Beyond silica: the quest for mesoporous semiconductors

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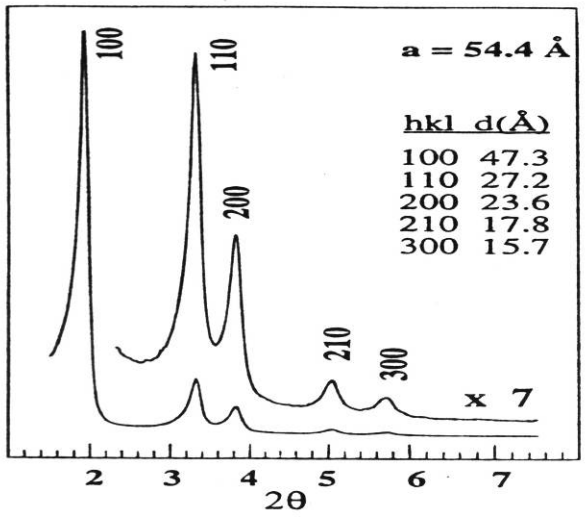
Outline

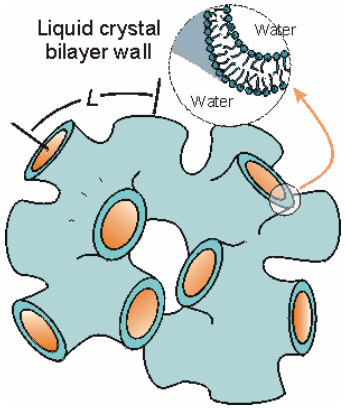
- Chalcogenide networks
- Wormholes, honeycombs and labyrinths..
- MCM-48 type chalcogenides
- Mesostructured elements
- Ge-Cubic (NU-Ge-1)
- Ge-hexagonal (NU-Ge-2)
- Ge-hexagonal (NU-Ge-3)
- Conclusions

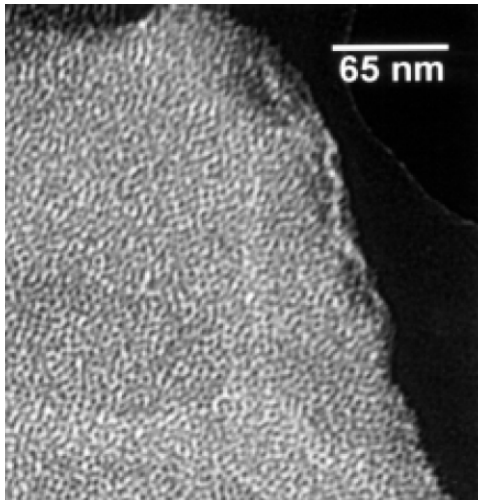
Mesoporous Oxides via Liquid Crystal Template Route

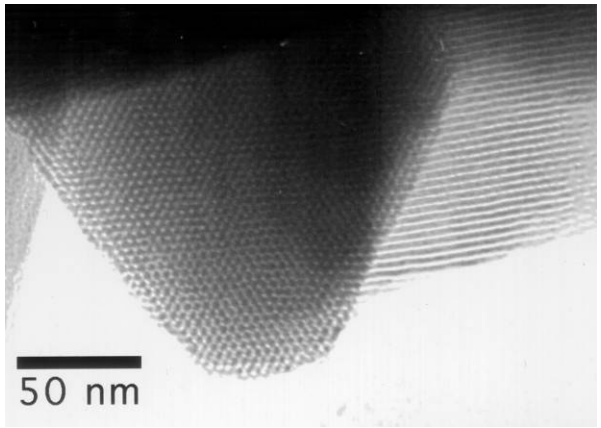
- Major Breakthrough ca 1989: general synthetic strategy to ordered mesoporous silicates by Mobil[1] (MCM-41, MCM-48 etc), opened the pathway for novel hybrid solids.
- Many mesoporous metal oxides have been synthesized based on MCM-X materials



- ***ZrO_2, V_2O_5, SnO_2, TiO_2***

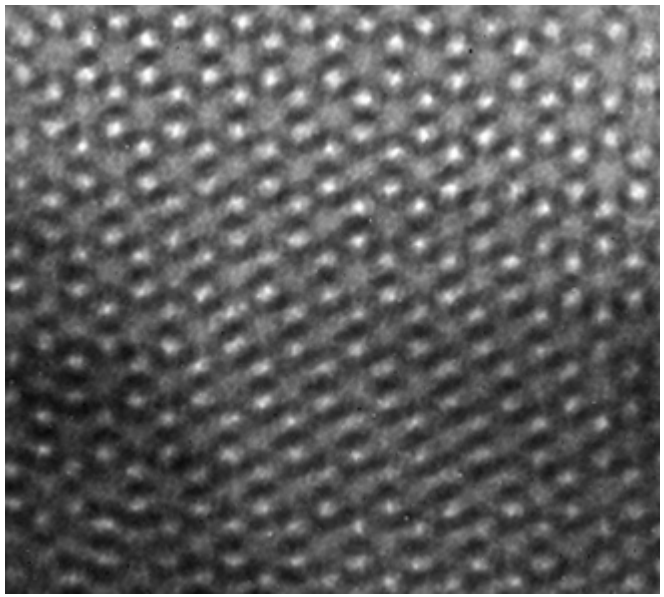




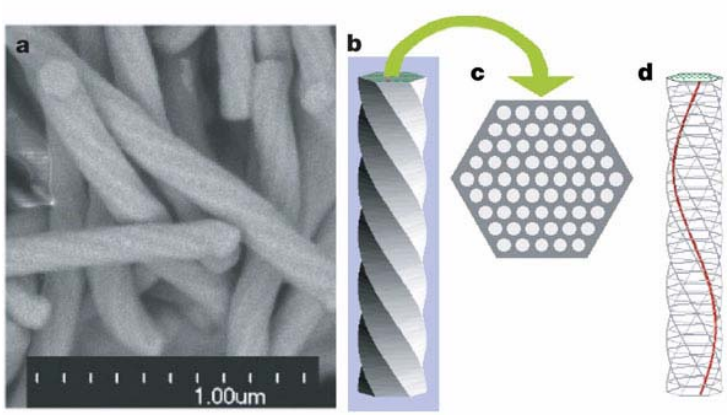


Tanev Pt, Pinnavaia TJ *Science* 267 (5199): 865-867 Feb 10 1995
Huo Qs, Margolese D I, Ciesla U, et al. *Nature* 368 (6469): 317-321, 1994
Kresge C T, Leonowicz M E, Roth W J, et al. *Nature* 359 (6397): 710-712, 1992

Mesoporous silica



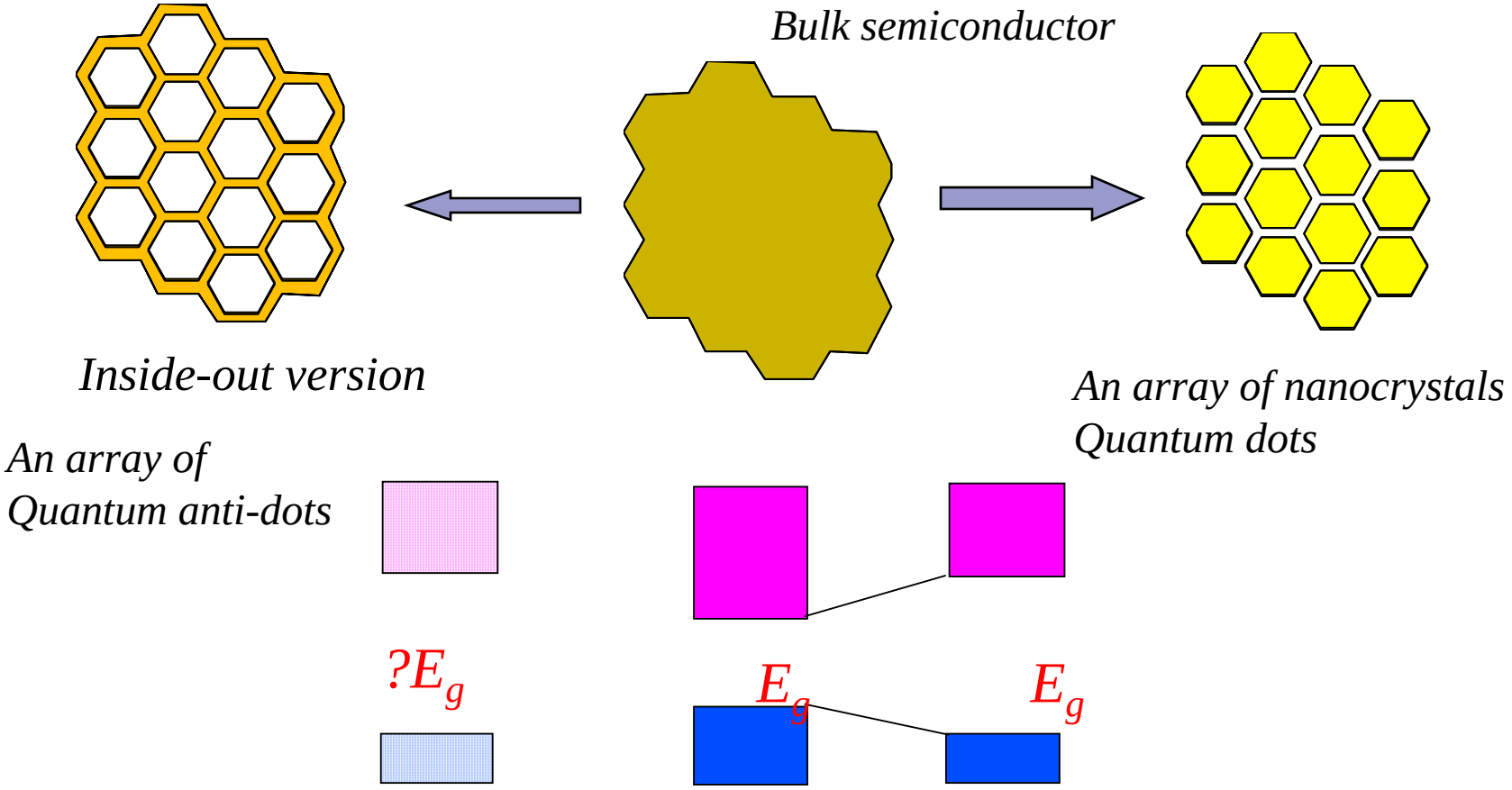
Cubic MCM-41



chiral mesoporous silica

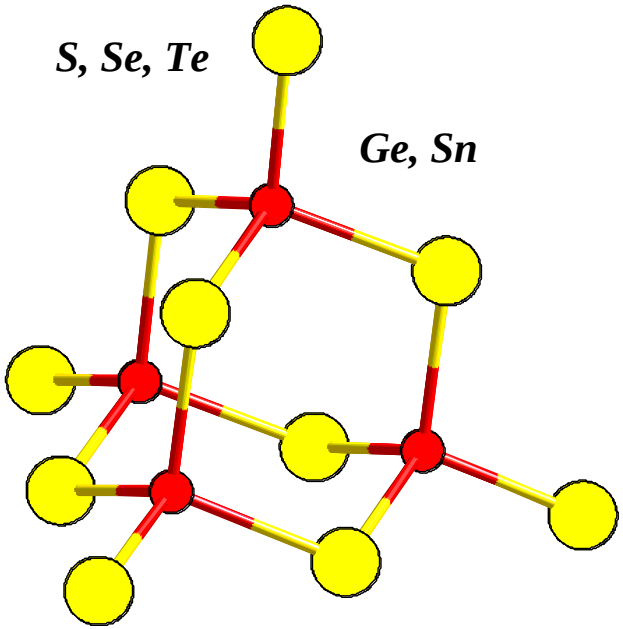
Shunai Che, Zheng Liu, Tetsu Ohsuna, Kazutami Sakamoto,
Osamu Terasaki and Takashi Tatsumi
Nature 429, 281-284(20 May 2004)

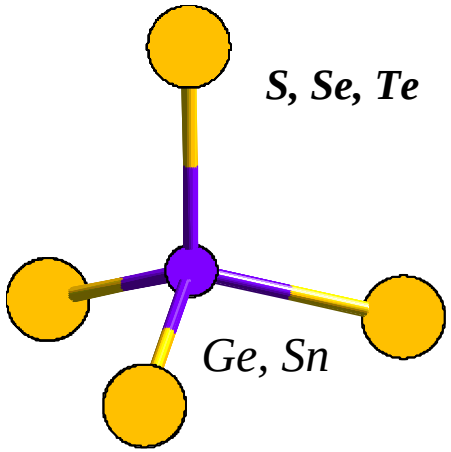
Porous Semiconductors (non-oxidic): A challenge

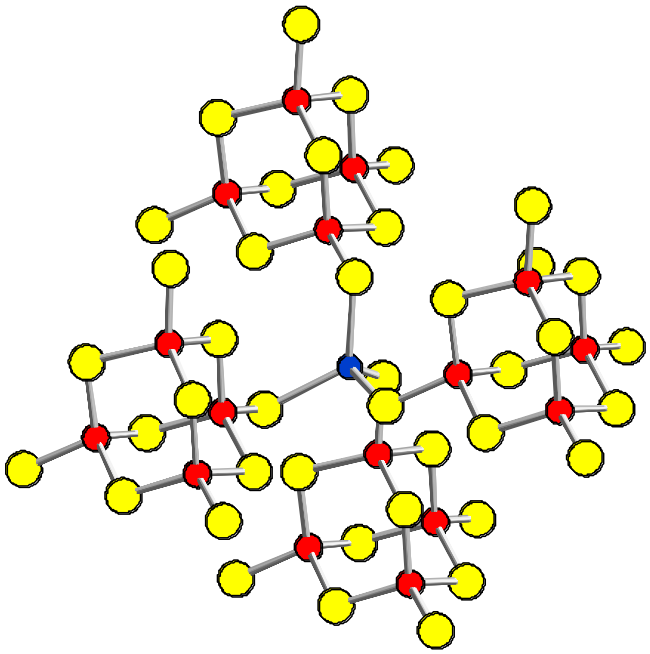


M. G. Kanatzidis, *Advanced Materials*, 2007, 19, 1165

Mesostructured Non-Oxidic Solids Based on the Tetrahedral Clusters and Metal Ions





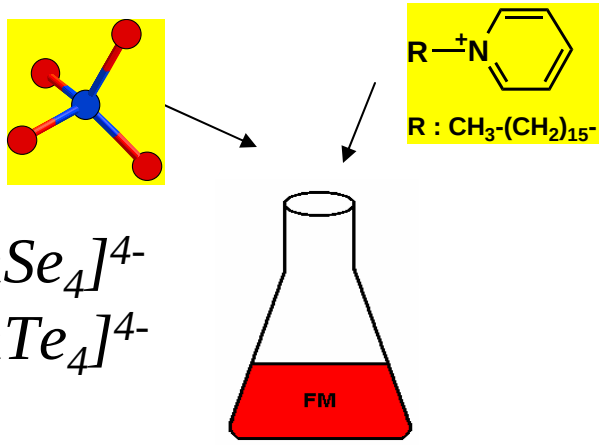


SiO_4 analogs
topologically similar structures?

1. M. Wachhold, K.K. Rangan, S.J.L. Billinge, V. Petkov, J. Heising, M.G. Kanatzidis, *Adv. Mater.* **2000,** 12(2) 85-91.
2. K. K. Rangan, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, *Chem. Mater.* **1999**, 10, 2629.
3. M.J. MacLachlan, N. Coombs, G.A. Ozin, *Nature* **1999**, 397, 681.
4. Riley AE, Tolbert SH *J. Am. Chem. Soc.* **2003**, 125 (15): 4551

Synthesis

Mesostructured Chalcogenide Phases



$[SnSe_4]^{4-}$
$[SnTe_4]^{4-}$

Supramolecular organization

Formamide : 20 ml

Surfactant : 10 mmol

K_4SnSe_4 : 1 mmol

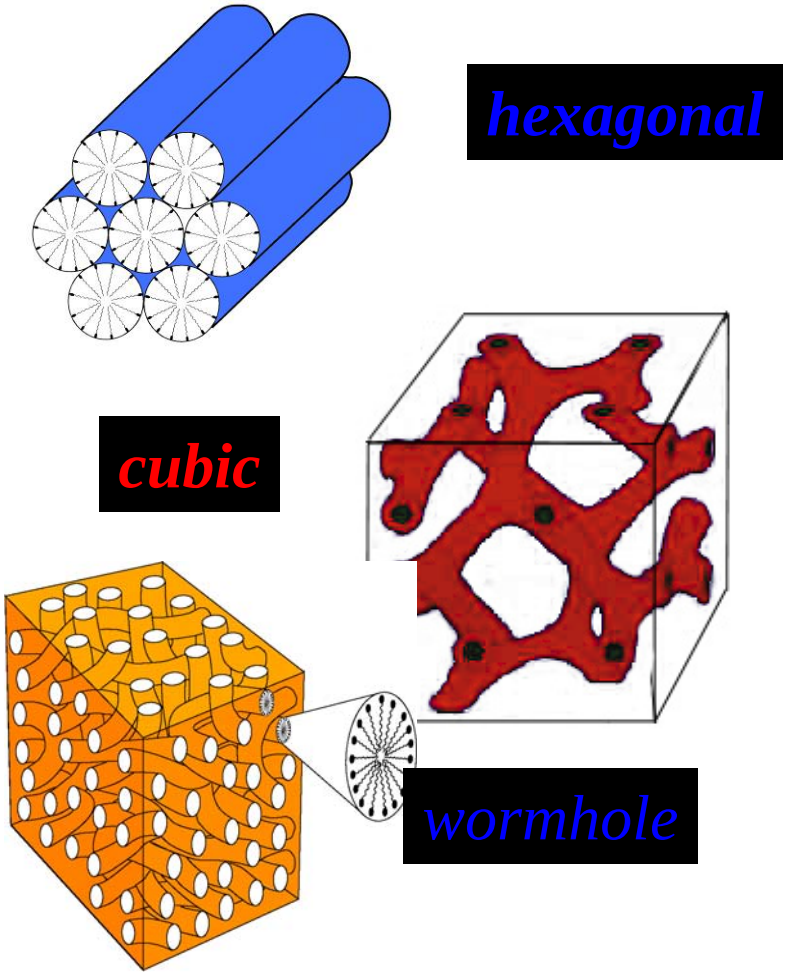
Temperature : 75 °C

Slow addition of M^{2+}/FM solution

M^{2+} : Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}

Immediate precipitation

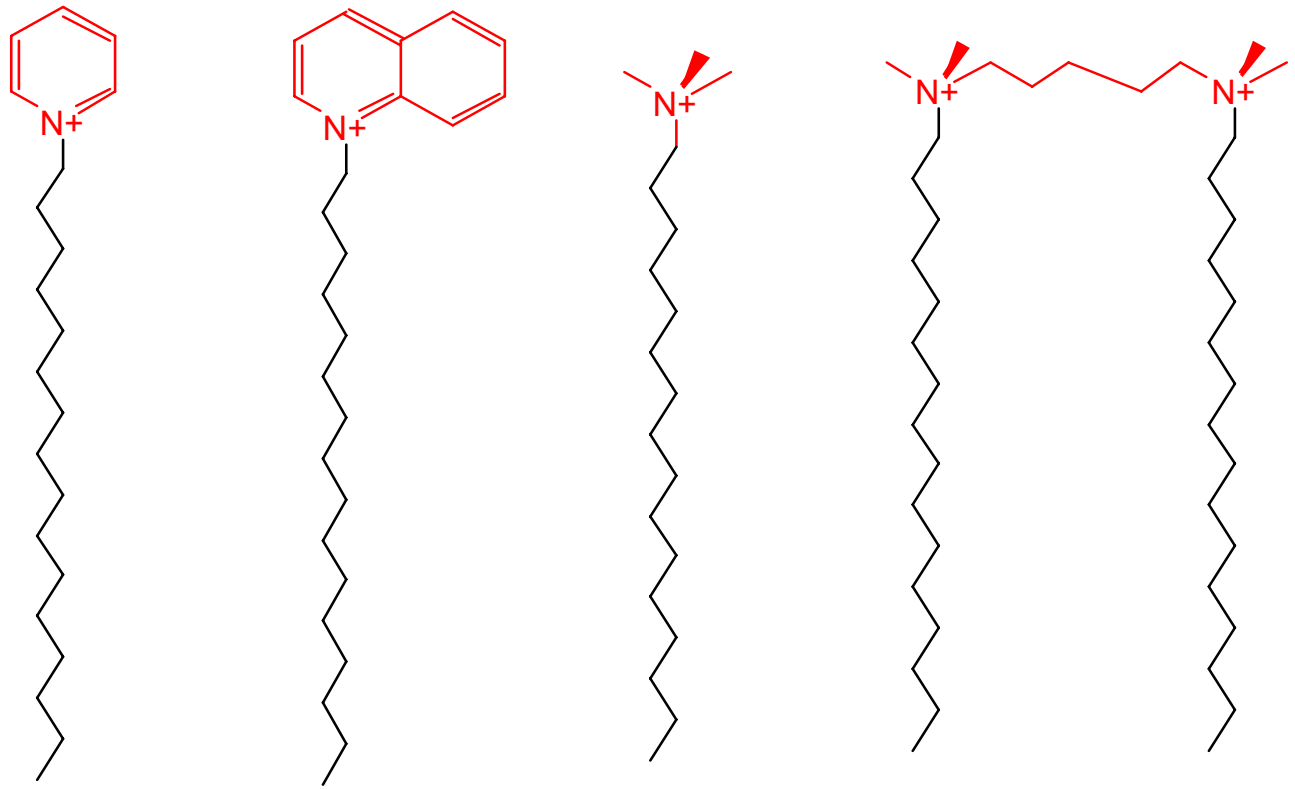
aging for 24h



Surfactants set the stage for inorganic framework assembly

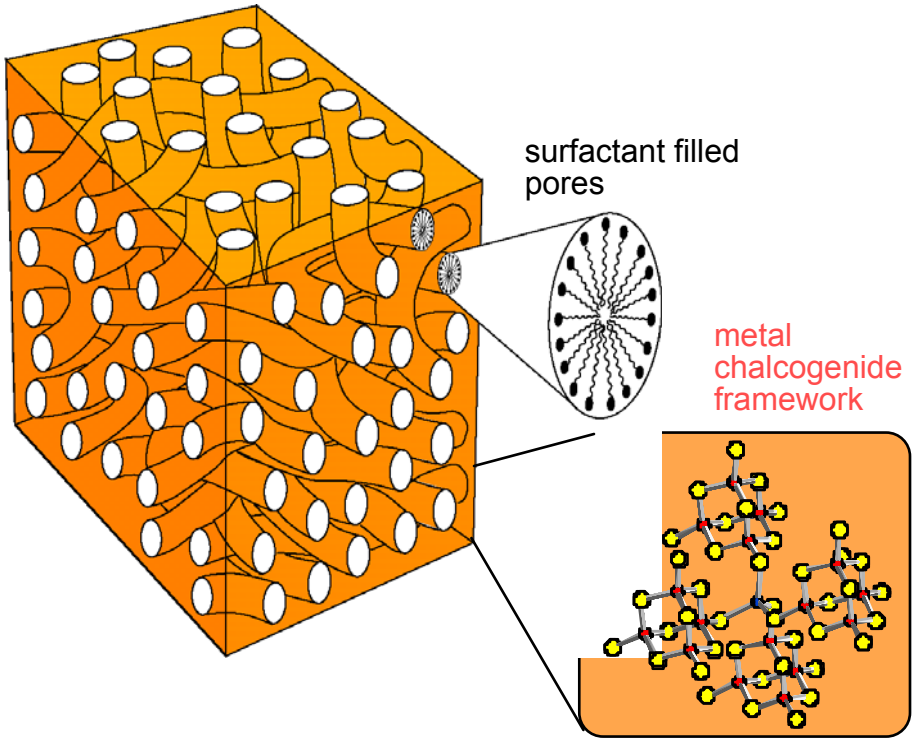
Examples

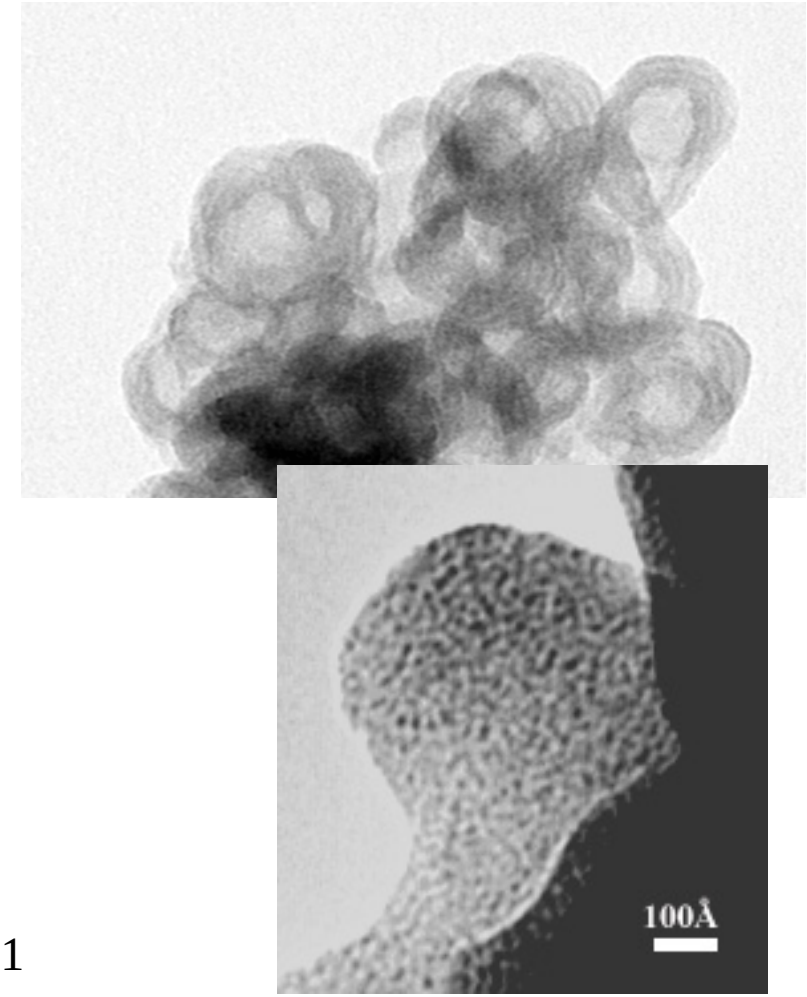
$R=C_nH_{2n+1}$



R-pyridinium *R-quinolinium* *R-TMA-* *Gemini-$C_{n\text{-}s\text{-}n}$*

Mesostructured Wormholes ~35 Å





Kanatzidis *et al Advanced Mater*. 2000, 12, 85-91

Influence of solvent

- In water: $(R\text{-}NMe_3)_2MGe_4Q_{10}$
  - Disordered wormhole
- In formamide: $(R\text{-}NME_3)_{2-x}M_{1+x}Ge_4Q_{10+\delta}$
  - Ordered hexagonal, cubic

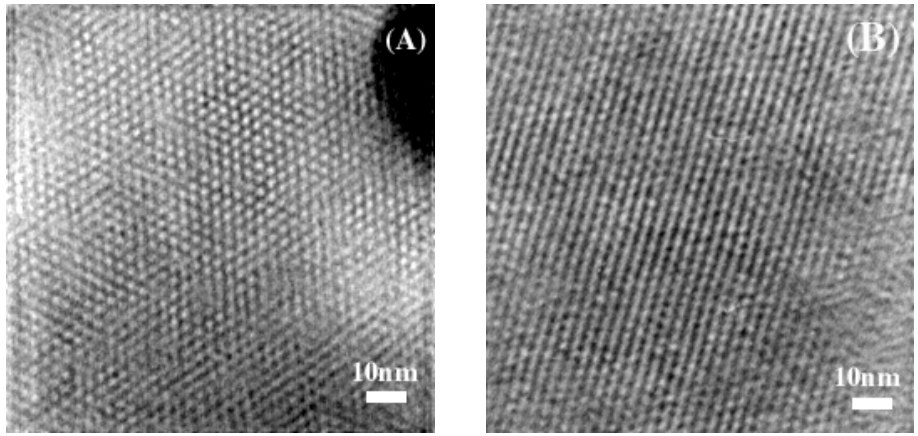
$$[Ge_4Q_{10}]^{4-} \rightleftharpoons [Ge_4Q_{10-x}]^{z-} + xQ^{2-}$$

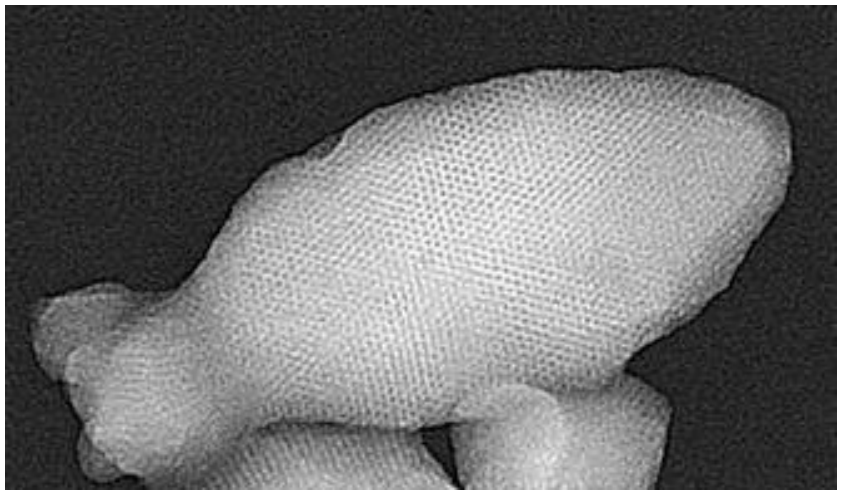
$$2[SnSe_4]^{4-} \rightleftharpoons [Sn_2Se_6]^{4-} + 2Se^{2-}$$

CP/M/Ge_4S_{10} (CPMGeS) M=Ga, In, Zn *J. Am. Chem. Soc.* 2000, *122*, 10230

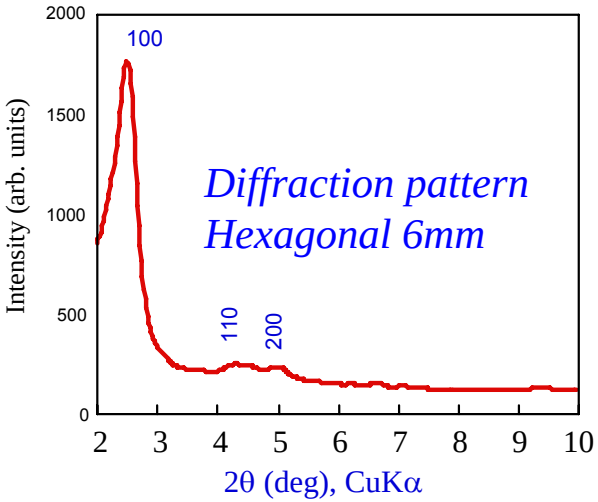
Walls are amorphous

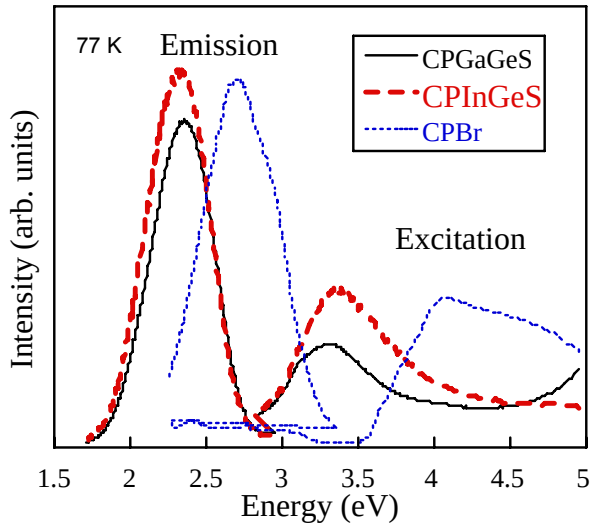
TEM images



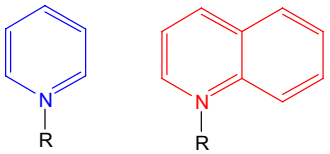


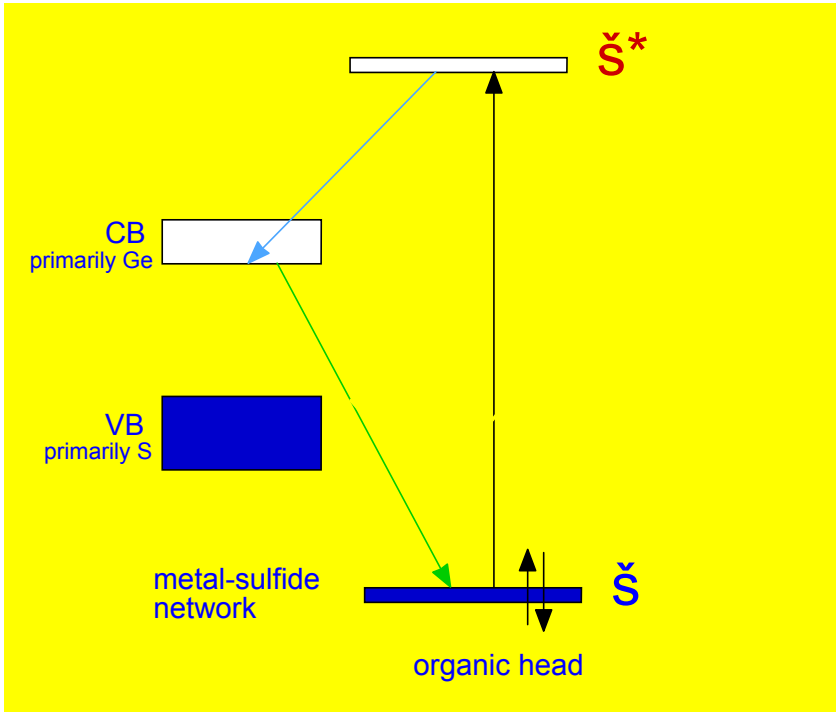
Thermally stable up to 220 °C

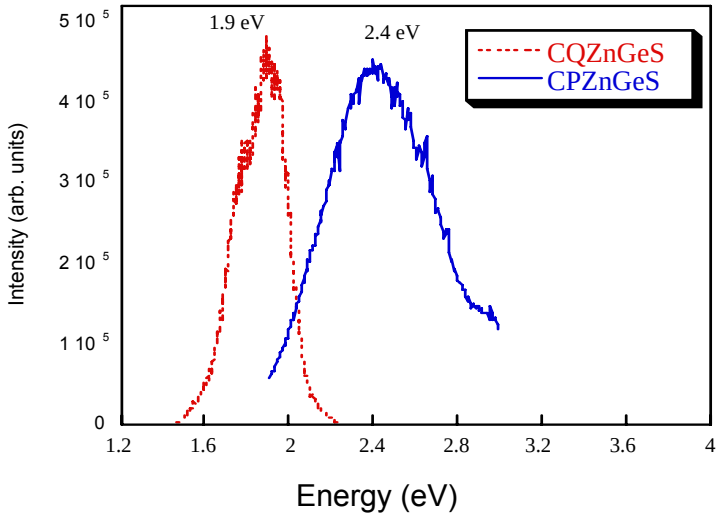


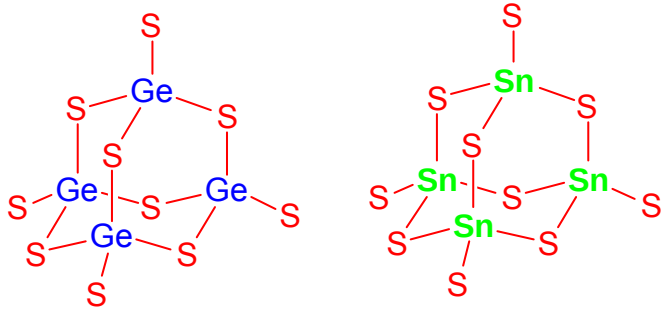


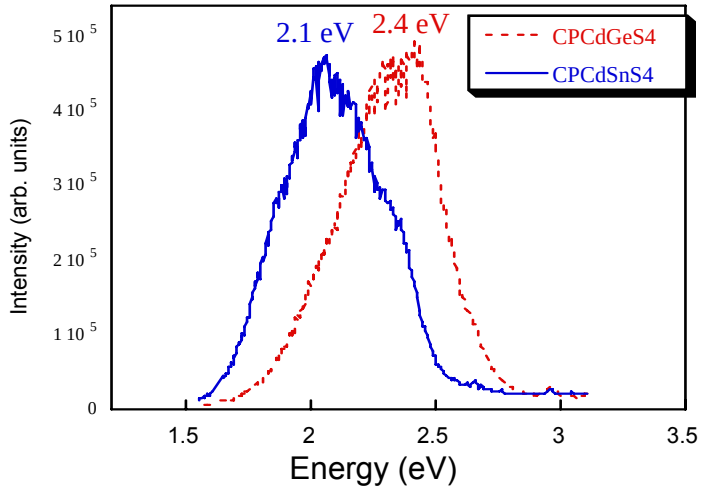
Photoluminescence





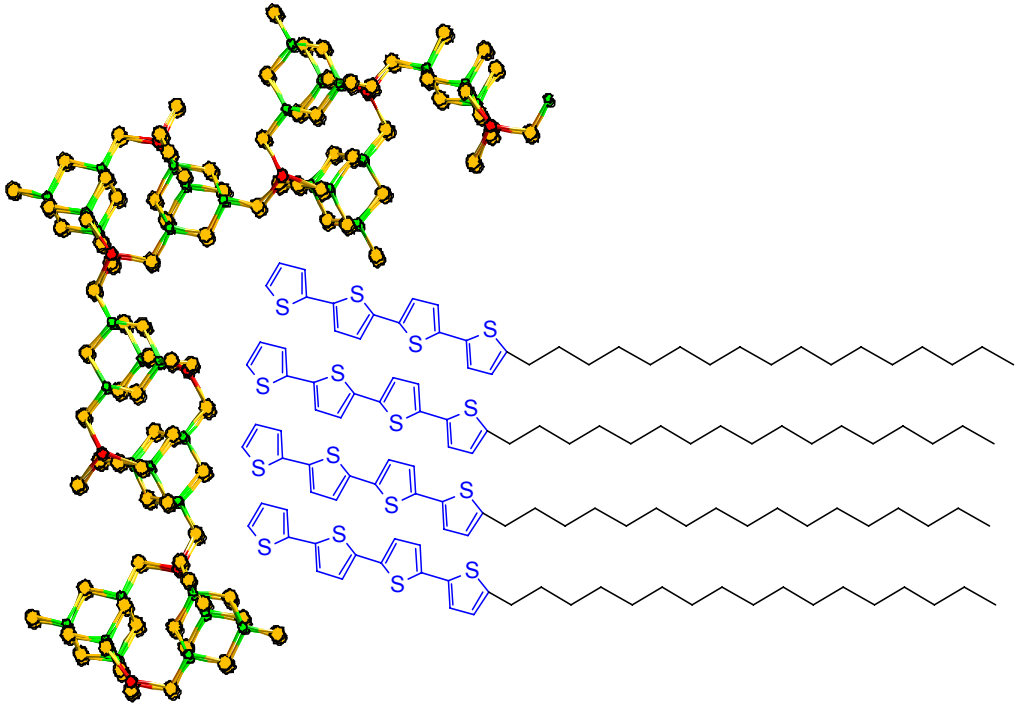


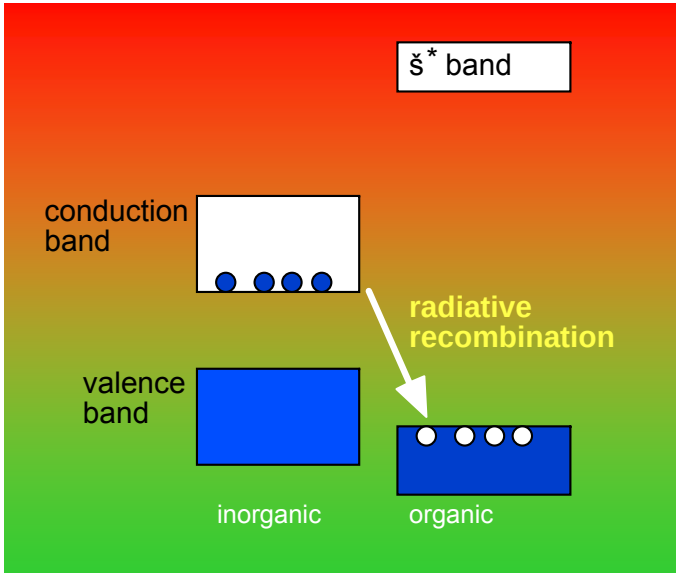




Perhaps we don't want to remove the surfactant!

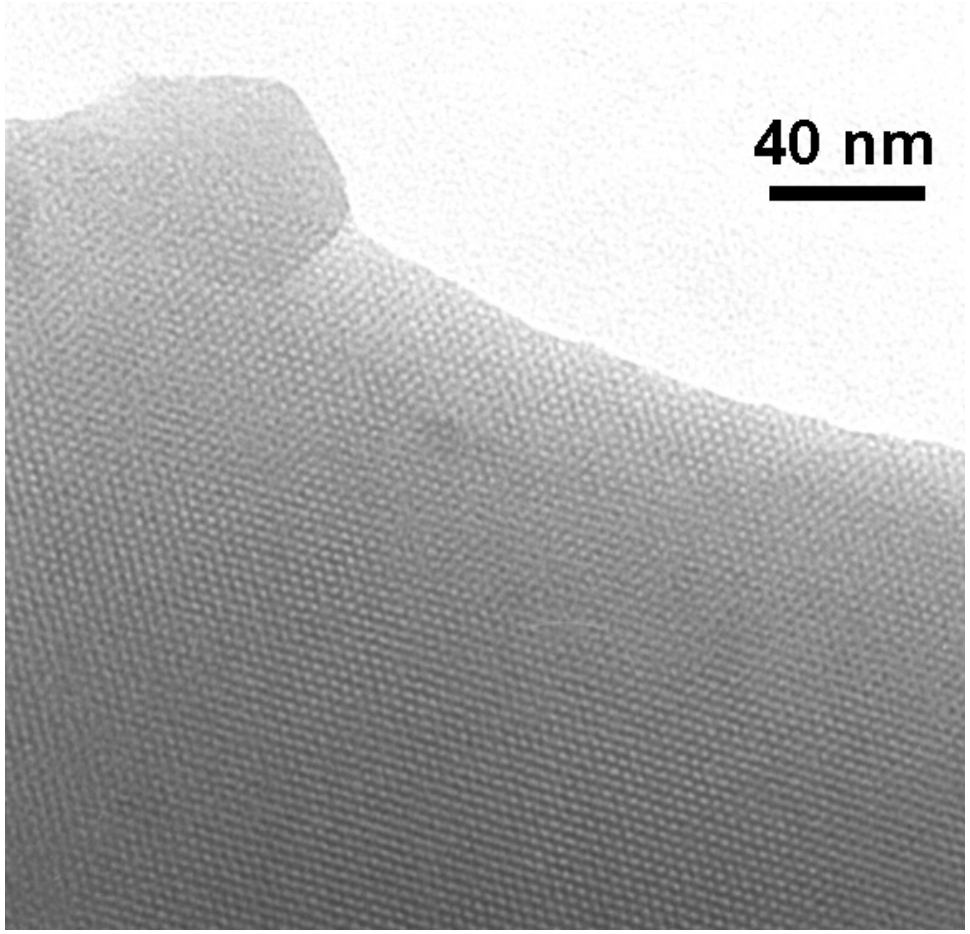
- Add functionality to the surfactant
  - Electronically active head groups or tails

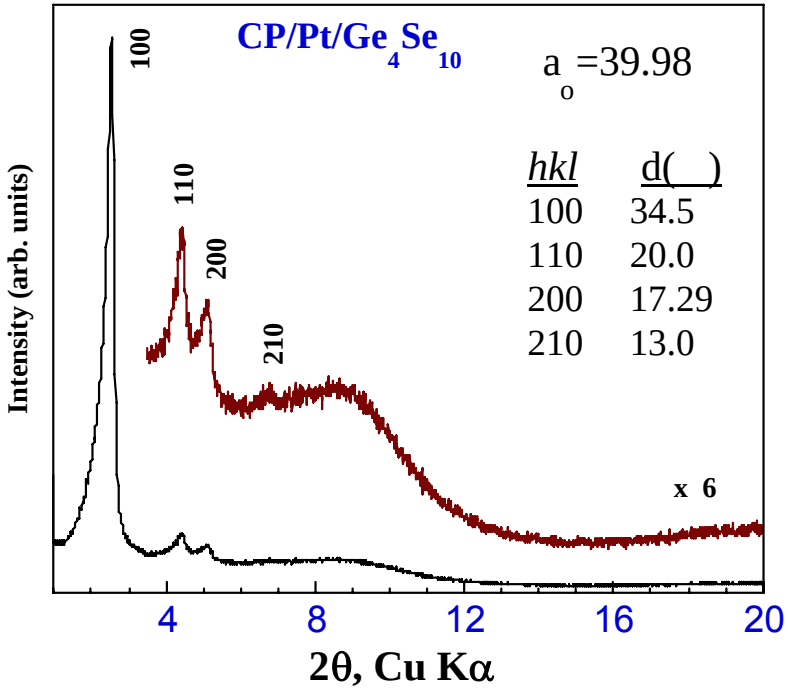




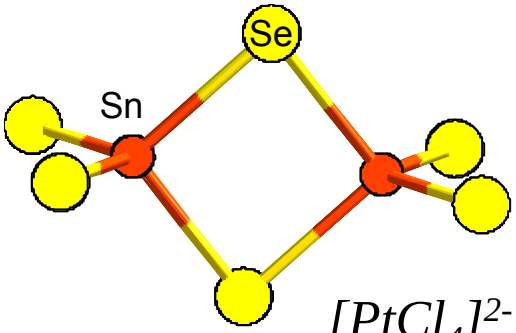
electroluminescence

Highly ordered CP-$PtGe_4Se_{10}$

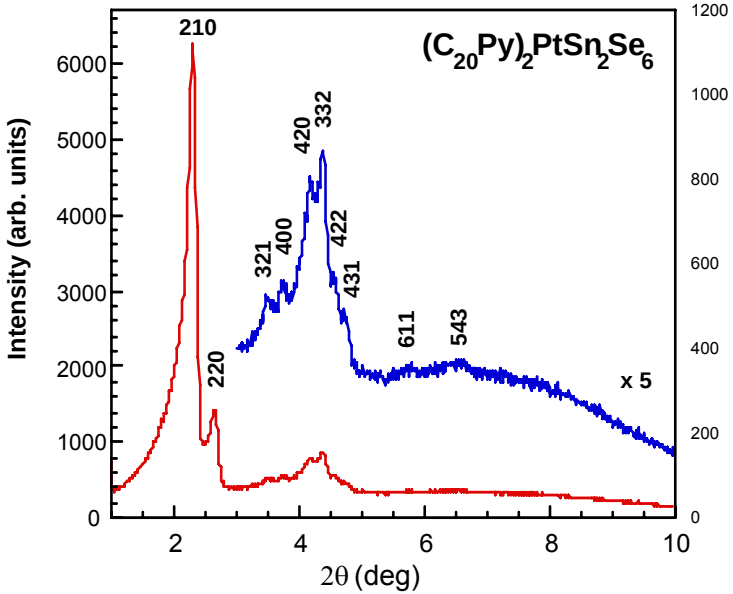


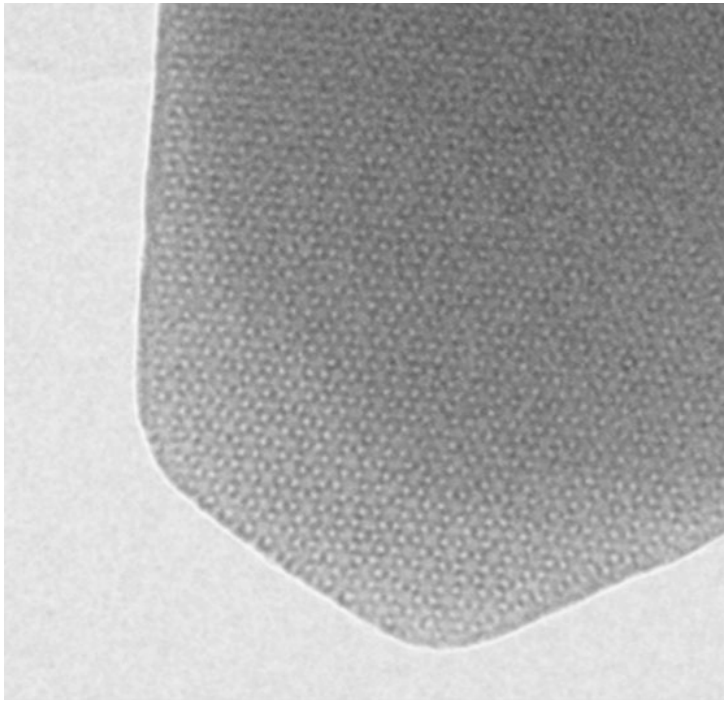


The system Pt^{2+} / $[Sn_2Se_6]^{4-}$

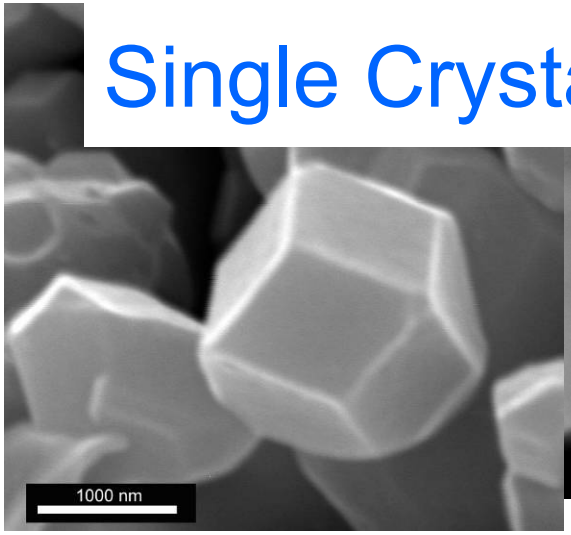


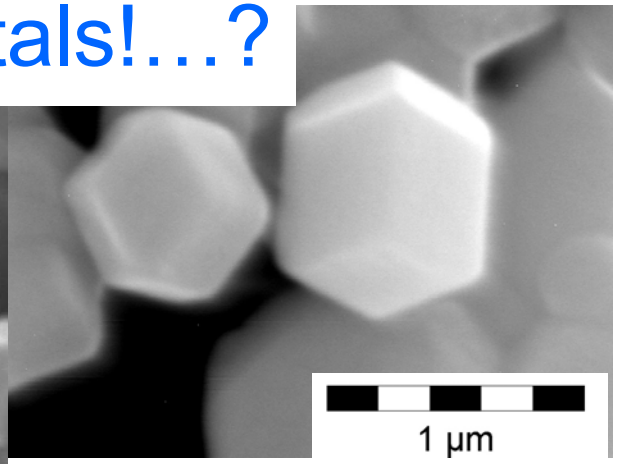
$[PtCl_4]^{2-} + [Sn_2Se_6]^{4-}$



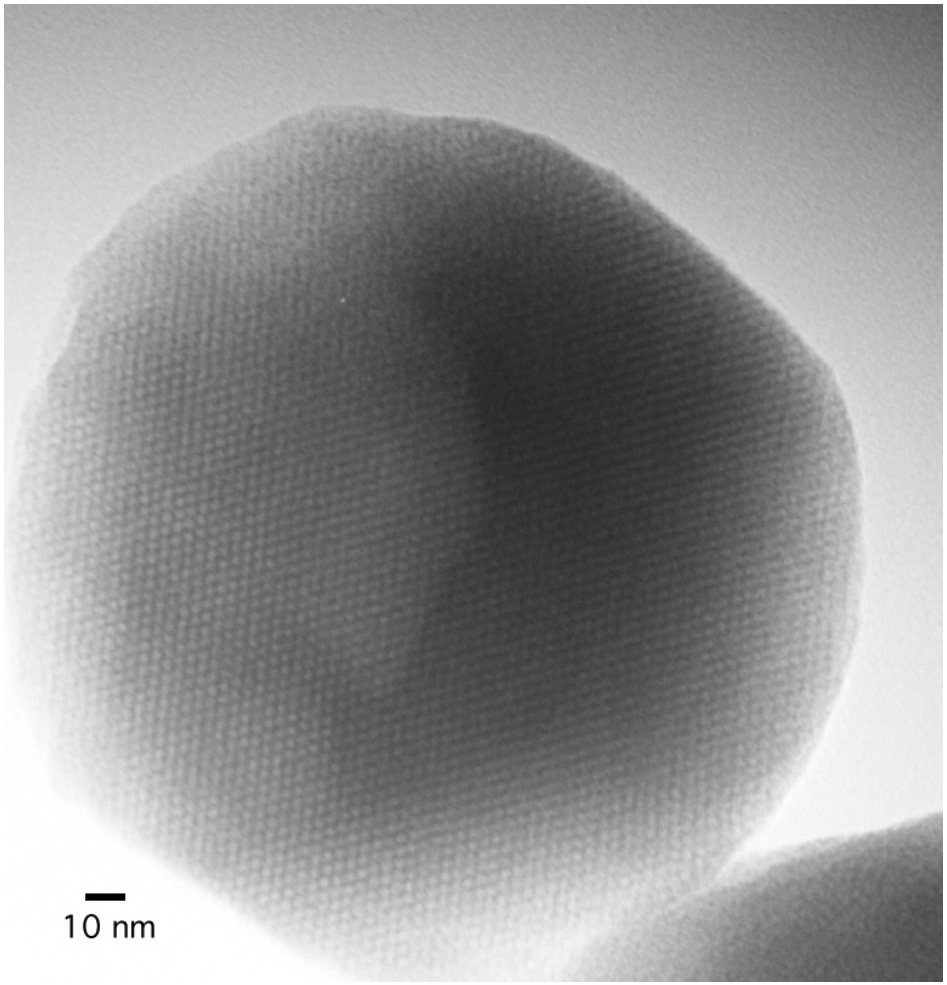


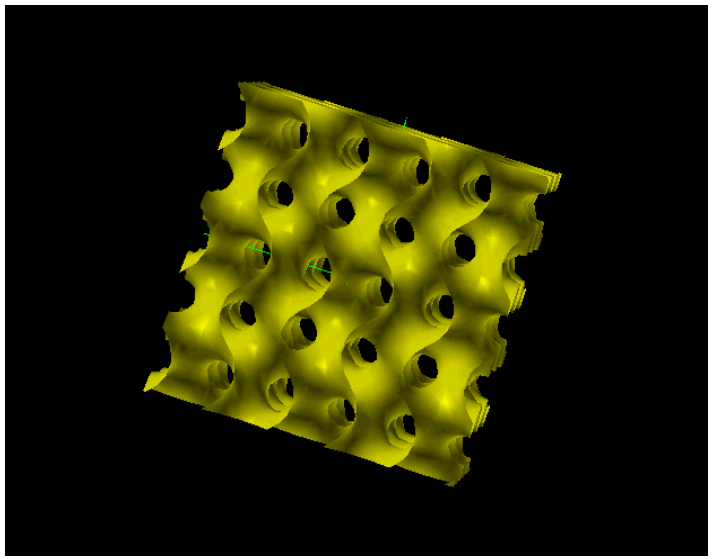
Single Crystals!…?





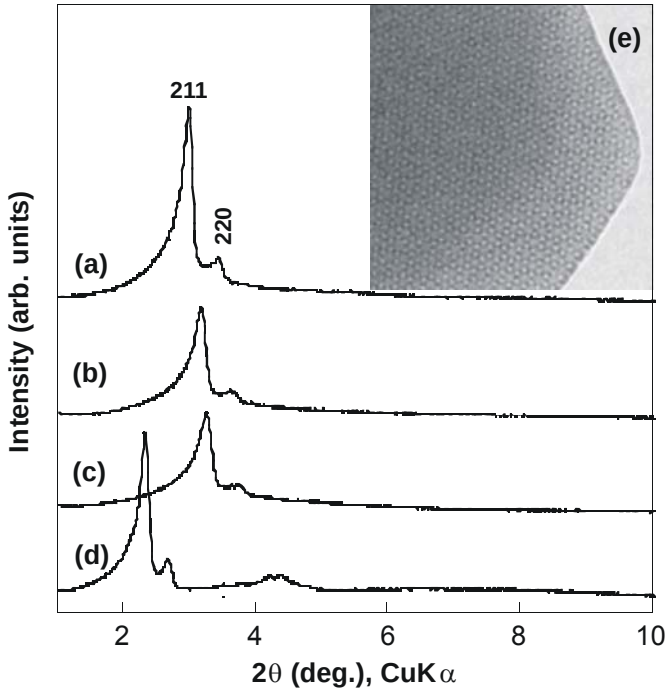
TEM of a Cubosome: [110] direction

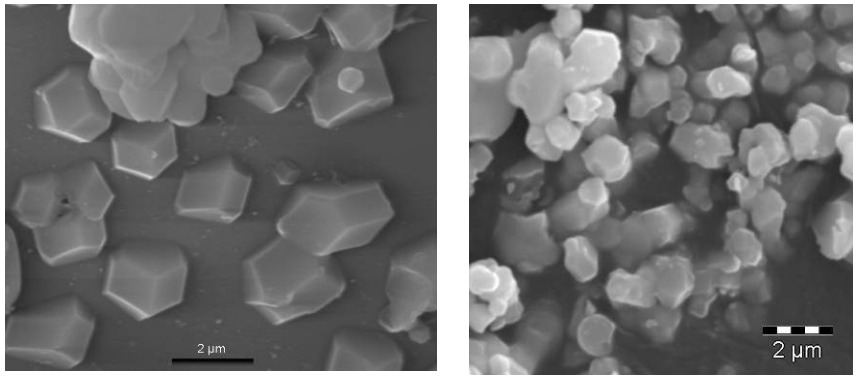




Unit cell edge: 95Å
V=857,375 Å^3
Density 1.8 g/cm3
~34000 atoms per cell

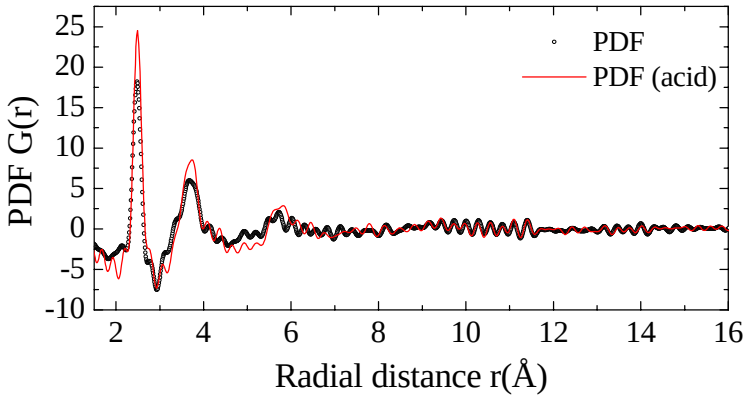
Acid stability and framework breathing





SEM images of (left) as-synthesized *c*-C_{20}PyPtSnSe. (right) H_2SO_4_C_{20}PyPtSnSe particles showing contracted grain size yet preserved cubosome morphology.

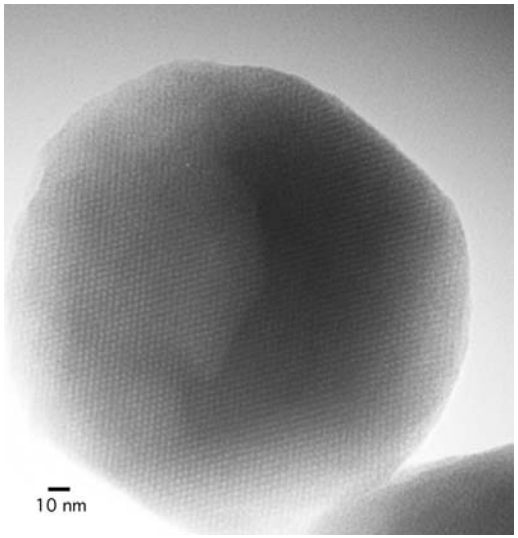
Sample	Powder XRD Data		Unit cell Constant, *a* (Å)	Vol. Contraction, (%)
	d_{211}/Å	d_{220}/Å		
HCl_C_{20}PyPtSnSe	29.9	25.9	73	54.4
H_2SO_4_C_{20}PyPtSnSe	28.0	24.5	69	61.8
HNO_3_C_{20}PyPtSnSe	27.4	23.9	67	64.6
c-C_{20}PyPtSnSe	38.6	33.3	95	

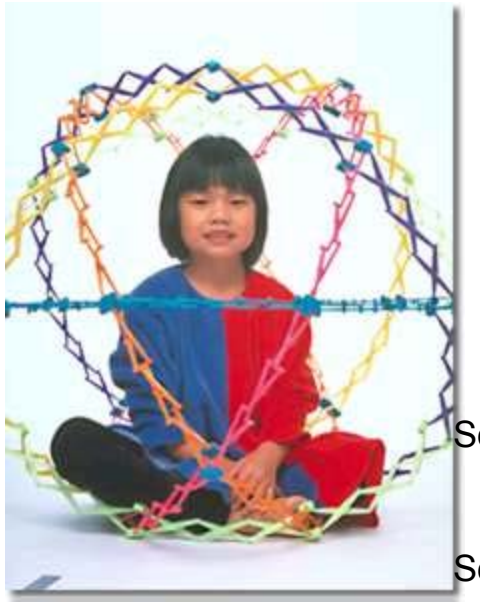


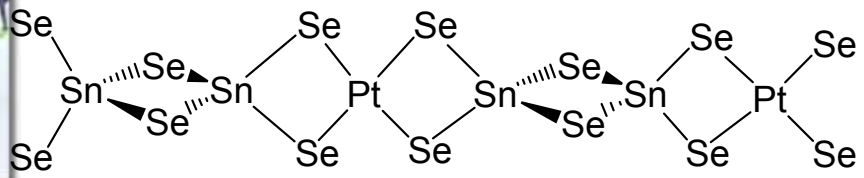
Trikalitis PN, Ding N, Malliakas C, et al. *J. Am. Chem. Soc*. **2004**, 126 (47): 15326.

How does cubic Pt-Sn-Se breath?

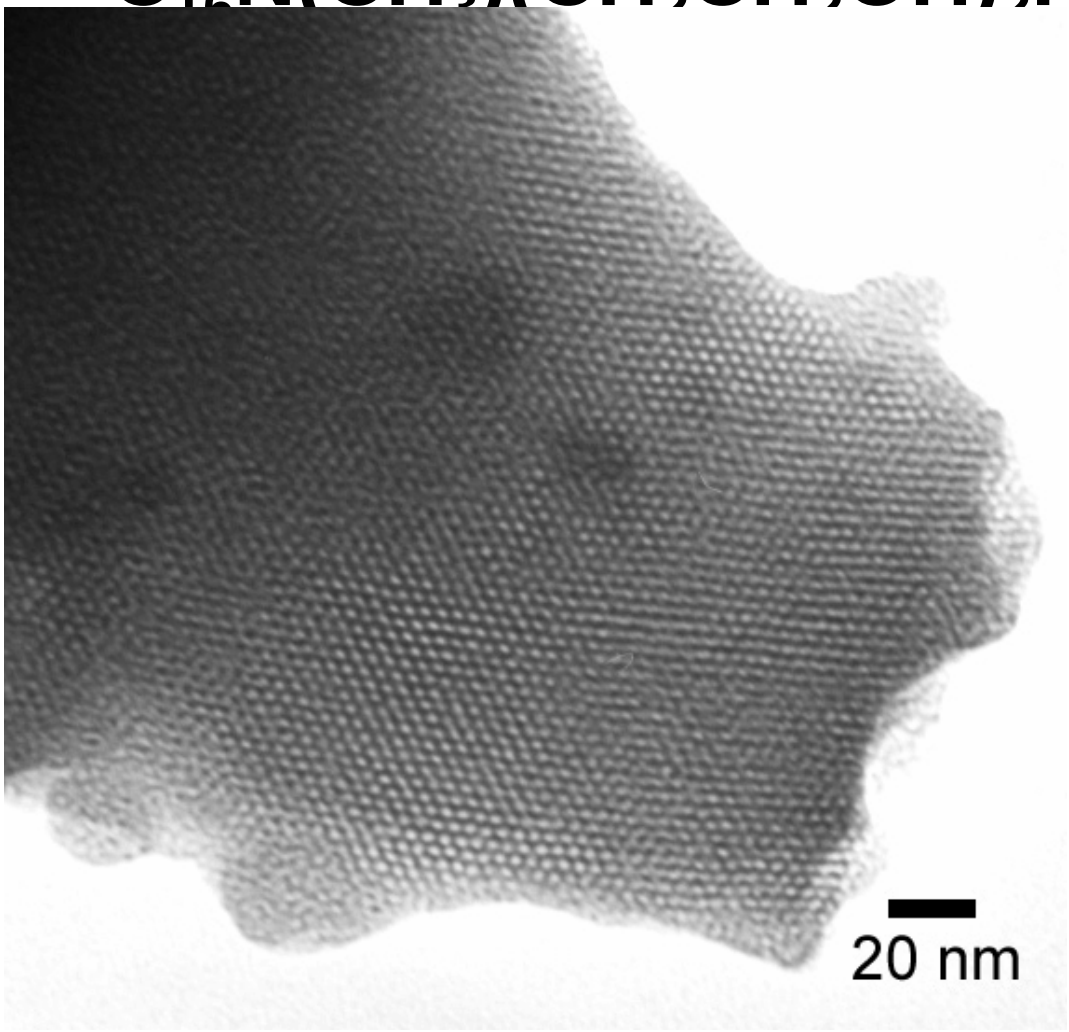
- A **Hoberman sphere** is a structure that resembles a geodesic dome, but is capable of folding down to a fraction of its normal size by the scissor-like action of its joints.

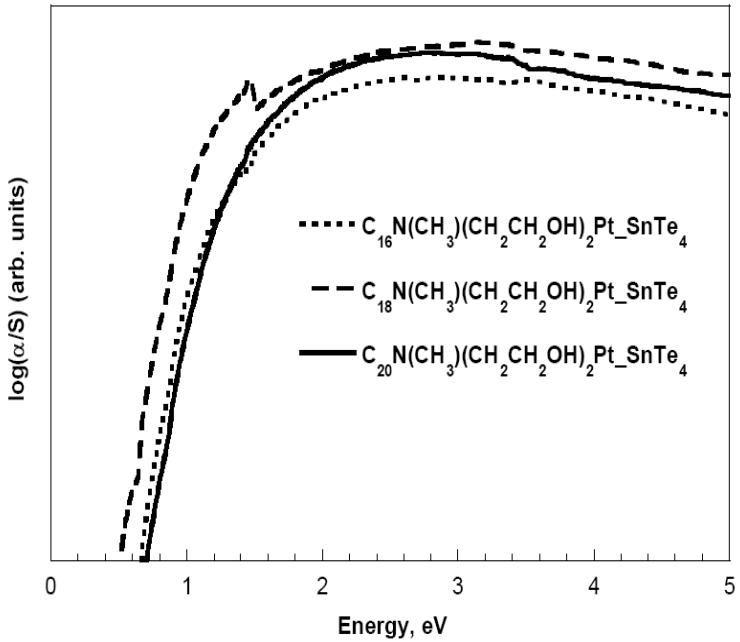






TEM images of $C_{16}N(CH_3)(CH_2CH_2OH)_2Pt\_SnTe_4$



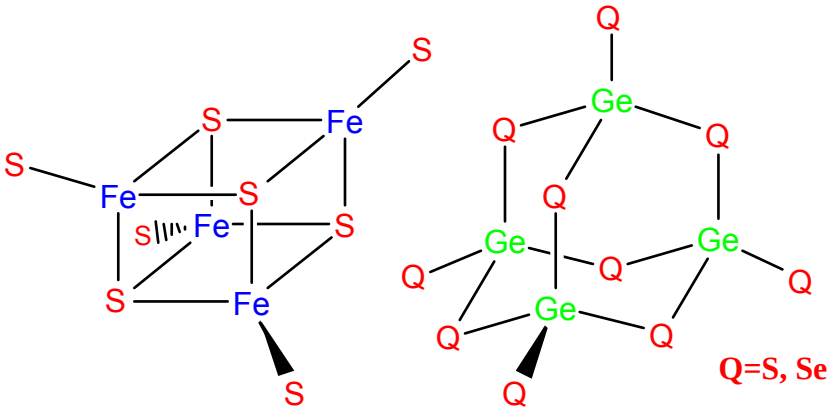


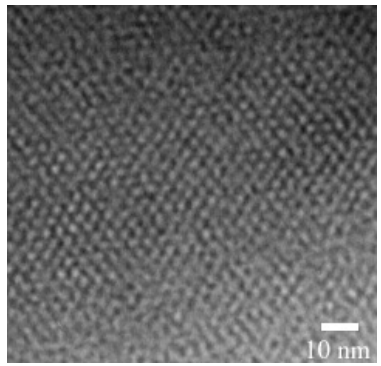
Extremely air sensitive.

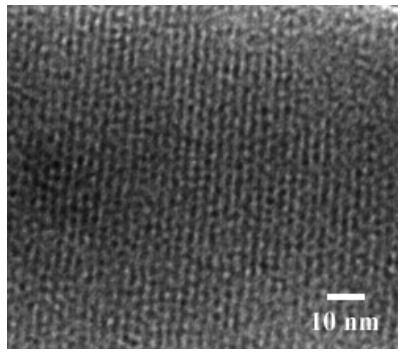
Biologically inspired nanocomposites (Fe_4S_4 ferredoxinoids)

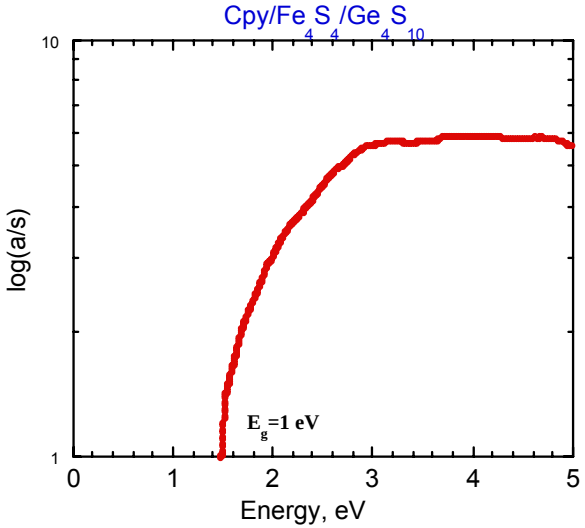
Fe4S4-MSU-1 and Fe4S4-M SU-2

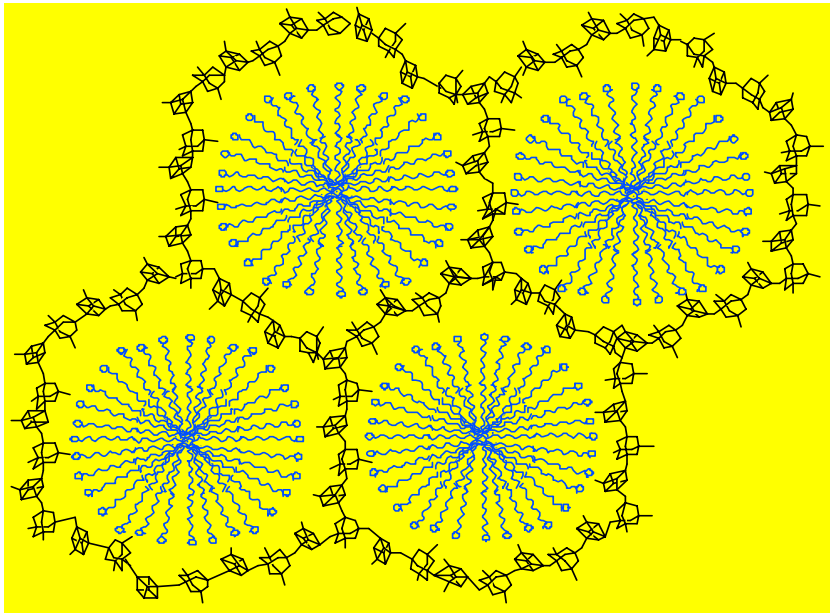
Angew Chemie 2000, 39, 4558





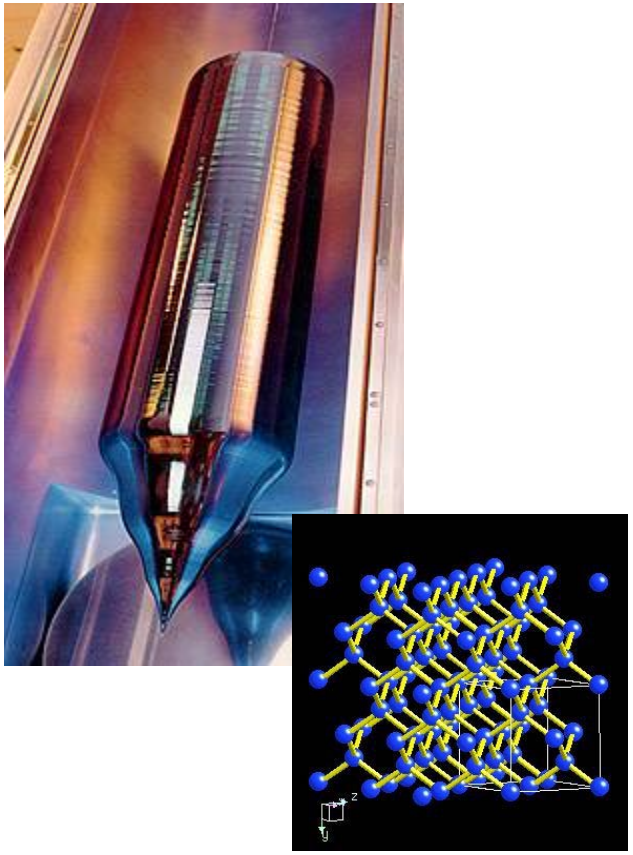


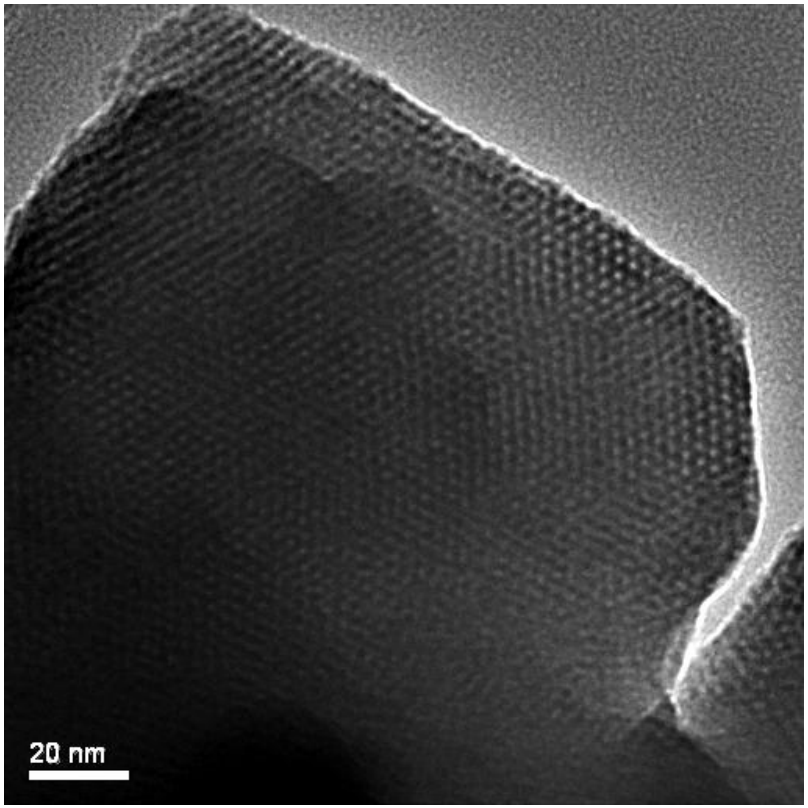




Mesoporous elements…

- Group IV: Si, Ge and Sn





Preparation of mesostructured Ge

Mg_2Ge + $GeCl_4$ + EMBHEAB ⟶ EMBHEA-$(Ge)_m$

NU-Ge-1

1 : 1 : 1.5 (molar ratio)

Mg_2Ge/FM at 75°C

+Surfactant (3h) $GeCl_4$ at 65°C

Aged at 85°C for 18h

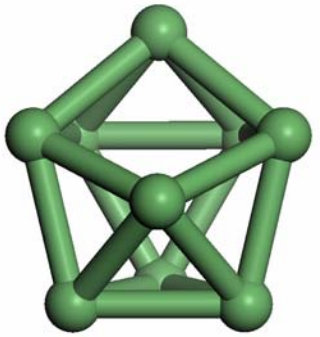
K_4Ge_9 + $GeCl_4$ + C_nMBHEAB ⟶ C_nMBHEA-$(Ge_9Ge)_m$

NU-Ge-2

1 : 1 : 6 (molar ratio)

in en/FM solution at 80°C for 18h

$[Ge_9]^{-4}$=

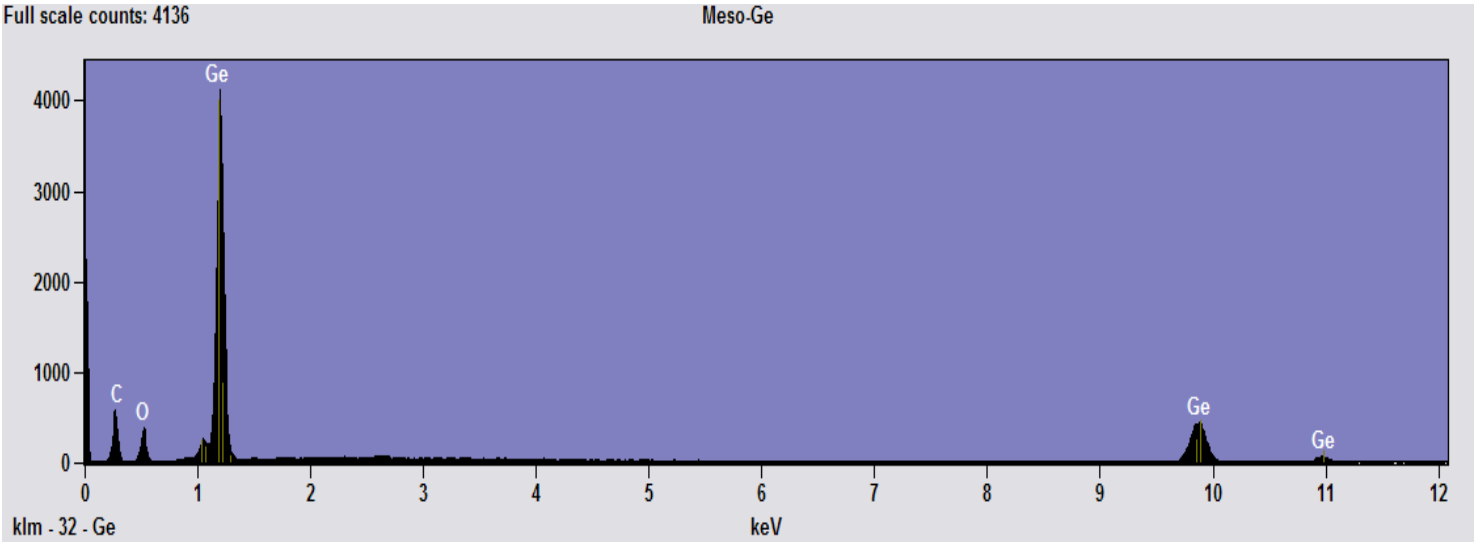


EMBHEAB = $C_{20}N(CH_3)(C_2H_4OH)_2Br$

After purification in $CHCl_3$

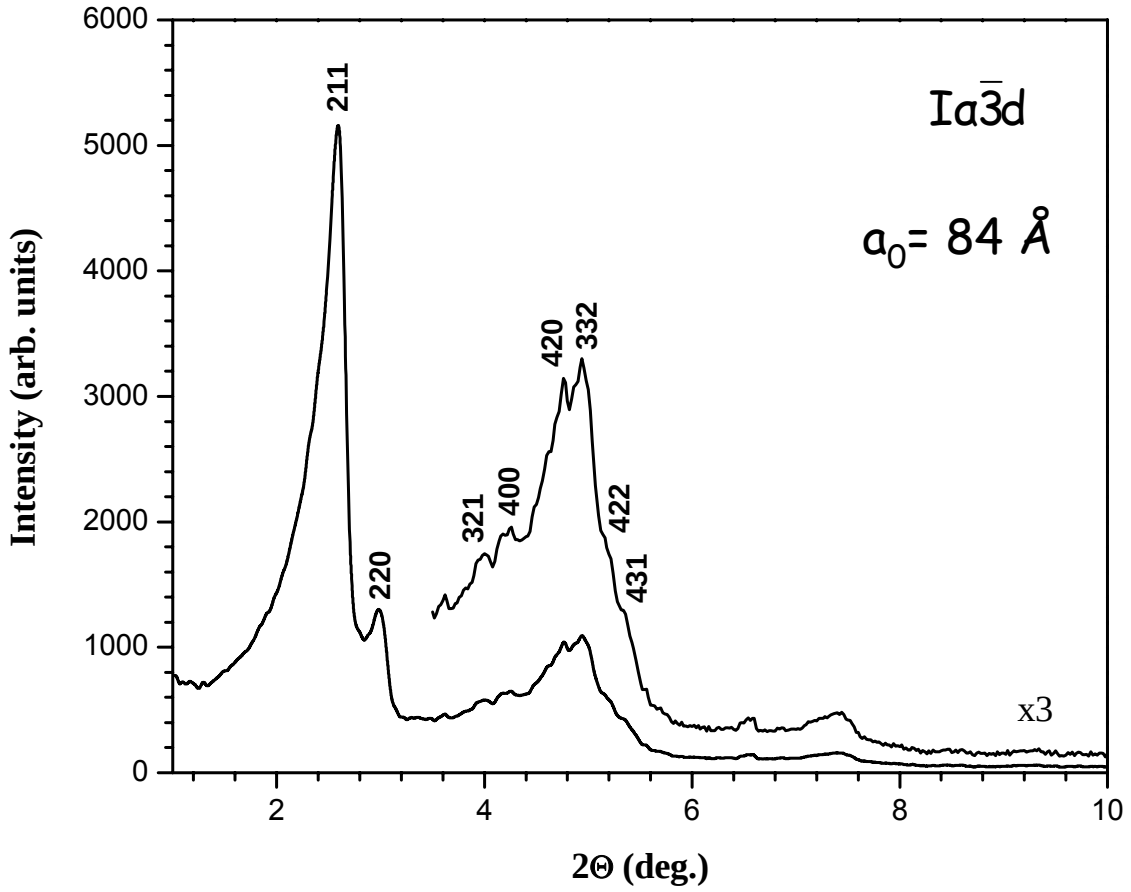
EMBHEA-$(Ge)_{m(s)}$ in $CHCl_{3(l)}$ (1 mg/1 ml) for 1h

EDS Analysis



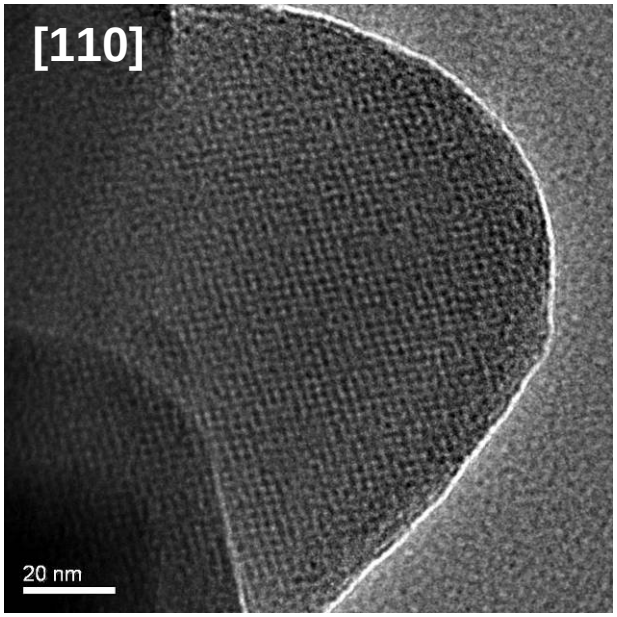
formula: $C_{20}N(CH_3)(C_2H_4OH)_2$-$[Ge]_{7.3}$

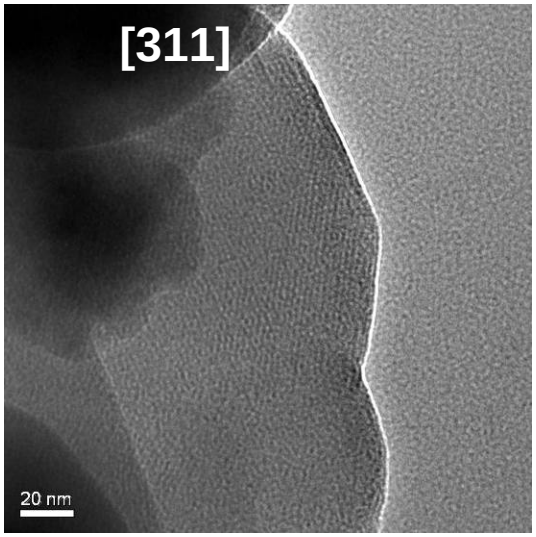
PXRD of EMBHEA-$(Ge)_{7.3}$: NU-Ge-1

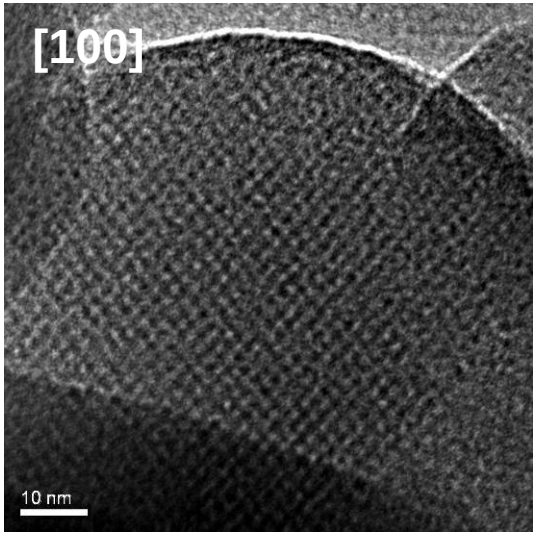


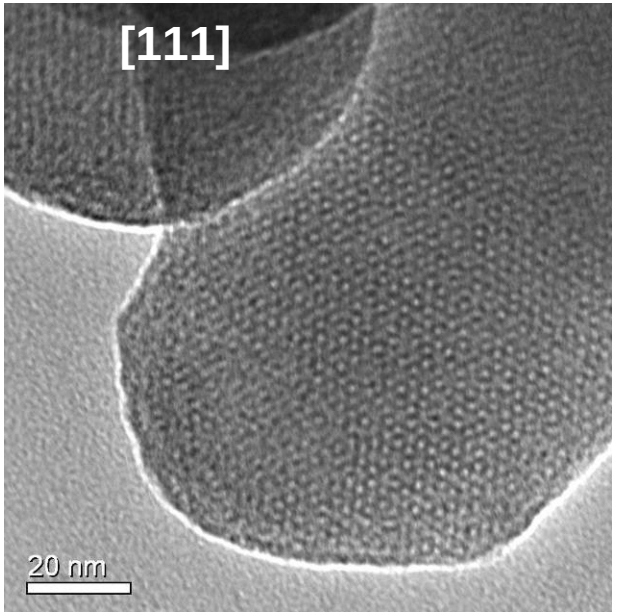
From Mg_2Ge → cubic

TEM Images of Cubic EMBHEA-$(Ge)_{7.3}$



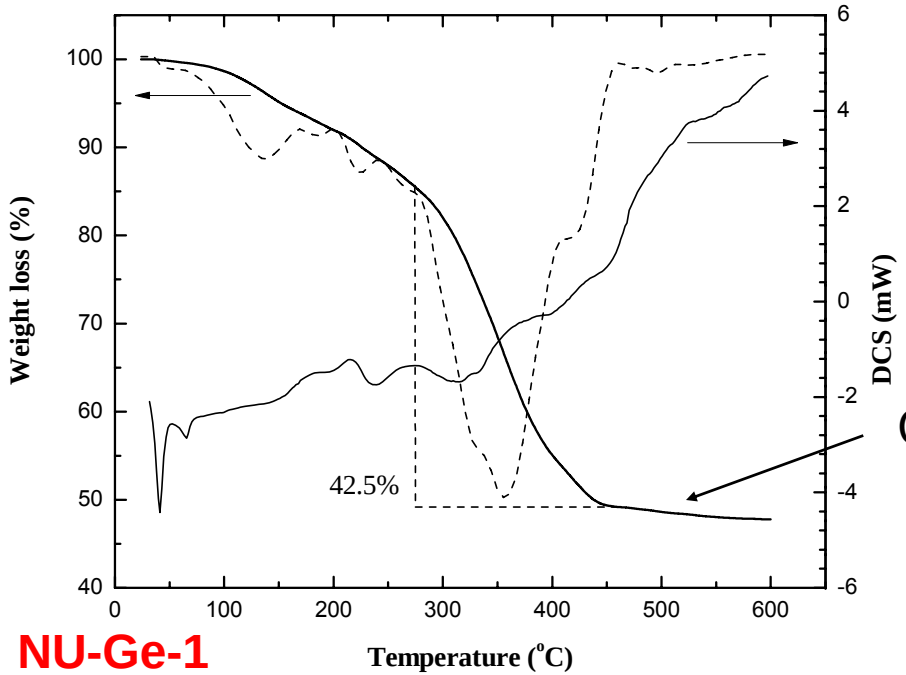






NU-Ge-1

TGA/DSC & CHN Analysis



NU-Ge-1

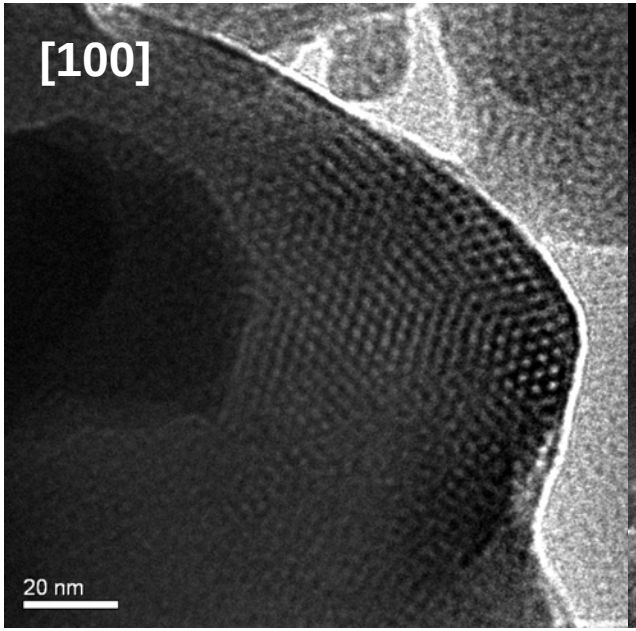
C (%)	H (%)	N (%)
32.24	5.97	1.61

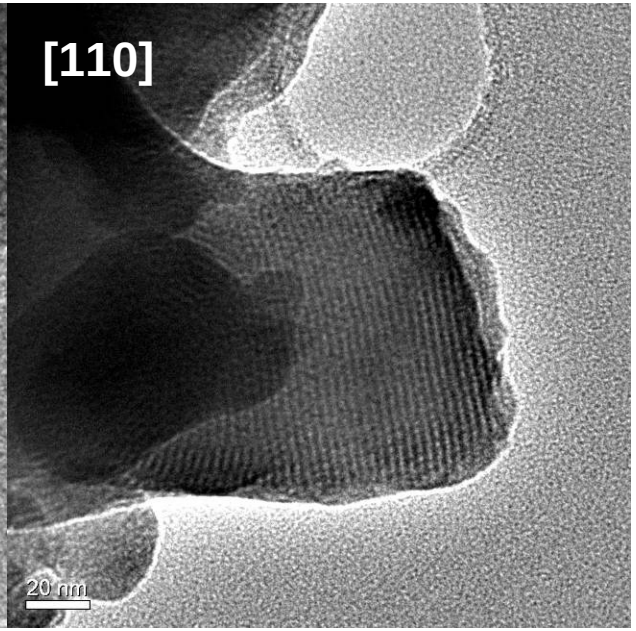
Crystalline Ge

formula: $C_{20}N(CH_3)(C_2H_4OH)_2$-$[Ge]_{7.3}$

Hexagonal

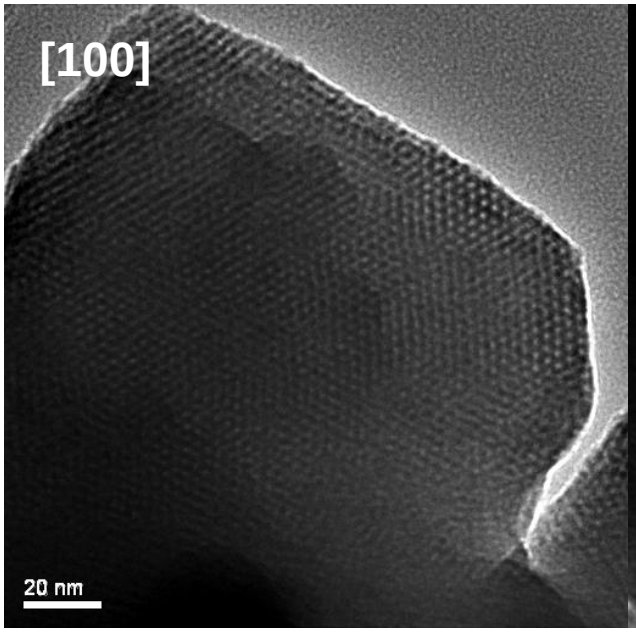
$C_{18}MBHEA_{0.91}$-(Ge_9Ge)

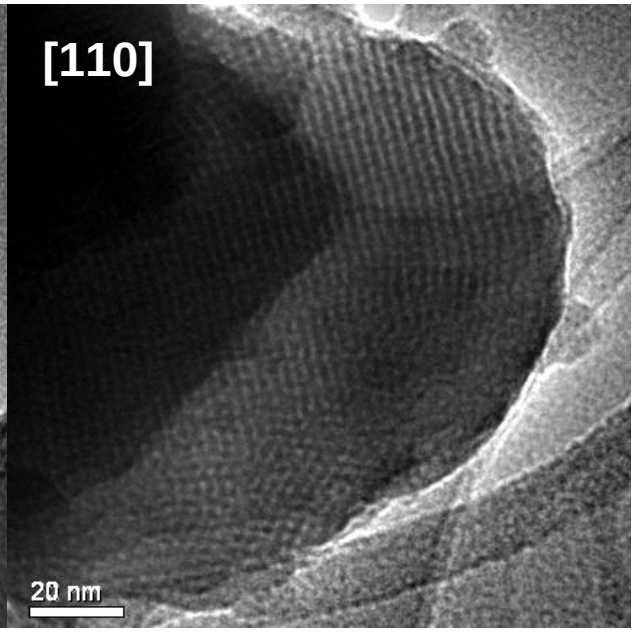




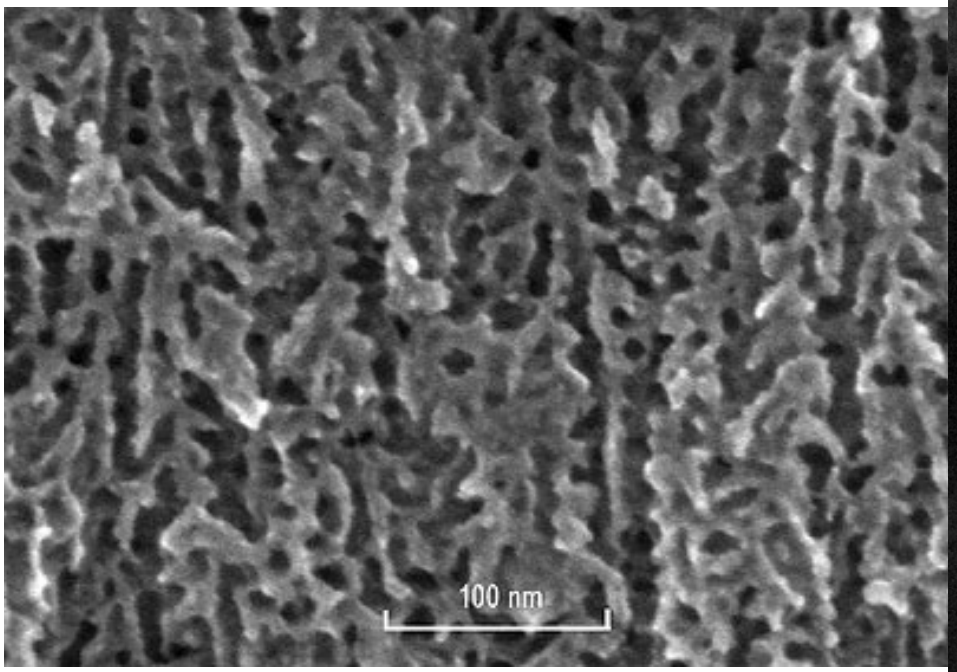
NU-Ge-2

$C_{20}MBHEA_{0.92}$-(Ge_9Ge)

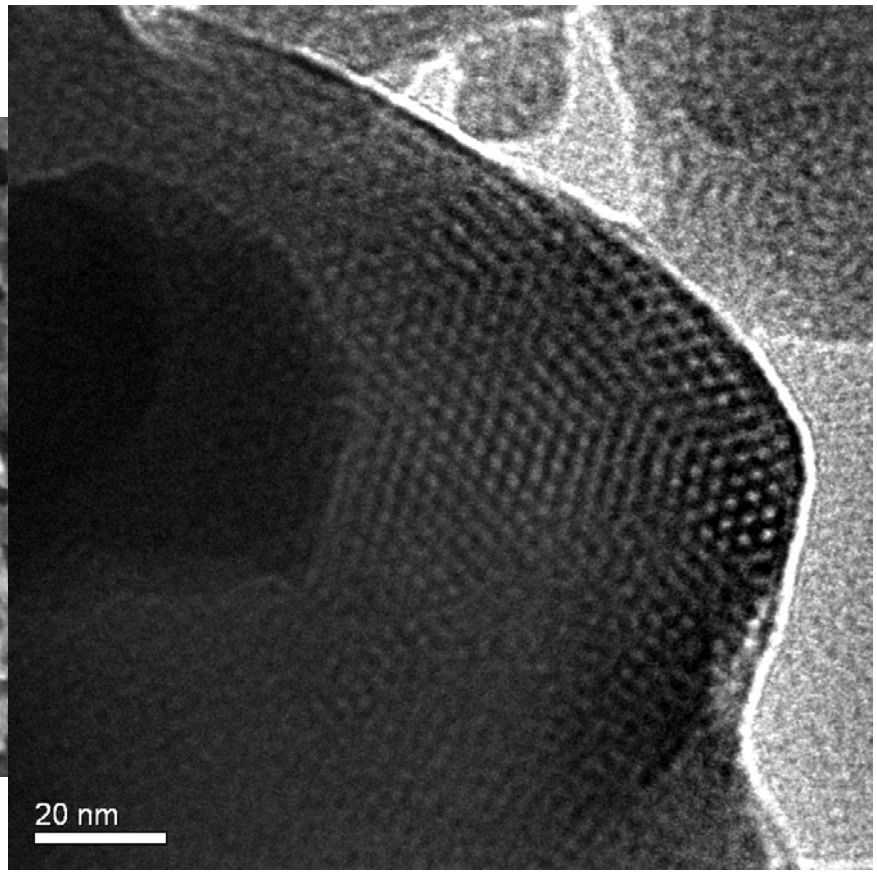




Porous silicon versus mesoporous Ge

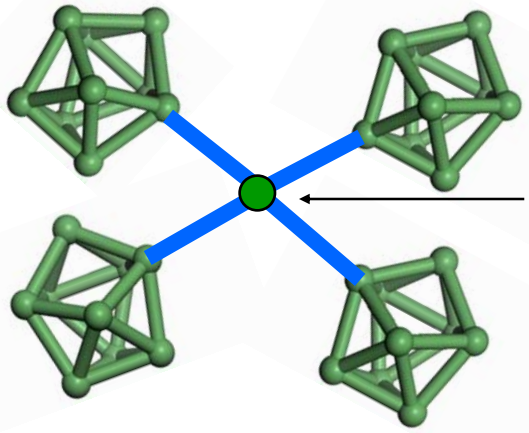


Porous silicon
Anodizing Si

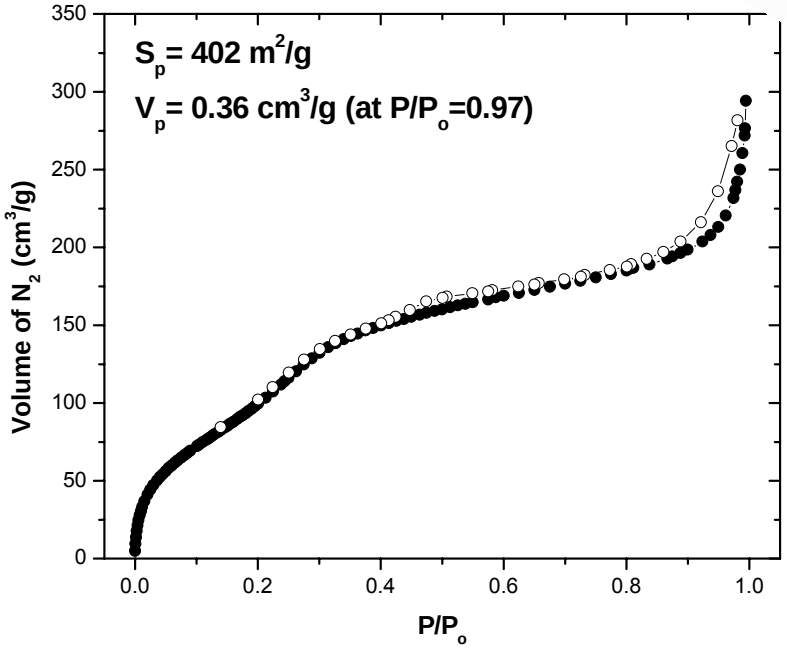


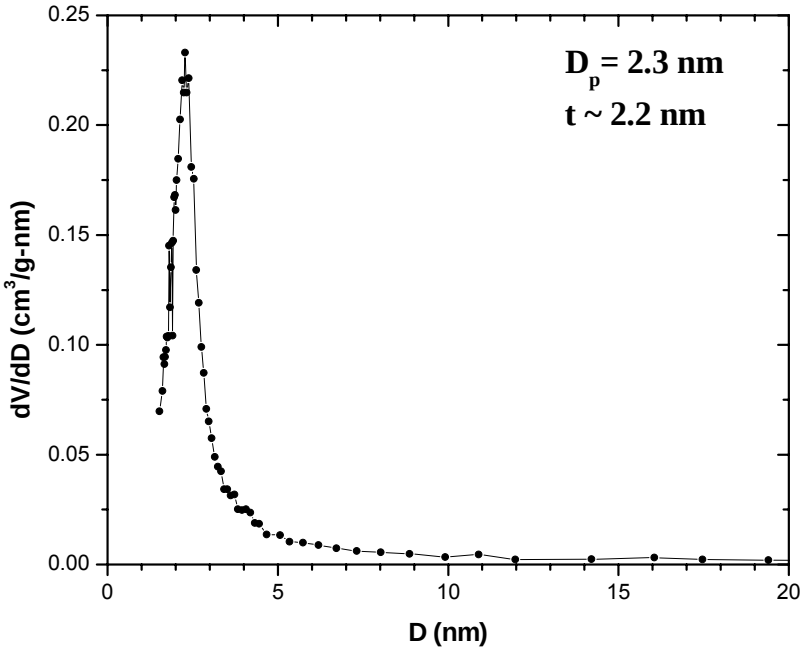
mesoporous Ge
Self-assembly

Mesoporosity of (C_{20-1})-$[(Ge_9)_m]$: NU-Ge-2

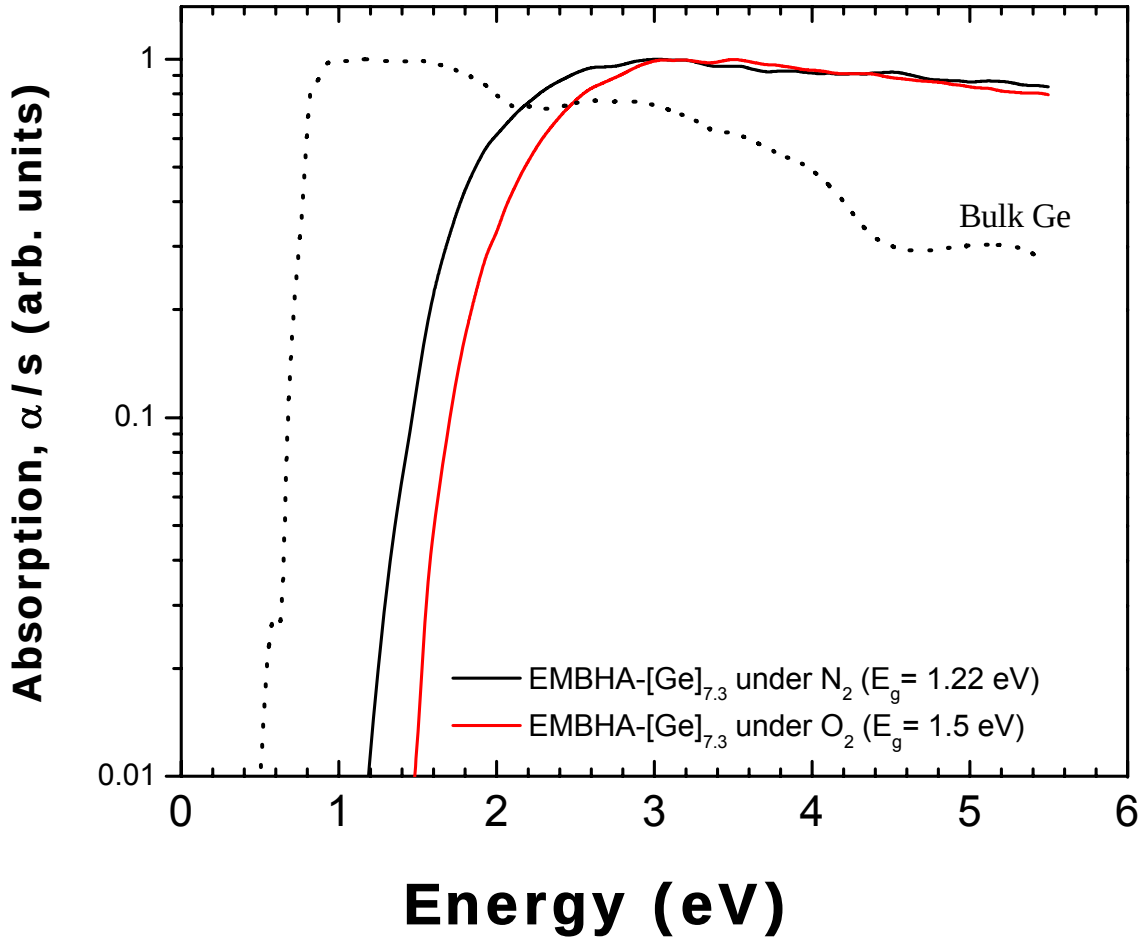


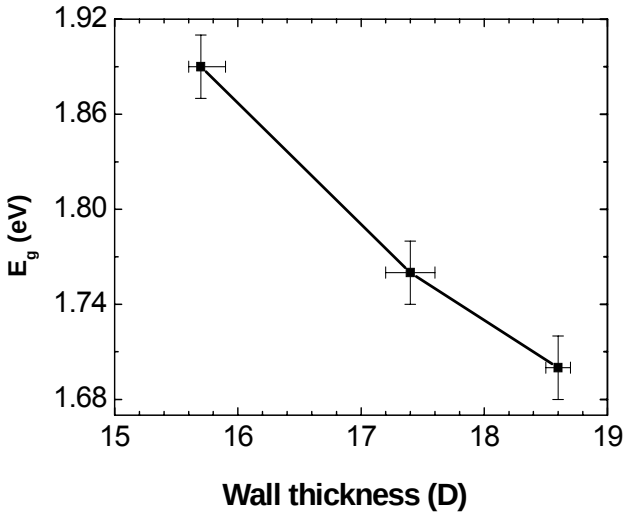
Linking Ge atom





Optical Properties of mesoporous-Ge: NU-Ge-2

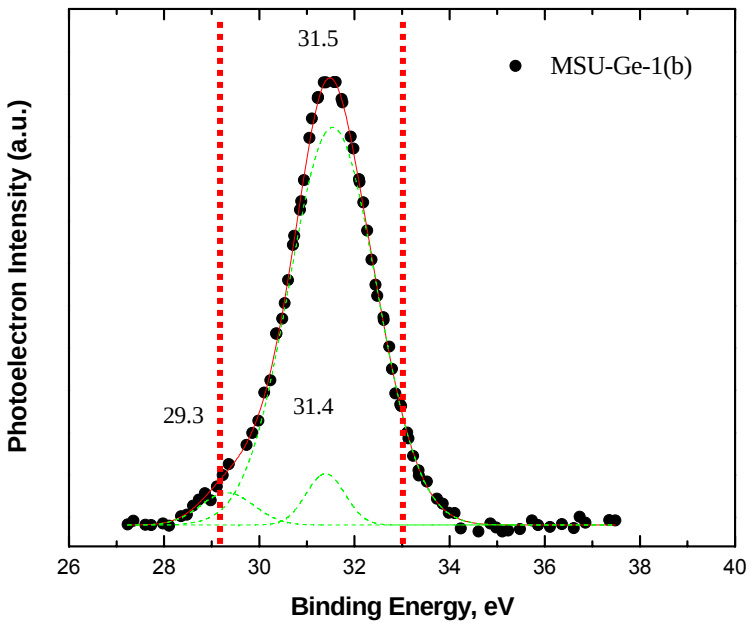


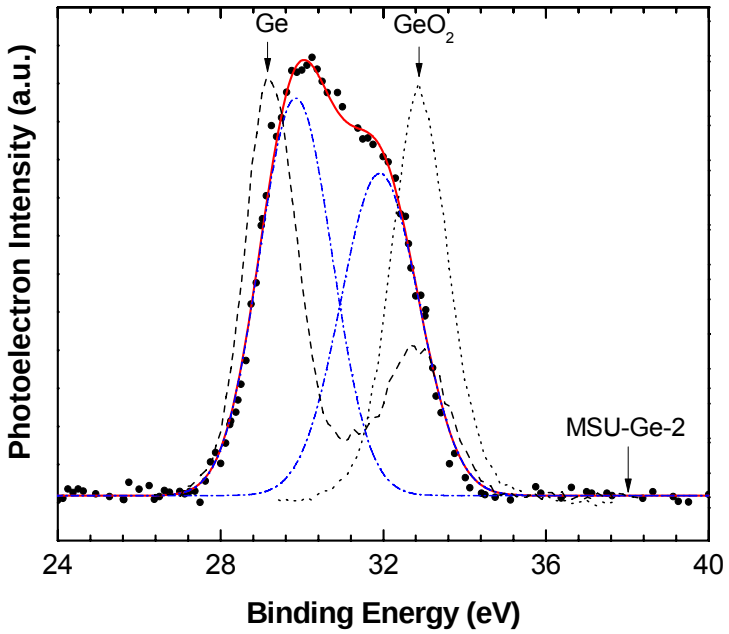


Oxidation

X-ray photoelectron spectroscopy

binding energy of Ge 3d peaks





Cubic 1 nm wall

Mg_2Ge

hexagonal 2 nm wall

From $[Ge_9]^{4-}$

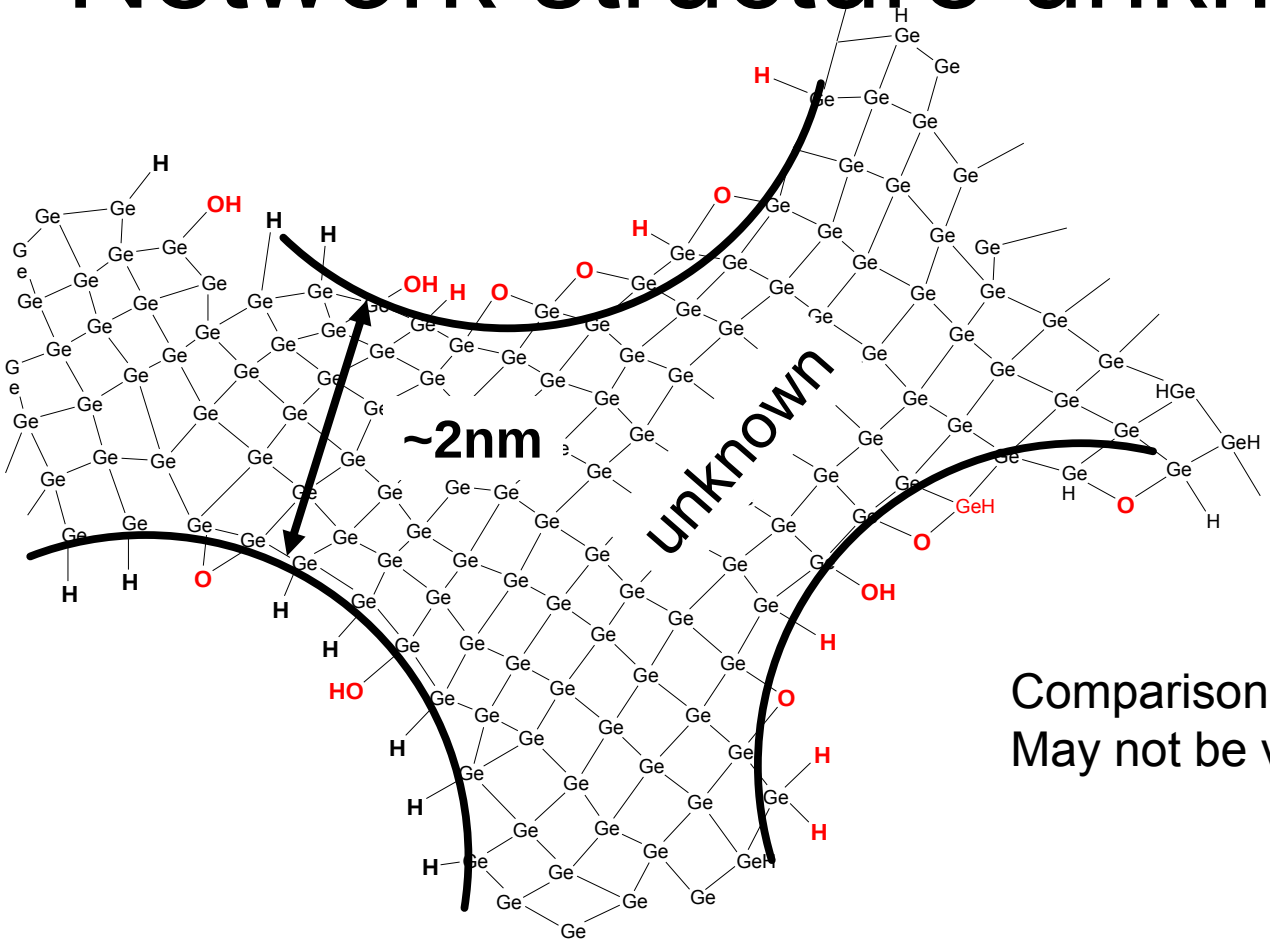
Is mesoporous Ge really a new form of Ge?

- Mesostructured cubic and hexagonal Ge not a new elemental form..
- They are compounds:

  $\{C_{20}N(CH_3)(C_2H_4OH)_2\}(Ge_{7.3})$

  $\{C_{20}N(CH_3)(C_2H_4OH)_2\}_{0.9}(Ge_{10})$
- Mesoporous hexagonal Ge: ~Ge_8H

Network structure unknown

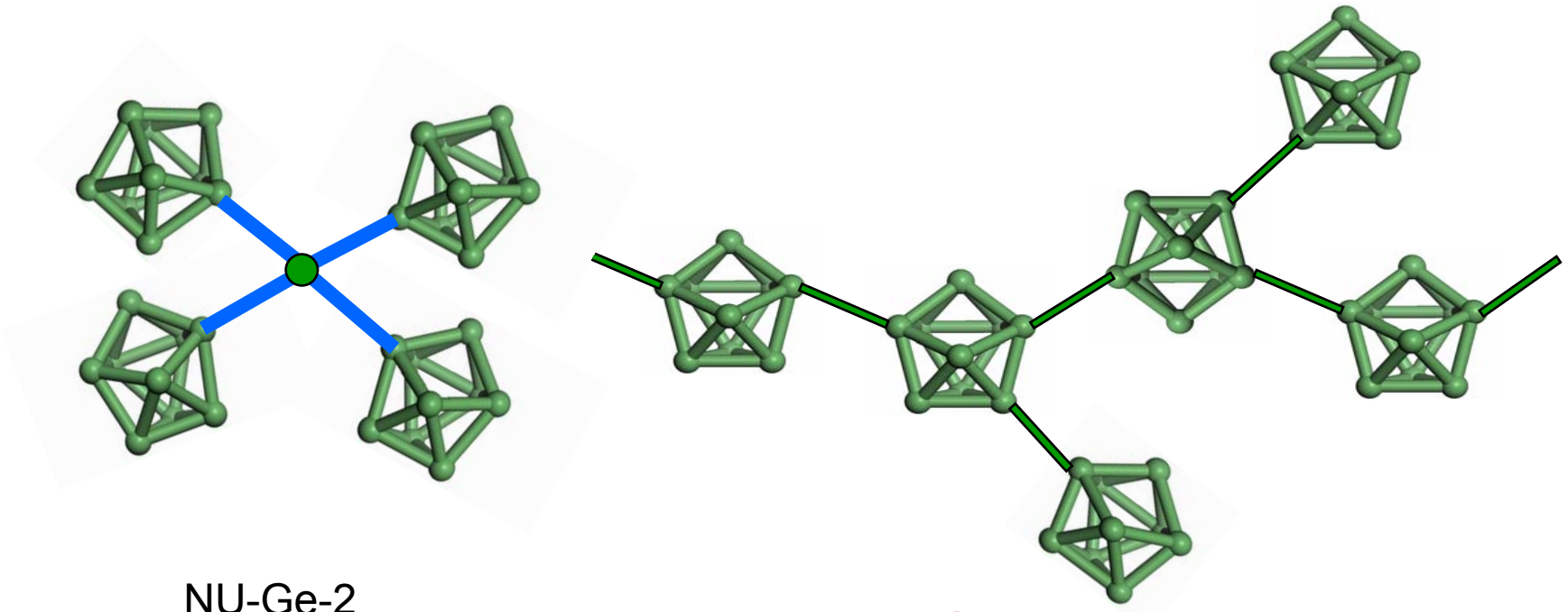


Comparison to Ge nanocrystals
May not be valid (unless size <2 nm)

$CaZn_{13}$, AlB_{12}

Formula: ~ $Ge_6(H,OH,O)$ to $Ge_{10}(H,OH,O)$

Mesoporous Ge from the oxidative self-polymerization of the deltahedral $[Ge_9]^{4-}$ cluster

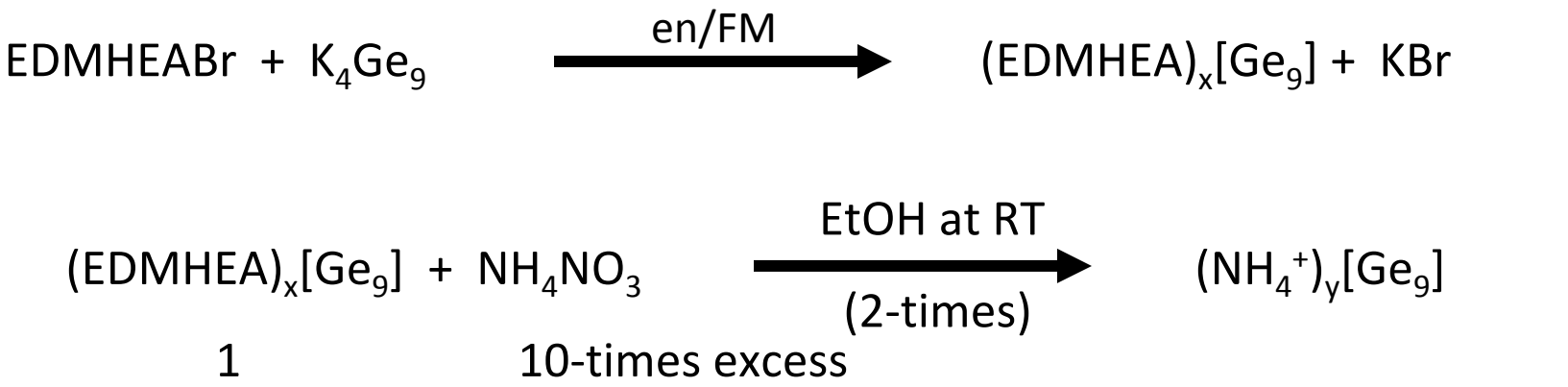


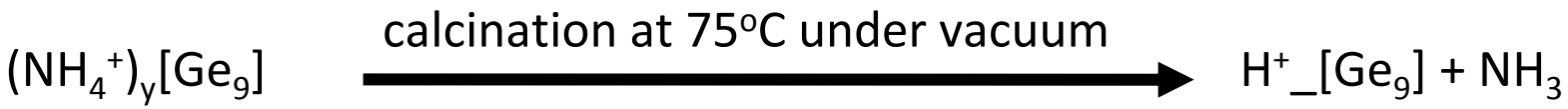
NU-Ge-2

NU-Ge-3

No linking Ge atoms

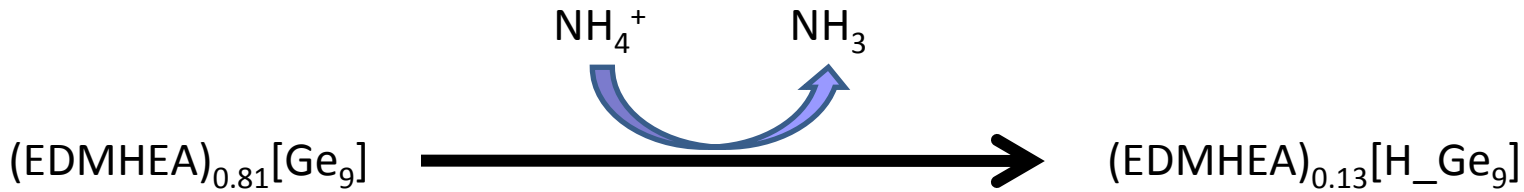
Oxidative self-polymerization of mesoporous (Ge9)-polymer: NU-Ge-3

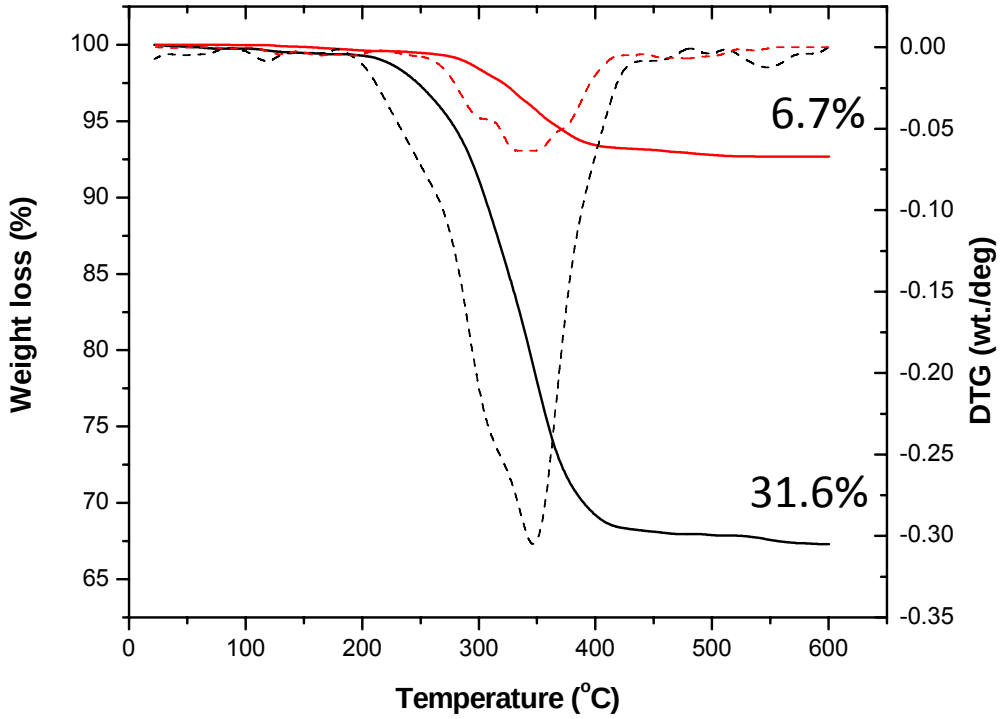




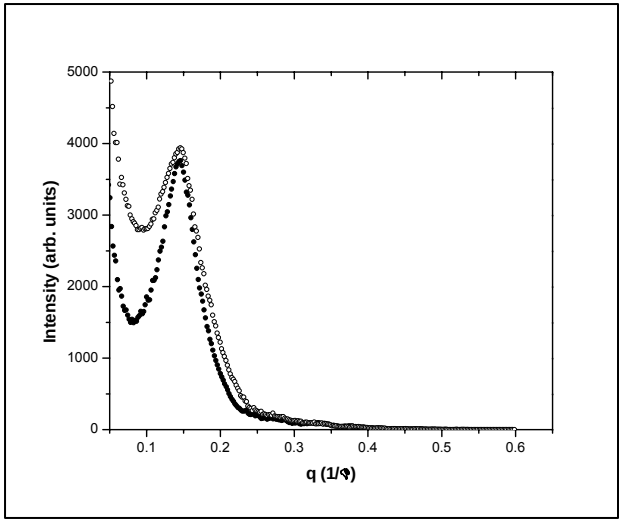
EDMHEABr: $C_{20}H_{41}N(CH_3)_2(C_2H_4OH)Br$

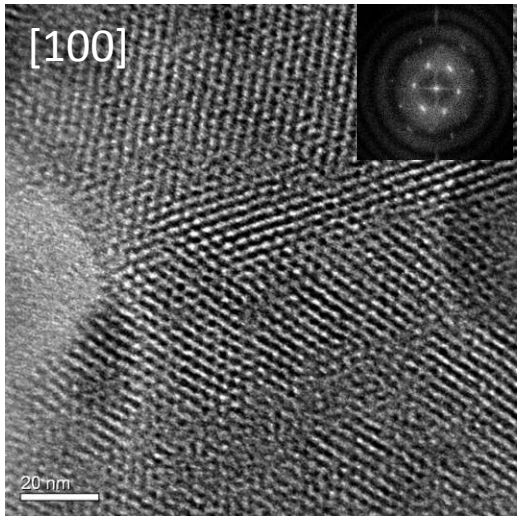
Chemical composition of (Ge_9)-polymer: NU-Ge-3

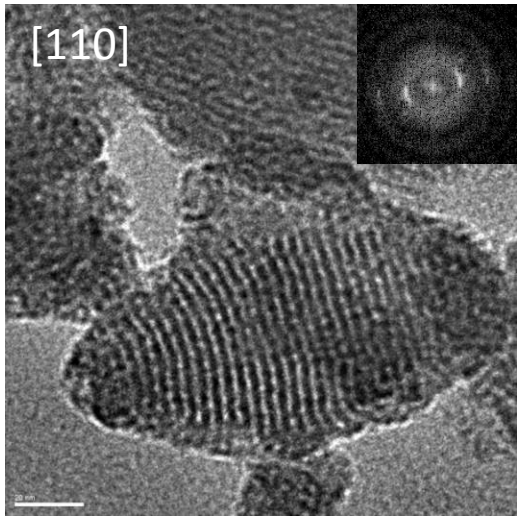




SAXS diffraction and TEM images of mesoporous (Ge_9)-NU-Ge-3



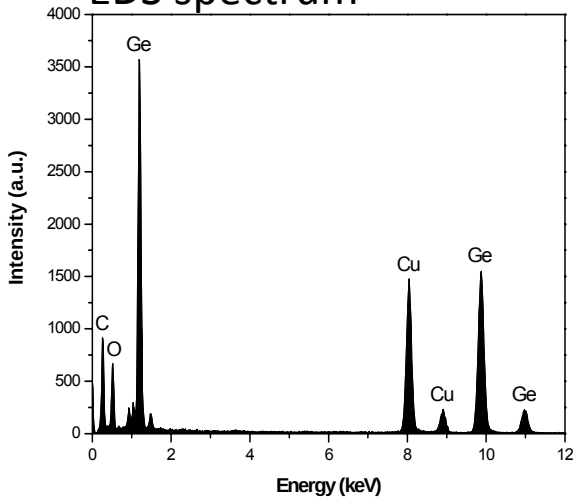




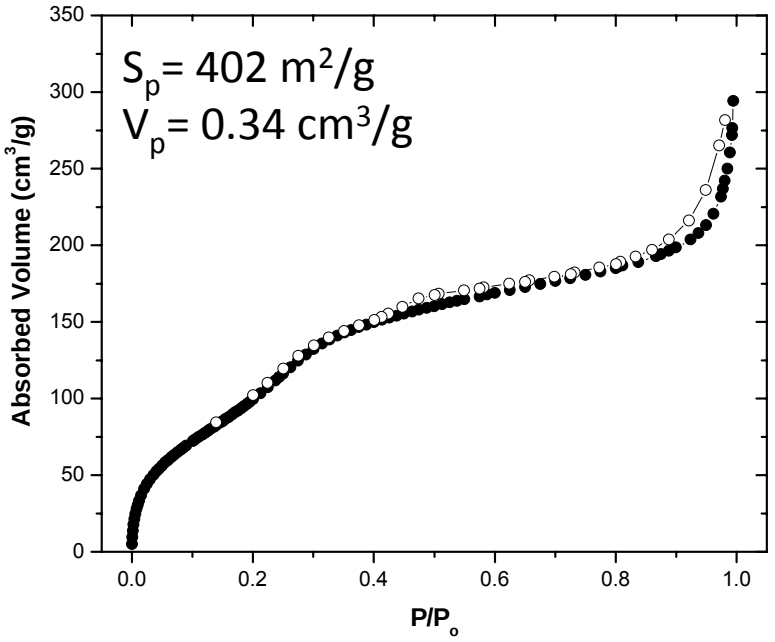
$(EDMHEA)_{0.81}[Ge_9]$ a_0=5.04 nm

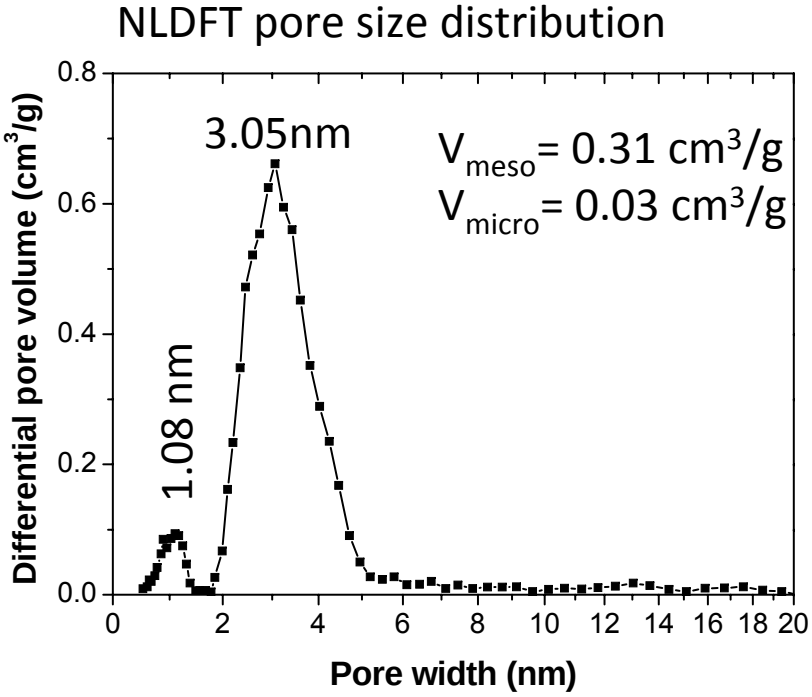
$(EDMHEA)_{0.13}[H\_Ge_9]$ a_0=4.94 nm

EDS spectrum

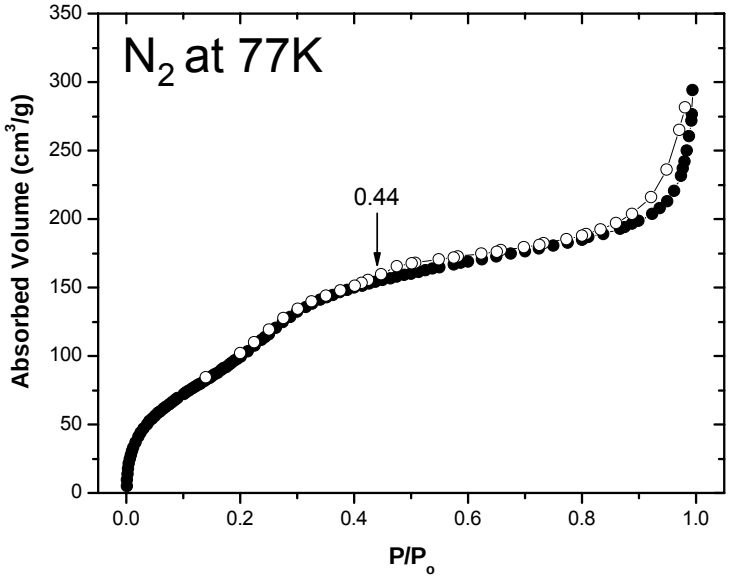


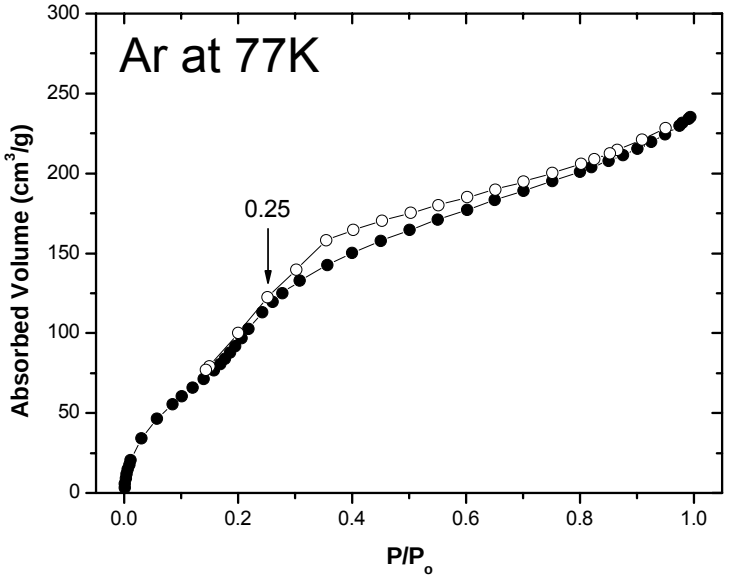
N_2 adsorption-desorption isotherm at 77K





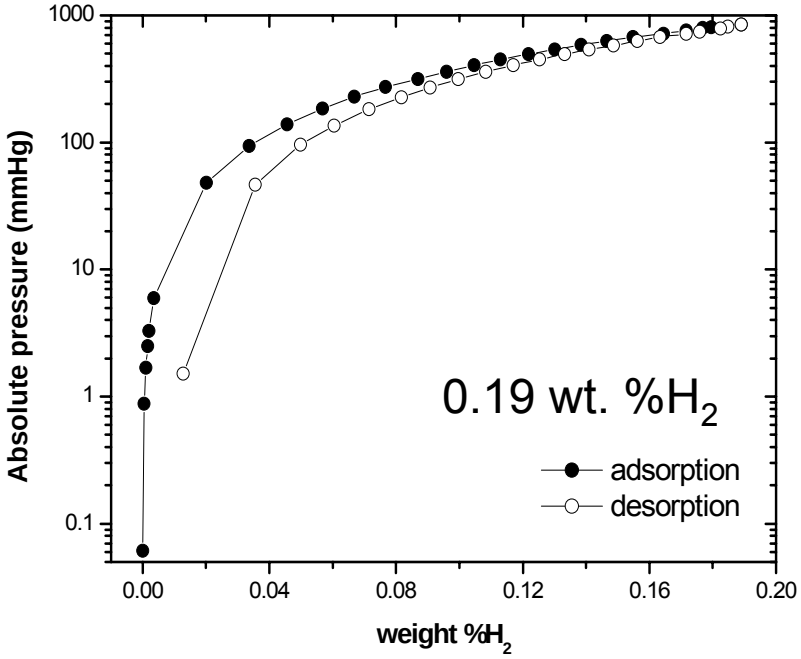
Pore blocking or cavitations effects?

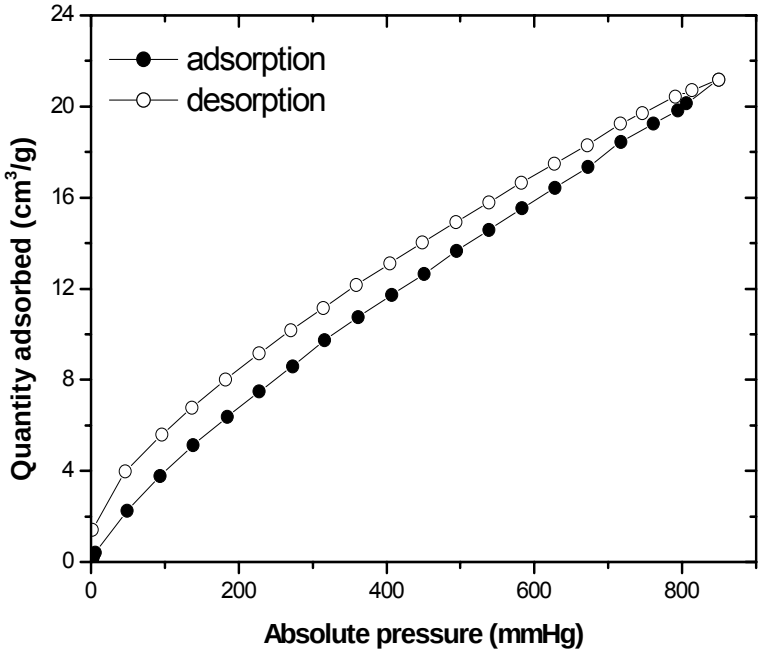




Adsorptive	**N_2**	**Ar**
Cross-section area	16.2 Å^2	14.2 Å^2
Surface area	402 m^2/g	385 m^2/g

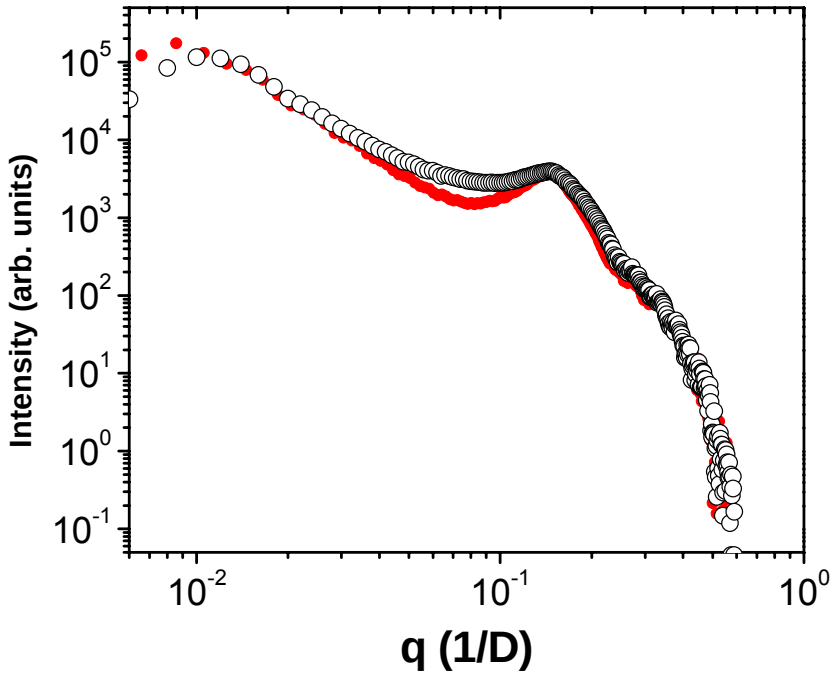
Hydrogen adsorption at 77K





$$(EDMHEA)_{0.13}[Ge_9] \xrightarrow{0.19\ wt.\ \%H_2} (EDMHEA)_{0.13}(H_2)_{1.3}[Ge_9]$$

Small angle x-ray scattering (SAXS) analysis: NU-Ge-3



$$S = \pi \cdot \phi \cdot (1-\phi)\left(\frac{K}{\rho \cdot Q}\right) = \pi \cdot \phi \cdot \left(\frac{K}{\rho_s \cdot Q}\right)$$

$$Q = \int_{q_{\min}}^{q_{\max}} (I(q) - b) q^2 dq + \frac{K}{q_{\max}}$$

$D_{SAXS} = l_p = 1/(1-\varphi)$ $l = 4^*\pi/Q^*K$

SAXS unit cell, a_0‡	49.4 Å (50.4 Å of as-prepared)
Surface area, S_{BET}†	402 m^2/g
Surface area, S_{SAXS}	417 m^2/g
Surface area, S_{NLDFT}	400 m^2/g
Gurvich pore volume (at P/P_o=0.95)	0.34 cm^3/g
SAXS mesopore width, D_{SAXS}	29.9 Å
Wall thickness, WT_{SAXS}§	19.5 Å

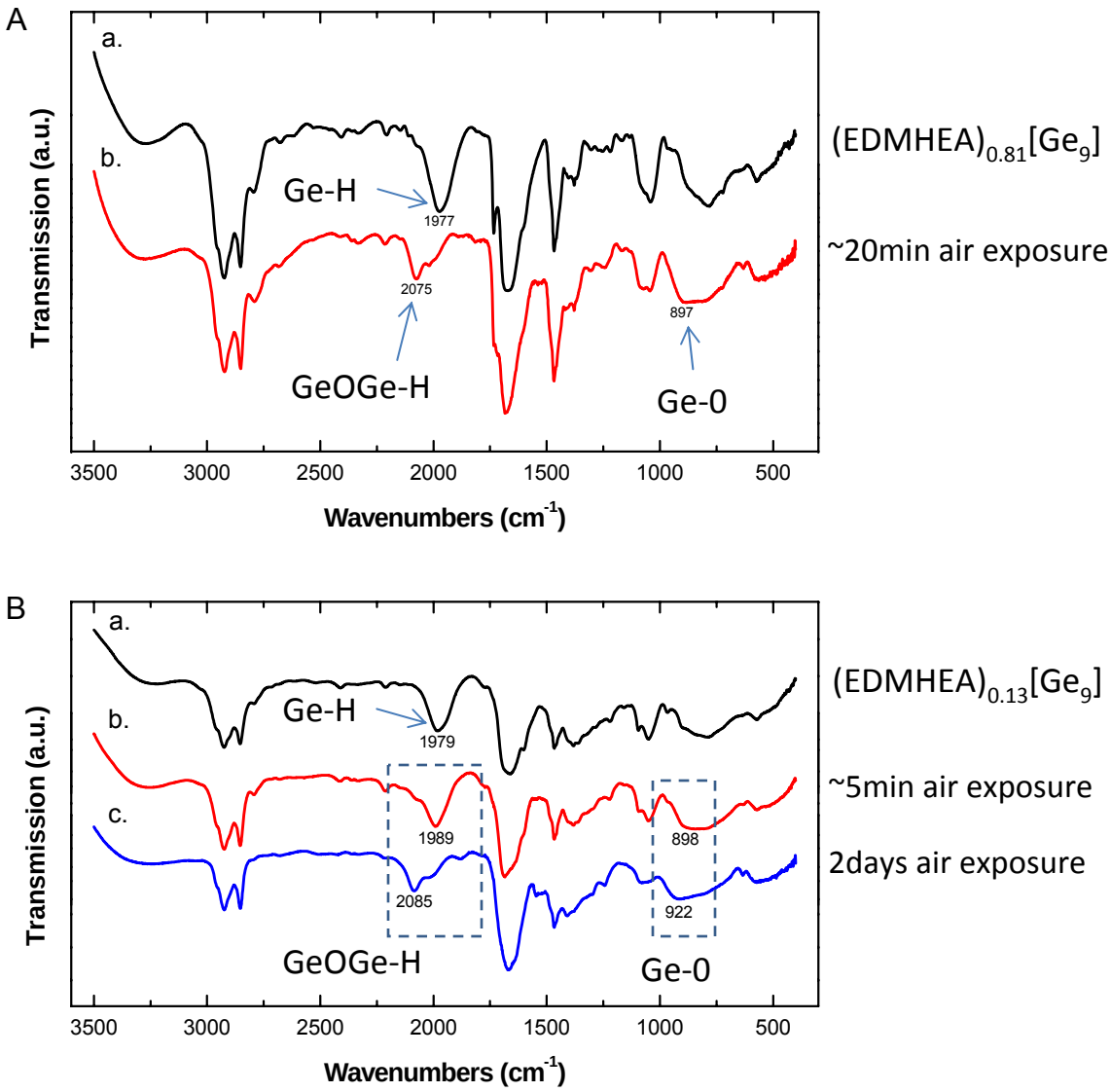
I(q) = *f*(q) (q=4π/λ sin(θ))

K – Porod's constant

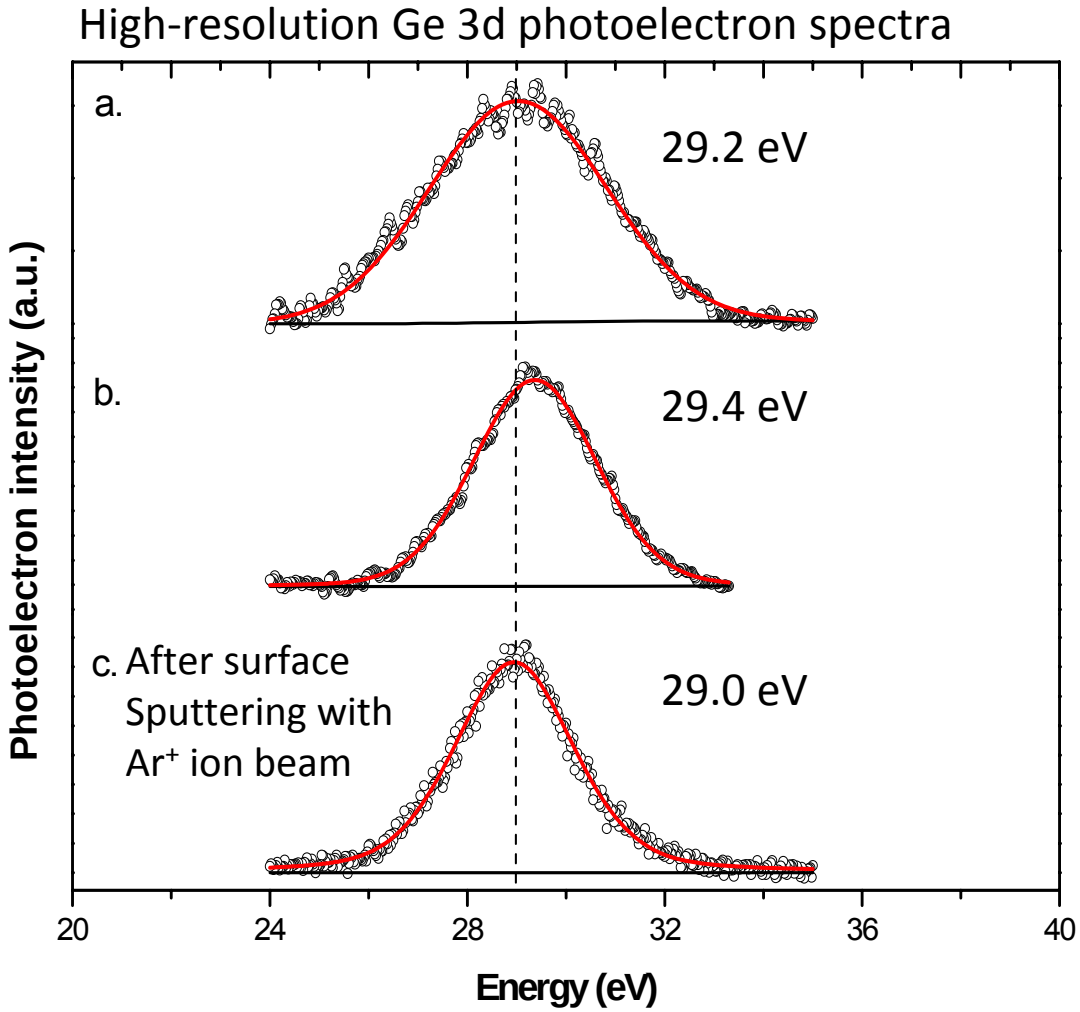
φ – fraction of pores (porosity)

ρ,ρ_S – bulk and skeleton densities

FTIR spectra of as-prepared (A) and mesoporous (B) materials



X-ray photoelectron spectroscopy (XPS) analysis of mesoporous NU-Ge-3



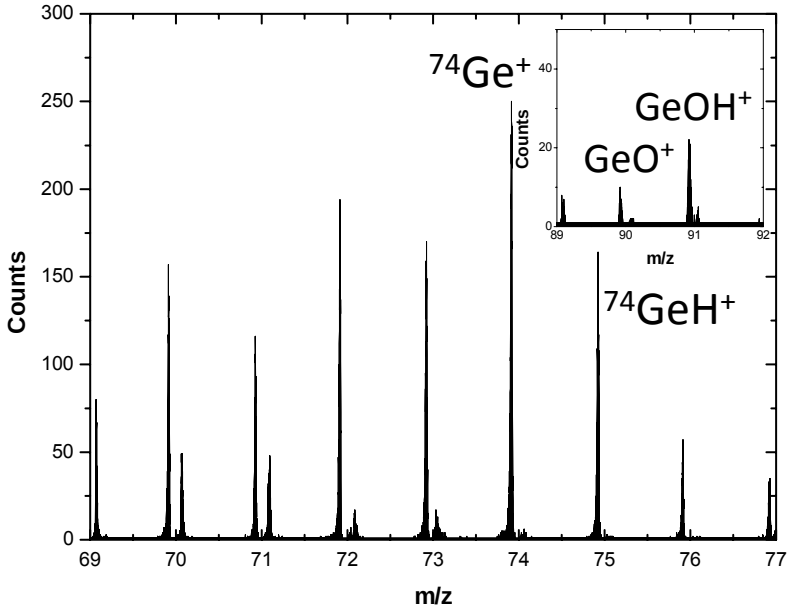
Ge^0 $3d_{5/2}$ = 29.0 eV

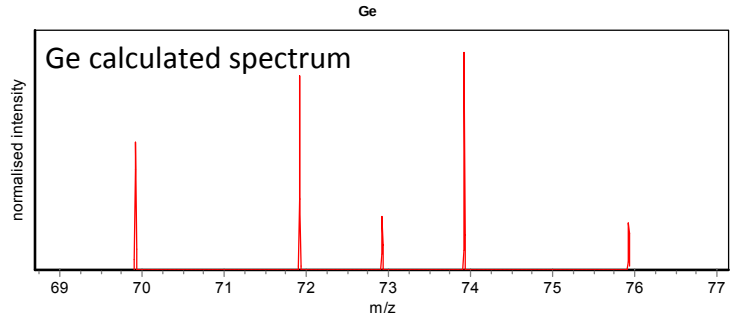
GeO_2 $3d_{5/2}$ = 32.5 eV

Ge-H and

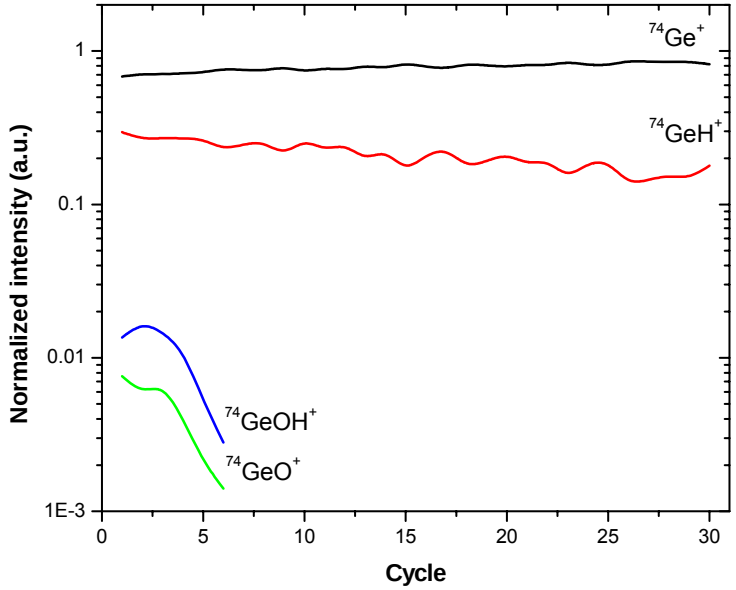
possibly Ge-OH (?)

Time-of-Flight secondary ion mass spectroscopy (ToF-SIMS) analysis of mesoporous NU-Ge-3



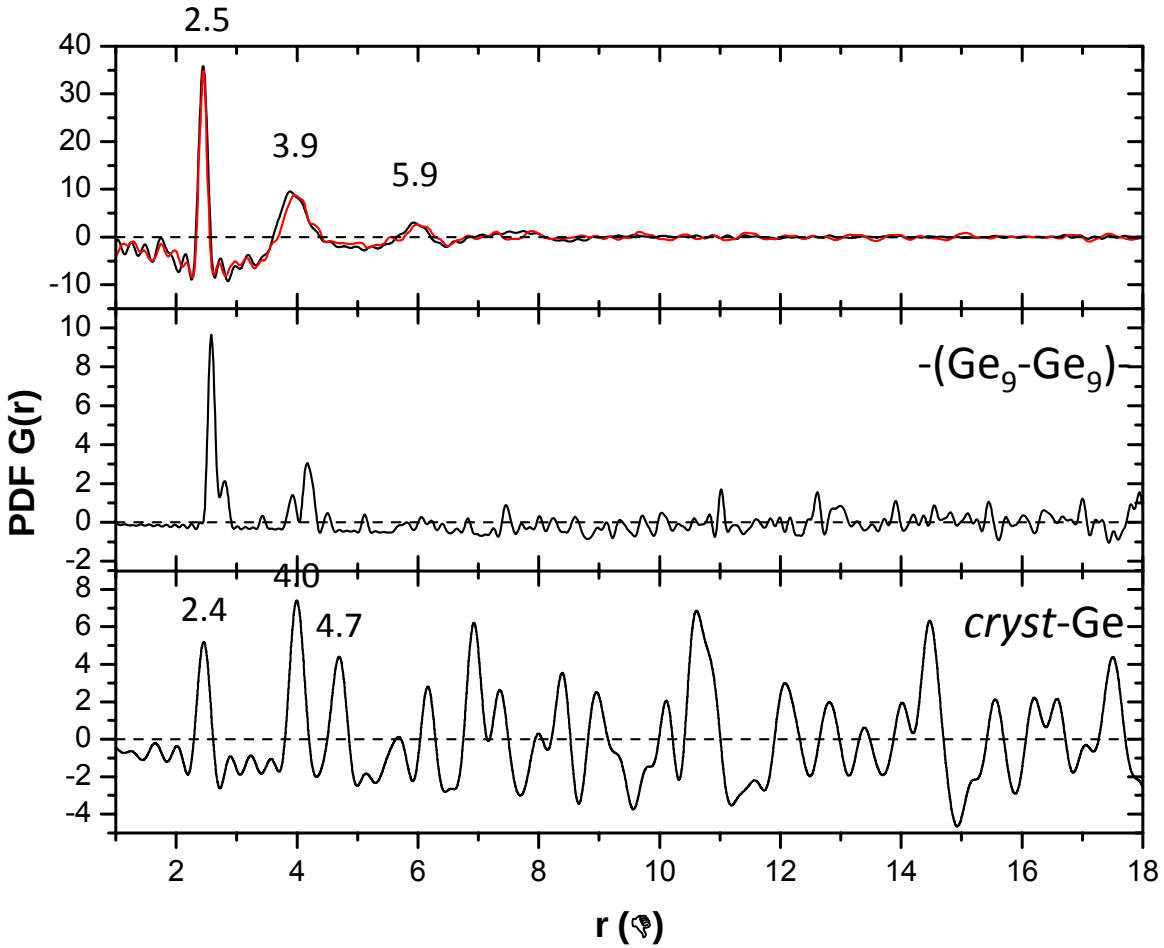


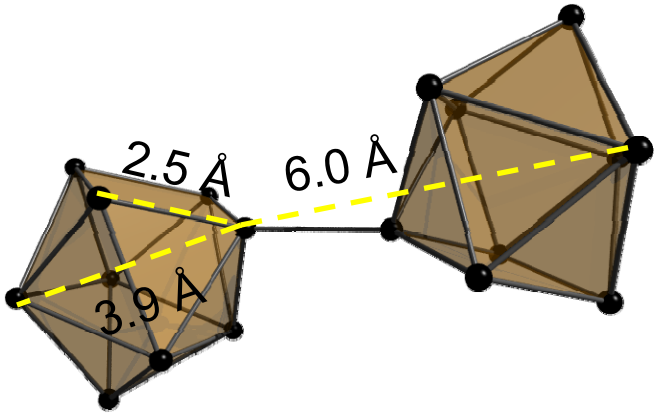
Depth profile*



*analysis time of 28s and sputtering time of 5s

Pair distribution function (PDF) analysis





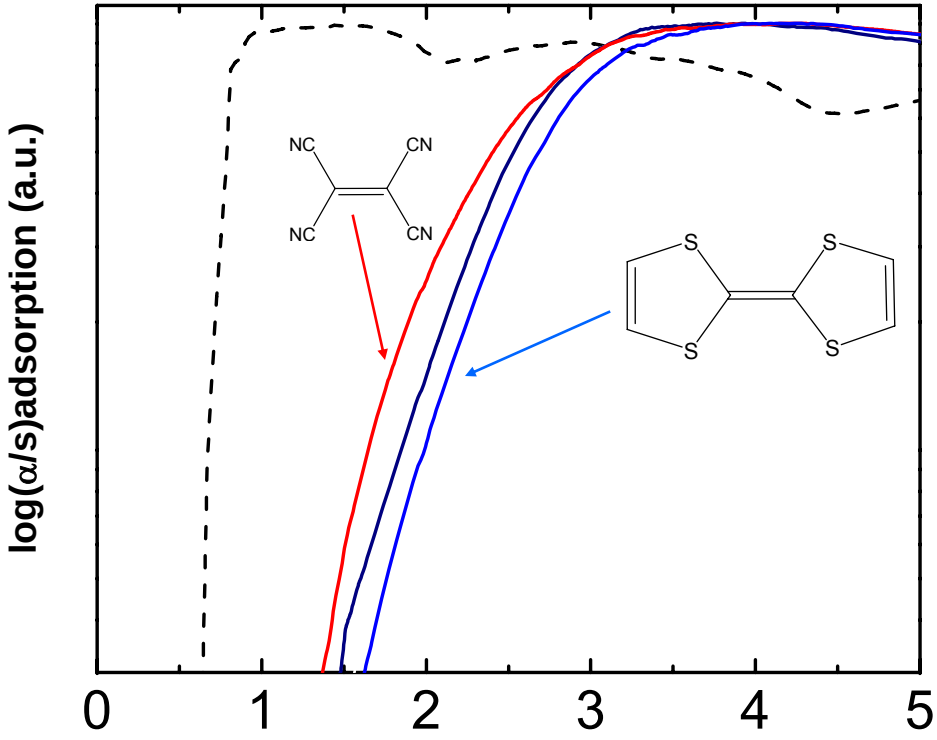
Oxidation coupling of $(Ge_9)^{4-}$: Possible mechanism

$$n(Ge_9)^{4-} \longrightarrow {}_{2\infty}\{Ge_9\}^0 + 4ne^-$$

$$EDMHEAB + nGe_9^{4-} + 2nNH_2(CH_2)_2NH_2 \longrightarrow (EDMHEA)_x[{}_{1\infty}\{Ge_9\}^{2n-}] + 2n(NH_2(CH_2)_2NH)^{1-} + nH_2$$

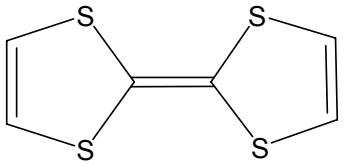
$$(EDMHEA)_x[{}_{1\infty}\{Ge_9\}^{2n-}] + 2nNH_2(CH_2)_2NH_2 \longrightarrow (EDMHEA)_x[{}_{2\infty}\{Ge_9\}^0] + 2n(NH_2(CH_2)_2NH)^{1-} + nH_2$$

Optical properties of mesoporous Ge: NU-Ge-3

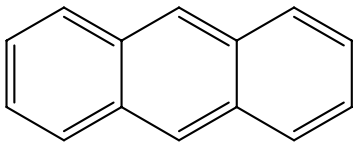


$(EDMHEA)_{0.81}[Ge_9]$ (668nm, 1.86eV)

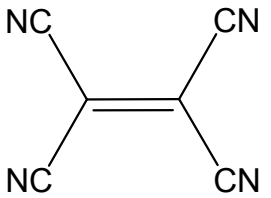
$(EDMHEA)_{0.13}[Ge_9]$ (663nm, 1.87eV)



TTF donor



anthracene



TCNE acceptor

Conclusions

- Mesoporous non-oxidic solids are a reality
- All known forms for mesostructured materials can be prepared.
- The scope and diversity of materials possible with non-oxide systems is wider than oxides.
- Mesoporous Ge: first porous elemental semiconductor
- Unique absorption as well as electronic and optical properties anticipated.

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