

## Learning Objectives for Networks

- Understand how **coordination numbers** lead to network topologies in crystal structures.
- Define key terms: **vertex** (linking point) and **linker/edge** (connection between vertices).
- Recognize that linkers can be **bonds, atoms, or polyatomic groups** (e.g., O in zeolites,  $\text{CN}^-$  in Prussian blue, dicarboxylates in MOFs).
- Distinguish between:
  - **Uninodal nets** (all vertices equivalent).
  - **Binodal nets** (two different kinds of vertices).
  - **Regular nets** (all vertices, edges, and angles equivalent).
- Apply network ideas to both **simple binary compounds** and **framework materials** (zeolites, MOFs).
- Relate real crystal structures (e.g.,  $\text{TiO}_2$  as a 6–3 binodal net) to their underlying network topology.

# Network Vocabulary

**Vertex** = Linking point (in our discussion the vertex will be generally be an atom, though in some cases it will be a cluster of atoms)

**Linker** = Connects vertices, can take various forms

- A bond, such as in diamond
- Atom, such as the oxygen atoms in a zeolite/silicate
- Molecule, such as a dicarboxylic acid in a MOF

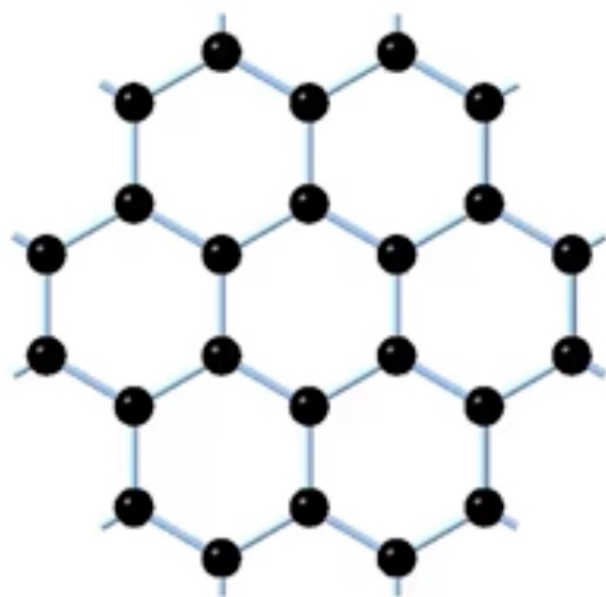
**Uninodal Network** = All vertices are the same

**Binodal Network** = Two types of vertices. We use the symbolism (N,M) connected net. For example,  $\text{TiO}_2$  is a (6,3) net.

**Regular Network** = All vertices, edges and angles are equivalent by symmetry

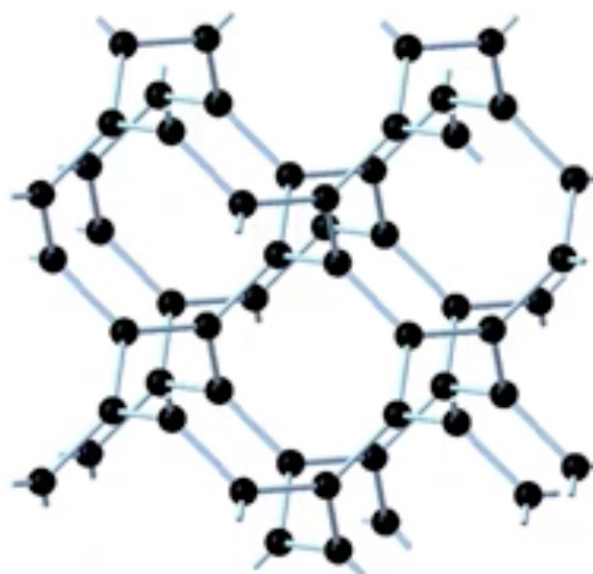
See: M. O'Keeffe, M. Eddaoudi, H. Li, T. Reinke & O.M. Yaghi, *J. Solid State Chem.* **152**, 3-20 (2000).

## Uninodal 3-Connected Nets



**Graphite (2D Net)**  
Space Group =  $P6_3mc$   
Site symmetry =  $3m$  ( $C_{3v}$ )

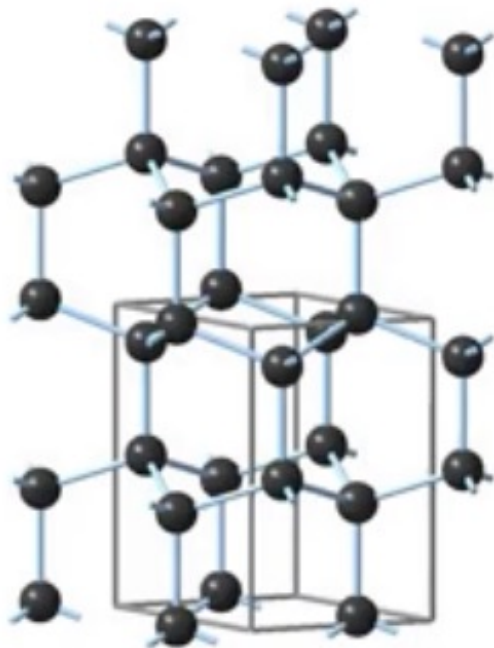
*Regular network*



**SrSi<sub>2</sub> (Silicon network)**  
Space Group =  $I4_132$   
Site symmetry =  $32$  ( $D_3$ )

---

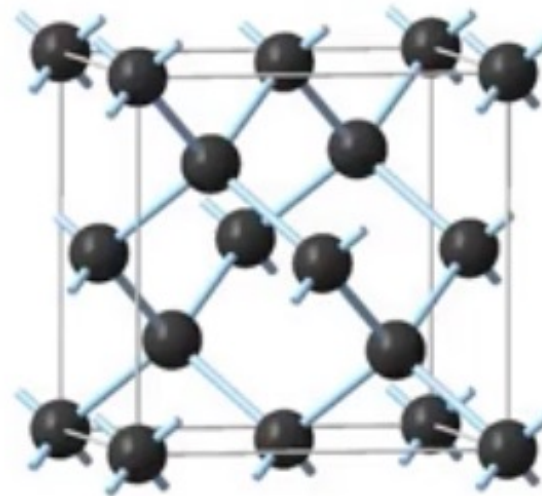
## Uninodal 4-Connected Nets



**Lonsdaleite**

Space Group =  $P6_3/mmc$   
Site symmetry =  $3m (C_{3v})$

*Regular network*

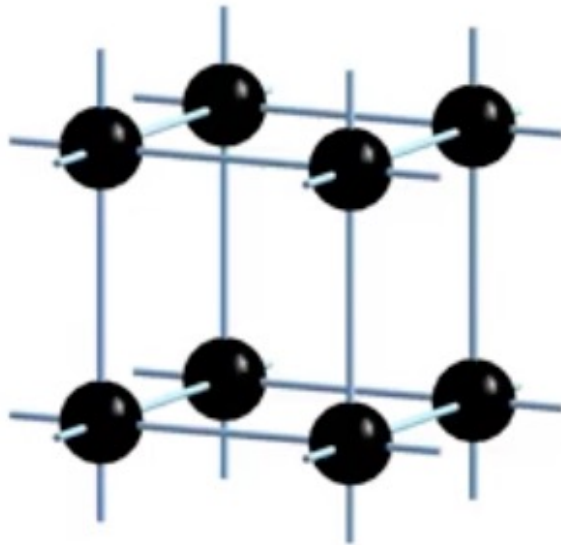


**Diamond**

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

# Uninodal 6- and 8-Connected Nets

*Regular network*

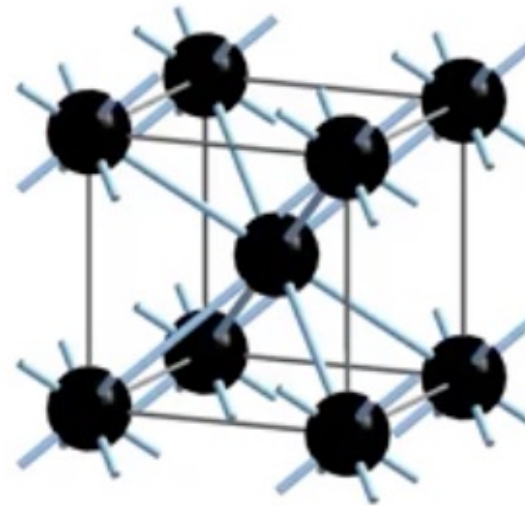


**Primitive cubic (Po)**

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

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

*Regular network*

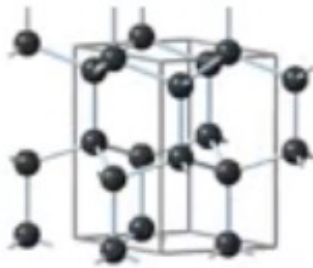


**Body-centered cubic (Fe)**

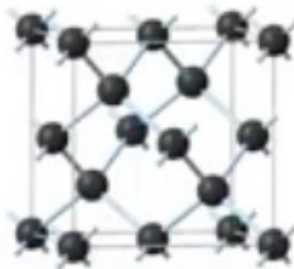
Space Group =  $Im\bar{3}m$

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

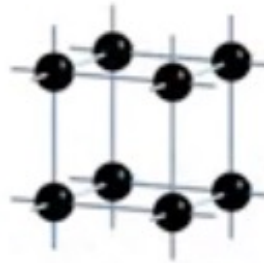
## Site Ordered Homeotypes



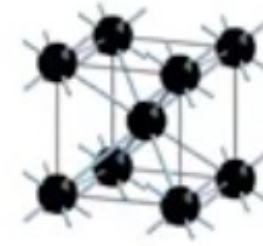
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )



4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )

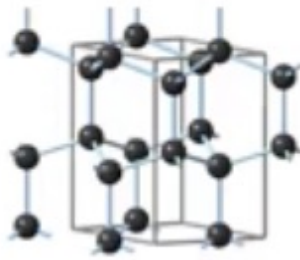


6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )

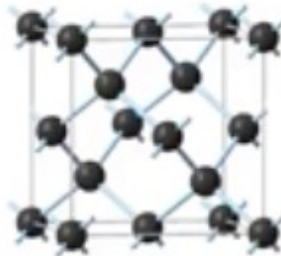


8-connected net  
**Body-centered Cubic**  
( $Im\bar{3}m$ )

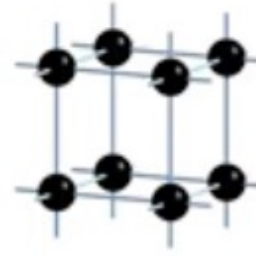
# Site Ordered Homeotypes



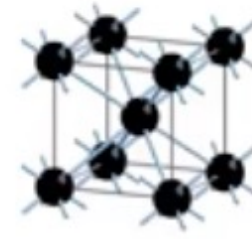
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )



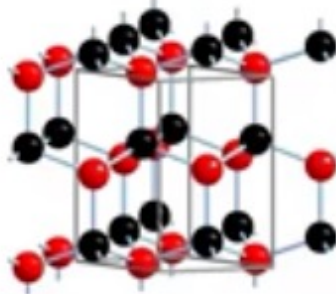
4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )



6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )

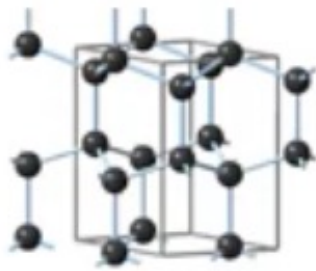


8-connected net  
**Body-centered Cubic**  
( $Im\bar{3}m$ )

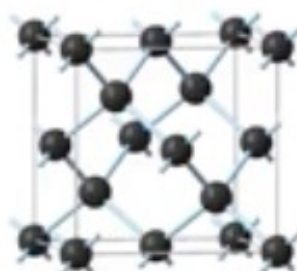


4,4-net  
**Wurtzite**  
( $P6_3mc$ )

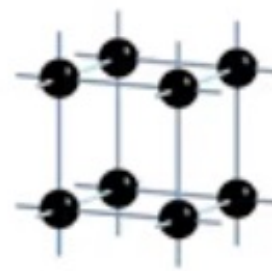
# Site Ordered Homeotypes



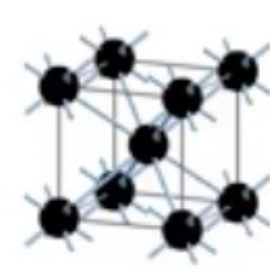
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )



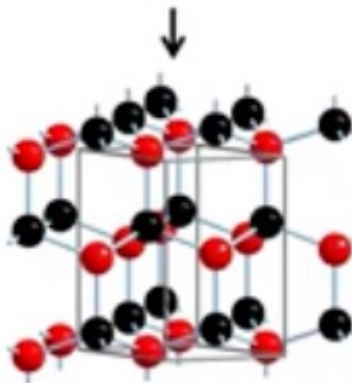
4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )



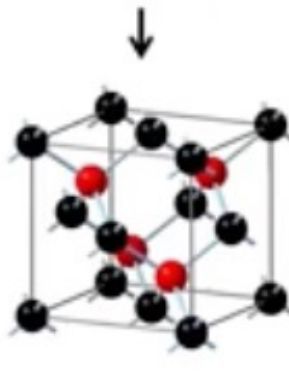
6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )



8-connected net  
**Body-centered Cubic**  
( $Im\bar{3}m$ )



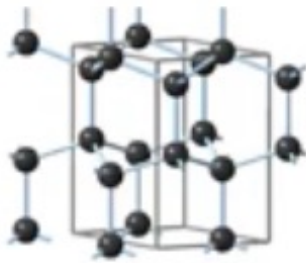
4,4-net  
**Wurtzite**  
( $P6_3mc$ )



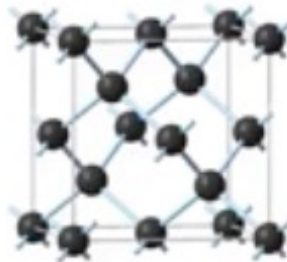
4,4-net  
**Sphalerite**  
( $F\bar{4}3m$ )



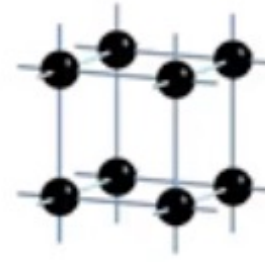
# Site Ordered Homeotypes



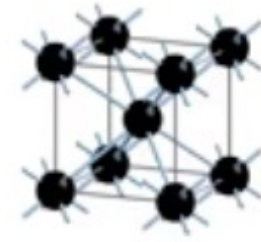
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )



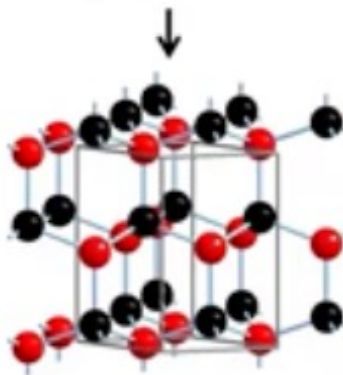
4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )



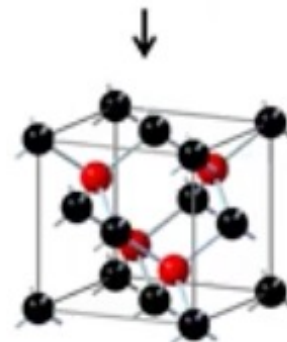
6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )



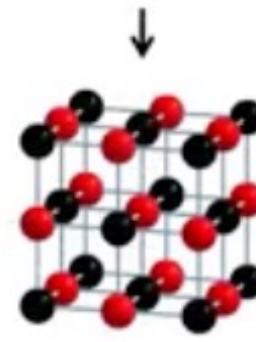
8-connected net  
**Body-centered Cubic**  
( $Im\bar{3}m$ )



4,4-net  
**Wurtzite**  
( $P6_3mc$ )



4,4-net  
**Sphalerite**  
( $F\bar{4}3m$ )

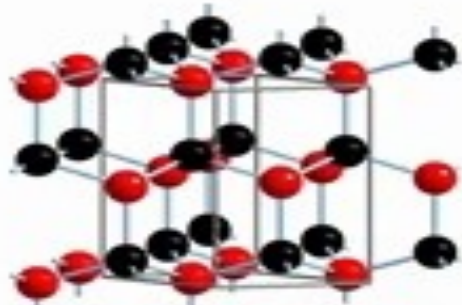


6,6-net  
**NaCl** ( $Fm\bar{3}m$ )

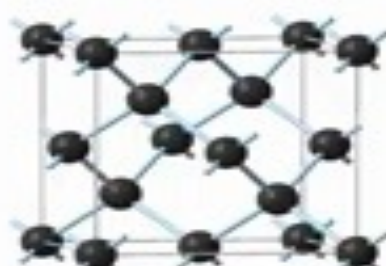
# Site Ordered Homeotypes



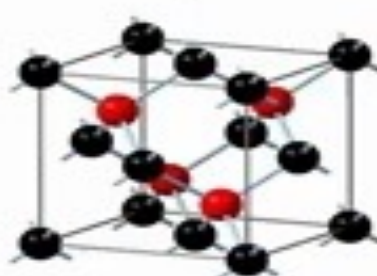
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )



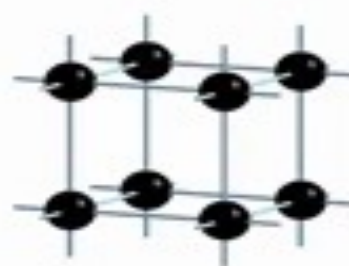
4,4-net  
**Wurtzite**  
( $P6_3mc$ )



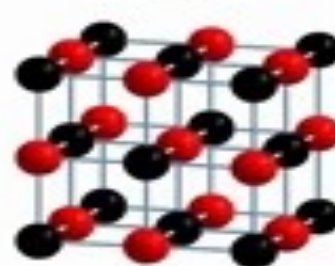
4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )



4,4-net  
**Sphalerite**  
( $F\bar{4}3m$ )



6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )



6,6-net  
**NaCl** ( $Fm\bar{3}m$ )



8-connected net  
**Body-centered  
Cubic** ( $Im\bar{3}m$ )

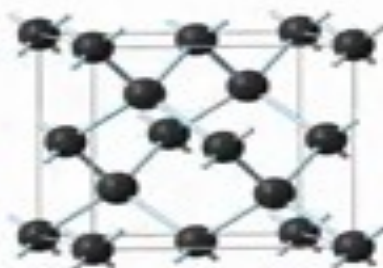


8,8-net  
**CsCl** ( $Pm\bar{3}m$ )

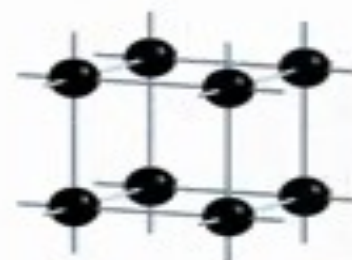
# Network Expansion



4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )  
Si(4f)



4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )  
Si(8a)

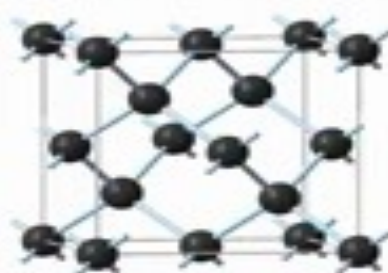


6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )  
Po(1a)

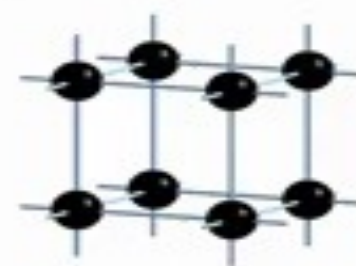
# Network Expansion



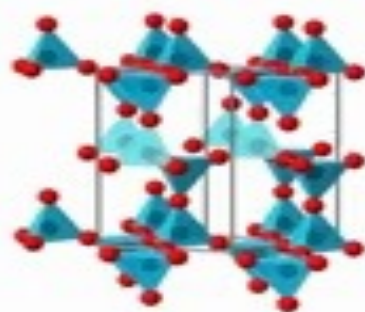
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )  
Si(4f)



4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )  
Si(8a)



6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )  
Po(1a)

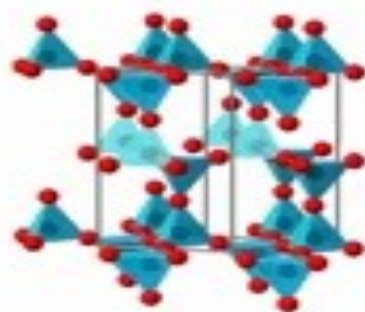


**Tridymite**  
( $P6_3/mmc$ )  
Si(4f), O(2c), O(6g)

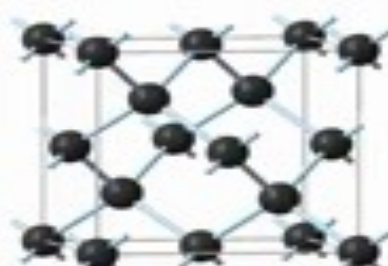
# Network Expansion



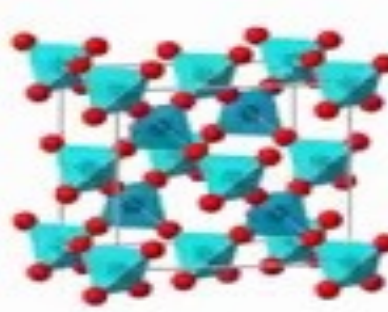
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )  
Si(4f)



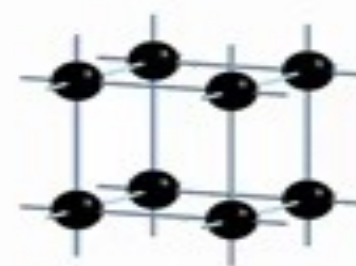
**Tridymite**  
( $P6_3/mmc$ )  
Si(4f), O(2c), O(6g)



4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )  
Si(8a)

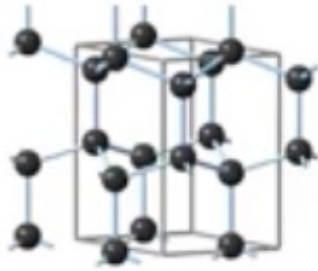


**Cristobalite**  
( $F\bar{4}3m$ )  
Si(8a), O(16c)

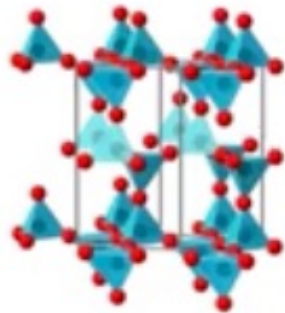


6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )  
Po(1a)

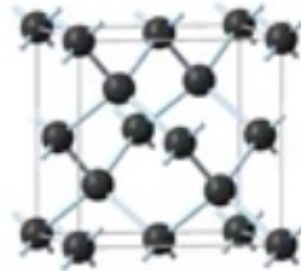
# Network Expansion



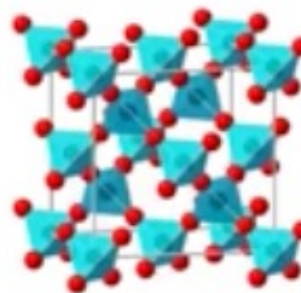
4-connected net  
**Lonsdaleite**  
( $P6_3/mmc$ )  
Si(4f)



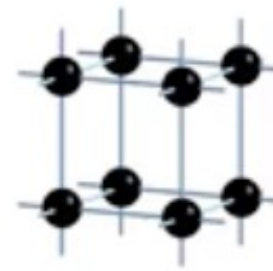
**Tridymite**  
( $P6_3/mmc$ )  
Si(4f), O(2c), O(6g)



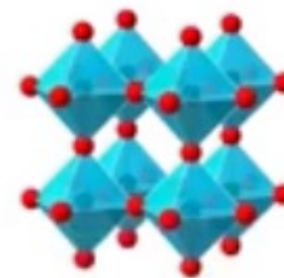
4-connected net  
**Diamond**  
( $Fd\bar{3}m$ )  
Si(8a)



**Cristobalite**  
( $F\bar{4}3m$ )  
Si(8a), O(16c)

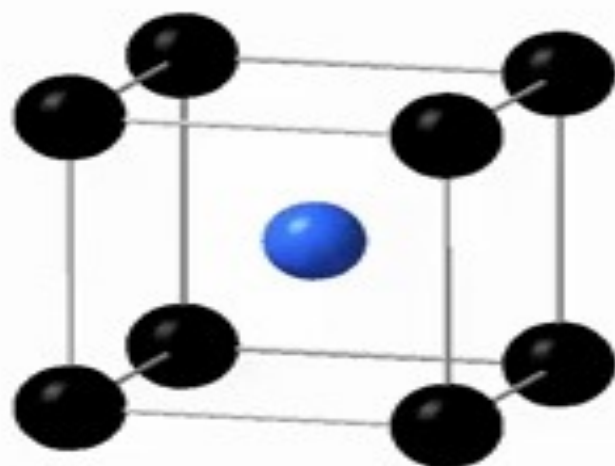


6-connected net  
**Primitive Cubic**  
( $Pm\bar{3}m$ )  
Po(1a)



**ReO<sub>3</sub>**  
( $Pm\bar{3}m$ )  
Re(1a), O(3d)

## Decoration



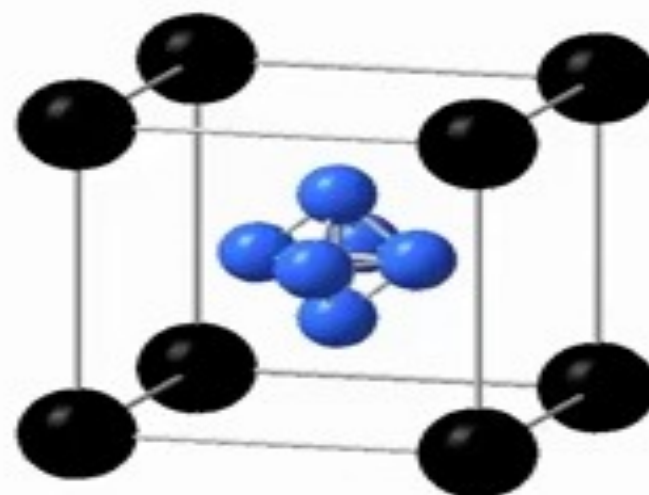
### CaTe (CsCl structure type)

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

$a = 3.387 \text{ \AA}$

Ca (1a) 0 0 0

Te (1b)  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$



### CaB<sub>6</sub>

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

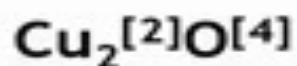
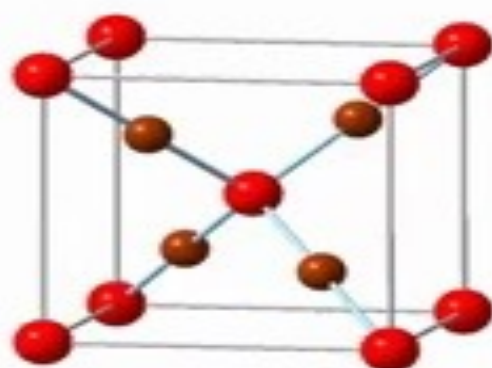
$a = 4.15 \text{ \AA}$

Ca (1a) 0 0 0

B (6f)  $\frac{1}{2} \frac{1}{2} 0.20$

# Interpenetration

Unit cell view

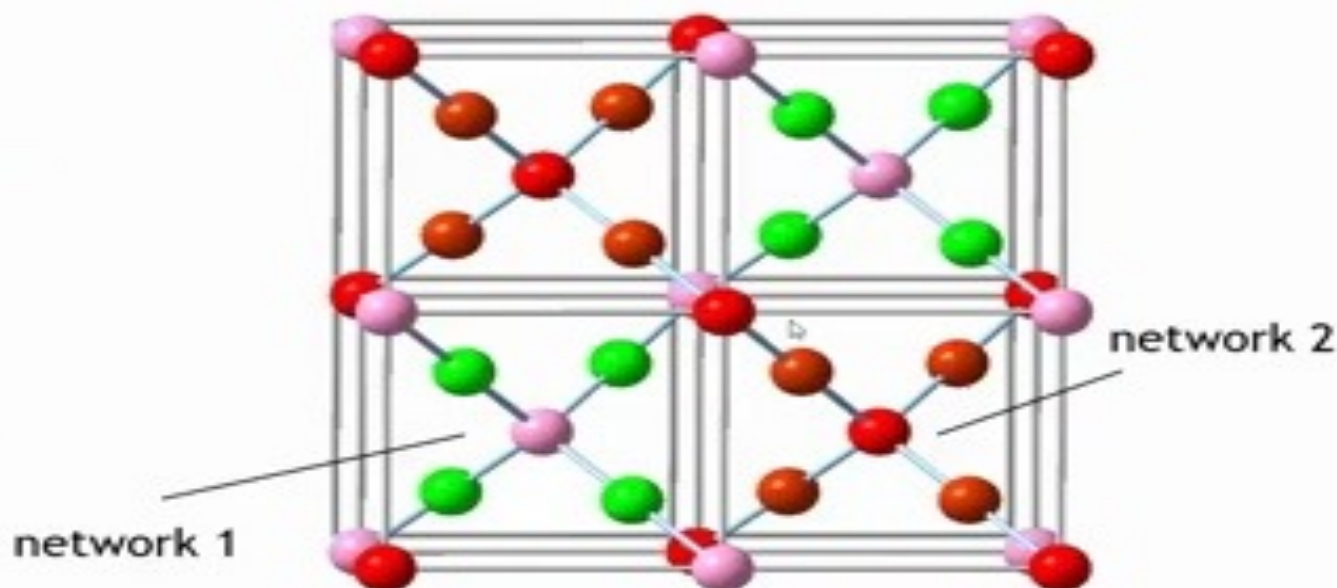


Space Group:  $Pn\bar{3}m$

$a = 4.257 \text{ \AA}$

Cu (2a) 0 0 0

O (4b)  $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$

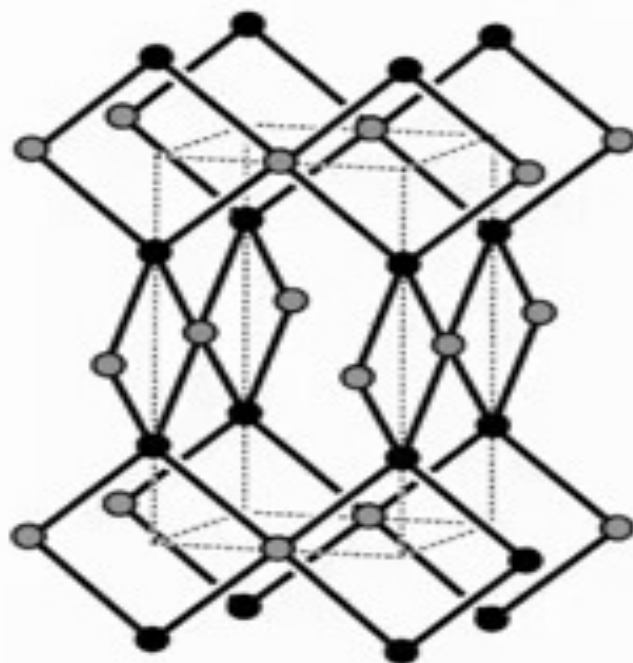


False colors have been used here to show how Cu<sub>2</sub>O can be described as two independent, yet interpenetrating cristobalite networks.

## Some Important Binodal Nets

(N,M)-Net	Coordination Figures		Net (Example)
4,2	Tetrahedron	Linear (bent)	SiO <sub>2</sub> (cristobalite, tridymite)
4,3	Tetrahedron	Triangle	Si <sub>3</sub> N <sub>4</sub>
4,4	Tetrahedron	Tetrahedron	ZnS (sphalerite, wurtzite)
4,3	Square	Triangle	Pt <sub>3</sub> O <sub>4</sub>
4,4	Square	Square	NbO
4,4	Square	Tetrahedron	Cooperite (PtS)
6,2	Octahedron	Linear	ReO <sub>3</sub>
6,3	Octahedron	Triangle	TiO <sub>2</sub> (rutile, anatase)
6,4	Octahedron	Tetrahedron	Corundum (Al <sub>2</sub> O <sub>3</sub> )
6,6	Octahedron	Octahedron	Rock salt (NaCl)
6,6	Octahedron	Trigonal prism	NiAs
8,4	Cube	Tetrahedron	Fluorite (CaF <sub>2</sub> )
8,8	Cube	Cube	CsCl

## (4,4) Nets



### Cooperite (PtS)

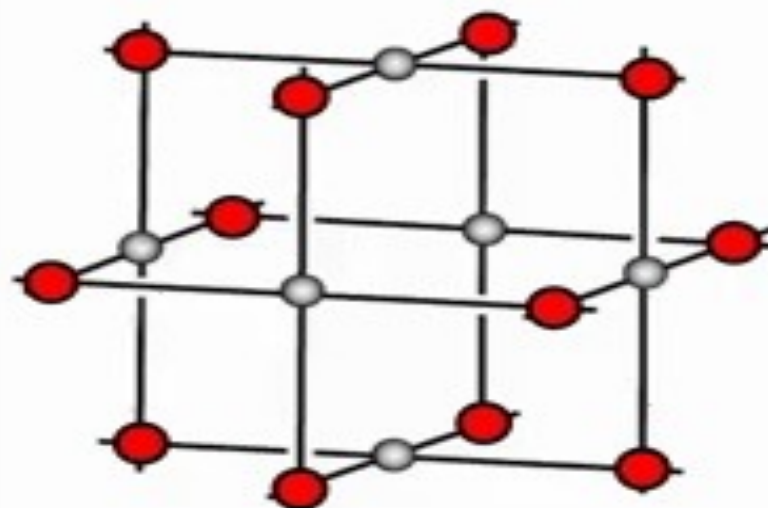
Space Group =  $P4_2/mmc$

$a = 3.48 \text{ \AA}$        $c = 6.11 \text{ \AA}$

Pt (2c) 0  $\frac{1}{2}$  0

S (2f)  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{4}$

*Regular network*



### NbO

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

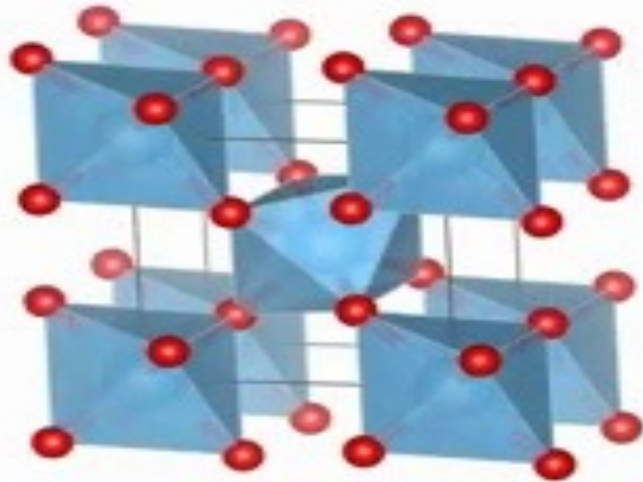
$a = 4.21 \text{ \AA}$

Nb (3c)  $\frac{1}{2}$   $\frac{1}{2}$  0

O (3d)  $\frac{1}{2}$  0 0

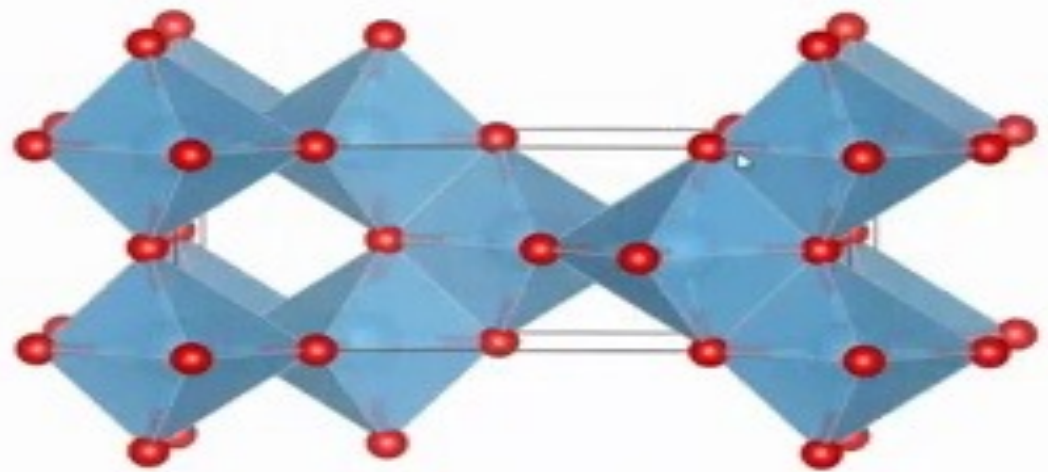
# Polymorphs of $\text{TiO}_2$

## Rutile



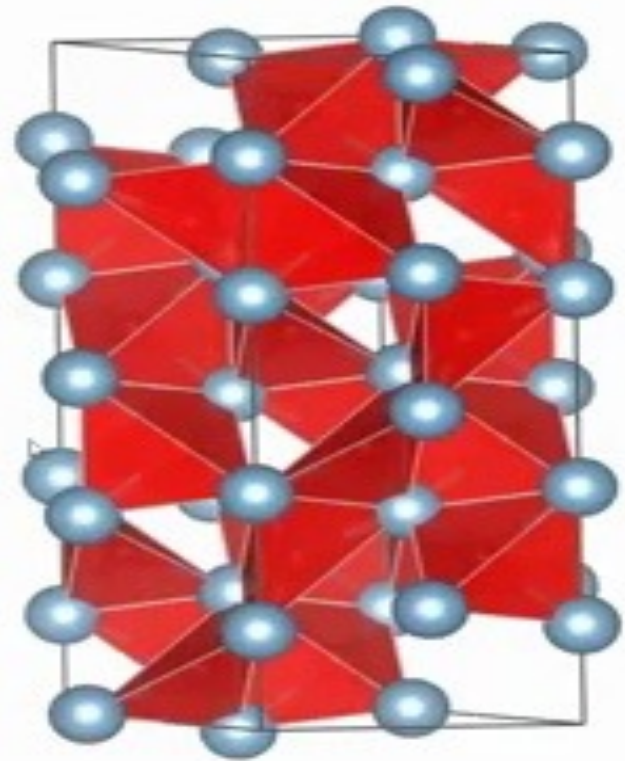
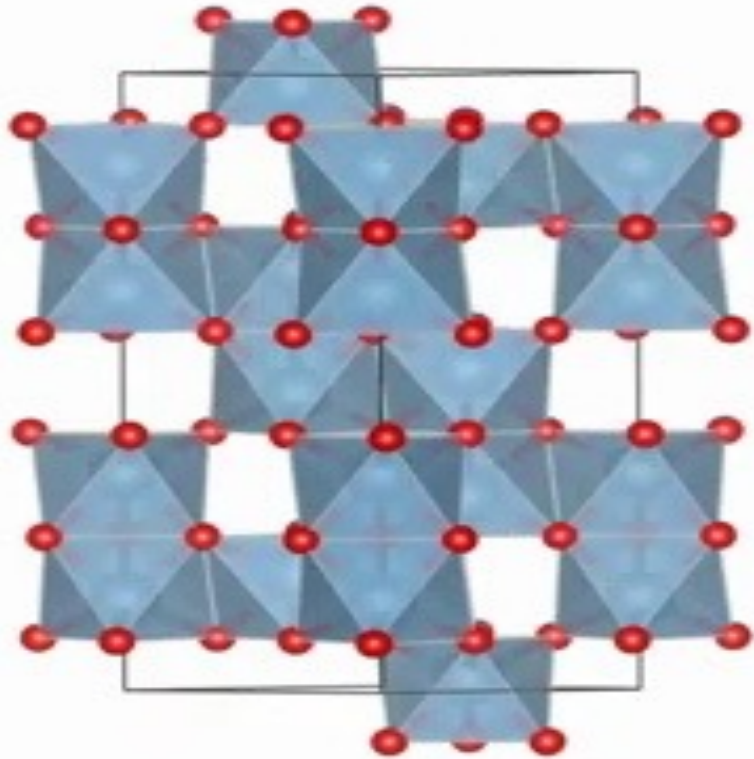
Space group:  $P4_2/mnm$   
 $Z = 2$   
Ti (2a)  $mmm$   
O (4f)  $2mm$

## Anatase



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

# Corundum



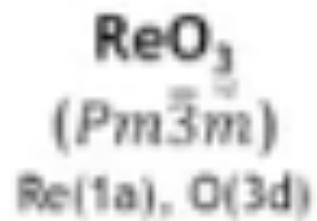
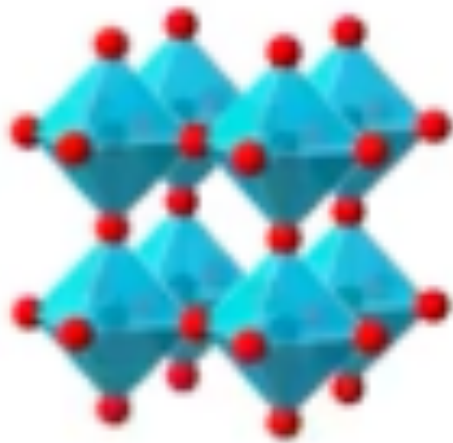
The (6,4) network formed by two of the most common environments - octahedron & tetrahedron - does not give a regular environment for either.

## Summary for Networks

- Networks describe **how atoms connect**, abstracted into **vertices and linkers**.
- **Uninodal nets**: all vertices identical (e.g., diamond, graphite, cubic/bcc nets).
- **Binodal nets**: two vertex types with different coordination (e.g., Ti 6–O 3 in  $\text{TiO}_2$ ).
- **Regular nets**: rare, highly symmetric cases where all vertices, edges, and angles are equivalent.
- **Transformations of nets**:
  - **Site ordering** → compounds like NaCl, CsCl, sphalerite, wurtzite.
  - **Network expansion** → insert atoms as linkers (e.g.,  $\text{ReO}_3$ , perovskite).
  - **Decoration** → replace simple vertices with polyatomic clusters (e.g.,  $\text{CaB}_6$ ).
  - **Interpenetration** → overlapping nets (e.g.,  $\text{Cu}_2\text{O}$ ).
- Binodal nets provide a systematic way to connect **empirical formulas, coordination numbers, and real crystal structures**.

## You try it now:

- 1.27  $\text{ReO}_3$  has a 3D network of octahedrally coordinated rhenium. Determine the  $N$ ,  $M$ -connectivity for this binodal network



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

Why:

- In  $\text{ReO}_3$ , Re atoms sit at the corners of a simple-cubic framework and each Re is **octahedrally coordinated** by O  $\rightarrow$  Re CN = 6.
- Each O lies midway along a Re-Re edge (think "perovskite without the A-cation"): every O **bridges exactly two Re**  $\rightarrow$  O CN = 2.
- There are **two node types** (Re and O), so it's **binodal**, and the node connectivities are **6 and 2**  $\rightarrow$  (6,2).

# Silicates and Microporous Solids

## Learning Objectives

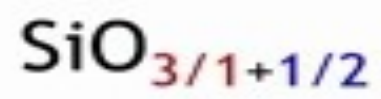
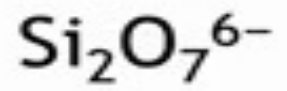
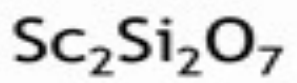
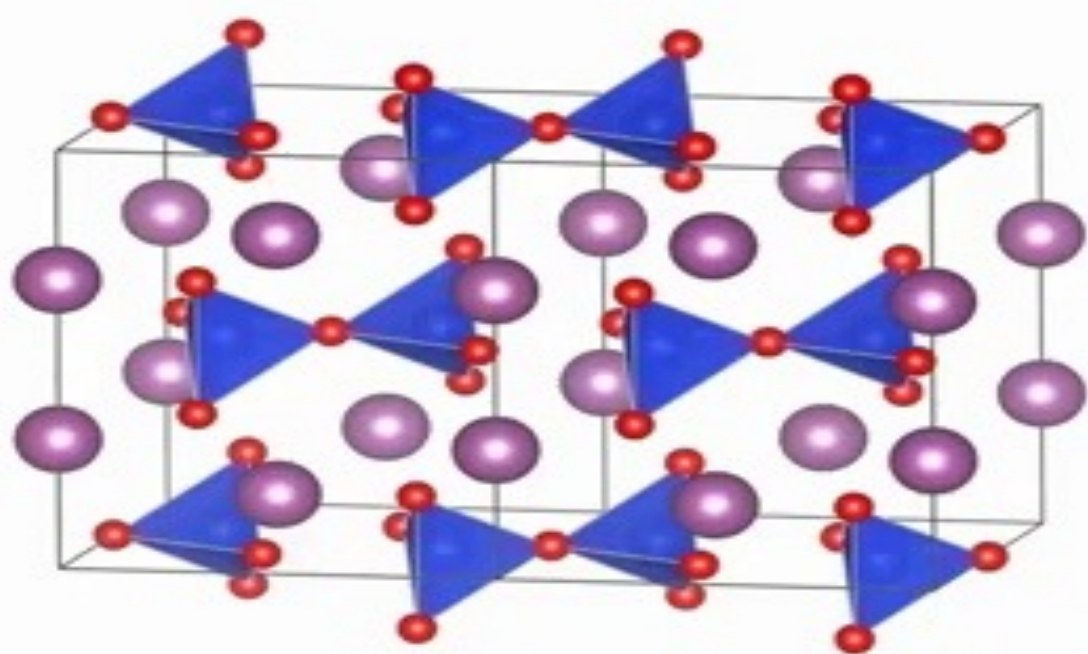
By the end of this lecture, you should be able to:

- Explain how silicate structures are built from corner-sharing  $\text{SiO}_4$  tetrahedra.
- Use the **Niggli formula** to relate oxygen: silicon ratios to structural motifs.
- Identify structural motifs (isolated tetrahedra, chains, rings, sheets, frameworks) from O:Si ratios.
- Describe how **zeolites** form from Al/Si tetrahedra and why cations create porosity.
- Recognize key zeolite building blocks (sodalite cage, zeolite A, faujasite) and their pore sizes.
- Distinguish microporous, mesoporous, and macroporous solids.
- Understand the basics of **MOFs** and how MOF-5 is constructed from nets.

# Silicates

- Silicates are the most common minerals in the earth's crust
- Silicates represent about one third of known inorganic crystal structure types
- Silicates generally share a number of common features
  - Tetrahedrally coordinated silicon
  - If connected tetrahedra are connected through corner sharing
- The O:Si ratio is an important parameter in dictating the extent to which the tetrahedra are connected

# Niggli Formula



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 <sub>2</sub>	SiO <sub>(4/2)</sub>	3D network of corner <sub>b</sub> connected tetrahedra
2.5			
3			
3.5			
4	ZrSiO <sub>4</sub>	SiO <sub>(4/1)</sub>	Isolated tetrahedra

bridging oxygen

terminal oxygen

## O:Si ratio and Niggli Formula

O:Si	Example	Niggli Formula	Network Connectivity
2	SiO <sub>2</sub>	SiO <sub>(4/2)</sub>	3D network of corner connected tetrahedra
2.5	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	SiO <sub>(1/1) + (3/2)</sub>	2D sheets of corner connected tetrahedra
3			
3.5			
4	ZrSiO <sub>4</sub>	SiO <sub>(4/1)</sub>	Isolated tetrahedra

bridging oxygen

terminal oxygen

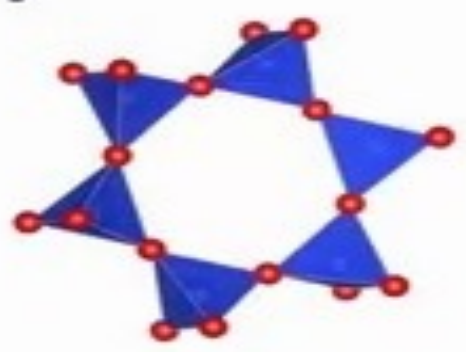
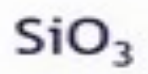
## O:Si ratio and Niggli Formula

O:Si	Example	Niggli Formula	Network Connectivity
2	SiO <sub>2</sub>	SiO <sub>(4/2)</sub>	3D network of corner connected tetrahedra
2.5	Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	SiO <sub>(1/1) + (3/2)</sub>	2D sheets of corner connected tetrahedra
3	Na <sub>2</sub> SiO <sub>3</sub>	SiO <sub>(2/1) + (2/2)</sub>	1D chains or rings of corner connected tetrahedra
3.5	Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	SiO <sub>(3/1) + (1/2)</sub>	dimers of corner connected tetrahedra
4	ZrSiO <sub>4</sub>	SiO <sub>(4/1)</sub>	Isolated tetrahedra

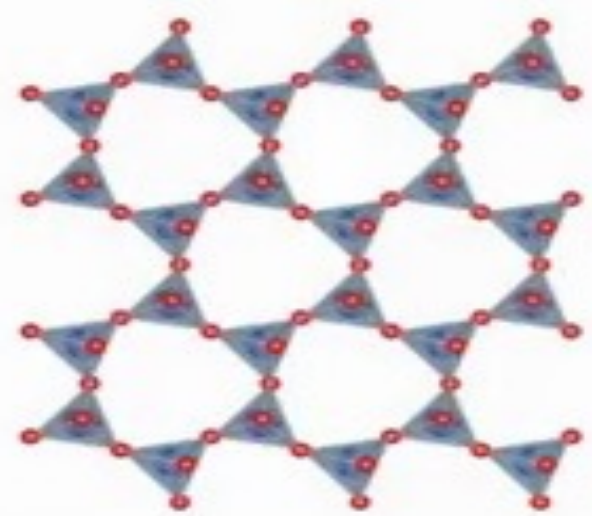
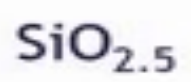
bridging oxygen

terminal oxygen

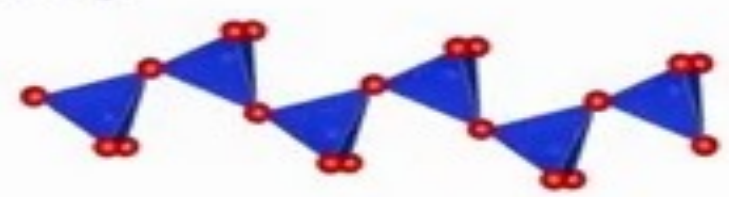
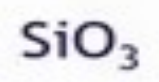
# Silicate Structures



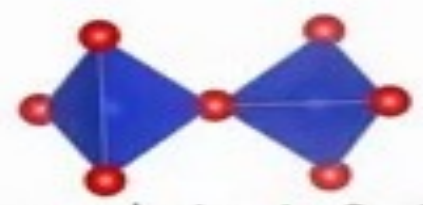
$\text{SiO}_{2/1+2/2}$  rings in beryl  
( $\text{Al}_2\text{Be}_2\text{Si}_6\text{O}_{18}$ )



$\text{SiO}_{1/1+3/2}$  sheets in mica



$\text{SiO}_{2/1+2/2}$  chains in  $\text{Na}_2\text{SiO}_3$



$\text{SiO}_{3/1+1/2}$  chains in  $\text{Sc}_2\text{Si}_2\text{O}_7$

# Porous Materials

**Zeolites** (Boiling stone) = Framework materials built from corner connected  $\text{SiO}_{4/2}$  and  $\text{AlO}_{4/2}$  tetrahedra

**Zeotypes** = Similar to zeolites but with other elements on the tetrahedral sites

**Metal Organic Frameworks (MOFs)** = Porous coordination polymers made up of clusters of metal ions or clusters connected by multidentate polyatomic ligands.

# Porous Materials

**Zeolites** (Boiling stone) = Framework materials built from corner connected  $\text{SiO}_{4/2}$  and  $\text{AlO}_{4/2}$  tetrahedra

**Zeotypes** = Similar to zeolites but with other elements on the tetrahedral sites

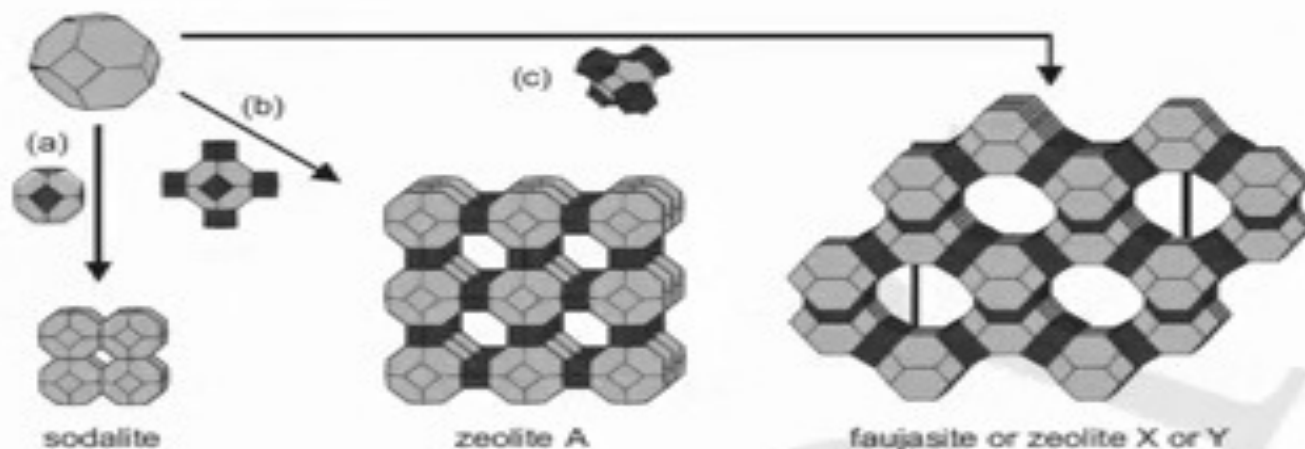
**Metal Organic Frameworks (MOFs)** = Porous coordination polymers made up of clusters of metal ions or clusters connected by multidentate polyatomic ligands.

- Microporous materials (pore size <2 nm)
- Mesoporous materials (pore size 2-50 nm)
- Macroporous materials (pore size >50 nm)

# Important Zeolites

Name	Framework	Ring	Accessible volume*	Channel dimensions
Sodalite	$\text{Al}_6\text{Si}_6\text{O}_{24}^{6-}$	6	0	---
Zeolite A	$\text{Al}_{12}\text{Si}_{12}\text{O}_{48}^{12-}$	8	21.4%	$4.1 \text{ \AA} \times 4.1 \text{ \AA}$
Faujasite	$\text{Al}_{58}\text{Si}_{134}\text{O}_{384}^{58-}$	12	27.4%	$7.4 \text{ \AA} \times 7.4 \text{ \AA}$

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



# Uninodal 4-Connected Nets

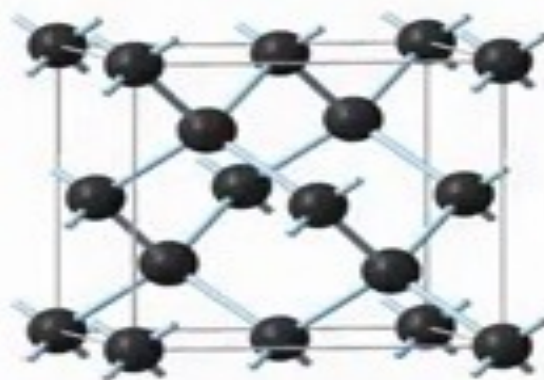


**Lonsdaleite**

Space Group =  $P6_3/mmc$

Site symmetry =  $3m$

Site symmetry =  $C_{3v}$

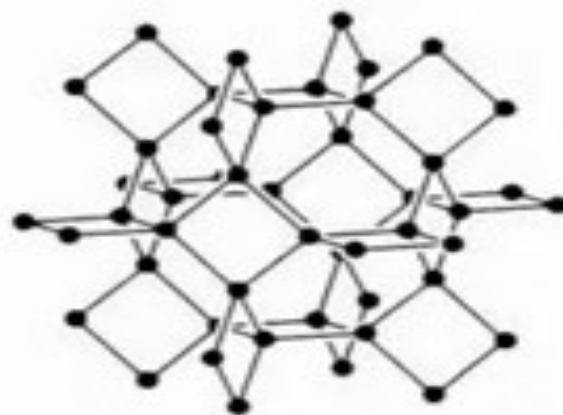


**Diamond**

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

Site symmetry =  $\bar{4}3m$

Site symmetry =  $T_d$



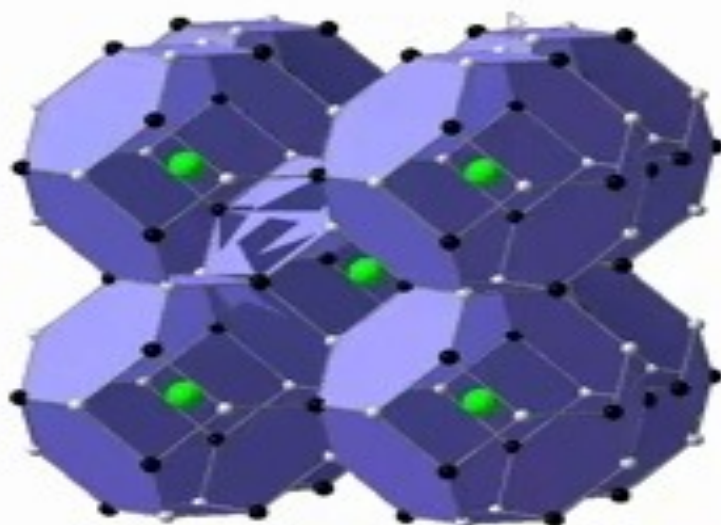
**Sodalite**

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

Site symmetry =  $\bar{4}m2$

Site symmetry =  $D_{2d}$

# Sodalite - $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$



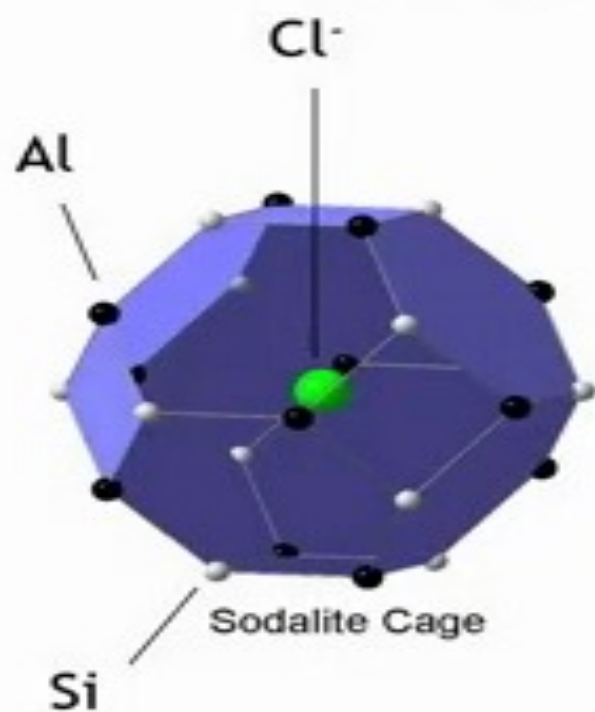
The sodalite cages share hexagonal faces (6-rings) to form a body centered cubic arrangement.

In sodalite the openings to the cages are sufficiently small (6 tetrahedra around the ring, openings of  $\sim 2.6 \text{ \AA}$ ) that guest molecules cannot get in or out (not microporous).

Space group:  $P\bar{4}3n$   
 $a = 8.875 \text{ \AA}$

Na1	8e	0.1777(2)	0.1777(2)	0.1777(2)
Al1	6d	1/4	0	1/2
Si1	6c	1/4	1/2	0
O1	24i	0.1387(3)	0.1484(3)	0.4375(2)
Cl1	2a	0	0	0

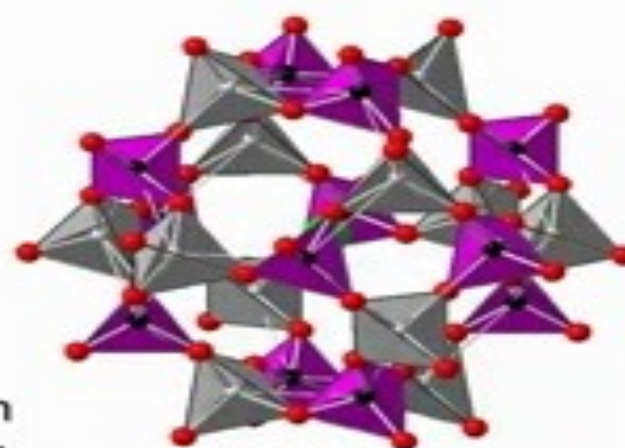
# Sodalite - $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$



Apply site ordering  
homeotypism,  
alternating Al and Si at  
the vertices



Apply a network  
expansion inserting an  
oxygen ion as a linker

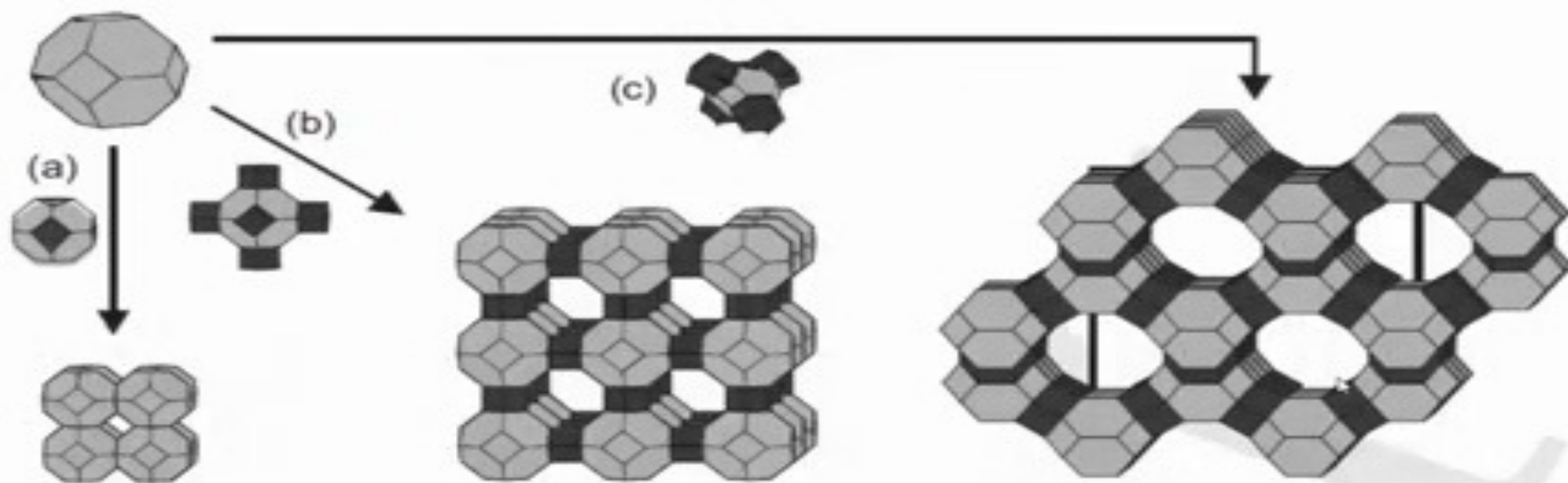


Alternating corner  
connected  $\text{AlO}_4$  and  
 $\text{SiO}_4$  tetrahedra

# Sodalite Cage



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



### Sodalite

Not porous

### Zeolite A

Connect 4-rings of  
the sodalite cages  
through a  
T-O-T bridge  
(T = Al/Si)  
Decorated primitive  
cubic network

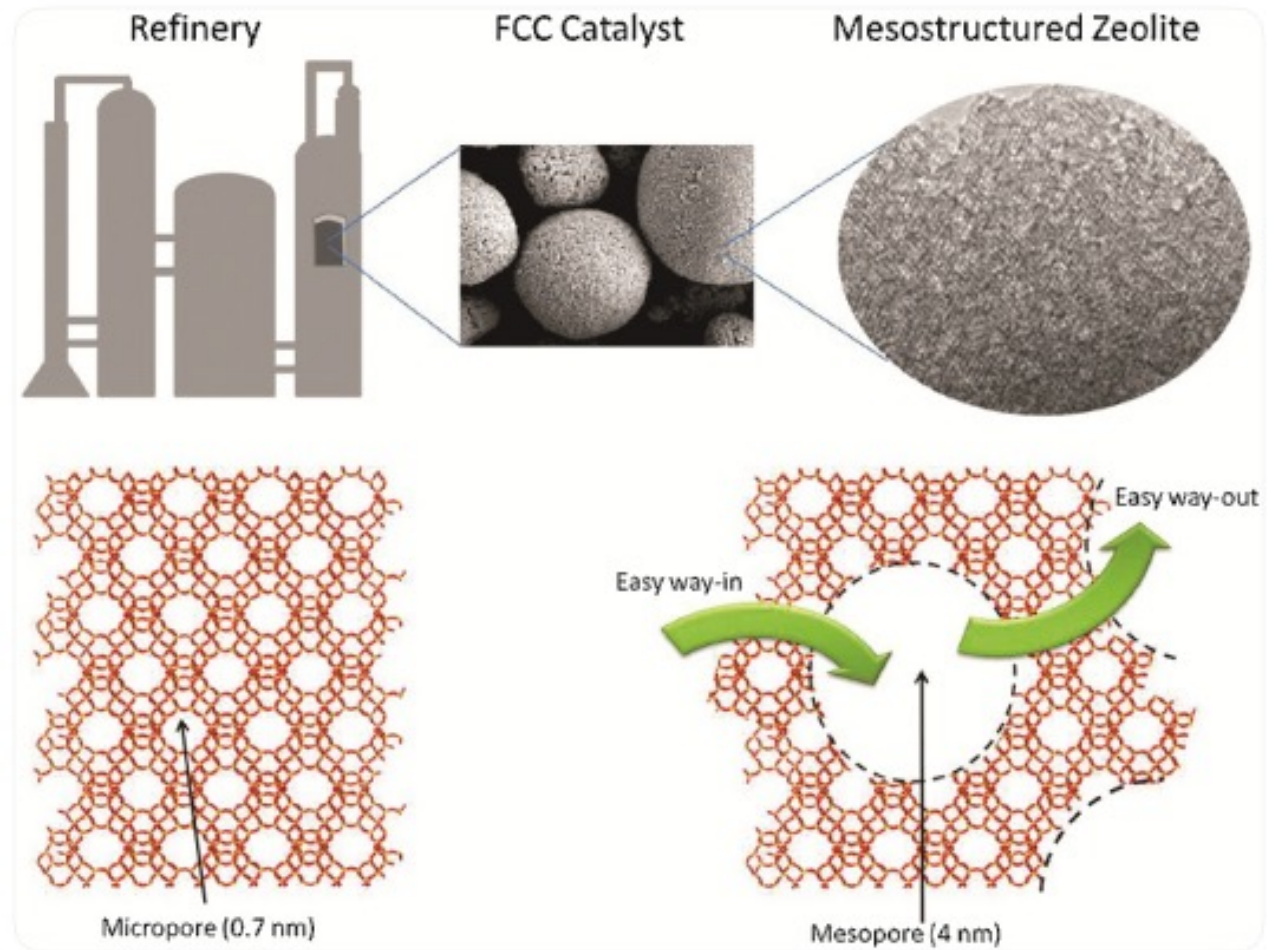
Pore diameter 4.1 Å

### Faujite

Connect 6-rings of  
the sodalite cages  
through a  
T-O-T bridge  
(T = Al/Si)  
Decorated diamond  
network

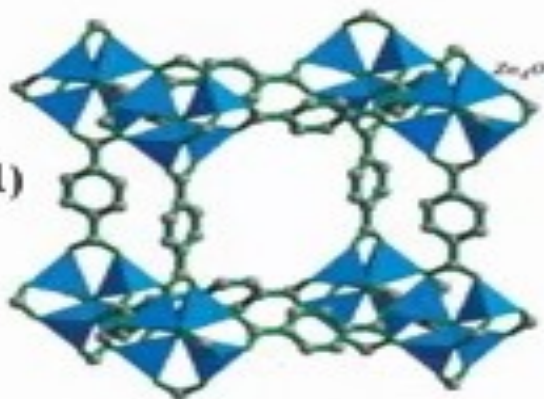
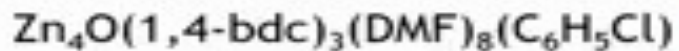
Pore diameter 7.4 Å

Hierarchical faujasite (zeolite Y) catalyst used in petroleum cracking. Micropores in the zeolite framework ( $\sim 0.7$  nm) provide the active catalytic sites, while additional mesopores ( $\sim 4$  nm), introduced by dealumination and leaching during catalyst preparation, act as diffusion channels. These mesopores allow larger hydrocarbon molecules to enter and exit, improving efficiency of the cracking process.

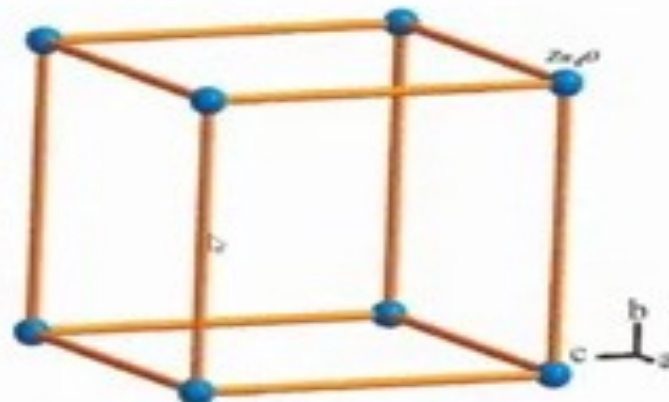


**fluid catalytic cracking (FCC) in petroleum**

# MOF-5

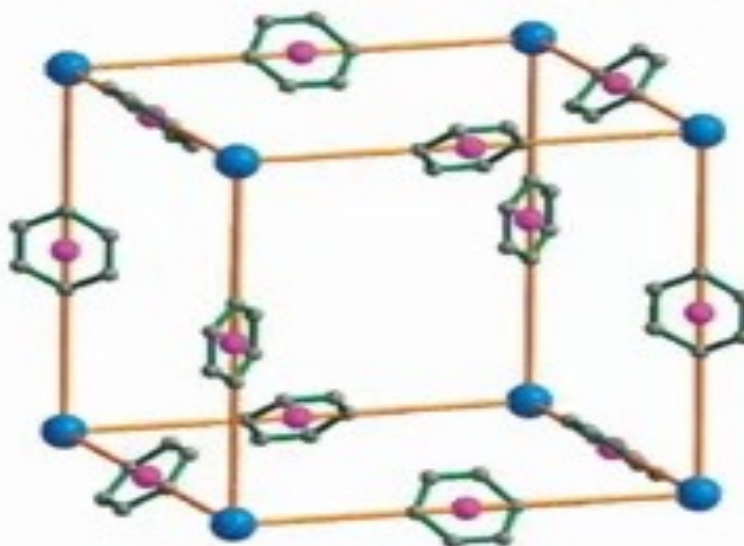


(a)



(b)

1. Start with 6-connected primitive cubic net
2. Decorate the vertices with  $\text{OZn}_4$  clusters
3. Expand with 1,4-benzenedicarboxylic acid linker



Taken from "Metal-Organic framework structures - How closely are they related to classical inorganic structures" S. Natarajan and P. Mahata, *Chem. Soc. Rev.* 2009, 38, 2304-2318.

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

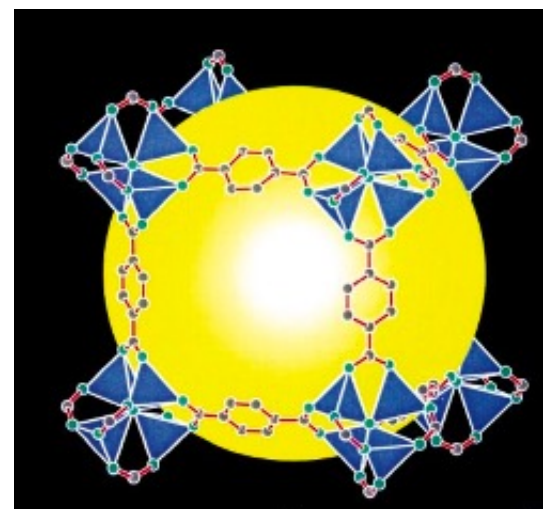
Hailian Li\*, Mohamed Eddaoudi†, M. O’Keeffe\* & O. M. Yaghi†

*Materials Design and Discovery Group, \* Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA*

*† Department of Chemistry, University of Michigan, 930 North University, Ann Arbor, Michigan 48109-1055, USA*

Open metal-organic frameworks are widely regarded as promising materials for applications<sup>1-15</sup> 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<sup>14,15</sup>. 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.





## 1. The status quo problem

- Ion-implant tools in chip fabs need toxic dopant gases: **arsine ( $\text{AsH}_3$ )**, **phosphine ( $\text{PH}_3$ )**,  **$\text{BF}_3$** , etc.
- Traditionally stored in **high-pressure steel cylinders** (pressures often  $>100$  psig).
- Hazards:
  - **Catastrophic leak risk** → a single bottle contains enough toxic gas to endanger workers and trigger fab-wide shutdowns.
  - **Regulatory & insurance burden** → fabs need redundant ventilation, scrubbing, and emergency protocols, raising costs.
  - **Cylinder heel (unused residual gas)** → waste that still poses disposal risks.

## 2. What the MOF cylinder changes

- MOFs **adsorb and store the gas inside their pores**, allowing the cylinder to hold the same usable inventory at **sub-atmospheric pressure (near vacuum to  $\sim 1$  atm)**.
- On use, the gas desorbs in a controlled way to feed the ion-implant tool.

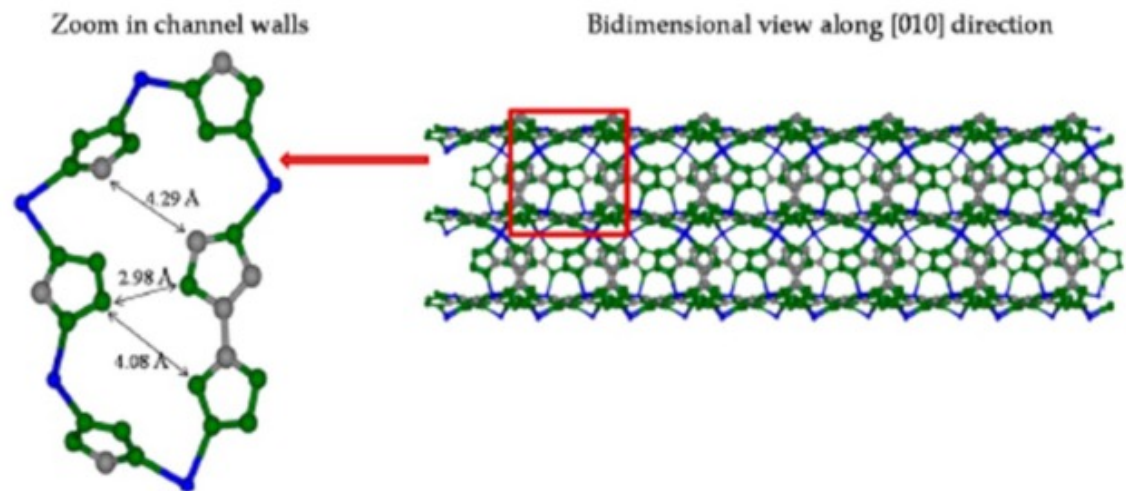
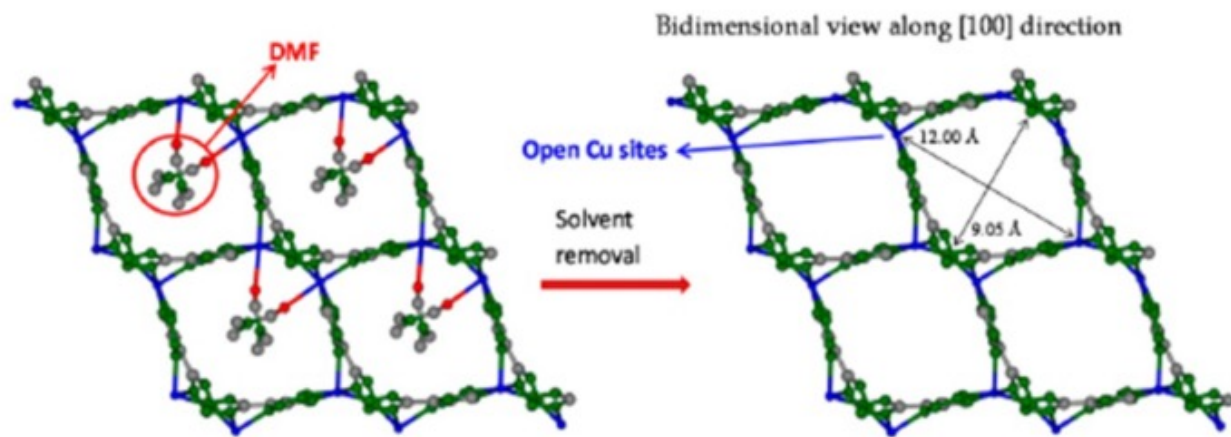


### 3. Why fabs pay for this

- **Massively reduced safety risk:** Even if the cylinder is breached, no pressurized toxic gas rushes out. That alone cuts the probability and severity of a catastrophic event.
- **Regulatory relief:** Lower safety classification than high-pressure bottles → lower facility cost, easier permitting, fewer insurance penalties.
- **Operational continuity:** Prevents fab shutdowns due to leaks or alarms, which are extremely expensive (>\$1M/day lost production).
- **Waste reduction:** Lower "heel" volumes mean less toxic waste to manage and dispose of.
- **Compatibility:** ION-X cylinders plug directly into existing ion-implant tools (no redesign needed).

### 4. The value proposition in one line

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.



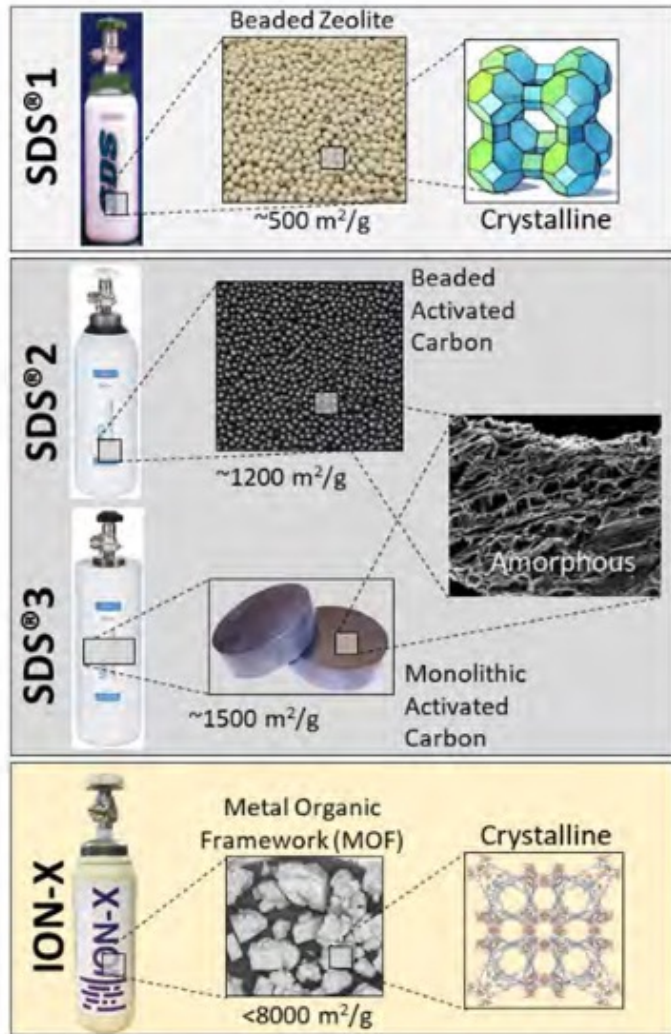


Fig. 2. Structural and physical properties of adsorbent materials used to store and deliver ion implant dopant gases

## 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,

*NuMat Technologies*

Skokie, IL, U.S.A.

j.arno@numat-tech.com

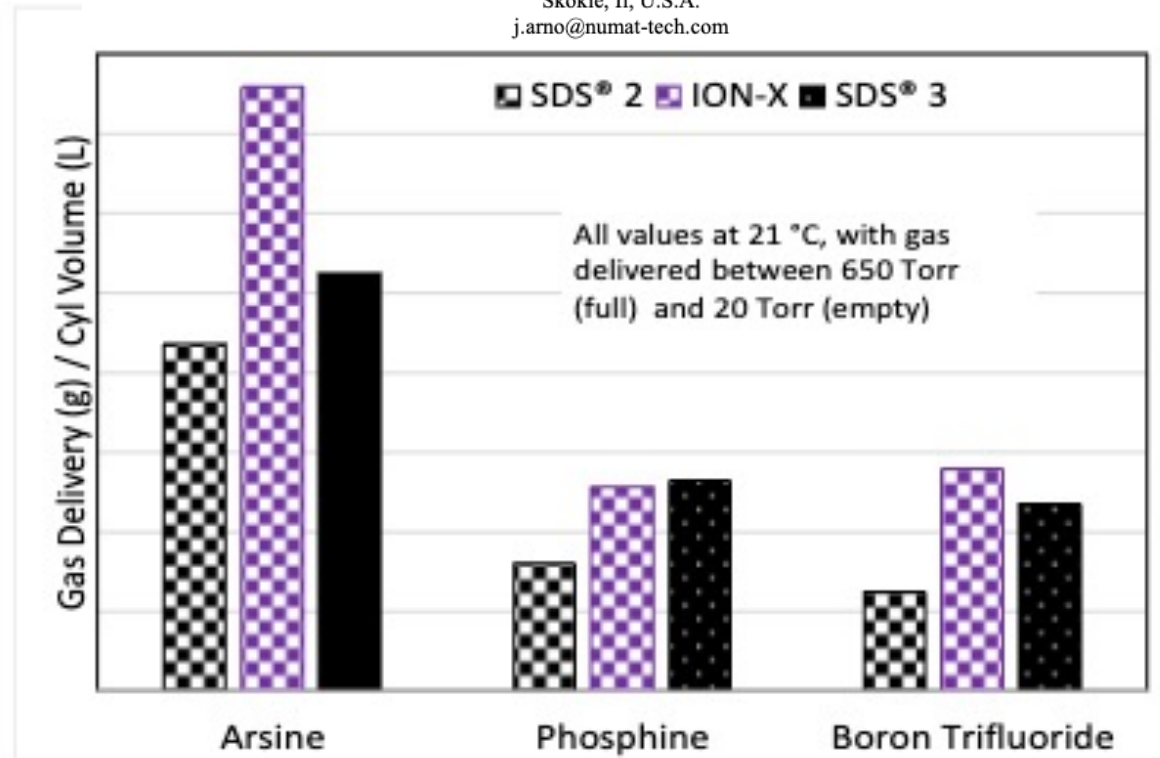


Fig. 3. Volumetric dopant gas delivery comparison between ION-X and activated carbon-based products

## 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

- Silicates dominate Earth's crust; their tetrahedral networks are defined by O:Si ratios.
- Structural motifs range from isolated tetrahedra ( $\text{SiO}_4^{4-}$ ) to 1D chains, 2D sheets, and 3D frameworks.
- Zeolites are Al/Si tetrahedral frameworks; charge-balancing cations generate accessible pores.
- Key zeolites (sodalite, zeolite A, faujasite) differ in connectivity and pore size (4–7.4 Å).
- Porous materials are classified as **microporous (<2 nm)**, **mesoporous (2–50 nm)**, **macroporous (>50 nm)**.
- MOFs (e.g., MOF-5) extend these ideas: metal–oxide clusters linked by organic ligands create highly porous, tunable frameworks.

## Homework

- 1.22 Write the Niggli formula and the simple crystal-chemical formula for the  $\text{CrO}_3$  structure that contains chains of corner-sharing chromium-centered tetrahedra.
- 1.23 Construct a bond graph or Niggli formula to determine if it is possible for all anions to be equivalent in a structure of tetrahedrally coordinated cations and stoichiometry of  $\text{C}_2\text{A}_3$ ? Which alternative Niggli formula complies best with the rule of parsimony?
- 1.24 Using the Niggli formula and the rule of parsimony, determine the stoichiometry that results from sharing (a) all corners, (b) all edges, and (c) all faces of a cation-centered cube of anions. Note the structure prototype where you recognize it.
- 1.25 Write the Niggli formula for  $\text{C}_3\text{N}_4$  made of identical  $\text{CN}_4$  tetrahedra. How many different types of nitrogen vertices are there? What is the coordination number of each?
- 1.26 In  $\beta\text{-Li}_3\text{N}$ , nitrogen is 11-coordinated. Write down the Niggli formula of the  $\text{NLi}_3$  polyhedron.

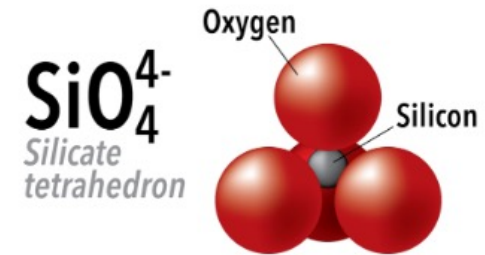
1.22

Corner sharing tetrahedra in 1-D chains ->  
CrO<sub>4</sub> tetrahedra

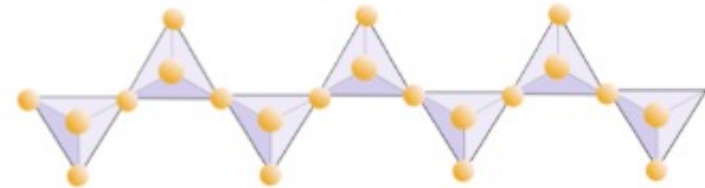
### What the Niggli formula describes

- It's a **connectivity-based formula** for one polyhedron (e.g., a tetrahedron or octahedron around a cation).
- It tells you how many anion vertices there are, and how many other polyhedra each vertex connects to.
- You always write it **per one cation-centered polyhedron**.
- C A(numerator/denominator + numerator/denominator ...)

**Niggli formula:** CrO<sub>2/2+2/1</sub>



### 1. Single Chain



## Crystal-Chemical Formula Algorithm

1. **List atoms:** Write down each unique cation and anion site.
2. **Tag cations:** Add coordination number (how many neighbors) + geometry (t = tetra, o = octa, etc.).
3. **Tag anions:** Mark how many cations each anion connects to: O[1] = terminal, O[2] = bridging, O[3] = 3-connected, etc.
4. **Check balances:**
  - Bonds from cations = bonds accepted by anions.
  - Count anions = formula stoichiometry.
  - Charges must cancel.
5. **Keep it simple:** Only include distinct sites/connectivities needed to show bonding.

**Given:** Cr is tetrahedral; tetrahedra link by **corners** to form **1D chains**.

**Sites:** Cr, bridging O ( $O_{br}$ ), terminal O ( $O_t$ ).

**Coordination & geometry:**

Cr[4t];  $O_{br}$ [2n] (bent Cr–O–Cr);  $O_t$ [1].

**Balances (per one Cr):**

- Stoichiometry:  $b + t = 3$ .
- Connectivity:  $4 = 2b + t$  (Cr has CN = 4).

**Solve:** subtract  $\Rightarrow b = 1$ , then  $t = 2$ .

**Crystal-chemical formula:**

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

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