Microstructural Kinetics Group

UNIVERSITY OF CAMBRIDGE
Department of Materials Science and Metallurgy

Fragility of Glass-Forming Liquids

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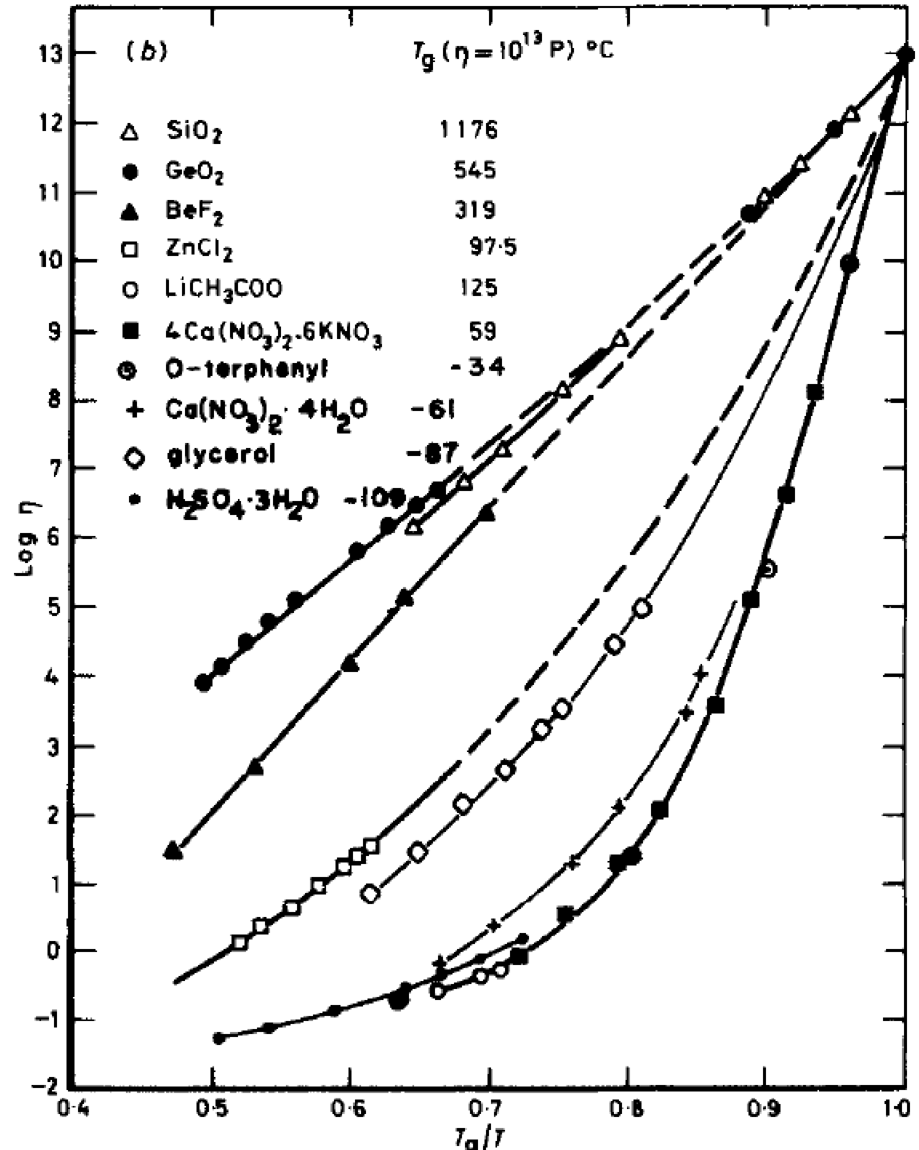
Symposium on Fragility
JNCASR, Bengaluru, India
5–8 January 2014

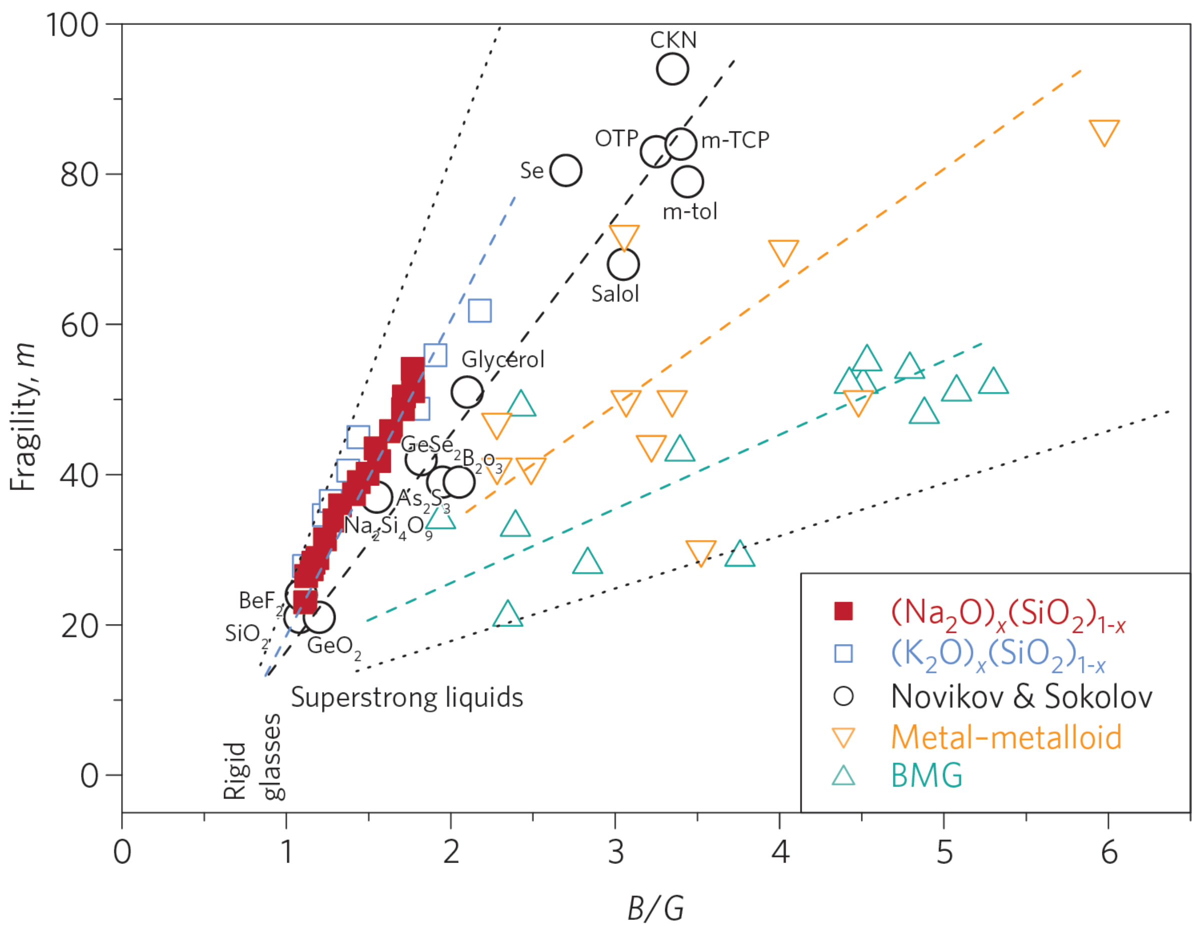
CA Angell, W Sichina

Thermodynamics of the glass transition: empirical aspects

Ann. NY Acad. Sci.
279 (1976) 53.

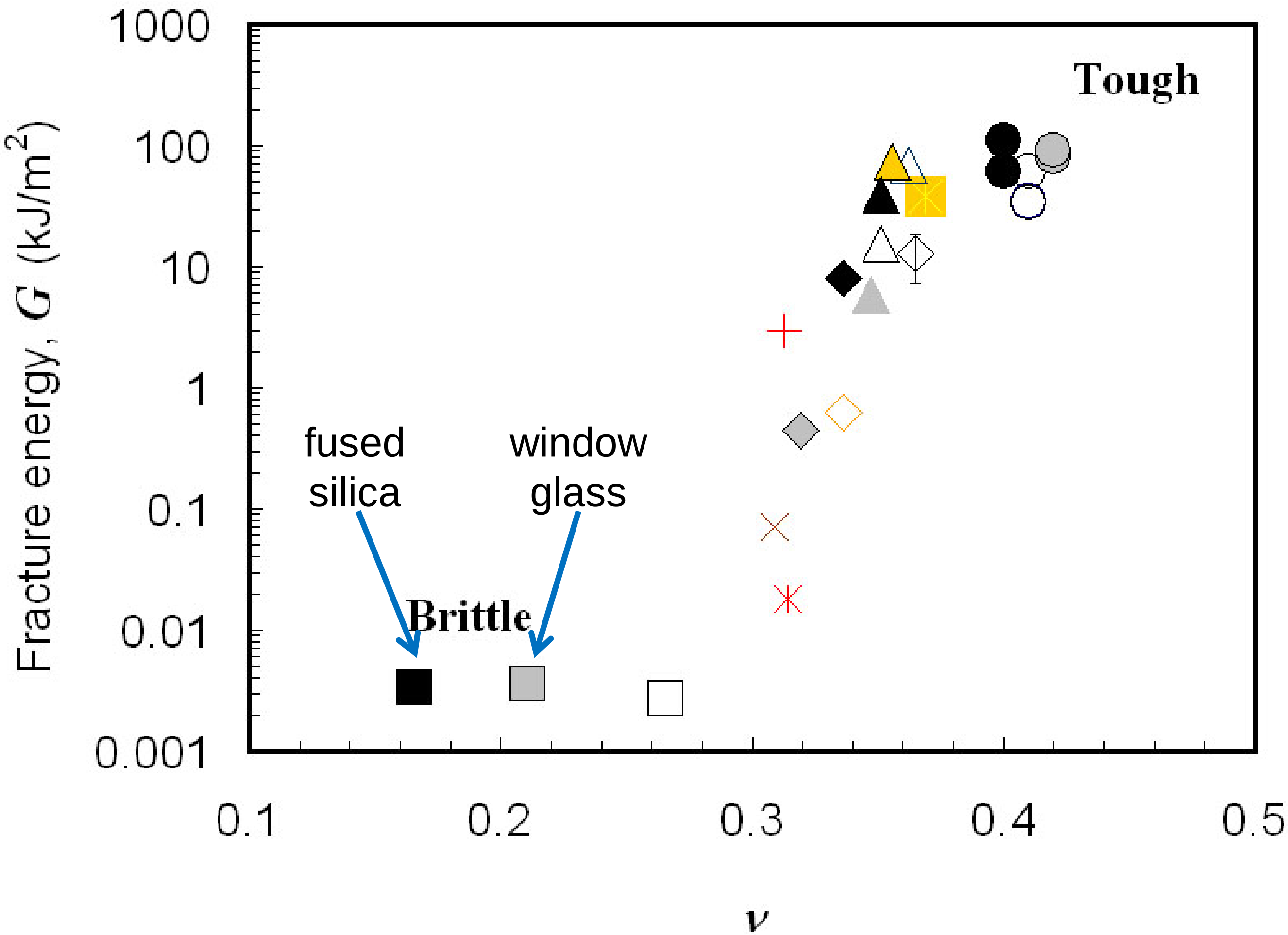


Fragility of the liquid



trend of Poisson's ratio of the glass, ν ⟶

GN Greaves, AL Greer, RS Lakes, T Rouxel: Poisson's ratio and modern materials, *Nature Mater.* **10** (2011) 823–837.

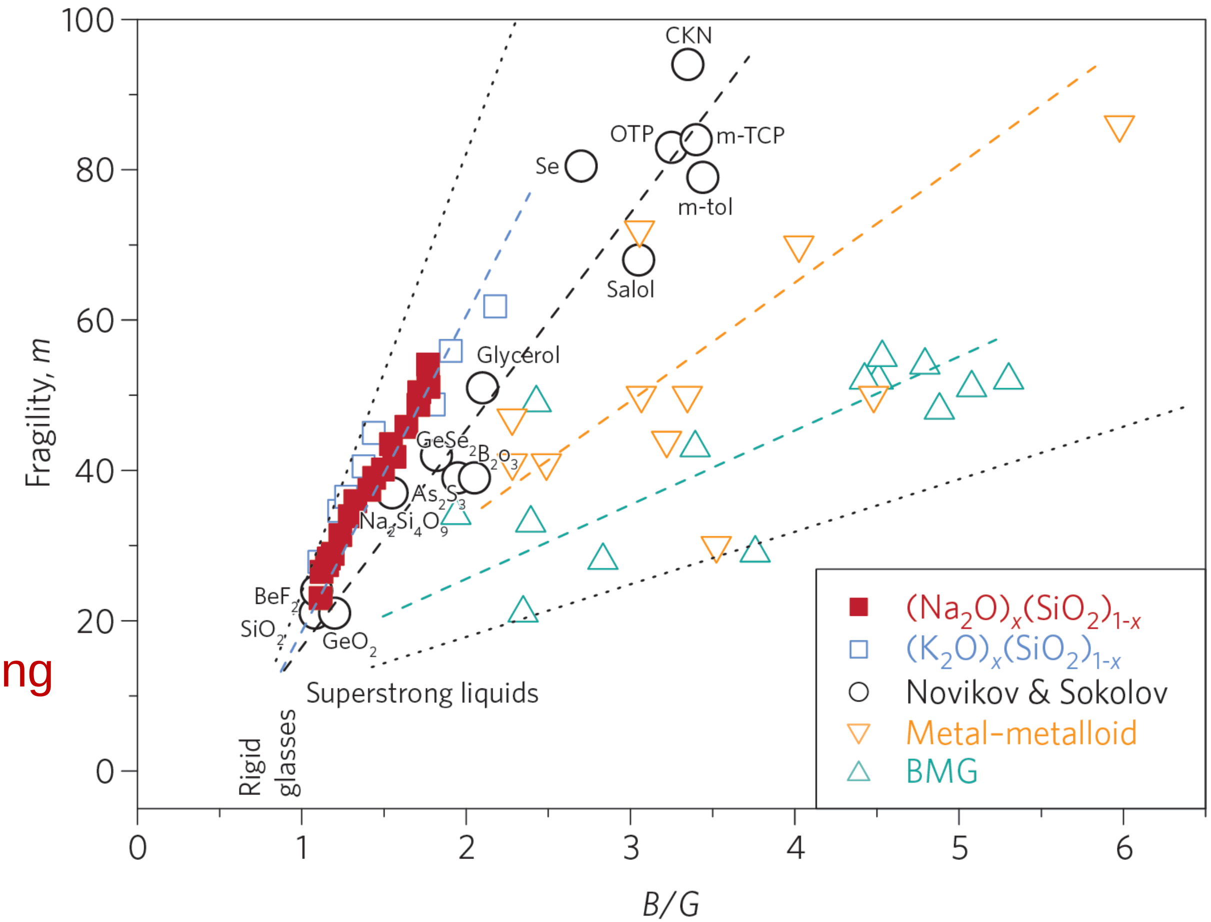


Data on metallic glasses of different compositions and after various annealing treatments. The critical value of Poisson's ratio, ν_{crit} = 0.31-0.32.

JJ Lewandowski, WH Wang AL Greer: Intrinsic plasticity or brittleness of metallic glasses, *Philos. Mag. Lett.* **85** (2005) 77.

The better the glass-forming ability, the more likely to be brittle!

better glass-forming ability



trend of Poisson's ratio, ν

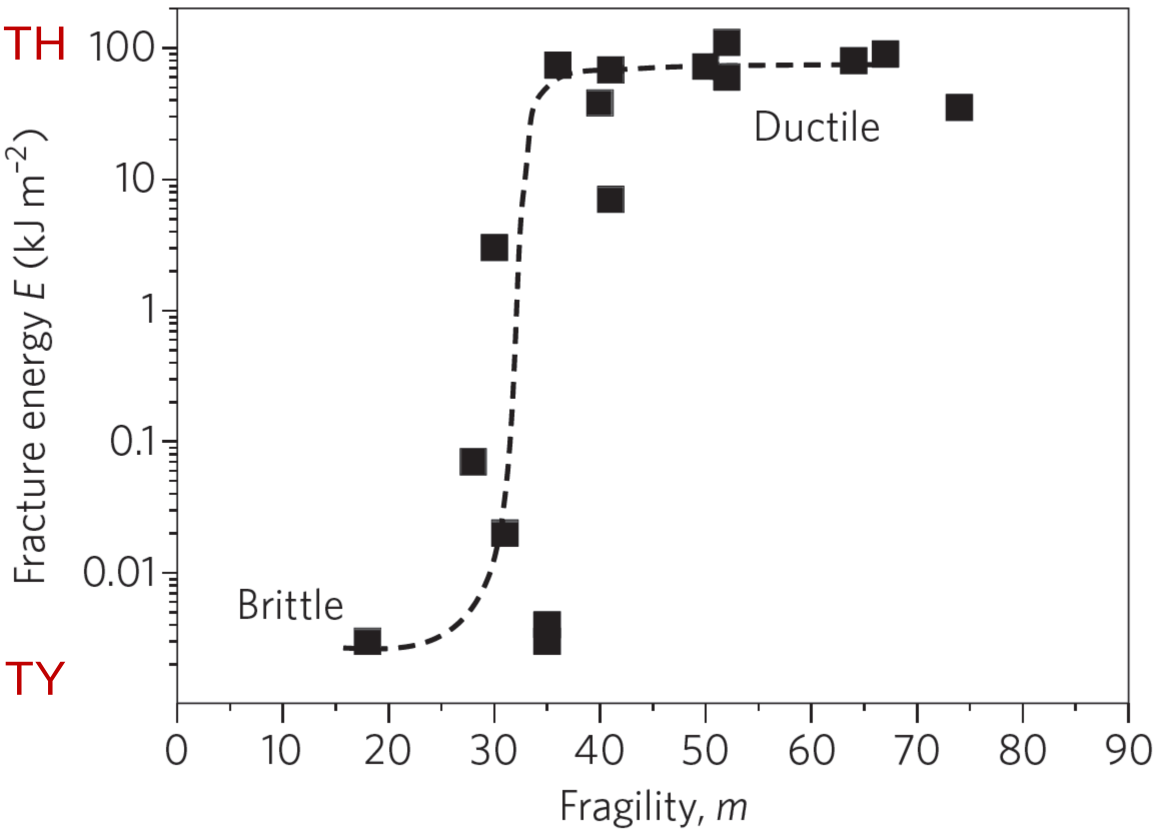
brittleness — plasticity

GN Greaves, AL Greer, RS Lakes, T Rouxel: Poisson's ratio and modern materials, *Nature Mater.* **10** (2011) 823–837.

An inverse correlation of fragility of the liquid with fragility of the glass!

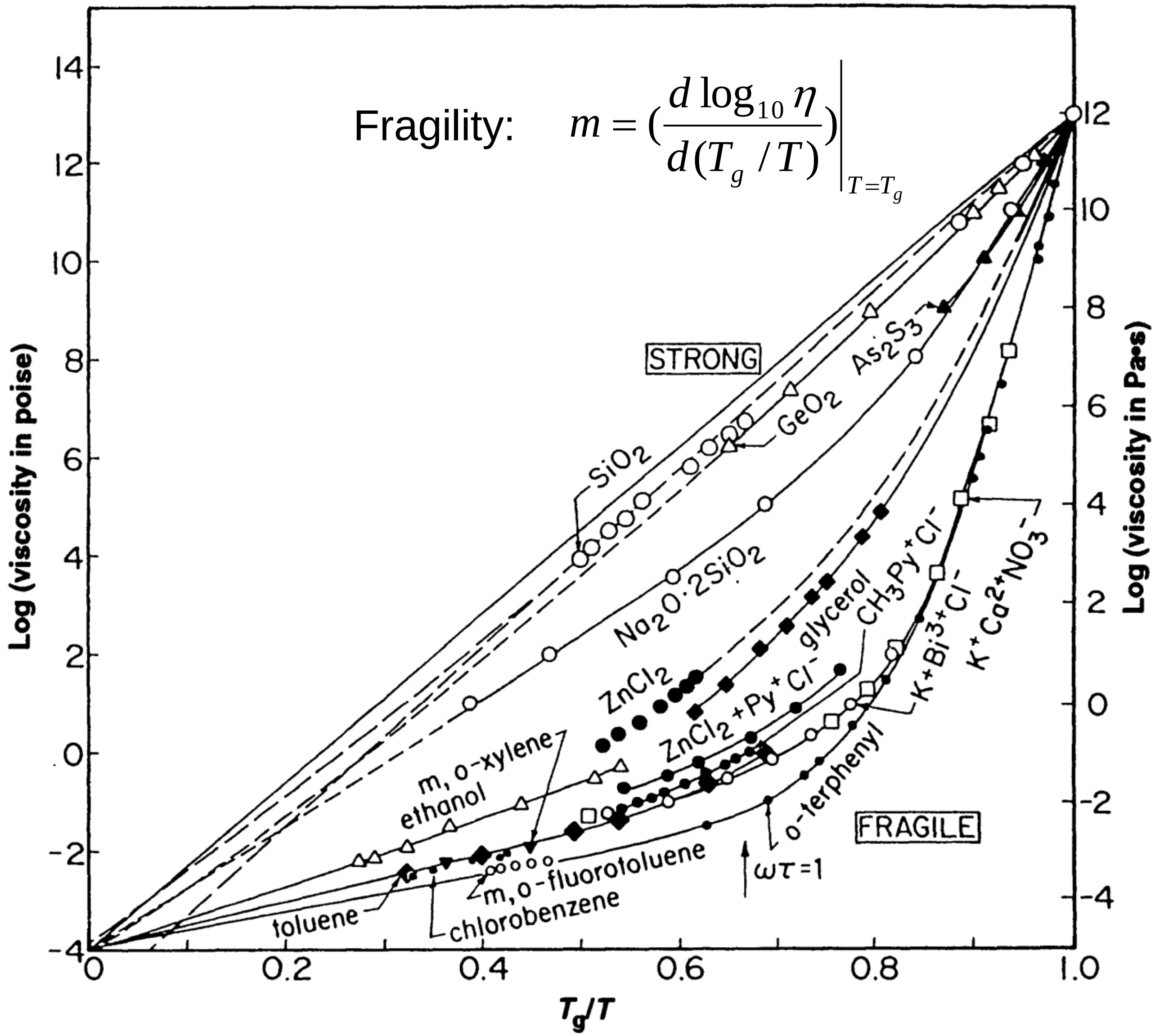
STRENGTH

FRAGILITY



GN Greaves, AL Greer, RS Lakes, T Rouxel:
Poisson's ratio and modern materials
Nature Mater. **10** (2011) 823–837.

Fragility: $m = \left(\dfrac{d \log_{10} \eta}{d(T_g / T)}\right)\Bigg|_{T=T_g}$



CA Angell: *Science* **267** (1995) 1924.

“Fragile” liquids … have structures which degrade rapidly on increase of temperature above the glass transition

CA Angell: ‘Strong and fragile liquids’ in *Relaxations in Complex Systems*, eds KL Ngai & GB Wright, Nat. Techn. Inf. Serv. (1985).

Liquids can be fragile because, in contrast with other condensed phases, their structures can change so much without destroying the integrity of the phase

CA Angell: this Symposium Volume, page 21.

Oxford English Dictionary

Fragility:
first recorded in English (from the French) in 1398, meaning moral weakness —

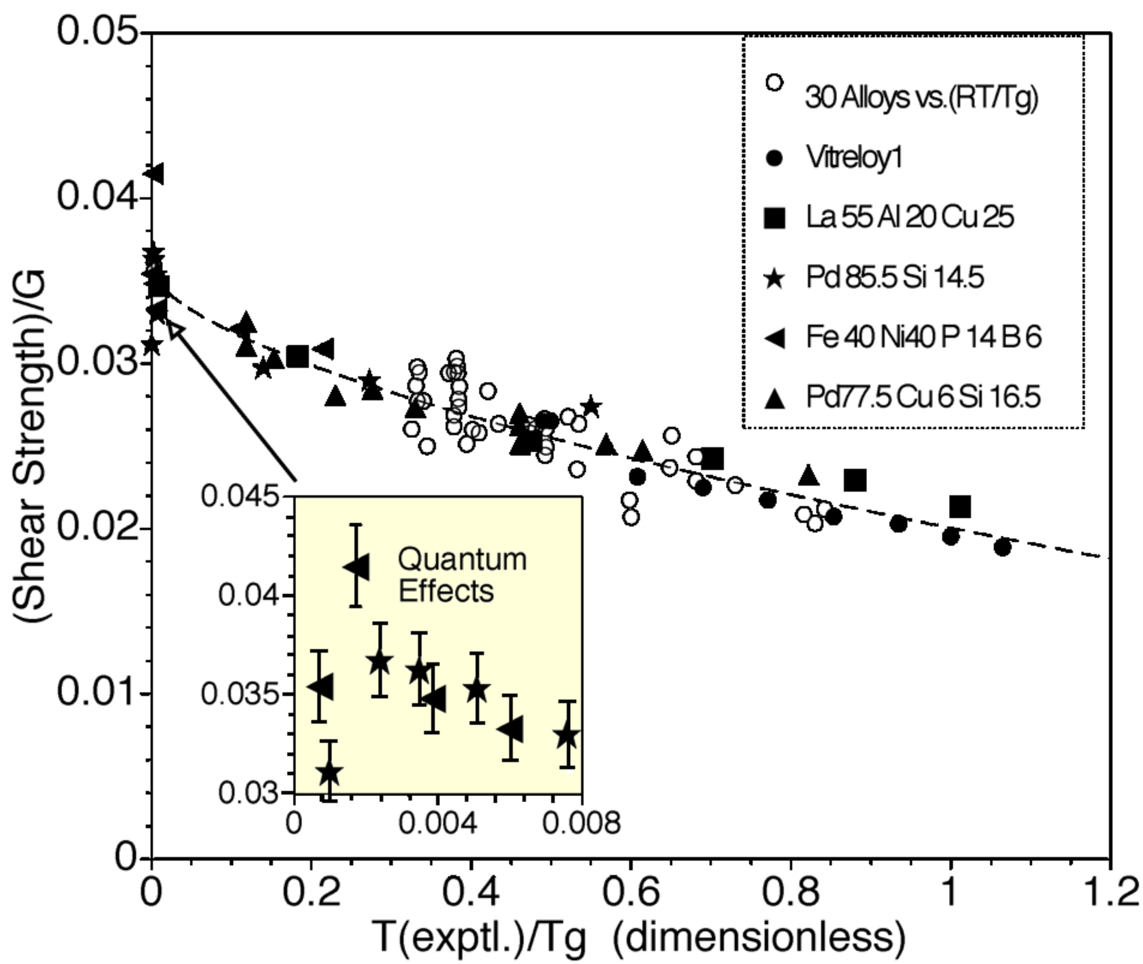
“bi humayne fragilyte … thou trespas ayenst the commaundement of almyghty god”

Fragile:
First recorded in English in 1513, meaning liable to err or fall into sin —

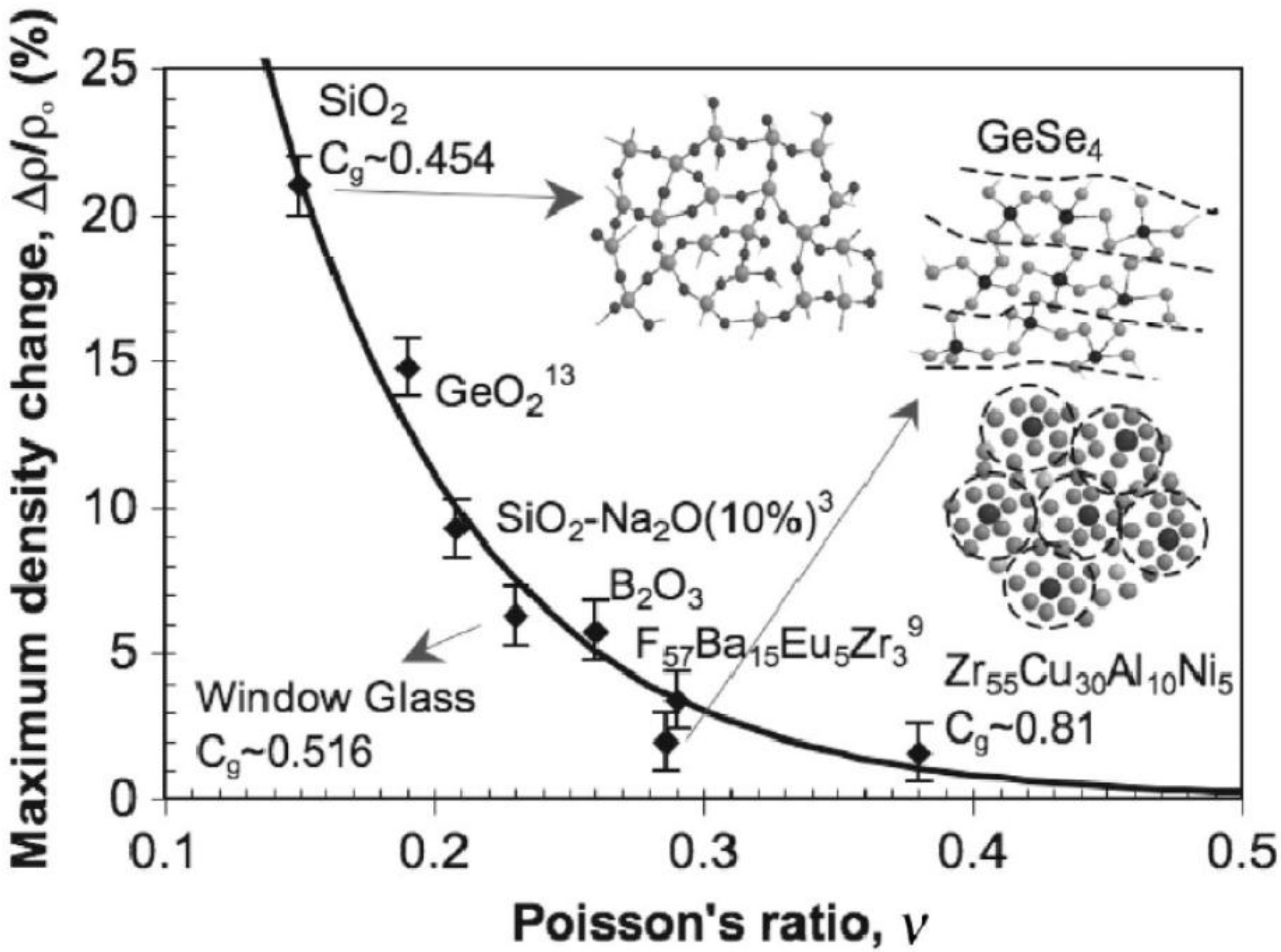
“More lyke an angell..Than a fragyll mayde, of sensuall appetyte … A wanton prynce, folowynge sensualyte And his fragyll appetyte.”

- The nature of the liquid:
  - structure, heterogeneity, relaxations, dynamics
  - dependence on T and V (P)
  - fragile-to-strong transitions
- Energy and entropy:
  - atomic/molecular interactions
  - energy landscapes
  - Adam-Gibbs model
  - relationships between kinetic and thermodynamic aspects
- How are the liquid and the glass related?
  - correlations of liquid properties with glass properties
  - e.g. with elastic properties notably Poisson’s ratio
  - liquid stability relative to the crystalline state
- Experimental techniques (physical and simulation), new directions
- Correlations

Elastic shear strain limit of metallic glasses

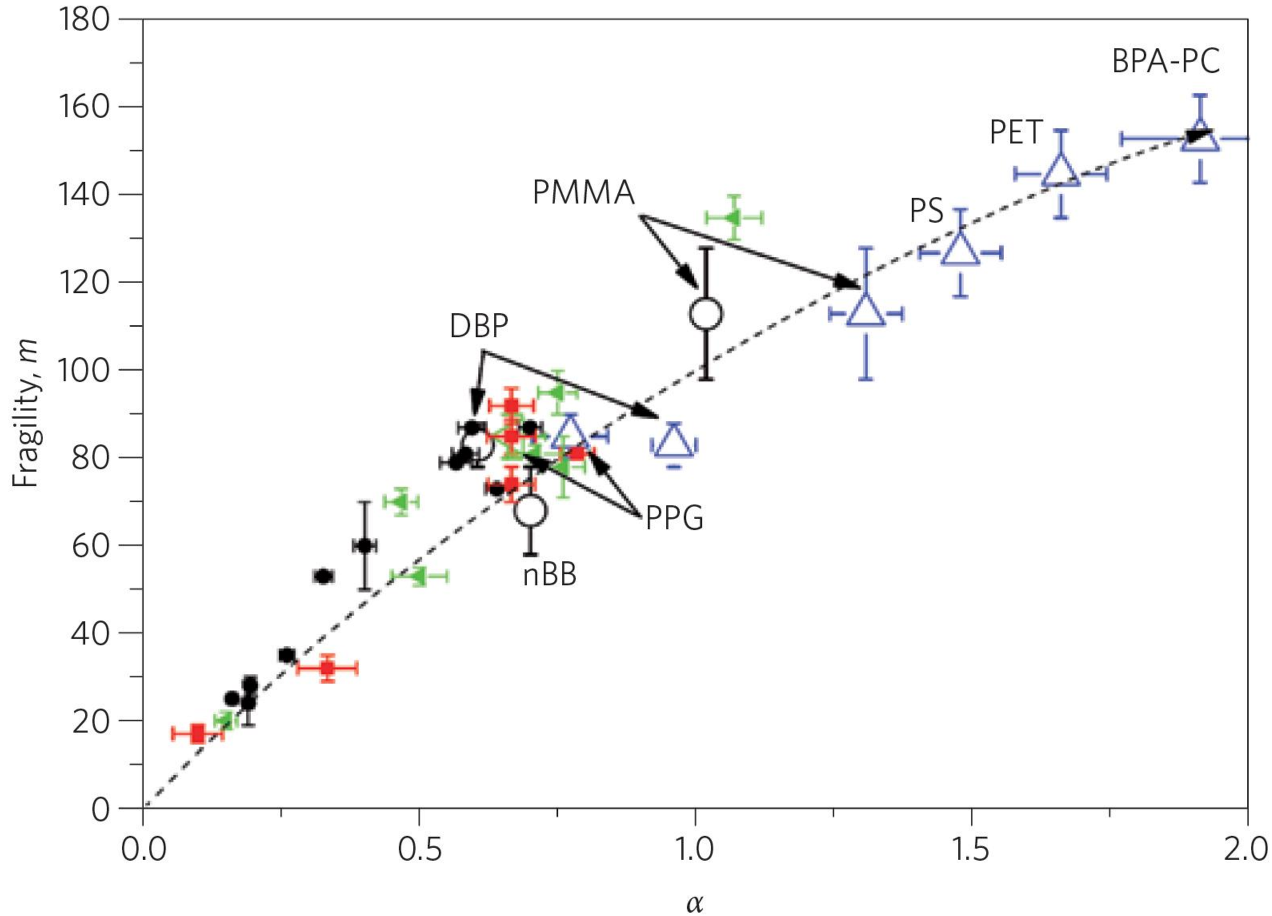


WL Johnson, K Samwer: A universal criterion for plastic yielding of metallic glasses with a $(T/T_g)^{2/3}$ temperature dependence, *Phys. Rev. Lett*. **95** (2005) 195501.



T. Rouxel, H. Ji, T. Hammouda, A. Moreac, Poisson's ratio and the densification of glass under high pressure. *Phys. Rev. Lett.* **100** (2008) 225501.

Scopigno correlation — between the kinetic fragility of the liquid and the vibrational properties of the glass (specifically the α parameter in the non-ergodicity factor)



Scopigno papers in Symposium volume, plus
GN Greaves, AL Greer, RS Lakes, T Rouxel: Poisson's ratio and modern materials, *Nature Mater.* **10** (2011) 823–837.

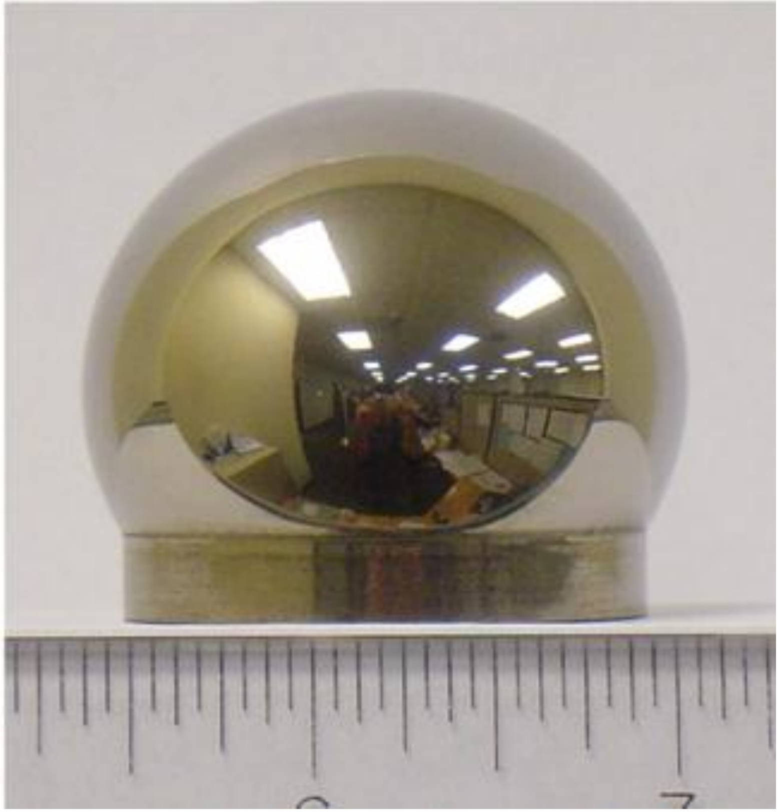
Correlations across and within glass-forming systems

- oxides and silicates
- polymers
- chalcogenides
- organics, molecular liquids
- ionics
- bio: carbohydrates, proteins (and their folding)
- metallic alloys
- water

We will focus on some practical aspects of FRAGILITY …

… for machines, memory, and survival!

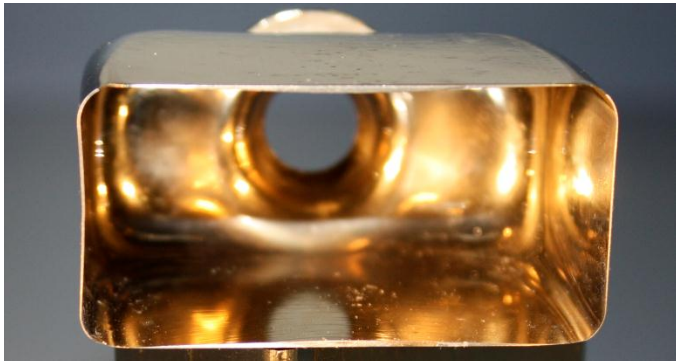

No 2 POT
ARCH

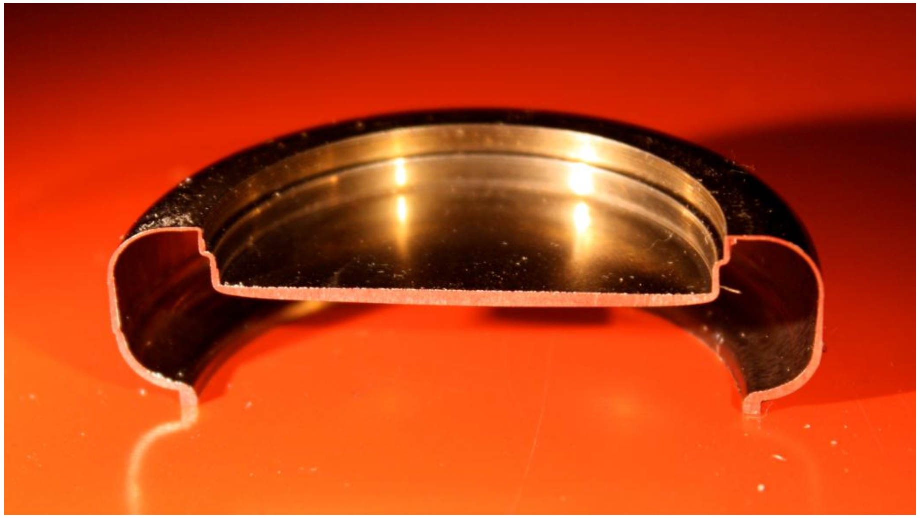


J Schroers *et al*., *Scripta Mater*. **57** (2007) 341.

Unachievable shapes for metals?

Hollow, thin, seamless, complex parts —





[courtesy: Jan Schroers, Yale]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APPLIED SCIENCE
ENGINEERING &
YALE SCHOOL OF
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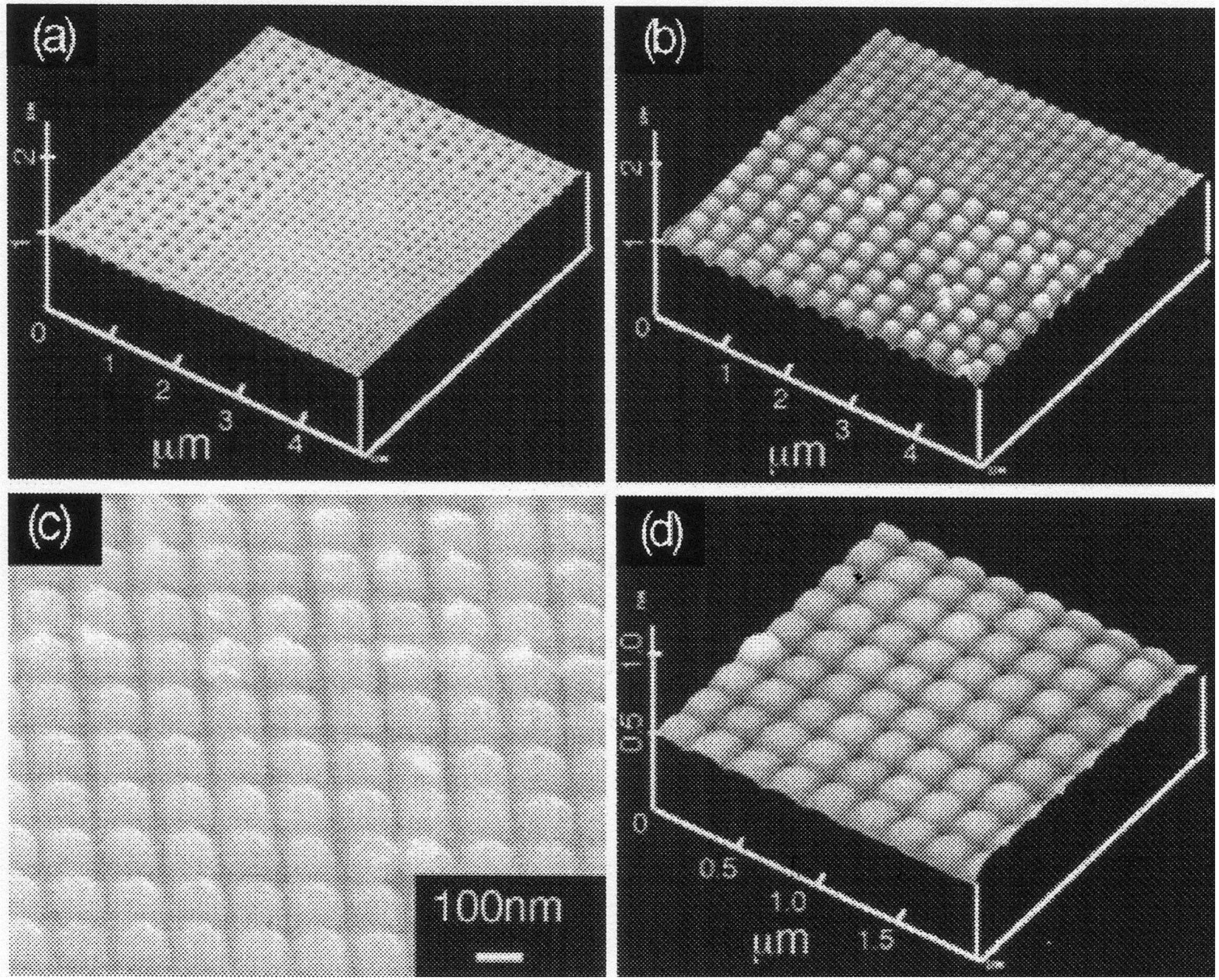
CHANEL
PARIS
EAU DE PARFUM

Microformability of BMGs

• of interest for micro- & nano-imprinting of surfaces



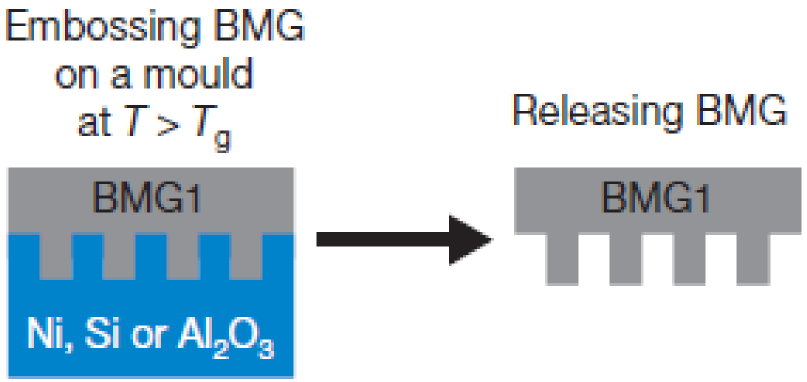
AFM and SEM images of a patterned (100) Si die and a Pt-based BMG imprinted with the die (10 MPa, 550 K, 300 s)

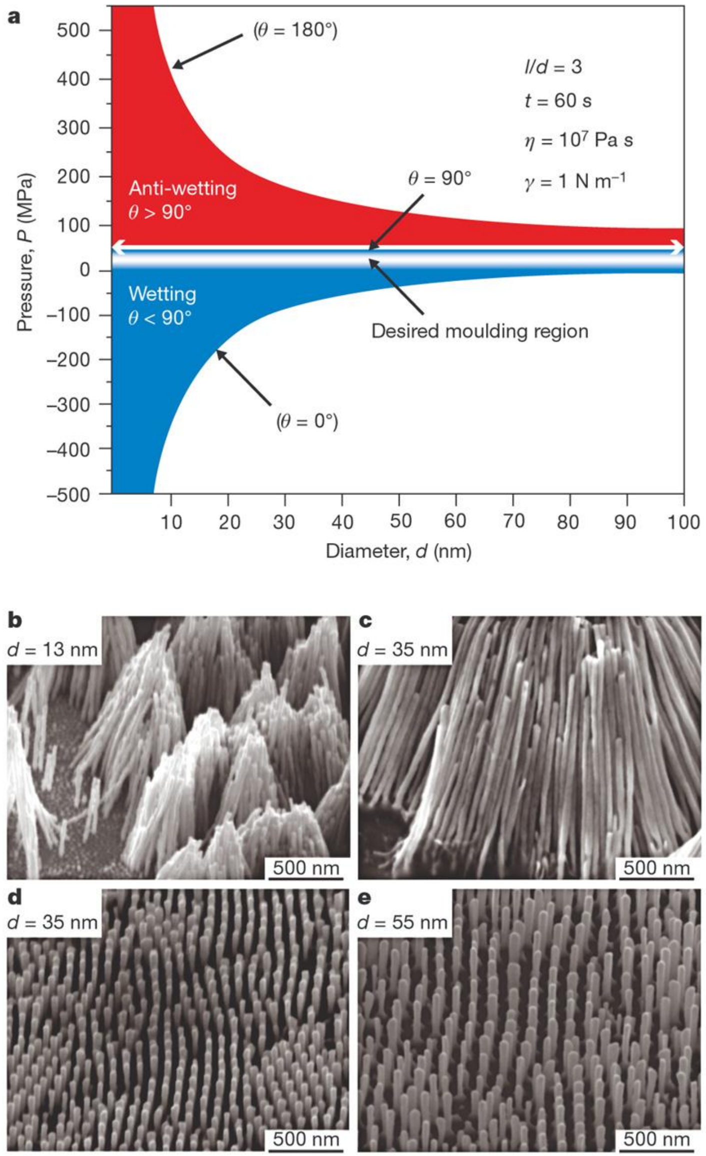
Y Saotome et al. The micro-nanoformability of Pt-based metallic glass and the nanoforming of three-dimensional structures, *Intermetallics* **10** (2005) 1241.

Nanomoulding with amorphous metals

Controlling metallic glass moulding on scales smaller than 100 nm

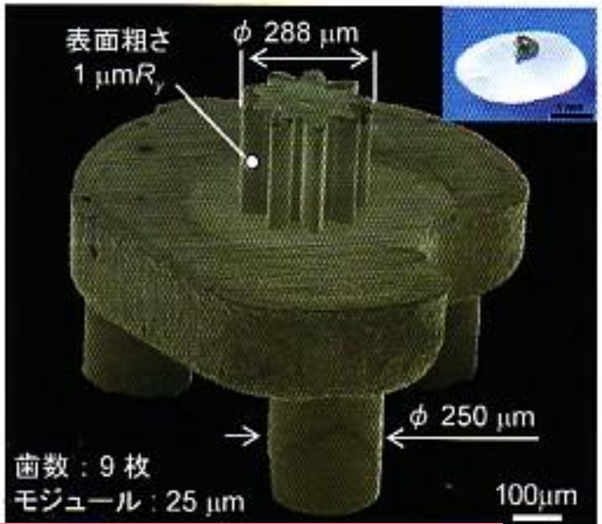
Pt-based BMG





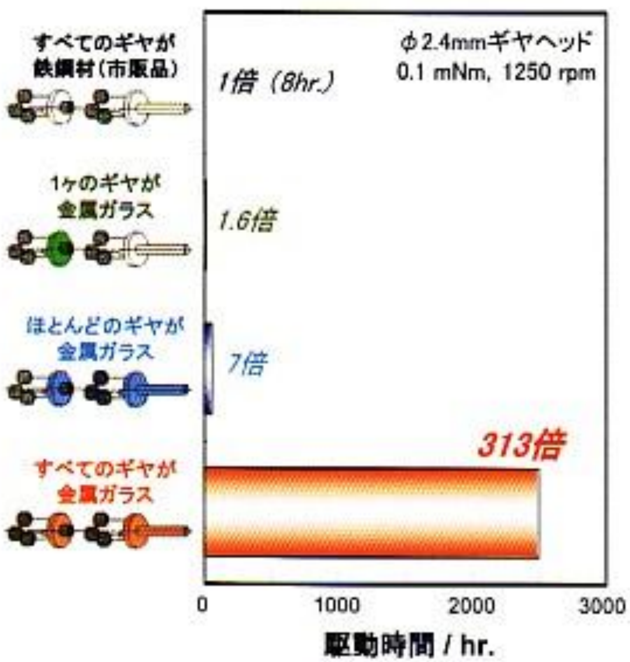
G Kumar, HX Tang, J Schroers, *Nature* **457** (2009) 868.

nature

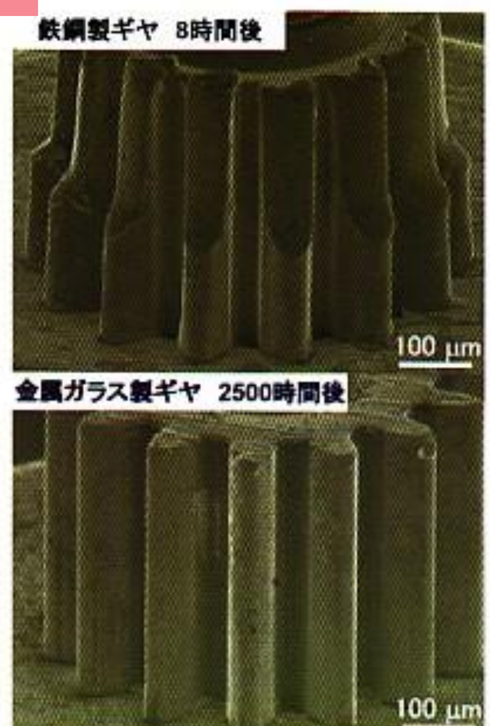


金属ガラス製超精密歯車を組み込んだ世界最小マイクロギヤードモータ

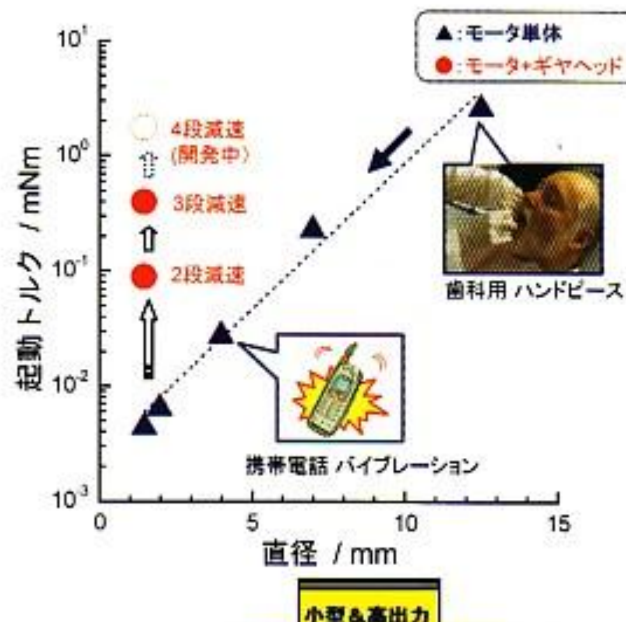
The world’s smallest motor



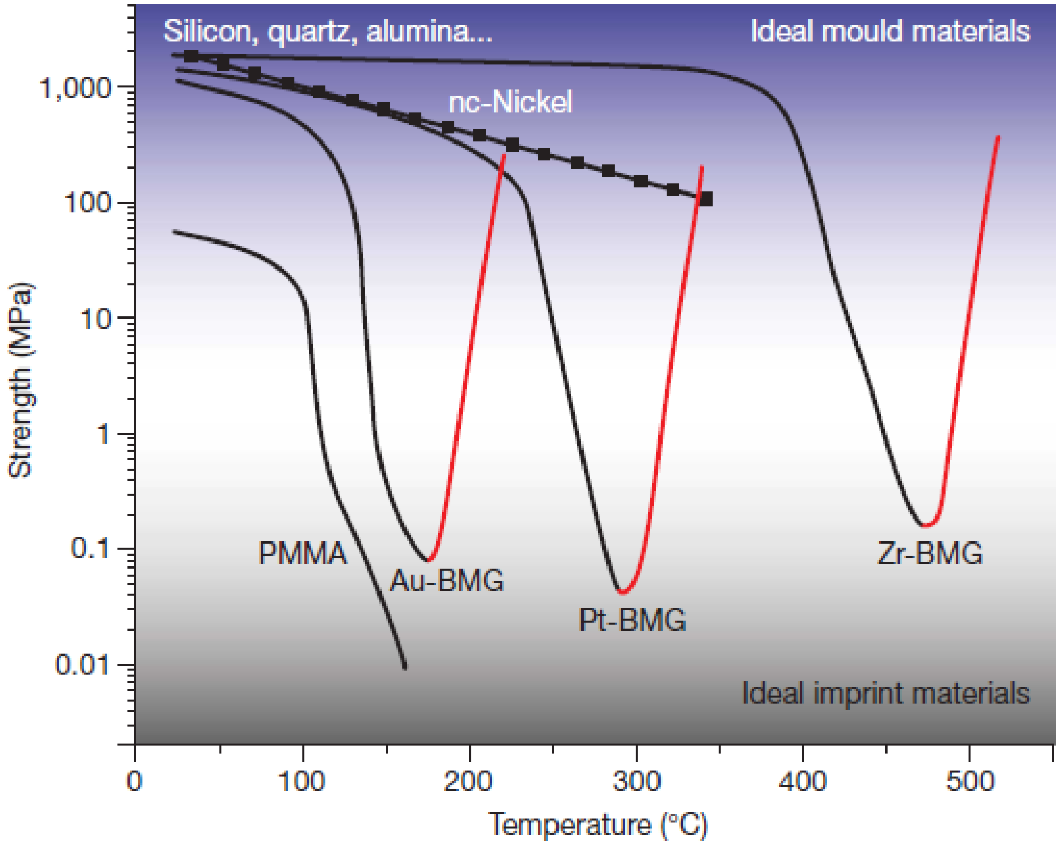
直径2.4 mmギヤヘッド（従来品）を用いた駆動時間比較



駆動試験後の歯車摩耗状況

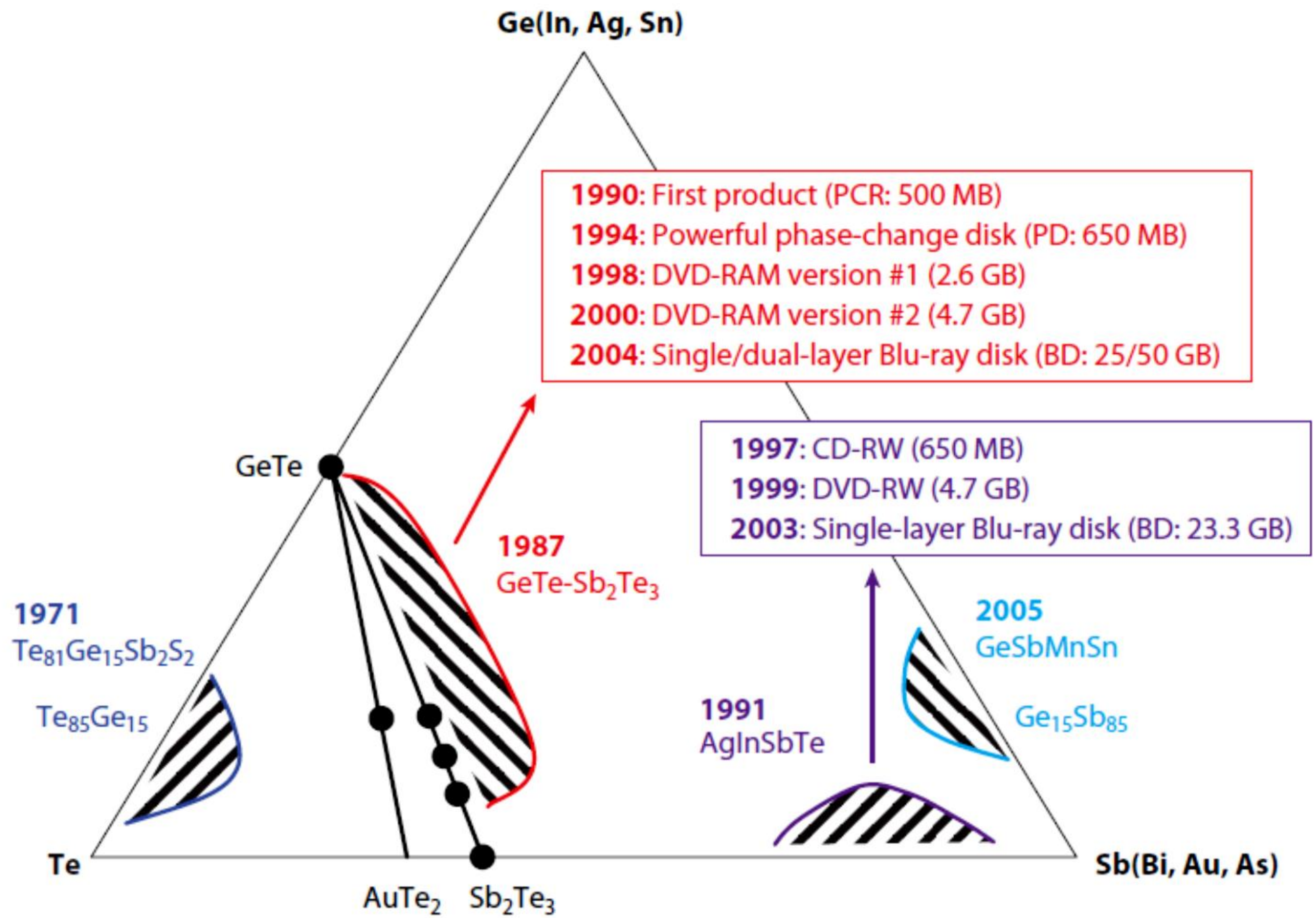


医療機器、ロボット等に適用可能



G Kumar, HX Tang, J Schroers, *Nature* **457** (2009) 868.

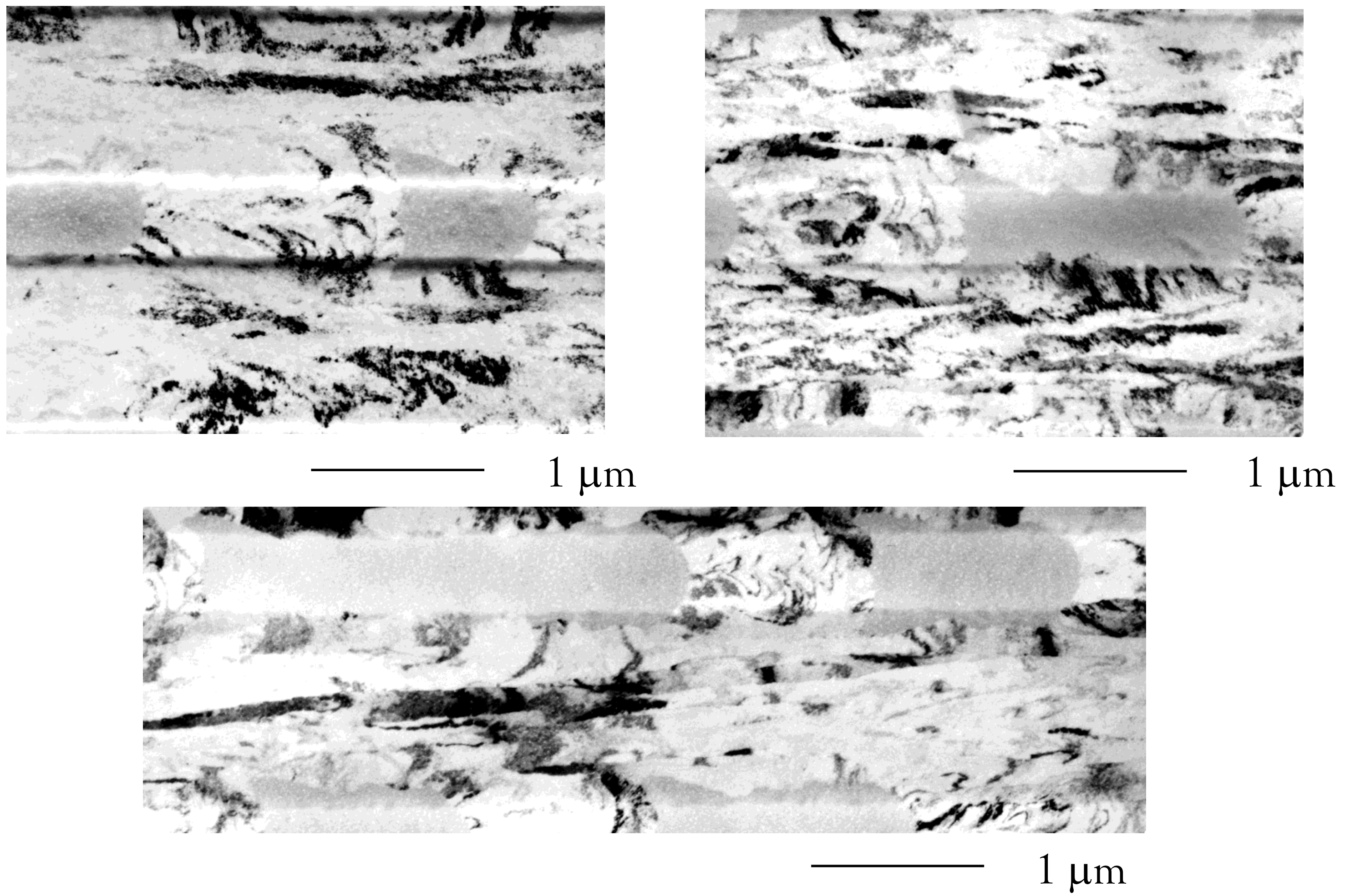
Chalcogenide glass-forming compositions



Ternary phase change diagram showing composition of phase-change alloys used in different types of commercialized optical data media.

S Raoux: Phase change materials, *Ann. Rev. Mater. Res.* **39** (2009) 25.

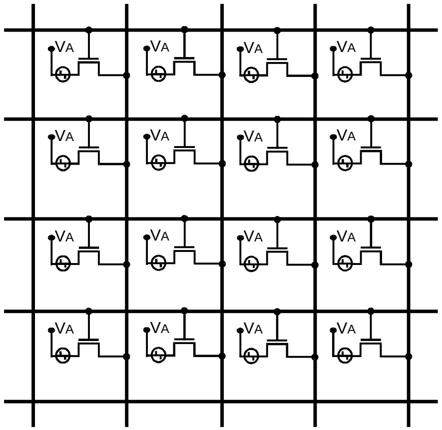
Chalcogenide (e.g. $Ge_2Sb_2Te_5$) thin film, 20 nm thick, in a CD-RW

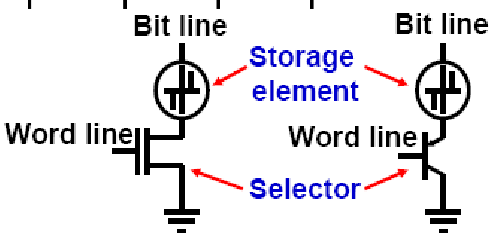


- data marks written by laser-melting: rapid cooling gives a glass
- reading is by laser, exploiting contrast in reflectivity ~ 20 % $R(\lambda)$

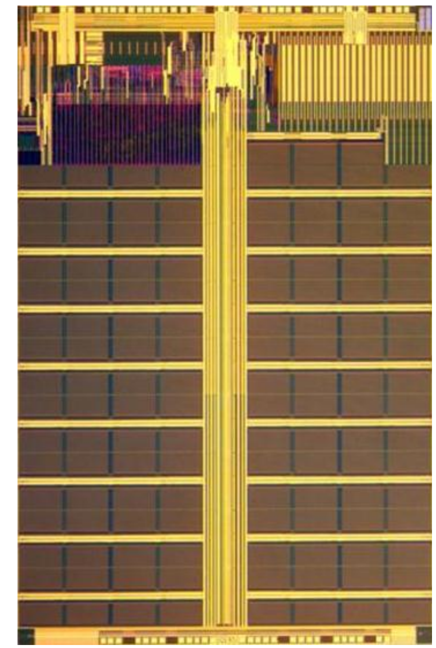
PC-RAM

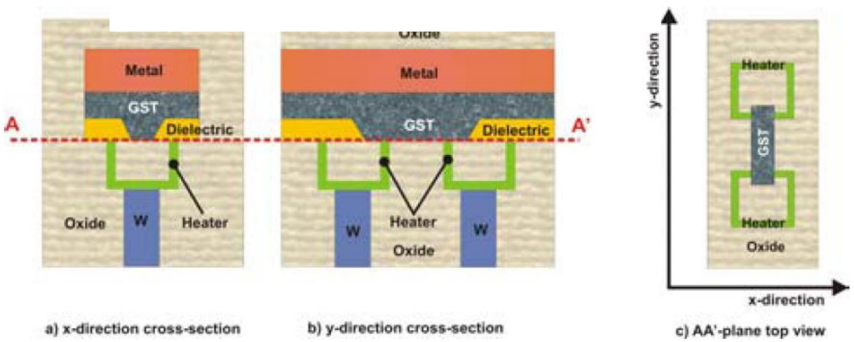
- example of Intel, STMicroelectronics 128 Mb µTrench cell architecture memory introduced to market in 2008



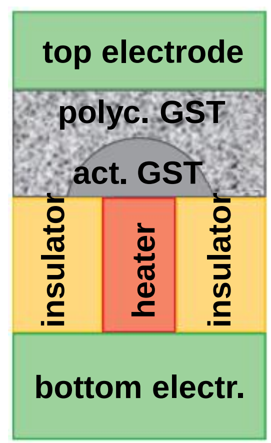


1T/1R cell structure
Die: 7 mm x 5 mm,
Unit cell die: 0.22 x 0.44 µm^2
Capacity: 128 Mbits
Reset: 400 µA, ~ 2V, 100 ns
Set: 250 µA, ~ 1.5V, 100 ns
Read: 20 µA, ~ 0.2 V
Technology: 90nm CMOS





µTrench – reducing electrode contact area

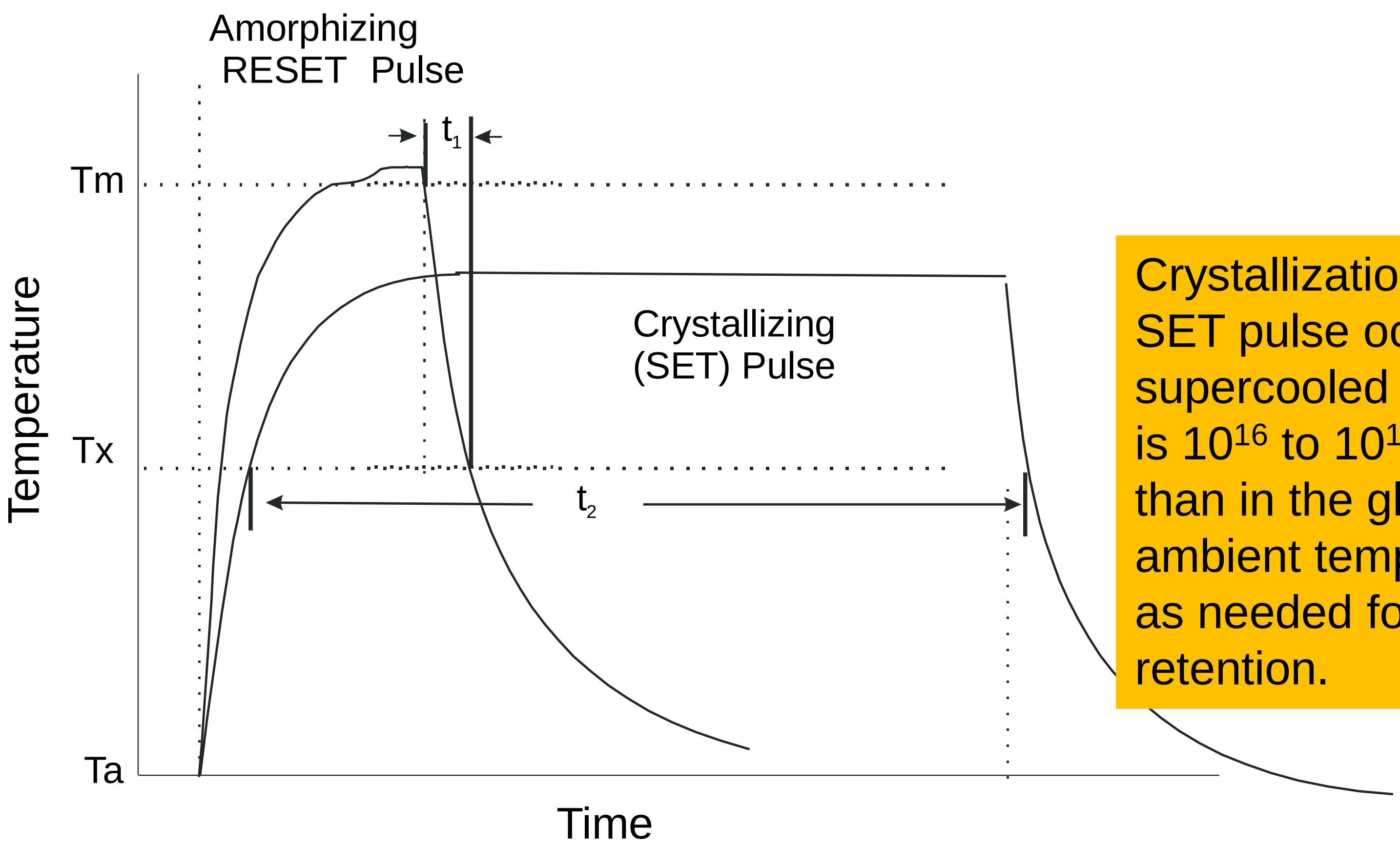


typical heater

- Picture of the 90 nm 128 Mb vehicle based on the self-aligned µTrench approach (Alverstone).

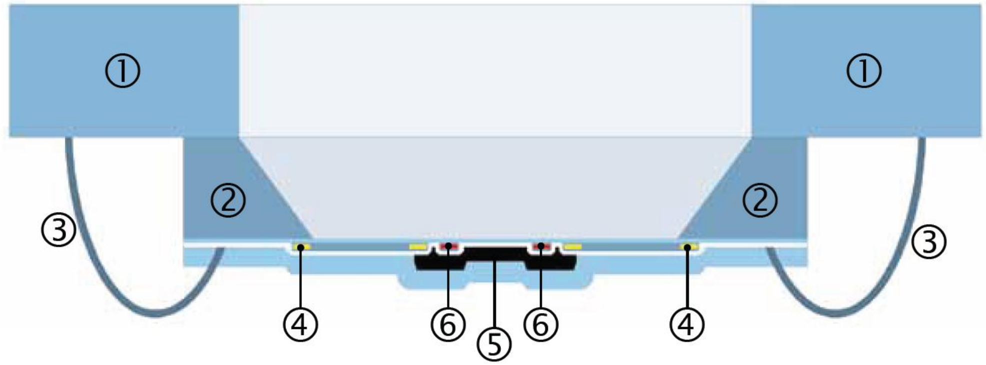
A. Pirovano et al., „Phase-change memory technology with self-aligned µTrench cell architecture for 90 nm node and beyond, *Sol. St. Electronics* **52** (2008) 1467.; S. Raoux, „Phase Change Materials" *Annu. Rev. Mater. Res.* **39** (2009) 25.

Programming of memory devices (schematic)

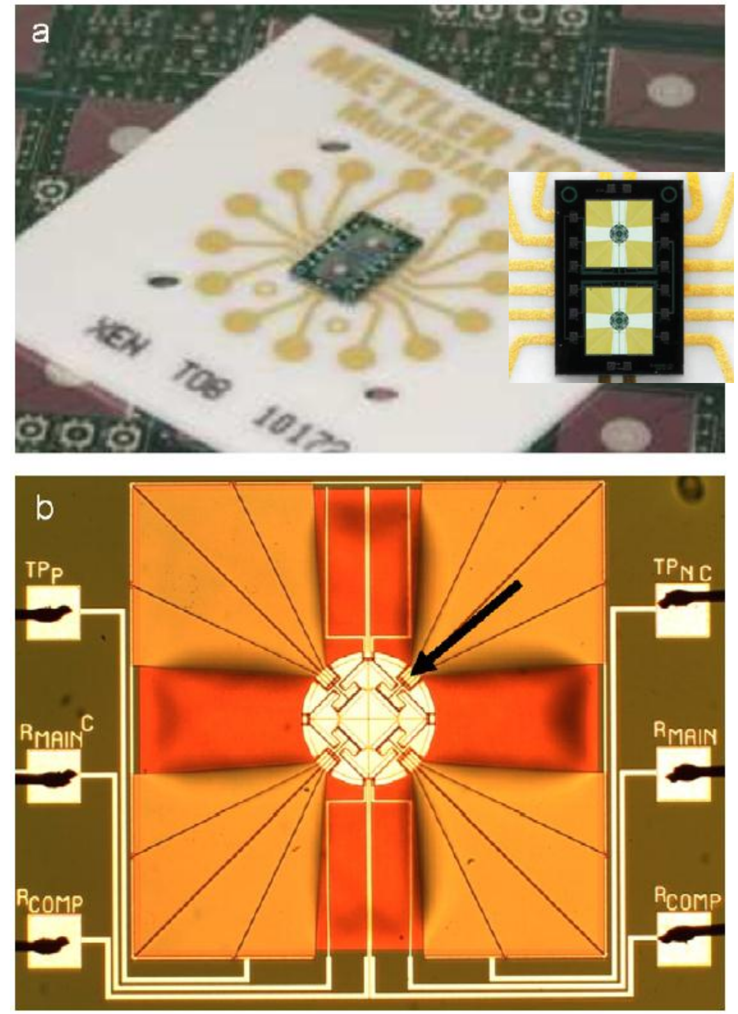


Crystallization during the SET pulse occurs in the supercooled liquid, and is 10^{16} to $10^{17}\times$ faster than in the glass at near-ambient temperatures as needed for data retention.

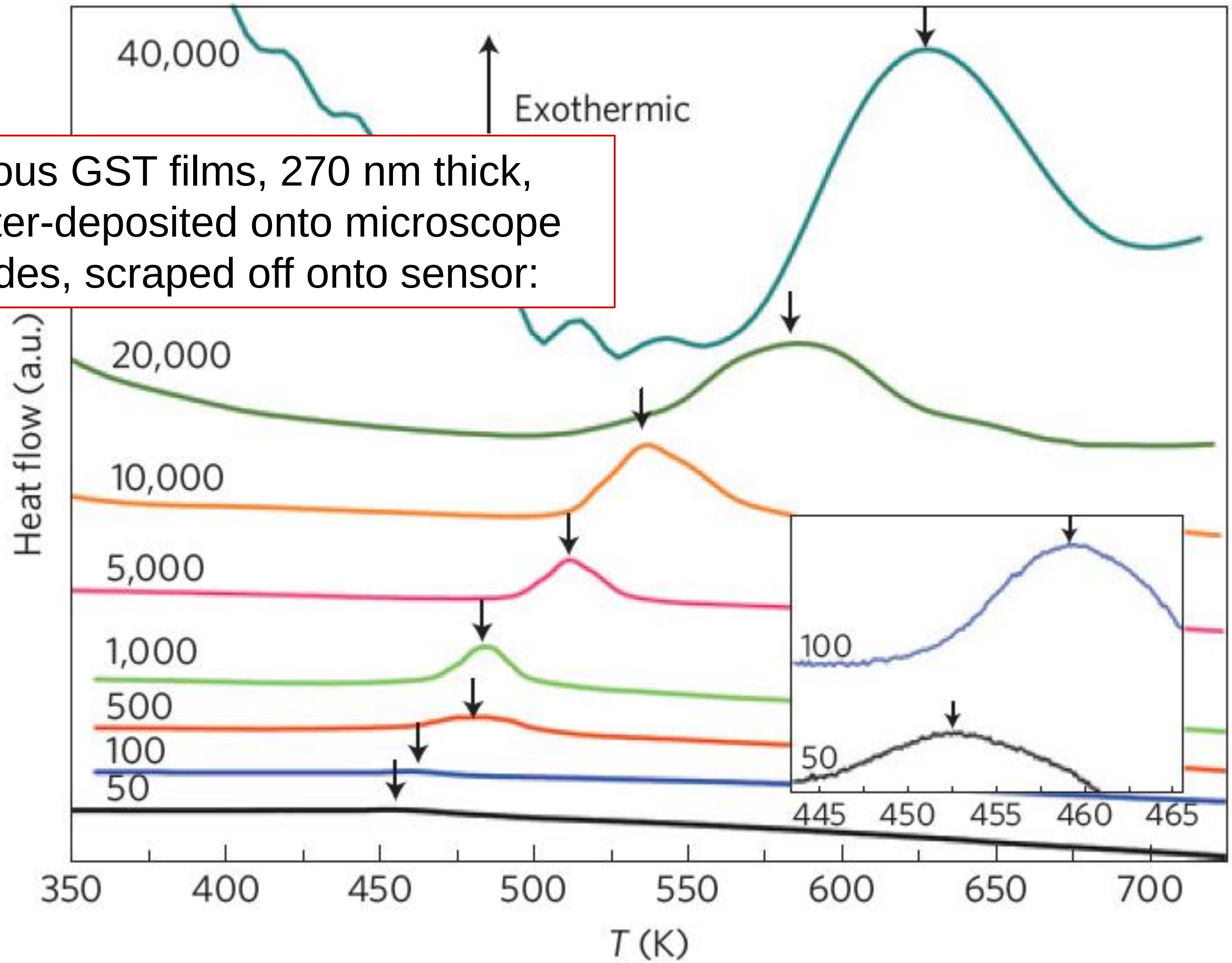
Ultra-fast DSC, Mettler-Toledo Flash DSC 1



1. Ceramic plate
2. Silicon frame
3. Connecting wire
4. Resistance heater
5. Aluminum plate (sample area)
6. Thermocouple

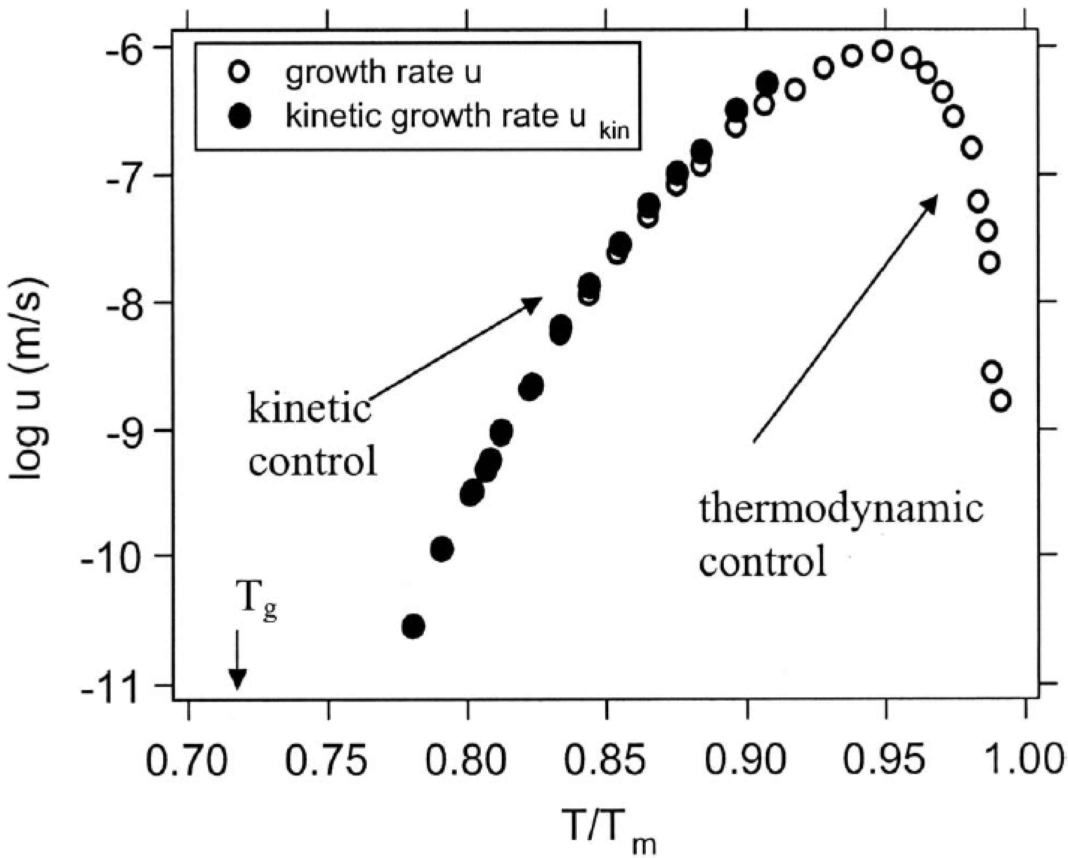


Amorphous GST films, 270 nm thick, RF sputter-deposited onto microscope glass slides, scraped off onto sensor:



J Orava, AL Greer, B Gholipour, DW Hewak, CE Smith: Characterization of supercooled liquid $Ge_2Sb_2Te_5$ and its crystallization by ultrafast-heating calorimetry, *Nature Mater*. **11** (2012) 279-283.

Crystal growth from supercooled liquid



Experimental $U(T)$ for 1,3,5-tri-α-naphthylbenzene

$$U = U_{\text{kin}} \times \left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right]$$

kinetic $\times$ thermodynamic

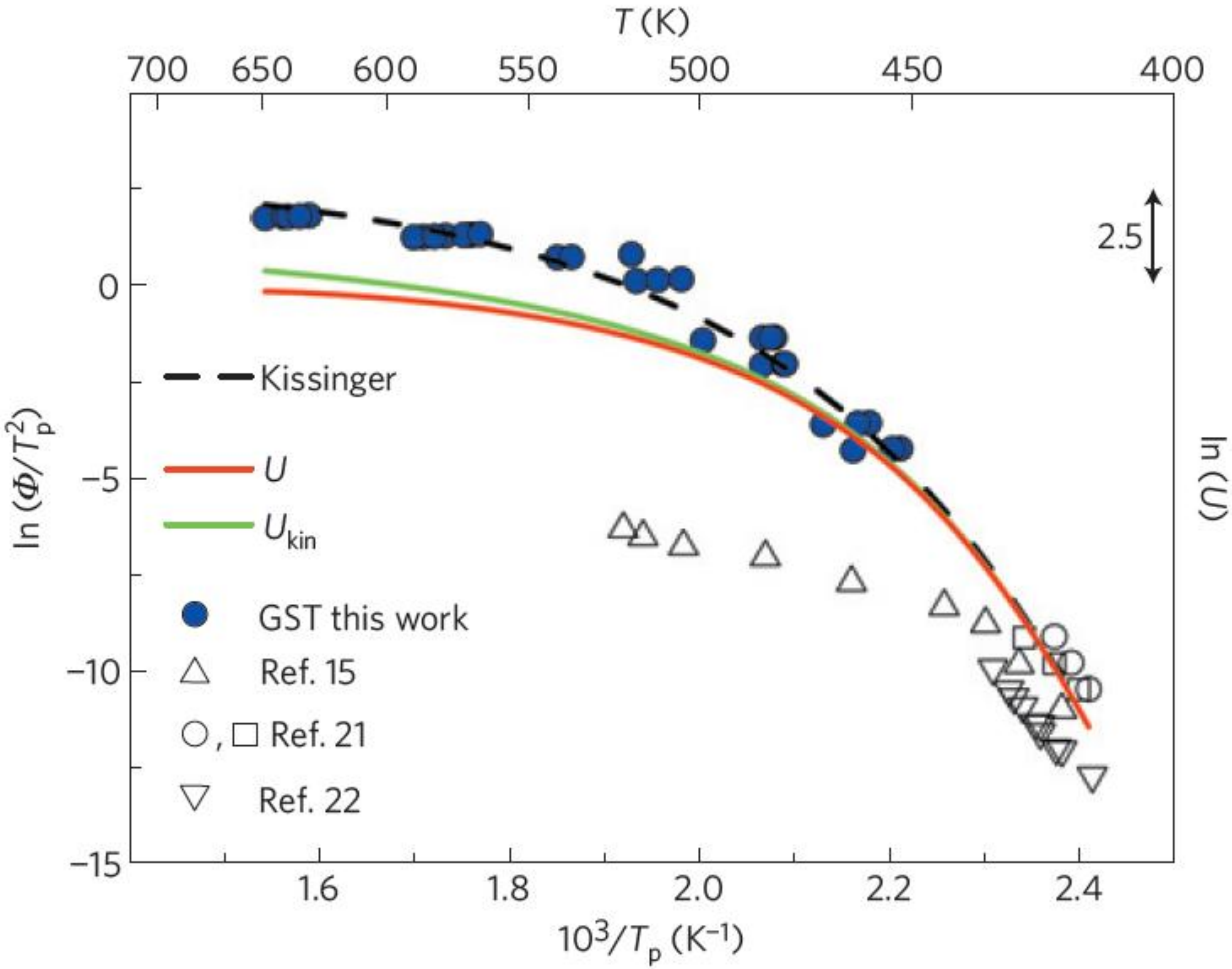
factor

***Diffusion*-limited growth**

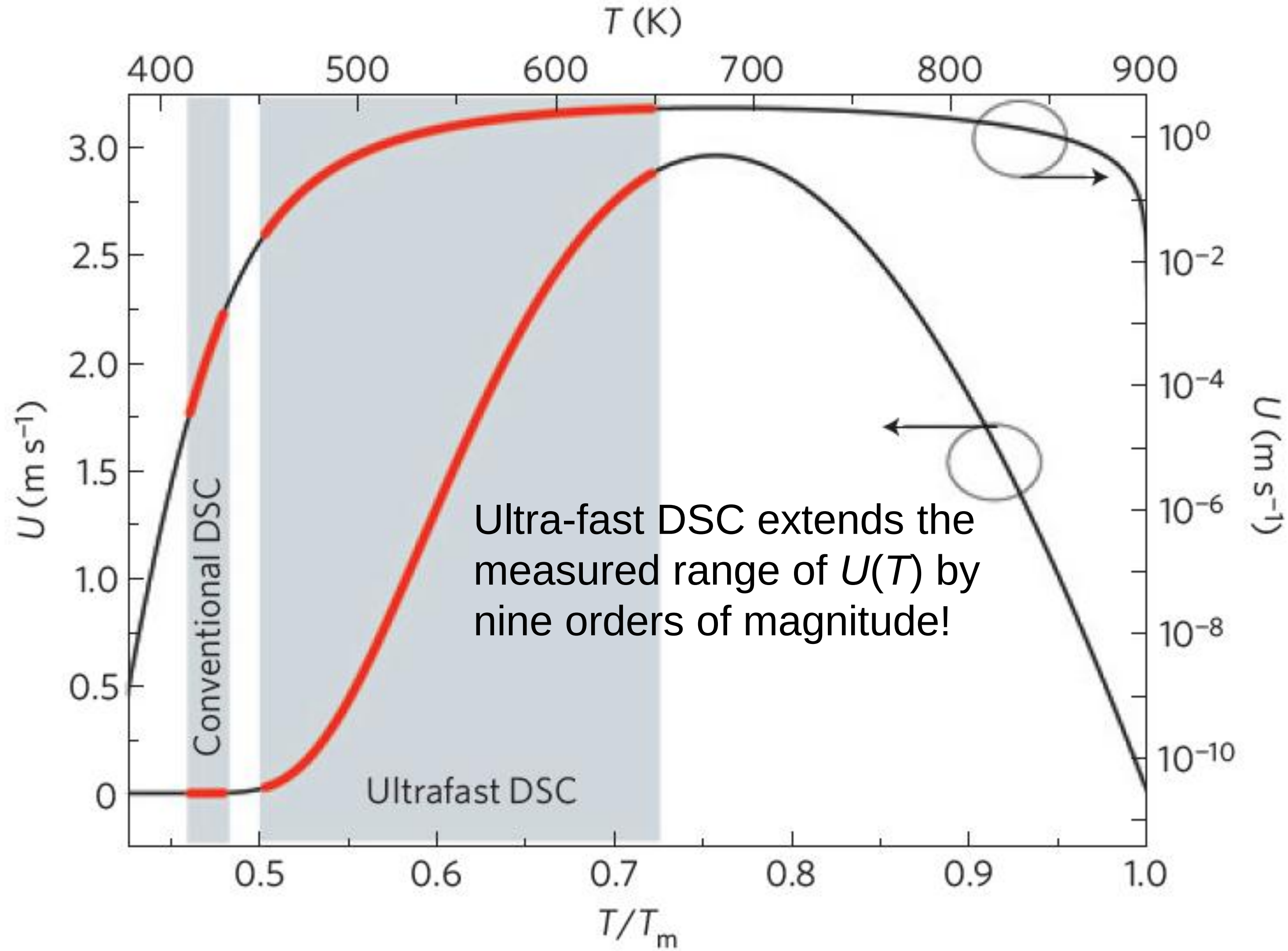
$U_{\text{kin}}(T) \propto 1/\eta(T)$

$\approx D(T)/a$

Ediger et al. *J. Chem. Phys.* **128** (2008) 034709.

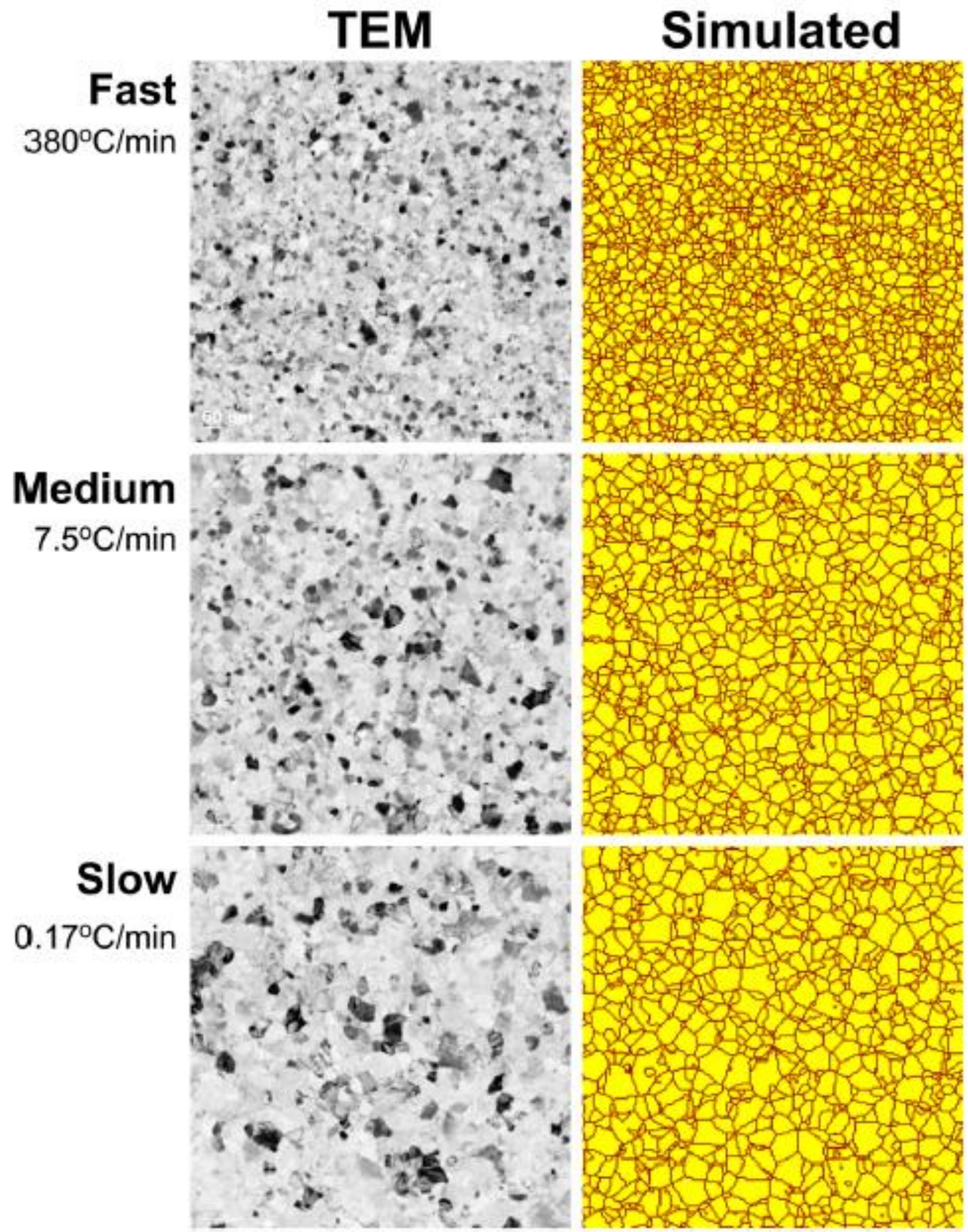


J Orava, AL Greer, B Gholipour, DW Hewak, CE Smith: Characterization of supercooled liquid $Ge_2Sb_2Te_5$ and its crystallization by ultrafast-heating calorimetry, *Nature Mater*. **11** (2012) 279-283.



J Orava, AL Greer, B Gholipour, DW Hewak, CE Smith: Characterization of supercooled liquid $Ge_2Sb_2Te_5$ and its crystallization by ultrafast-heating calorimetry, *Nature Mater*. **11** (2012) 279-283.

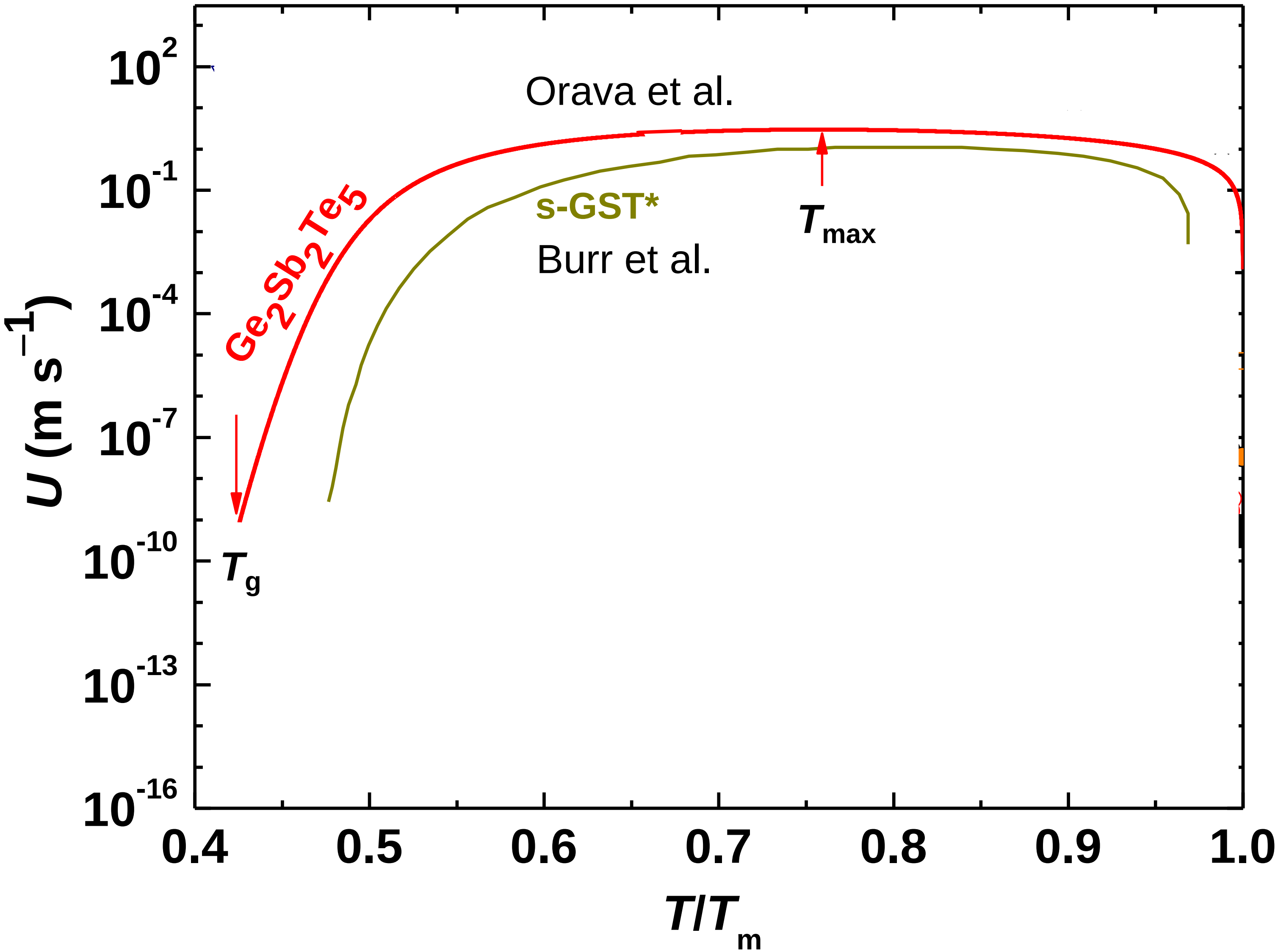
Other studies of crystallization of amorphous GST:



GW Burr, P Tchoulfian, T Topuria, C Nyffeler, K Virwani, A Padilla, RM Shelby, M Eskandari, B Jackson, B-S Lee

"Observation and modeling of polycrystalline grain formation in $Ge_2Sb_2Te_5$"

J. Appl. Phys. **111** (2012) 104308.



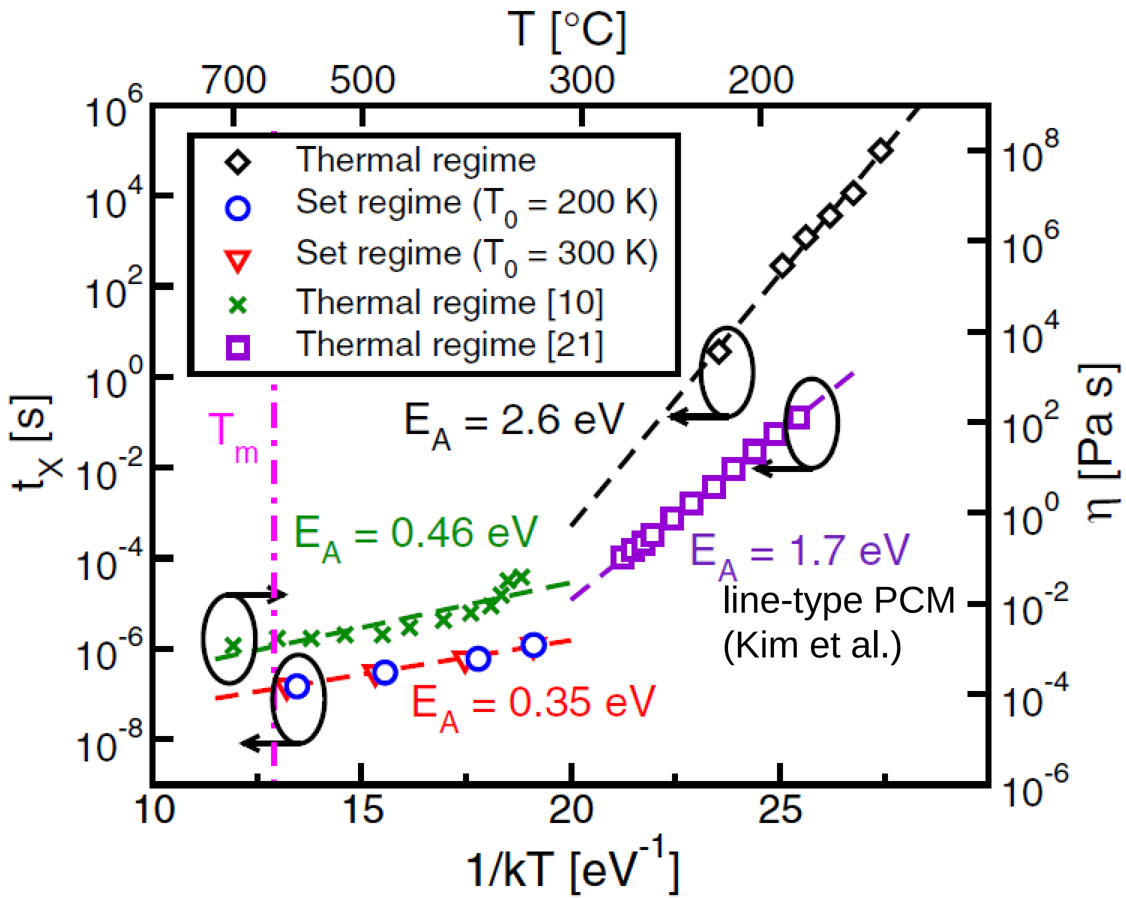
Orava et al.
Ge2Sb2Te5
s-GST*
Burr et al.
Tmax
Tg
U (m s−1)
T/Tm
10^2
10^-1
10^-4
10^-7
10^-10
10^-13
10^-16
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Non-Arrhenius crystallization kinetics in PCM devices

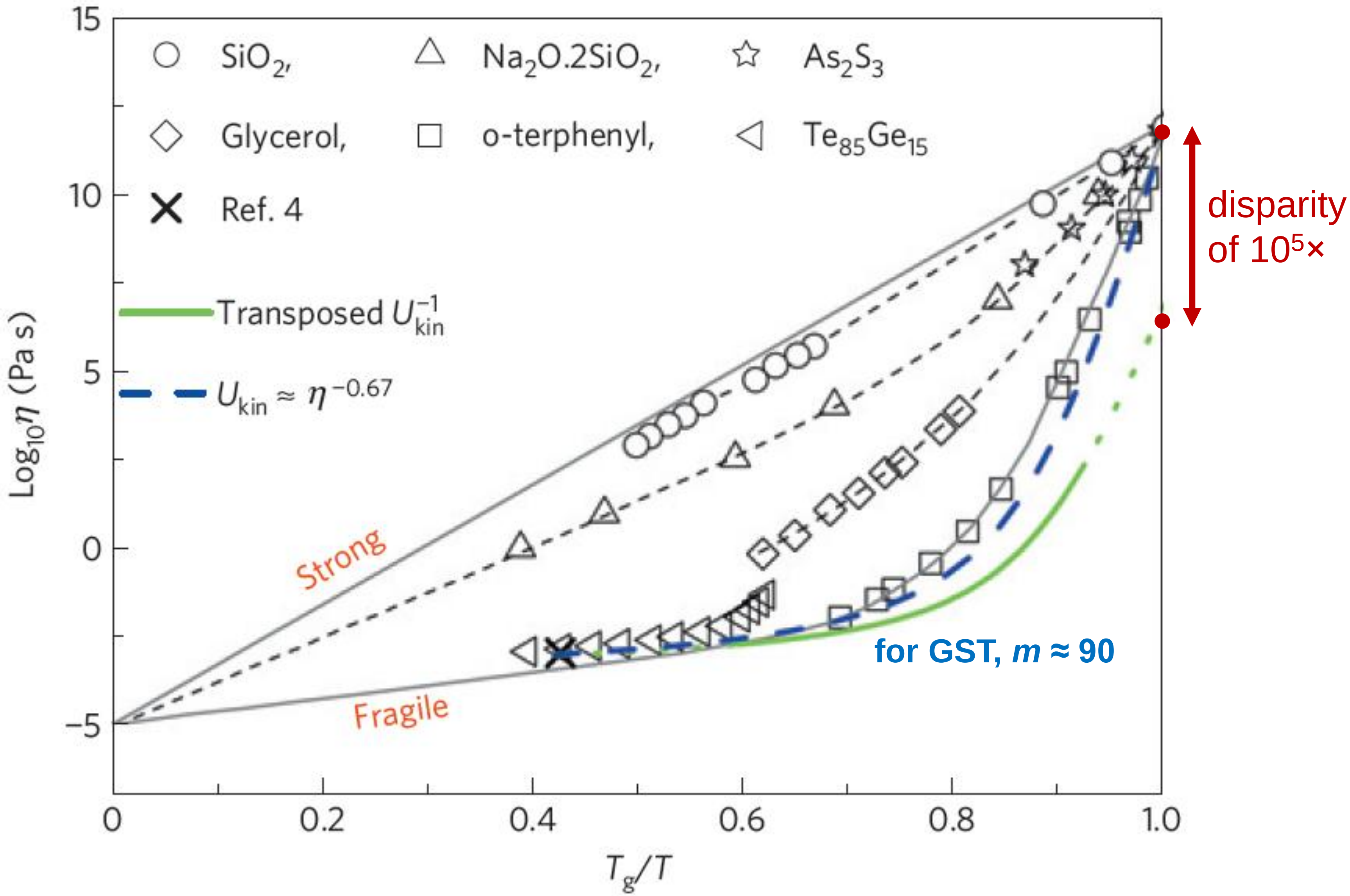
PCM structures with GST

Thermal annealing at *T* < 250ºC gives a high activation energy ($Q \approx 2$ eV)

At higher temperatures the activation energy is much lower



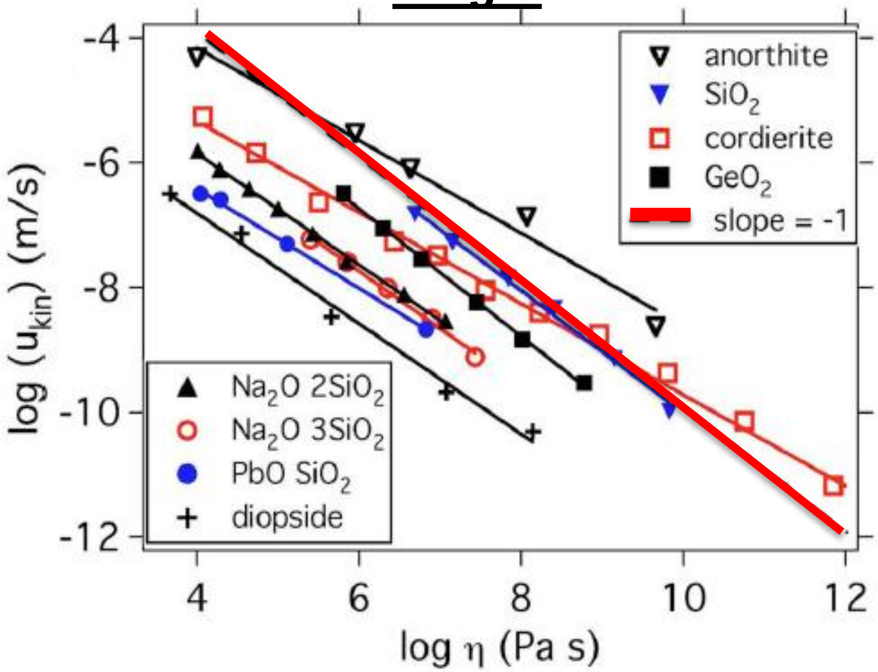
N Ciocchini, M Cassinerio, D Fugazza, D Ielmini: "Non-Arrhenius pulse-induced crystallization in phase change memories" IEEE Conf Proc, 4th IEEE International Memory Workshop (2012) 31.2.1–4.



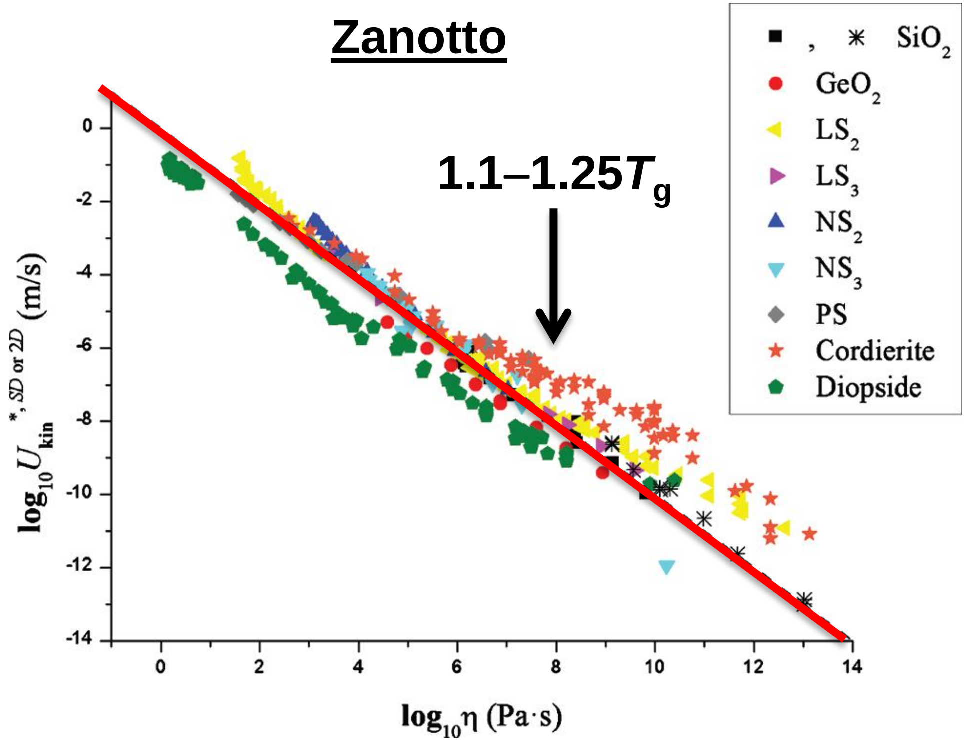
J Orava, AL Greer, B Gholipour, DW Hewak, CE Smith: Characterization of supercooled liquid $Ge_2Sb_2Te_5$ and its crystallization by ultrafast-heating calorimetry, *Nature Mater*. **11** (2012) 279-283.

Crystal growth: decoupling from viscosity

Ediger



Zanotto



$$U = \boxed{U_{\mathrm{kin}}}\left[1-\exp\left(-\frac{\Delta G}{RT}\right)\right]$$

$$U_{\mathrm{kin}} \propto \eta^{-\xi}$$

Breakdown in Stokes-Einstein equation

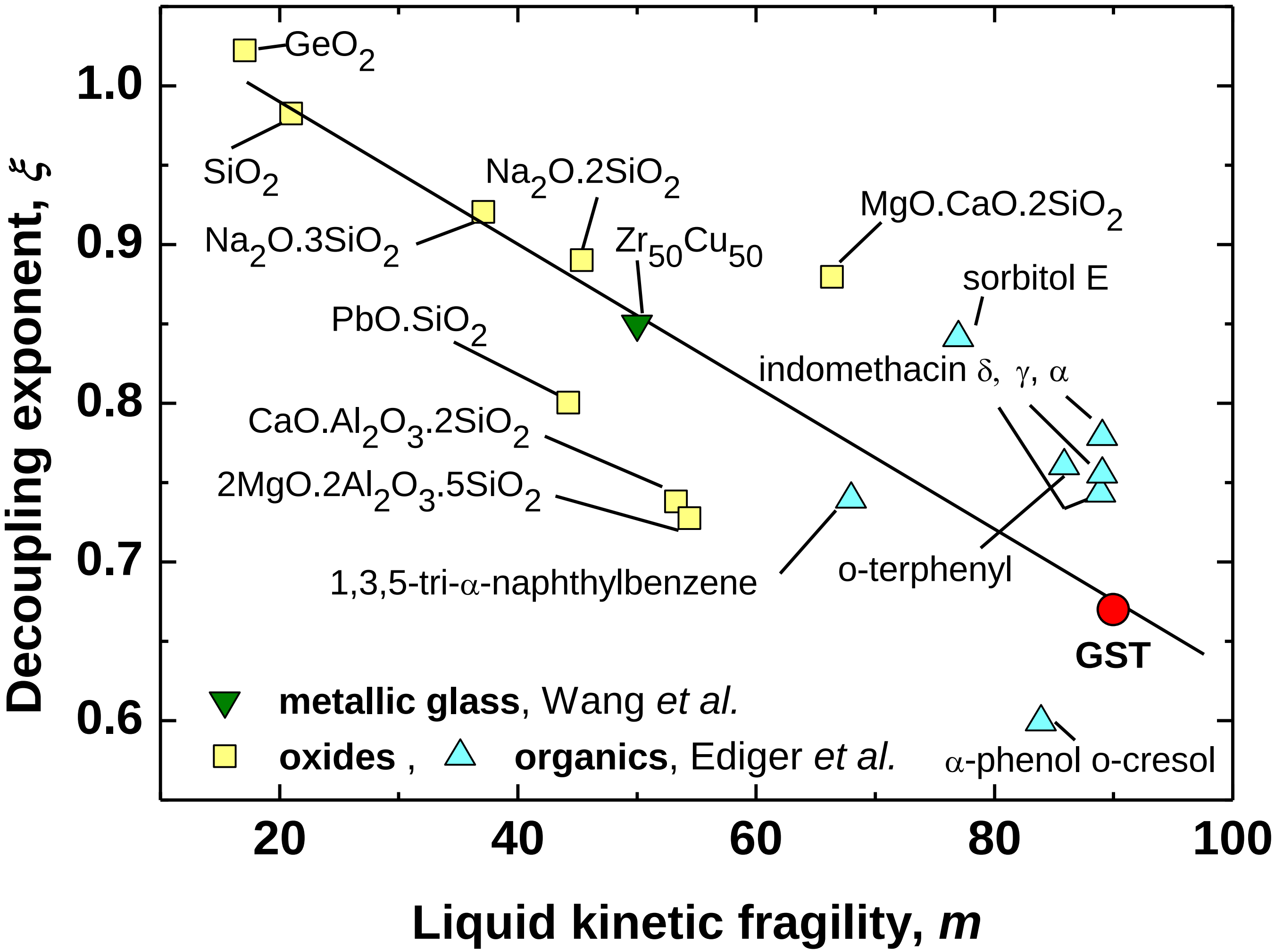
$\eta = k_B T/3\pi a D \quad (U_{\mathrm{kin}} = D/a)$

ξ = 1 no decoupling

$\xi \leq 1$, the value of decoupling parameter ξ is smaller for larger decoupling

Ediger et al. *J Chem Phys* **128** (2008) 034709; Zanotto et al. *J Chem Phys* **133** (2010) 174701.

General picture of decoupling (empirical relation)



just above T_g, the crystal growth rate is much faster than would be predicted from the viscosity

Orava et al. *Nature Mater*. **11** (2012) 279.
Ediger et al. *J. Chem. Phys*. **128** (2008) 034709.
Wang et al. *Phys. Rev. B* **83** (2011) 014202.

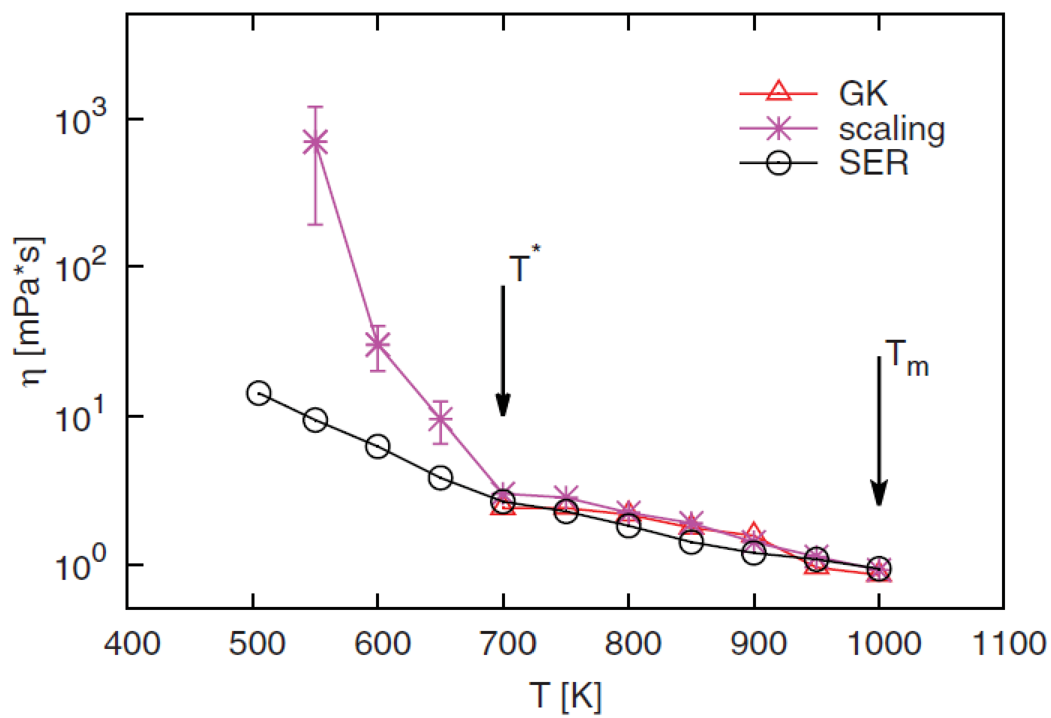
Molecular-dynamics simulations of supercooled liquid GeTe:
— breakdown of the Stokes-Einstein relation

Supercooled liquid GeTe has a high fragility:

m = 104 to 111

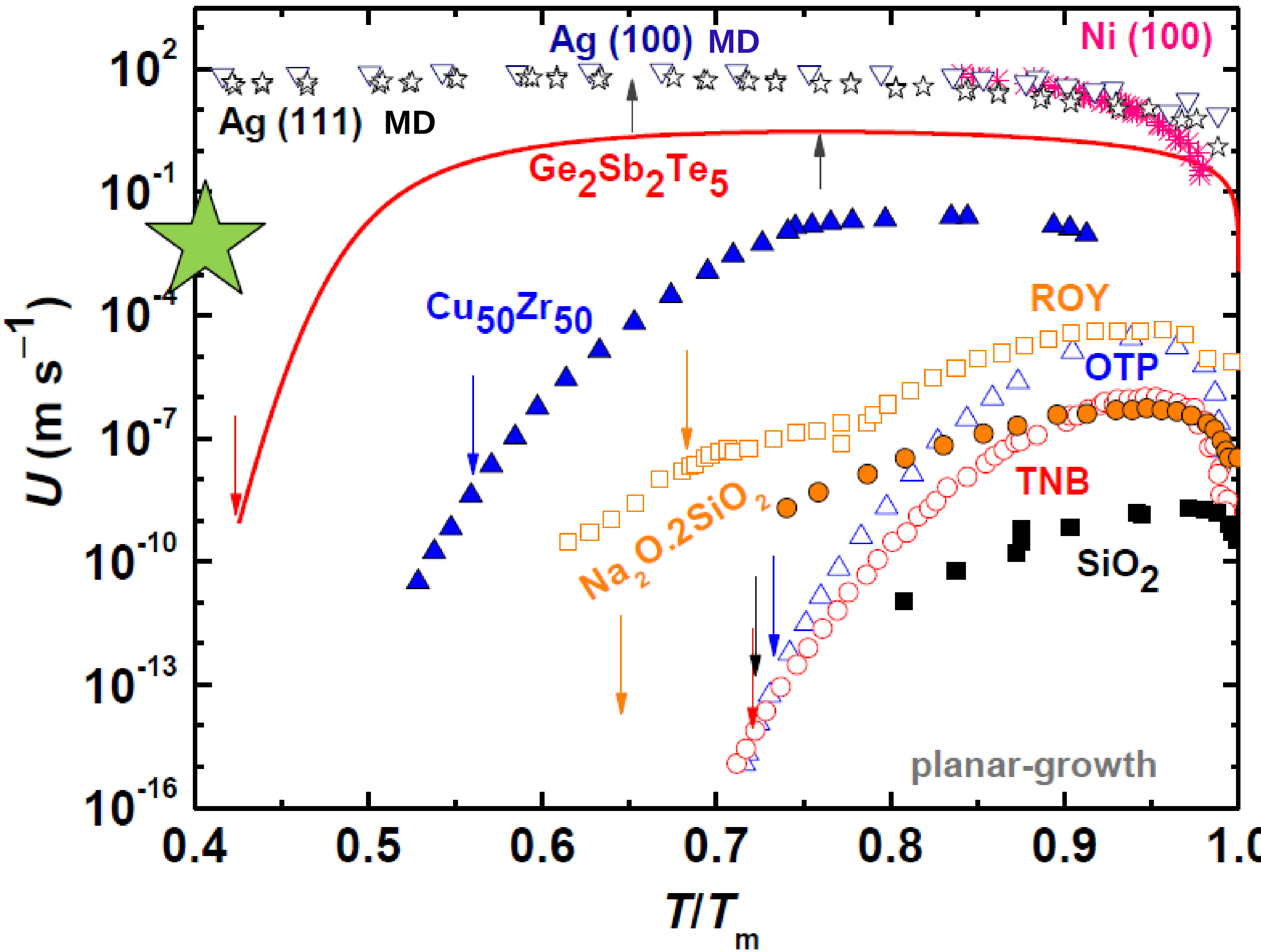
(uncertainty in T_g)

At low temperature, η is some $10^3\times$ greater than would be predicted from the average D



GC Sosso, J Behler, M Bernasconi: “Breakdown of Stokes–Einstein relation in the supercooled liquid state of phase change materials” *Phys. Status Solidi B* **249** (2012) 1880–1885.

Comparison of crystal-growth rates in supercooled liquids



GST lies:

between pure metals and glass-forming alloys

between *diffusion*-limited and *collision*-limited growth

— a largely unexplored area!

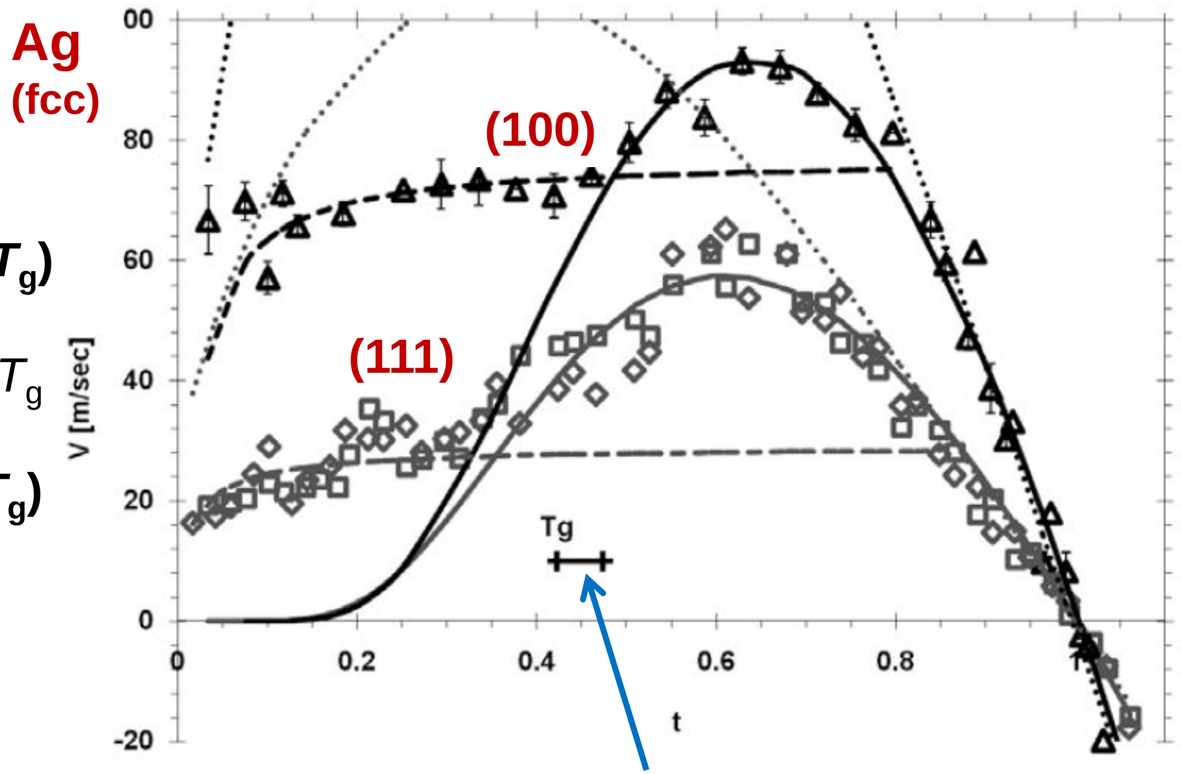
Wang et al. *Phys. Rev. B* **83** (2011) 014202.
Nascimento et al. *J. Chem. Phys*. **133** (2010) 174701.
Ashkenazy et al. *Acta Mater*. **58** (2010) 524. Sun et al. *J. Chem. Phys*. **31** (2009) 074509.

Molecular-dynamics simulations of the freezing of pure metals

Two regimes:

High-temperature ($T>T_g$)
- thermally activated
- maximum in U above T_g

Low-temperature ($T<T_g$)
- athermal (very low activation energy)



T_g is in just the same range for GST

Y Ashkenazy, RS Averback: " Kinetic stages in the crystallization of deeply undercooled body-centered-cubic and face-centered-cubic metals"
Acta Mater **58** (2010) 524–530.

Can pure metals form true glasses?

- generally considered that pure metals cannot form glasses
- metallic liquids have low viscosity
- metallic crystal structures are simple and easily formed
- amorphous metals can be formed by quench condensation (vapour deposition onto substrates) but they soon crystallize on heating:

Crystallization of quench-condensed amorphous metals:
Many studies, including:

W Buckel & R Hilsch: Einfluss der Kondensation bei tiefen Temperaturen auf den elektrischen Widerstand und die Supraleitung für verschiedene Metalle, *Z. Phys.* **138** (1954) 109-129.

KH Behrndt: Formation of amorphous films, *J. Vac. Sci. Technol*. **7** (1970) 385-398.

W Felsch: Schichten aus amorphem Eisen, *Z. Phys.* **195** (1966) 201-214.

C Markert, D Lützenkirchen-Hecht, R Wagner & R Frahm: In situ surface-sensitive X-ray investigations of thin quench condensed bismuth films, *EPL,* **86** (2009) 46007.

Crystallization of quench-condensed amorphous metals:

- semi-metals (Bi & Ga) do form amorphous deposits at 4.2 K, but ..
- .. their crystallization temperatures are very low (14–25 K)

- crystallization temperatures are higher for thinner films
- amorphous Bi, 6 nm thick has T_x as high as 42 K

- ccp metals don’t form amorphous films at all, without some alloying/impurities

- amorphous Fe crystallizes as low as 3.3 K, but ..
- .. can be stabilized up to 300 K by impurities

These results have been taken to mean that, even if a glassy pure metal could be formed by ultra-rapid quenching, it would have very limited stability,   BUT ….

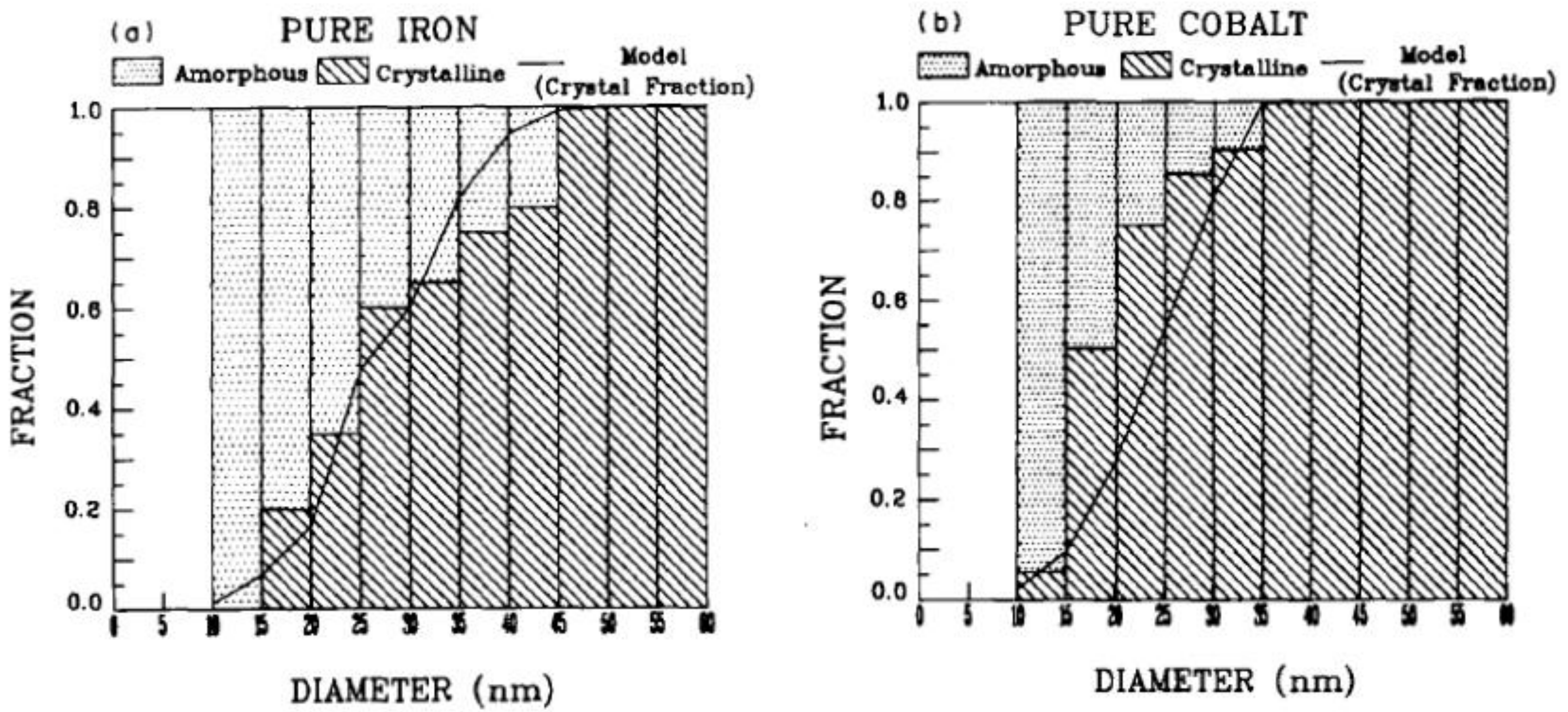
Electrohydrodynamic atomization of liquid pure metals in vacuum

- gives droplets 2 nm to 100 μm in diameter
- radiative cooling, containerless solidification
- a 60 μm droplet would encounter only 1 gas molecule in critical cooling range
- crystal nucleation is difficult (no substrate, clean, small volume)
- some partially or fully glassy spheres were found for a wide range of elements: Co, Fe, Ge, Mo, Nb, Ni, Ta, Ti, V, W, Zr

YW Kim, HM Lin & TF Kelly: Solidification structures in submicron spheres of iron-nickel alloys: Experimental observations, *Acta Metall.* **36** (1988) 2525-2536.

YW Kim, HM Lin & TF Kelly: Amorphous solidification of pure metals in sub-micron spheres, *Acta Metall.* **37** (1989) 247-255.

YW Kim & TF Kelly: The solidification structures in submicron droplets of Fe-Co alloys, *Acta Metall. Mater.* **39** (1991) 3237-3249.

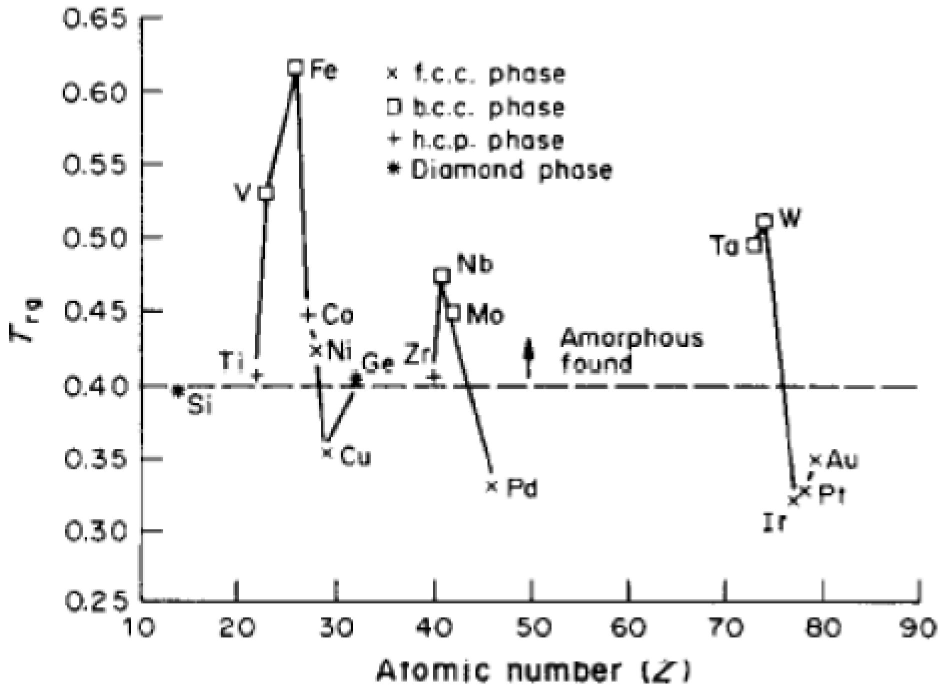


• spheres of Fe have a 50:50 chance of being glassy for ~ 30 nm diam

• for 30 nm Co spheres, the critical cooling rate for glass formation ≈ 10^7 K s^{-1}

Suggested reduced glass-transition temperatures,
$T_{rg} = T_g/T_m$ →

Suggested T_g for Ni is 732 K



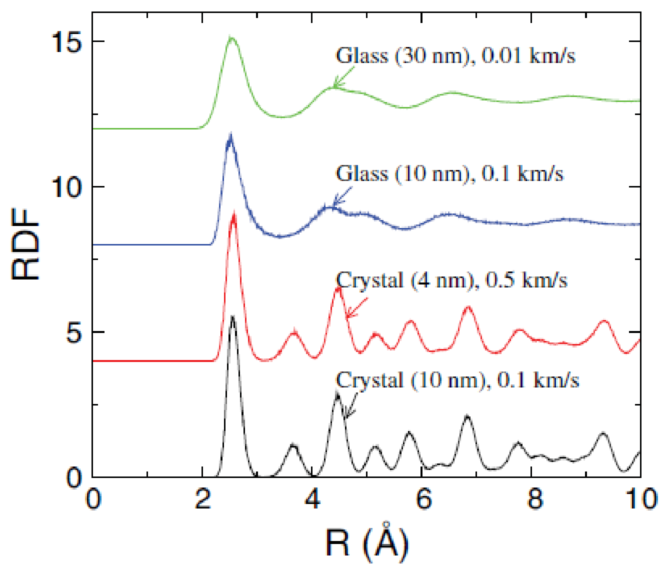
From MD for liquid Ni, Rodriguez & Soler suggest $T_g \approx 750$ K

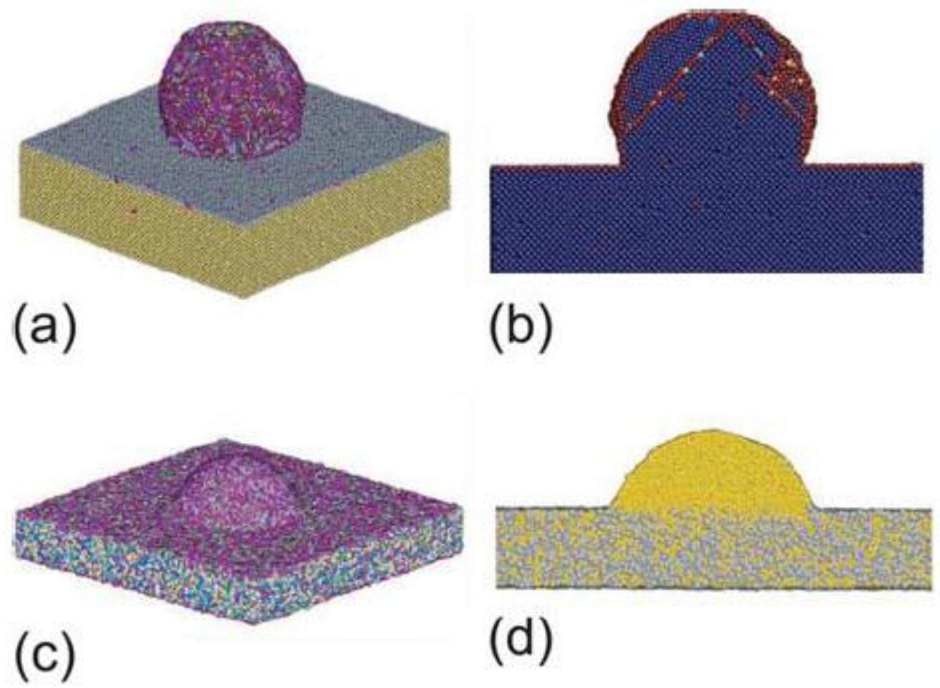
YW Kim, HM Lin & TF Kelly: Amorphous solidification of pure metals in sub-micron spheres, *Acta Metall.* **37** (1989) 247-255.

O Rodríguez de la Fuente & JM Soler: Structure and stability of an amorphous metal, *Phys. Rev. Lett.* **81** (1998) 3159-3162.

MD simulations of the quenching of 30 nm droplets (10^6 atoms) of liquid pure Cu onto a solid amorphous Cu-Zr substrate:

— quenching at 10^{12} to 10^{13} K s^{-1} gives fully glassy deposits, stable to >600 K





Q An, SN Luo, WA Goddard, WZ Han, B Arman & WL Johnson:
Synthesis of single-component metallic glasses by thermal spray of nanodroplets on amorphous substrates,
Appl. Phys. Lett. **100** (2012) 041909.

Can pure metals form true glasses?

How can these results on formation of stable glasses be reconciled with the results on quench-condensed films?

nature materials

ARTICLES

PUBLISHED ONLINE: 6 JANUARY 2013 | DOI: 10.1038/NMAT3521

Ultrastable glasses from *in silico* vapour deposition

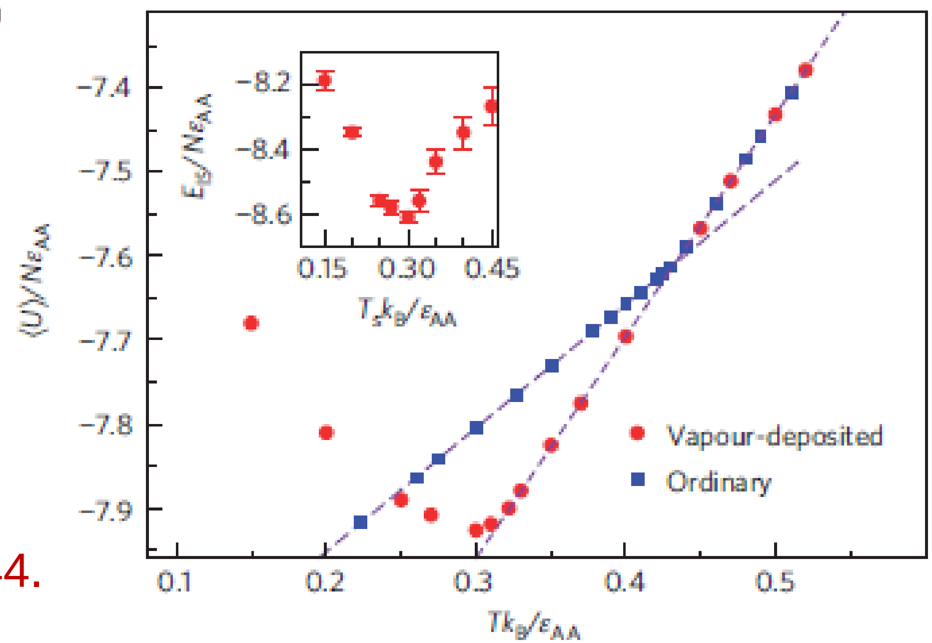
Sadanand Singh[1], M. D. Ediger[2] and Juan J. de Pablo[1,3,4]*

Glasses are generally prepared by cooling from the liquid phase, and their properties depend on their thermal history. Recent experiments indicate that glasses prepared by vapour deposition onto a substrate can exhibit remarkable stability, and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. Here we create ultrastable glasses by means of a computer-simulation process that mimics physical vapour deposition. These stable glasses have, far below the conventional glass-transition temperature, the properties expected for the equilibrium supercooled liquid state, and optimal stability is attained when deposition occurs at the Kauzmann temperature. We also show that the glasses' extraordinary stability is associated with distinct str

and the relative lack of irregular polyhedra.

binary mixture of LJ particles

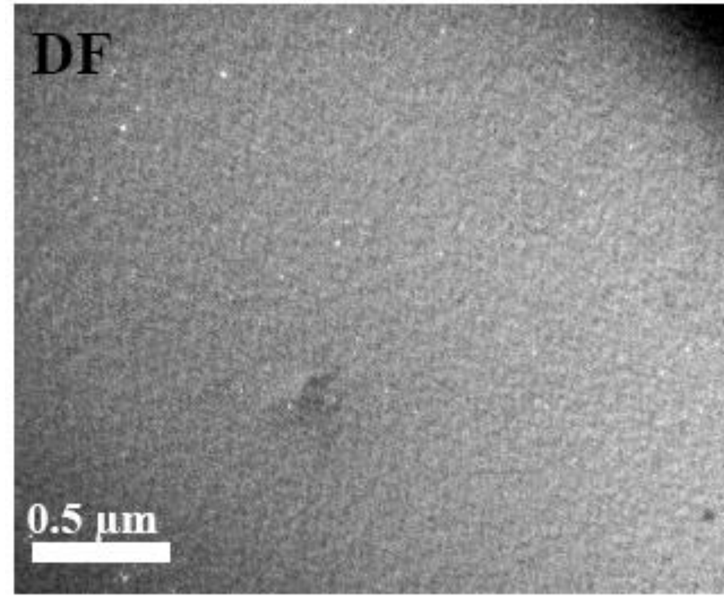
potential energy

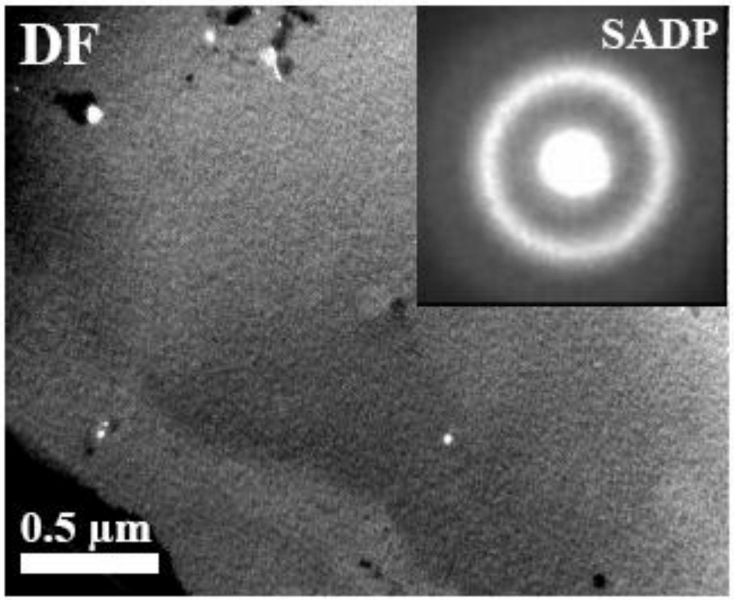


Nature Mater. **12** (2013) 139-144.

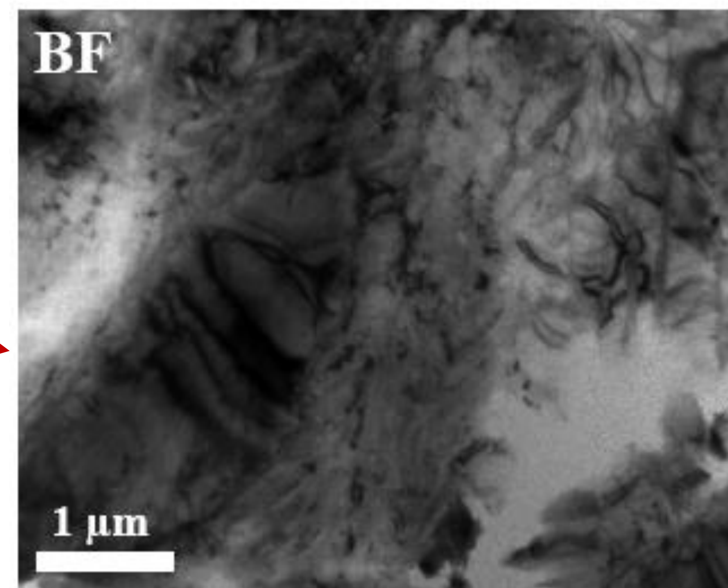
Plastic deformation of metallic glass $Zr_{55}Al_{10}Cu_{30}Ni_5$

shot-peening at room temp.
→ AMORPHIZATION



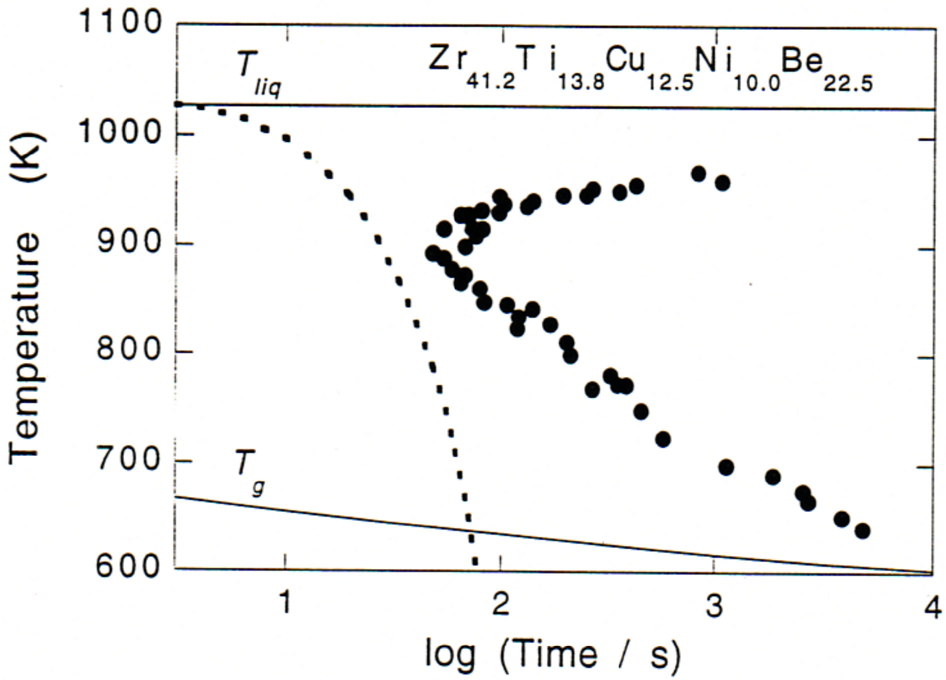


shot-peening at 77 K
→ CRYSTALLIZATION



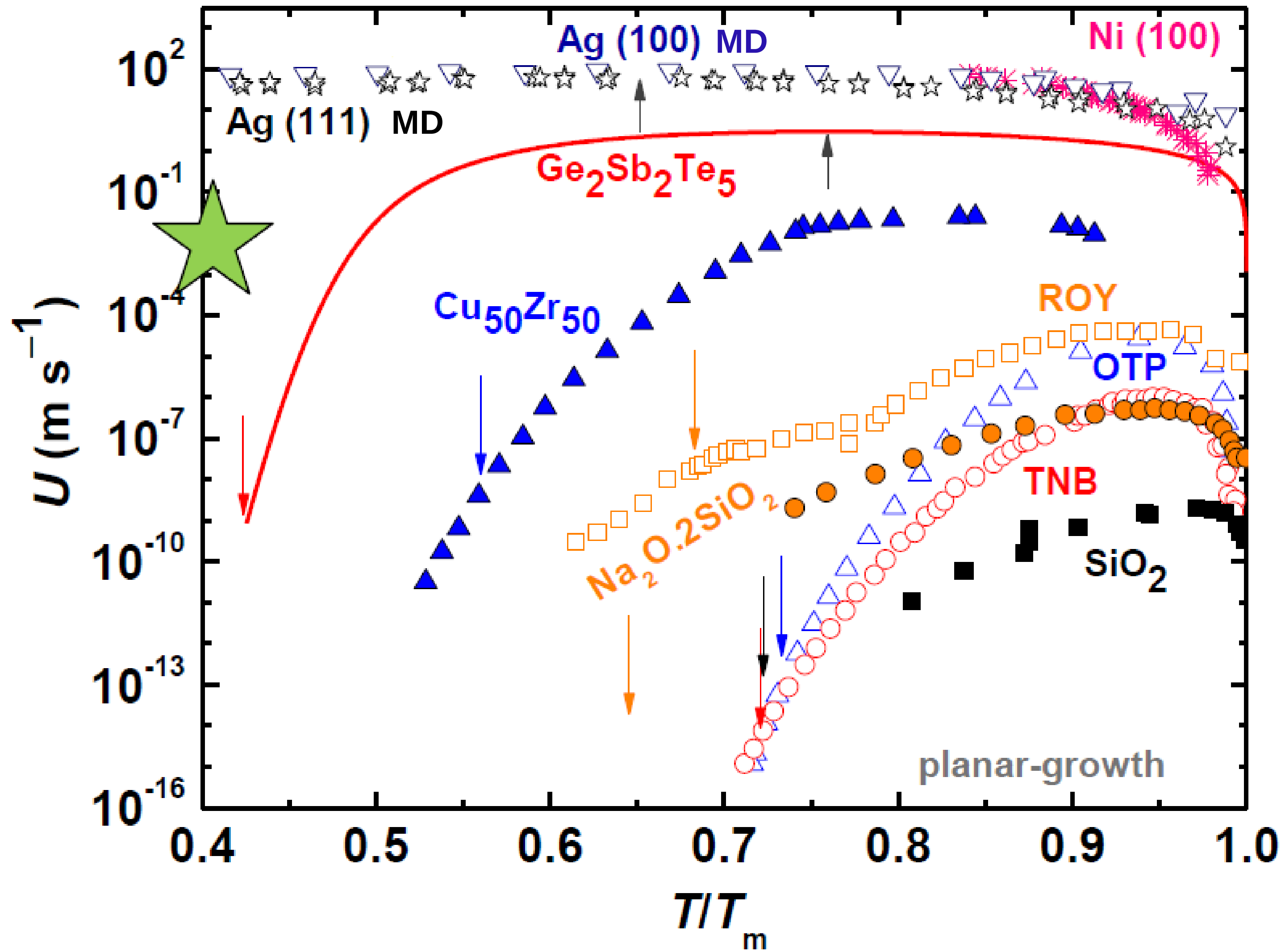
FO Méar, B Doisneau, AR Yavari, AL Greer: Structural effects of shot-peening in bulk metallic glasses, *J. Alloys Comp.* **483** (2009) 256-259.

Bulk Metallic Glasses



- multicomponent compositions aid glass formation
- the critical cooling rate is low (~1 K s^{-1})
- glasses can be formed in bulk
  (maximum diameters mm up to a few cm)

Comparison of crystal-growth rates in supercooled liquids



Wang et al. *Phys. Rev. B* **83** (2011) 014202.
Nascimento et al. *J. Chem. Phys*. **133** (2010) 174701.
Ashkenazy et al. *Acta Mater*. **58** (2010) 524. Sun et al. *J. Chem. Phys*. **31** (2009) 074509.

Fast transformers

The pronounced temperature dependence of crystal-growth speed in phase-change materials not only rationalizes their favourable characteristics for non-volatile memory applications, but also suggests a profound new insight into their fundamental properties.

Matthias Wuttig and Martin Salinga

Unravelling the mysteries of chocolate making, comprehending the formation of amethyst geodes, or producing advanced steels requires an understanding of the relevant crystallization phenomena. Phase-change materials pose a similar challenge. They can be rapidly and reversibly switched between the amorphous and crystalline states, which is accompanied by a significant change of their optical and electrical properties[1]. This renders these materials suitable for optical and electronic data-storage applications that require the structural transformation to occur extremely rapidly once the material is heated to sufficiently high temperatures. In a study of the crystallization dynamics at ultrahigh heating rates, reported in *Nature Materials*, Jiri Orava and colleagues now provide a new insight into our understanding of these fast transformations in phase-change materials that make them so attractive for memory devices[2].

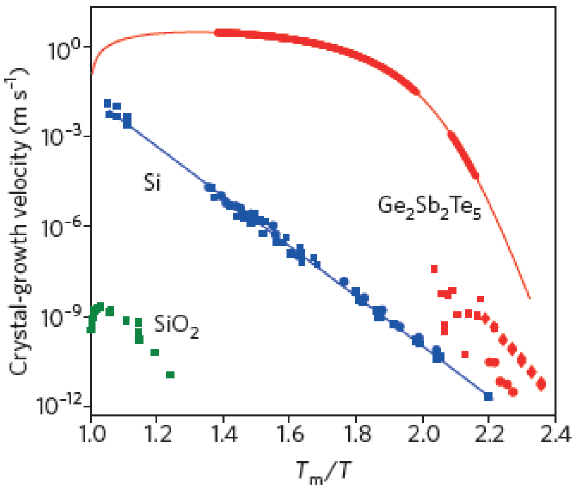


Figure 1 | Crystal-growth speeds. In comparison to the behaviour of Si (ref. 10) and SiO_2 (ref. 11), which show a temperature-independent activation energy for crystal growth, phase-change materials such as $Ge_2Sb_2Te_5$ show a very different, fragile behaviour. The red squares[12], circles[13] and diamonds[14] show results from earlier experiments at lower temperatures.

pulse is utilized to enable fast crystallization. Although these experiments have demonstrated that crystallization indeed can be completed within a few nanoseconds,

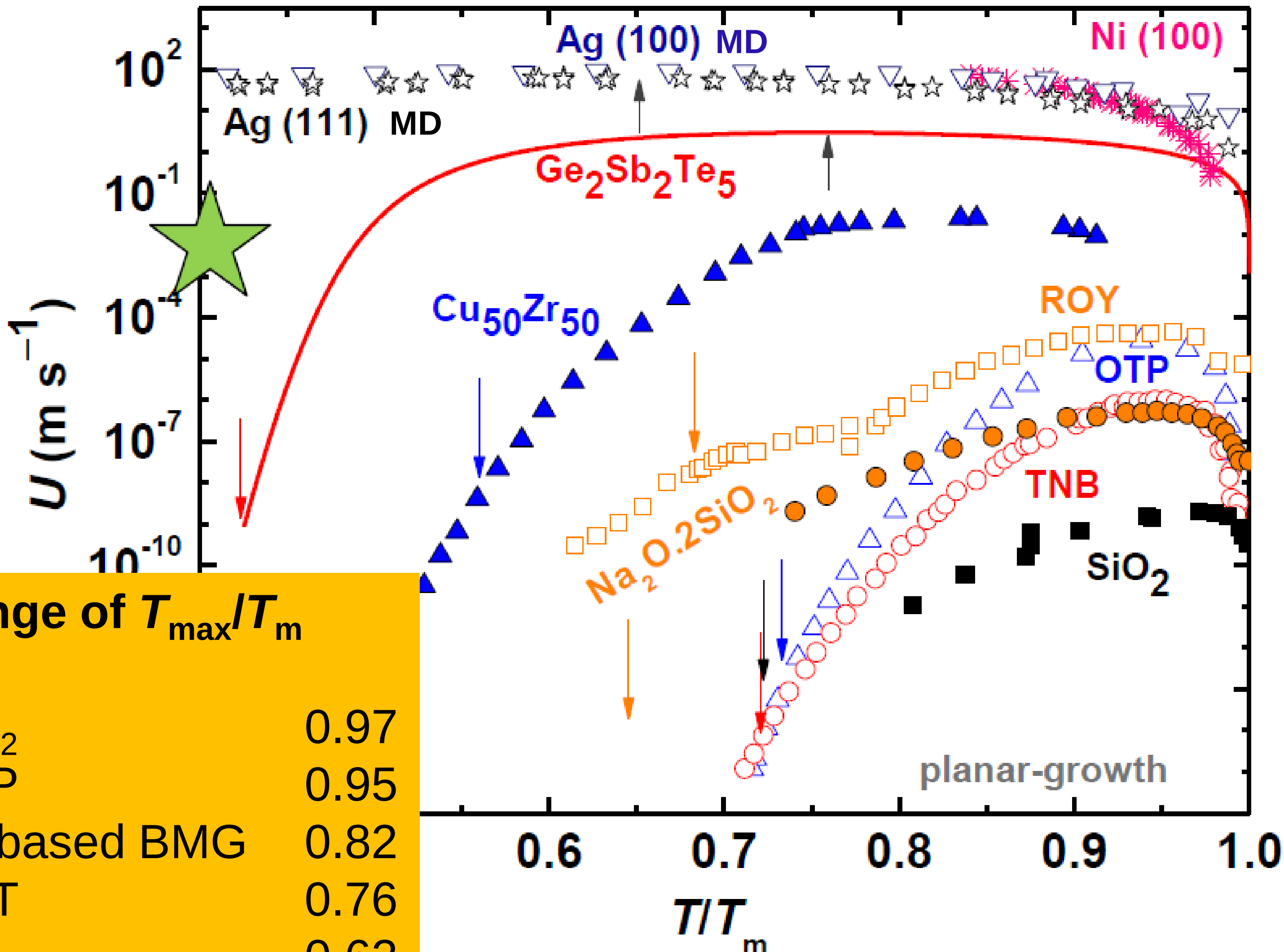
"…. one can wonder if non-volatile memories employing phase change materials could also be realized with well-known materials such as Si or GaAs ….”

M Wuttig, *Phys. Status Solidi B* **249** (2012) 1843–1850.

differential scanning calorimetry (DSC), which measures the energy required to heat a sample. In comparison to existing designs, here they utilize an ultrafast-heating calorimeter that enables heating rates of

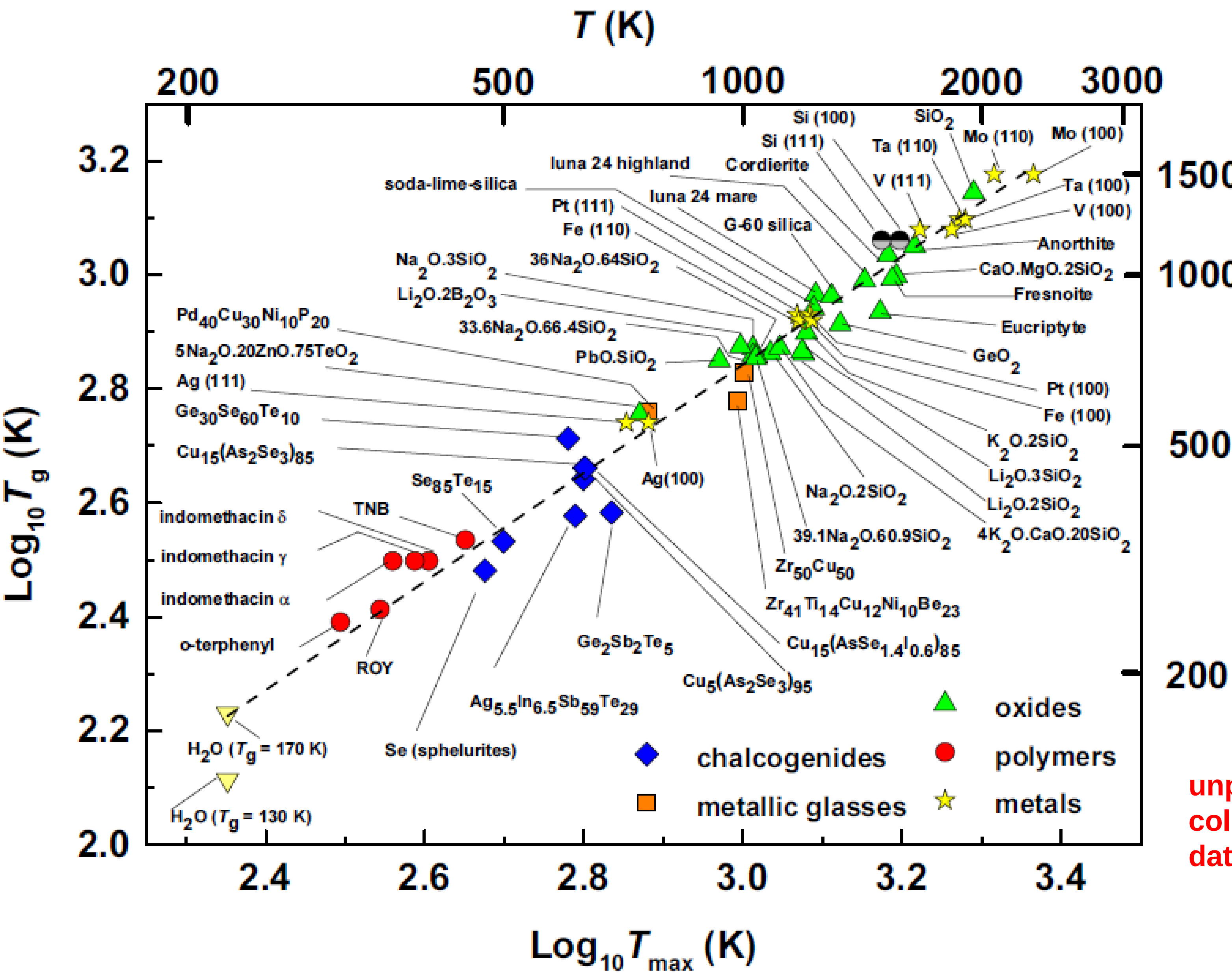
Nature Materials **11** (2012) 270-271 (News & Views)

Comparison of crystal-growth rates in supercooled liquids

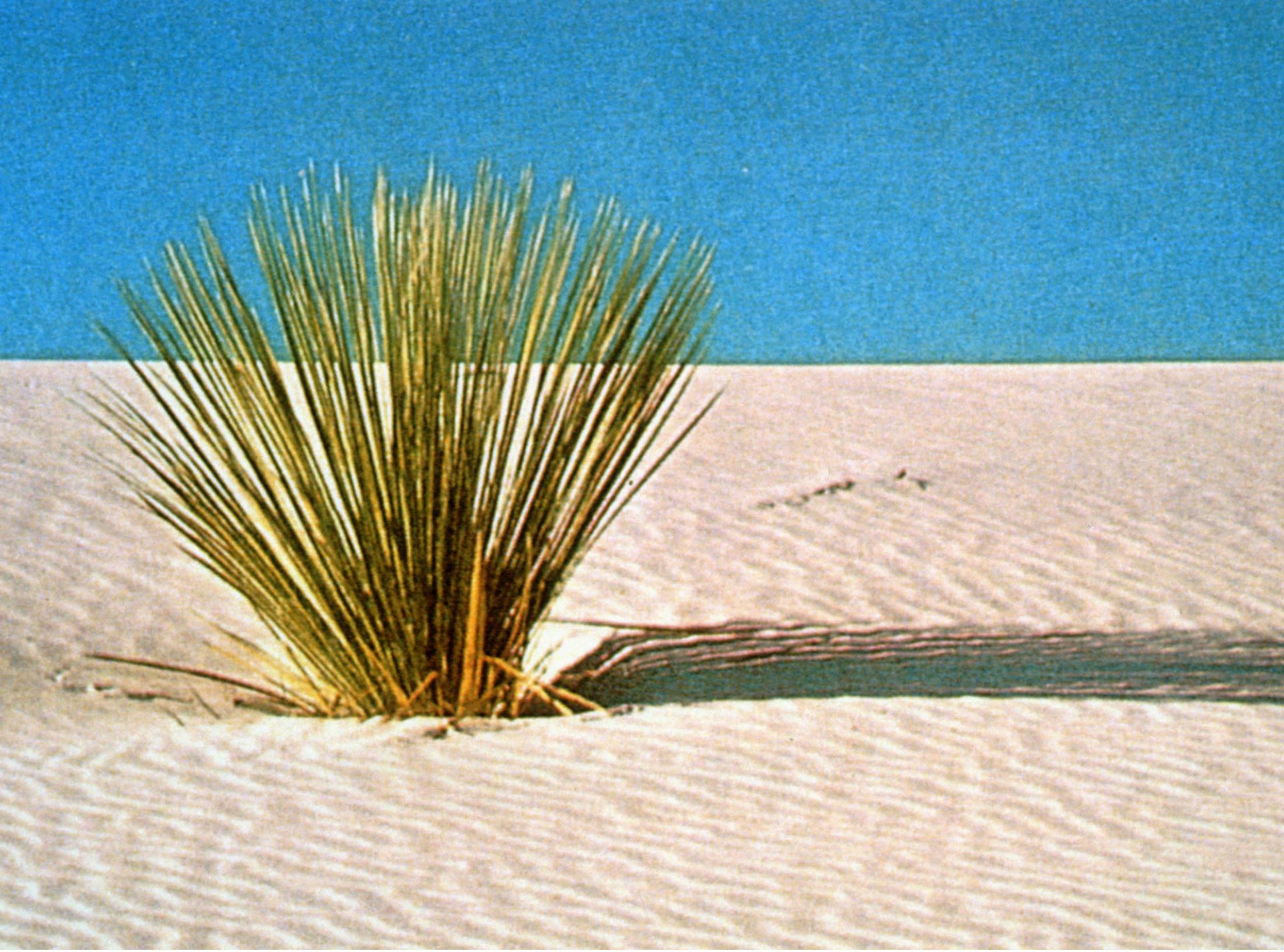


Range of T_{max}/T_m	
SiO_2	0.97
OTP	0.95
Pd-based BMG	0.82
GST	0.76
Ag	0.62
Ta	0.55

Wang et al. *Phys. Rev. B* **83** (2011) 014202.
Nascimento et al. *J. Chem. Phys*. **133** (2010) 174701.
Ashkenazy et al. *Acta Mater*. **58** (2010) 524. Sun et al. *J. Chem. Phys*. **31** (2009) 074509.

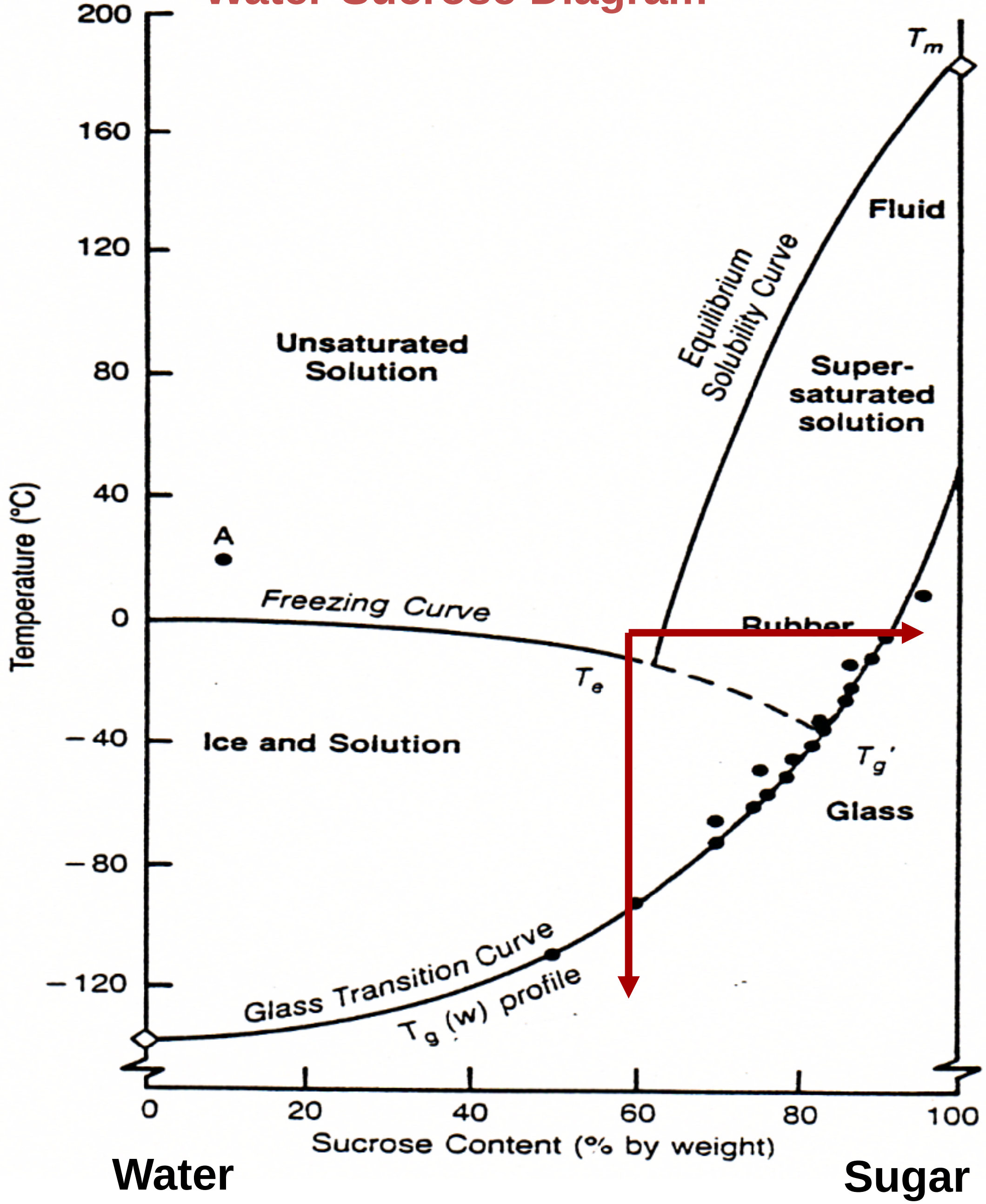


unpublished collection of data



***Turbellaria* flatworms**
— primitive, no respiratory or circulatory systems

Water-Sucrose Diagram



— shows key points about avoiding crystal formation (ice or sugar or salts) in cells

- crystal formation is replaced by formation of a sugar-based glass
- need dehydration and/or cooling

Northern Wood Frog
Rana sylvatica

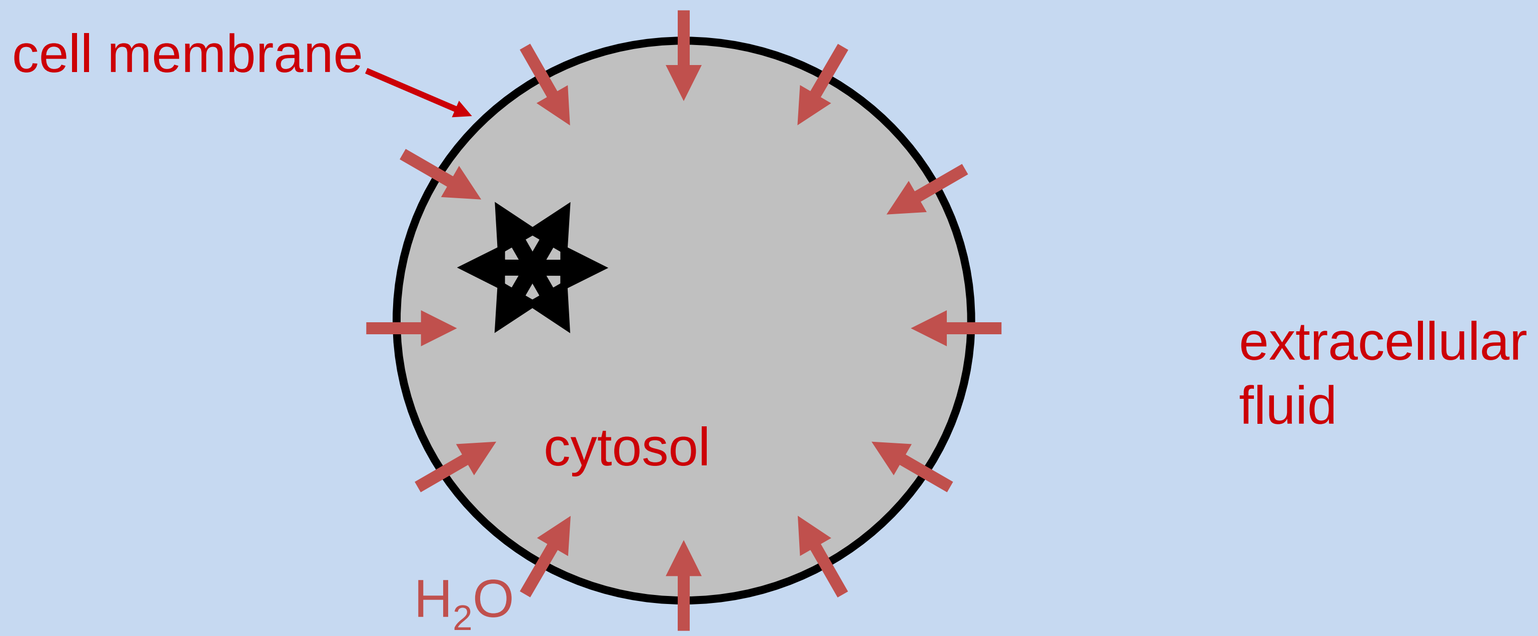
— the only frog found north of the Arctic circle

— when frozen, the frog’s breathing, blood flow and heartbeat stop

Ice formation inside a cell

— is fatal

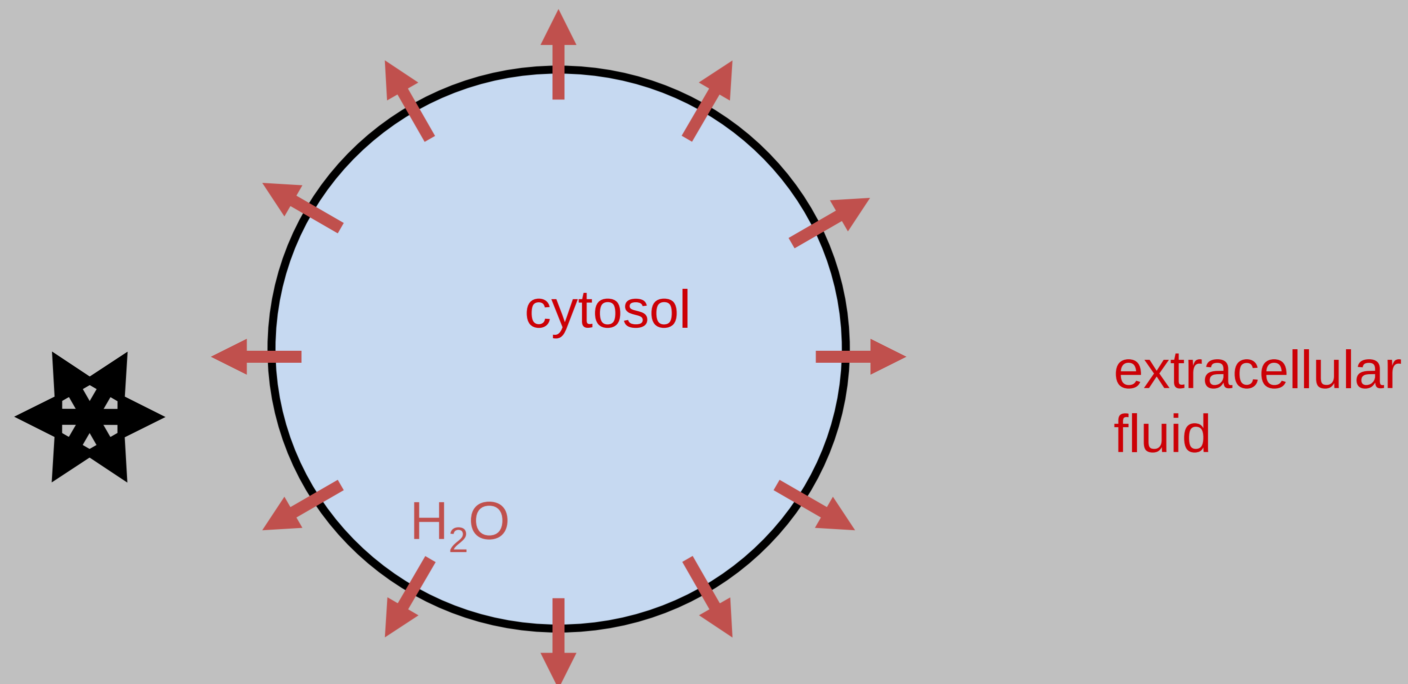
- the salt concentration rises in the remaining cytosol
- water is drawn into the cell by osmosis from the extracellular fluid
- the cell continues to swell and eventually bursts



Ice formation in the extracellular fluid

— is beneficial

- the salt concentration rises in the extracellular fluid
- water is drawn from the cell by osmosis from the extracellular fluid
- the cell shrinks and the cytosol is dehydrated into a sugar glass



It is of interest for:

- *Rana sylvatica*
- pharmaceutical industry
- medical science

— to know more about the strength or fragility of liquids forming glasses by dehydration (and glasses into liquids on rehydration)

GM Fahy, DR MacFarlane, CA Angell, HT Meryman:

Vitrification as an approach to cryopreservation,

Cryobiology **21** (1984) 407–426.

Best wishes to Austen (angell, not fragyll) on his 80th!

Many happy returns of the day…

Thanks to Austen for stimulating such fruitful fields of research

We look forward to a very successful Fragility Symposium

— and also to many happy returns of the event!