compliance, and downtime.

OPEN CU SITES IN A MOF CHANNEL



ION-X PERFORMANCE AT AXCELIS

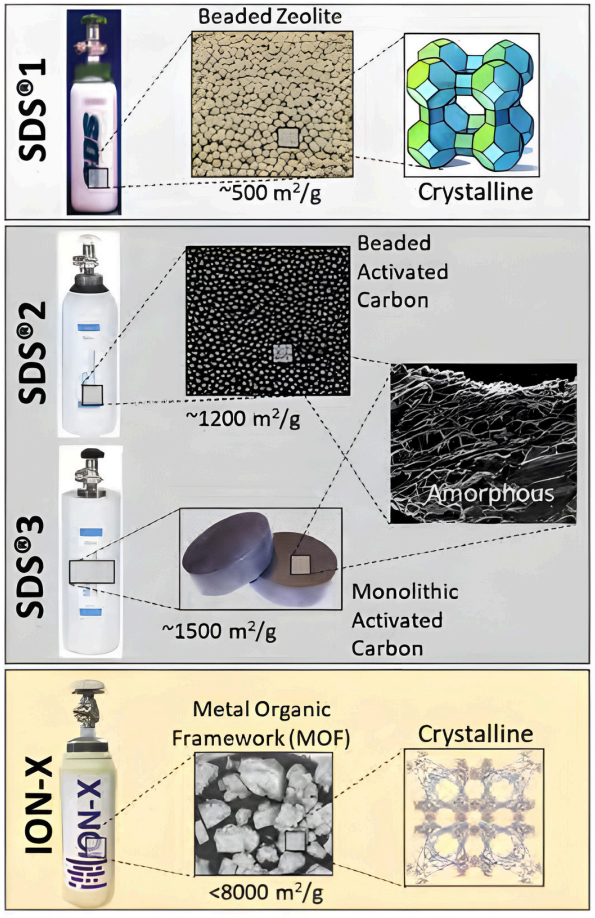


Fig. 2. Structural and physical properties of adsorbent materials used to store and deliver ion implant dopant gases

ION-X Dopant Gas Delivery System Performance Characterization at Axcelis

J. Arnó, O. K. Farha, W. Morris, P. W. Siu, G. M Tom, M. H. Weston, P. E. Fuller,
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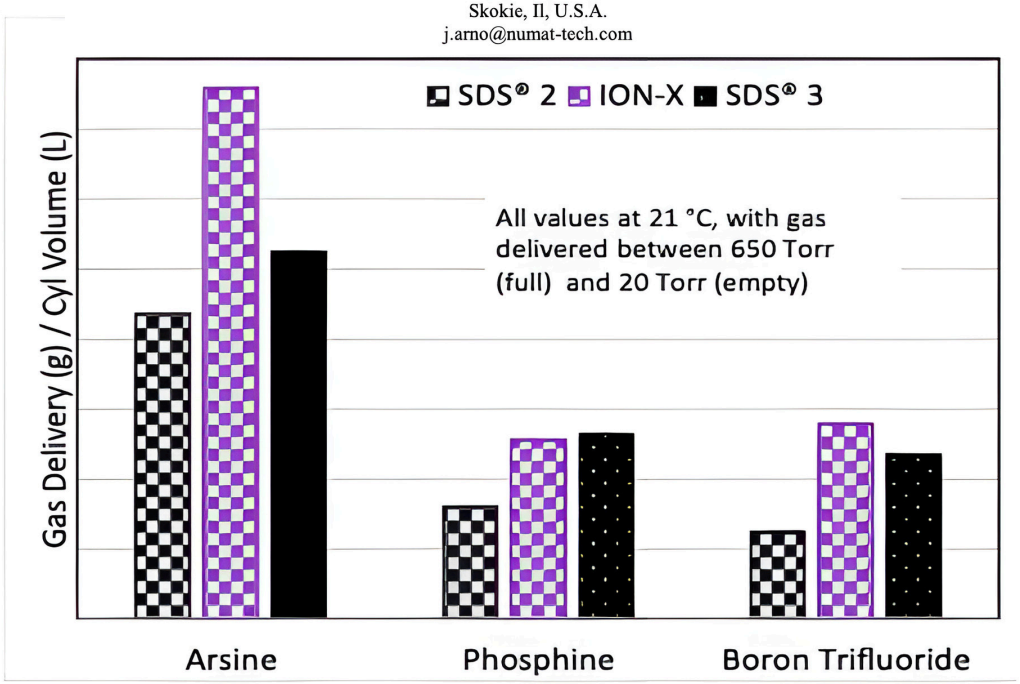


Fig. 3. Volumetric dopant gas delivery comparison between ION-X and activated carbon-based products

J. Arnó and co-workers, NuMat Technologies, Skokie, IL — Figs. 2 and 3

ION-X (MOF) VS SDS (CARBON) CYLINDERS

Metric	ION-X (MOF)	SDS (Carbon)
Gas delivered	Higher usable capacity (20–50% more for some gases)	Lower deliverable, larger residual heel
Flow stability	Stable delivery down to very low pressures (few Torr)	Delivery falls off sooner; larger heel
Residual gas (heel)	Very low; most gas is recoverable	Higher heel, more waste
Purity / contamination	Low metals, stable across cycles	Acceptable, but batch variability possible
Reproducibility	Highly consistent (crystalline pores)	More variability (heterogeneous carbon)
Safety	Sub-atmospheric storage	Also sub-atmospheric storage (same safety principle)

SUMMARY

One tetrahedron, linked more and more openly: the O:Si ratio sets the motif, and the motif sets the size of the pore.

Silicates	Dominate Earth's crust; their tetrahedral networks are defined by O:Si ratios
Motifs	Isolated tetrahedra, 1D chains, 2D sheets, and 3D frameworks
Zeolites	Al/Si tetrahedral frameworks; charge-balancing cations generate accessible pores
Key zeolites	Sodalite, zeolite A, and faujasite differ in connectivity and pore size, 4 to 7.4 Å
Pore classes	Microporous below 2 nm, mesoporous 2 to 50 nm, macroporous above 50 nm
MOFs	Metal–oxide clusters linked by organic ligands: the same network ideas, made highly porous and tunable

MOF-5 closes the loop: decorate a cubic net, expand the linker, and the pore grows to order.

YOU TRY IT NOW: PROBLEM 1.22

Given	CrO_3 is built from chains of corner-sharing chromium-centered tetrahedra
Find	the **Niggli formula** and the simple **crystal-chemical formula** for this structure

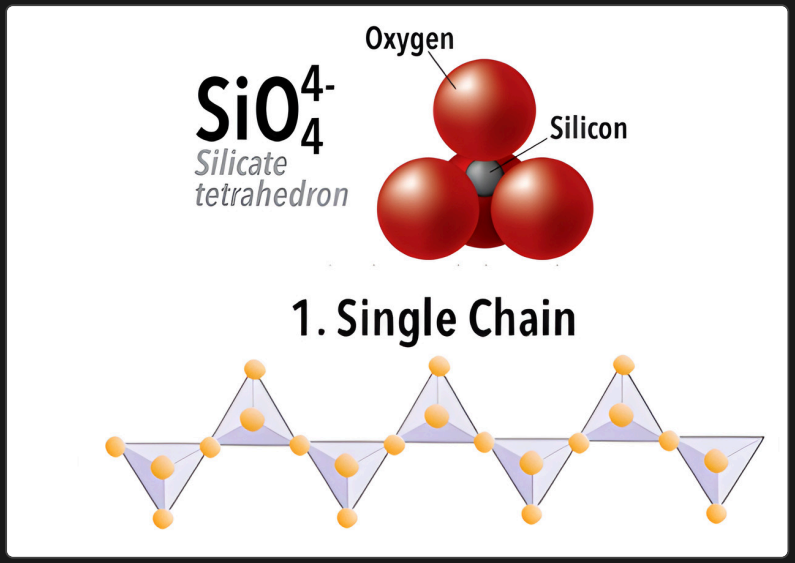
NIGGLI FORMULA: COUNTING THE CORNERS

Structure	Corner-sharing tetrahedra in 1-D chains → **CrO_4 tetrahedra**
Niggli formula	one **cation-centered polyhedron**: each oxygen as **how many** over **how many share it**

Bridging O	Terminal O
2 corners join the next tetrahedron	the other 2 are this Cr's alone
2/2	2/1

$$CrO_{2/2 + 2/1}$$

2/2 is 1 and 2/1 is 2, so we recover **CrO_3**, and the numerators 2 + 2 give **CN(Cr) = 4**.



Silicate tetrahedron SiO_4^{4-}: oxygen and silicon labelled, above "1. Single Chain". Cr sits where Si does.

CRYSTAL-CHEMICAL FORMULA ALGORITHM

1. List atoms	Write down each unique cation and anion site
2. Tag cations	Add the coordination number, how many neighbors, and the geometry: **t** tetrahedral, **o** octahedral, and so on
3. Tag anions	Mark how many cations each anion connects to: **O[1]** terminal, **O[2]** bridging, **O[3]** 3-connected
4. Check balances	Bonds from cations = bonds accepted by anions; the anion count = the formula stoichiometry; the charges must cancel
5. Keep it simple	Only the distinct sites and connectivities needed to show the bonding

WORKED SOLUTION: CrO_3

Given	Cr is tetrahedral; tetrahedra link by **corners** to form **1D chains**
Sites	Cr, bridging O (O_{br}), terminal O (O_t)
Coordination	Cr[4t]; O_{br}[2n] (bent Cr–O–Cr); O_t[1]

Balances, per one Cr

Stoichiometry	Connectivity	Solve
$b + t = 3$	$4 = 2b + t$	subtract $b = 1,\ t = 2$

$$^{1}_{\infty}[\mathrm{Cr}[4t]\ \mathrm{O}[2n]\ \mathrm{O}_2[1]]$$

One crystallographically distinct **infinite chain**; each Cr tetrahedral; one **bridging** O per formula (nonlinear) and two **terminal** O.

PRACTICE QUESTIONS

Work the Lecture 6 practice questions before the next class.

Open the Lecture 6 practice questions