Cavities and Chemical Disorder in Chalcogenide Glasses

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Outline

- Introduction
- Cavities in Insulating Glasses and Ionic Diffusion/Exchange
  - Ge-S glasses
  - Diffraction studies and DFT-MD modelling
  - Definition of cavities
  - Ag tracer diffusion
  - Anderson-Stuart model for ionic transport
  - Chemical sensing and ion exchange
- Chemical Disorder in Glassy As_2Te_3
  - Collapse of $(As_4Te_6)_\infty$ ribbon: a possible scenario
  - Diffraction data and RMC/DFT modelling
  - Glassy As_2Te_3 under high pressure
- Conclusions

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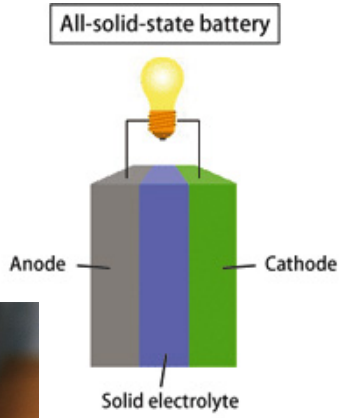
Chalcogenide Glasses



Infrared Optics
Passive and active optical devices

Phase-Change Materials
DVD, Blu-Ray

All-Solid State Batteries
(Li_2S-P_2S_5)

Chemical and Biosensors

Chalcogenide vs. Oxide/Halide Glasses

Pure chalcogens are glass-formers, especially Selenium

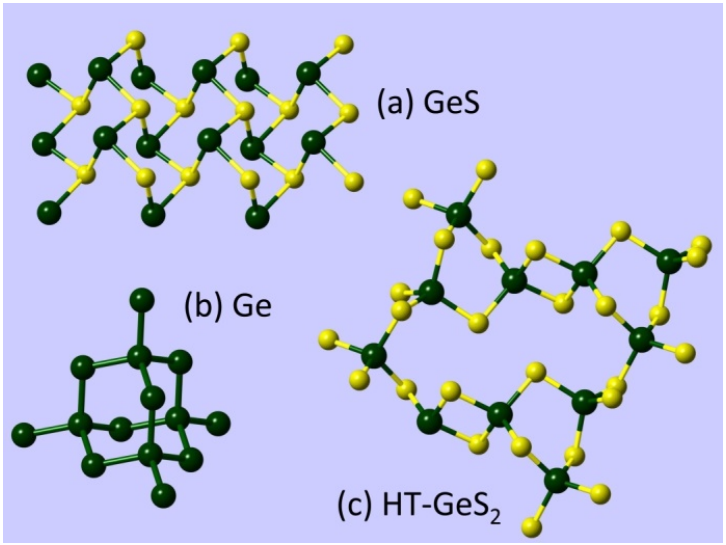
Wide glass-forming range not limited to stoichiometric compositions

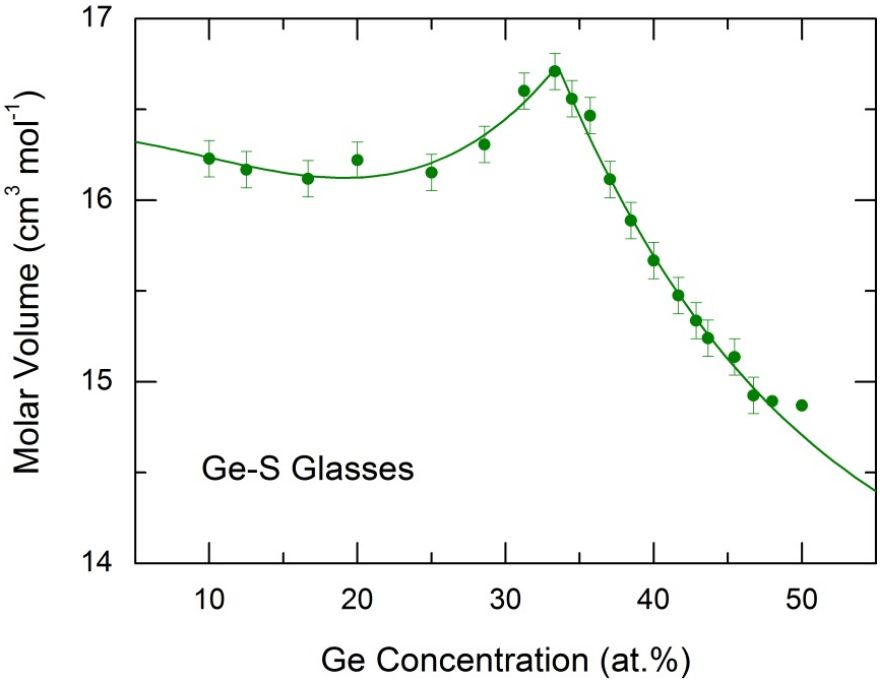
Chemical disorder

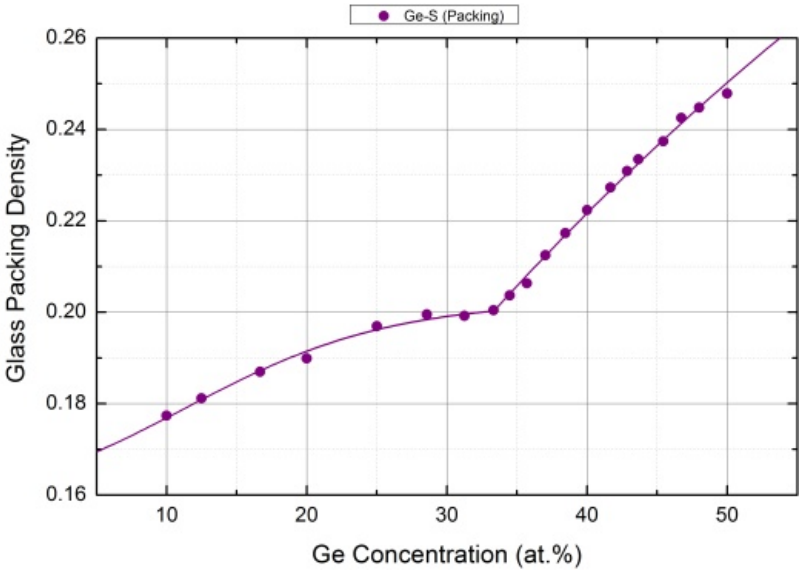
Mixed chalcogen glasses

Cavities in Insulating Glasses and Ionic Diffusion / Exchange

Ge-Rich Sulphide Glasses: Molar Volume & Packing Density





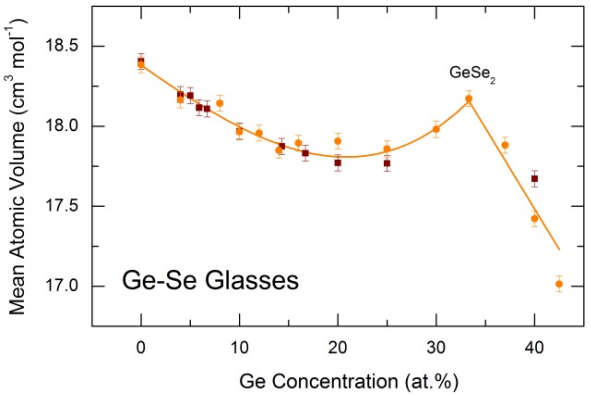


$$\rho = \frac{V_a^0}{V_a},$$

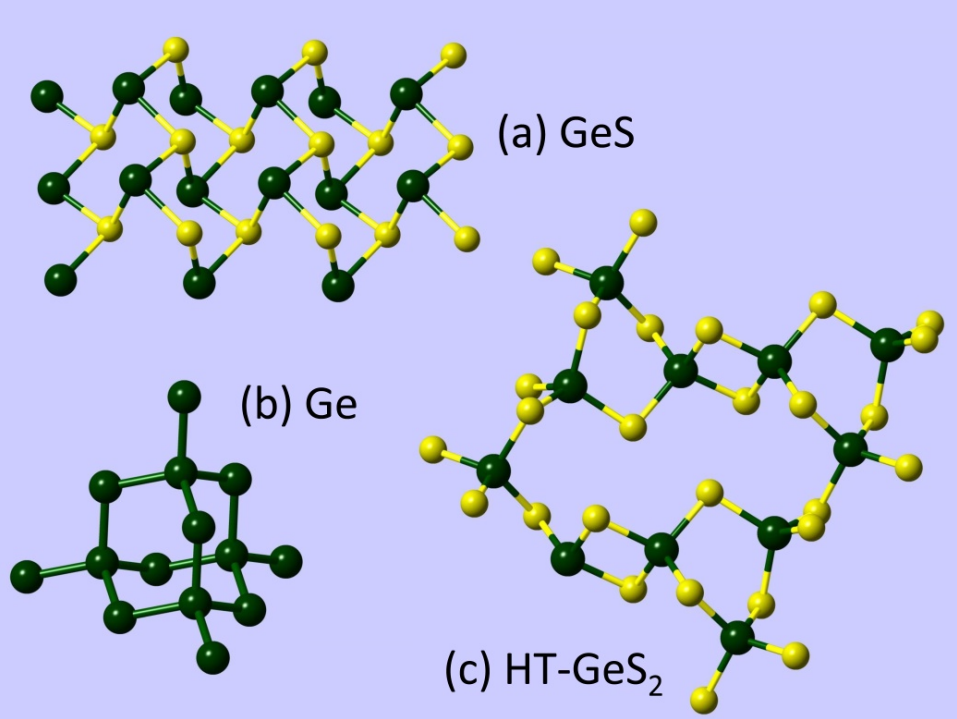
$$V_a^0 = \sum_i c_i \frac{4\pi}{3} r_i^3,$$

$$V_a = \frac{\sum_i c_i M_i}{d\, N_A},$$

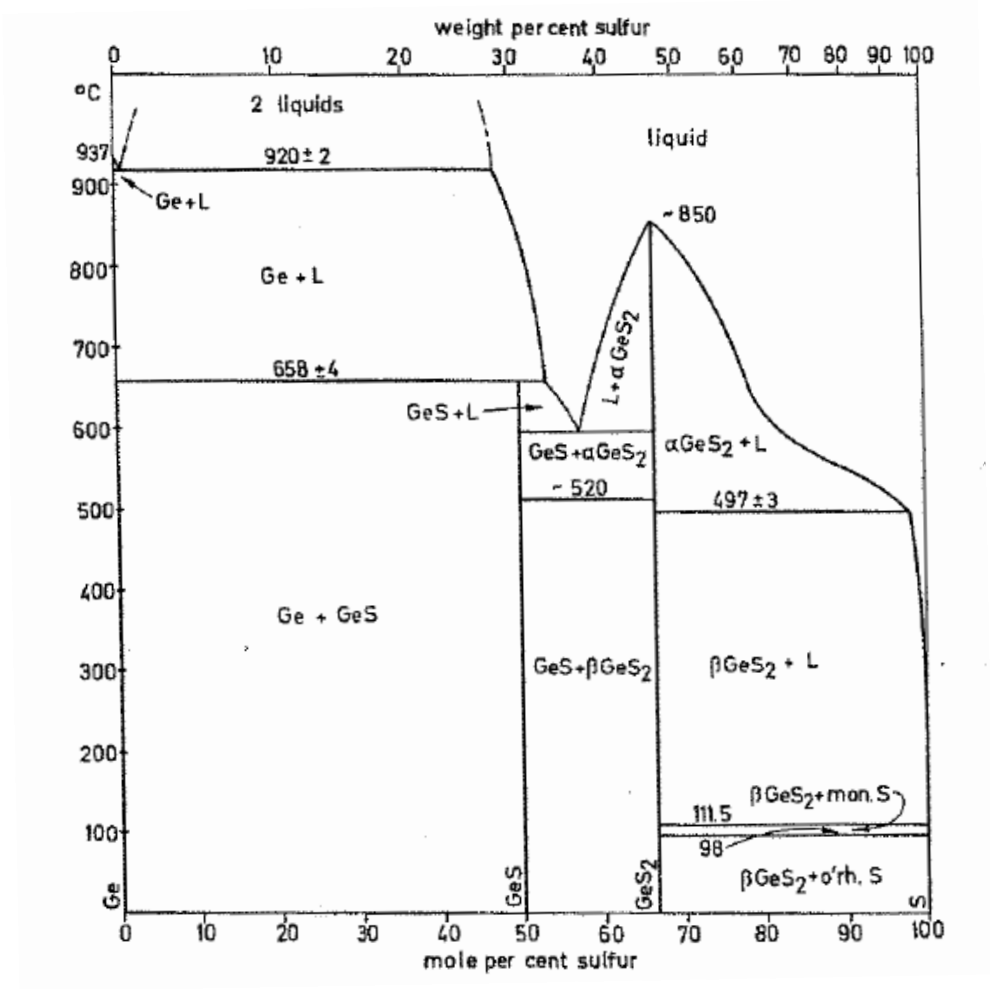
Packing density



Ge-Rich Sulphide Glasses



(a) Orthorhombic GeS, (b) cubic Ge and (c) monoclinic HT-GeS_2 crystalline forms related to the structural motifs present in Ge-rich sulphide glasses.



W. Viane, G. H. Moh, N. Jb. Miner. Abb. (1973)

Two Structural Hypotheses

Chemically-ordered random network or 4-2 model, Lucovsky et al. (1974) based on Philipp's model: SiO_x (1972)

Distorted NaCl or 3-3 model Bienenstock (1973)

GeS_4: $\bar{y}^4$,

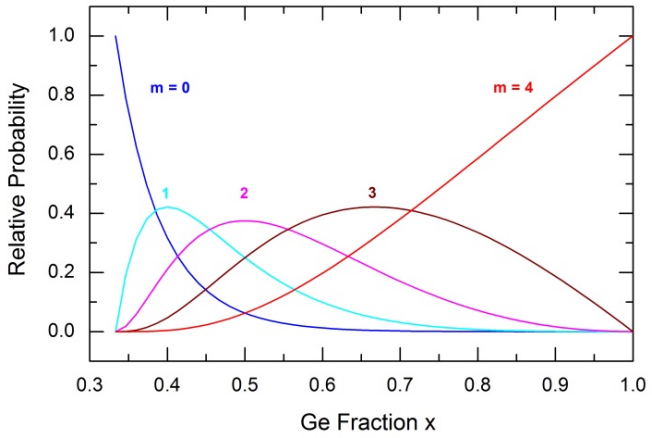
$Ge(GeS_3)$: $4\bar{y}^3\bar{x}$,

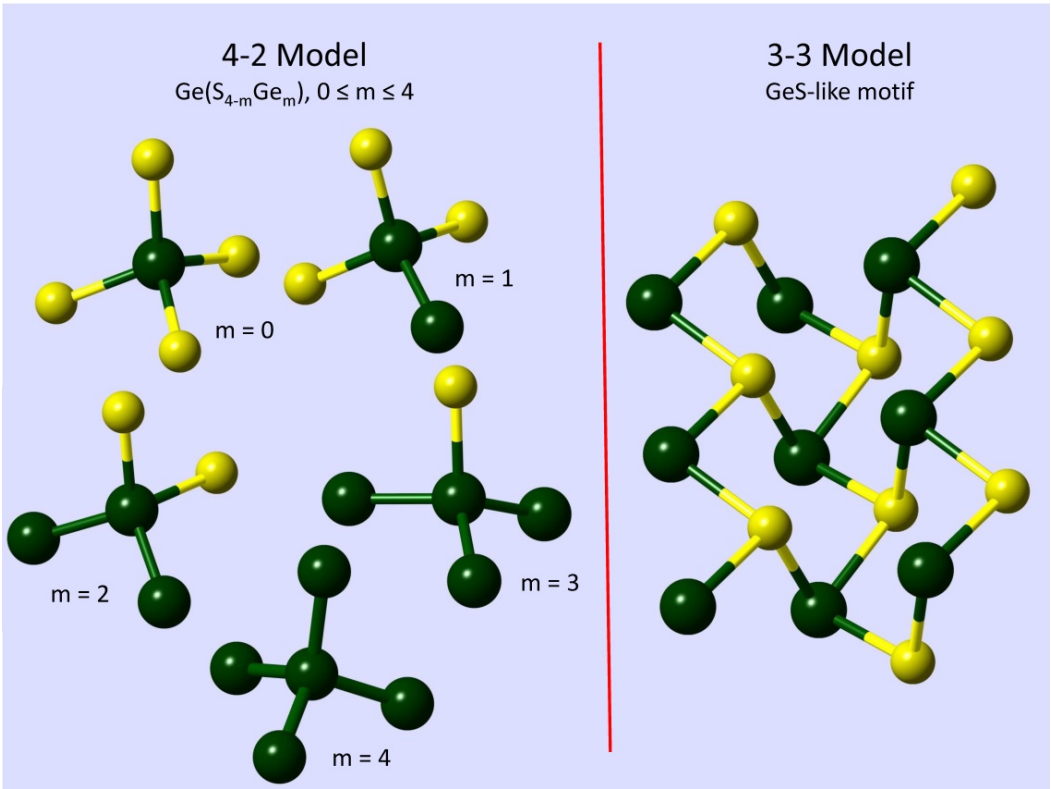
$Ge(Ge_2S_2)$: $6\bar{y}^2\bar{x}^2$,

$Ge(Ge_3S)$: $4\bar{y}\bar{x}^3$,

$GeGe_4$: $\bar{x}^4$.

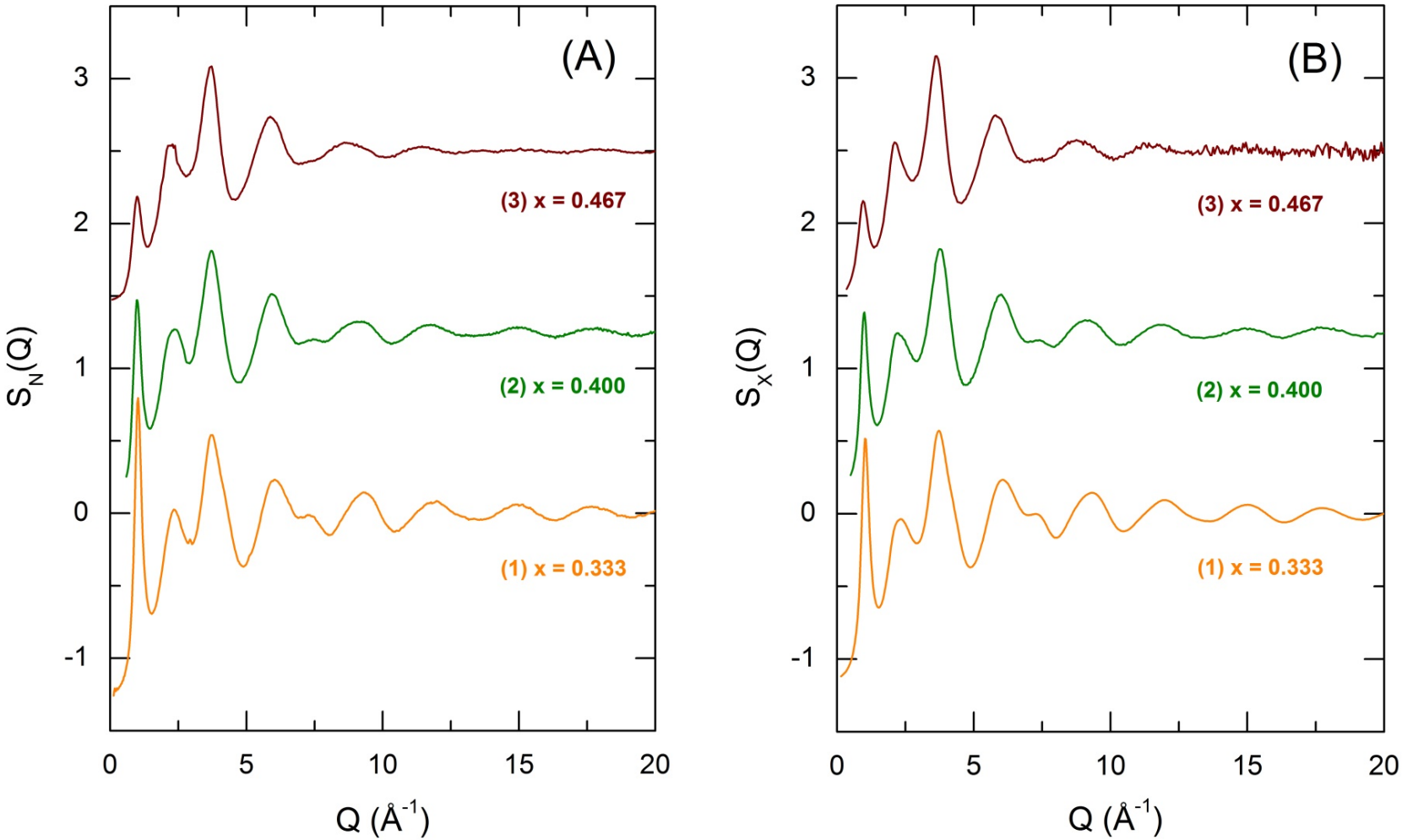
$$\bar{y} = \frac{1-x}{2x} \text{ and } \bar{x} + \bar{y} = 1$$





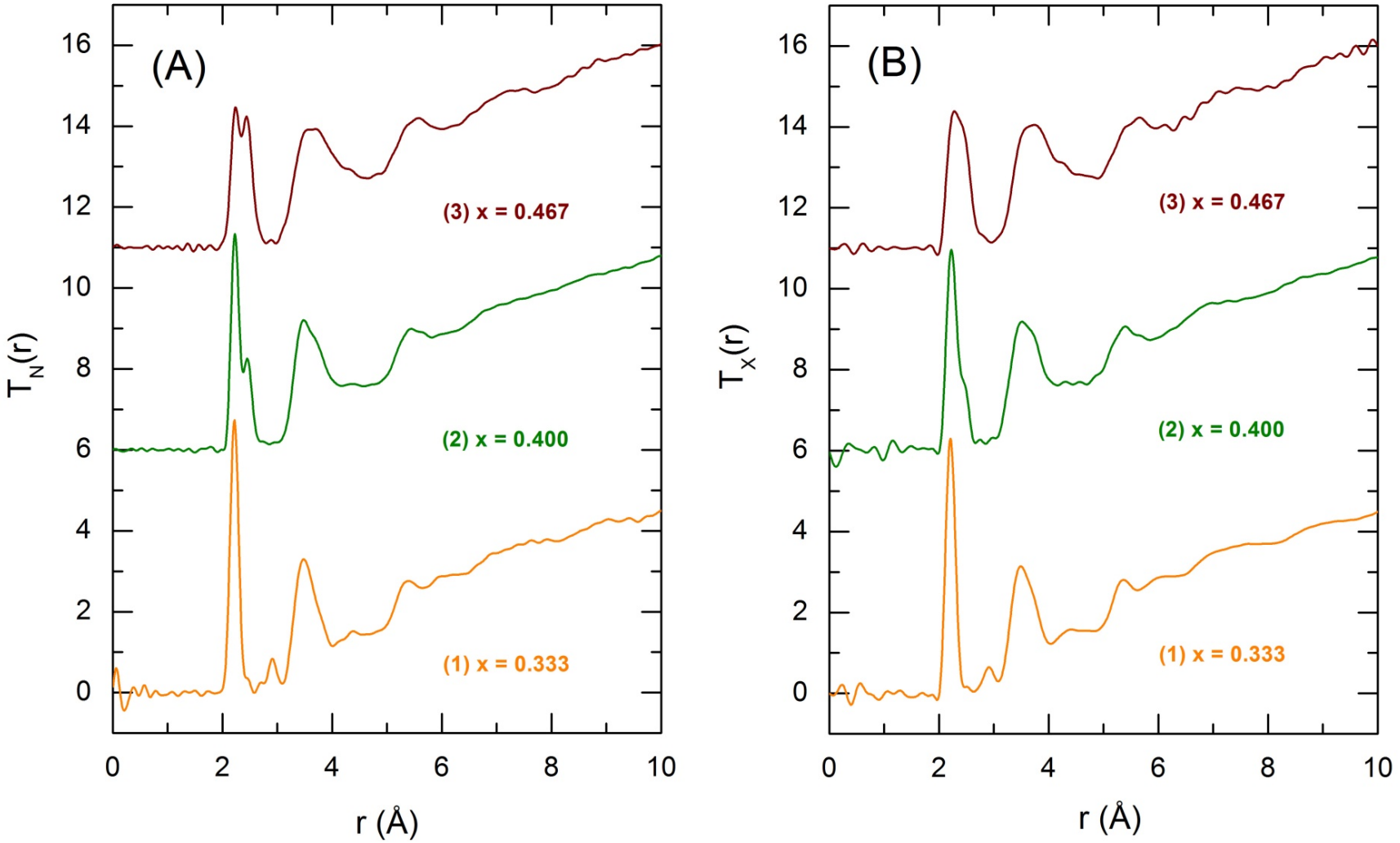
No compelling evidence in the last 40 years, rather contradictory reports

Pulsed Neutron and High-Energy X-Ray Diffraction of Ge-Rich Glasses (Q-Space)



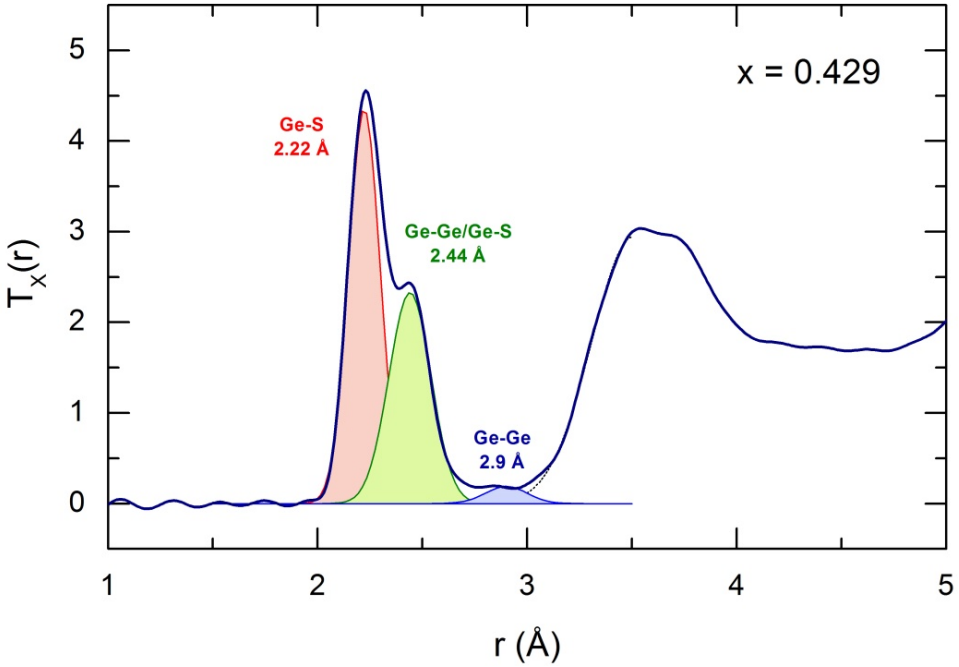
A. Bytchkov et al., PCCP (2013)

Pulsed Neutron and High-Energy X-Ray Diffraction of Ge-Rich Glasses (r-Space)

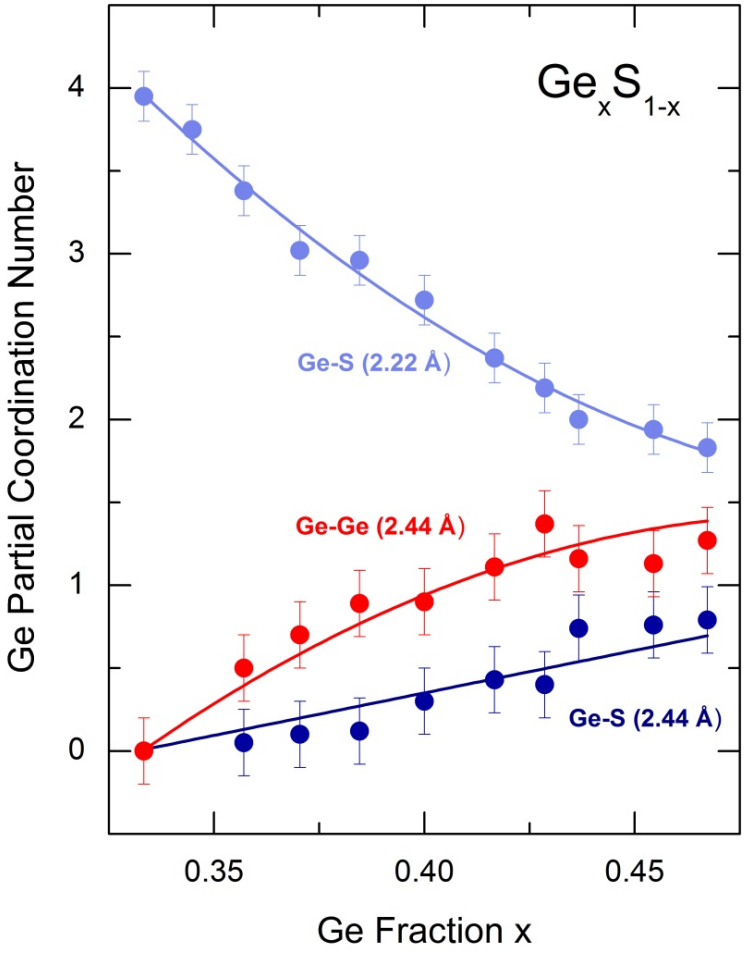


A. Bytchkov et al., PCCP (2013)

Pulsed Neutron and High-Energy X-Ray Diffraction of Ge-Rich Glasses (Fitting)



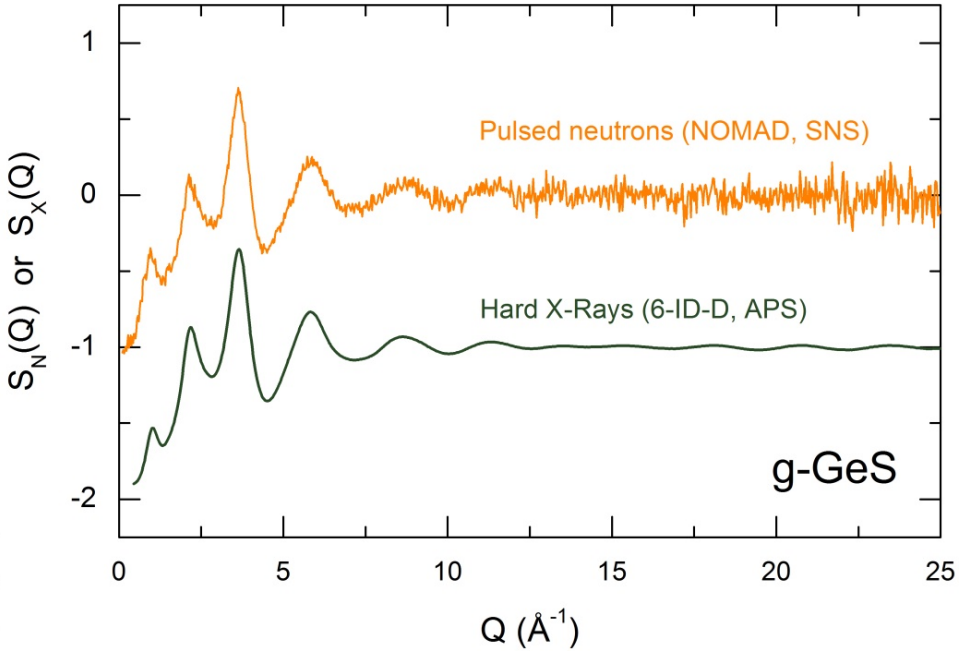
W^N_{GeGe}/W^N_{GeS} = 1.44
W^X_{GeGe}/W^X_{GeS} = 1.30

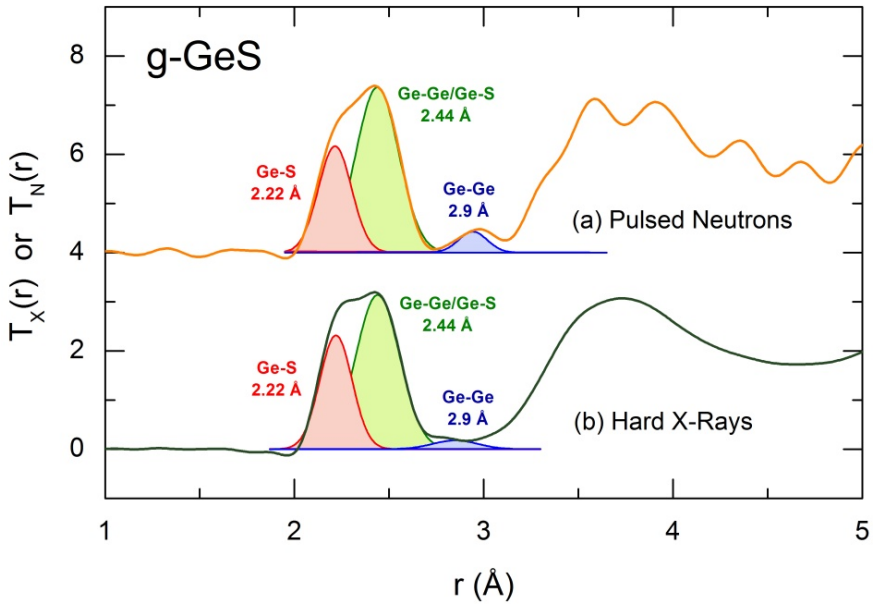


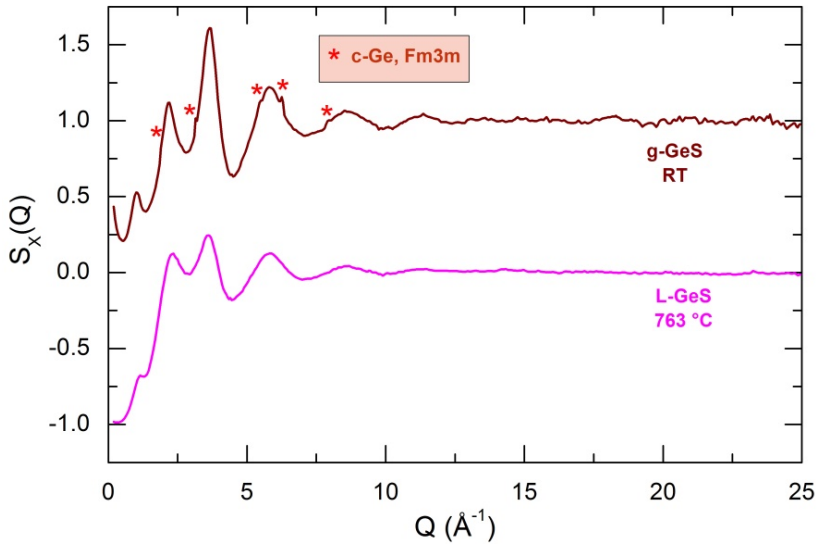
$N_{Ge-X} = N_{Ge-S} + N_{Ge-Ge} \approx 4$ ($0.33 \leq x \leq 0.46$)
What happens in glassy GeS?

A. Bytchkov et al., PCCP (2013)

Glassy GeS: Neutron Diffraction on a 2.6 mg Sample

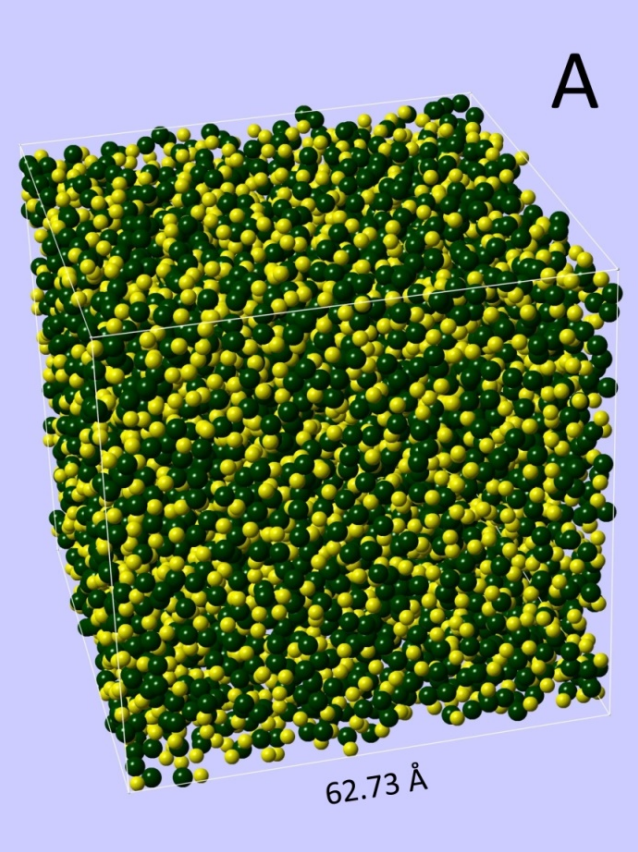






$N_{Ge-X} = N_{Ge-S} + N_{Ge-Ge} \approx 3.6$!!!

Ge-Rich Sulphide Glasses: RMC, DFT, DFT-MD



Partial Functions
Coordination
Local Environment
Angles
Connectivity/Chains
Rings
Characteristic Motifs
Voids/Cavities

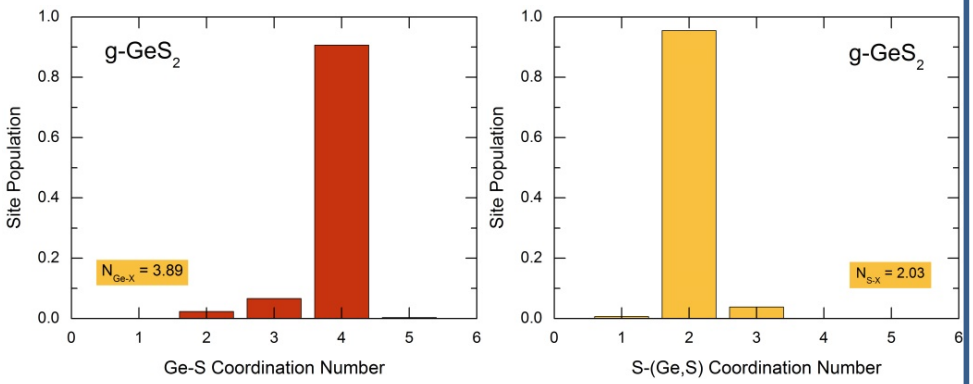
RMC → initial cfg for DFT → DFT-MD
DFT/DFT-MD Angles → optimised RMC

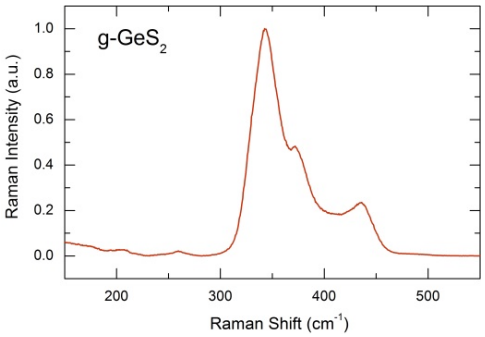
RMC: 5k – 10k atoms
DFT: 1000 – 2500 atoms
DFT-MD: ≤ 1000 atoms

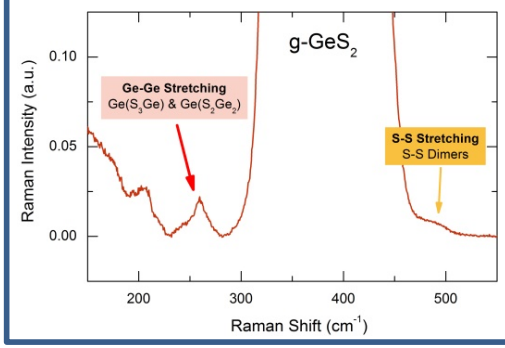
	RMC	DFT	DFT-MD
Energy	0	-(1 to 3) eV/atom	-0.3 eV/atom
Average displacement	0	1.0-1.5 Å	
Electronic structure	Metal	Semiconductor	

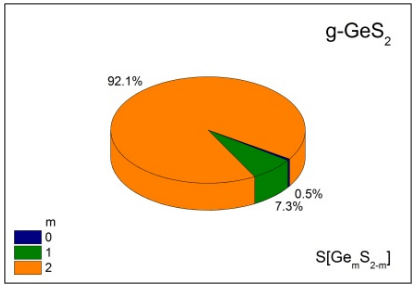
Ge-Rich Sulphide Glasses: Some DFT/DFT-MD Results

g-GeS_2









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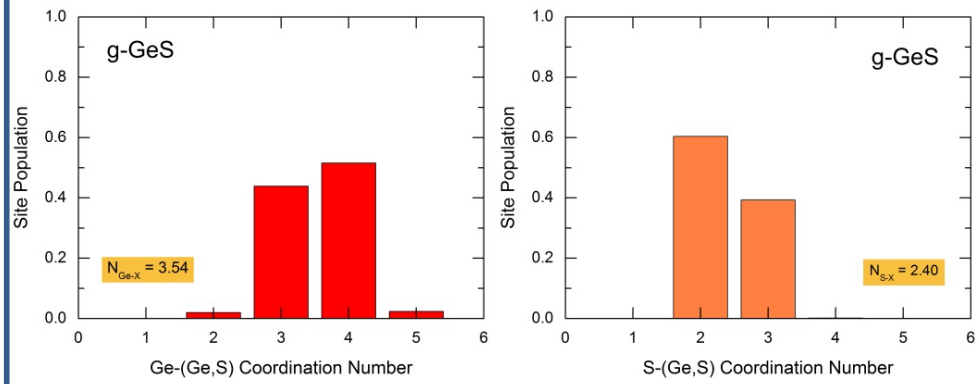
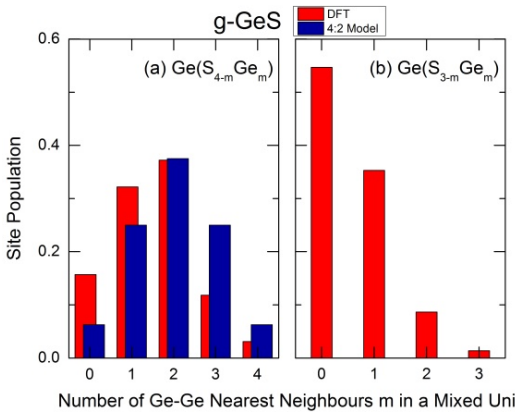
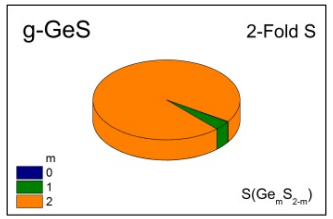
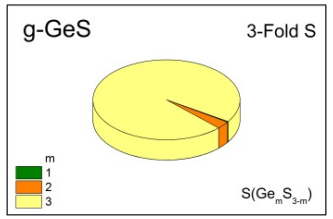
g-GeS









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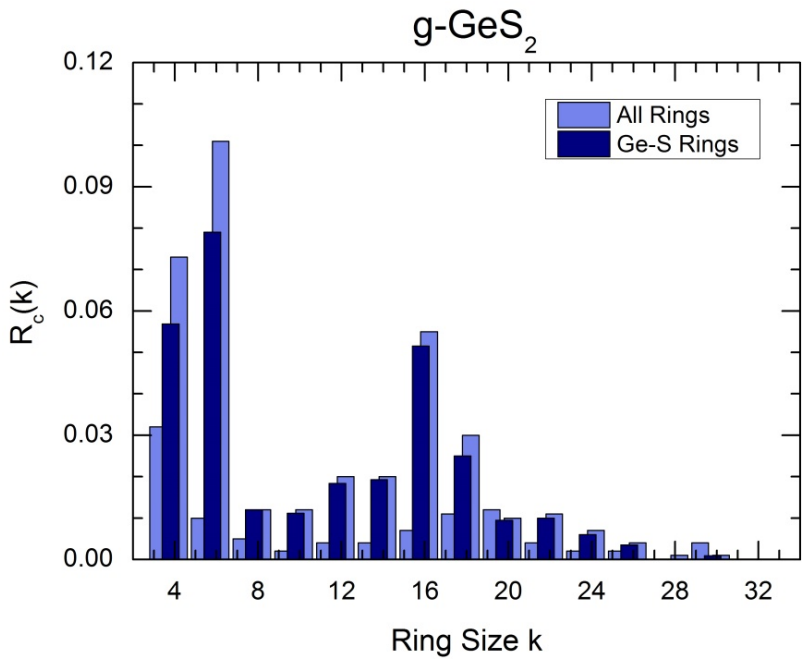
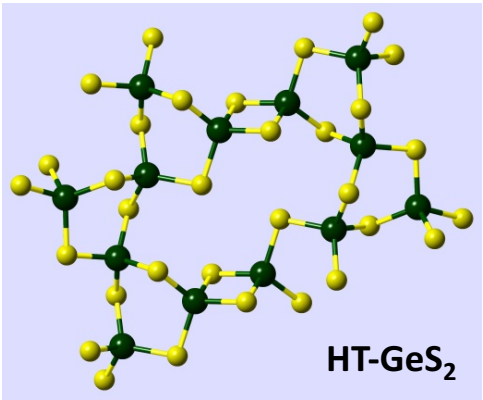
Ge-Rich Sulphide Glasses: Rings

g-GeS_2





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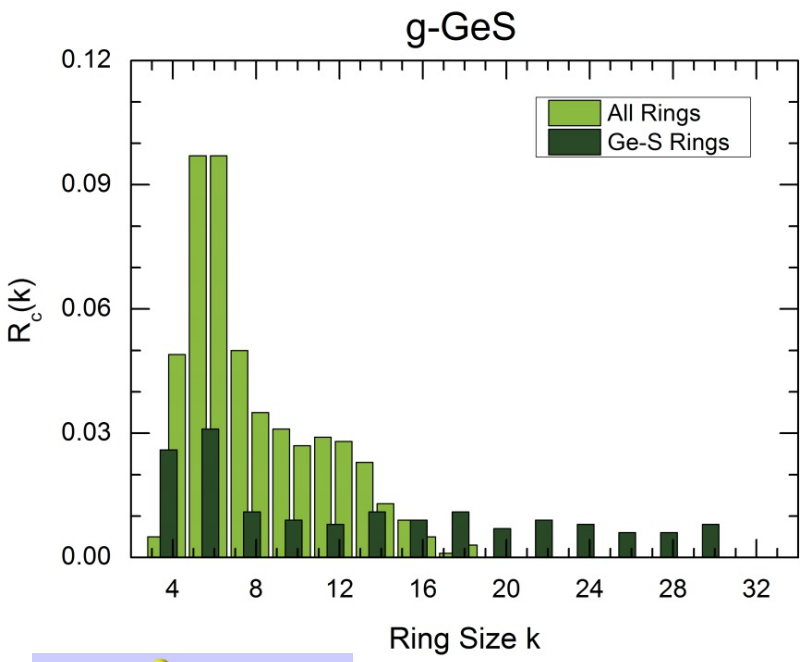
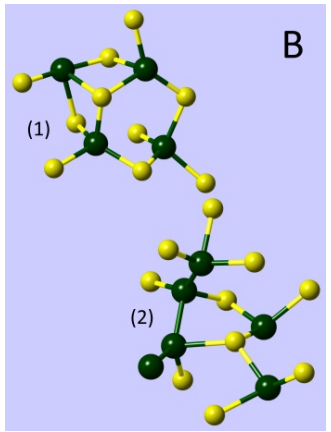
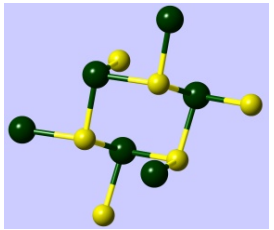
g-GeS







c-GeS

A. Sokolov, D. Fontanari

Conclusion 1

Ge-Rich Sulphide Glasses

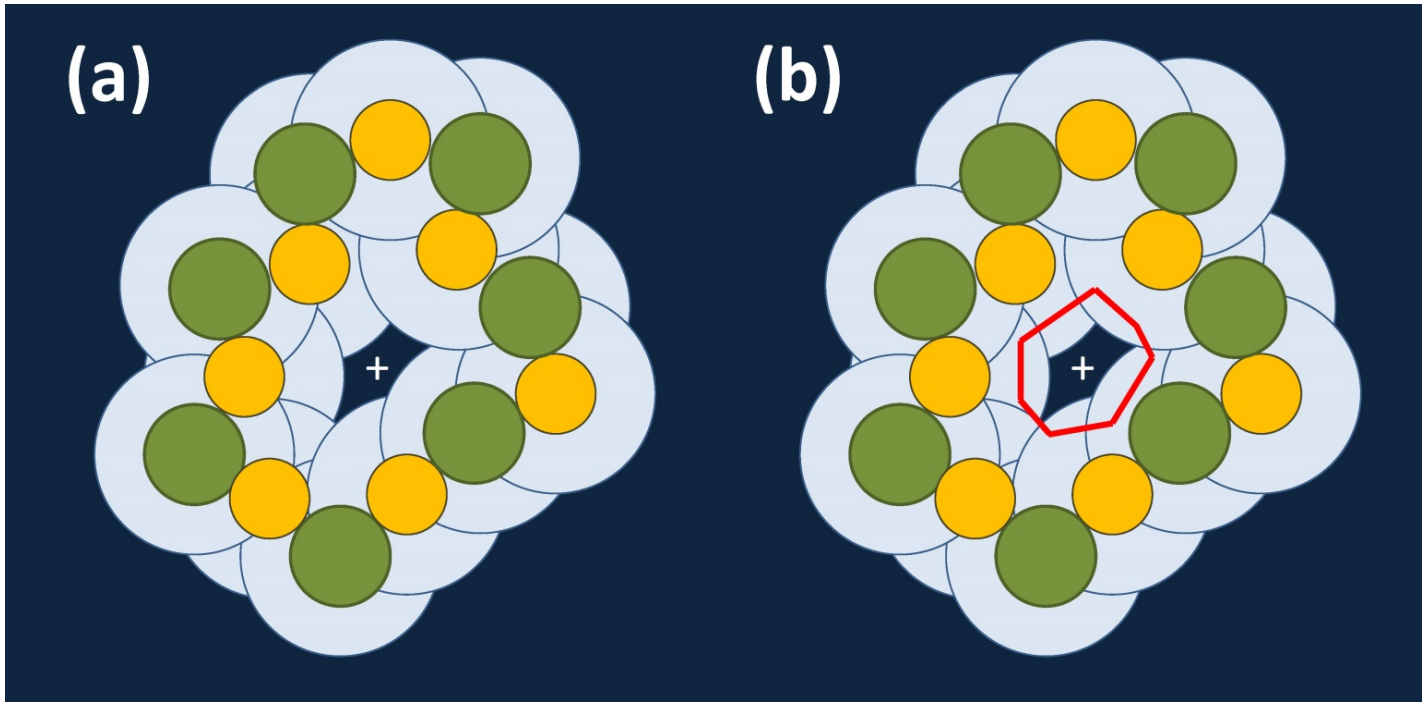
Neither the 4:2 nor the 3:3 model alone can explain the structural features of Ge-rich sulphide glasses. The complicted structure of these glasses is related to incongruent melting of GeS roughly presented by the following reaction:

$2GeS \rightleftarrows GeS_2 + Ge$

Quenching the melt into a glass gives first a variety of mixed tetrahedra $Ge(S_{4-m}Ge_m)$, then (below 658 °C) a variety of mixed trigonal units $Ge(S_{3-m}Ge_m)$.

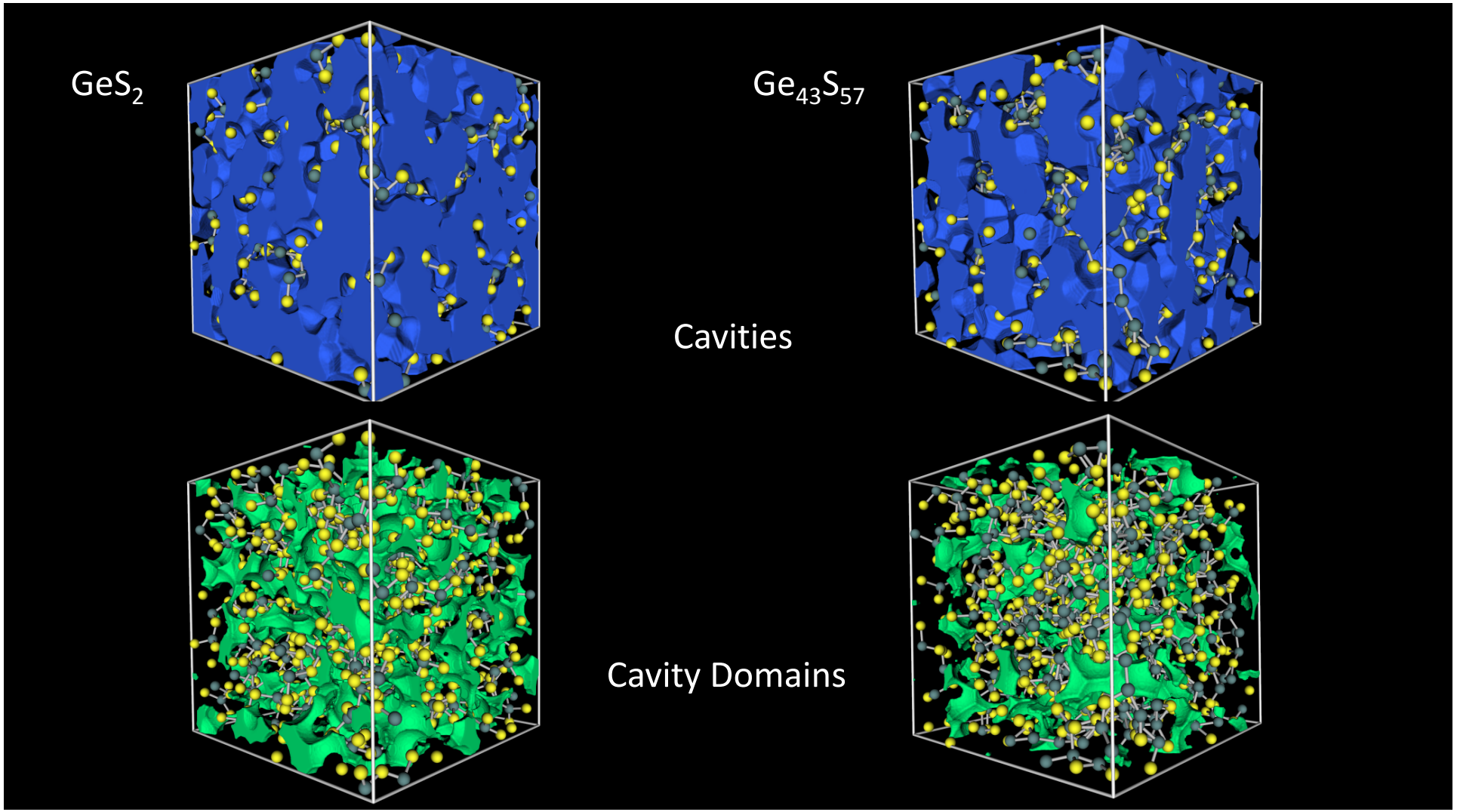
Calculating Cavities

Jaakko Akola & Robert Jones



Schematic representation of cavities in Ge-S glasses: the covalent radius of Ge (green) is set to 1.25 Å, that of S (yellow) to 1.0 Å. The cutoff radius r_C (light blue) is 2.5 Å. (a) A cavity domain with its center; (b) a Voronoi polygon (red) built using the cavity domain center.

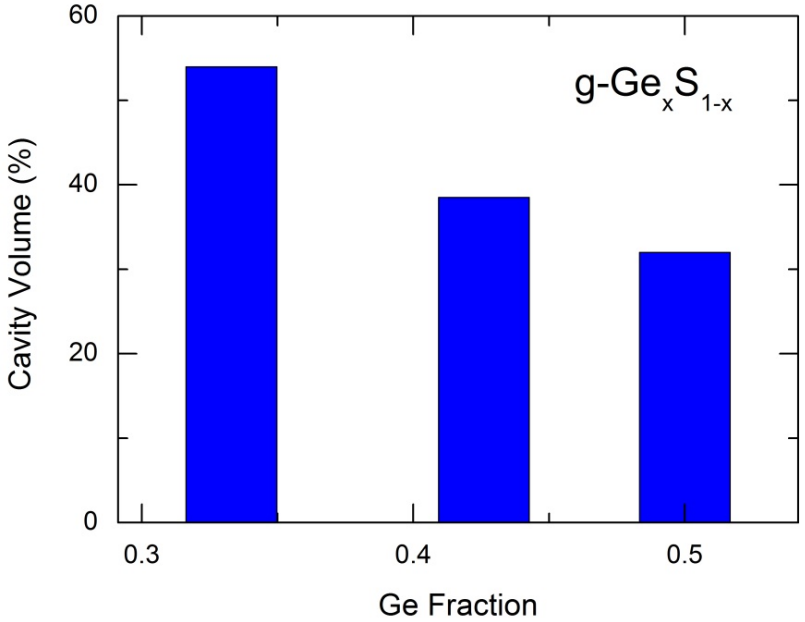
RMC, DFT-MD Modelling of GeS_2 and $Ge_{43}S_{57}$ Glasses and Cavity Calculations

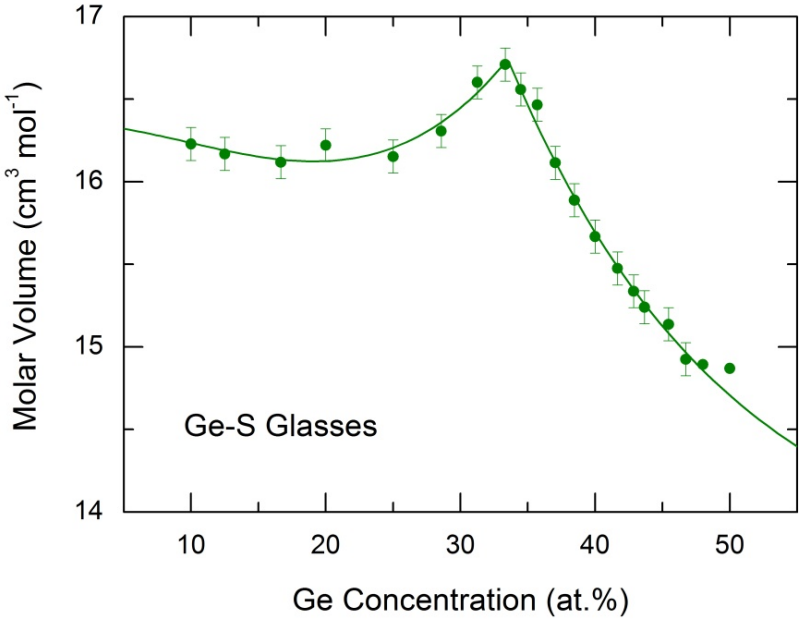


GeS_2, r_C = 2.5 Å, **53-55 %** cavities

$Ge_{43}S_{57}$, r_C = 2.5 Å, **36-41 %** cavities

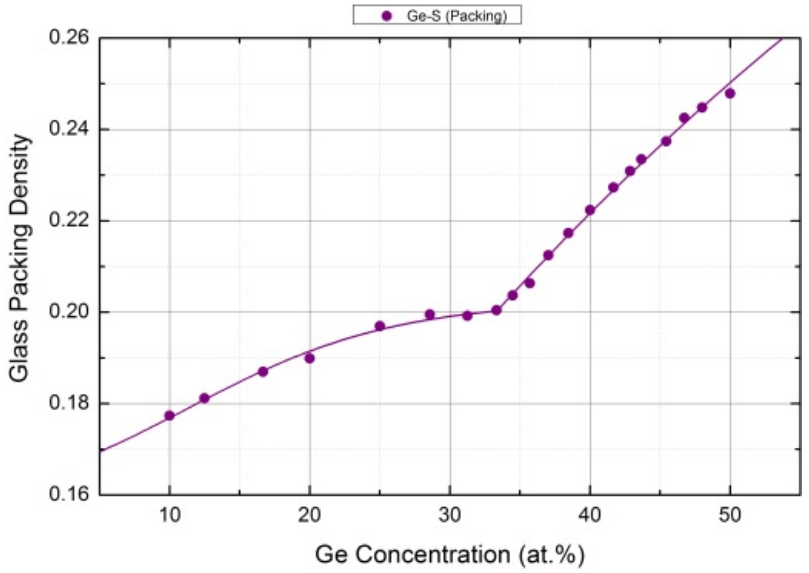
Ge-Rich Sulphide Glasses: Cavities vs. Molar Volume and Packing Density



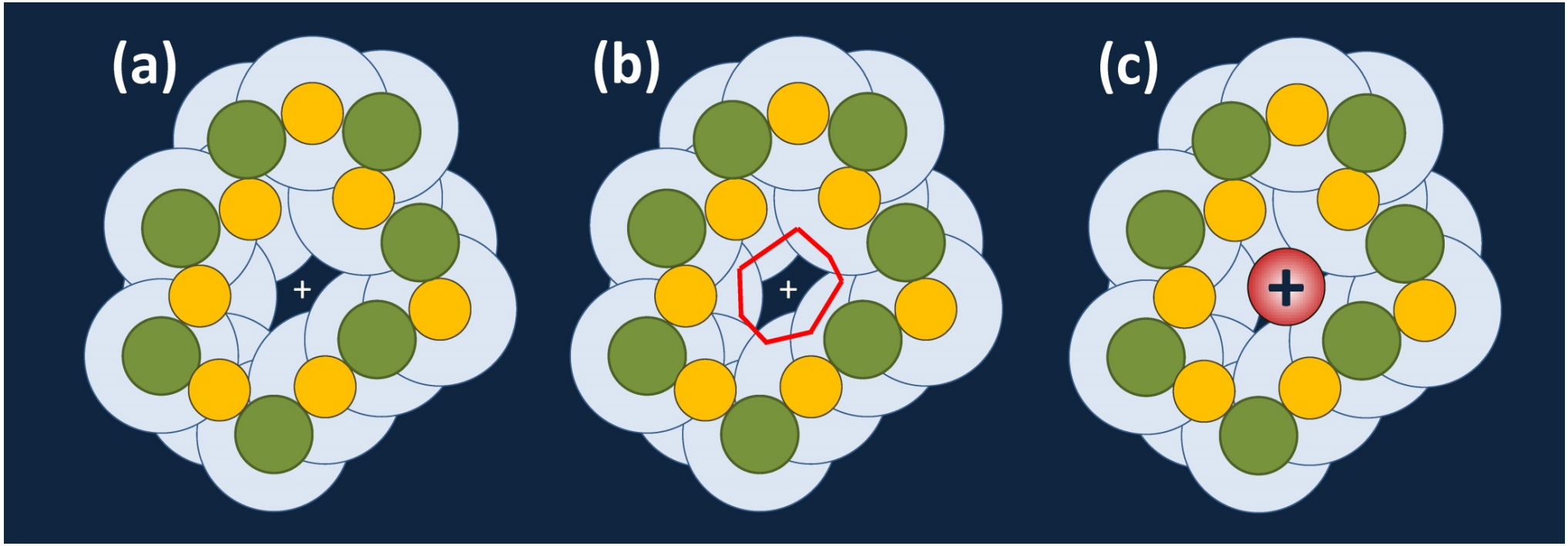


$$\frac{V_{cav}(GeS_2)}{V_{cav}(GeS)} = 1.69$$

How could we check this trend and the existence of cavities?

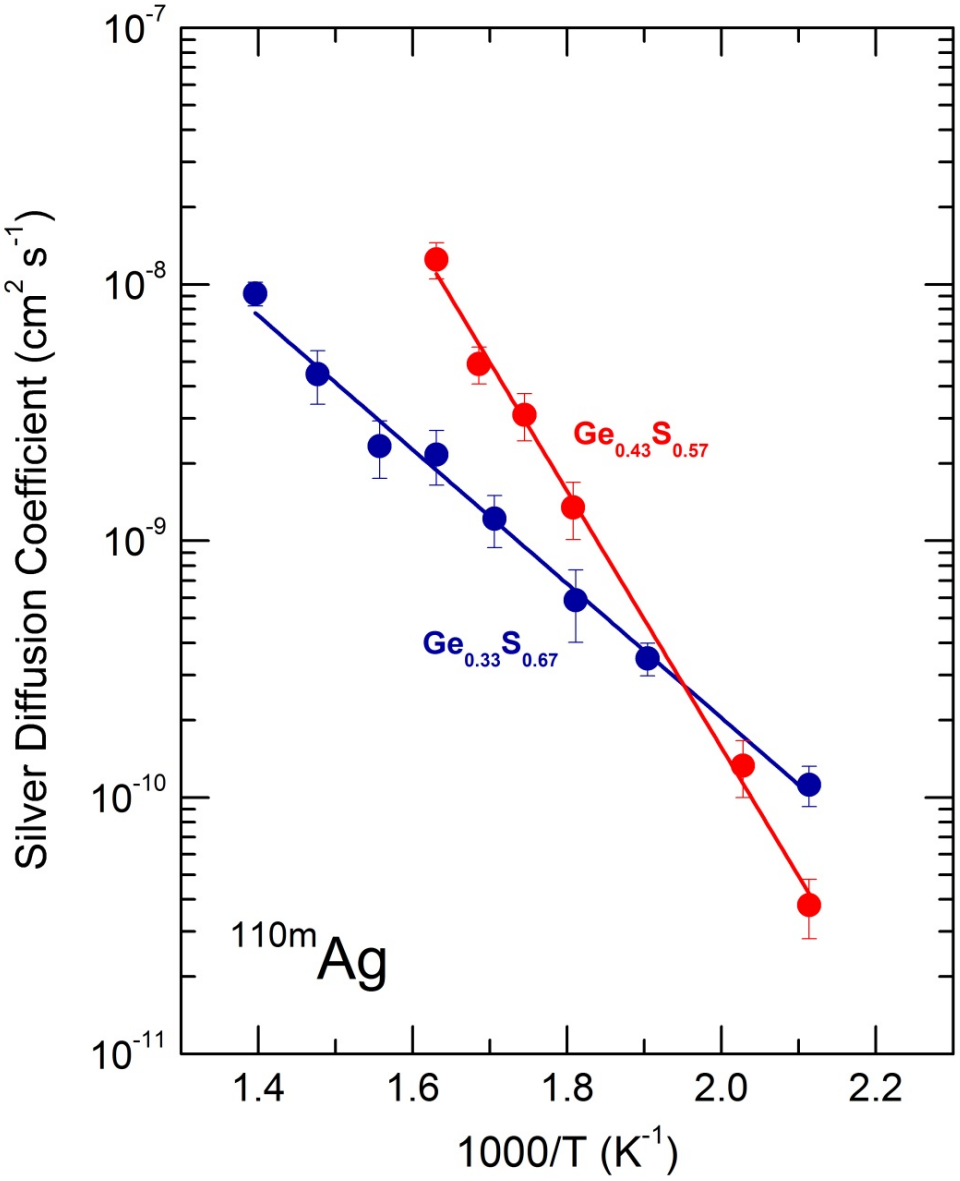


Cavity Domains as Residence Sites for Mobile Ions



Schematic representation of cavities in Ge-S glasses: the covalent radius of Ge (green) is set to 1.25 Å, that of S (yellow) to 1.0 Å. The cutoff radius r_C (light blue) is 2.5 Å and the Ag^+ ionic radius 1.26 Å. (a) A cavity domain with its center; (b) a Voronoi polygon (red) built using the cavity domain center; (c) an Ag^+ ion residing in a cavity formed around the cavity domain center.

^{110m}Ag Tracer Diffusion Ge-Rich Sulphide Glasses



Diffusion Activation Energy	
GeS_2	0.52(2) eV
$Ge_{43}S_{57}$	0.99(3) eV

I. Alekseev

Anderson-Stuart Model (1954)

$$E_d = E_b + E_s, \quad (1)$$

where

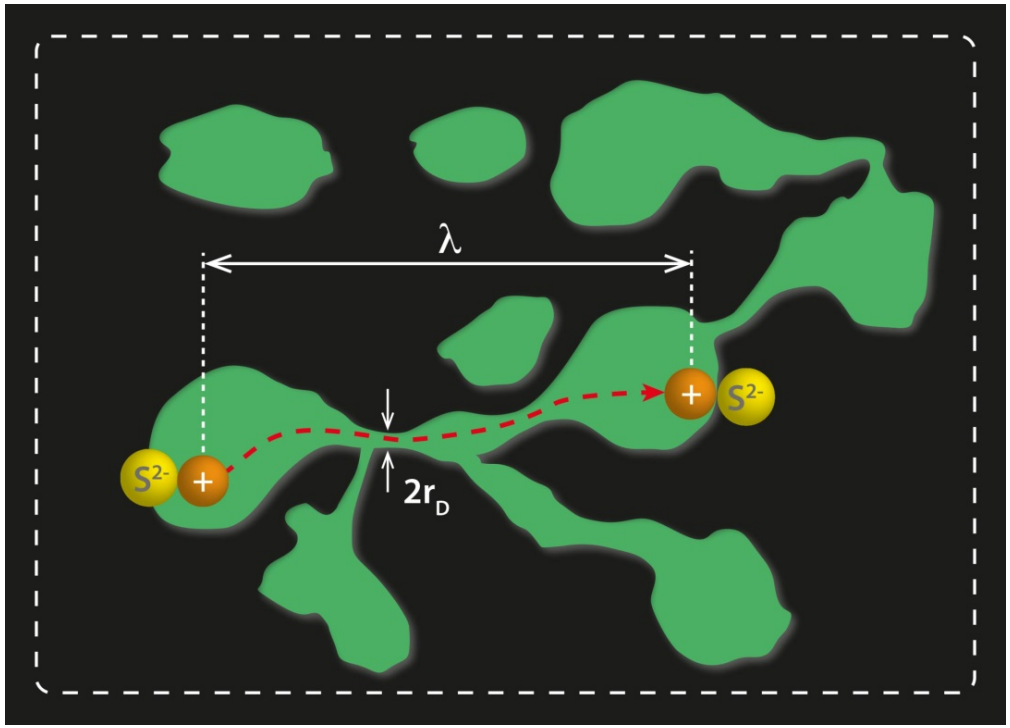
$$E_b = \frac{z_i z_0 e^2}{4\pi\epsilon_0\epsilon_r}\left(\frac{1}{r_i + r_0} - \frac{2}{\lambda}\right), \quad (2)$$

and

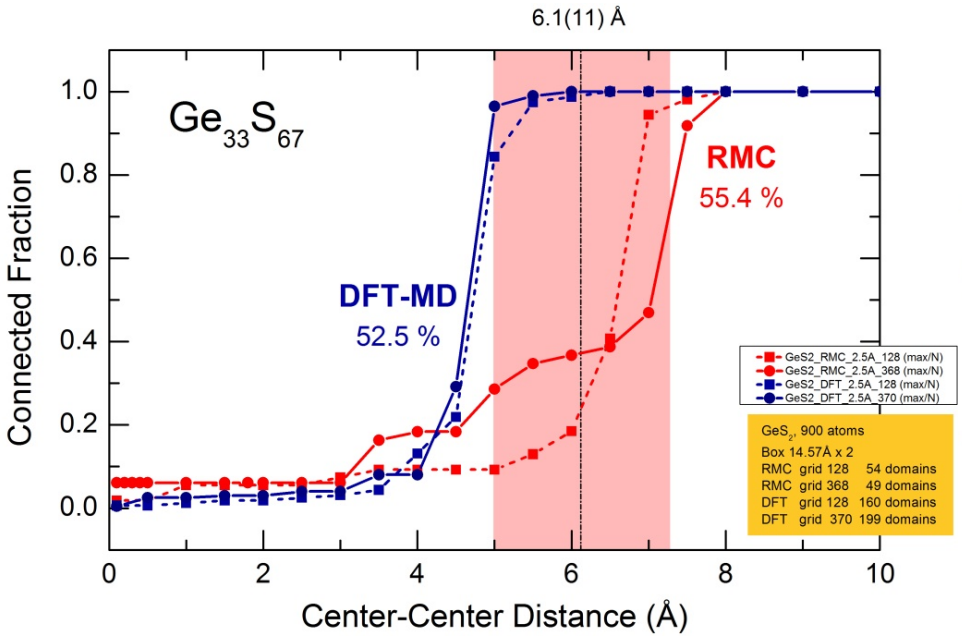
$$E_s = \frac{1}{2}\pi G\lambda(r_i - r_D)^2, \quad (3)$$

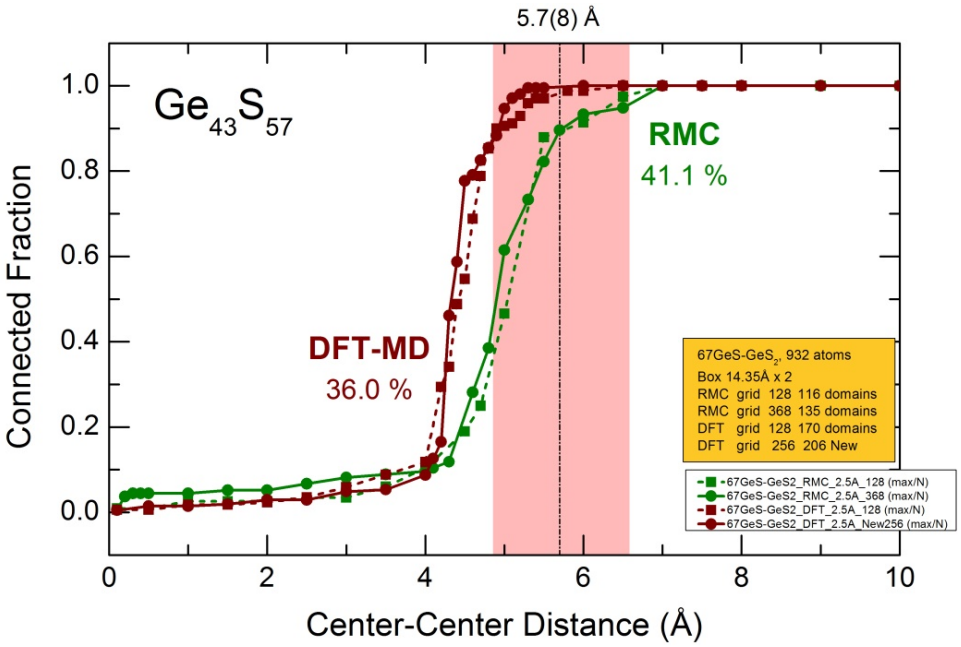
z_i, z_0, r_i, r_0 are the charge and the radii of the mobile cation and non-bridging anion, respectively, G is the shear modulus, λ is the site (cavity) separation distance, r_D is a doorway radius.

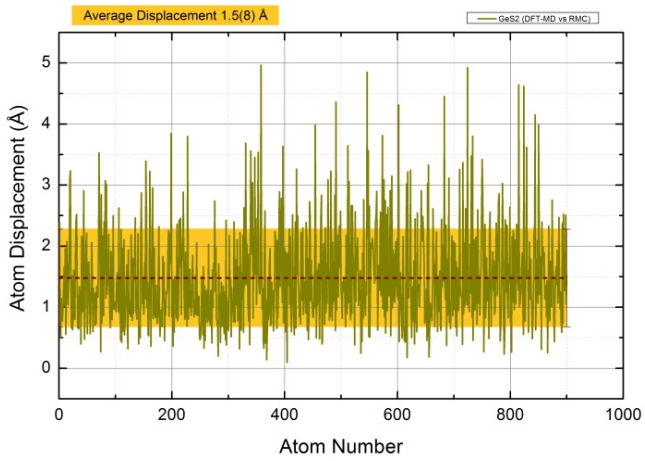
The elastic energy term E_s, eq. (3), was modified by McElfresh and Howitt in 1986.

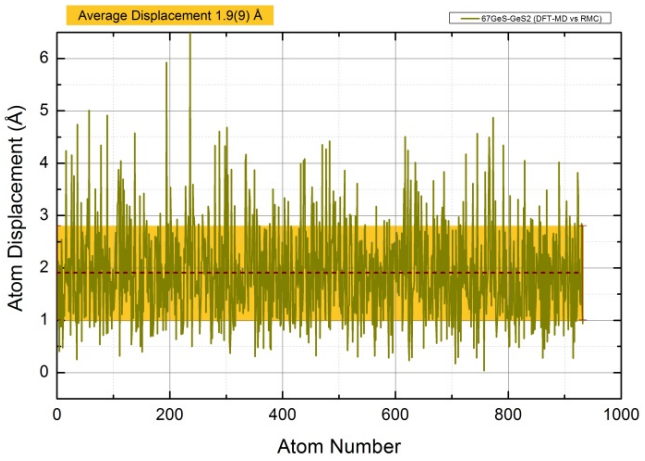


Percolating Cavity Through Cavity Domains Looking for λ

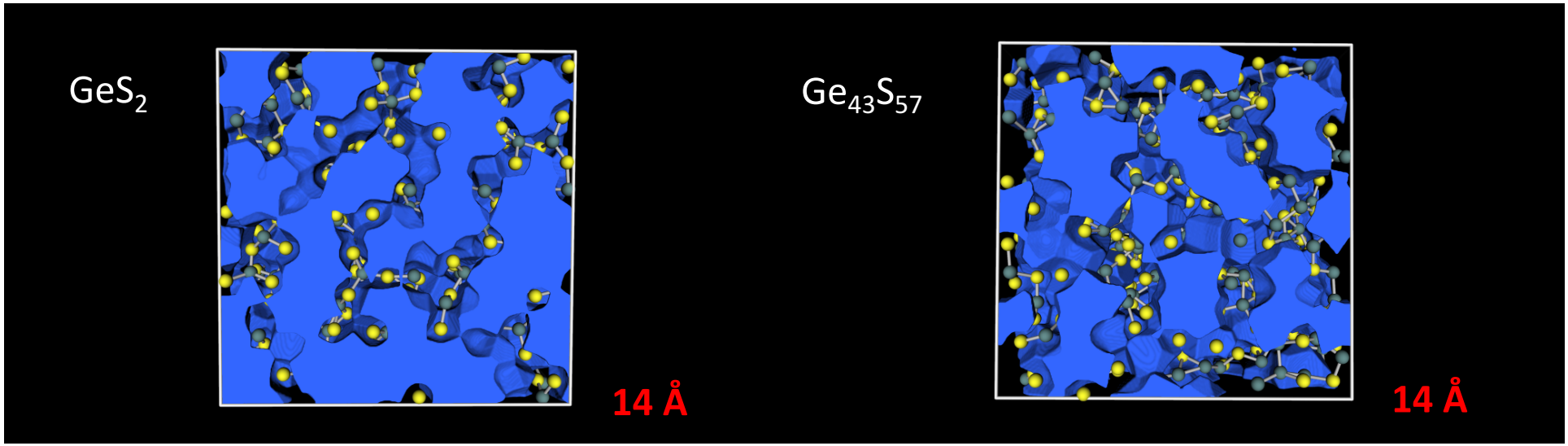






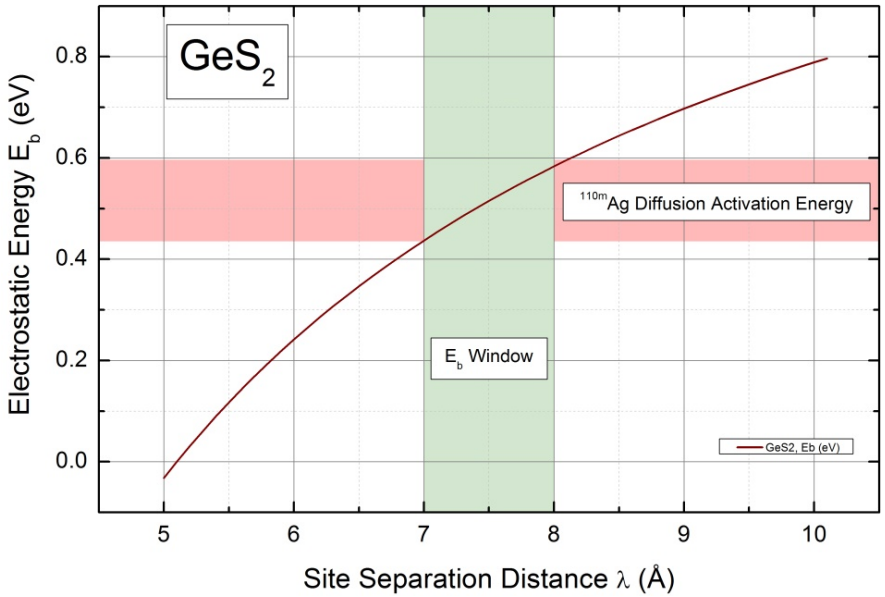


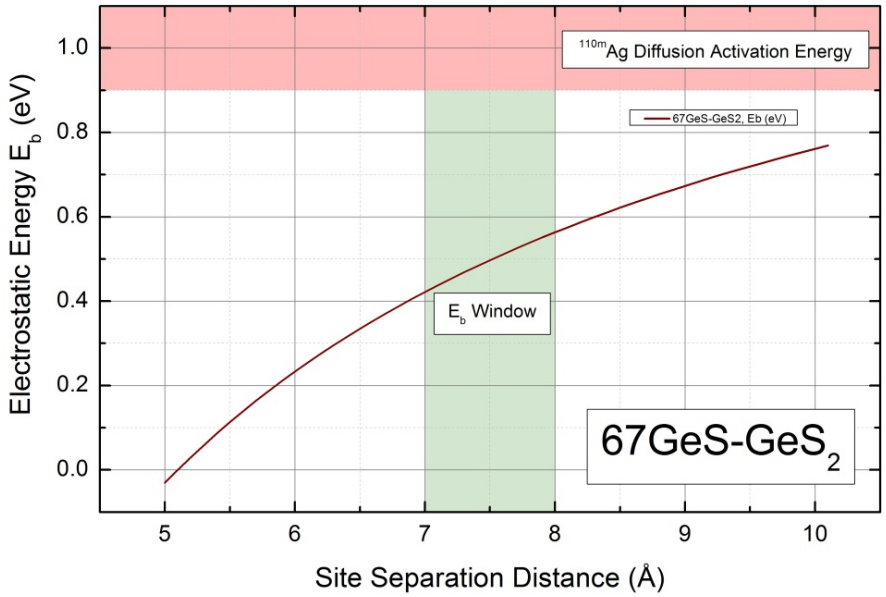
Percolating Cavity Through Cavity Domains Looking for r_D

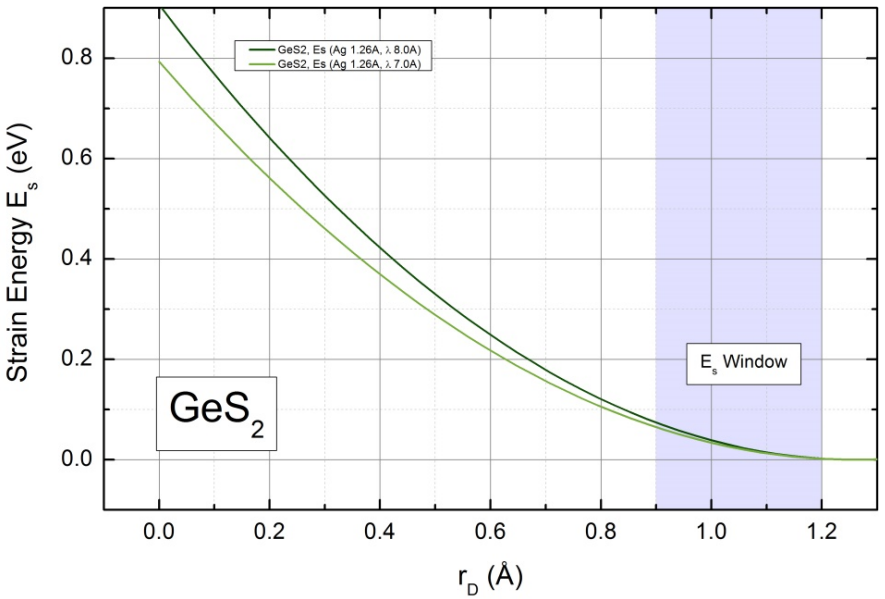


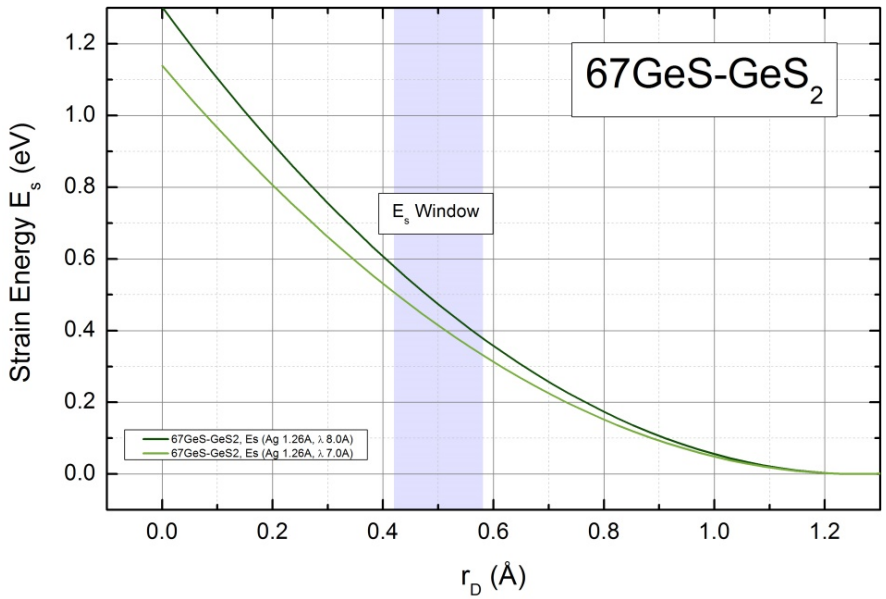
$r_D(GeS_2) > r_D(Ge_{43}S_{57})$

Calculating E_b and E_s



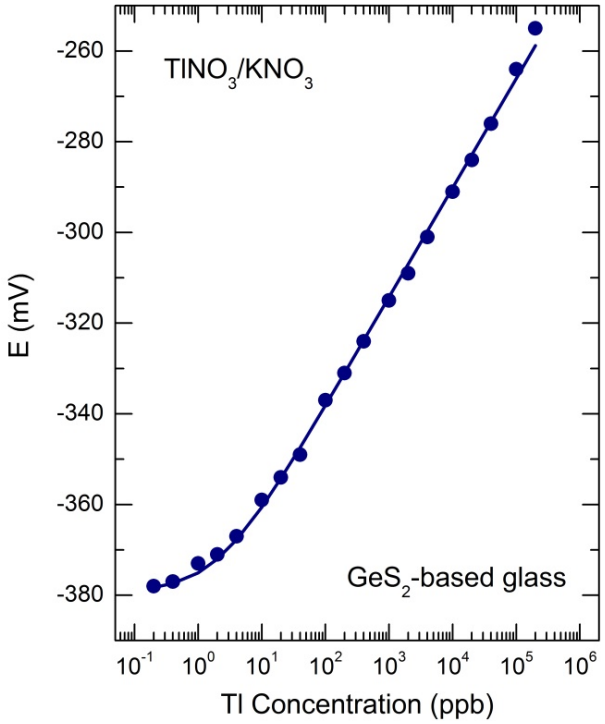


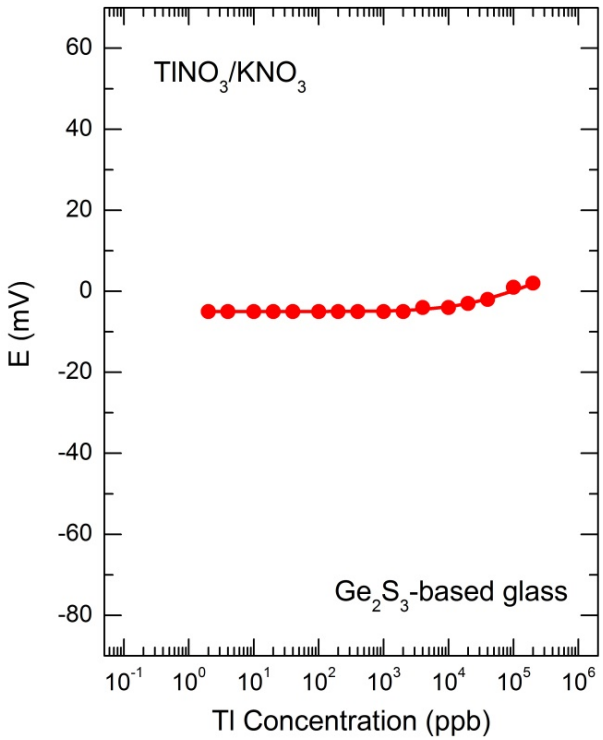




Tl^+ Ion Sensitivity of GeS_2- and Ge_2S_3-Based Glasses

Chalcogenide glasses are promising materials for heavy-metal chemical sensors



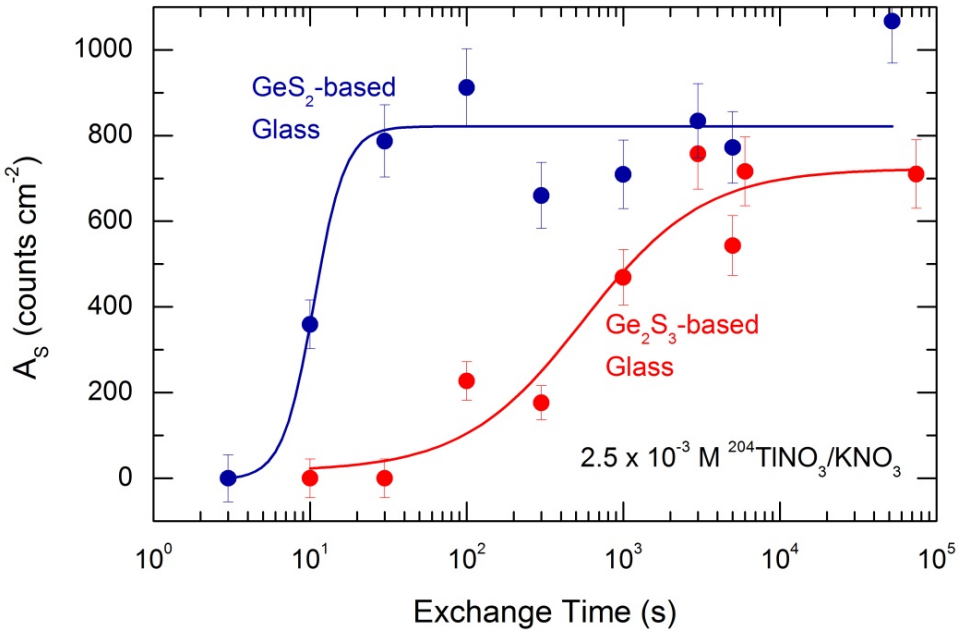


Tl^+ ion radius is 1.59 Å.
Are the cavities at the glass surface involved in the Tl^+ ion exchange ?

Tl^+ chemical sensors based on **GeS_2** glasses show excellent performance with a low detection limit of 2 ppb Tl. Chemically-similar compositions based on **Ge_2S_3** glasses exhibit eratic behaviour and poor sensitivity.

A. Paraskiva, M. Bokova, M. Milochova

^{204}Tl Ion Exchange Between Solution and GeS_2- or Ge_2S_3-Based Glasses



Fast ^{204}Tl exchange between thallium nitrate and **GeS_2** based glass correlates with remarkable sensitivity of chemical sensors and enhanced cavity volume in glassy GeS_2. Bad sensor performance of **Ge_2S_3** based glasses is associated with slow ^{204}Tl exchange and reduced volume of cavities in vitreous Ge_2S_3.

A. Paraskiva, I. Alekseev

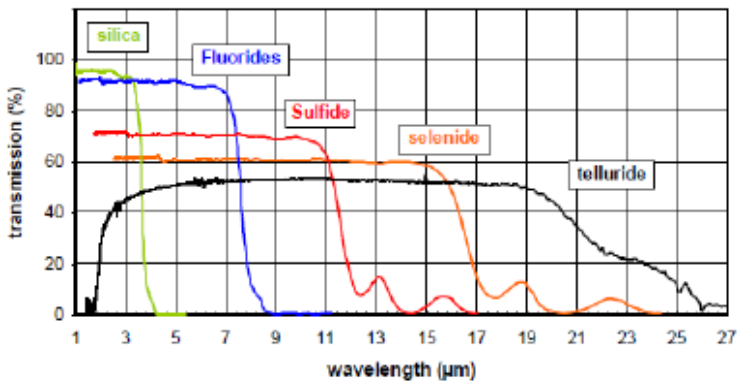
Conclusion 2

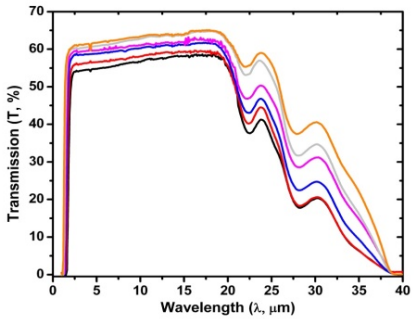
Silver tracer diffusion in insulating Ge-rich sulphide glasses and thallium ion exchange for GeS_2- and Ge_2S_3-based glasses show a good correlation with calculated volume and connectivity of cavities.

The cavity calculations could be used to re-animate the Anderson-Stuart model for ionic transport in insulating glasses.

Chemical Disorder in As_2Te_3: Bonding Preferences, Ribbon Structure or Metallisation

Telluride Glasses: Far-IR Transmittance and Phase-Change Memories



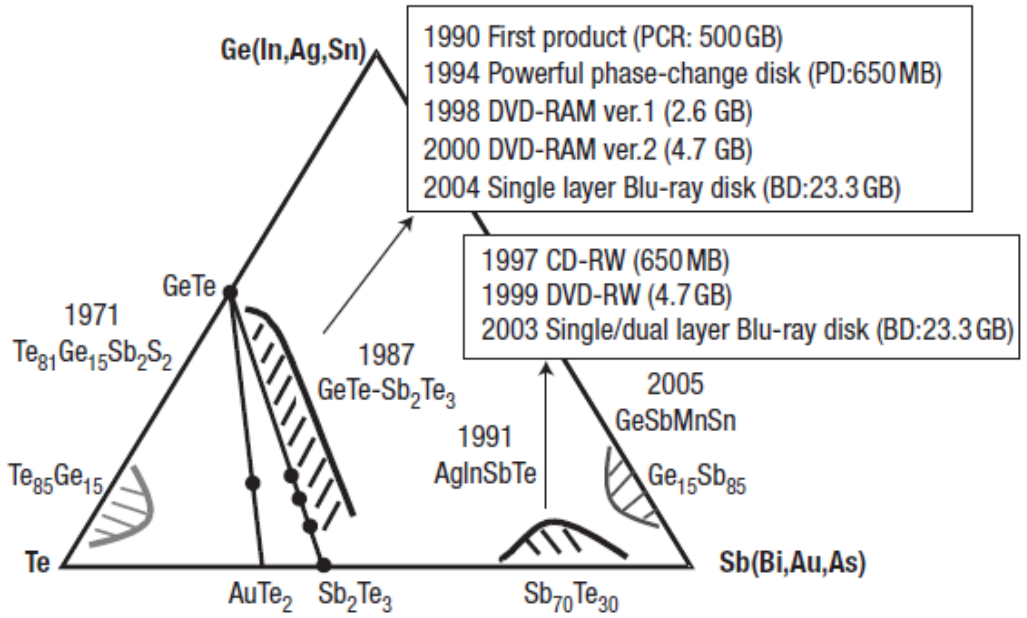


D. Le Coq et al. (2017)

Selective remote IR spectroscopy of various biotoxin and gas species

Thermal imaging

Interstellar IR detection of life signature at exoplanetary systems, etc.



M. Wuttig, N. Yamada, NMat (2009)

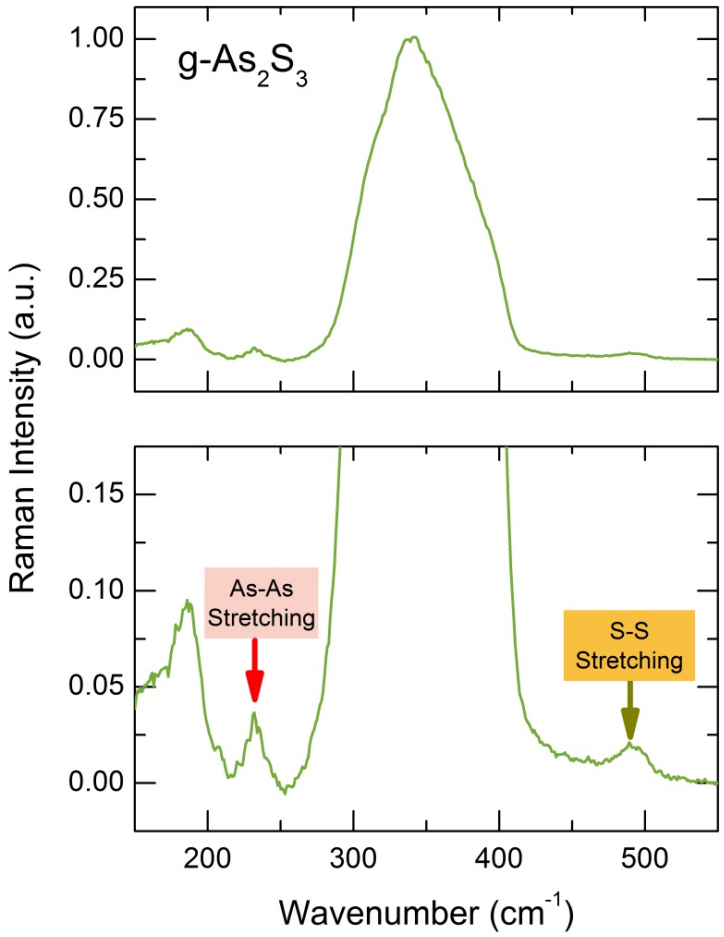
Phase-change materials for rewritable data storage

Non-volatile electronic memory

Mostly Ge-Sb-Te glasses, much less attention to As-Te, in particular, As_2Te_3

As_2Te_3 vs. As_2S_3 Glasses: Raman

g-As_2S_3



$$\frac{[As-As]}{[As-S]+[As-As]} = 0.02\text{-}0.03$$

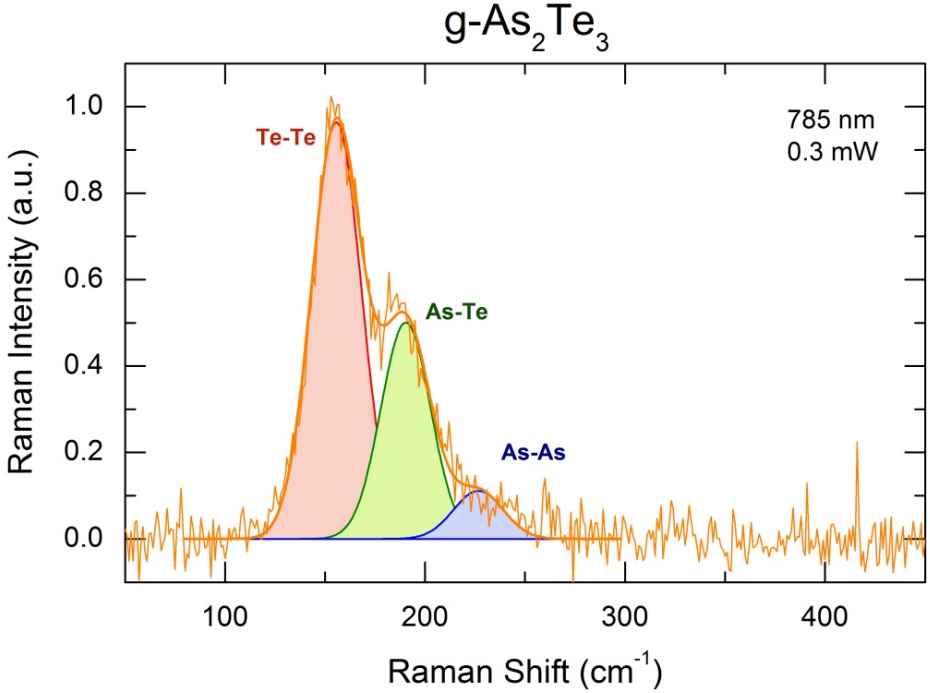
Usual degree of chemical disorder

g-As_2Te_3

A stoichiometric glass with highest chemical disorder

(1993-2017)

$$0.23 \leq \frac{[As-As]}{[As-Te]+[As-As]} \leq 0.58$$



A. Tverjanovich et al. (2012)

Possible Origin of High Chemical Disorder in As_2Te_3

(1) Similar bonding energies:

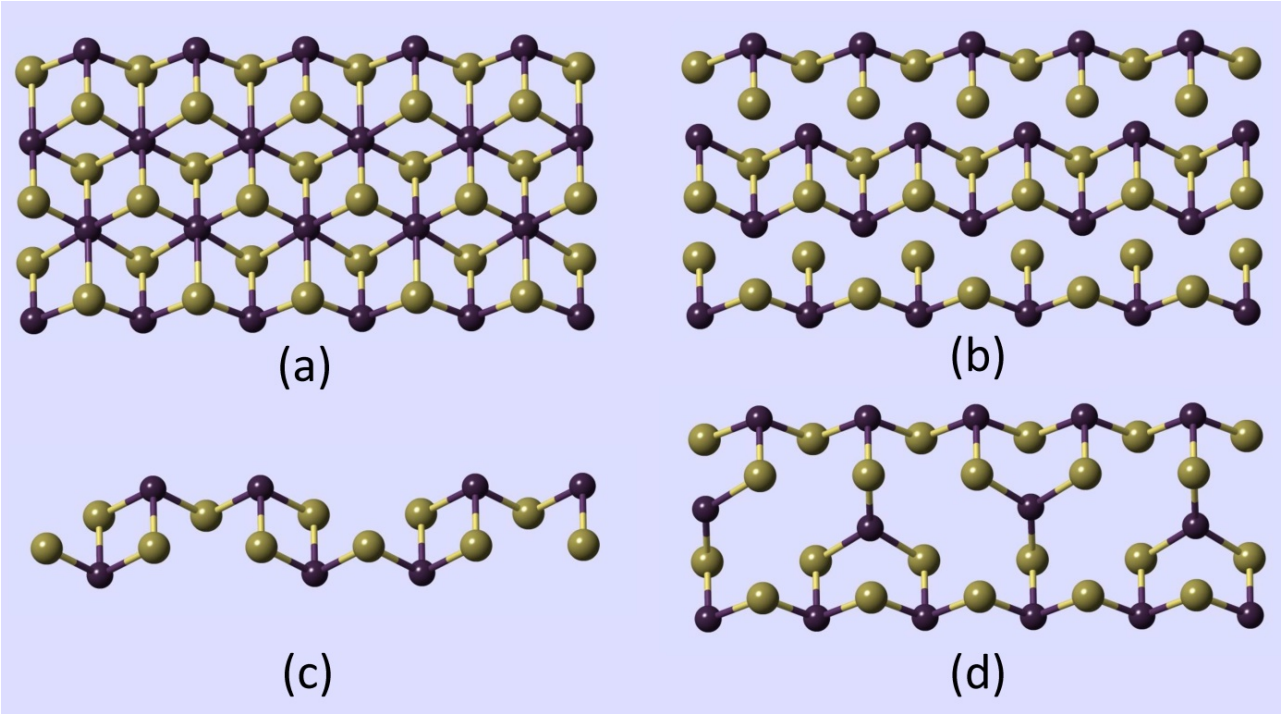
As-As	134.2 kJ/mol
As-Te	137.0 kJ/mol
Te-Te	137.9 kJ/mol

P(As-Te)/P(As-As)@500 °C ≈ 1.3 and ↘ with T ↗
P(As-S)/P(As-As)@500 °C = 10-20

(2) Specific crystal structure different from that in c-As_2S_3 or As_2Se_3

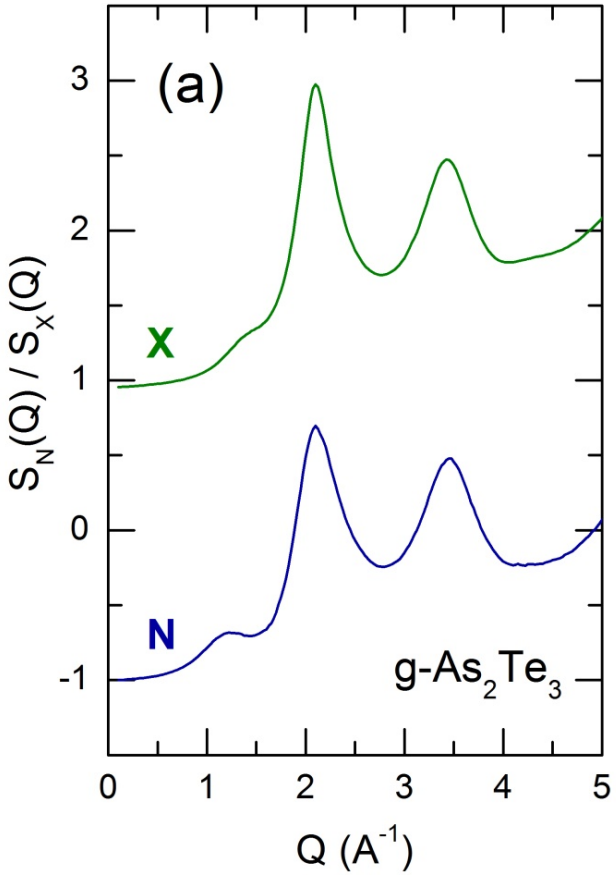
(3) Low-T metallisation in the melt
within 250 °C above T_m = 381 °C

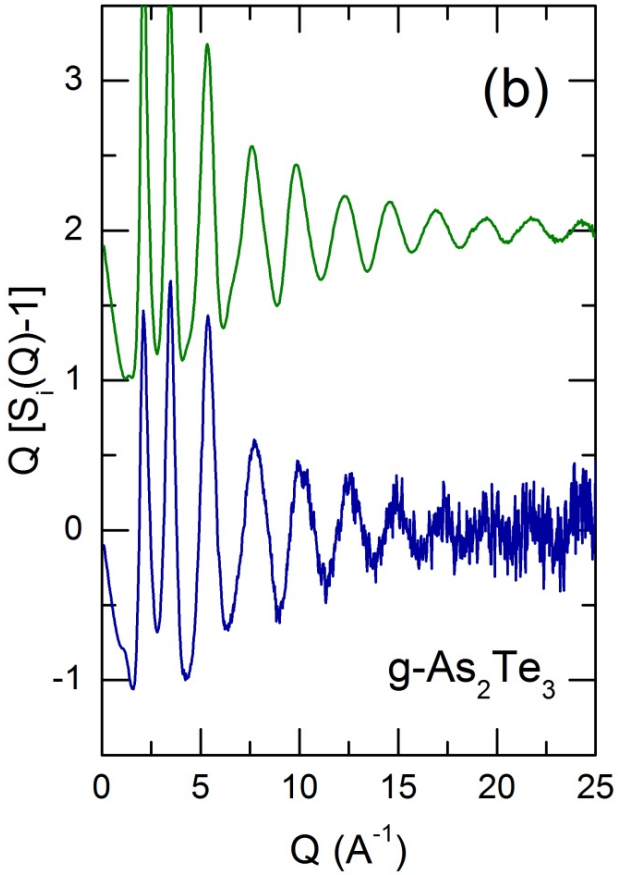
Collapse of $(As_4Te_6)_\infty$ Ribbon in the Melt: A Possible Scenario



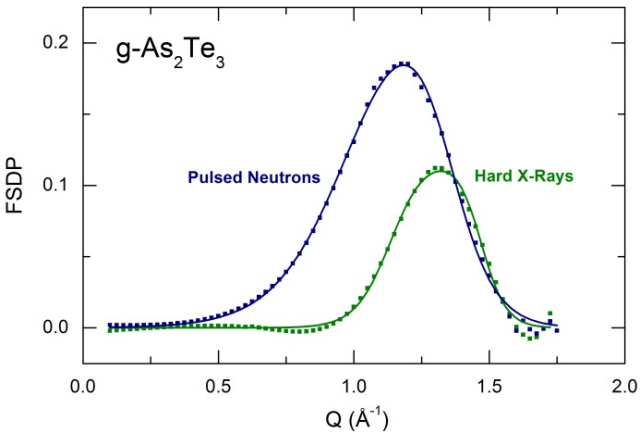
(a) Hypothetical transformation of an $(As_4Te_6)_\infty$ ribbon in crystalline α-As_2Te_3 into two chemically ordered motifs of *g*-As_2Te_3; (b) the bonding/non-bonding limit is set at 2.85Å, the central string, ES-$AsTe_{3/3}$, loses every third As atom transforming (c) into a chain consisting of $AsTe_{3/2}$ pyramids with alternate edge- and corner-sharing, (d) the two lateral chains with remaining As species are forming a new As-Te ribbon consisting of As_3Te_3 and As_6Te_6 rings.

Looking for Chemically Ordered Motifs in g-As_2Te_3

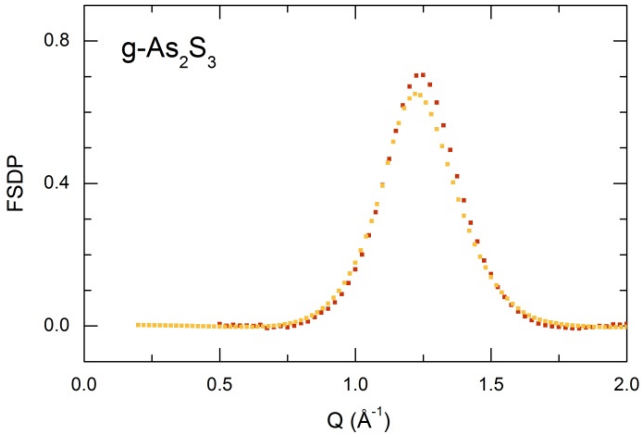




g-As_2Te_3

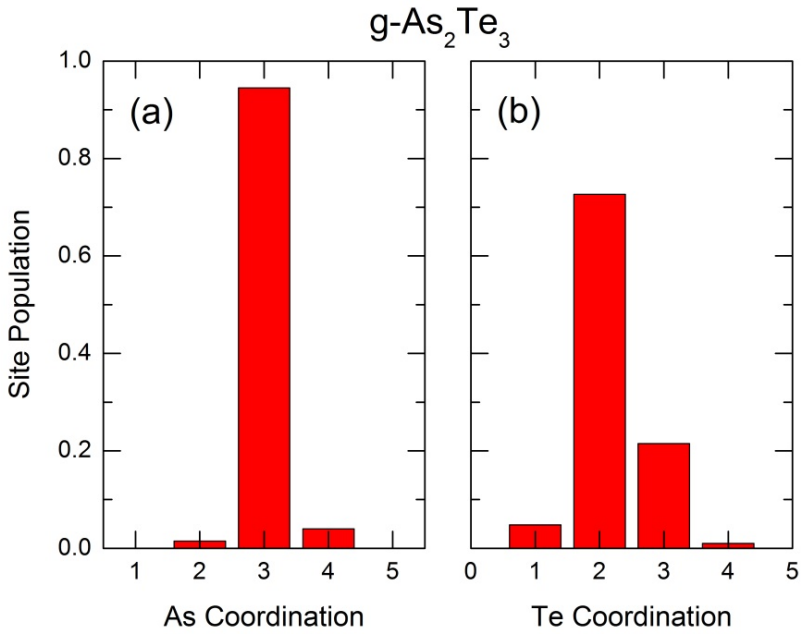


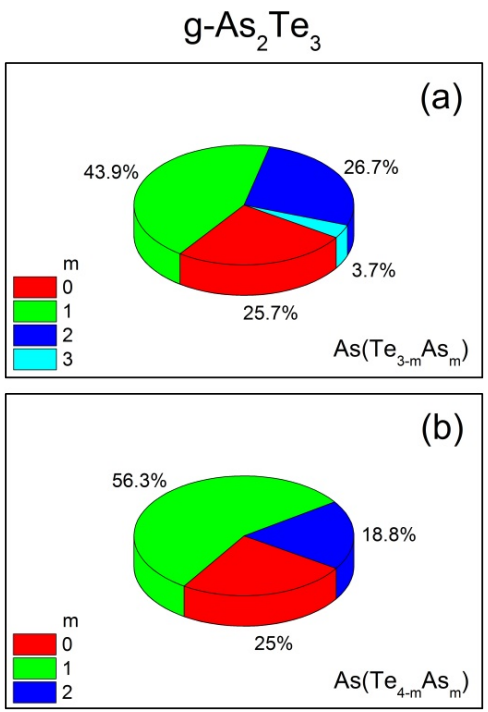
g-As_2S_3

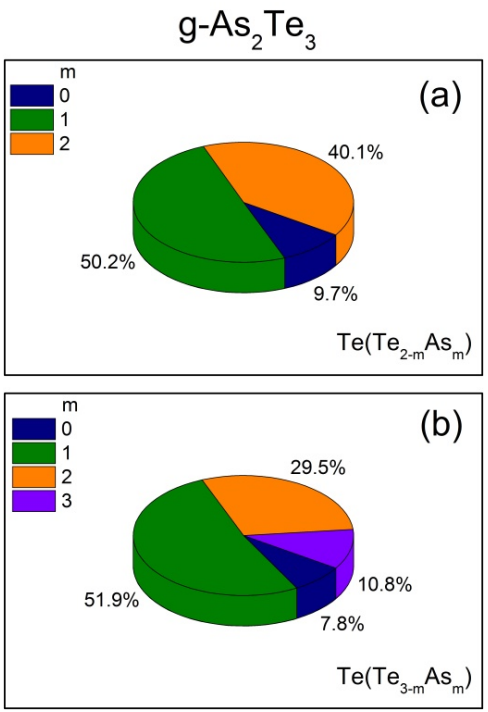


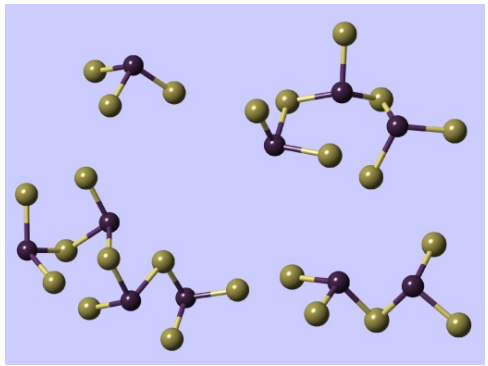
RMC/DFT Modelling of g-As_2Te_3

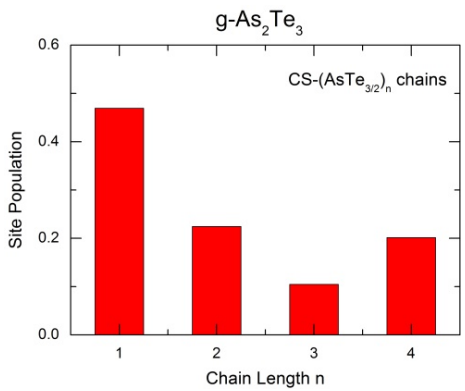
N_{As-X} = 3.025; N_{Te-X} = 2.19

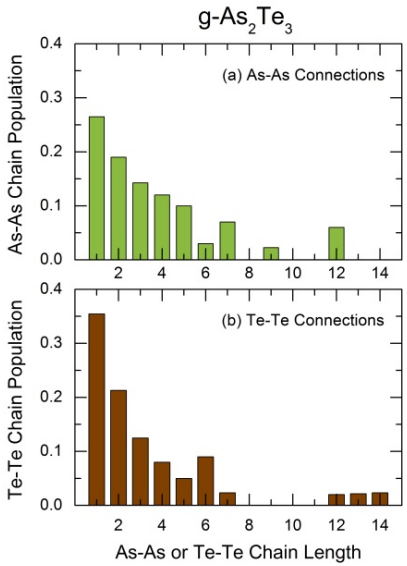


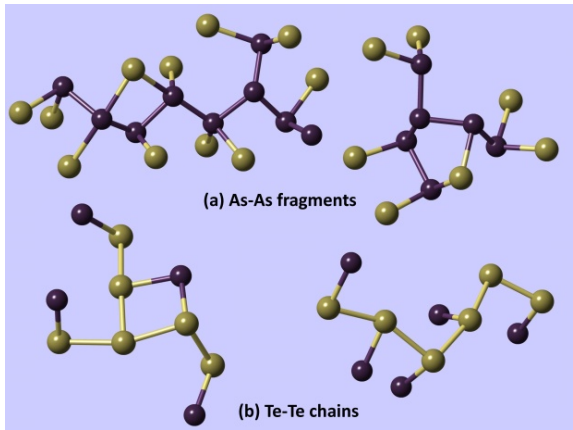












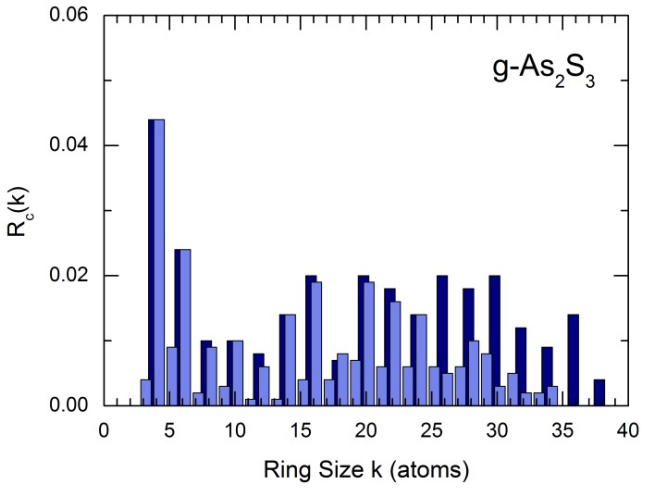
Chemically-ordered fragments exist only as CS oligomeric chains

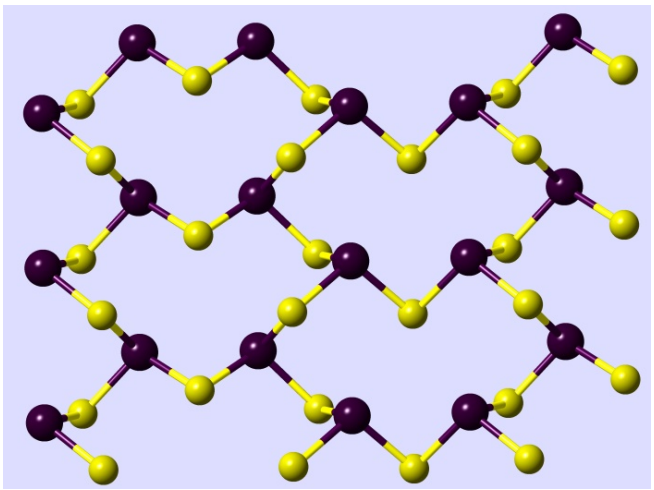
S. Kohara, Y. Onodera (2017)

Glassy As_2Te_3 vs. As_2S_3: Rings

S. Kohara, A. Sokolov

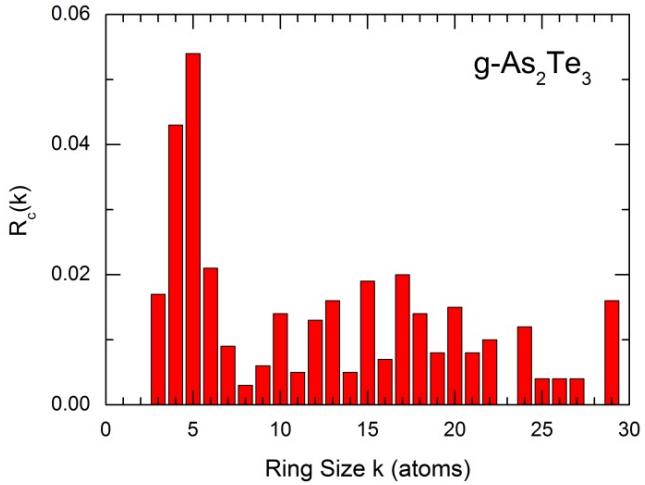
g-As_2S_3

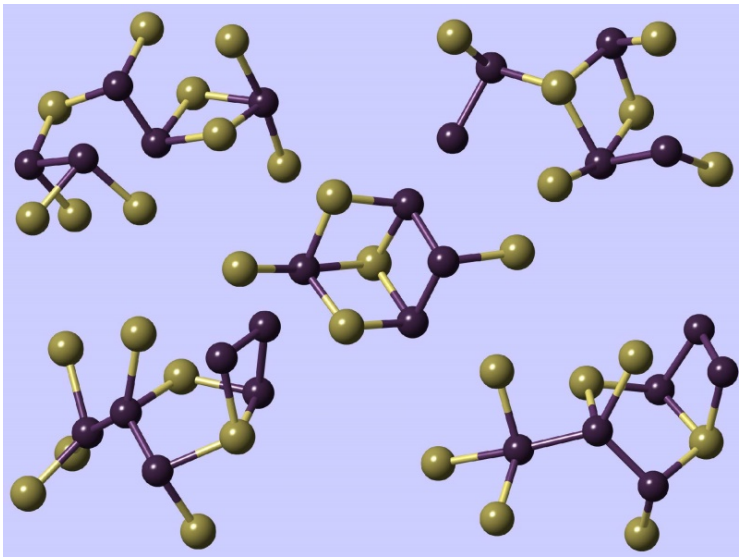




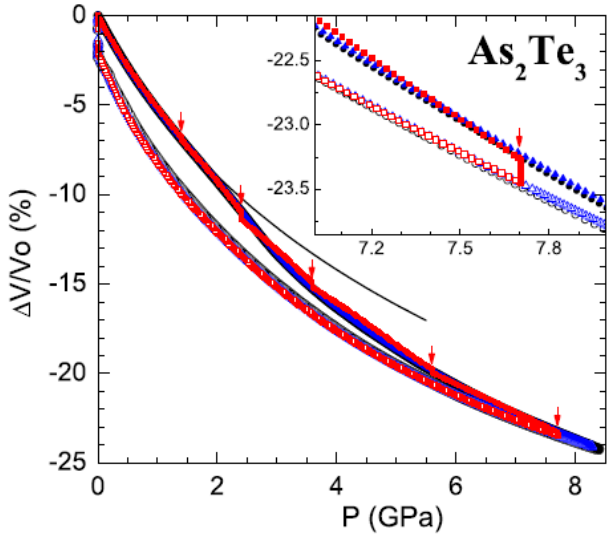
c-As_2S_3

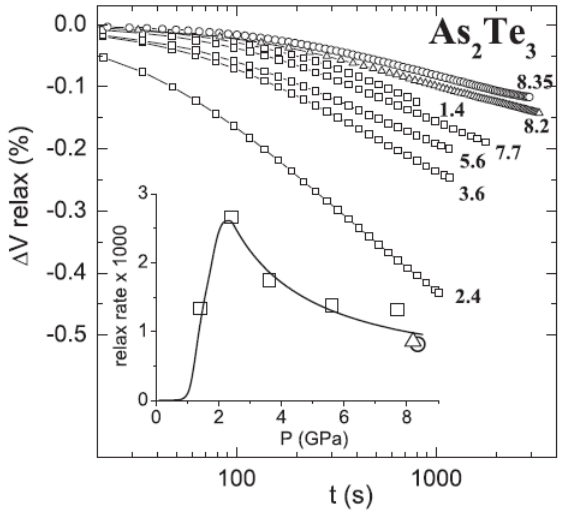
g-As_2Te_3

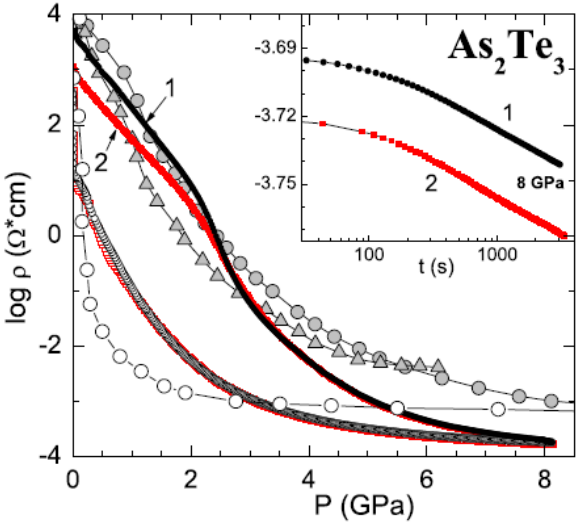




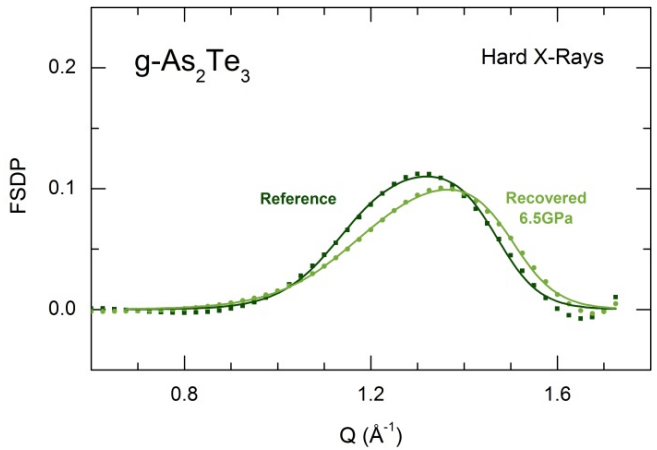
Glassy As_2Te_3 under High Pressure

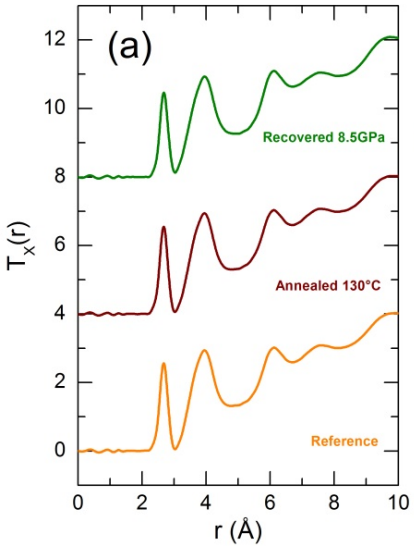


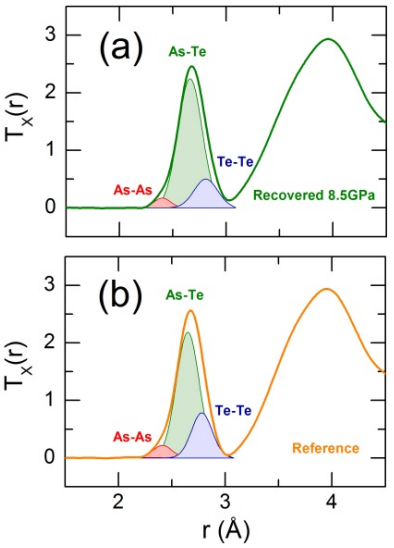


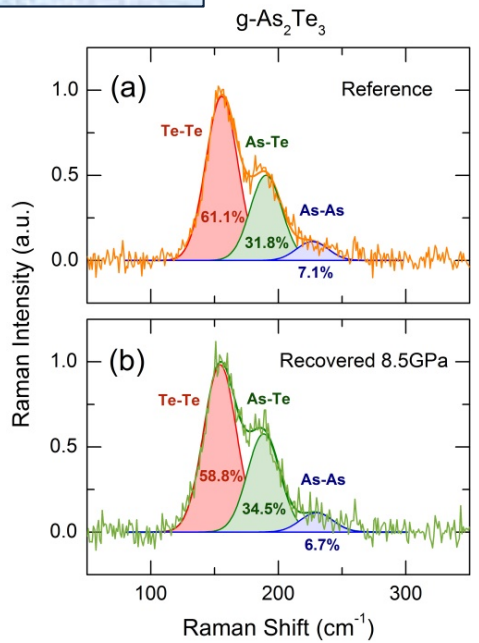


Ex-situ HE-XRD and Raman measurements (4 months after HP)









V. Brazhkin et al. PRB (2017)

Conclusion 3

Glassy As_2Te_3 exhibits a significant chemical disorder (up to 30-35 %) related to either very similar As-As, As-Te and Te-Te bond energies, or to a low-T metallisation in the glass-forming melt. The local and intermediate-range ordering of g-As_2Te_3 is reminiscent of both the collapse of $(As_4Te_6)_\infty$ ribbons and to, a less extent, the local coordination increase in the metallic melt.

High-pressure measurements of g-As2Te3 show several interesting phenomena under high pressure up to 8.5 GPa: (i) a remarkable softening of the bulk modulus and a sharp maximum of the relaxation rate at 2.5 GPa indicative of polyamorphism; (ii) smooth metallization at a pressure of 5 GPa with a resistivity decrease of 8 orders of magnitude, and (iii) some unexpected chemical ordering after the high-pressure treatment.

Thanks