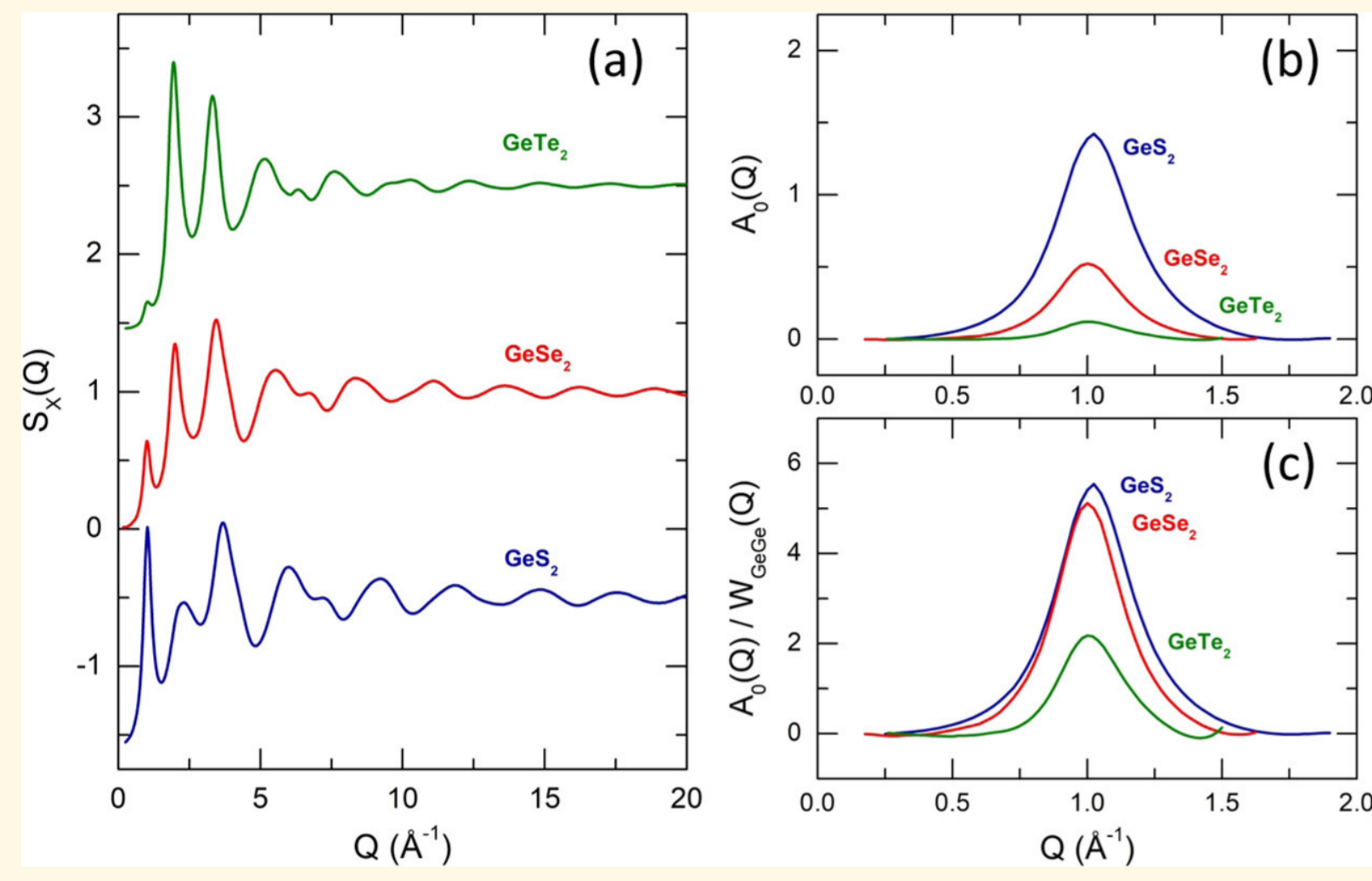


Bulk Glassy GeTe₂ compared to GeS₂ and GeSe₂

High-Energy X-ray Diffraction (HE-XRD)



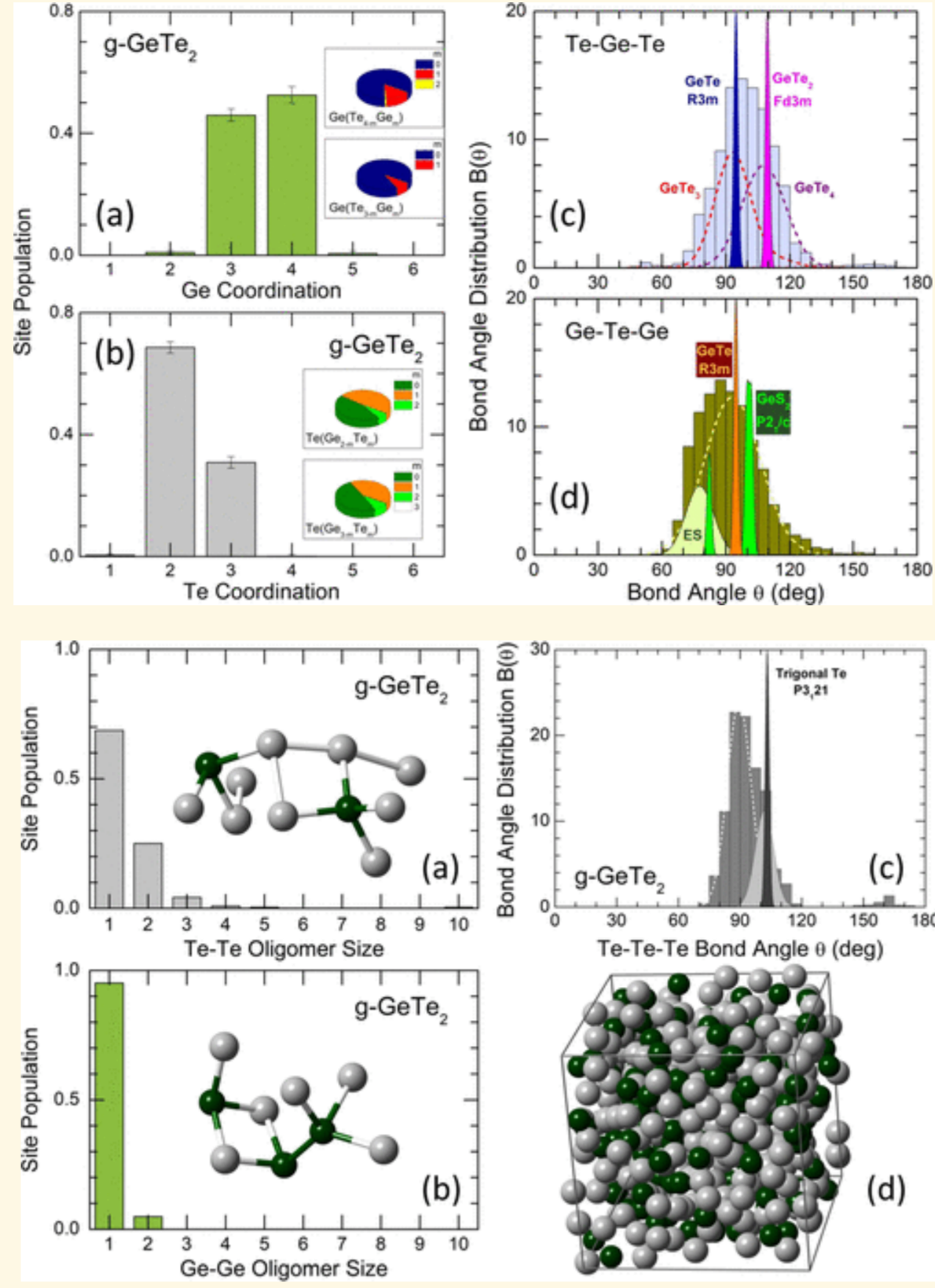
Bulk glassy GeTe₂ differs from the lighter GeX₂ members:

- 46% of trigonal germanium,
- 31% of three-fold coordinated tellurium,
- only 20% of edge-sharing tetrahedra or pyramids,
- significant population of dominant Te-Te dimers and Te_n oligomers, n ≤ 10.

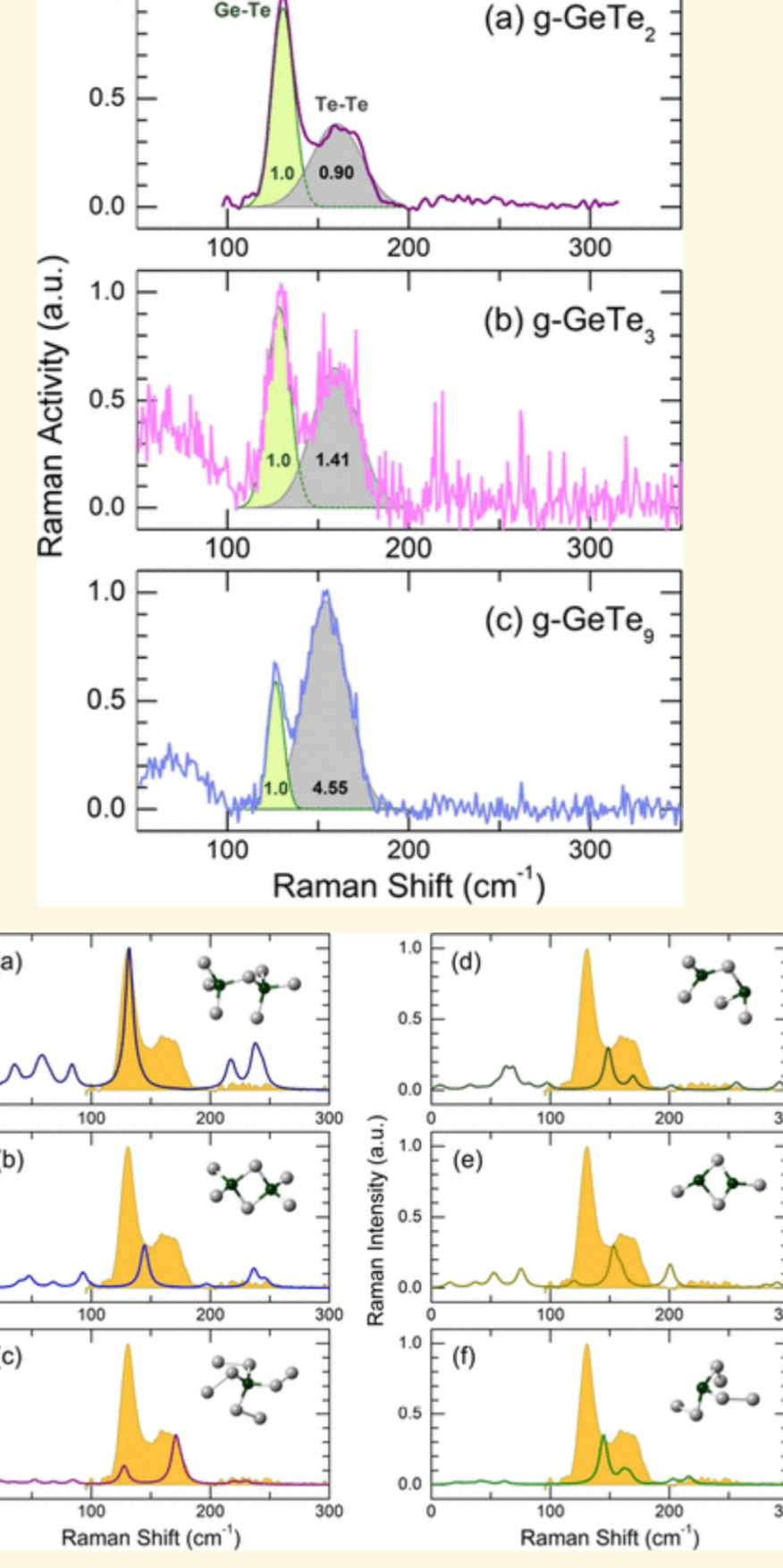
Thermodynamic metastability of germanium ditelluride:
GeTe₂ ⇌ GeTe + Te.

References: [1] A. Tverjanovich, et al., Bulk Glassy GeTe₂: A Missing Member of the Tetrahedral GeX₂ Family and a Precursor for the Next Generation of Phase-Change Materials, Chem. Mater. 33, 1031–1045 (2021); [2] M. R. Konnikova, et al., GeTe₂ Phase Change Material for Terahertz Devices with Reconfigurable Functionalities Using Optical Activation, ACS Appl. Mater. Interfaces 15, 9638–9648 (2023)

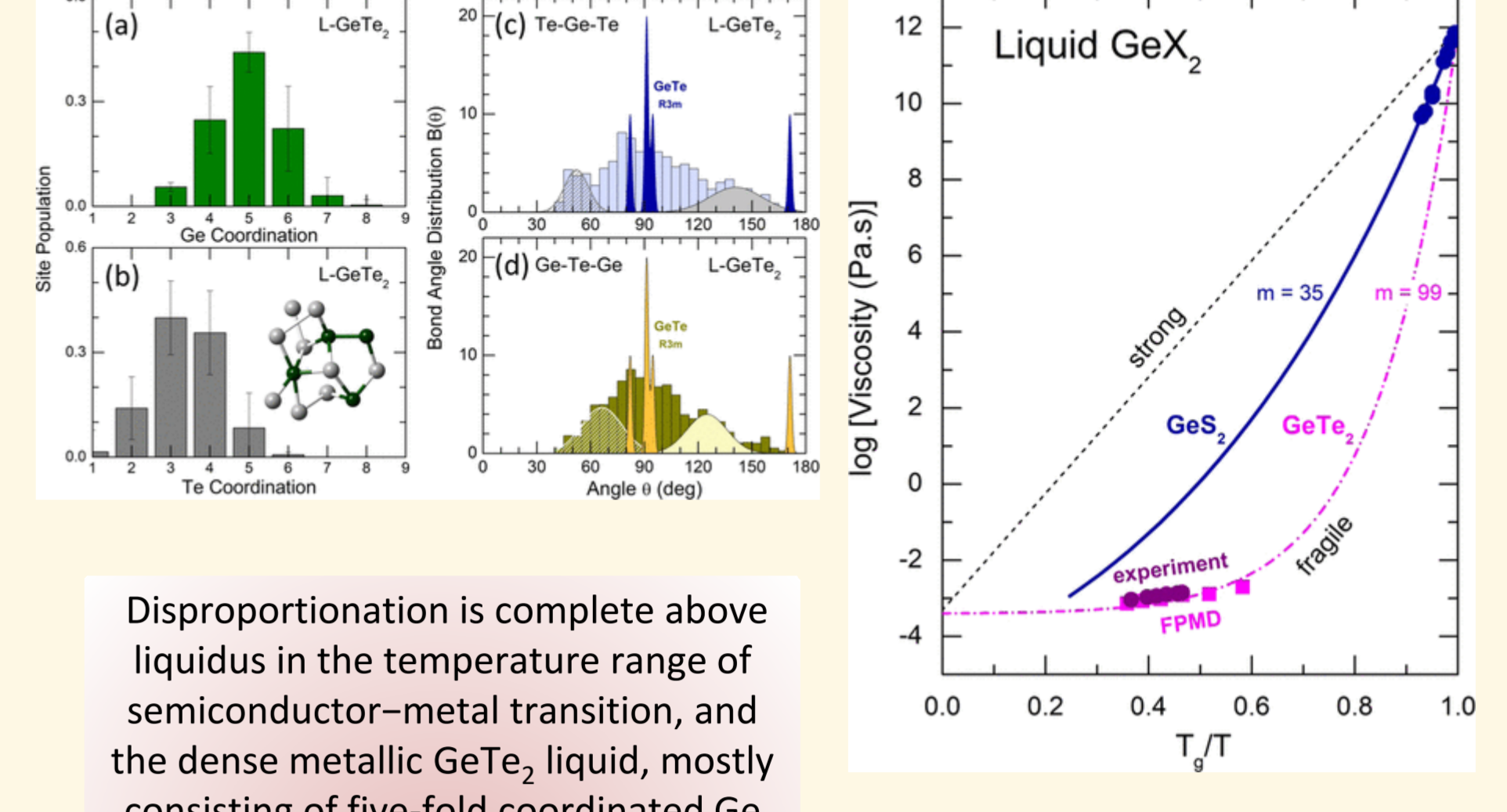
First-Principles Molecular Dynamics (FPMD)



Raman & DFT



Liquid GeTe₂ and a Semiconductor-Metal Transition

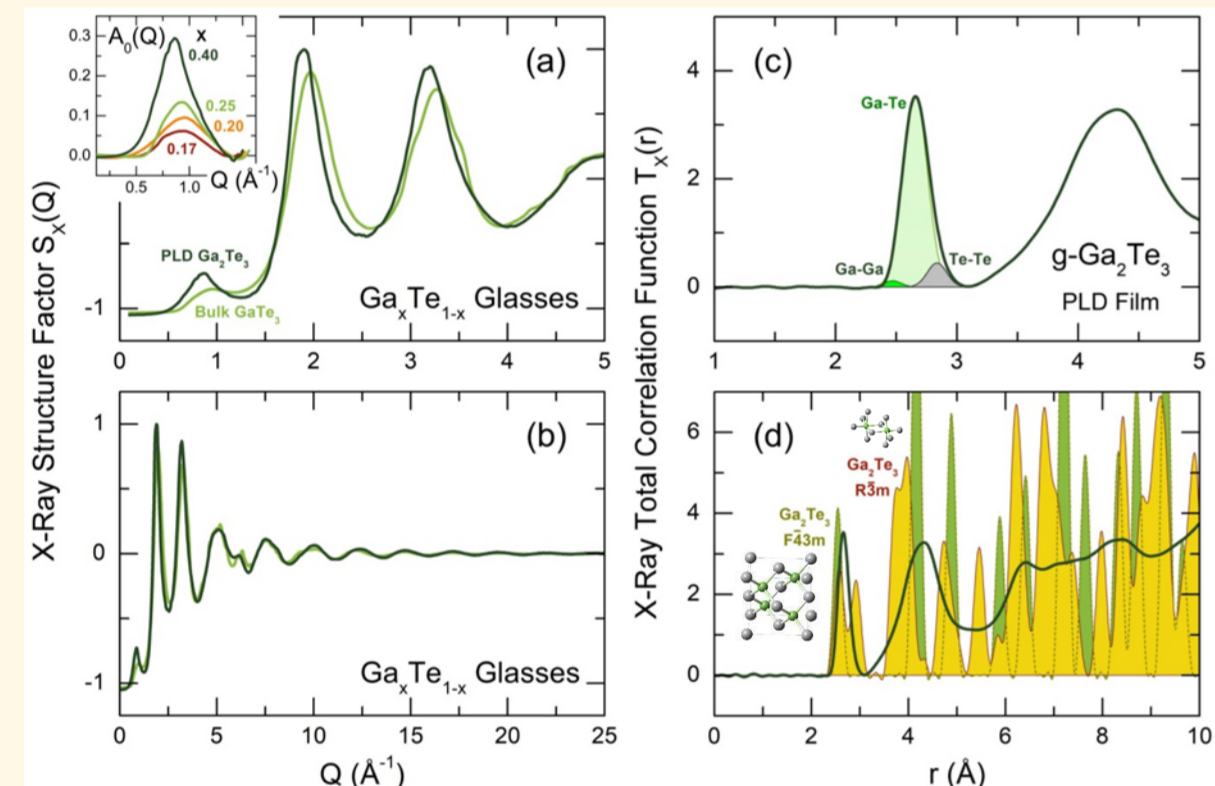


Disproportionation is complete above liquidus in the temperature range of semiconductor-metal transition, and the dense metallic GeTe₂ liquid, mostly consisting of five-fold coordinated Ge species, exhibits high fluidity, strong fragility (m = 99 ± 5), and presumably a fast structural transformation rate combined with low atomic mobility in the vicinity of the glass transition temperature, favorable for reliable long-term data retention in nonvolatile memories.

GeTe₂ is a promising precursor for the next generation of phase-change materials, especially coupled with additional metal doping, depolymerizing the tetrahedral interconnected glass network and accelerating (sub)nanosecond crystallization.

Ga-Te liquids, glasses and PLD films

Ga₂Te₃: specific SET crystal structure



Basically, g-Ga₂Te₃ is similar to cubic Ga₂Te₃
BUT

- chemical disorder,
- 42% ES-Ga₄,
- IRO: a disordered version of F43m & R3m

Expected small electric and optical contrast !?

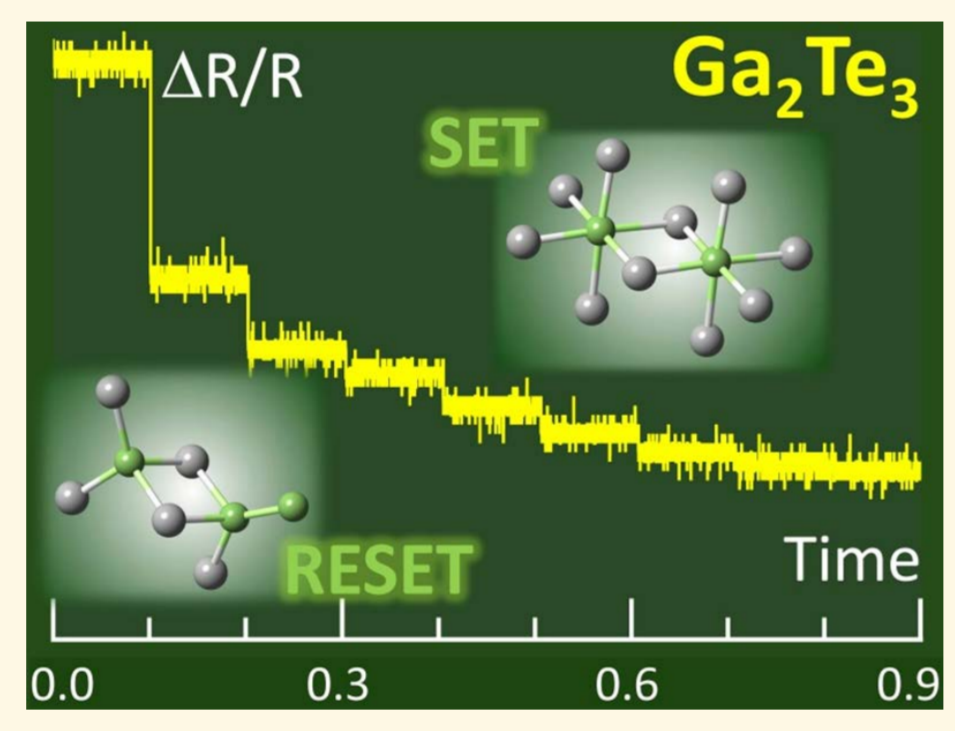
Hypothesis
Specific SET crystal structure is not necessarily a stable fcc Ga₂Te₃ phase

Remnants of high-pressure motifs are detected in amorphous phase

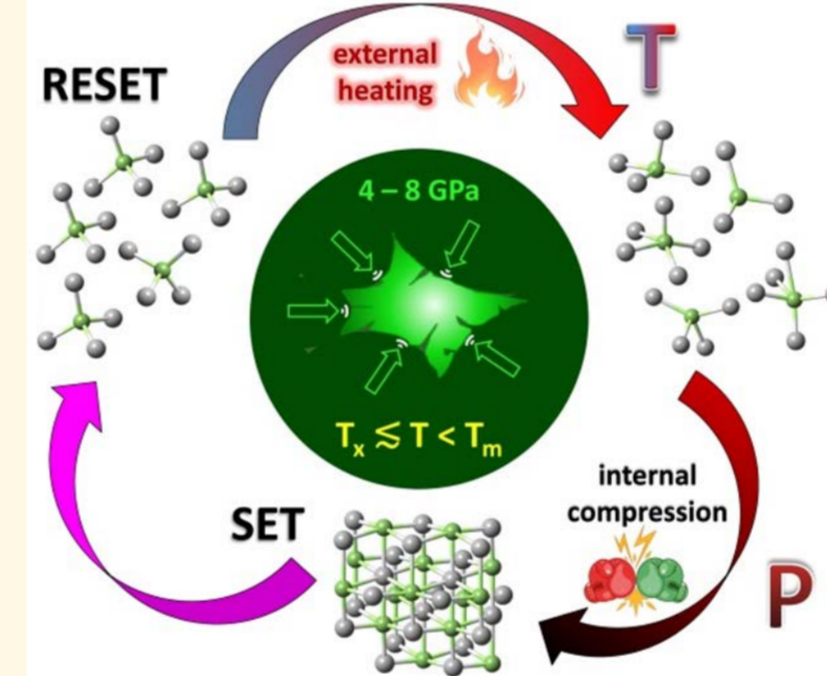
References: [1] M. Bokova, et al., Unraveling the atomic structure of bulk binary Ga-Te glasses with surprising nanotectonic features for phase-change memory applications, ACS Appl. Mater. Interfaces 13, 37363–37379 (2021). [2] A. Tverjanovich, M. Khomenko, C. J. Benmore, S. Berznev, A. Sokolov, D. Fontanari, A. Kiselev, A. Lotin, E. Bychkov, Atypical phase-change alloy Ga₂Te₃: atomic structure, incipient nanotectonic nuclei, and multilevel writing, J. Mater. Chem. C 9, 17019–17032 (2021). [3] M. Kassem, C. J. Benmore, T. Usuki, K. Ohara, A. Tverjanovich, M. Bokova, V. V. Brazhkin, E. Bychkov, Transient Mesoscopic Immiscibility, Viscosity Anomaly, and High Internal Pressure at the Semiconductor-Metal Transition in Liquid Ga₂Te₃, J. Phys. Chem. Lett. 13, 10843–10850 (2022). [4] A. Tverjanovich, C. J. Benmore, M. Khomenko, A. Sokolov, D. Fontanari, S. Berznev, M. Bokova, M. Kassem, E. Bychkov, Decoding the Atomic Structure of Ga₂Te₃ Pulsed Laser Deposition Films for Memory Applications Using Diffraction and First-Principles Simulations, Nanomaterials 13, 2137 (2023).

Ga-Te: Nanotectonics

A very unusual phenomenon
nanotectonic compression
simultaneous co-crystallization of ambient and high-pressure polymorphs (usually stable at 4–8 GPa) on heating!

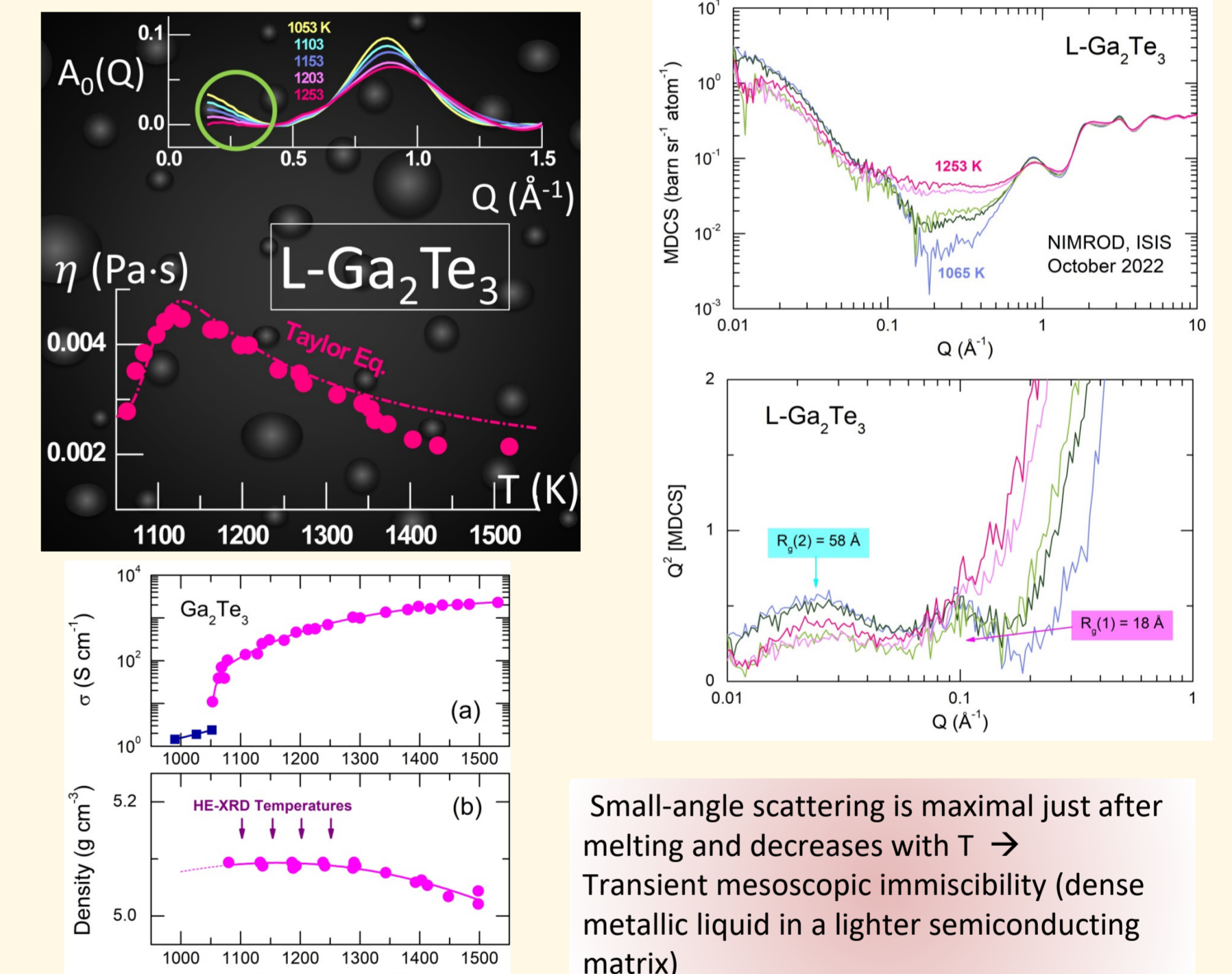


The metallic high-pressure forms are beneficial for PCM performance and energy consumption ensuring higher electrical and optical contrast



Beneficial for PCM applications increasing optical and electrical contrast between the SET and RESET states and decreasing power consumption

Liquid Ga₂Te₃: Viscosity Anomaly and Semiconductor – Metal Transition



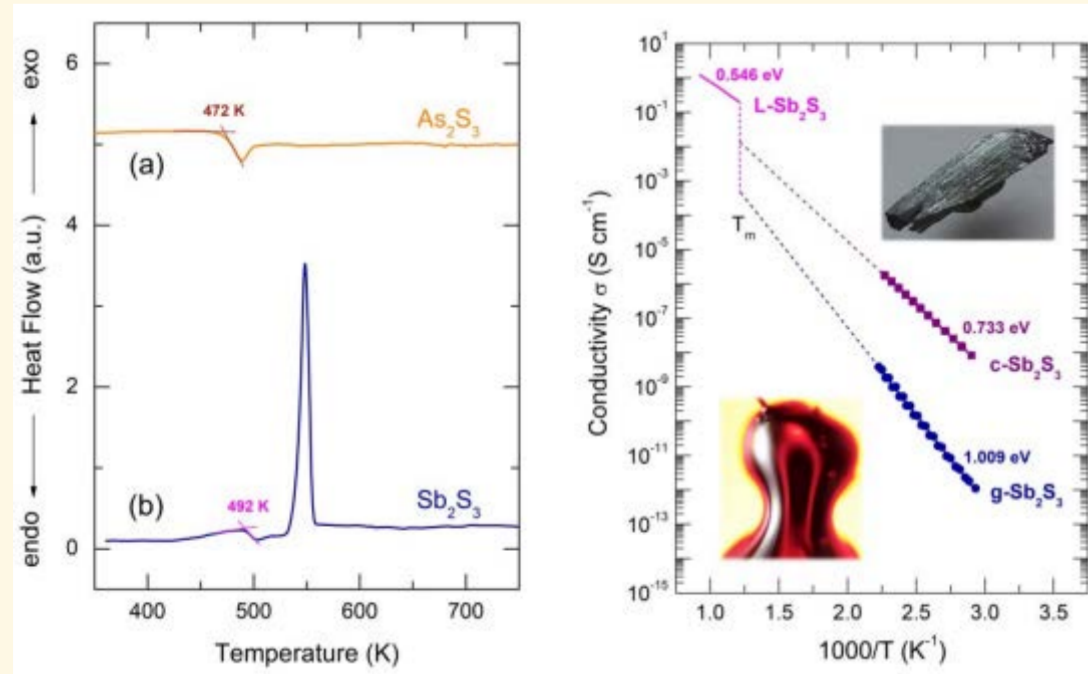
Liquid Ga₂Te₃ shows a viscosity η(T) anomaly just above melting when η(T) first increases and only then starts decreasing.

Small-angle scattering is maximal just after melting and decreases with T → Transient mesoscopic immiscibility (dense metallic liquid in a lighter semiconducting matrix)

Transient mesoscopic immiscibility is an additional mechanism to the fragile-strong transition in PCM

Glassy and liquid Sb₂S₃

Thermal & electric properties

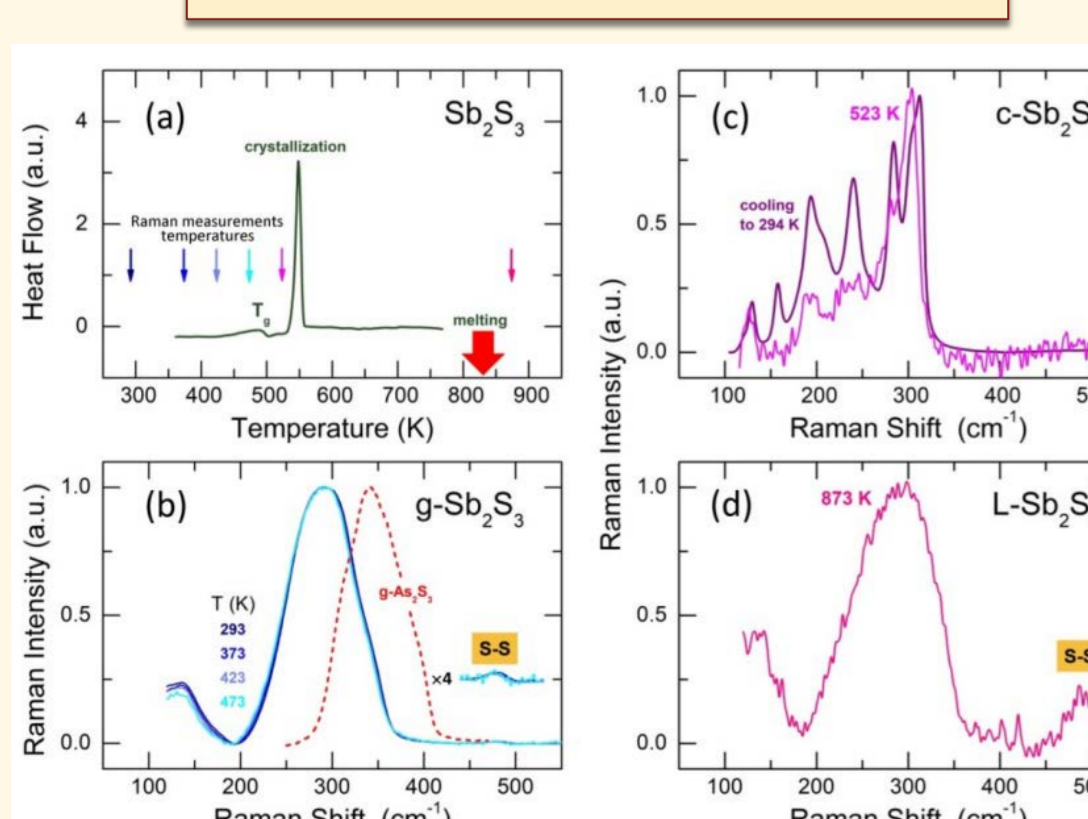


- 4.5 orders of magnitude difference in σ₂₉₈ between g-Sb₂S₃ and c-Sb₂S₃.
- Conductivity increases on melting by 3 orders of magnitude

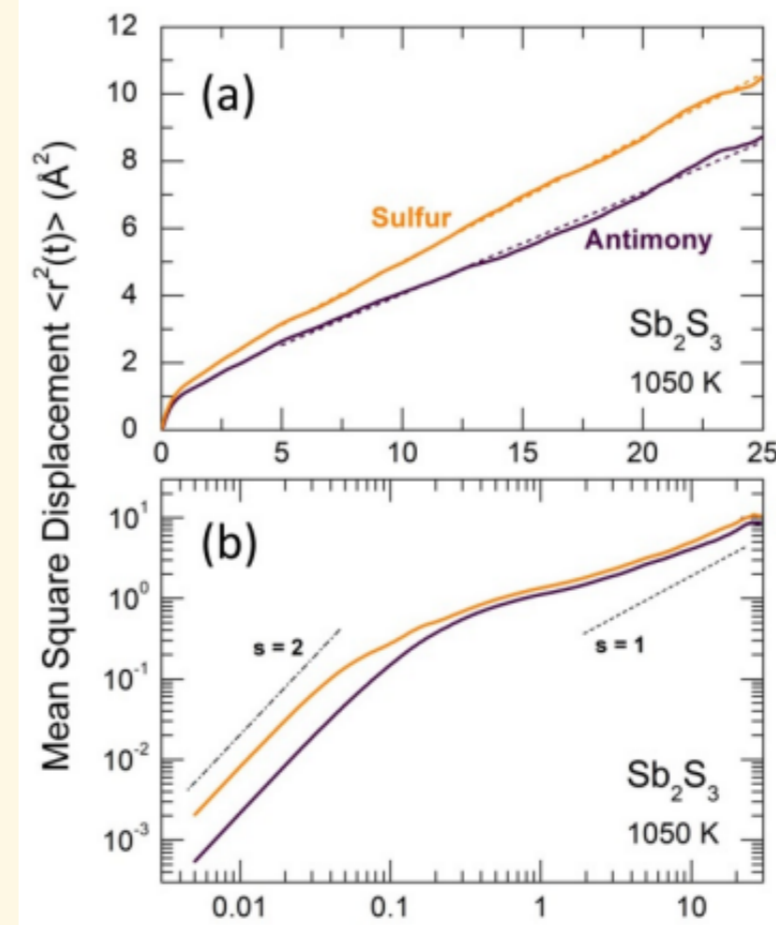
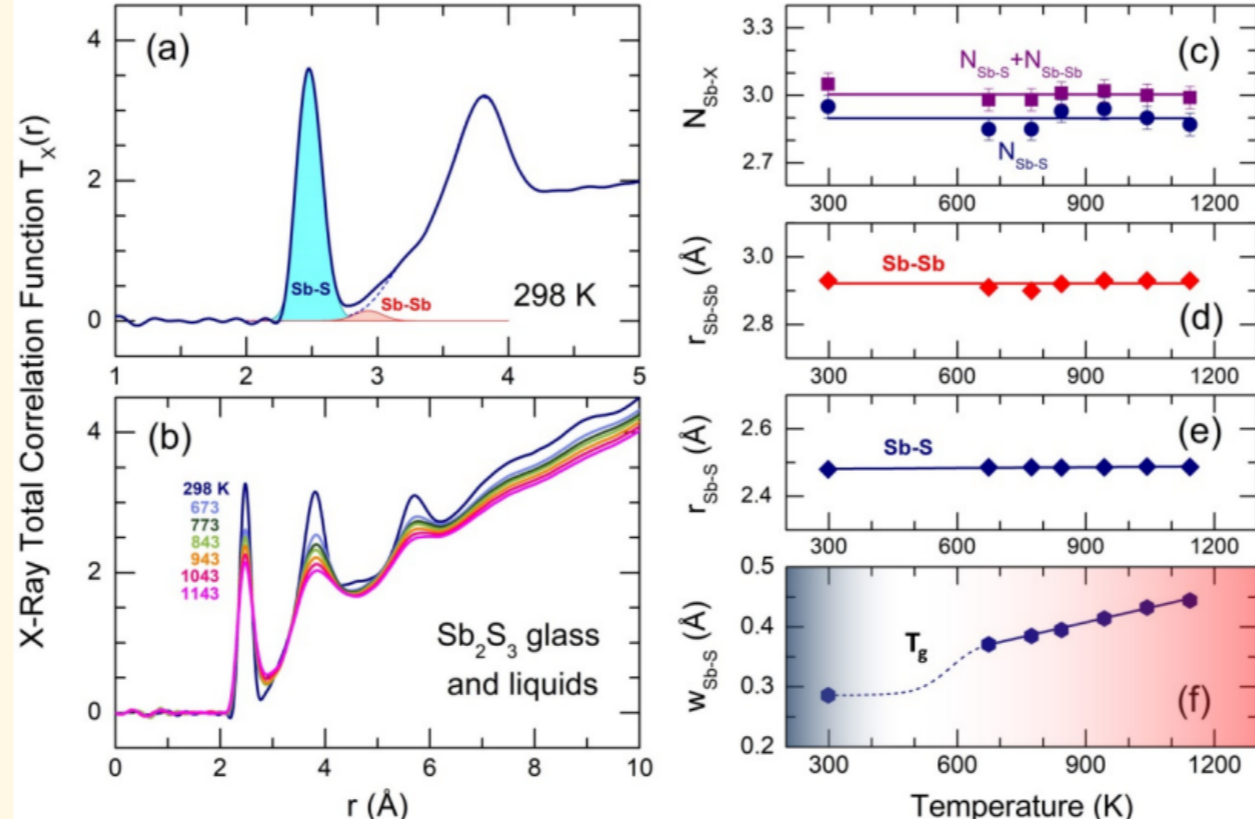
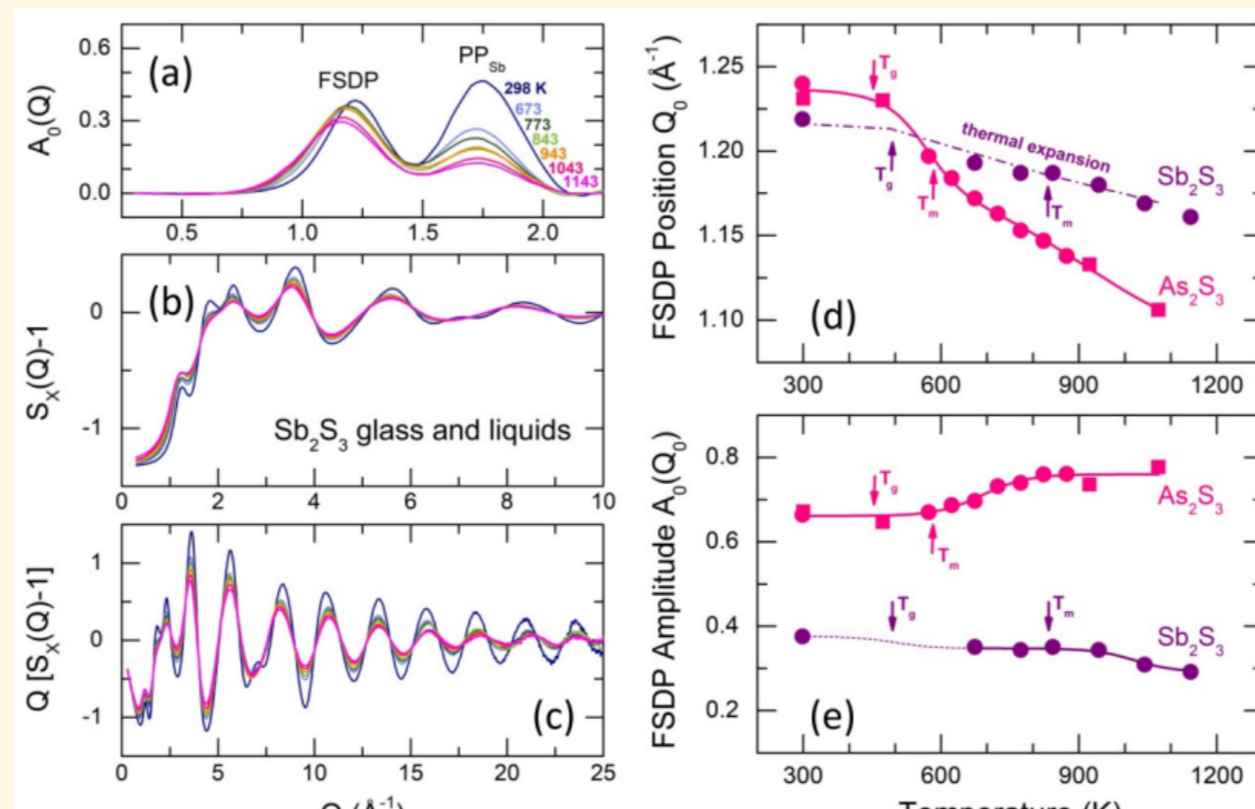
- Asymmetric feature centred at 292 cm⁻¹ (similar to g-As₂S₃)
- DFT simulations of Sb₁₂S₁₈ & Sb₁₂S₁₆ clusters reproduce well the experimental data
- Rapid crystallisation at 523 K ; Cooling down to room-temperature leads to typical orthorhombic c-Sb₂S₃ spectrum

- Glass structure hardly evolves at T ≤ Tg
- L-Sb₂S₃ (873 K) reminiscent of g-Sb₂S₃ except for intense S-S stretching

Raman & DFT



HE-XRD : Q-space and r-space



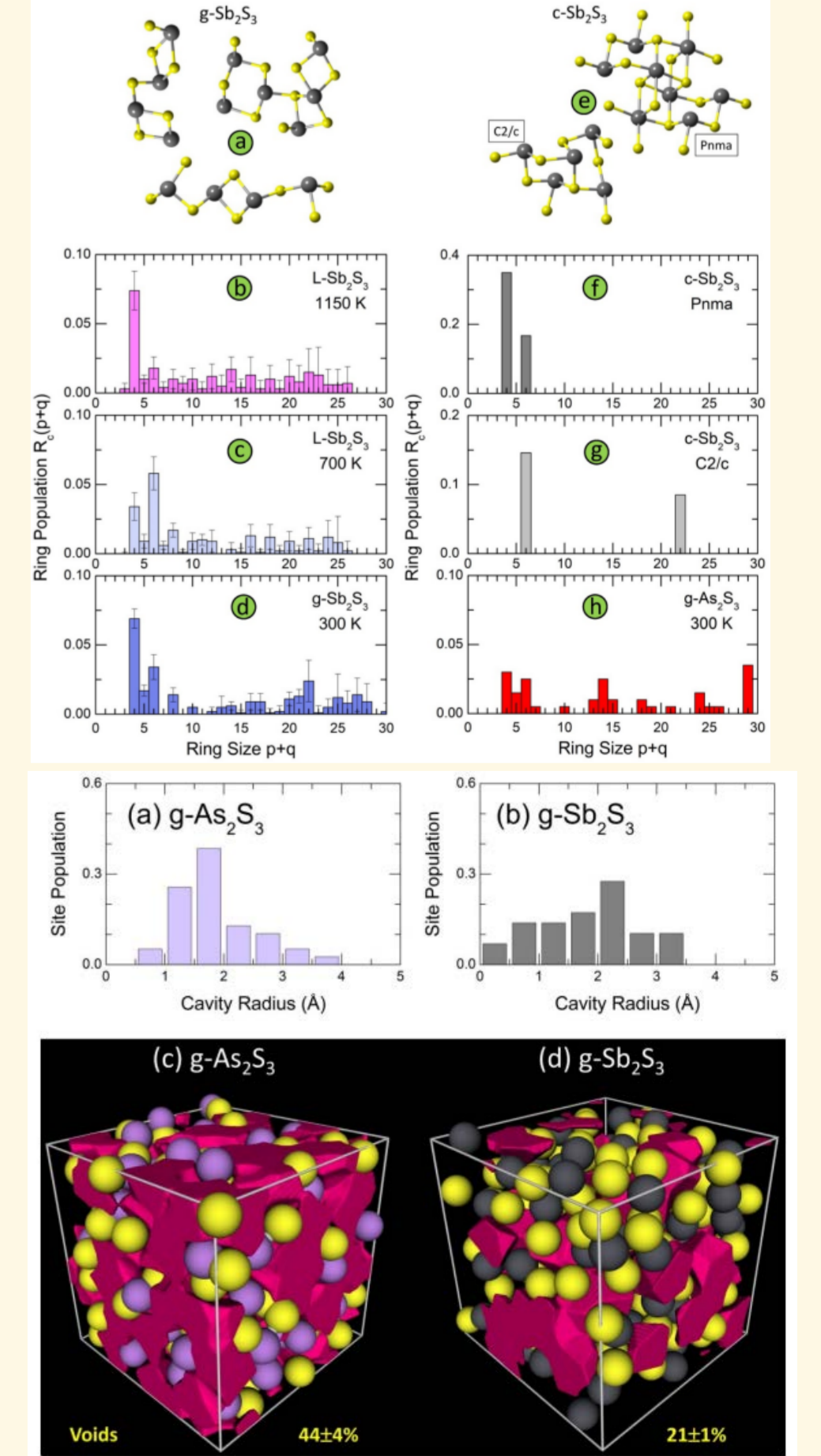
Sb₂S₃ vs. As₂S₃:

- More densified network in vitreous sulphides with increasing atomic number
- comparable glass transition temperatures, similar shape of the Raman spectra, identical picnide and sulfur local coordination and resembling ring statistics
- 2D layered structure build from defect octahedral SbS₃ entities in g-Sb₂S₃ vs 1D structure composed of infinite (Sb₂S₃)_n ribbons in c-Sb₂S₃

PCM :

- enhanced fragility of liquid Sb₂S₃ favorable for the rapid SET-RESET transition; fragility index m = 59 is approaching those of the benchmark telluride PCMs
- good retention of amorphous phase in the vicinity of Tg and at lower T
- anionic (Se) and/or cationic (Bi) substitution maybe used to decrease the temperature of a SC-M transition, thus improving the dynamics of the SET-RESET change

FPMD



References: M. Kassem, C. J. Benmore, A. Tverjanovich, T. Usuki, M. Khomenko, D. Fontanari, A. Sokolov, K. Ohara, M. Bokova, S. Kohara, E. Bychkov, Glassy and liquid Sb₂S₃: insight into the structure and dynamics of a promising functional material, J. Mater. Chem. C 11, 4654–4673 (2023).