“From Models for the Atomic Structure of Glass To Organic-Inorganic Glasses"

Neville Greaves

gng25@cam.ac.uk
www.msm.cam.ac.uk/

Laboratory of Extreme Glassy State, State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China.

Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK.

1. Models for the Atomic Structure of Glass:

    A. Continuous Random networks
    B. Modified Random Networks

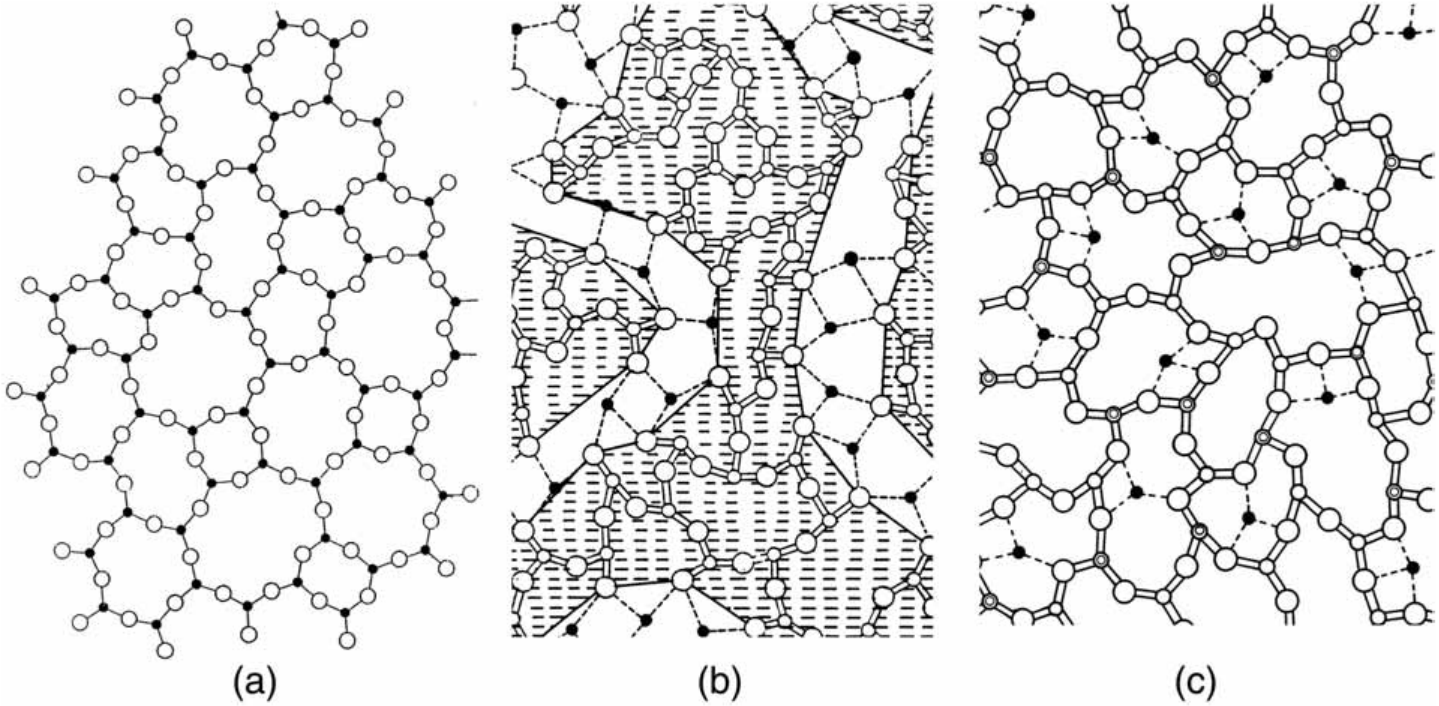
2. Organic-Inorganic Hybrid Glasses

    A. Examples of Organic-Inorganic Structures
    B. Amorphization, Melting and Vitrification of ZIF-4
    C. Other Melt-Quenched Hybrid Glasses
    D. Porous Hybrid Glasses
    D. Collapse Transitions for ZIF-8

1. Models for atomic structure of glass

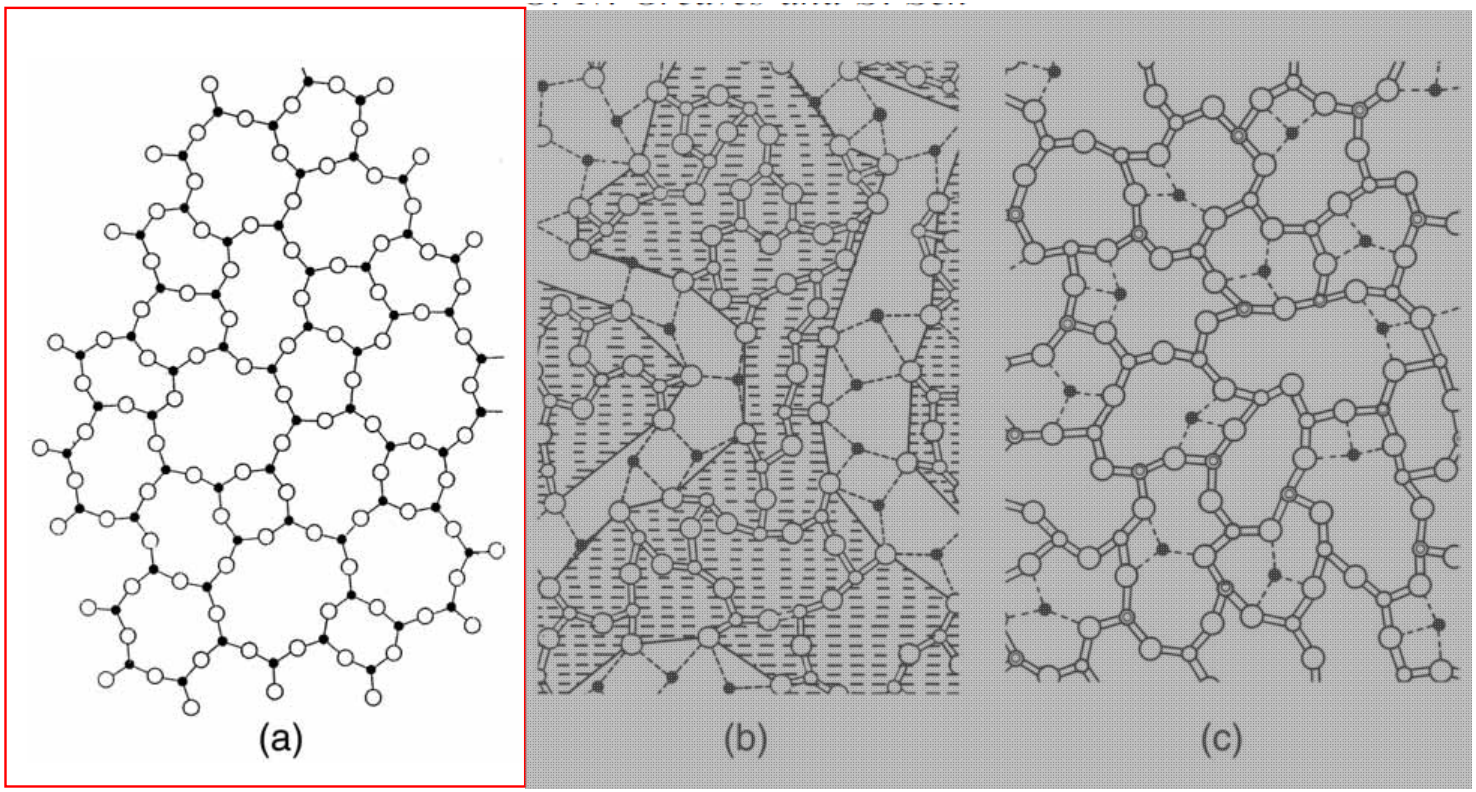
2D Models for atomic structure of glass

G. N. Greaves and S. Sen



Greaves GN and Sen S, *Advances in Physics* 56,1-166 (2007)

A. Continuous Random Network

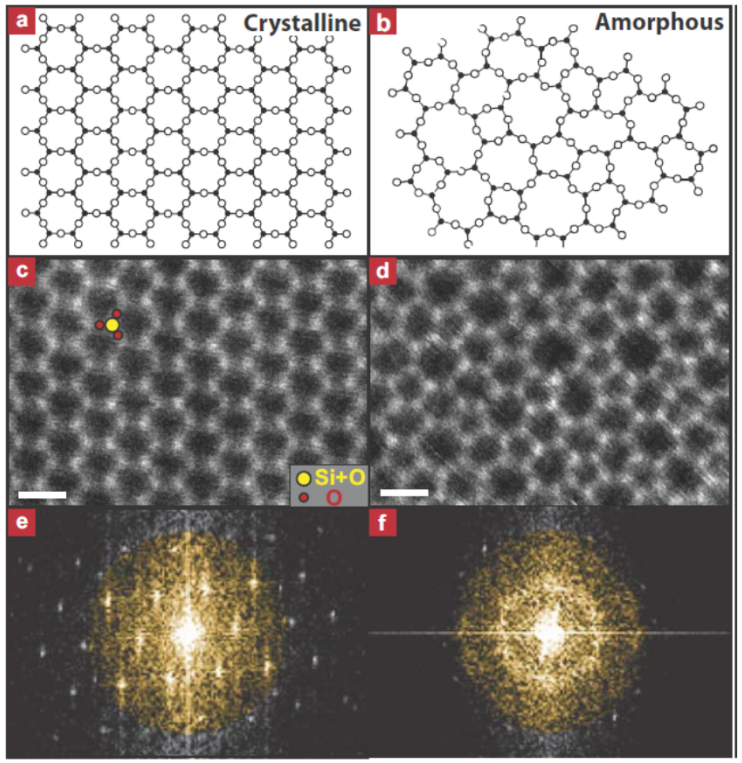


Zachariasen WH (1932) J Am Chem Soc 54:3841–3851.

2D Continuous Random Network Realised on Graphene

Imaging the Atoms in a Two-Dimensional Silica Glass on Graphene

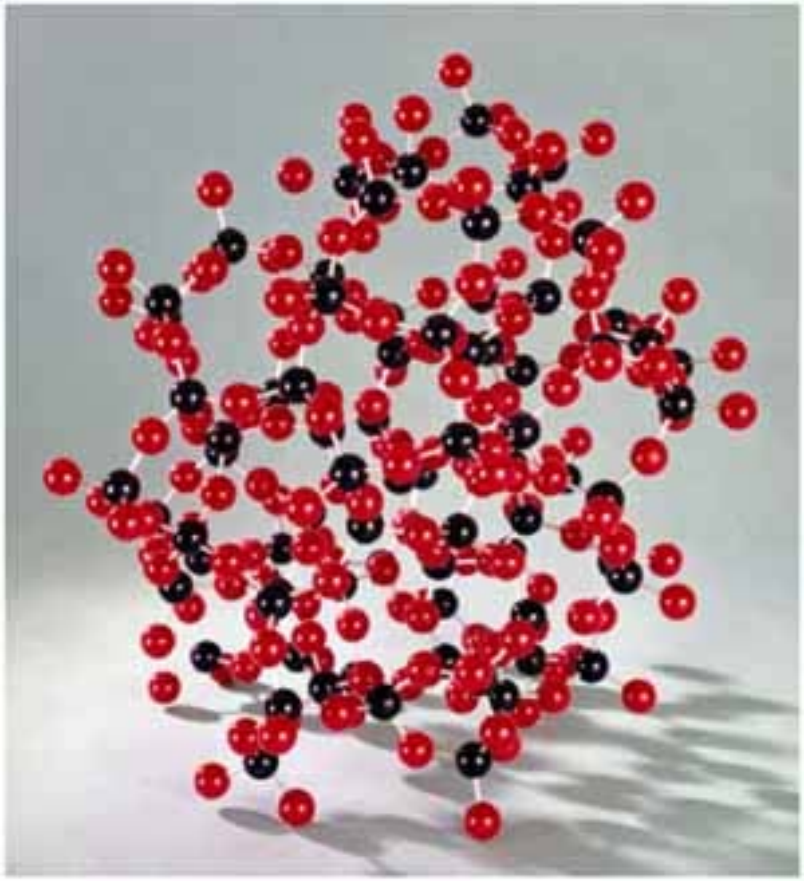
P.Y Huang et al
Microsc. Microanal. 18 (Suppl 2), 2012
Microscopy Society of America



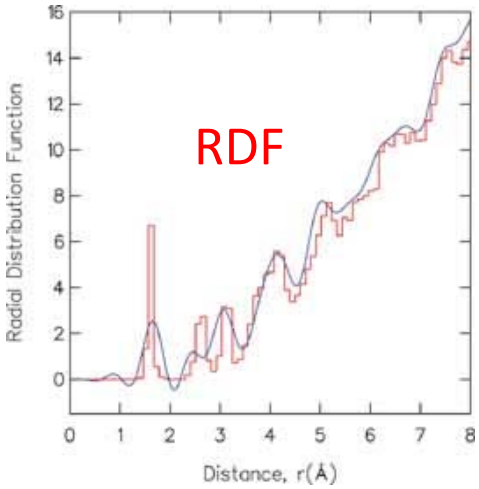
1496
doi:10.1017/S1431927612009336

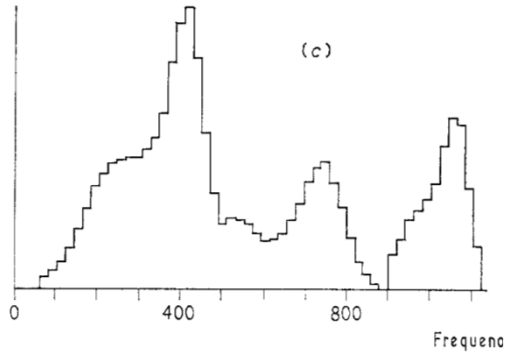
Microsc. Microanal. 18 (Suppl 2), 2012

3D CRN of SiO_2 Glass



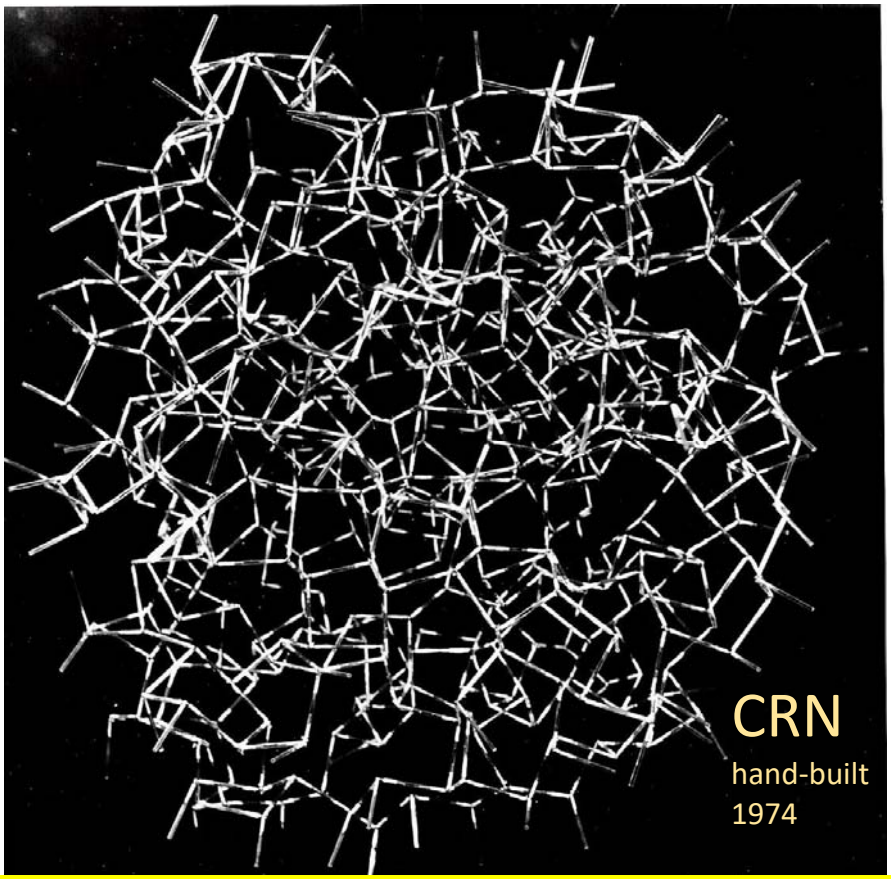
Hand built CRN for SiO_2
Bell and Dean, J. Phys. C (1968) 1, 299-301

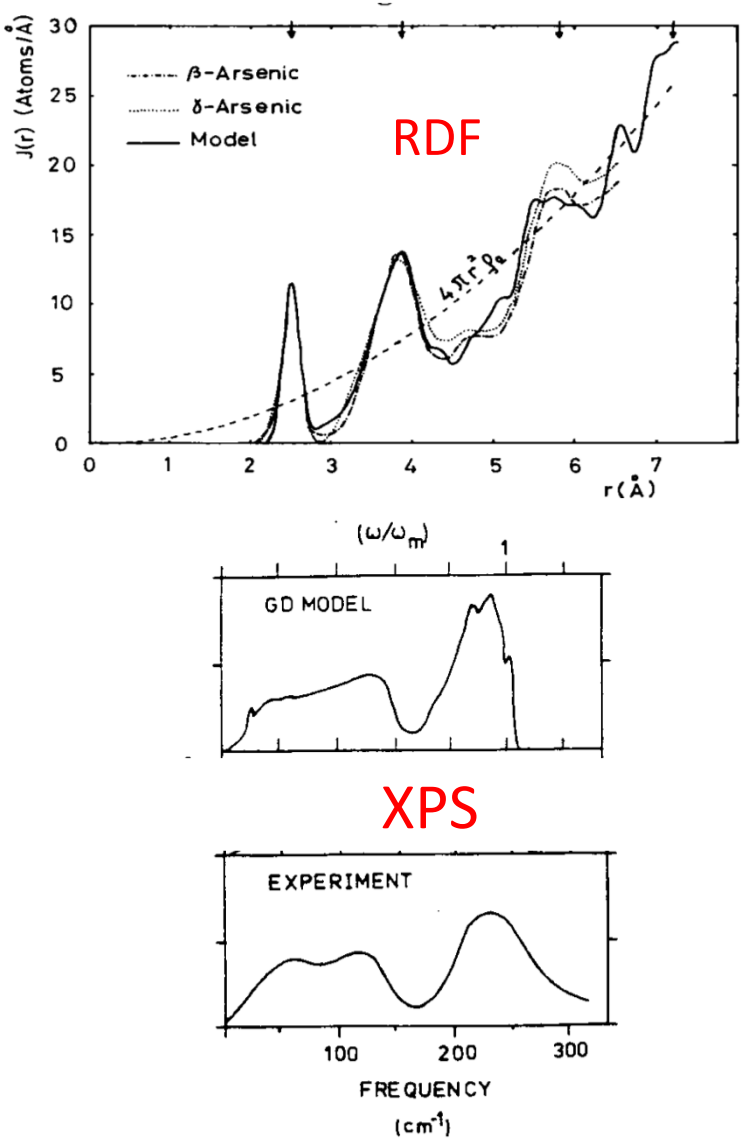




Vibrational Density of States

3D CRN for Glassy As and P





Hand built CRN

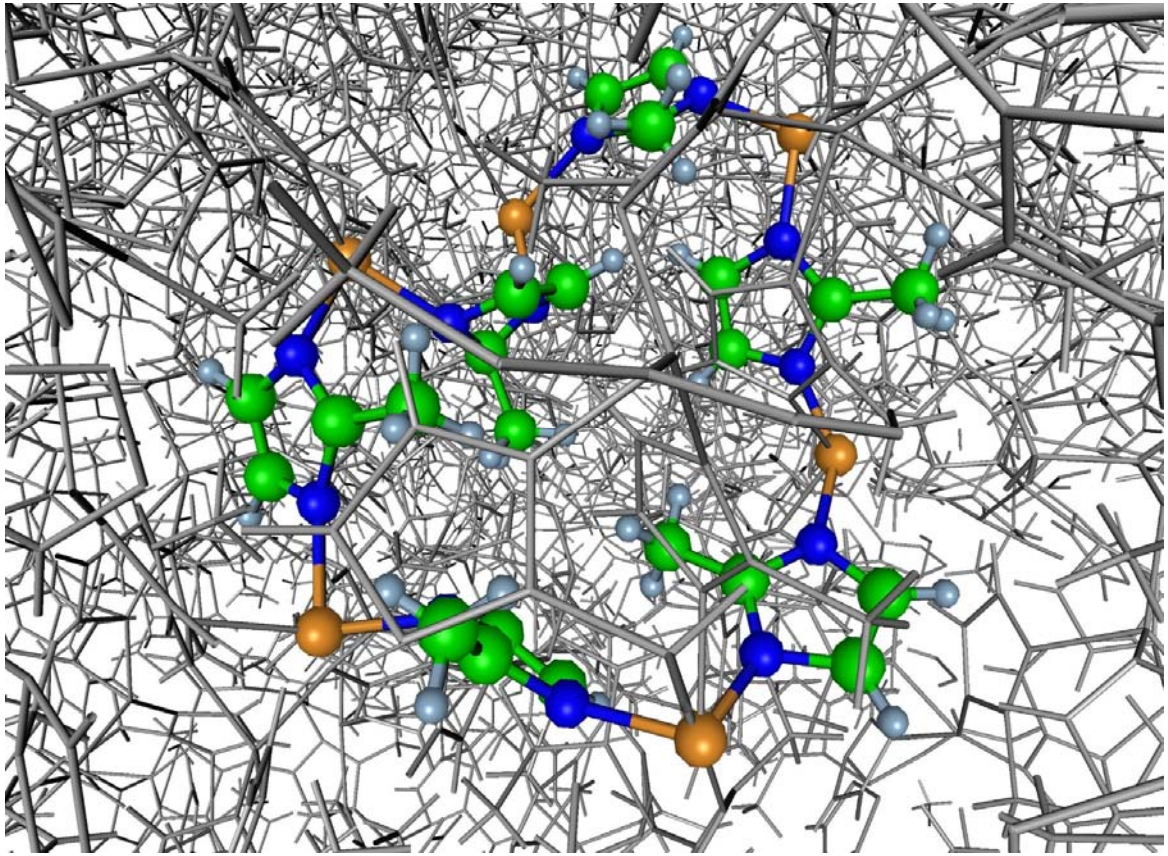
Continuous Random Network with three-fold Coordination

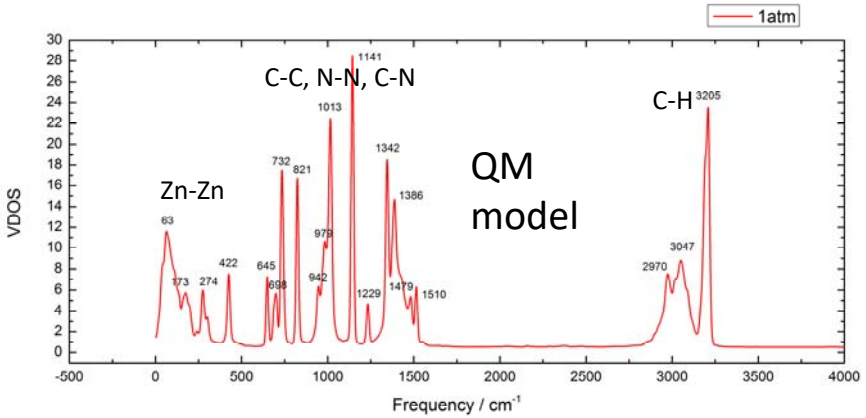
Greaves G N and Davis E A

Phil. Mag. 29 1201-1206 (1974)

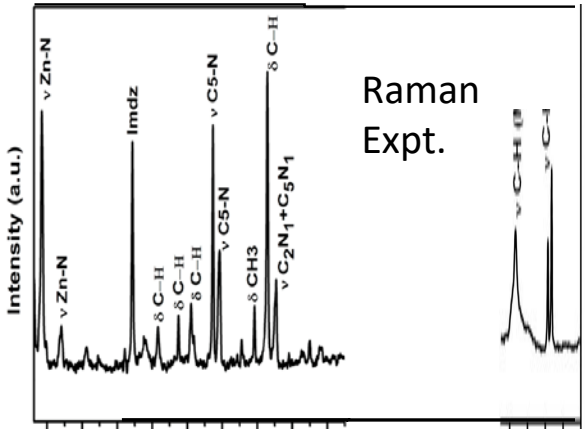
Advances in Physics 28, 49-141 (1979)

3D CRN for ZIF-8 Hybrid Glass



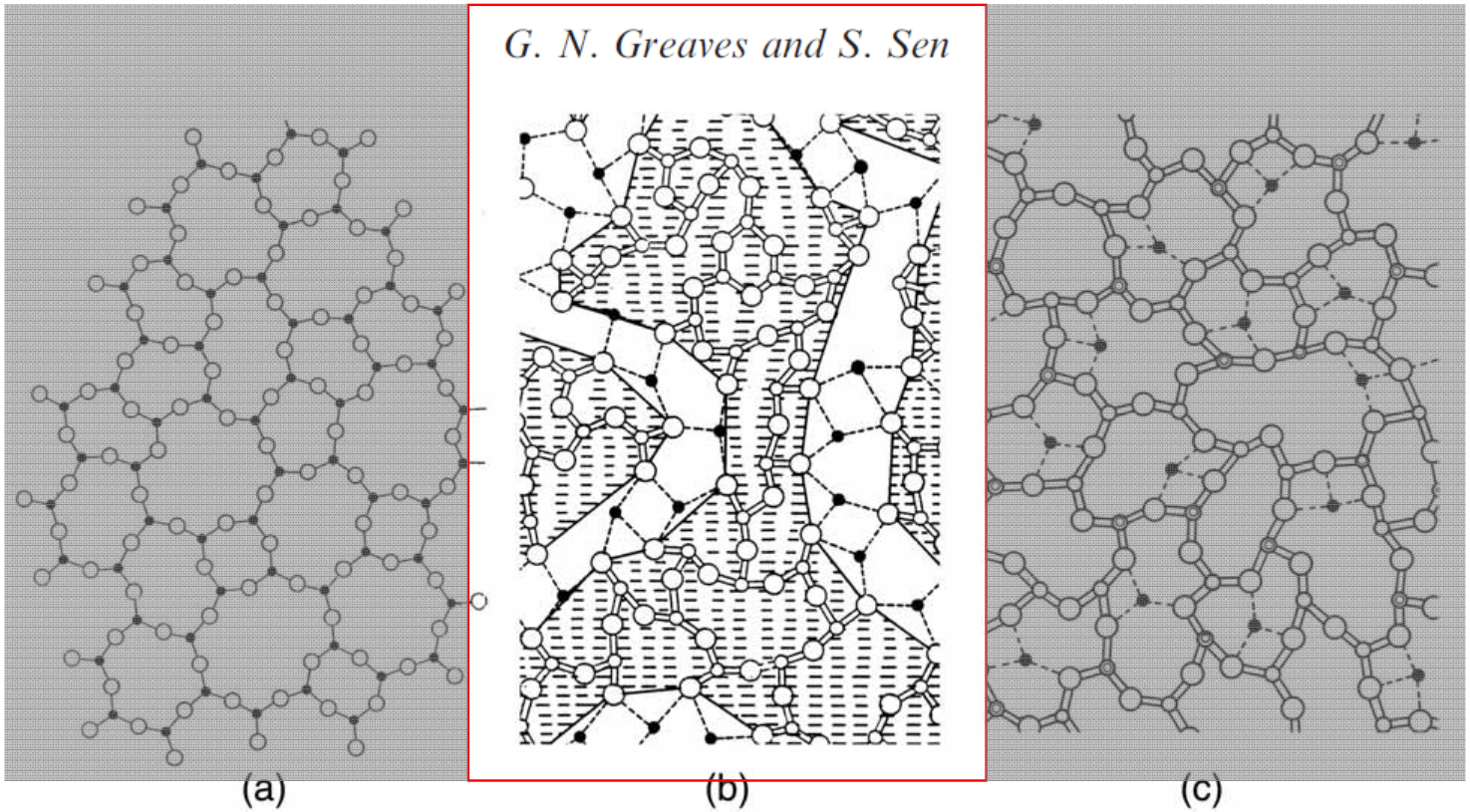


Vibrational Density of States



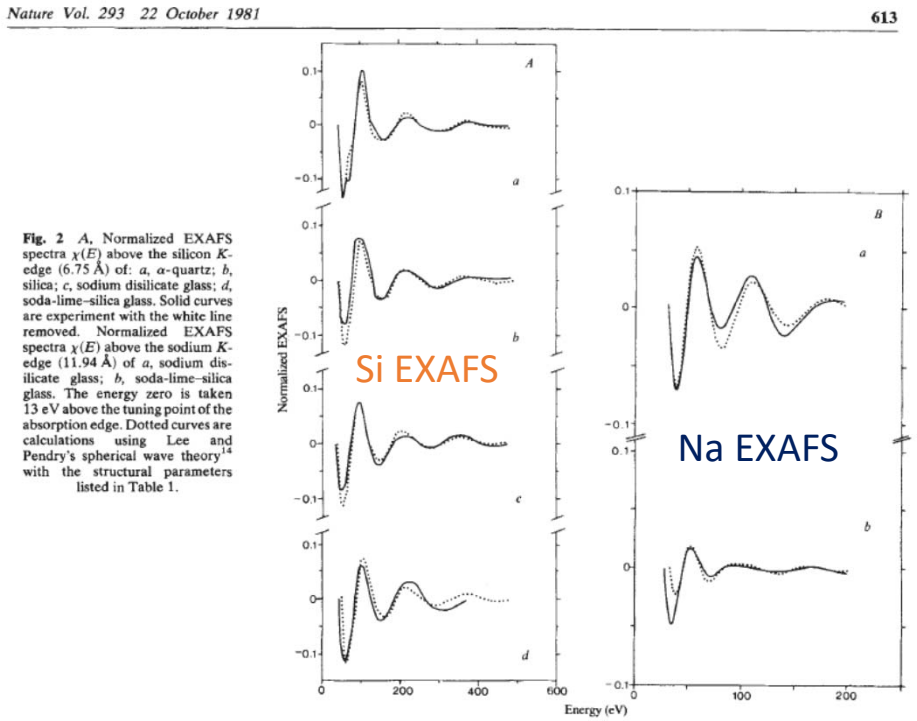
Bennett, Tang, Yue, Greaves et al
Nature Communications **6** 8079 pp. 1-7 (2015)

B. Modified Random network



EXAFS and the Structure of Glass
Greaves G N, *J. Non-Cryst. Solids,* 71, 203-217 (1985)

First EXAFS experiments to be made on glass: ACO Orsay 1980/81

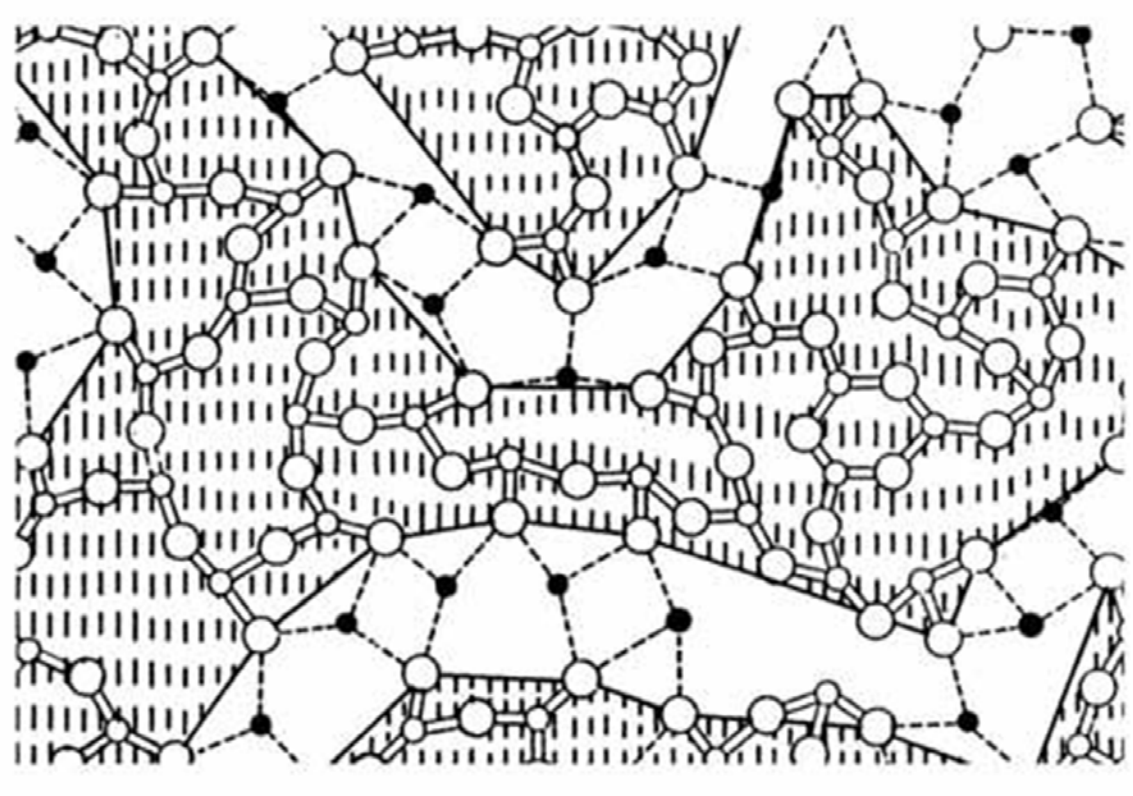


First EXAFS experiments to be made on glass:

ACO Orsay 1981

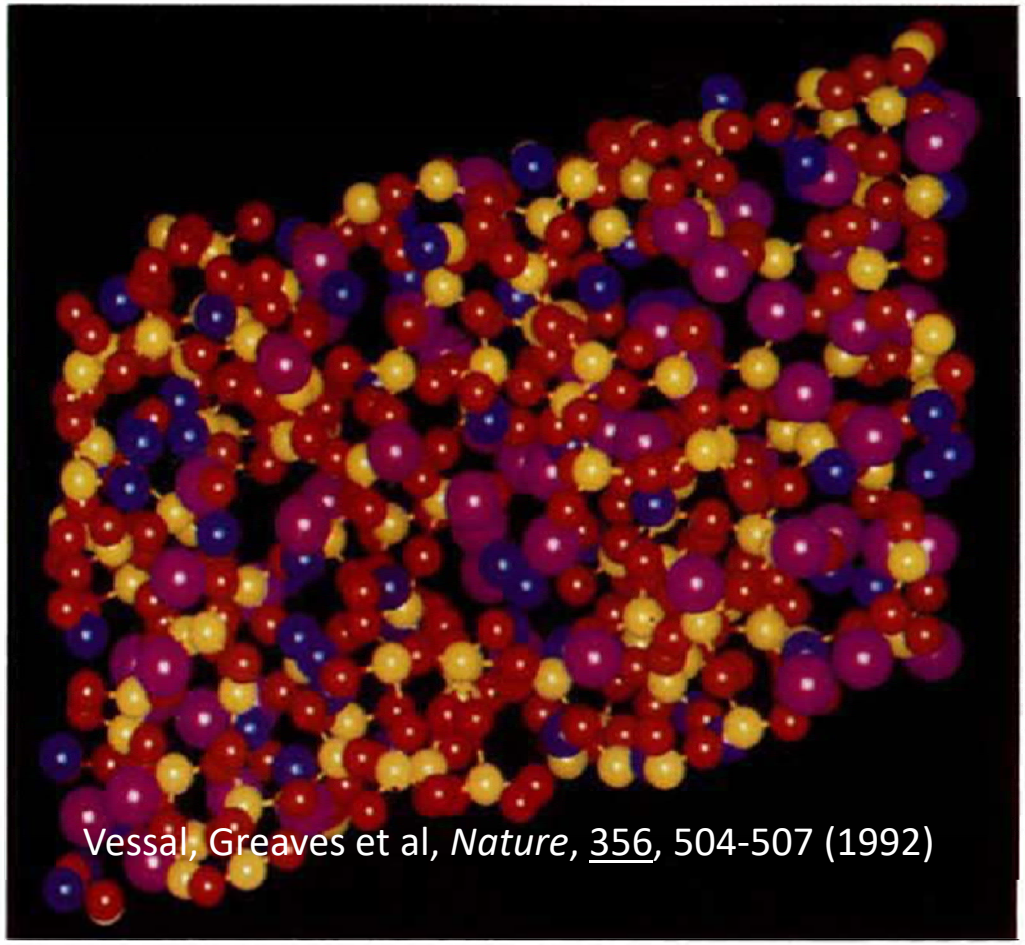
Greaves et al, *Nature*, 293, 611-616 (1981)

Modified Random network



EXAFS and the Structure of Glass
Greaves G N, *J. Non-Cryst. Solids,* 71, 203-217 (1985)

MD Realisation of Alkali Channels



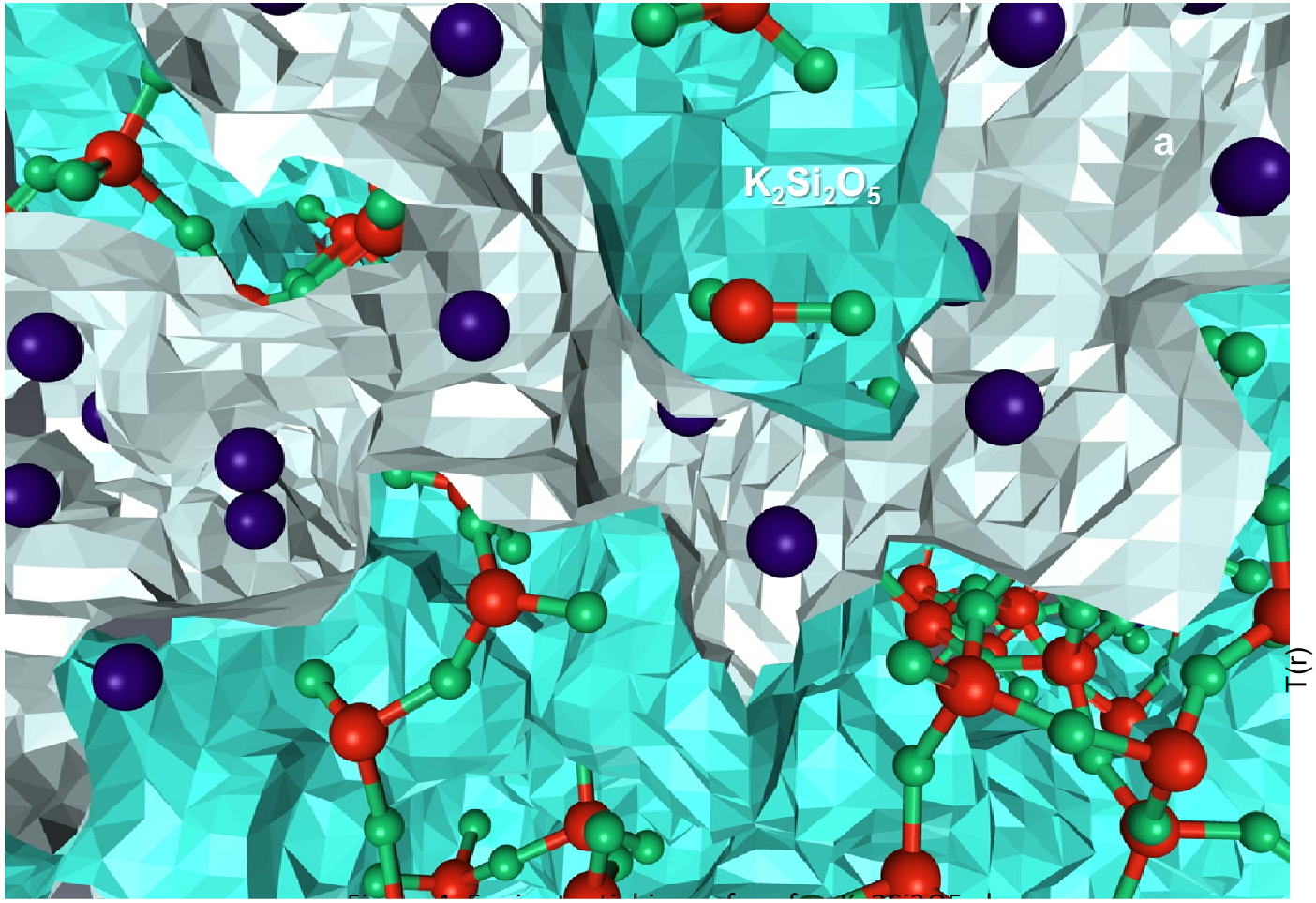
Na

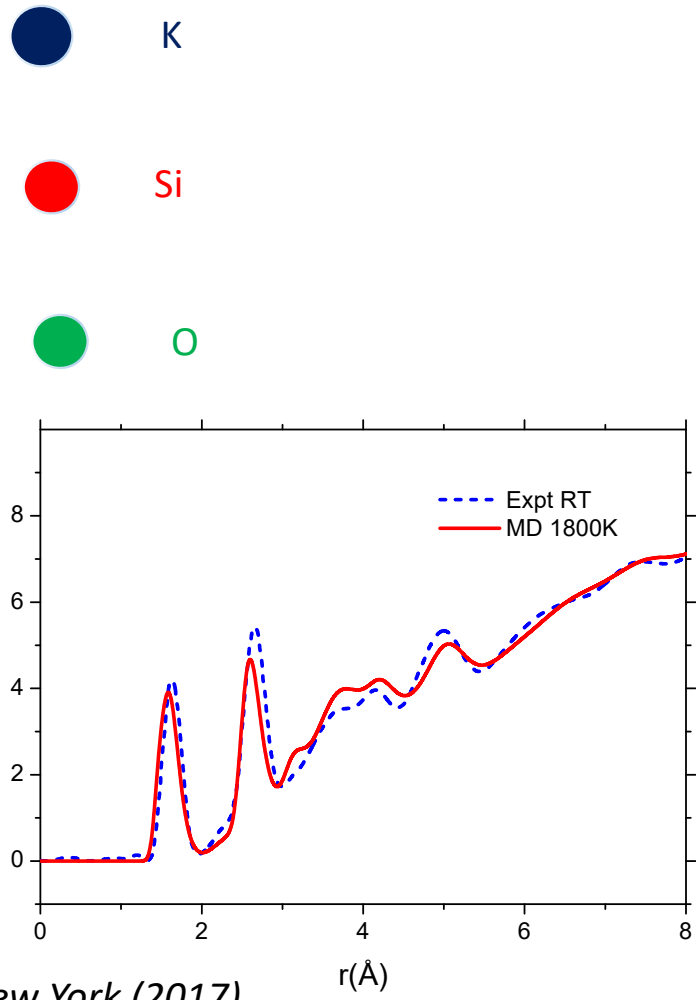
Rb

O

Si

Visualisation of Alkali Channels





Greaves, Extended Structure of Glass, Encyclopedia of Glass, Ed. P. Richet; Wiley: New York (2017).

2. Organic-Inorganic ‘Hybrid’ Glasses

Discovery of new glass system after: Silicates, chalcogenides, molecular, metallic glasses

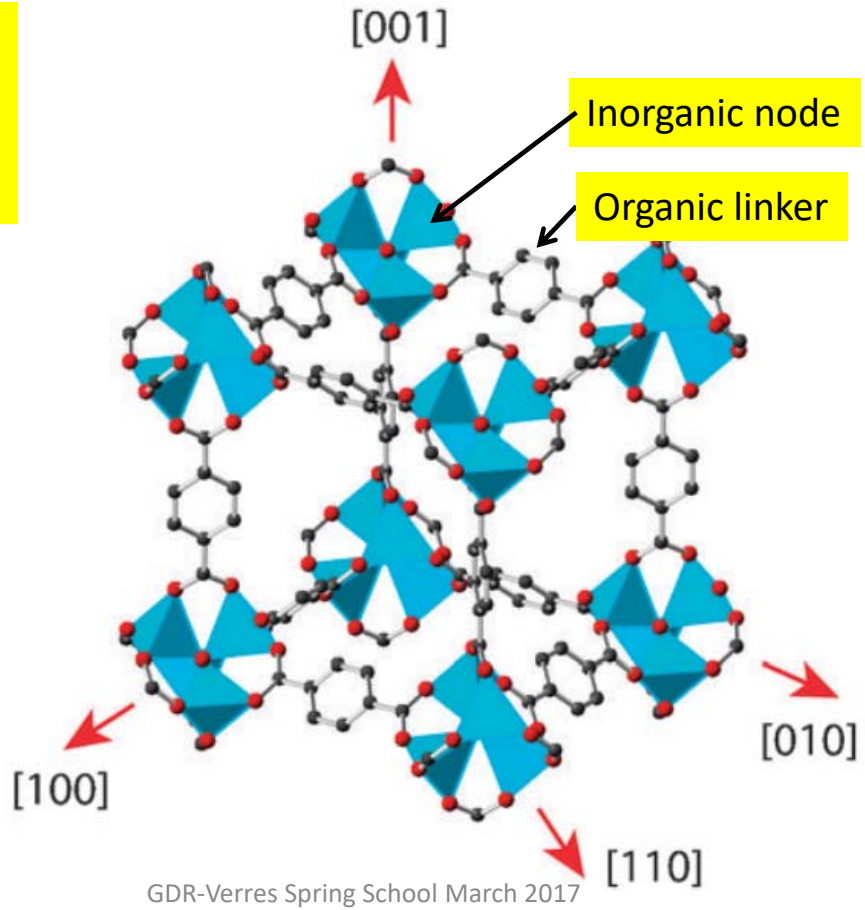
Nature Communications **6** 8079 pp. 1-7 (2015)

A. Examples of Organic-Inorganic Structures

Metal Organic Frameworks (MOFs)
Example: $ZnO_4(BDC)_3$

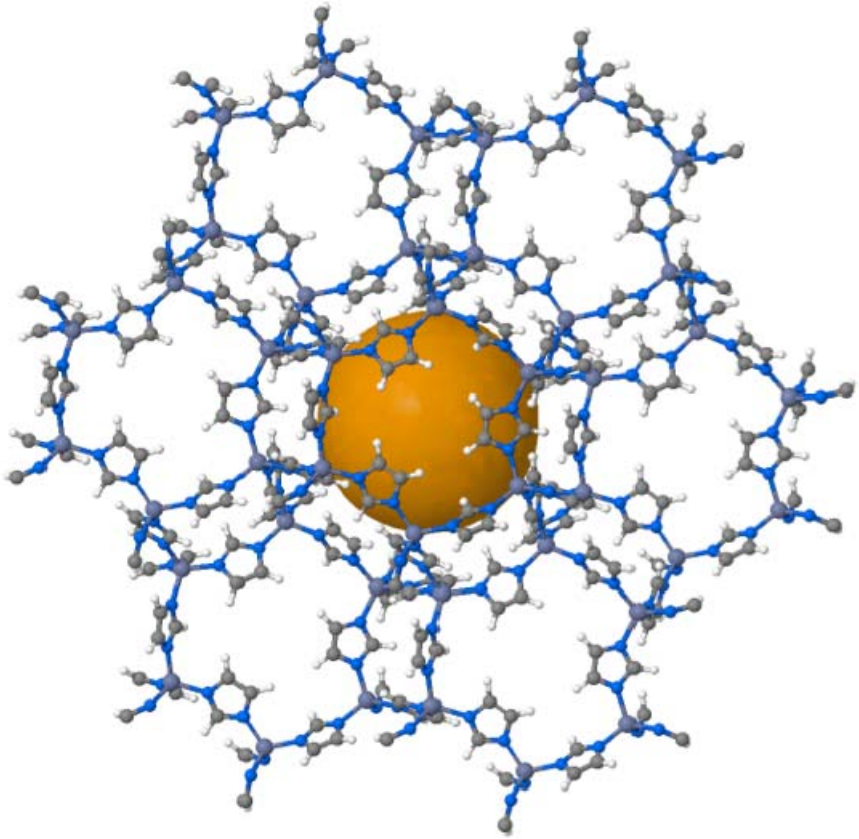
Benzenedicarboxylate

Zn
C
O

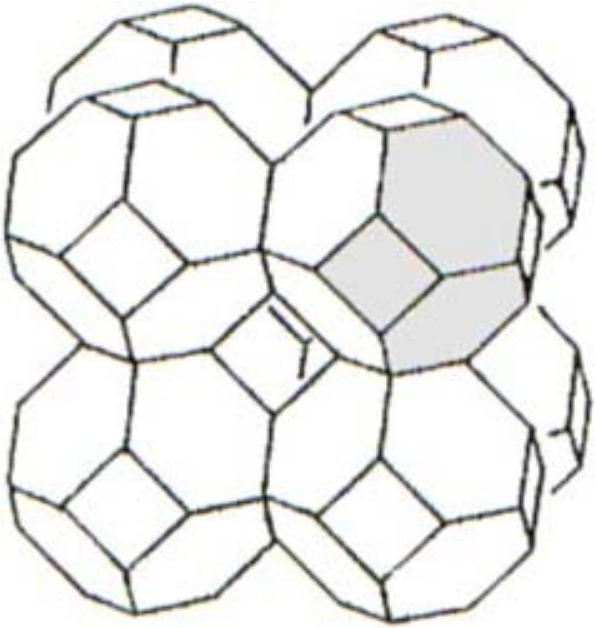


Zinc Imidazolate Frameworks (ZIFs)
Example: ZIF-8
Zn(2-methylimidazolate)$_2$

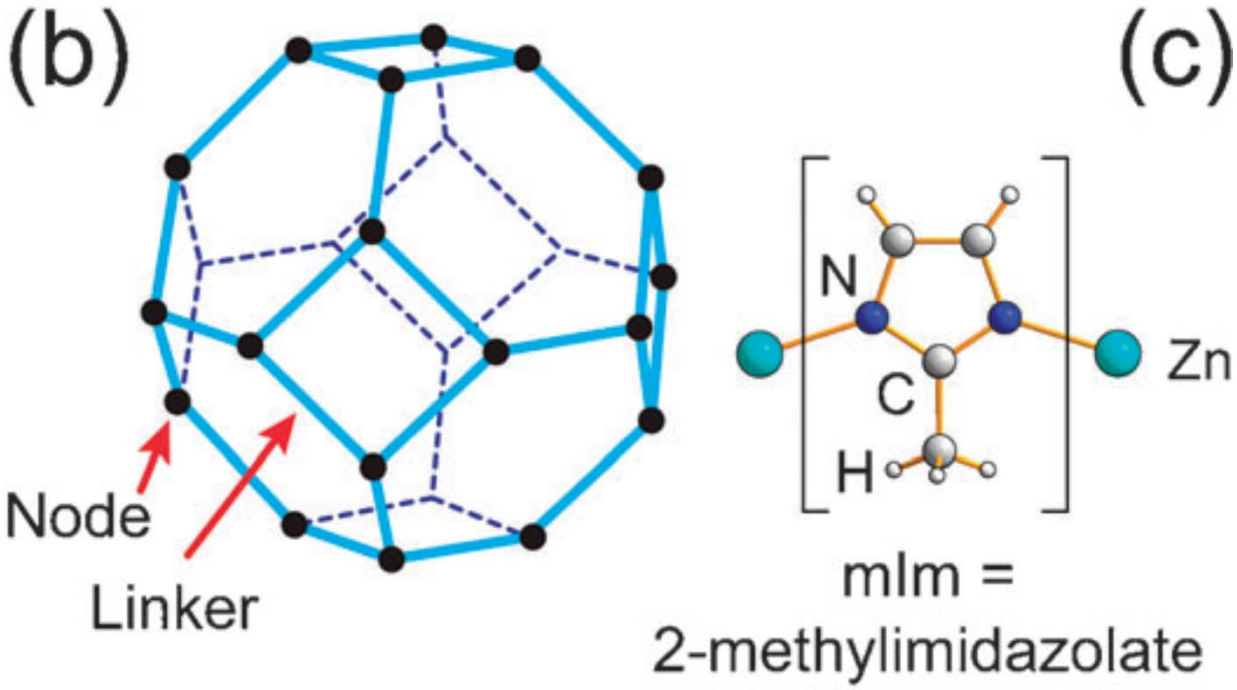
ZIF-8



Iso-structural Zeolite: Sodalite

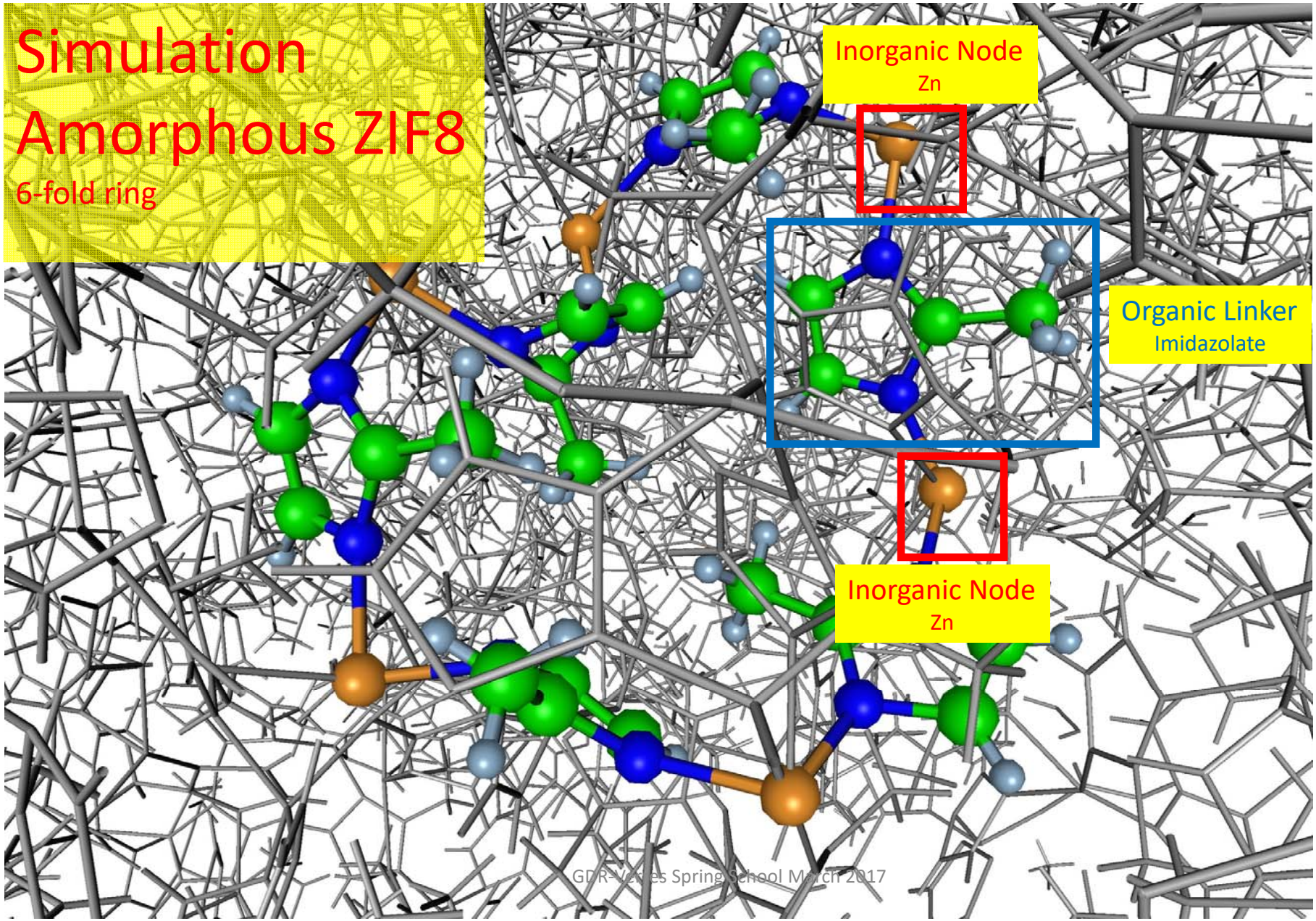


Nodes and Linkers



Simulation
Amorphous ZIF8

6-fold ring

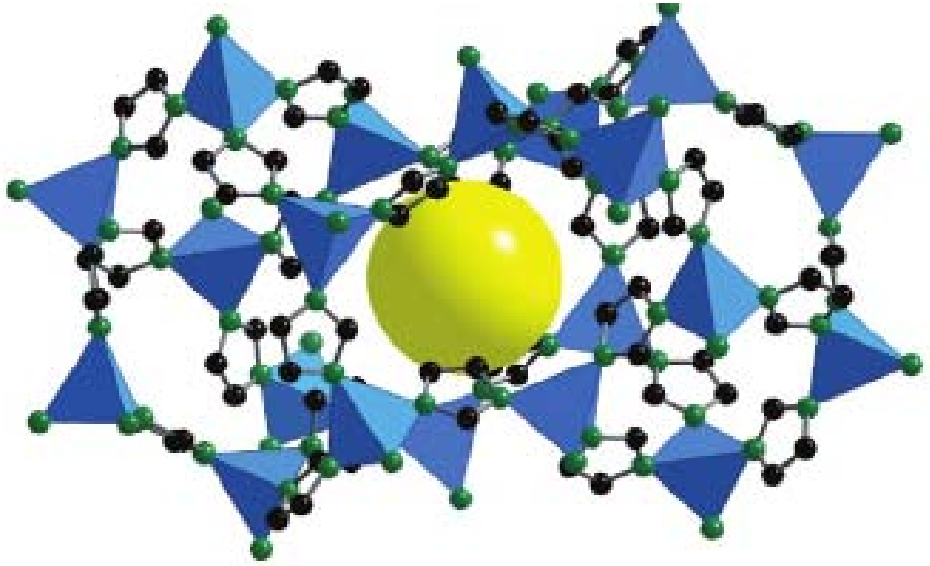


B. Amorphization, Melting and Vitrification of ZIF-4

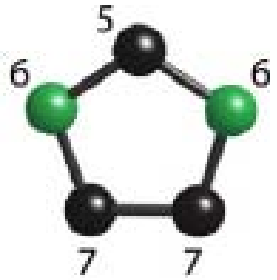
Zn(imidazolte)$_2$

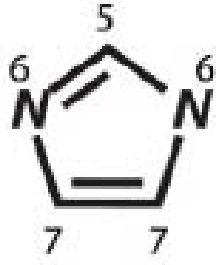
Structure of ZIF-4

Zn(imidazolte)$_2$

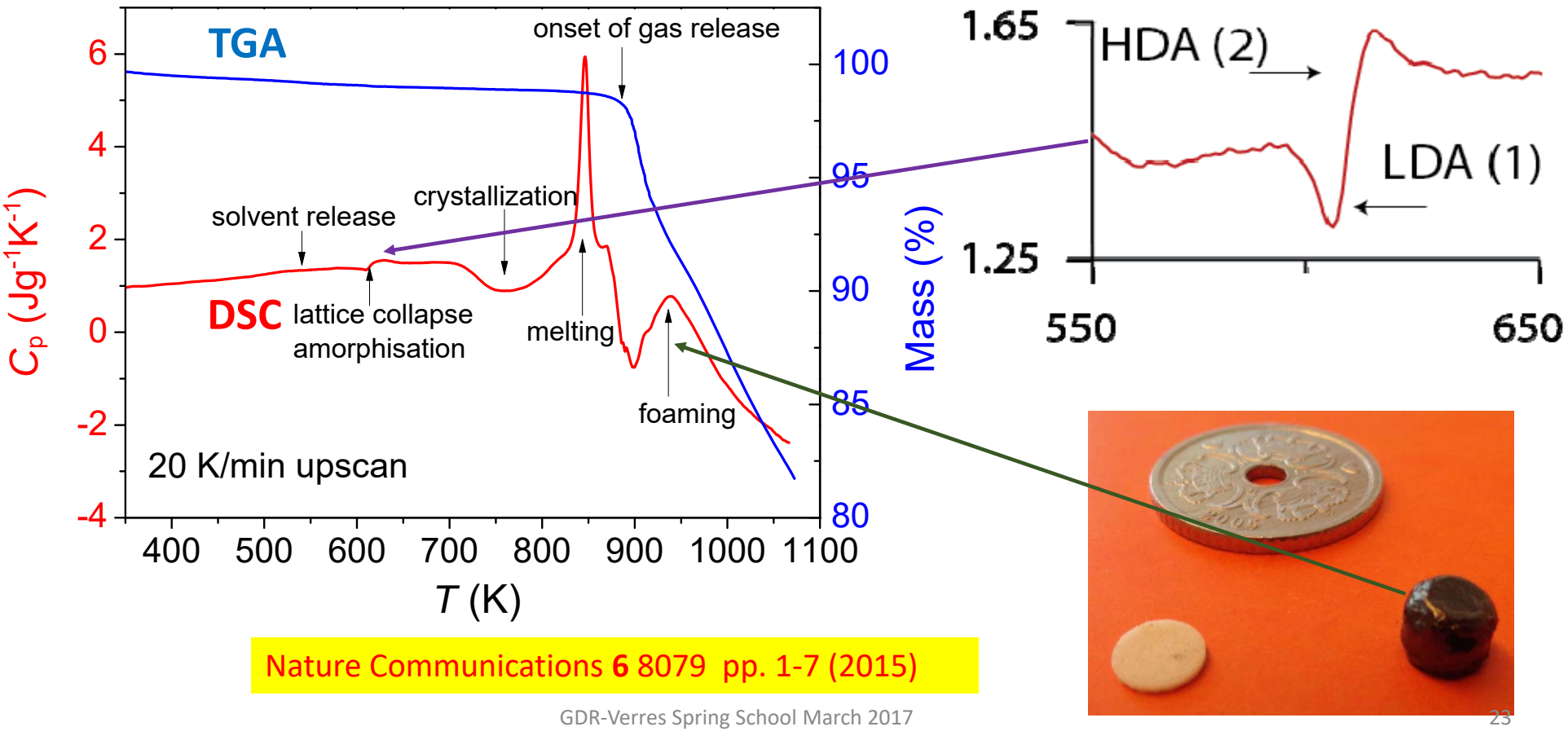


ZIF-4 - $Zn(C_3N_2H_3)_2$



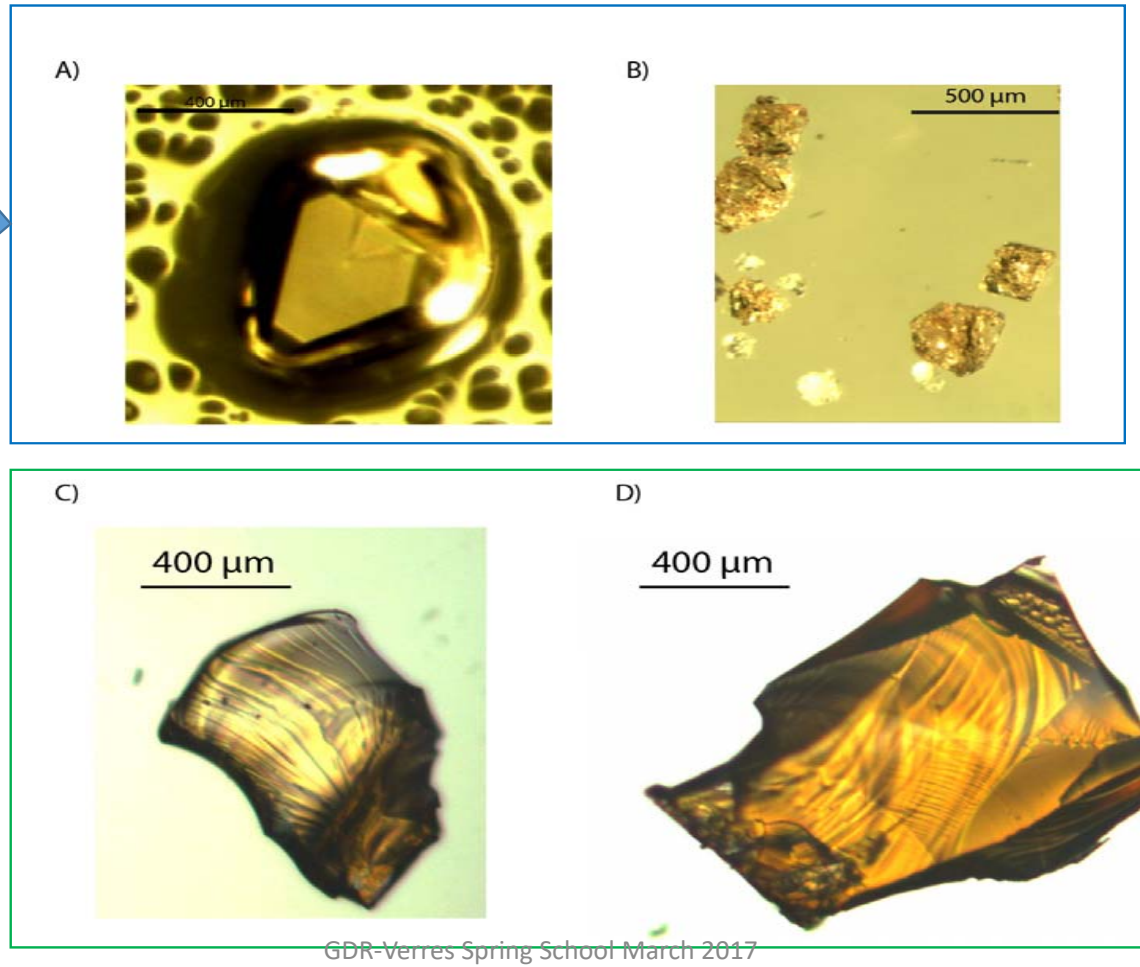


From ZIF4 to melt-quenched glass



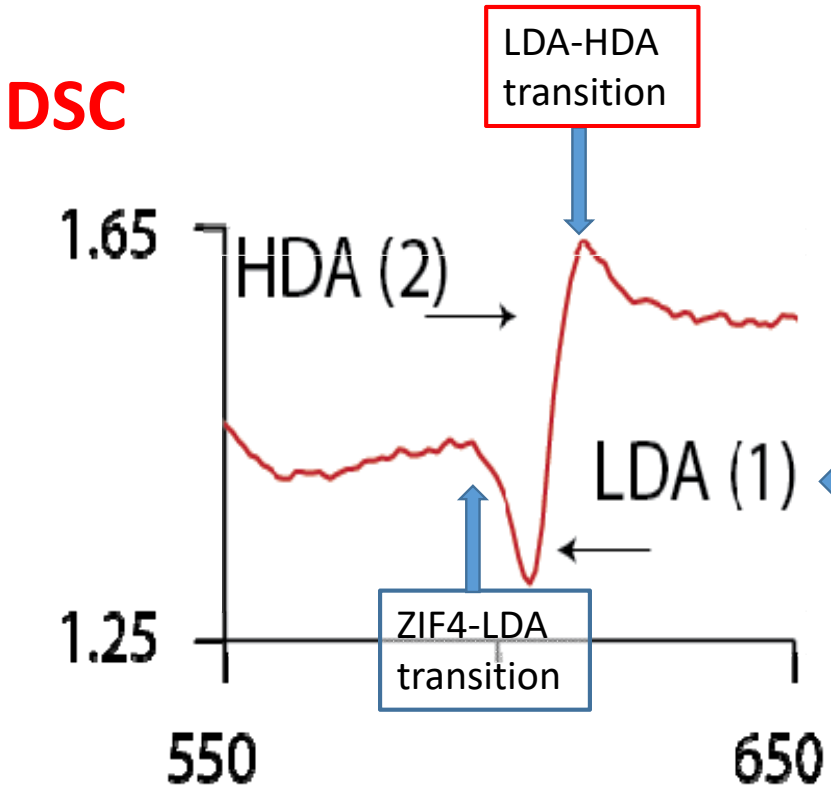
Nature Communications **6** 8079 pp. 1-7 (2015)

Crystals (A,B) and Melt Quenched Glasses (C,D) from ZIF4



Hybrid Glasses through **amorphization** of ZIF4

Low Density Amorphous (LDA) and High Density Amoprphous (HDA) phases

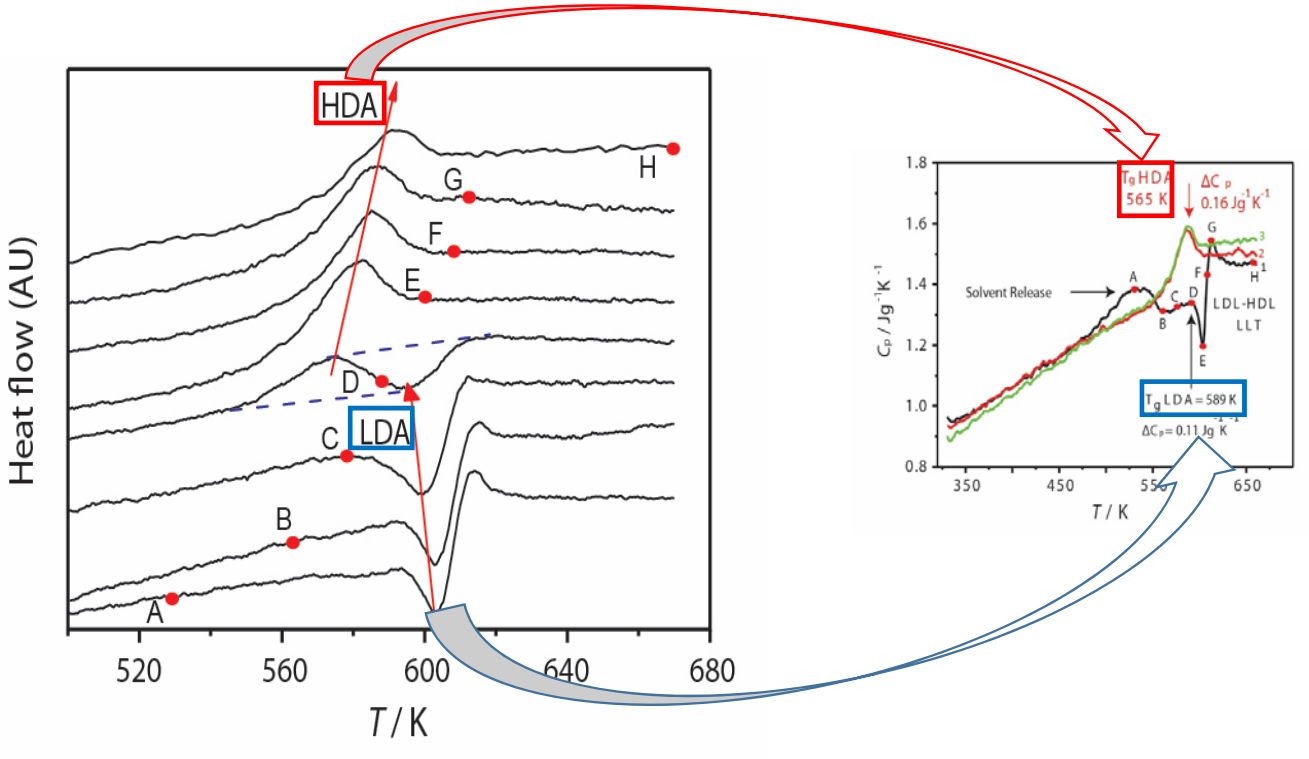


Probing the dynamics of instability in zeolitic materials, Greaves GN and Meneau F
J. Phys.: Condens. Matter 16, S3459-S3472 (2004)
Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids, Greaves GN* and Sen S
Advances in Physics 56,1-166 (2007)

DSC – separate polyamorphs identified during ZIF4 collapse

Low Density Amorphous (LDA) and High Density Amoprphous (HDA) phases

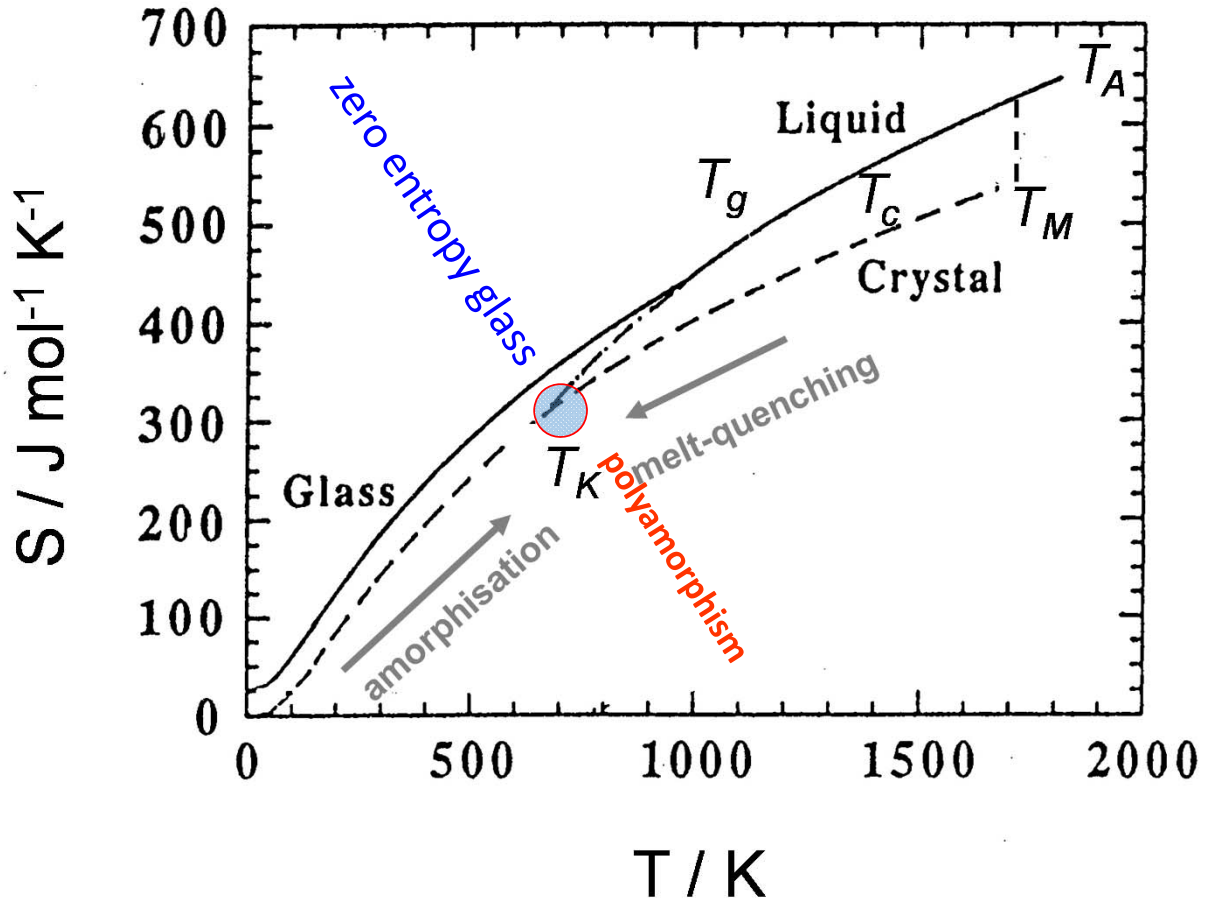
annealing (A-H) followed by upscans



Bennett, Tang, Yue, Greaves et al Nature Communications **6** 8079 pp. 1-7 (2015)

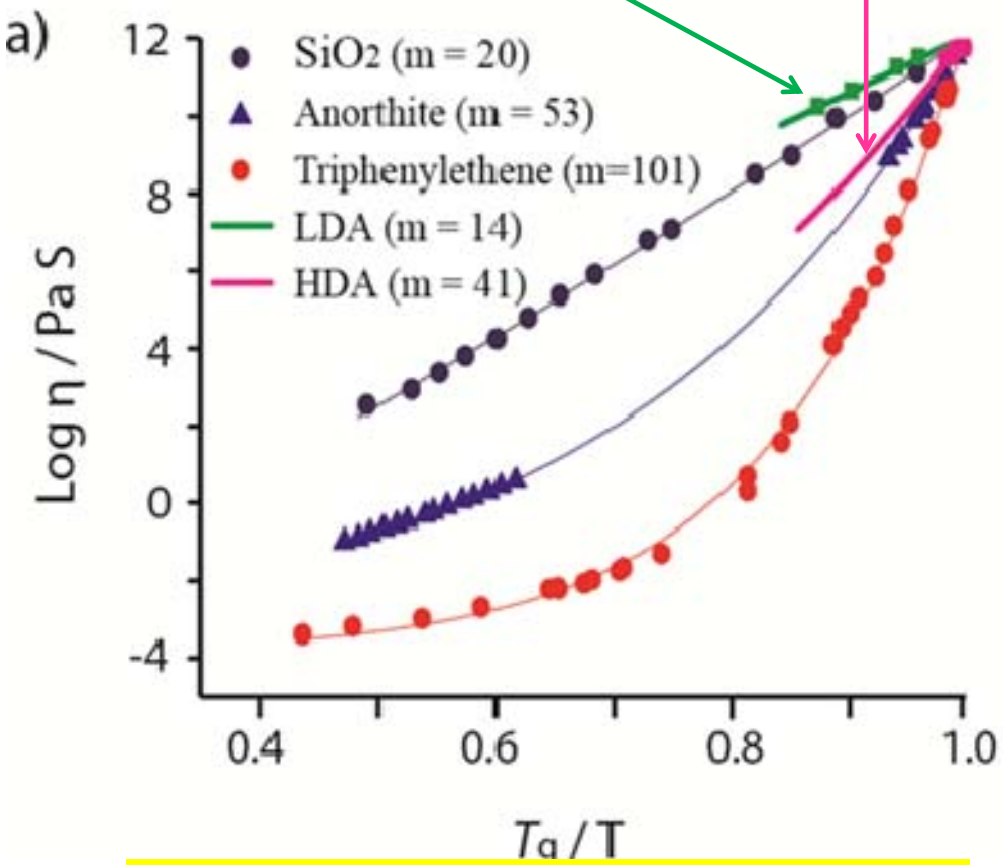
Routes to Perfect Glasses

Greaves GN and Sen S 2007 *Advances in Physics* **56** 1-166



Angell Plot – Polyamorphism in Organic-Inorganic Glasses

superstrong LDL cf. fragile HDL

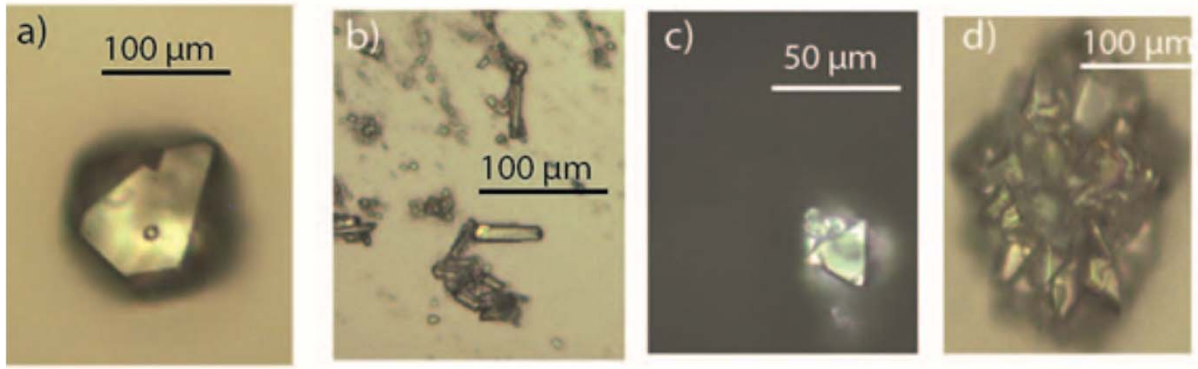


Nature Communications **6** 8079 pp. 1-7 (2015)

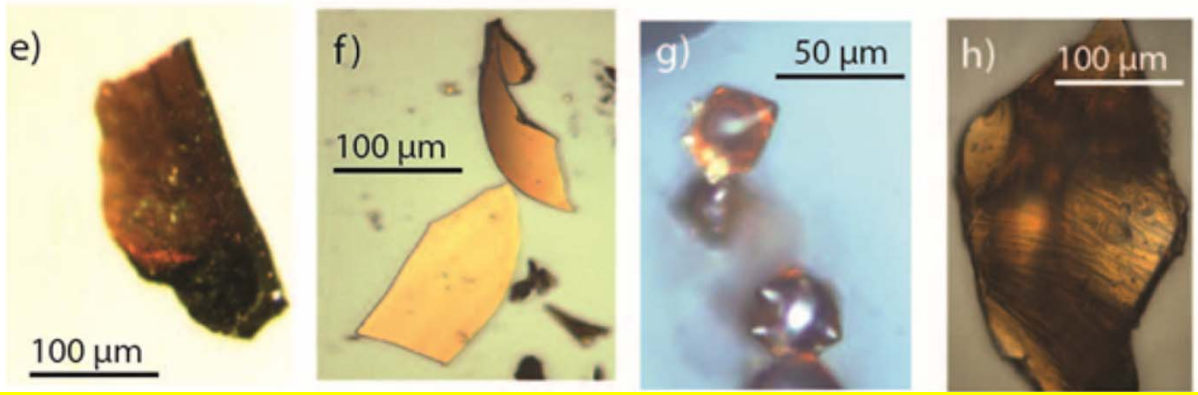
C. Other Hybrid Glasses

Other ZIF Hybrid Glasses

ZIF4 Zn(IM)2 GIC TIF4 ZIF62



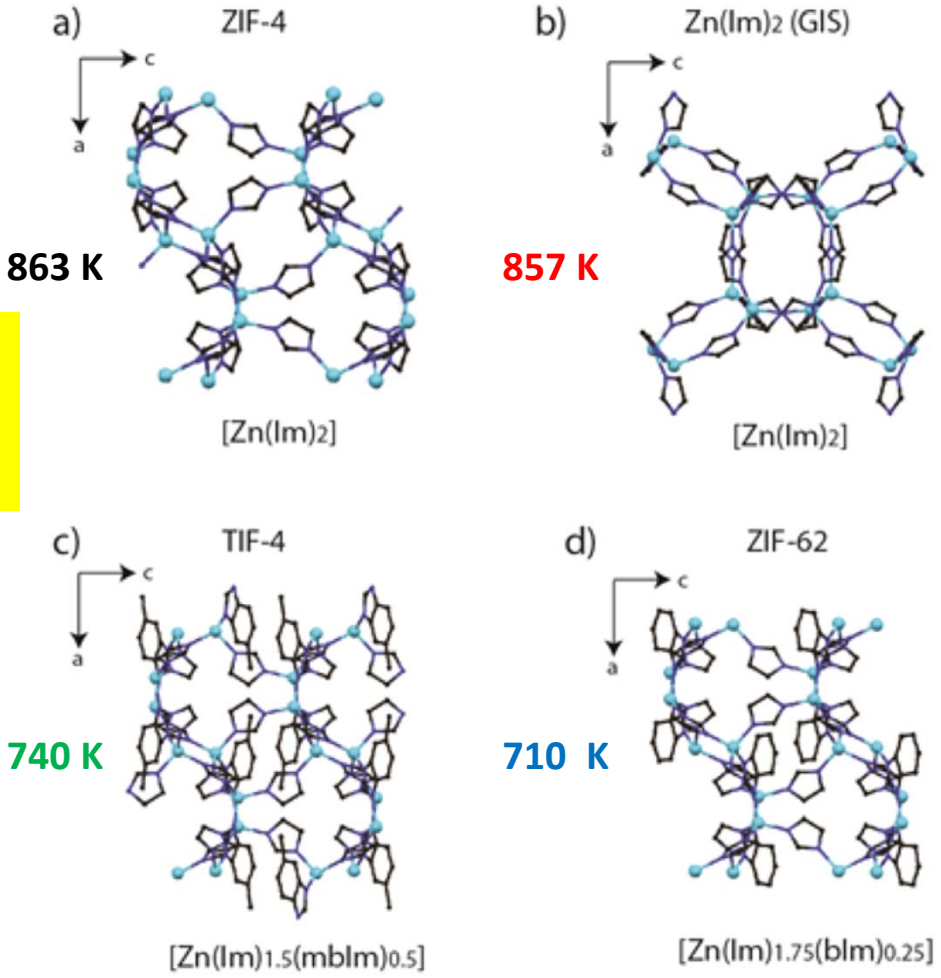
Crystals



Glasses

Melt-Quenched Glasses of Metal–Organic Frameworks
T. D. Bennett, Y-Z Yue, P. Li, A. Qiao, H. Tao, G.N. Greaves, T. Richards, G. I. Lampronti, S. A. T. Redfern, F. Blanc,´ O. K. Farha, J. T. Hupp, A. K. Cheetham, and D. A. Keen
J. Am. Chem. Soc. 2016, **138**, 3484–3492

Melting Points of ZIF Hybrid Glasses

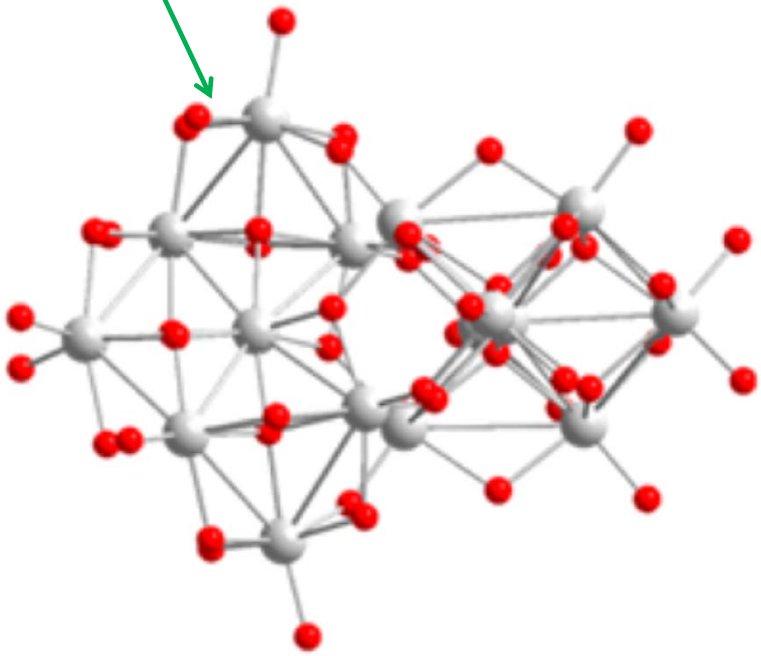


J. Am. Chem. Soc. 2016, **138**, 3484−3492

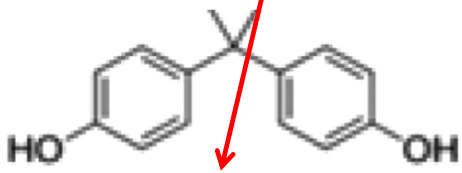
C. Porous Hybrid Glasses

Nanoporous MOF Glasses

Ti-oxo clusters with bisphenol linkers

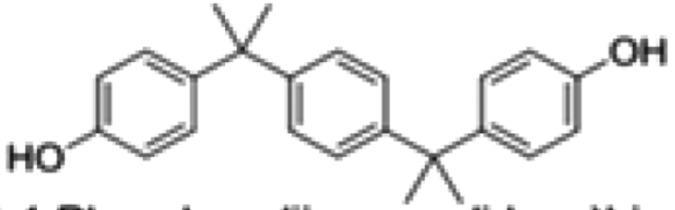


rigid



2,2-Bis(4-hydroxyphenyl)propane
(Bisphenol-A)

semi-rigid

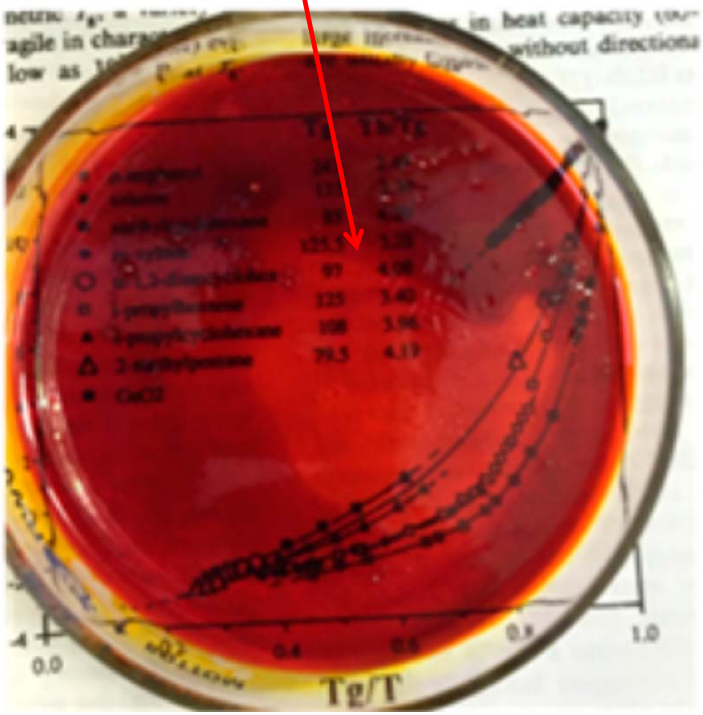


4,4'-(1,4-Phenylenediisopropylidene)bisphenol
(Bisphenol-A)

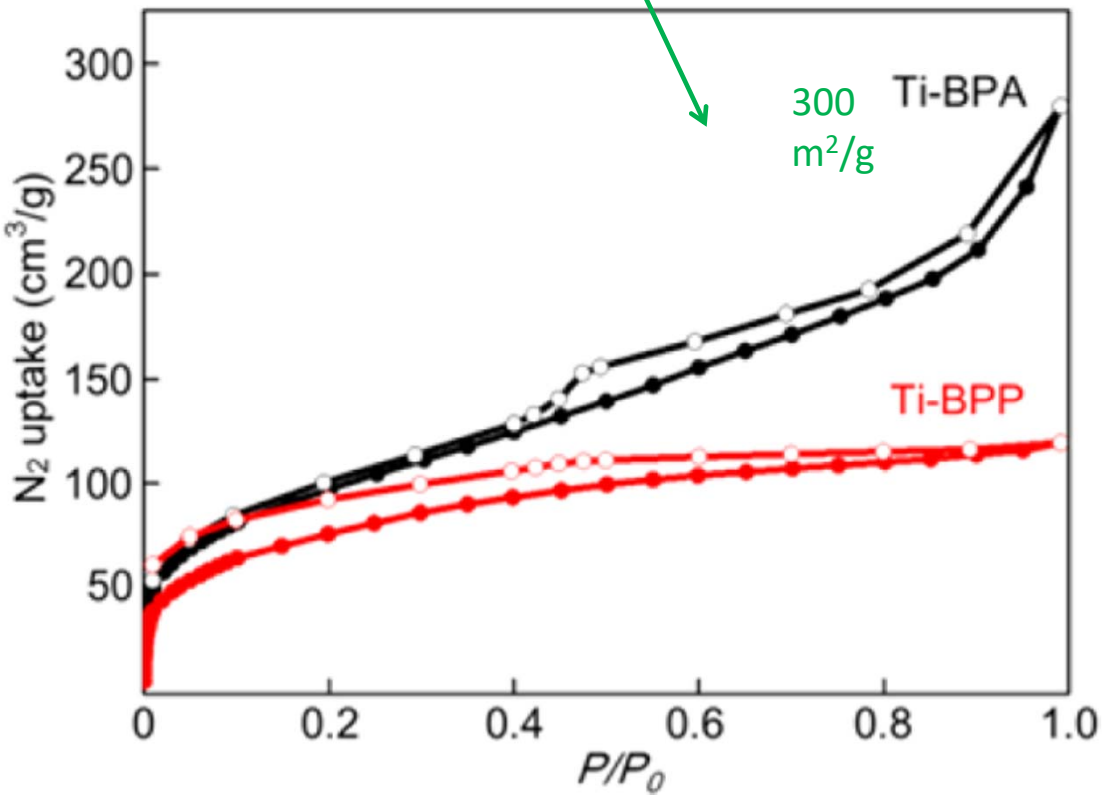
Nanoporous Transparent MOF Glasses with Accessible Internal Surface
Y Zhao, S-Y Lee, N Becknell, O M Yaghi and C. A Angell
J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b07078

Nanoporous MOF Glasses

Transparent Glass



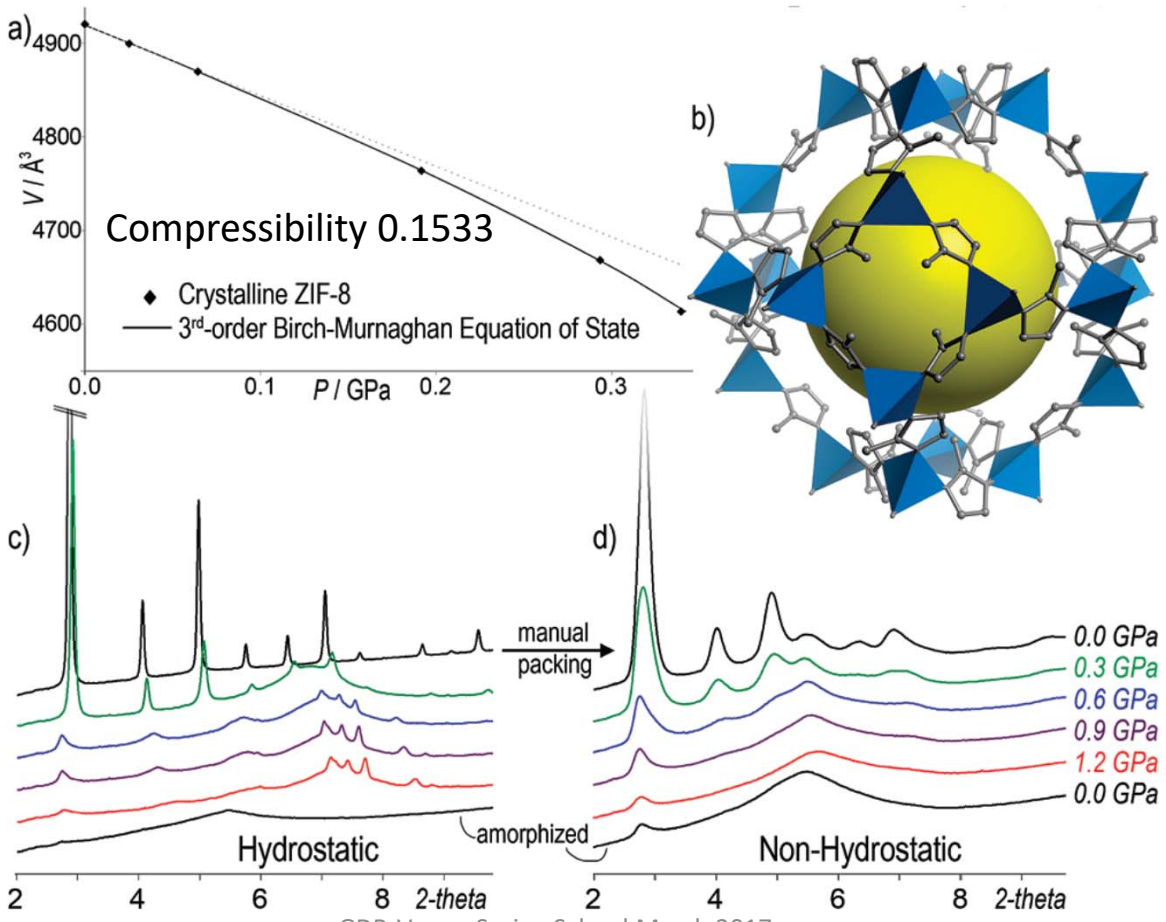
N_2 Adsorbance



D. Crushing ZIF-8

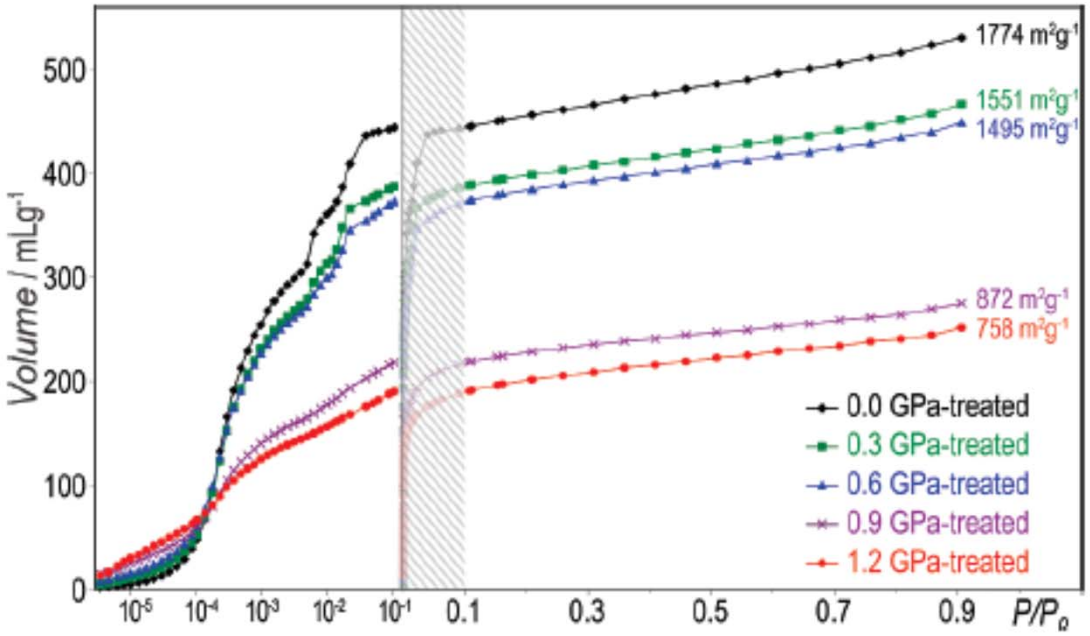
Crushing ZIF8 to a Glass

Chapman, Halder and Chupas, **J. AM. CHEM. SOC. 2009**, *131*, 17546–17547



Crushing ZIF8 to a Glass

Chapman, Halder and Chupas, **J. AM. CHEM. SOC. 2009**, *131*, 17546–17547



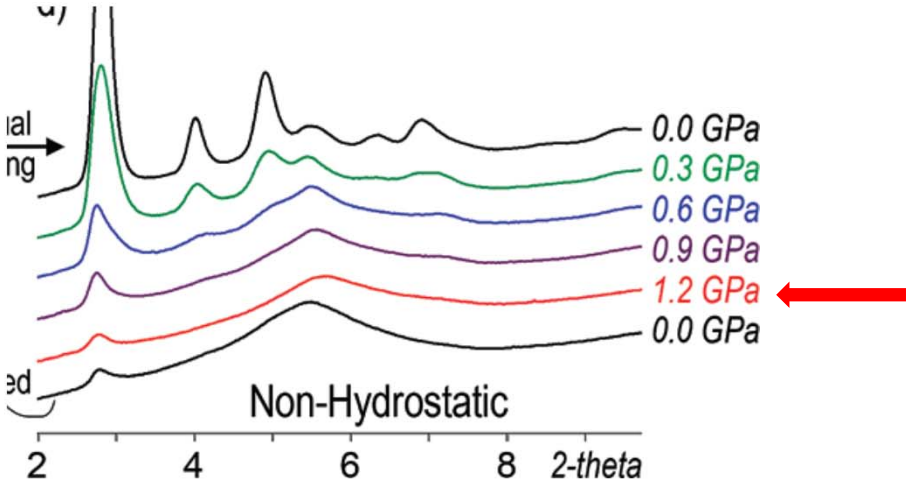
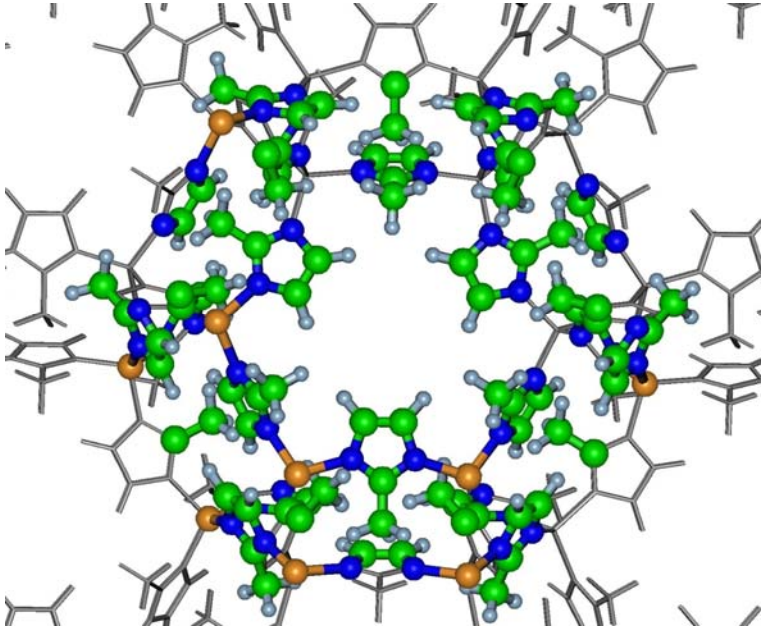


Figure 2. N_2 sorption isotherms for pressure-treated ZIF-8. A logarithm-scale expansion of the low pressure regime is given (left).

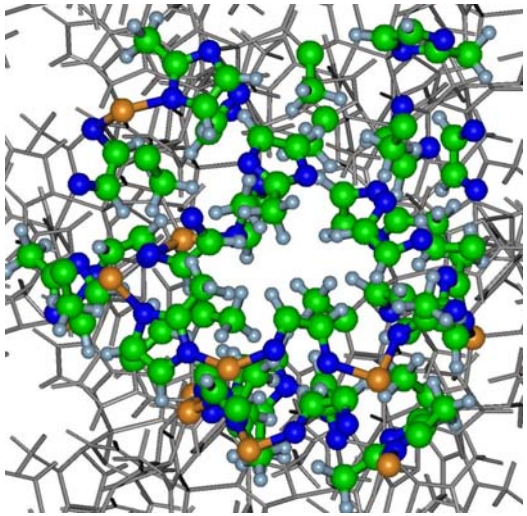
Simulating Crushing ZIF8 to a Glass

DFT MD Wenlin Chen PhD thesis 2016

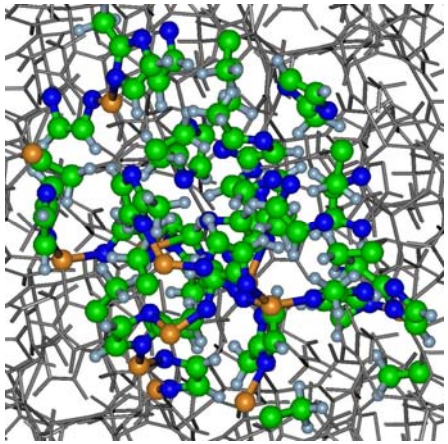
1 atmos



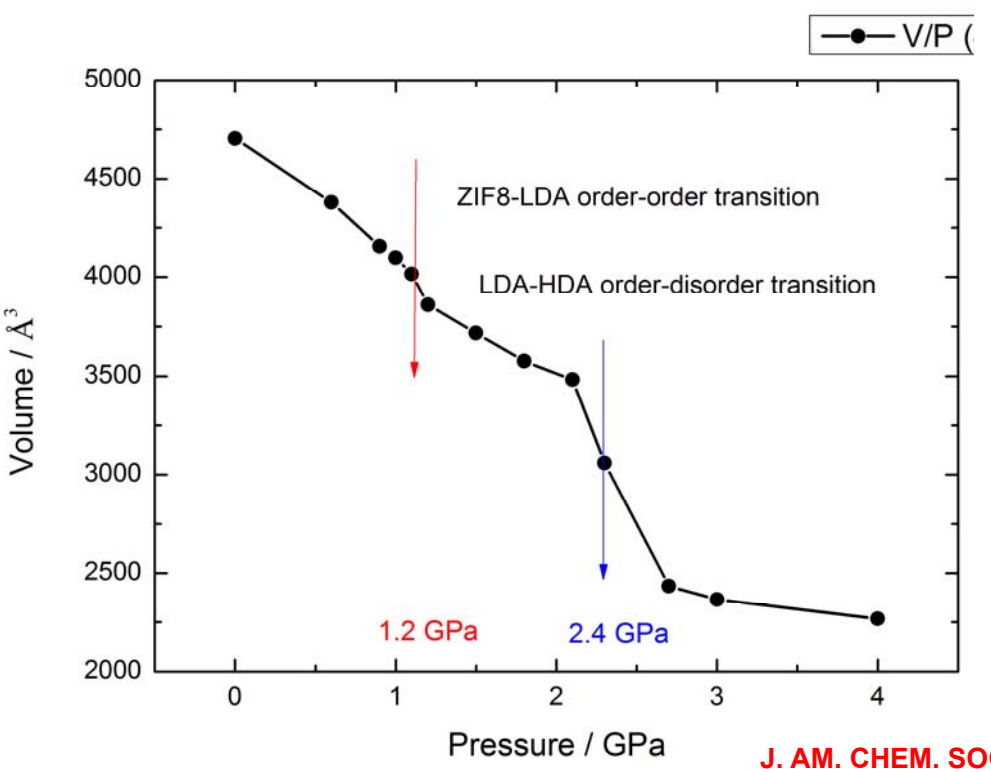
1.2 GPa

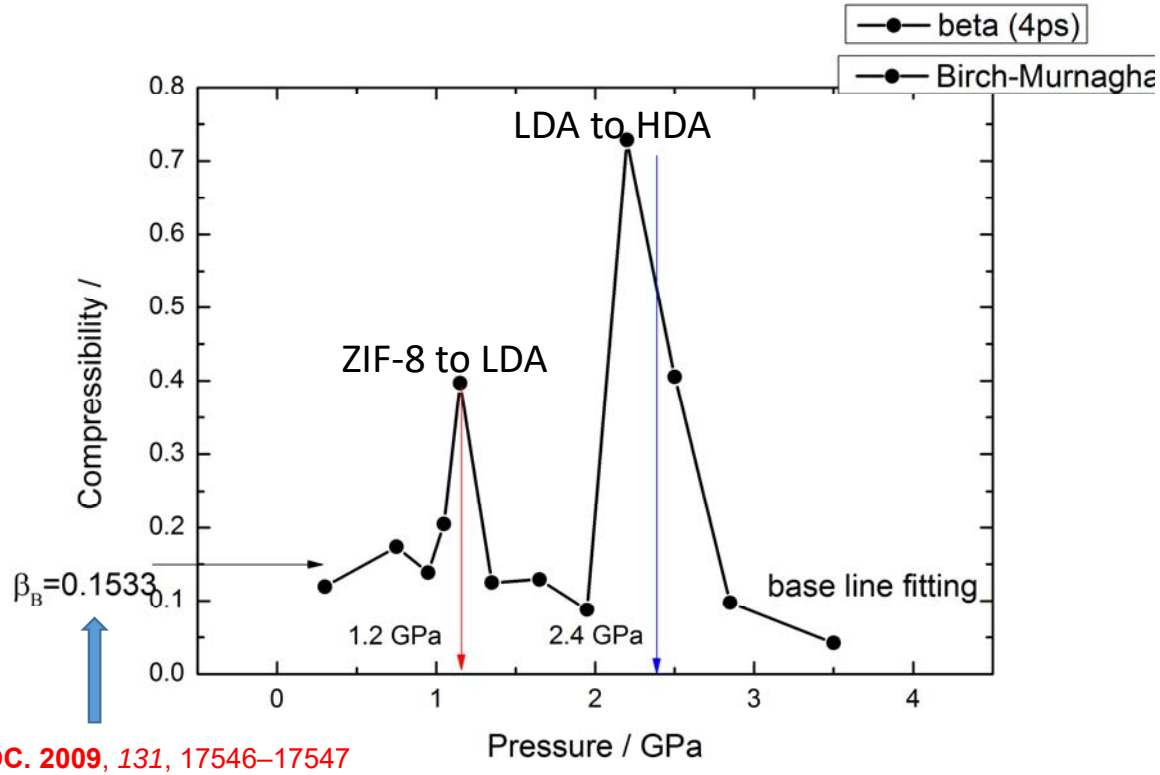


3 GPa



Crushing ZIF8
Volume versus Pressure ➡ Compressibility

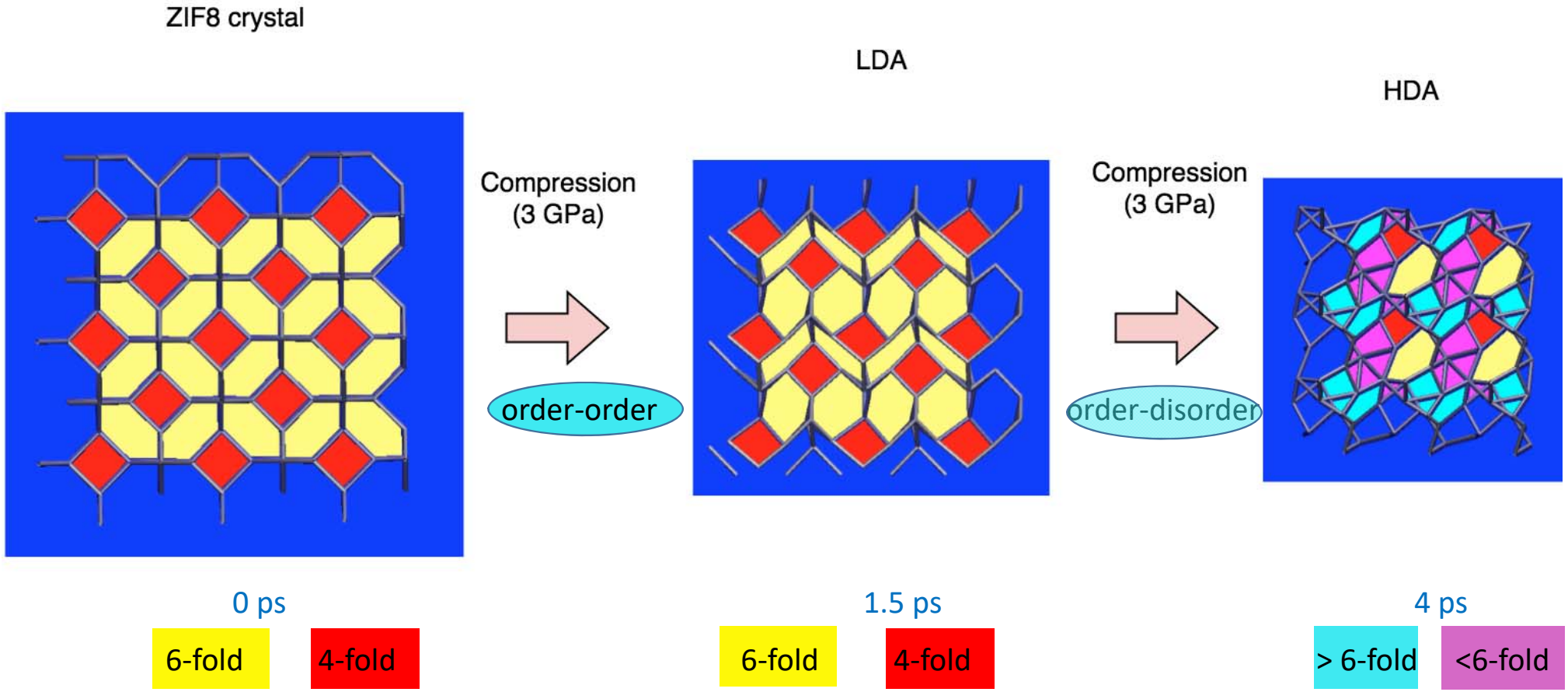




J. AM. CHEM. SOC. 2009, *131*, 17546–17547

Network Topology ZIF8

Zn-Zn rings through **compression**



"From Models for the Atomic Structure of Glass To Organic-Inorganic Glasses"

1. Models for the Atomic Structure of Glass:

    A. Continuous Random networks
    B. Modified Random Networks

2. Organic-Inorganic Hybrid Glasses

    A. Examples of Organic-Inorganic Structures
    B. Amorphization, Melting and Vitrification of ZIF-4
    C. Other Melt-Quenched Hybrid Glasses
    D. Porous Hybrid Glasses
    D. Collapse Transitions for ZIF-8