Lehigh University
Lehigh Preserve

US-Japan Winter School

Semester Length Glass Courses and Glass Schools

Winter 1-1-2008

# Lecture 10, Part 2: Engineered strengthening of glass

Tanguy Rouxel
*Universite de Rennes, France*

Follow this and additional works at: https://preserve.lehigh.edu/imi-tll-courses-usjapanwinterschool

Part of the Materials Science and Engineering Commons

## Recommended Citation

Rouxel, Tanguy, "Lecture 10, Part 2: Engineered strengthening of glass" (2008). *US-Japan Winter School*. 29.
https://preserve.lehigh.edu/imi-tll-courses-usjapanwinterschool/29

This Video is brought to you for free and open access by the Semester Length Glass Courses and Glass Schools at Lehigh Preserve. It has been accepted for inclusion in US-Japan Winter School by an authorized administrator of Lehigh Preserve. For more information, please contact preserve@lehigh.edu.

# Designing glasses to meet specific mechanical properties

**Tanguy ROUXEL**
LARMAUR, FRE-CNRS 2717, Université de Rennes 1

- Introduction: The Scales of Concern
- Elastic Moduli And The Short To Medium Range Order In Glass
- Hardness And Indentation Behavior

Strength of simply annealed window glass ~ 45 MPa CEN EN 572-2

Strength of heat strengthened float glass ~ 70 MPa CEN EN 1863-2

Strength of coated float glass ~ 120 MPa CEN EN 12150-2

Strength of tempered glass ~ 150 to 250 MPa

Strength of ion-exchanged glass ~ 450 to 750 MPa

Theoretical strength ~ 10 to 15 GPa!

Young's modulus of window glass ~ 72 MPa

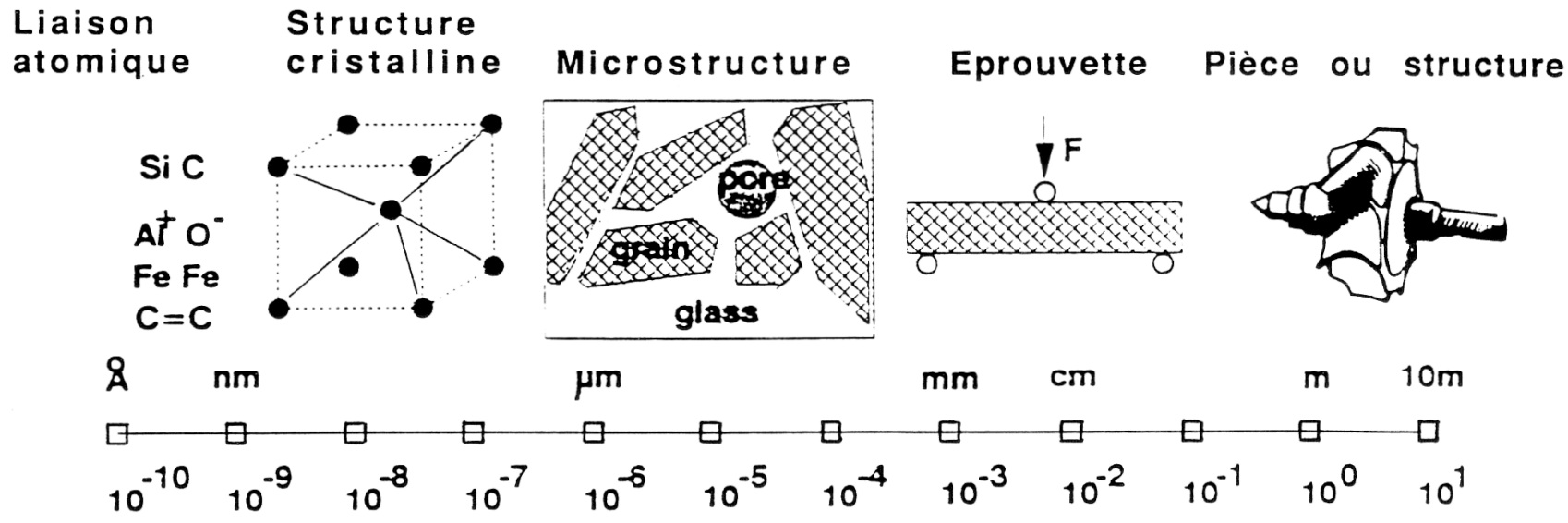
No change since the 17$^{th}$ century!

*J.T. Littleton said « We never test the strength of glass: all we test is the weakness of its surface » (1941)*
*F.W. Preston added, « We do not test the properties of the glass at all, but only those of the surrounding atmosphere »*

*(J. App. Phys. 13, [10], 623-634 (1942))*

***There is much room for improvement!***

# Typical multiscale approach in mehanical design

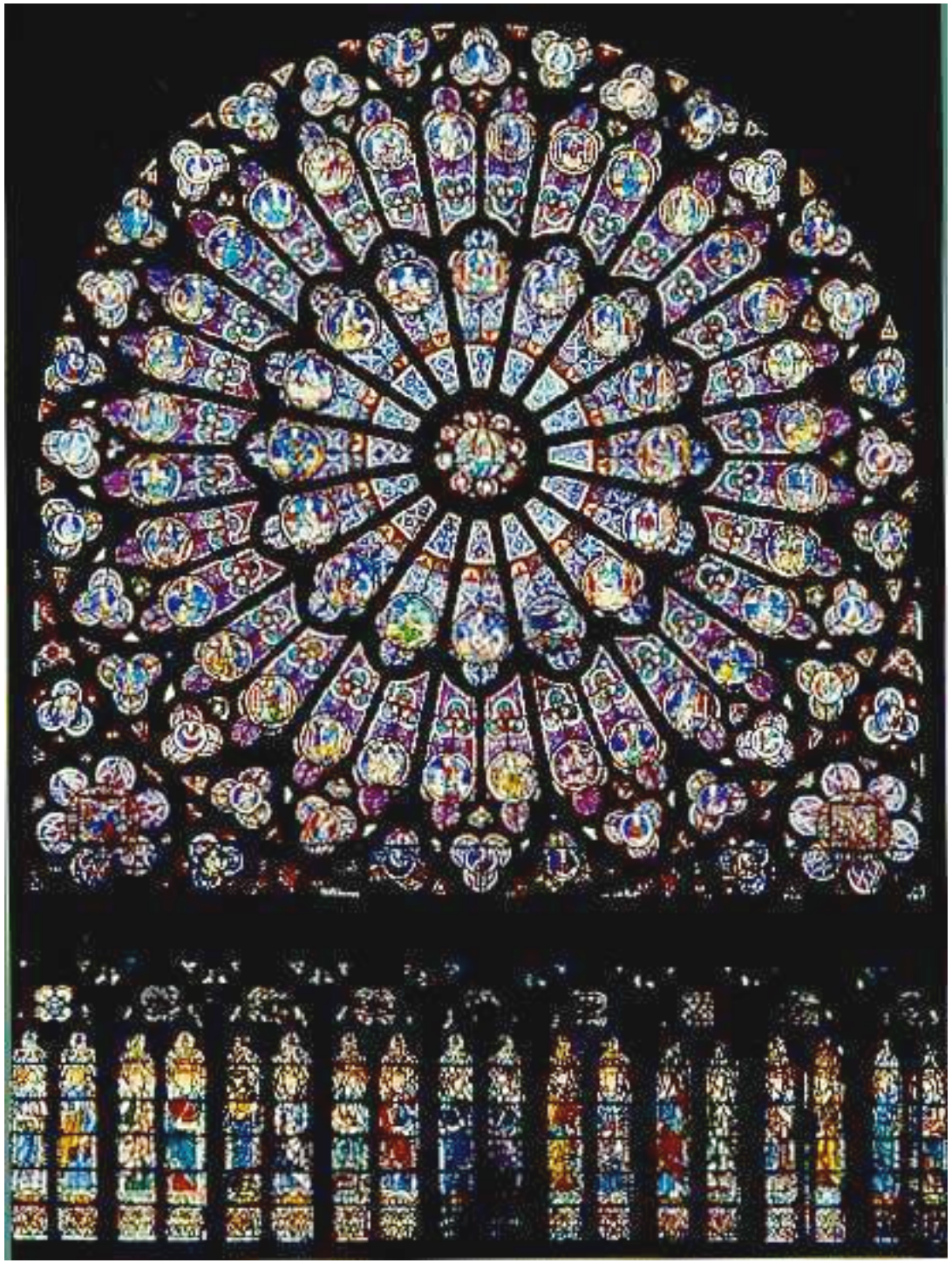



Chemical-Physics

Mechanical behavior (constitutive law)

Modelling (FEM) - Application

**Q1: Can we applied this approach to glass parts?**
**Q2: What for? Since glass is mostly not bearing the load!**



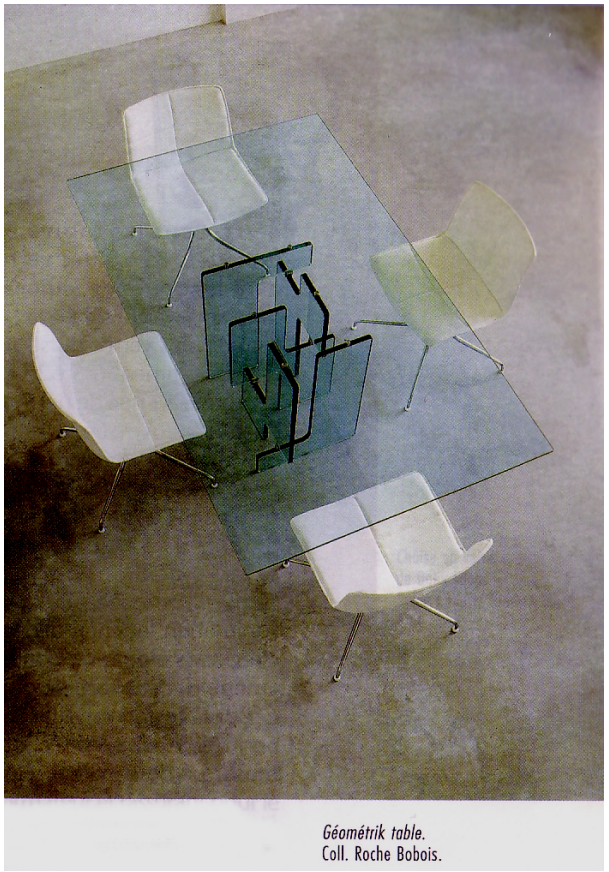
*Cathedral of Notre Dame, Paris*

Glass has played an important role in architecture as the material that opens up a building to light

Considered functions: transparency, aesthetics, insulation

Major drawback: glass windows weaken the structure

*Grandes Serres of "La cité des sciences et de l'industrie" at la Villette (Paris)*



*Géométrik table.*
Coll. Roche Bobois.

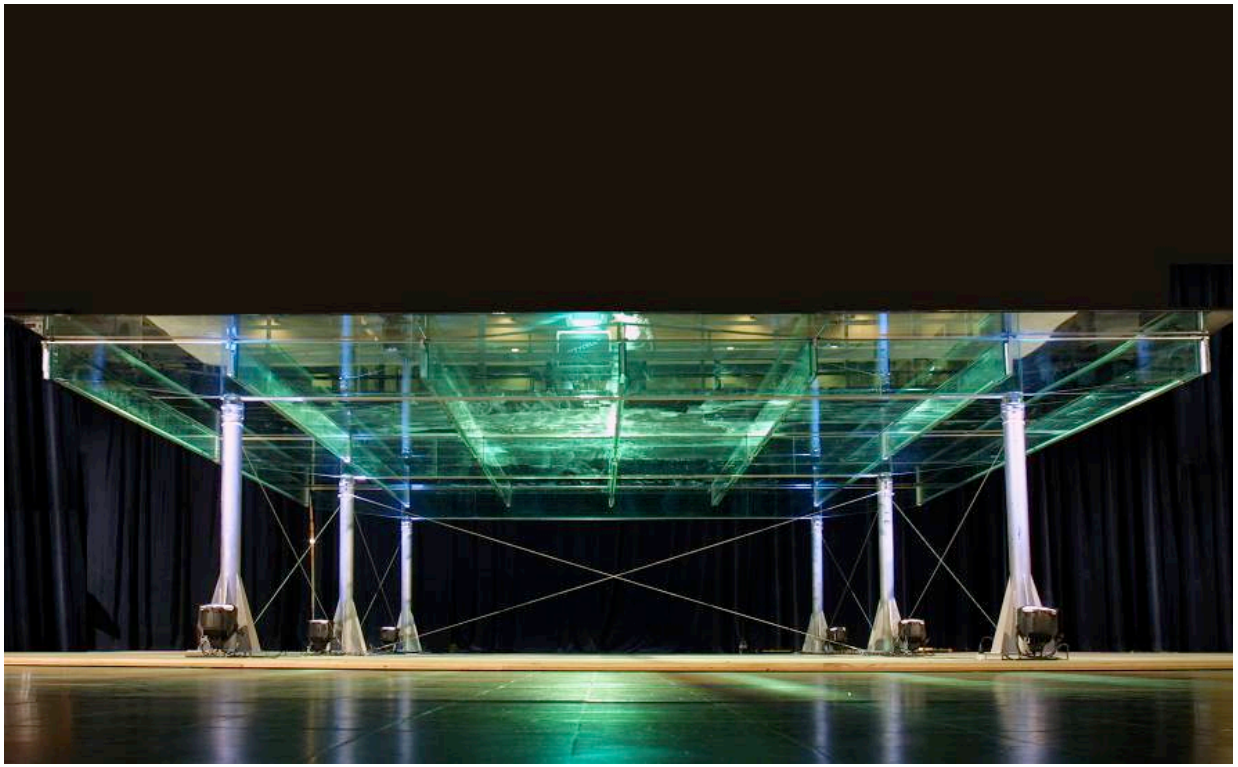
Although glass appeared to take a leading role it was still only a material that separated the interior and exterior untill some twenty years ago when loaded glass sheets started to be used in large structures

*Apple store, New York*

*TU Delft project of a beam-shape aquarium*

*(Courtesy F.A. Veer, TU Delft, Netherlands)*

*TU Delft all glass paviljon 2004*

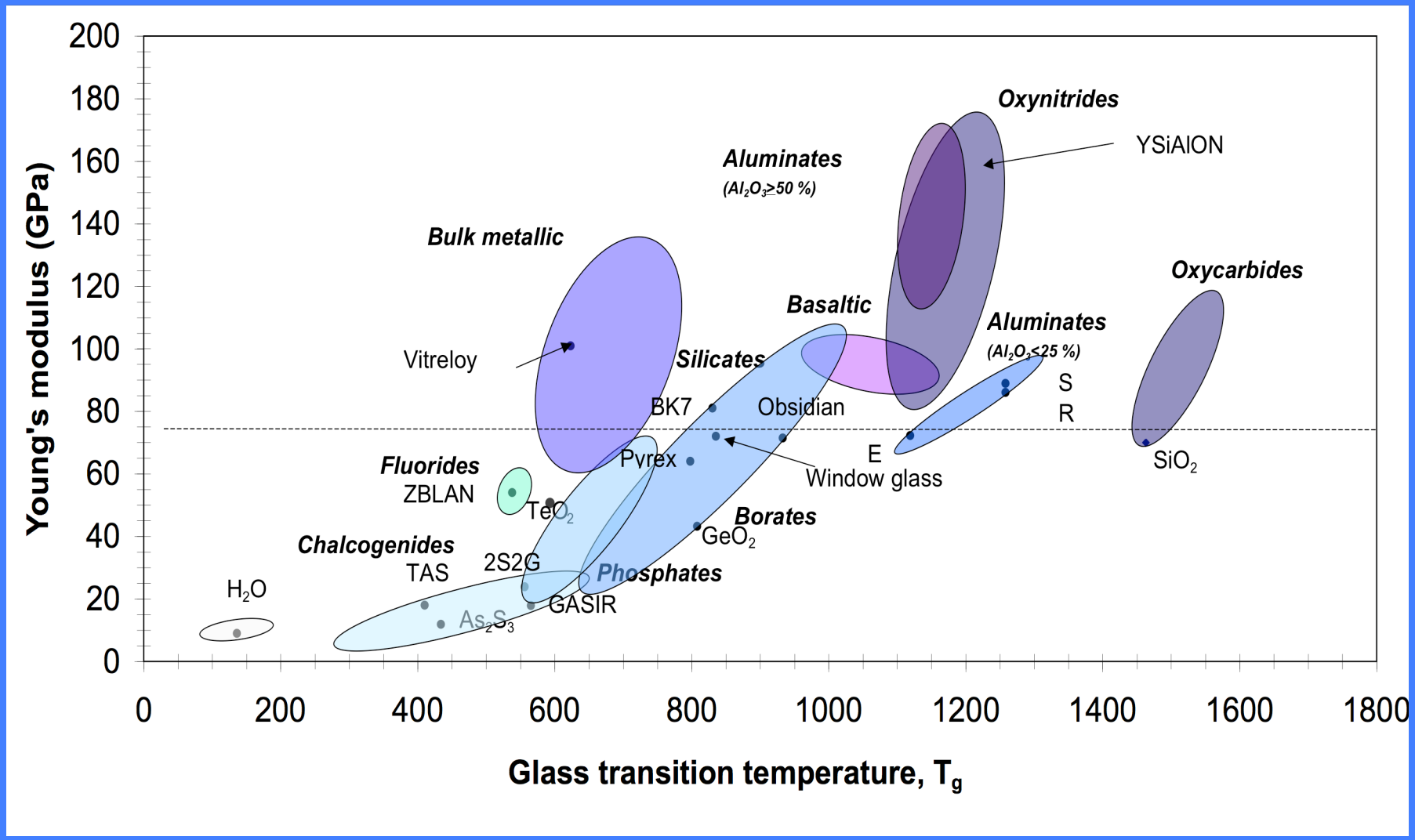


Q: How far can we go?

# I. Elasticity

**Search for glasses possessing high elastic moduli:**

- Increase computer hard disk rotating speed
- Lower the weight of windows (saving energy in transportation systems)
- Increase structure stiffness (buildings, bio-materials implants)
- Optimize ceramic sintering additives
- Design glass and glass-ceramic matrices with better performance for aerospace industry

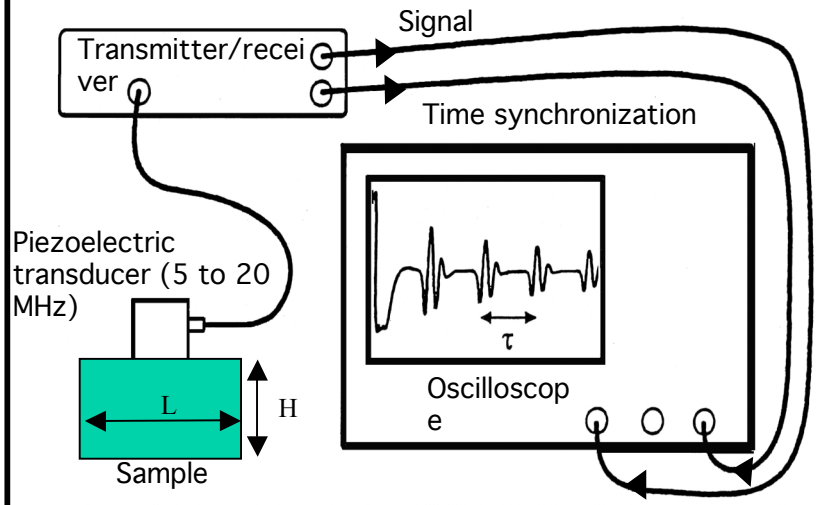



*J. Am. Ceram. Soc. 90 [10] 3019-3039 (2007)*

- There is no direct correlation between E and Tg
- Elastic moduli are expressed in Pascals, i.e. in $J/m^3$ , and are thus governed by the volume density of energy

# Measurement of elastic moduli by ultrasonic echography

## Measurements at ambient temperature

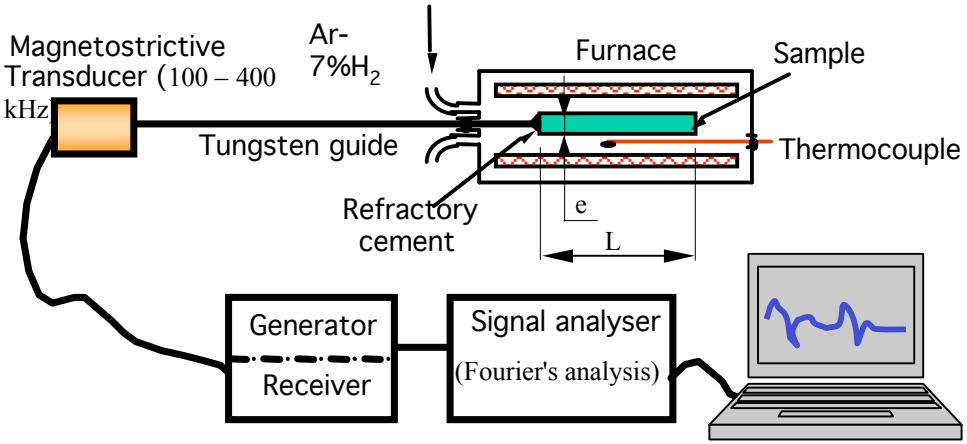



Elastic wave in semi-infinite medium : $\lambda \ll L$ and $\lambda \ll H$

$$E = \rho\,(3V_l^2 - 4V_t^2)/((V_l/V_t)^2 - 1)$$
$$G = \rho\,V_t^2$$
$$\nu = E/(2G) - 1$$

Where: $\rho$: specific mass
$V_l$: longitudinal wave velocity
$V_t$: transverse wave velocity

## High temperature measurements




Long beam bar mode : $e \ll L$ and $e \ll \lambda$ (10 to 100 mm)

$$E = \rho\,V_l^2$$

## Small size specimens: Acoustic microscopy

When $(L,H) < \lambda$, regular piezoelectric transducers are unable to efficiently promote the propagation of shear waves through the specimen. Focused piezoelectric transducers can be used to propagate surface-type waves, also called Rayleigh waves, which velocity is given by: $V_R = \zeta V_t$, where $\zeta$ is a function of Poisson´s ratio, or of the $V_l/V_t$ ratio. $V_R$ and $V_l$ are measured and $V_t$ is optimised to satisfy the following equation:

$$V_R = \frac{V_t\,(0.715 - (V_t/V_l)^2)}{0.750 - (V_t/V_l)^2}$$

# From the atom and to the continuum

Simple (simplistic) case of a Lennard-Jones potential (1st Grüneisen rule)

$$K = V_o \left.\frac{\partial^2 U}{\partial V^2}\right|_{Vo} = \frac{mn}{9V_o} U_o$$

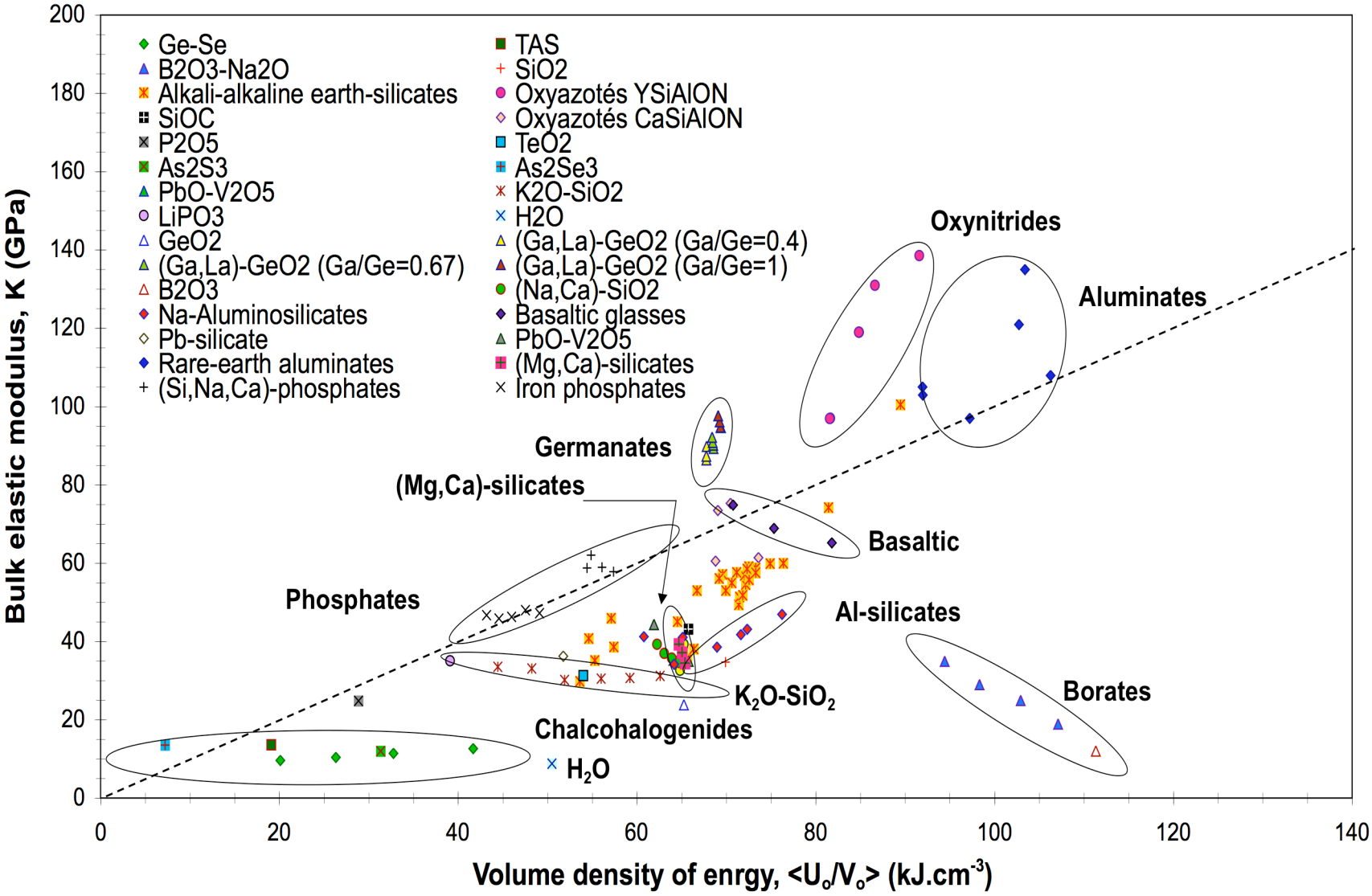
Multiconstituent glass:

$$\left\langle \frac{U_o}{V_o} \right\rangle = \Sigma\, f_i \Delta H_{ai} / (\Sigma\, f_i M_i / \rho_i)$$

$\rho_i$ : density
$f_i$ : molar fraction of the $i^{th}$ constituent
$M_i$ molar mass of the $i^{th}$ constituent

For the $i^{th}$ constituent $A_xB_y$, according to an ordinary Born-Haber cycle:

$$\Delta H_{ai} = x\,\Delta H_f^o(A,g) + y\Delta H_f^o(B,g) - \Delta H_f^o(A_xB_y)$$




$$K = V_o \left.\frac{\partial^2 U}{\partial V^2}\right|_{Vo} = \frac{mn}{9V_o} U_o$$

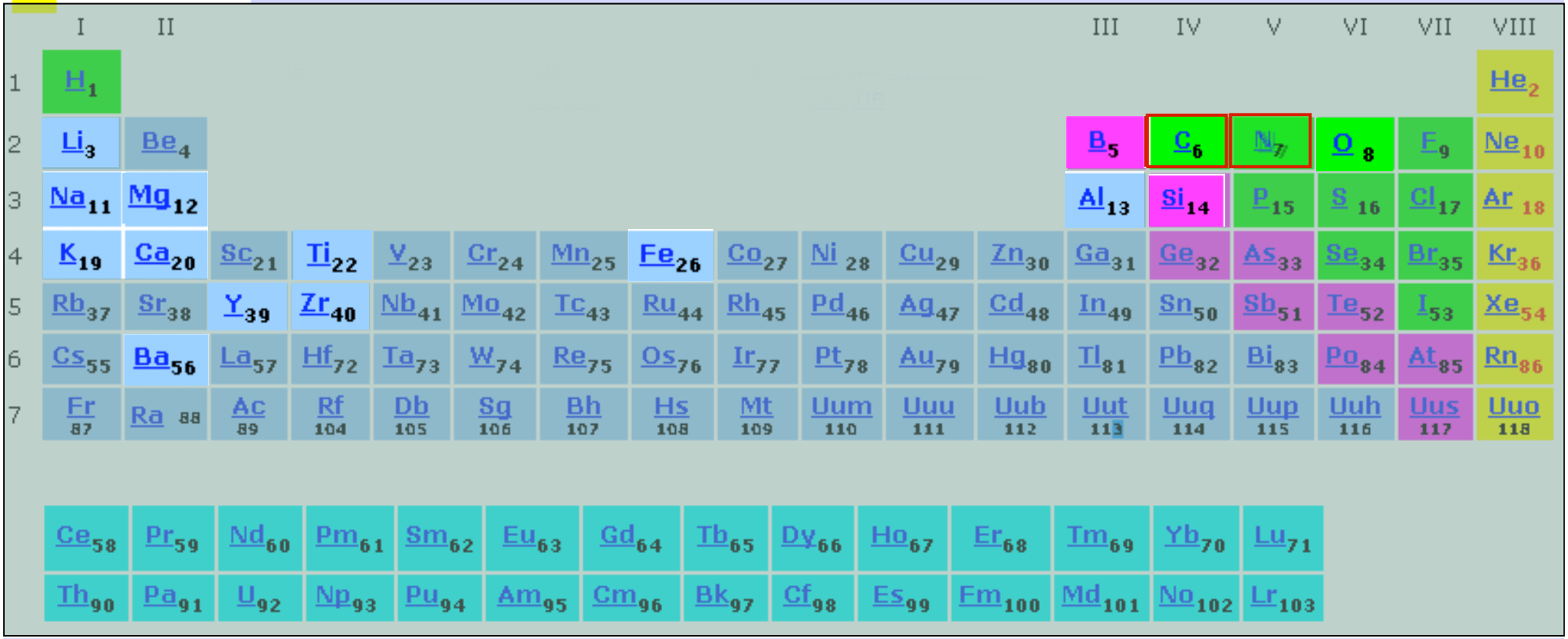
--------- ➡ n=1 and m=9

**Silicate glasses:**

Glass formers (Si, Al, B, Zr)

Modifyers and charge compensators (Li, Na, K, Ca, Ba)

Anions: O, N or C



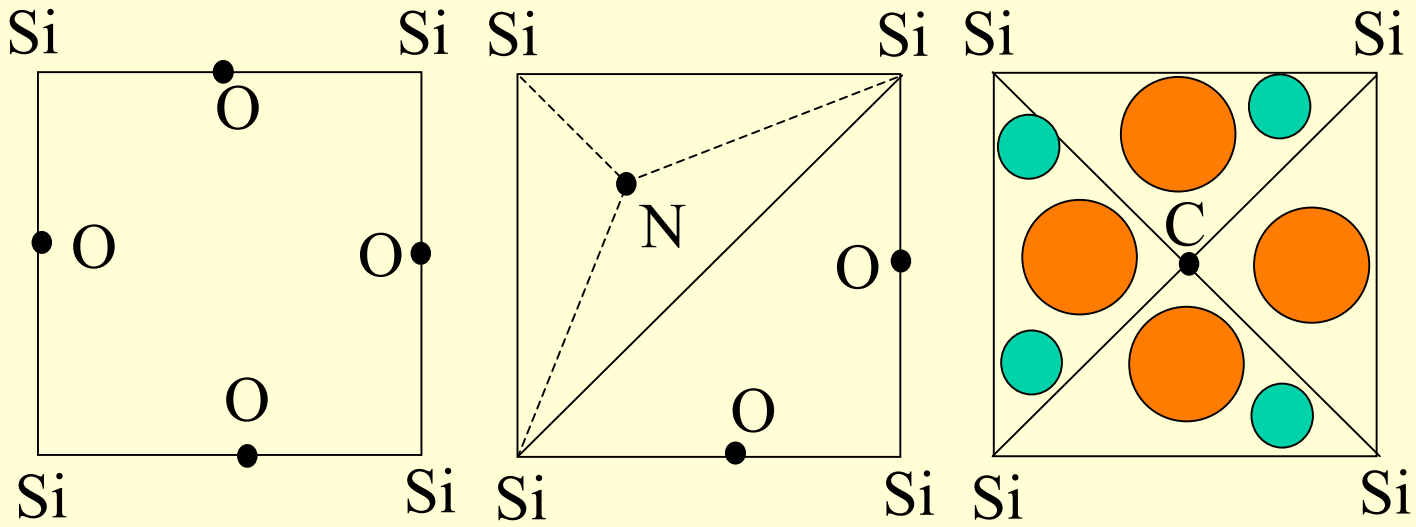

Cation substitution: modifyers ⇒ Uo ↘ ; formers ⇒ Cg ↘

Intermediate elements occupying former or interstitial sites: Hf, Be, Zr, Ti, Li and Th.

Electronegativities: 1.25 to 1.75.

$E_{max}$=145 GPa: magnesium aluminates + 25 mol.% de BeO.

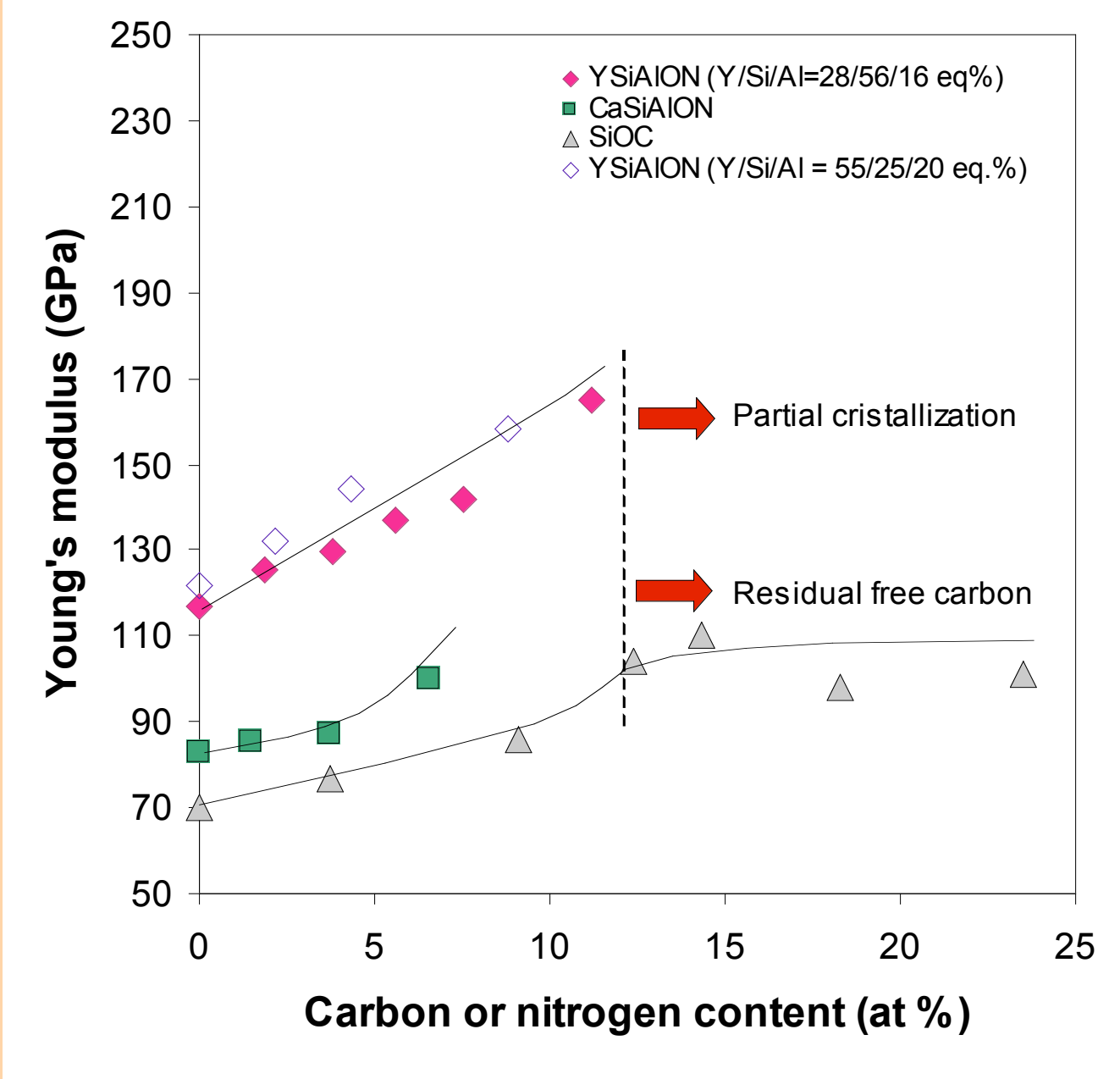
Anionic substitutions: more efficient but Tg ↗




E oxycarbides and E oxynitrides >> E oxides

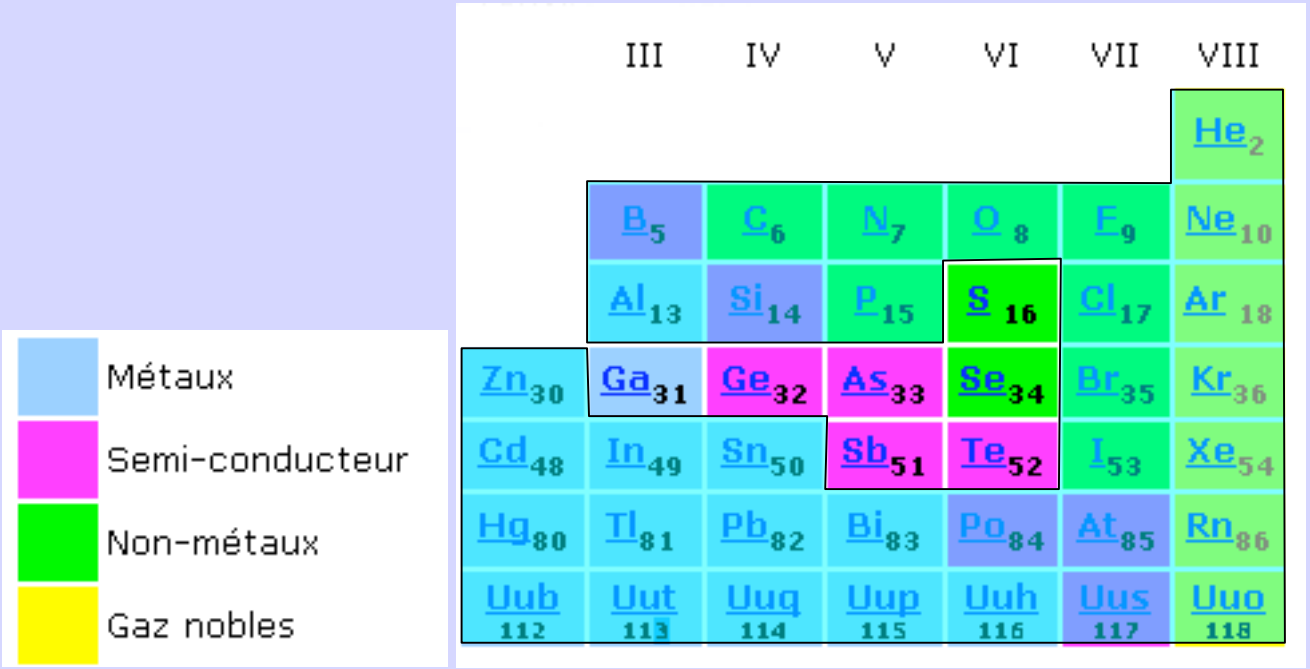
However: $U_{oSiC}$(447) kJ/mol)~$U_{oSi\text{-}N}$(437 kJ/mol)<$U_{oSi\text{-}O}$(800 kJ/mol)

*This is more the architecture (reticulation) of the network than the individual bond stiffnes that governs the glass elasticity*

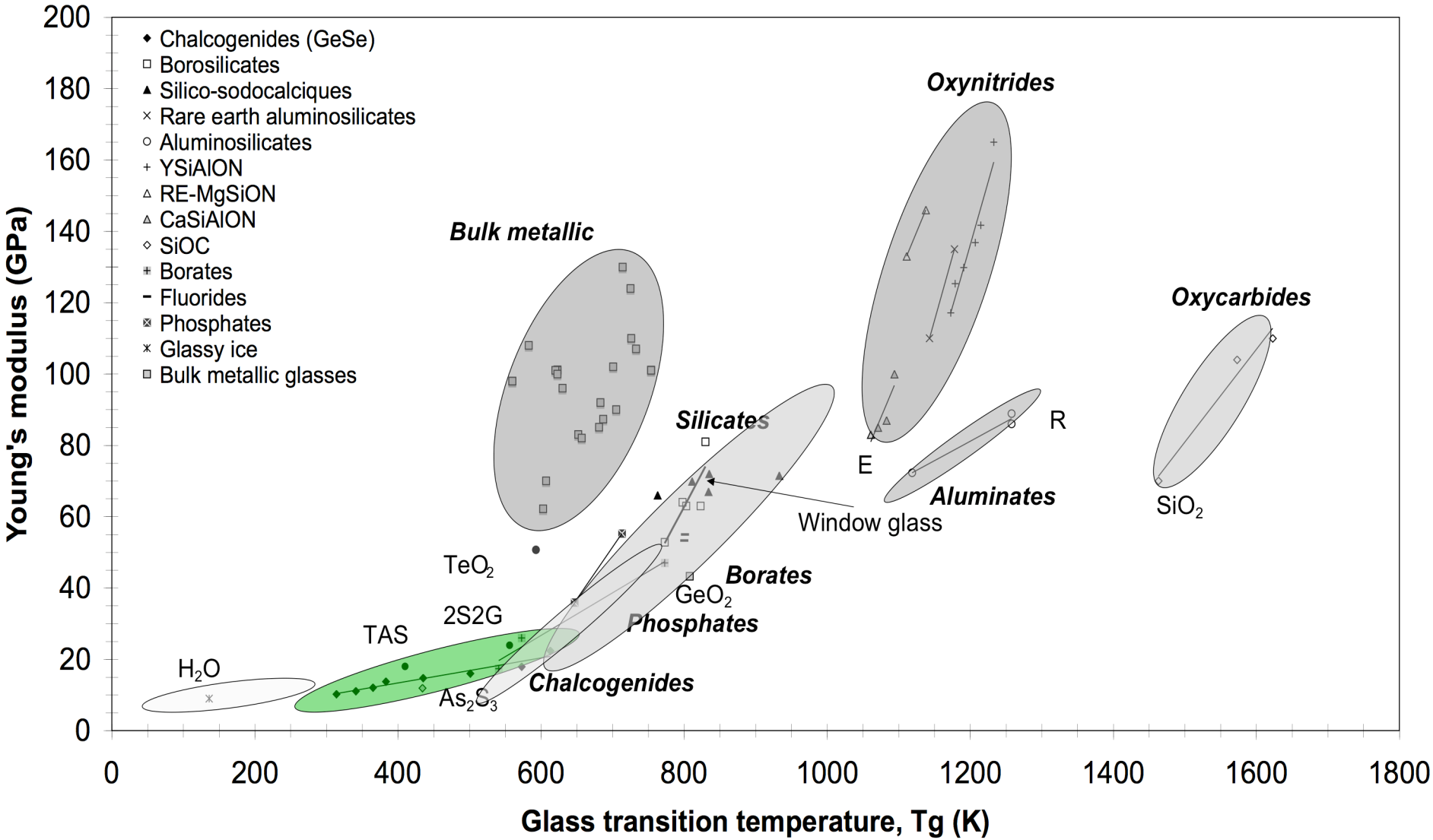

YSiAlON (Y/Si/Al=28/56/16 eq%)
CaSiAlON
SiOC
YSiAlON (Y/Si/Al = 55/25/20 eq.%)
Partial cristallization
Residual free carbon
Young's modulus (GPa)
Carbon or nitrogen content (at %)
250
230
210
190
170
150
130
110
90
70
50
0
5
10
15
20
25

## Chalcohalogenide glasses

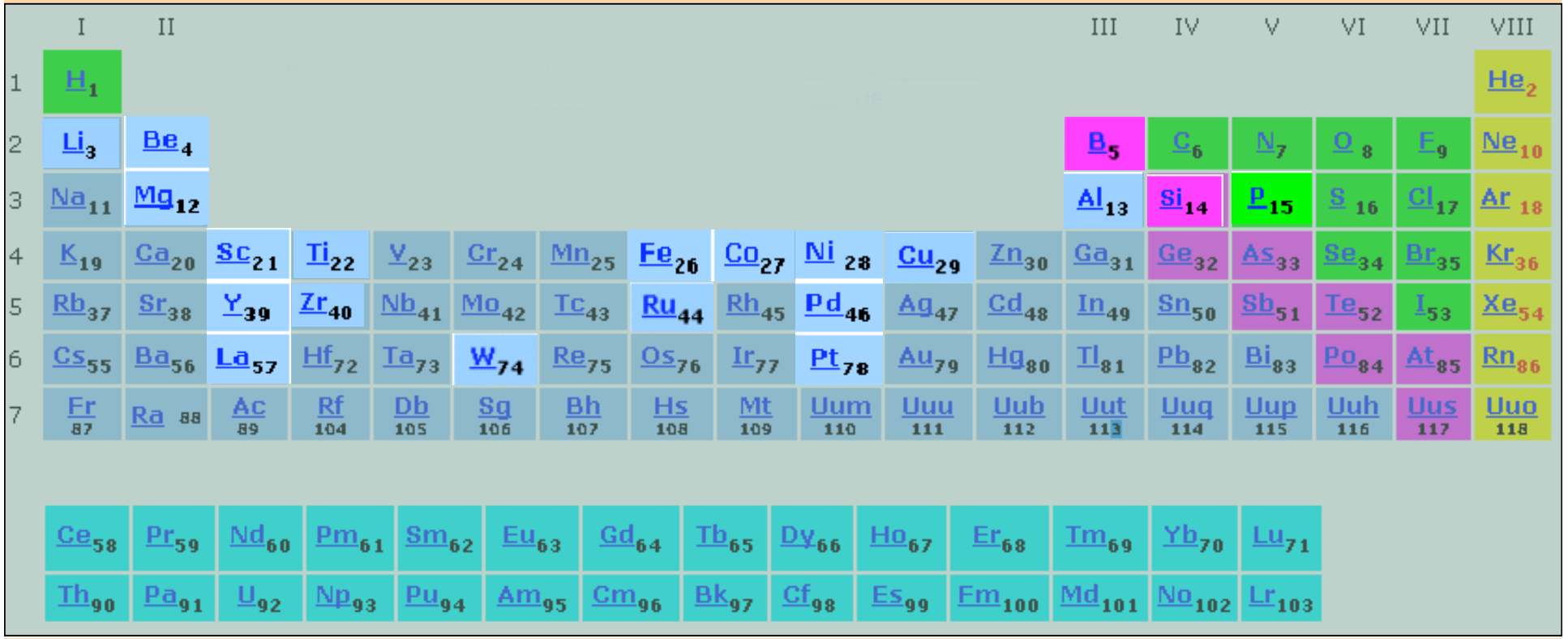
Chalcogen elements (S, Se, Te) (Col. 16)
Groups III, IV or/and V




***Examples: TAS: $Te_2As_3Se_5$ / $GeSe_4$ / 2S2G: $Ga_5Sb_{10}Ge_{25}Se_{60}$ / GASIR: $Ge_{22}As_{20}Se_{58}$***


Chalcogenides (GeSe)
Borosilicates
Silico-sodocalciques
Rare earth aluminosilicates
Aluminosilicates
YSiAlON
RE-MgSiON
CaSiAlON
SiOC
Borates
Fluorides
Phosphates
Glassy ice
Bulk metallic glasses
Young's modulus (GPa)
Glass transition temperature, Tg (K)
Bulk metallic
Oxynitrides
Oxycarbides
Silicates
Borates
Phosphates
Chalcogenides
Aluminates
E
R
Window glass
TeO2
2S2G
TAS
H2O
As2S3
GeO2
SiO2

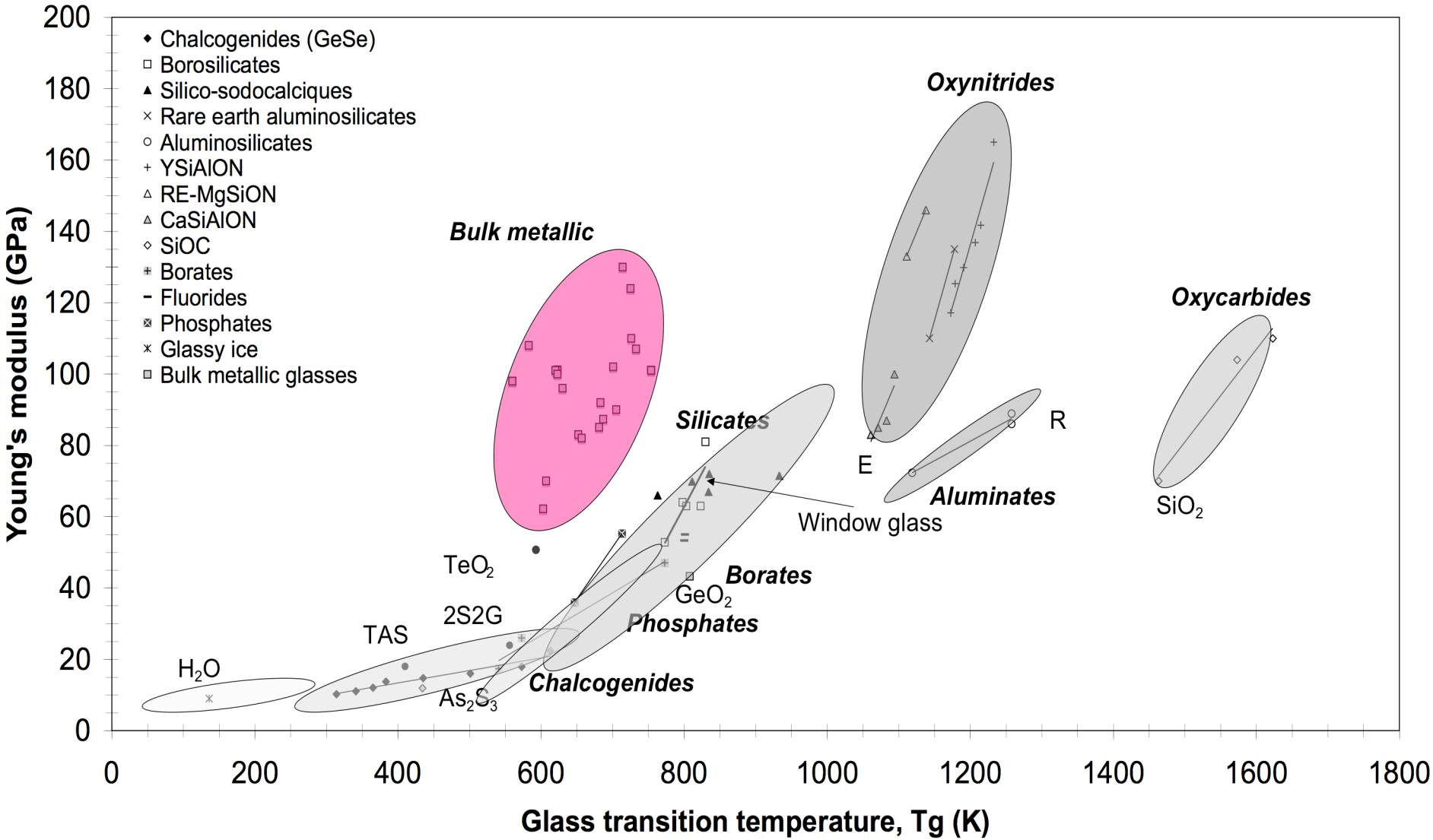
# Bulk Metallic Glasses

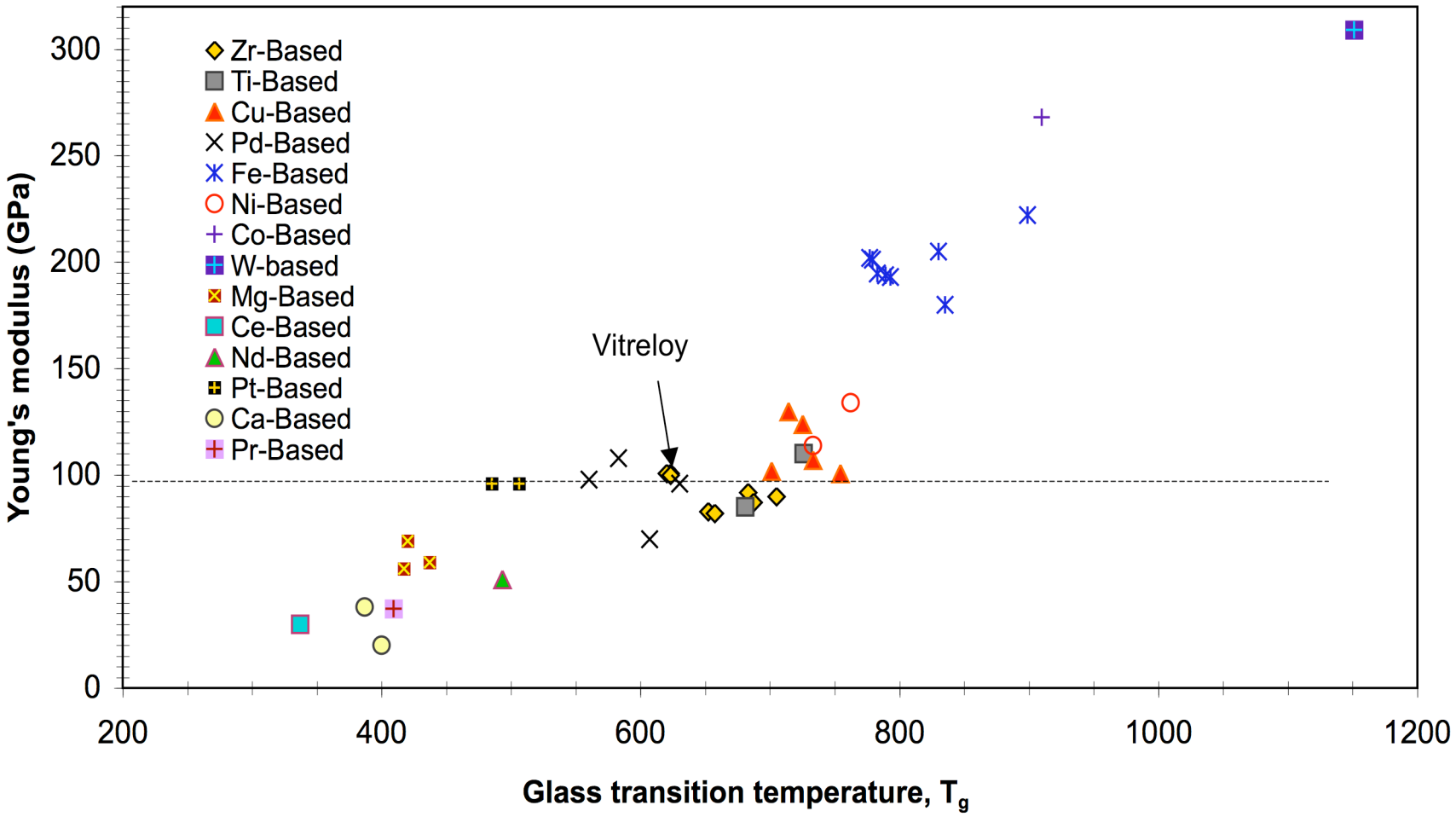



Atoms with much different atomic radii favour a chemical disorder and are used to synthesize BMG's: A metal (Be, Al, ...) + A transition metal (groups 3 to 12) from the right-hand side of the periodic table (Cu, Ni,...) + A transition metal from the left-hand side (Zr, Ti, Hf, Nb, ...), and a metalloid

Ex: $Zr_{60}Al_{10}Ni_{10}Cu_{15}Pd_5$ ; $Zr_{65}Al_{10}Ni_{10}Cu_{15}$

As a result, BMG's are characterized by a high atomic packing density and exhibit relatively high elastic moduli

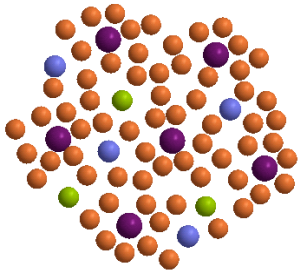

Chalcogenides (GeSe)
Borosilicates
Silico-sodocalciques
Rare earth aluminosilicates
Aluminosilicates
YSiAlON
RE-MgSiON
CaSiAlON
SiOC
Borates
Fluorides
Phosphates
Glassy ice
Bulk metallic glasses
Young's modulus (GPa)
Glass transition temperature, Tg (K)
Bulk metallic
Oxynitrides
Oxycarbides
Silicates
Borates
Phosphates
Chalcogenides
Aluminates
E
R
Window glass
TeO2
2S2G
TAS
H2O
As2S3
GeO2
SiO2



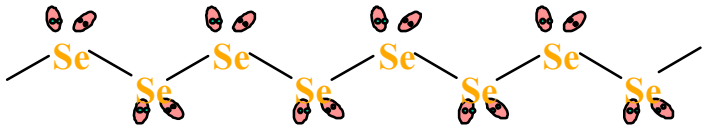

- Diferent chemical systems lead to identical elastic moduli
- This observation stems from the fact that BMG's show up with very different atomic packing density depending on their composition. For instance, Pt-based glasses have much higher packing density than Cu-Based alloys

# Molecular scale:

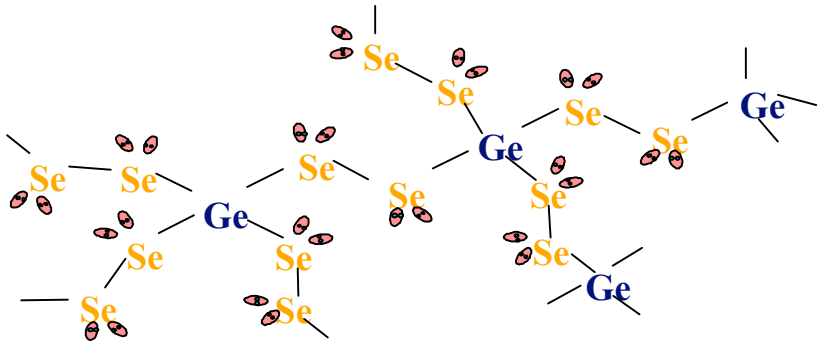
0D: Clusters, litlle short to medium range ordering



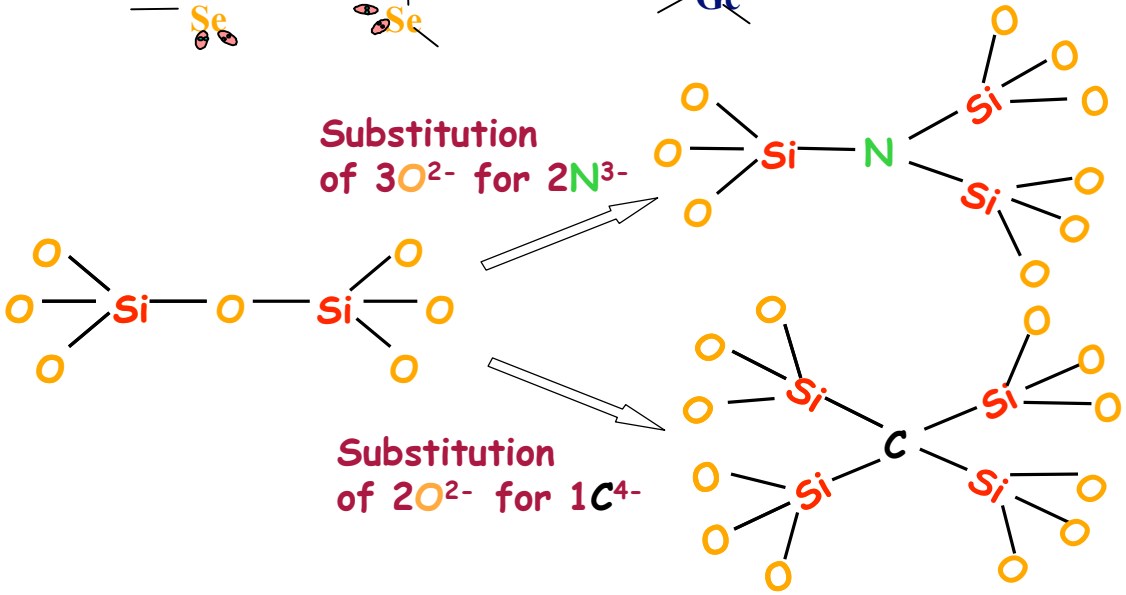
1D: Chains and rings



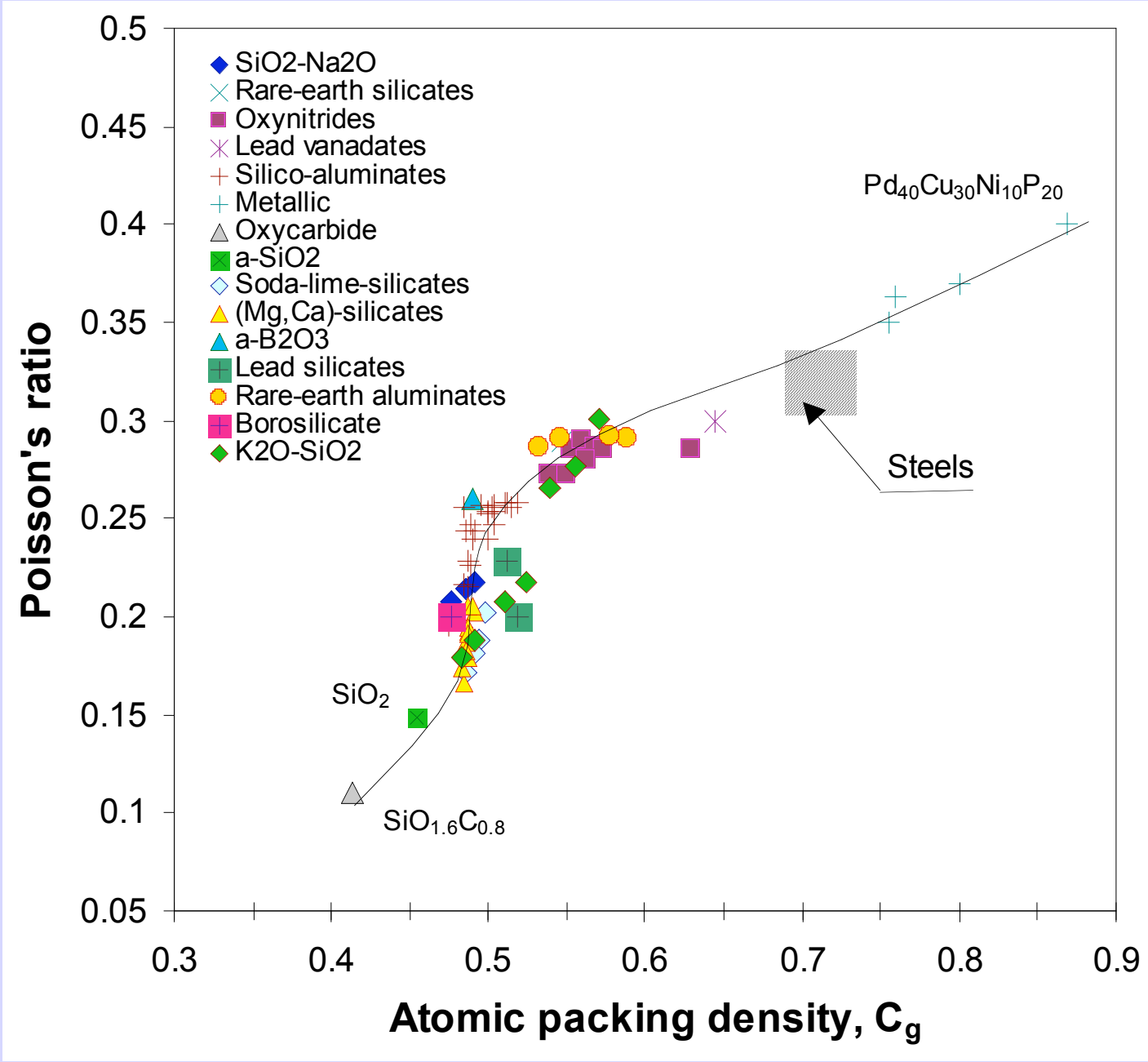

2D: Layers



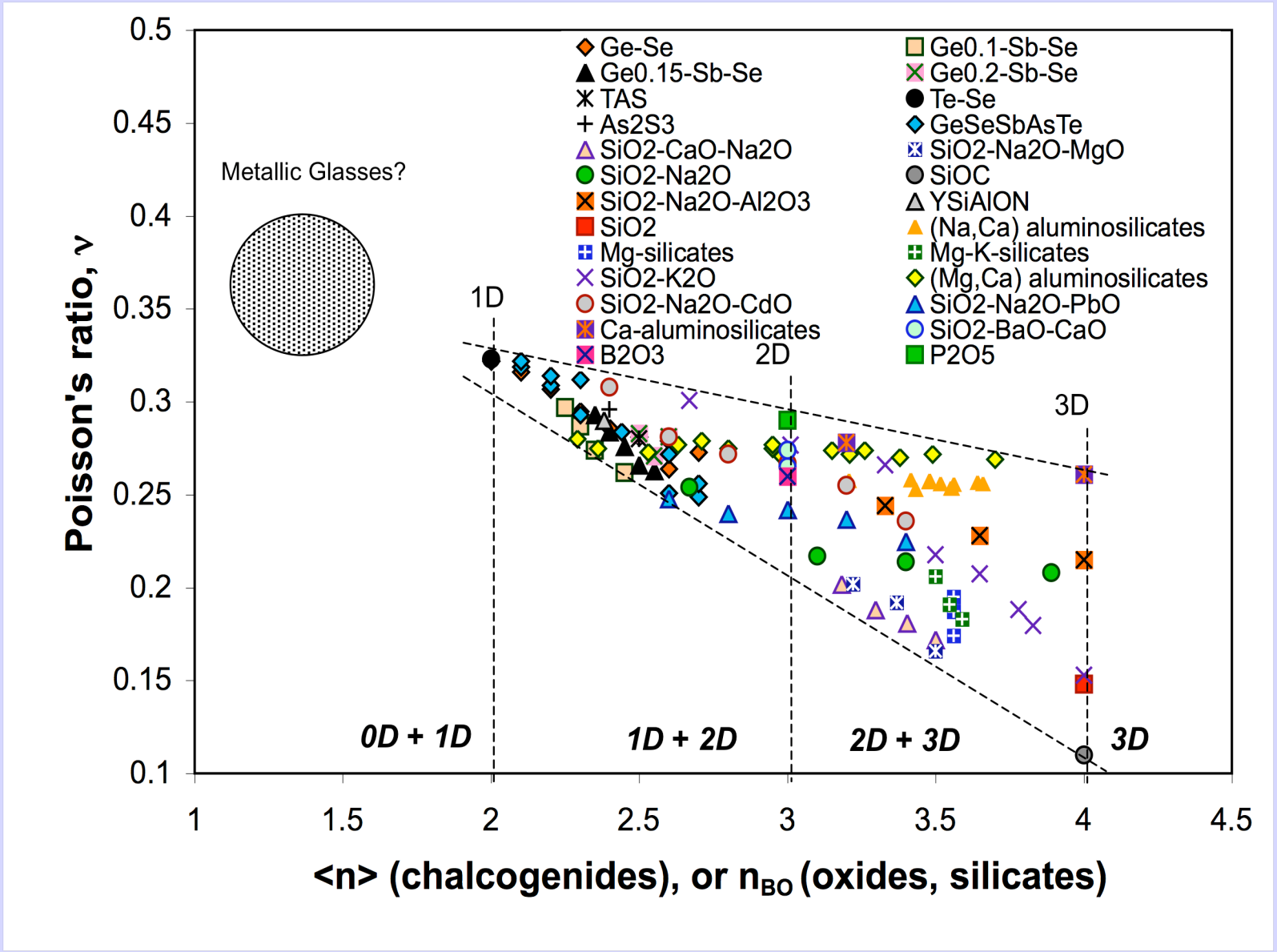

3D: 3D units and crosslinking



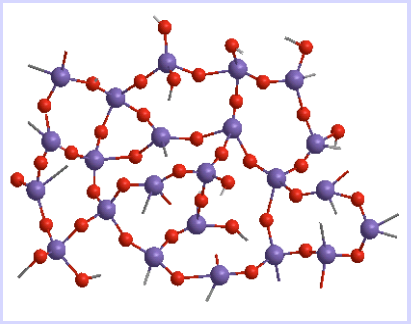
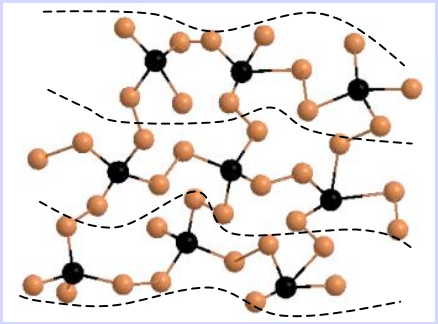
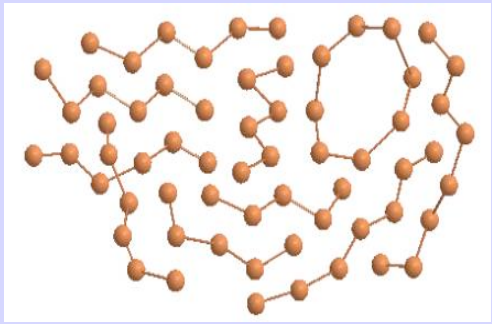
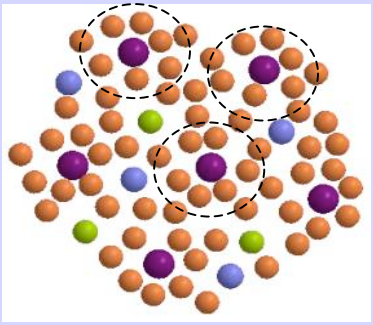
# Influence of the atomic packing density

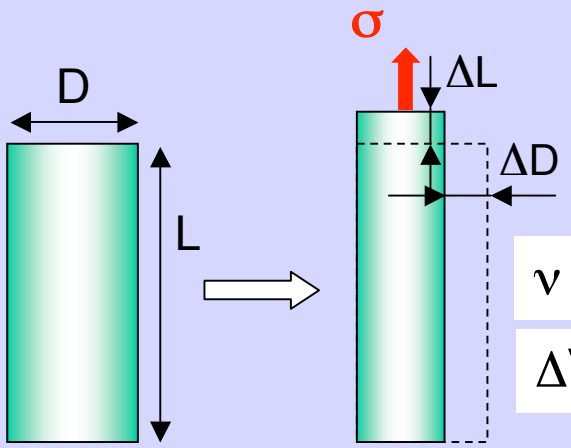


# Poisson's ratio and dimensionality



# Poisson's ratio and atomic network dimensionality

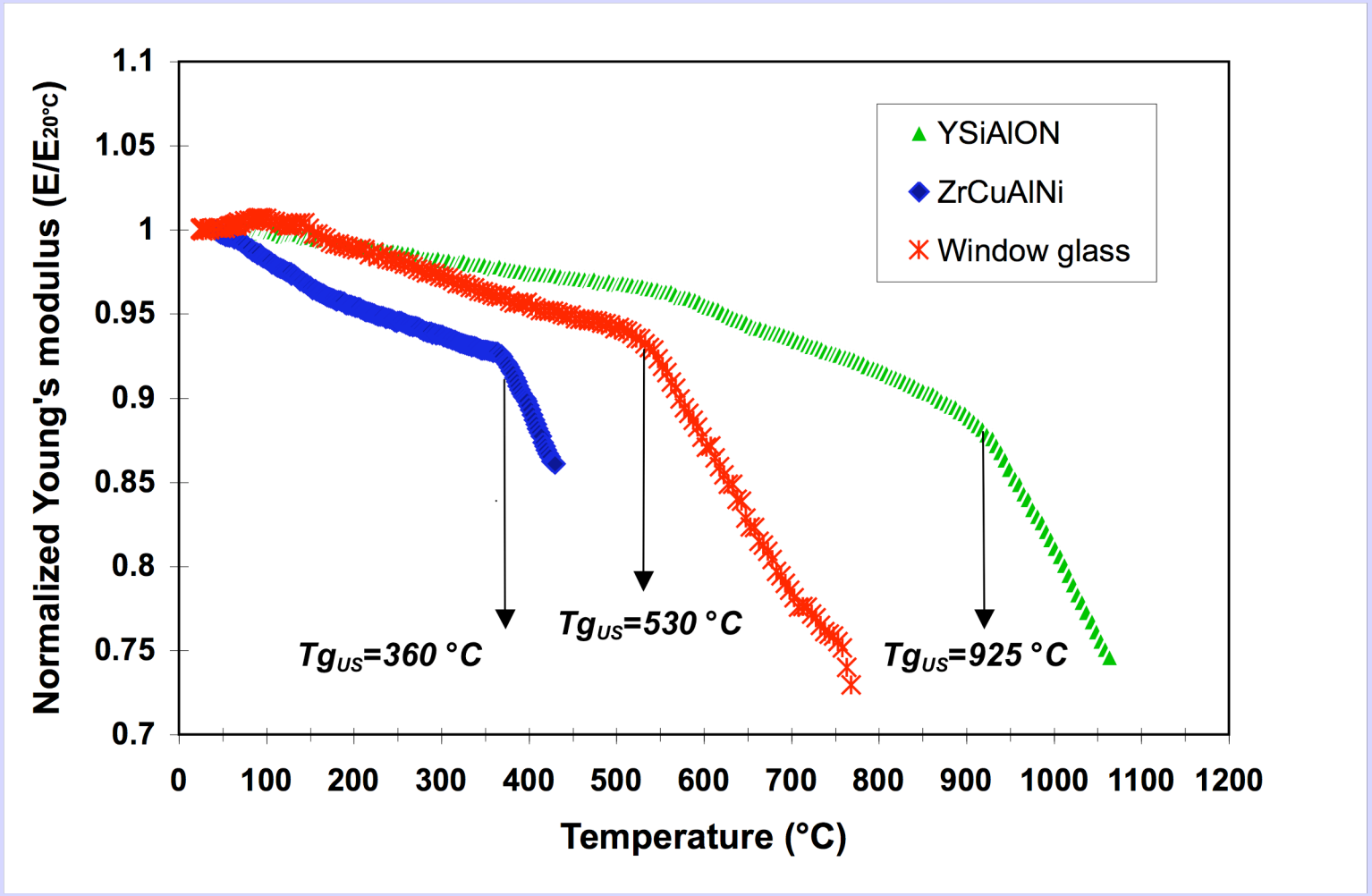
| $a\text{-}SiO_2$ | $GeSe_4$ | a-Se | $Zr_{55}Cu_{30}Al_{10}Ni_5$ |
|---|---|---|---|
|  |  |  |  |
| $\nu \approx 0.16$ | $\nu \approx 0.286$ | $\nu \approx 0.323$ | $\nu \approx 0.37$ |
| 3D | 2D | 1D | 0D? |

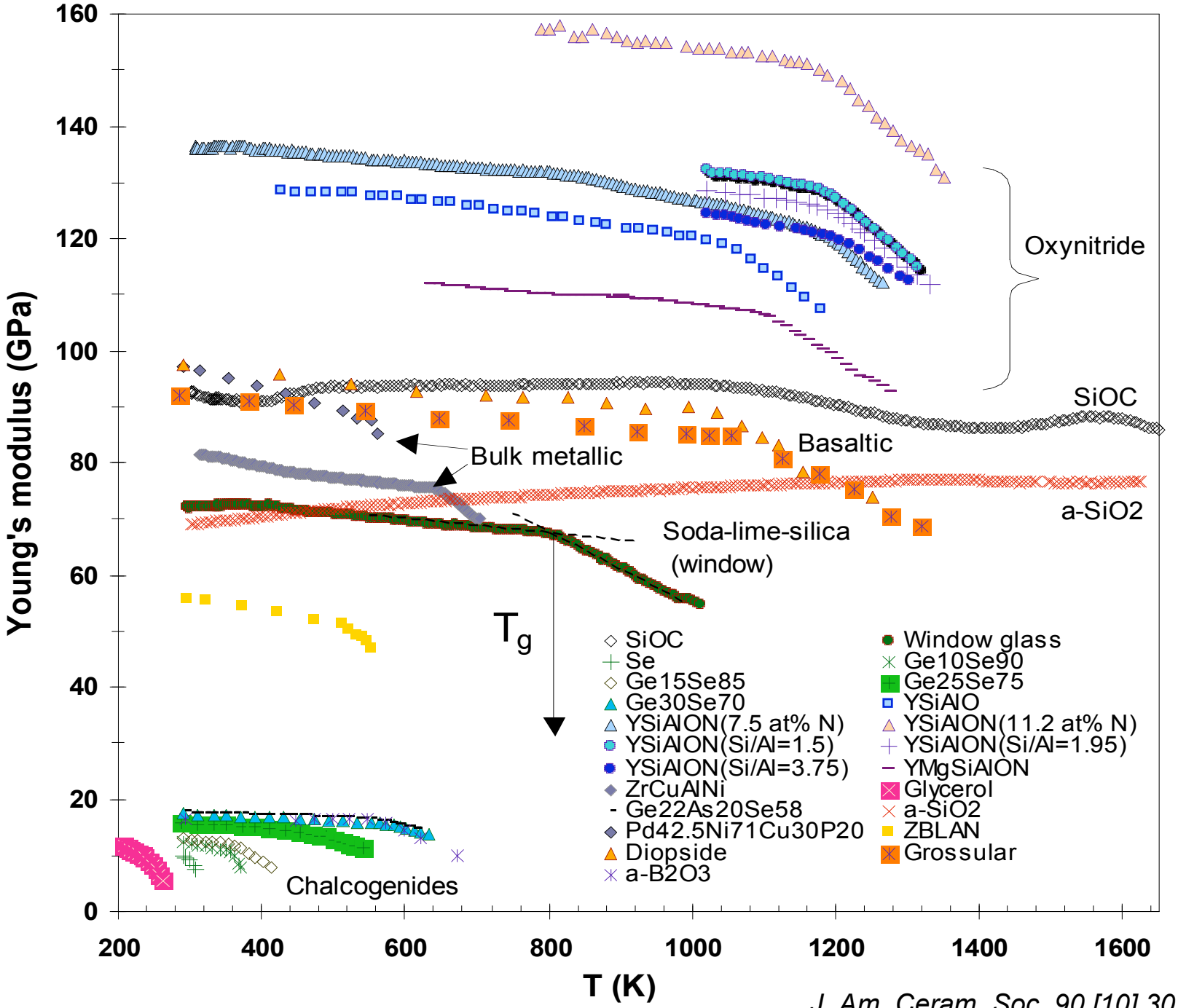



$\nu = -\varepsilon_t/\varepsilon_l = - L/D \times \Delta D/\Delta L$

$\Delta V/V = \text{Trace } \varepsilon = (1-2\nu)\sigma/E$

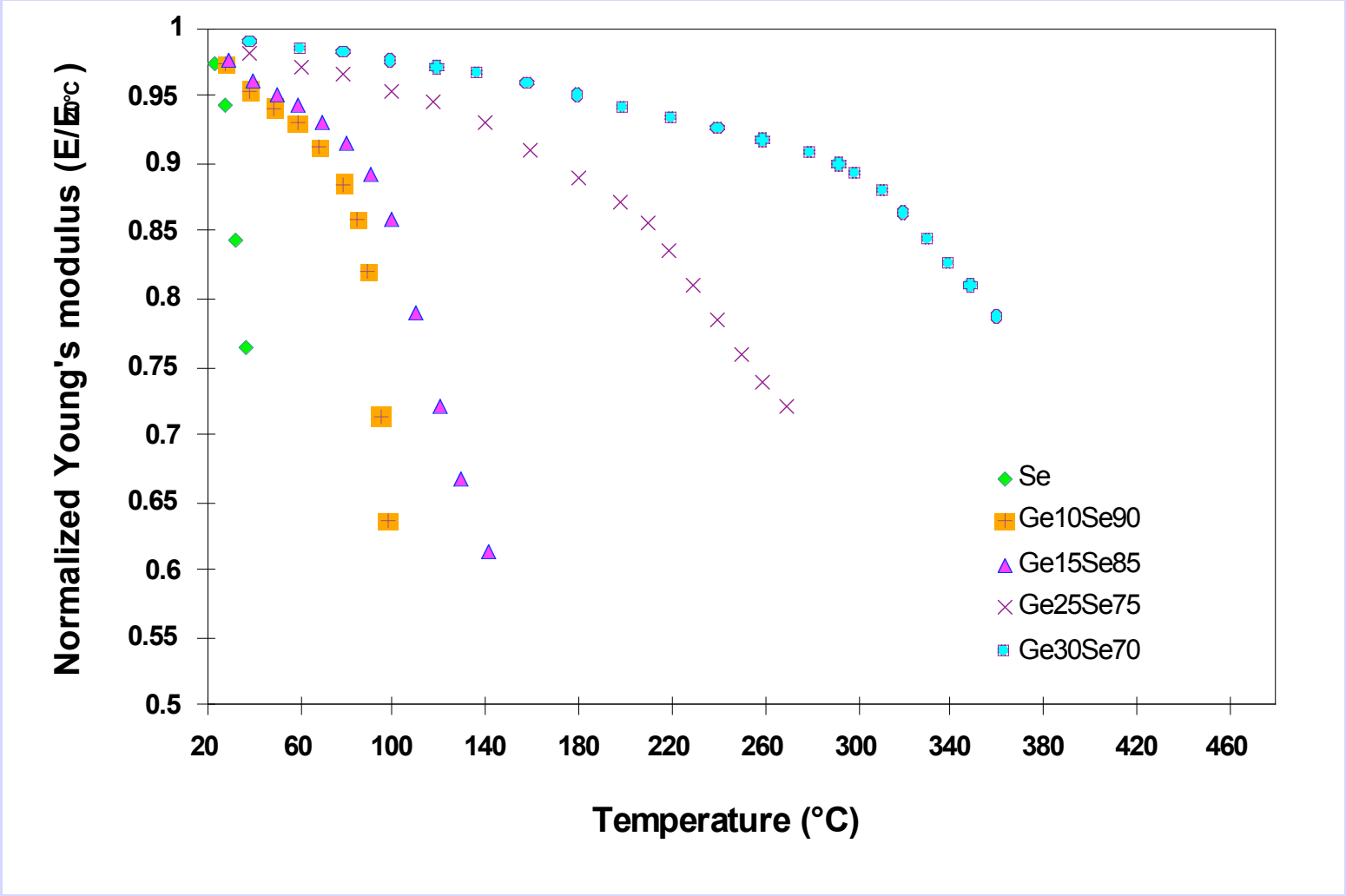
- **HIGH TEMPERATURE ELASTICITY**

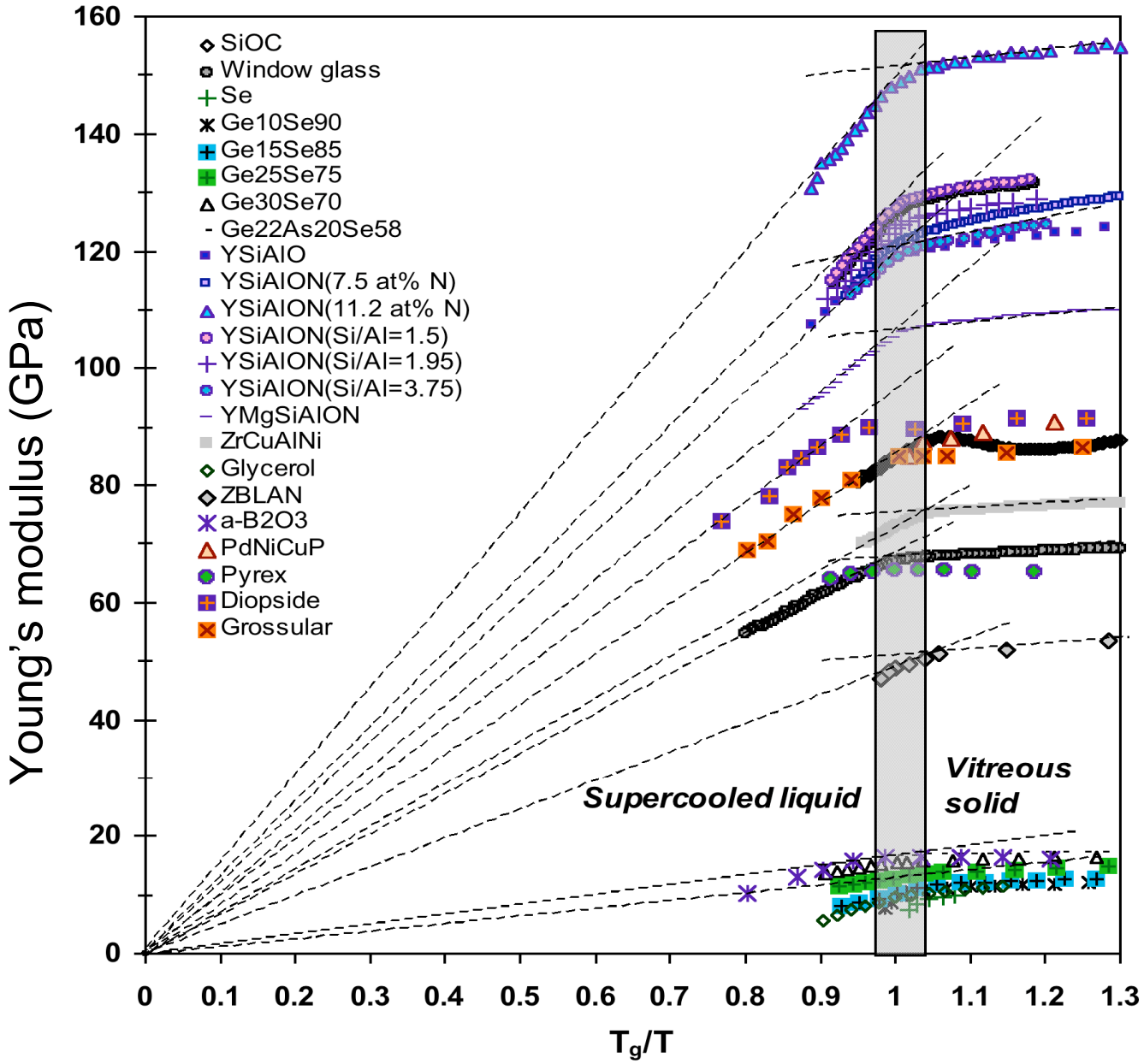

Normalized Young's modulus (E/E20°C)
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
Temperature (°C)
YSiAlON
ZrCuAlNi
Window glass
Tg_US=360 °C
Tg_US=530 °C
Tg_US=925 °C





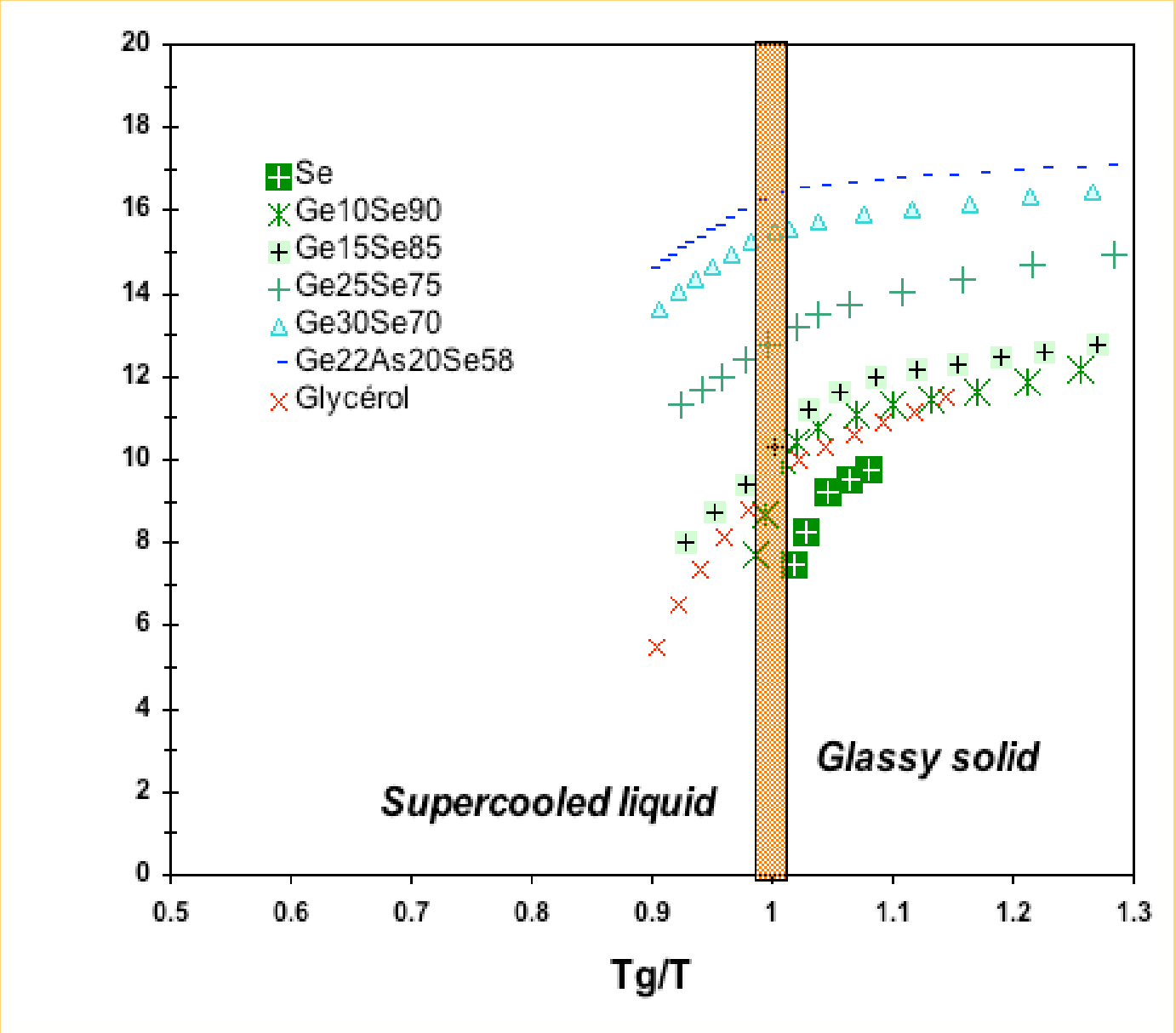

*J. Am. Ceram. Soc. 90 [10] 3019-3039 (2007)*


Normalized Young's modulus (E/E20°C)
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
20
60
100
140
180
220
260
300
340
380
420
460
Temperature (°C)
Se
Ge10Se90
Ge15Se85
Ge25Se75
Ge30Se70






For glasses with E>10 GPa: $E=E(T_g)T_g/T$


Se
Ge10Se90
Ge15Se85
Ge25Se75
Ge30Se70
Ge22As20Se58
Glycérol
Supercooled liquid
Glassy solid
Tg/T
0
2
4
6
8
10
12
14
16
18
20
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3

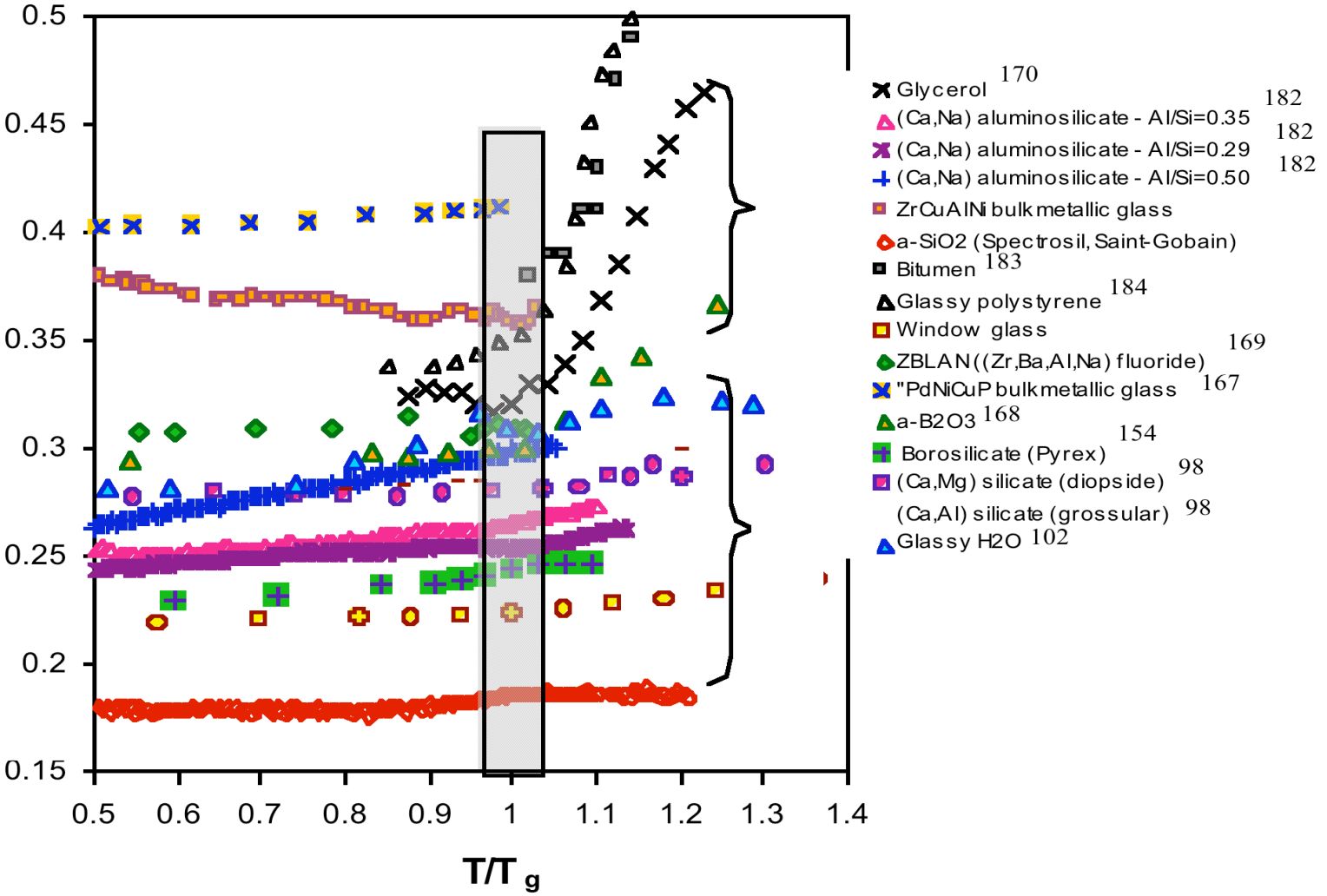
$$\beta = \frac{1}{1 - \frac{T}{E}\frac{\partial E}{\partial T}}$$

## « Strong » versus « Fragile » Glasses (Angell)

$\Phi(t)=\sigma(t)/\sigma(0)=\exp[-(t/t)^{\beta}]$

| Glass | $T_g$ (K) | E (293 K) (GPa) | E ($T_g$) (GPa) | $dE/dT(T_g^+)$ (MPa/K) | $\beta$ (~$T_g$)[2] | $\beta$[3] (littérature) |
|---|---|---|---|---|---|---|
| Glycérol[170] | 186 | 6 | 9.5 | -190 | 0.2 | 0.65[174] or 0.435[175] |
| $Ge_{10}Se_{90}$[165] | 365 | 12.1 | 10 | -230 | 0.07 | 0.6[176] |
| $Ge_{15}Se_{85}$[165] | 383 | 13.8 | 10.3 | -80 | 0.22 | 0.62[176] |
| $Ge_{25}Se_{75}$[165] | 501 | 16.1 | 12.8 | -38 | 0.38 | 0.63[176] |
| $Ge_{30}Se_{70}$[165] | 573 | 17.9 | 15.5 | -34 | 0.42 | 0.63[176] |
| $Ge_{22}As_{20}Se_{58}$[166] | 565 | 18 | 16.4 | -29 | 0.43 | 0.63[176] |
| $Y_{12.3}Si_{18.5}Al_7O_{54.7}N_{7.5}$[40] | 1183 | 150 | 122 | -103 | 0.45 | 0.8[177] |
| $Y_{4.86}Mg_{6.3}Si_{16.2}Al_{11.8}O_{54.9}N_{5.92}$[171] | 1120 | 134 | 122 | -105 | 0.52 | 0.75[178] |
| $Zr_{55}Cu_{30}Al_{10}Ni_5$[172] | 673 | 81.4 | 72.9 | -108 | 0.65 | 0.7[179] |
| Window glass[1) 173] | 835 | 72 | 56 | -67 | 0.53 | 0.55[173] or 0.45[175] |
| $SiC_{0.375}O_{1.25}$[58] | 1623 | 110 | 84.8 | -52 | 0.61 | 0.66[58] |

# ν as a probe of the depolymerization process






*J. Am. Ceram. Soc. 90 [10] 3019-3039 (2007)*

# Conclusion

## ELASTICITY

1) There is no direct relationship between elastic moduli and $T_g$.

2) Poisson's ratio ($\nu$) correlates with the atomic packing density and with the glass network dimensionality (polymerization degree)

3) High elastic moduli are favoured by structural disorder and in the search for stiff glasses, atomic packing density seems to predominate over the bond strength

4) The temperature dependence of the elastic properties above Tg can be discussed in the light of the "fragile" versus "strong" character of the liquid. The temperature sensitivity of v in the liquid range can be viewed as a consequence of the depolymerization occurring above Tg. v depends much on temperature above Tg but stays mostly lower than 0.5 up to T=1.3 Tg except for weakly cross-linked materials such as chain-polymers.

Acknowledgements:

*Ralf Riedel, TU Darmstadt, Germany*
*Gian-Domenico Sorarù, University of Trento, Italy*
*Stuart Hampshire, University of Limerick, Ireland*
*Satoshi Yoshida, University of Shiga prefecture, Japan*
*Yoshihito Kawamura, University of Kumamoto, Japan*
*Yoshihiko Yokoyama, University of Tohoku, Sendai, Japan*
*Christian Gault, Hervé Lemercier et Marc Huger, ENSCI, Limoges*
*Pascal Gadaud, ENSMA, Poitiers, France*
*Franck Augereau, LAIN, Montpellier, France*
*Vincent Keryvin, jean-Pierre Guin et Jean-Christophe Sangleboeuf, LARMAUR, Rennes, France*
*The glass and ceramics laboratory, Rennes, France*