Winter 1-1-2008

Lecture 10, Part 1: Engineered strengthening of glass

Tanguy Rouxel
Universite de Rennes, France

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 strenghtened 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 17th century!

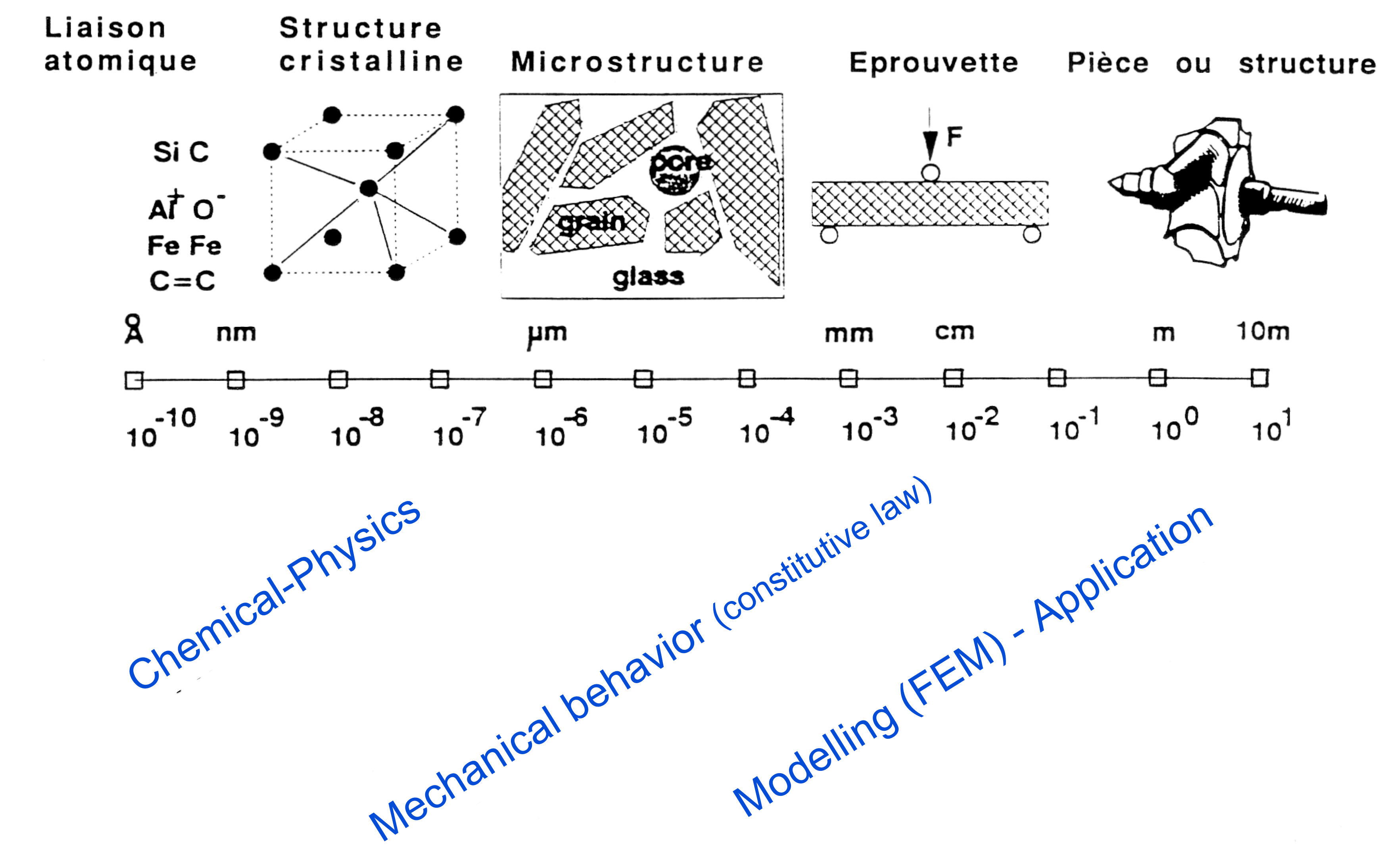
J.T. Littleton said « We never test the strength of glass: all we test is the weakness of its surface » (1941)
F.W. Preston added, « We do not test the properties of the glass at all, but only those of the surrounding atmosphere »

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

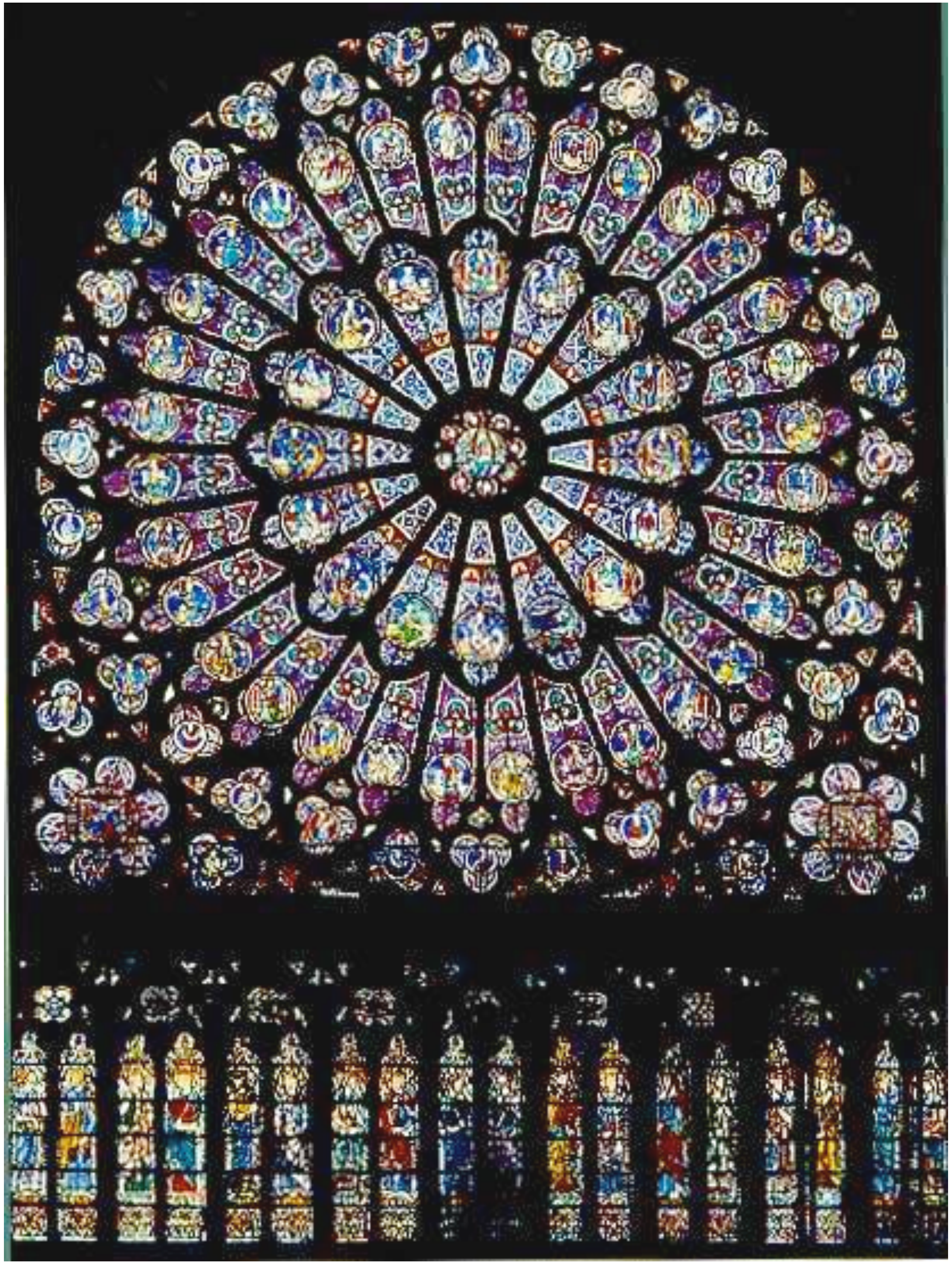
↓

There is much room for improvement!

Typical multiscale approach in mehanical design



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



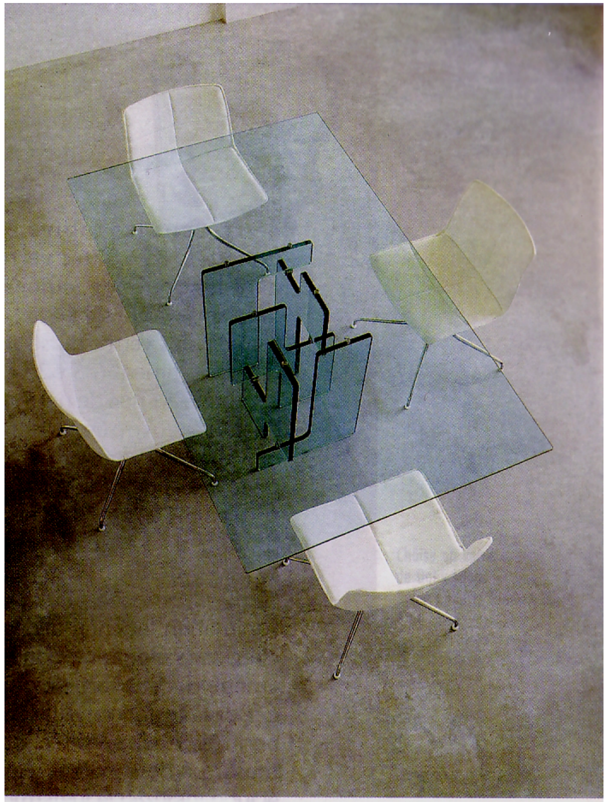
Cathedral of Notre Dame, Paris

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.

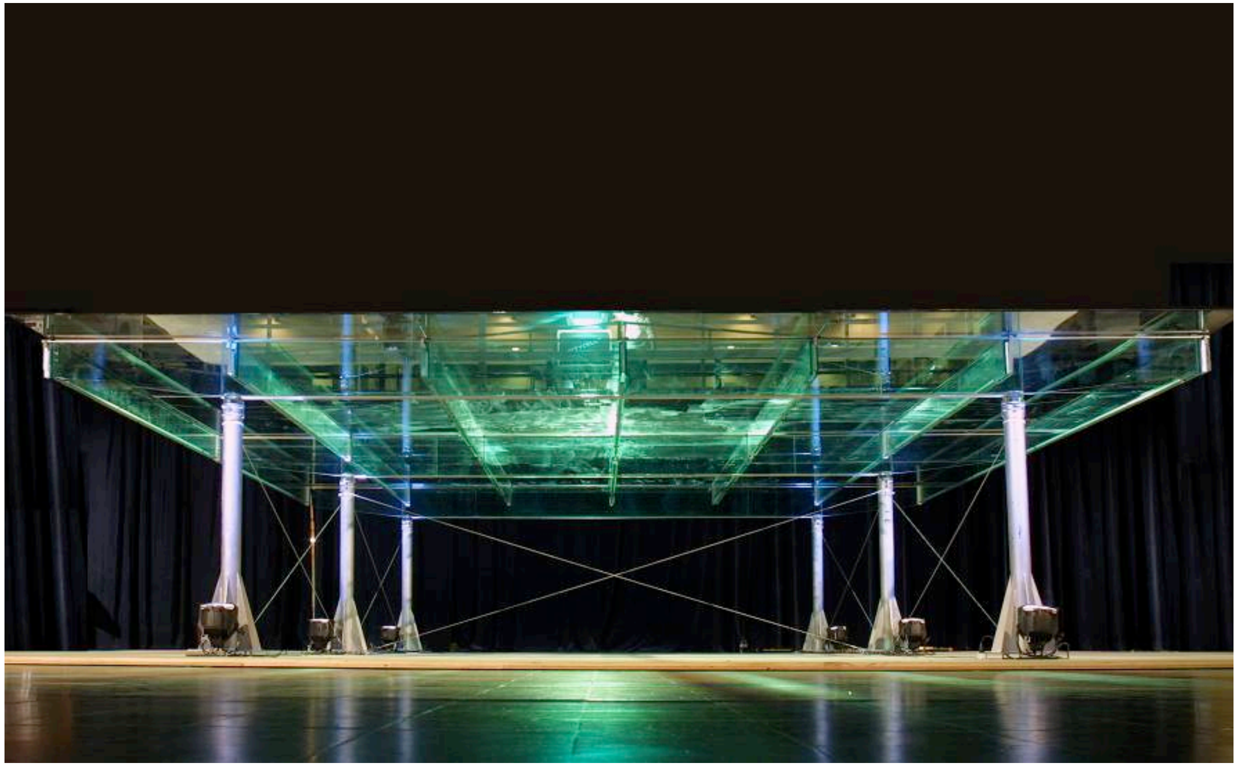
Although glass appeared to take a leading role it was still only a material that separated the interior and exterior untill some twenty years ago when loaded glass sheets started to be used in large structures

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

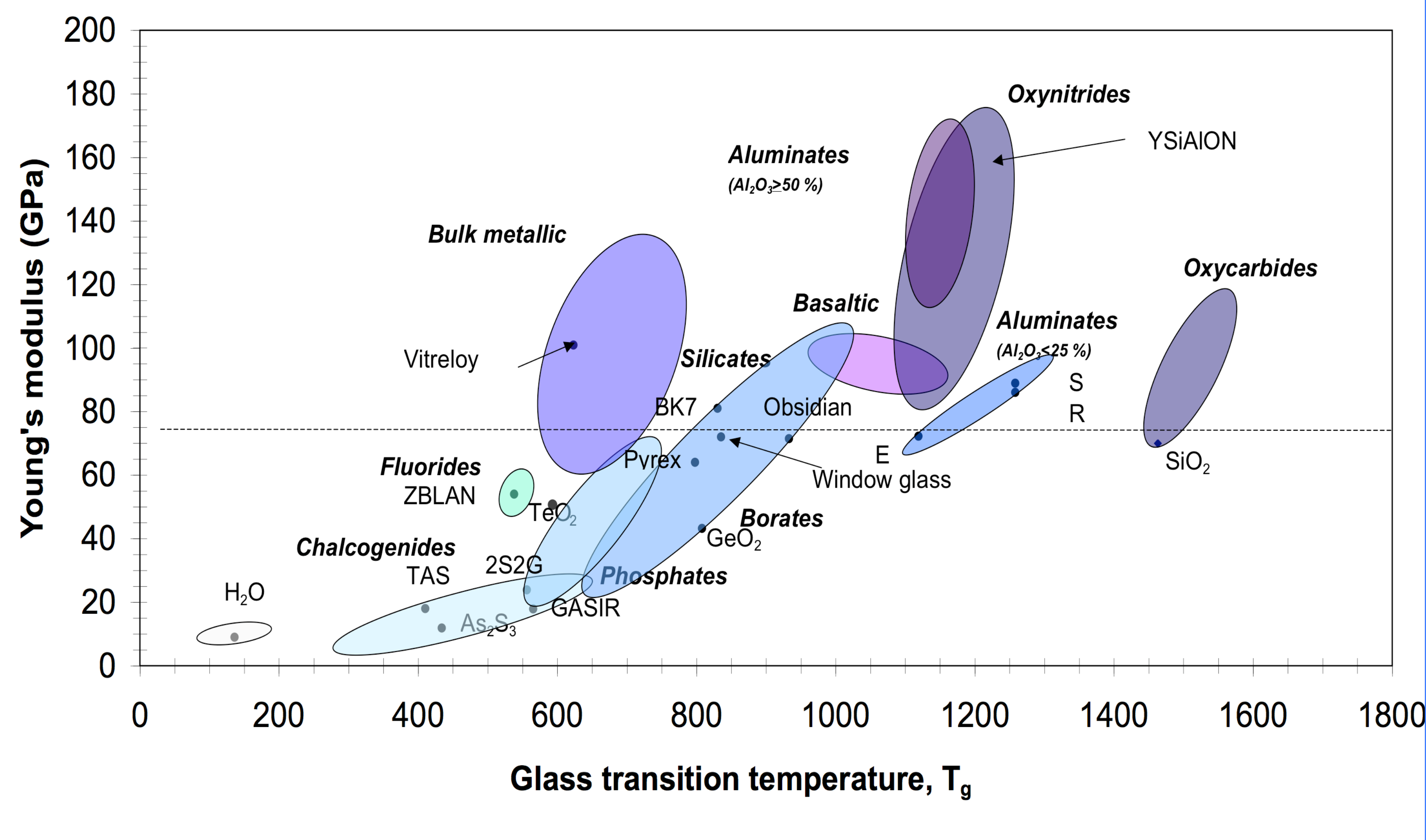


Q: How far can we go?

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

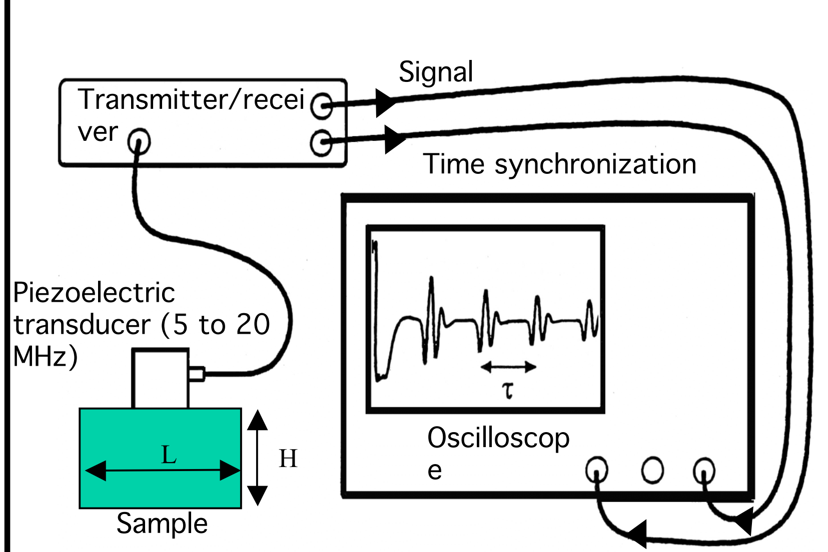


J. Am. Ceram. Soc. 90 [10] 3019-3039 (2007)

- 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

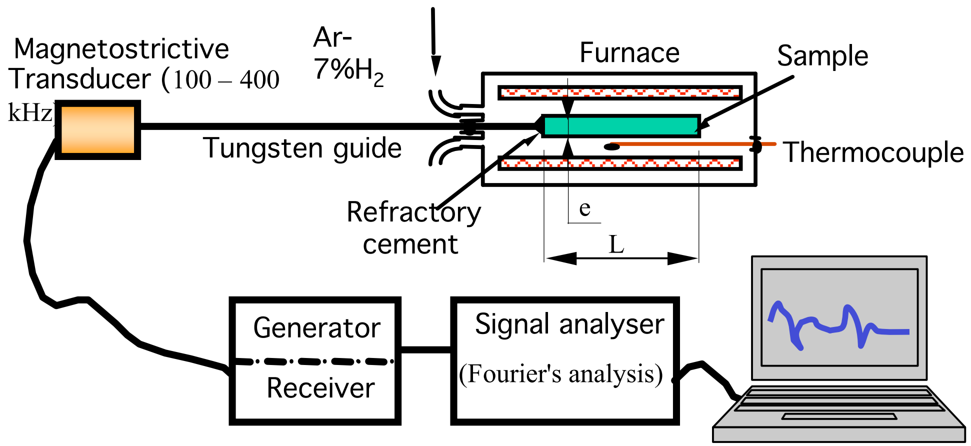


Elastic wave in semi-infinite medium : λ<<L and λ << H

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

Where: ρ: specific mass
V_l: longitudinal wave velocity
V_t: transverse wave velocity

High temperature measurements



Long beam bar mode : e<<L and e << λ (10 to 100 mm)

$E = \rho\,V_l^2$

Small size specimens: Acoustic microscopy

When (L,H)<λ, 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 ζ 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)

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

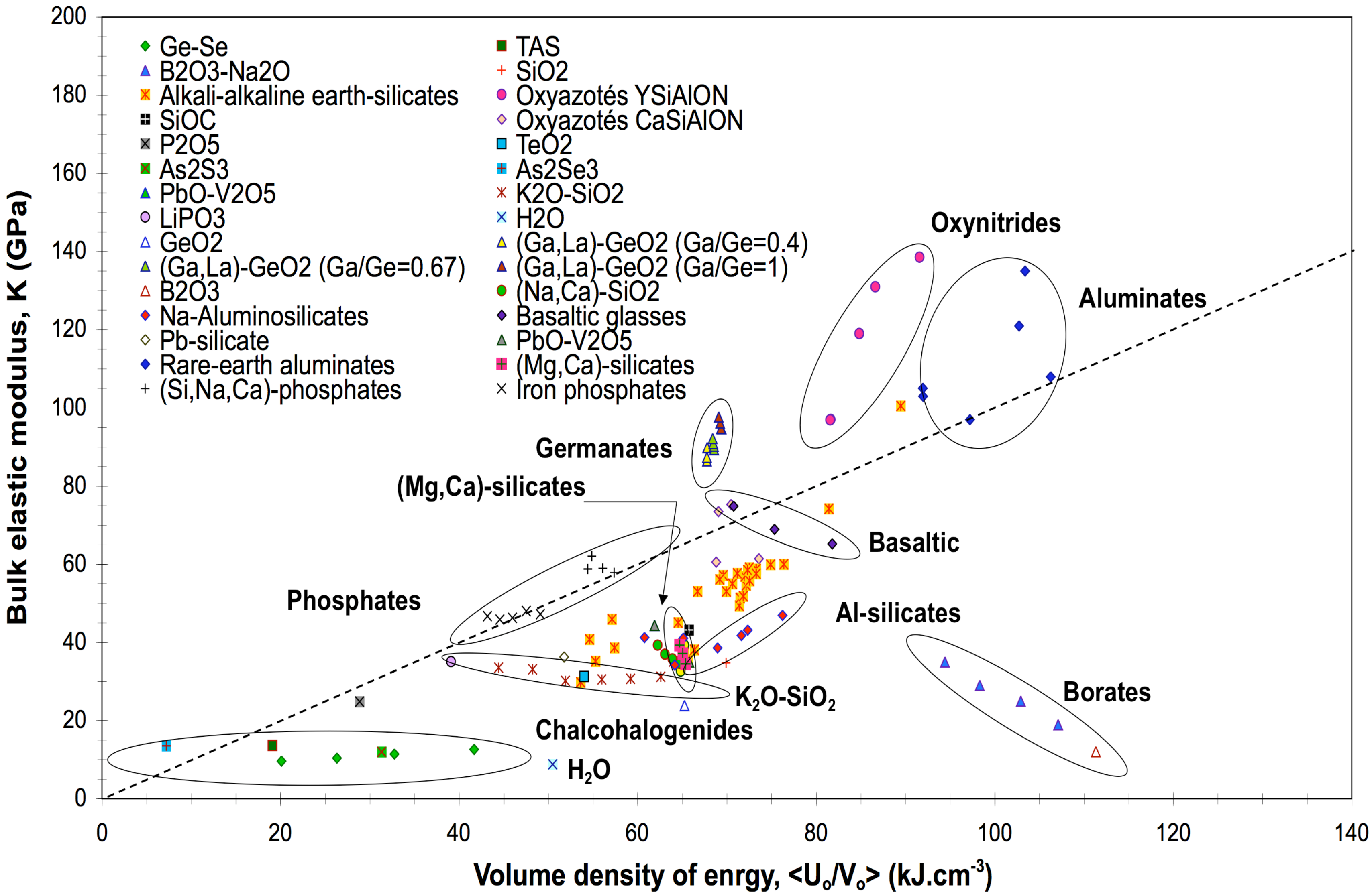
Multiconstituent glass:

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

ρ_i : density
f_i : molar fraction of the ith constituent
M_i molar mass of the ith constituent

For the ith constituent A_xB_y, according to an ordinary Born-Haber cycle:

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



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

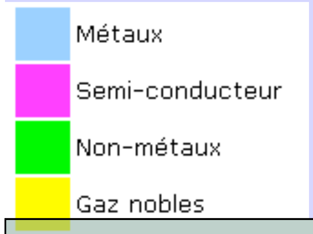
--------- → n=1 and m=9

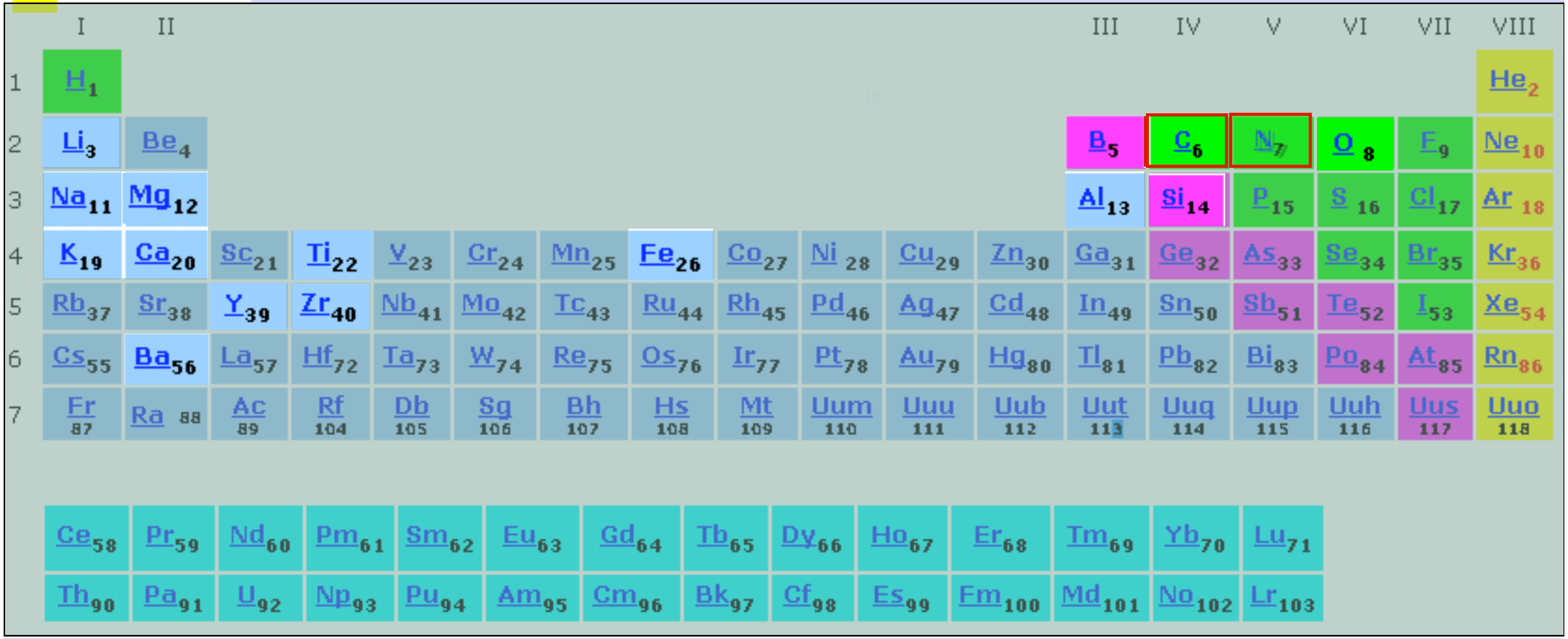
Silicate glasses:

Glass formers (Si, Al, B, Zr)

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

Anions: O, N or C





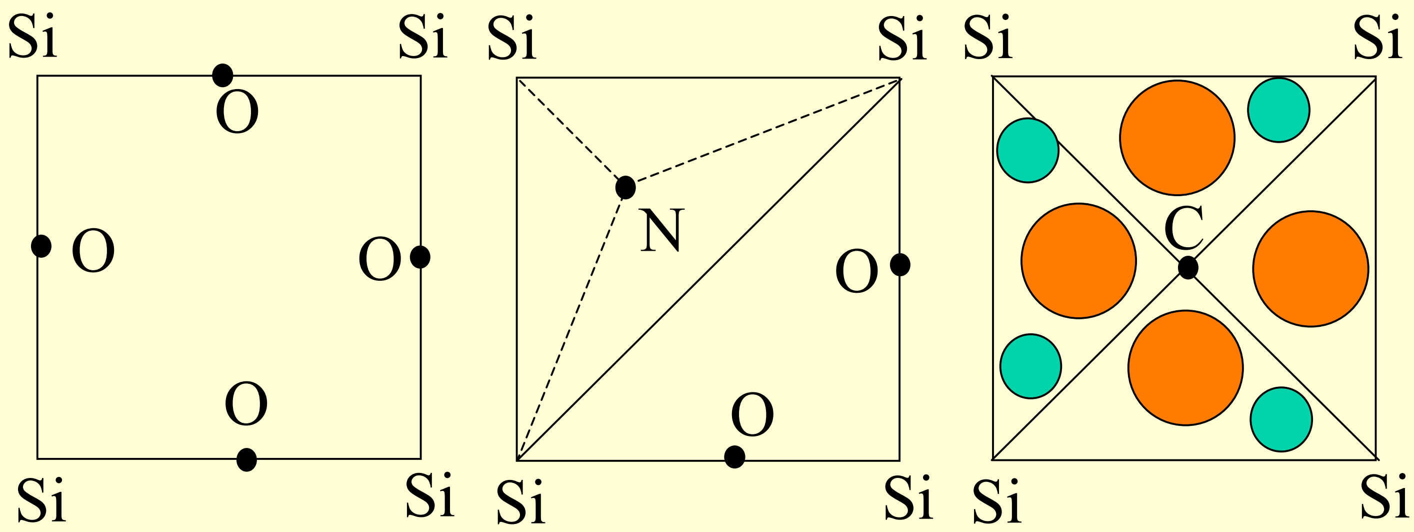
➡ Cation substitution: modifyers ⇒ Uo ↘; formers ⇒ Cg ↘

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.

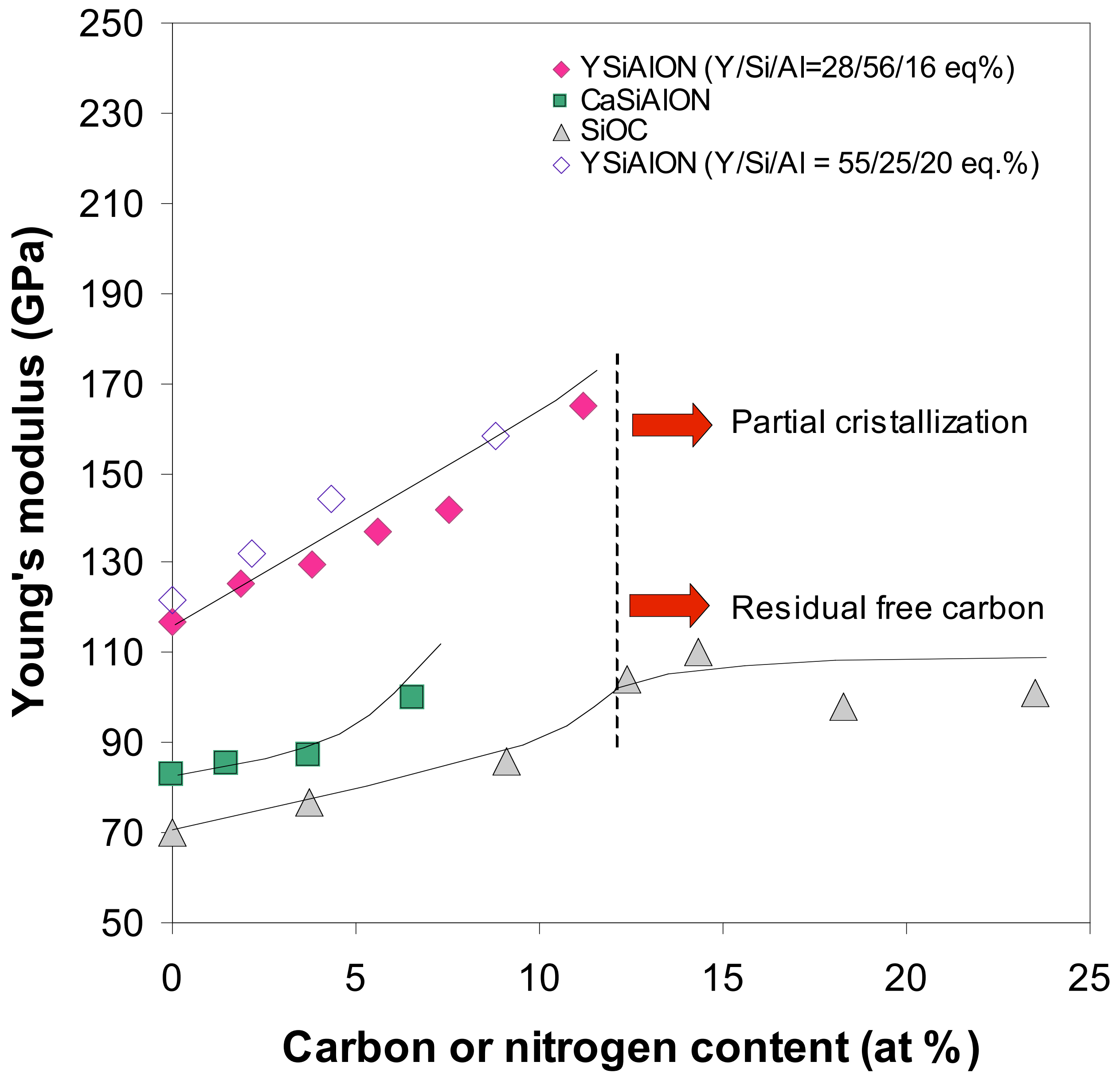
Anionic substitutions: more efficient but Tg ↗



E oxycarbides and E oxynitrides >> E oxides

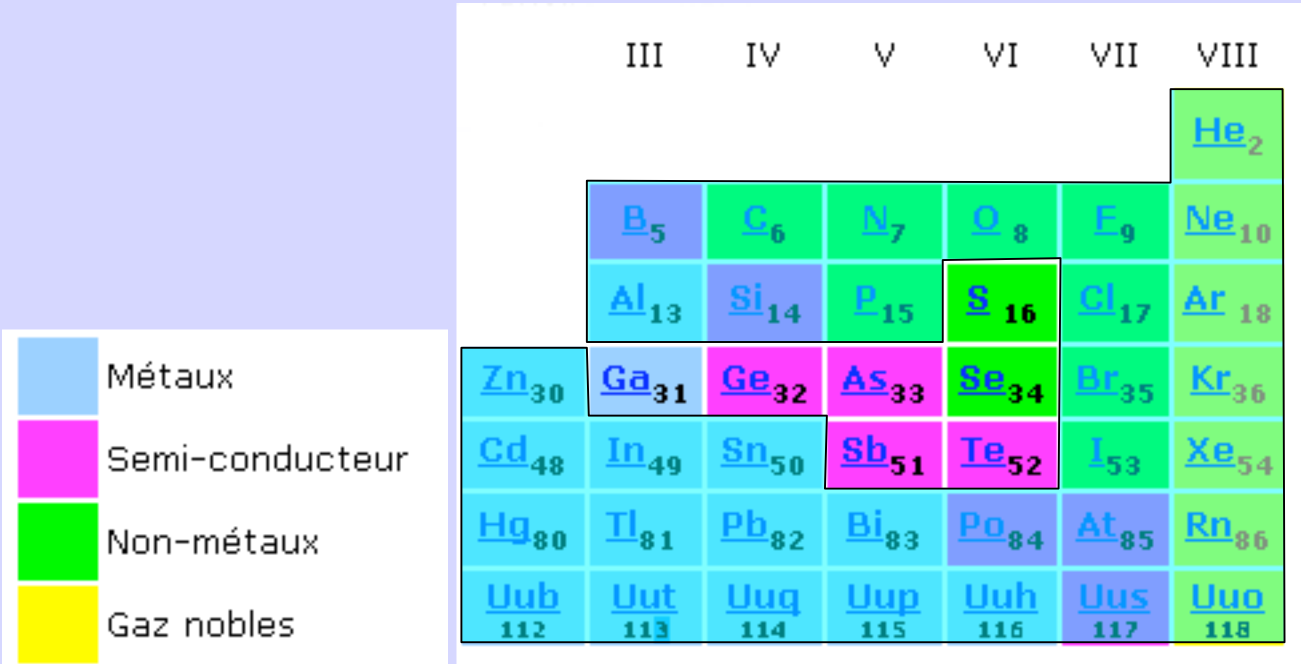
However: U_{oSiC}(447) kJ/mol)~$U_{oSi\text{-}N}$(437 kJ/mol)<$U_{oSi\text{-}O}$(800 kJ/mol)

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

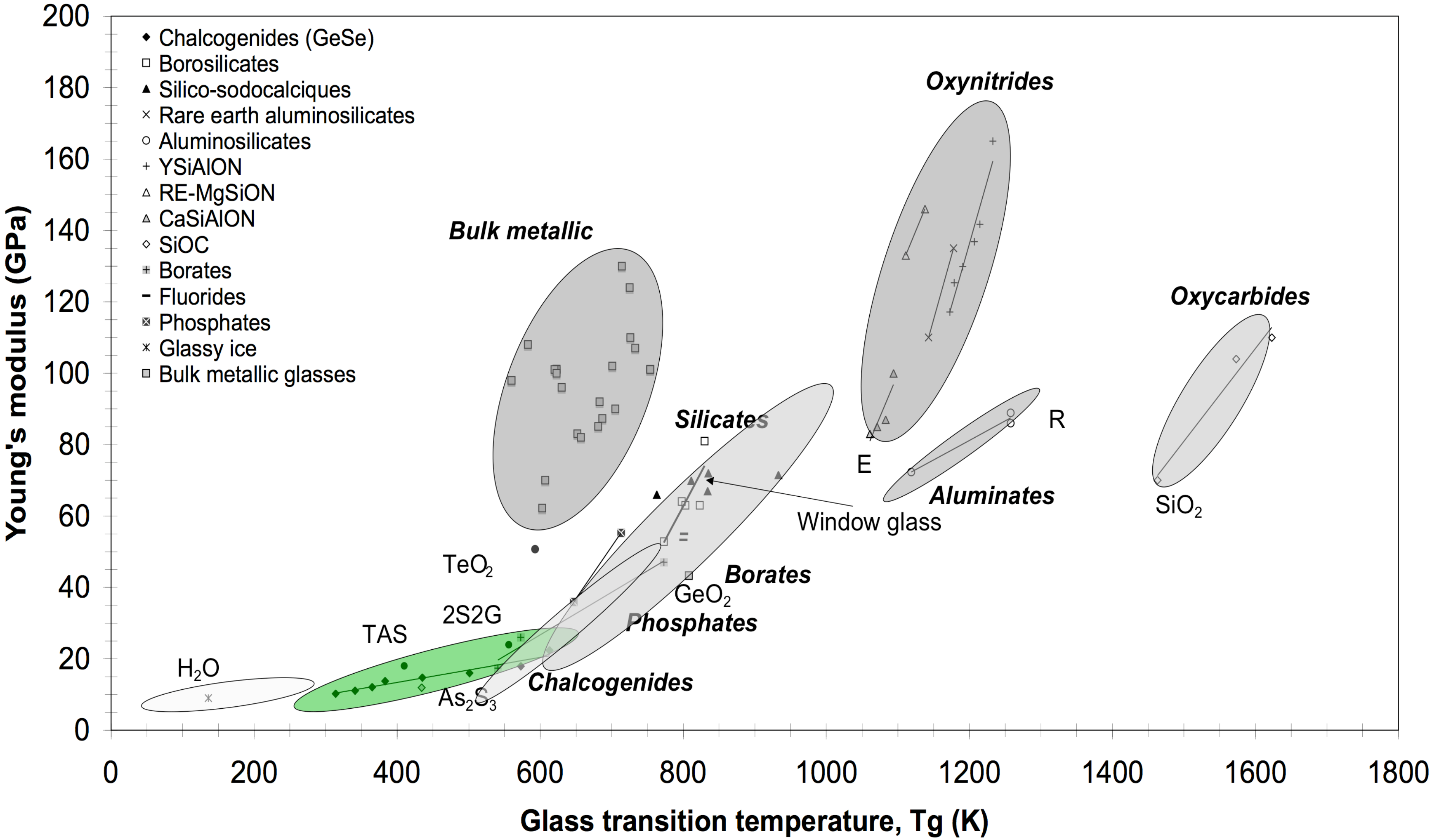

Young's modulus (GPa)
250
230
210
190
170
150
130
110
90
70
50
0
5
10
15
20
25
Carbon or nitrogen content (at %)
YSiAlON (Y/Si/Al=28/56/16 eq%)
CaSiAlON
SiOC
YSiAlON (Y/Si/Al = 55/25/20 eq.%)
Partial cristallization
Residual free carbon

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
Bulk metallic
Oxynitrides
Oxycarbides
Silicates
Aluminates
Window glass
Borates
Phosphates
Chalcogenides
E
R
SiO_2
TeO_2
2S2G
TAS
H_2O
GeO_2
As_2S_3
Young's modulus (GPa)
Glass transition temperature, Tg (K)
0
20
40
60
80
100
120
140
160
180
200
0
200
400
600
800
1000
1200
1400
1600
1800

Bulk Metallic Glasses

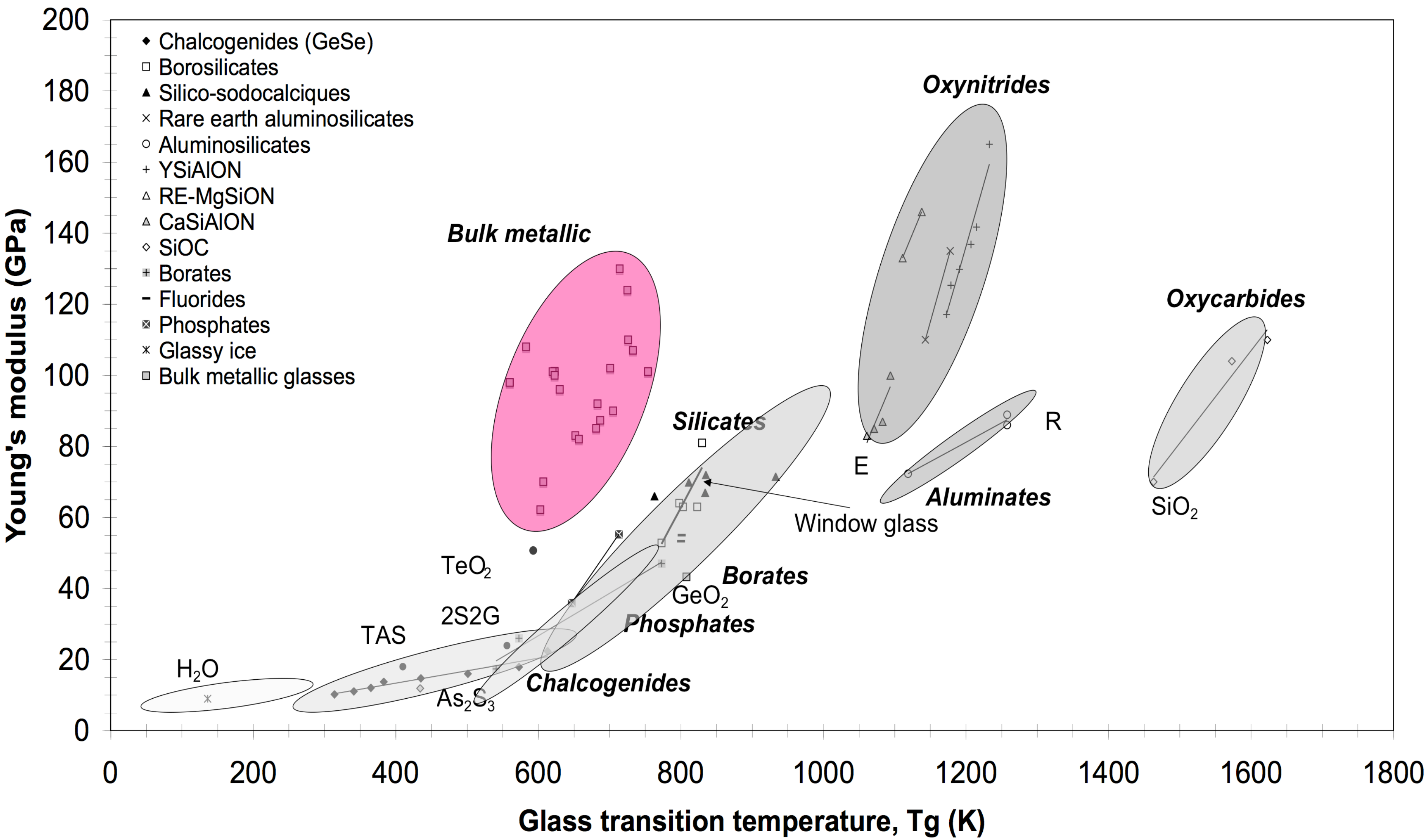
	I	II											III	IV	V	VI	VII	VIII
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uum 110	Uuu 111	Uub 112	Uut 113	Uuq 114	Uup 115	Uuh 116	Uus 117	Uuo 118

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

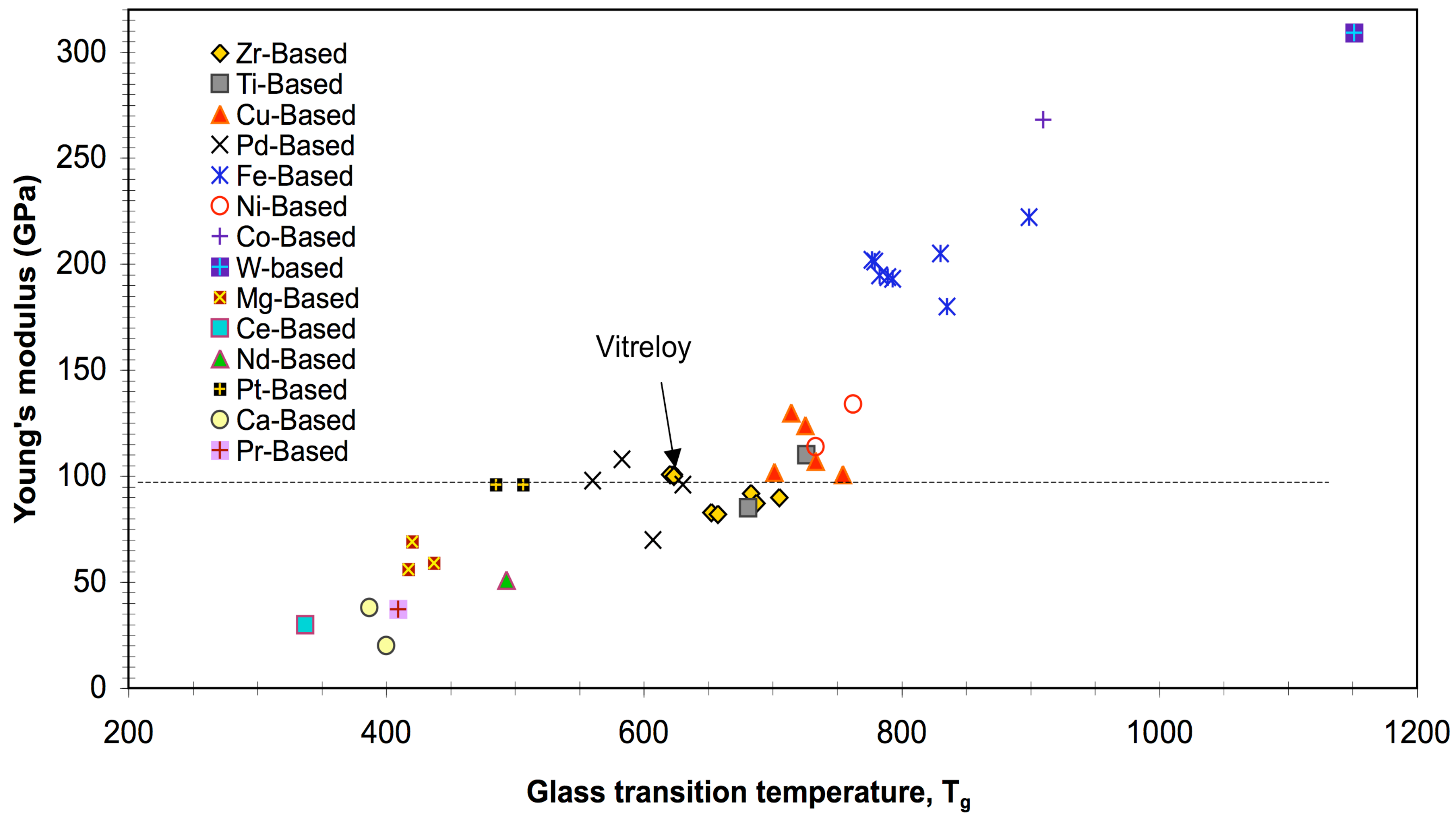
Atoms with much different atomic radii favour a chemical disorder and are used to synthesize BMG's: A metal (Be, Al, ...) + A transition metal (groups 3 to 12) from the right-hand side of the periodic table (Cu, Ni,...) + A transition metal from the left-hand side (Zr, Ti, Hf, Nb, ...), and a metalloid

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



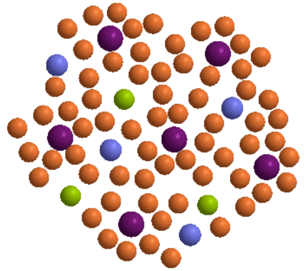
Young's modulus (GPa)
Glass transition temperature, Tg (K)
Chalcogenides (GeSe)
Borosilicates
Silico-sodocalciques
Rare earth aluminosilicates
Aluminosilicates
YSiAlON
RE-MgSiON
CaSiAlON
SiOC
Borates
Fluorides
Phosphates
Glassy ice
Bulk metallic glasses
Bulk metallic
Oxynitrides
Oxycarbides
Silicates
Aluminates
Window glass
Borates
Phosphates
Chalcogenides
TeO_2
2S2G
TAS
H_2O
As_2S_3
GeO_2
E
R
SiO_2
0
20
40
60
80
100
120
140
160
180
200
0
200
400
600
800
1000
1200
1400
1600
1800



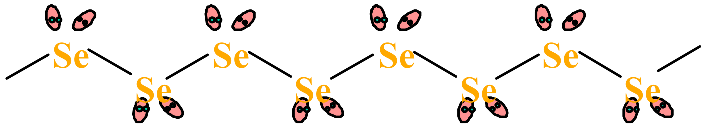
- Diferent chemical systems lead to identical elastic moduli
- This observation stems from the fact that BMG's show up with very different atomic packing density depending on their composition. For instance, Pt-based glasses have much higher packing density than Cu-Based alloys

Molecular scale:

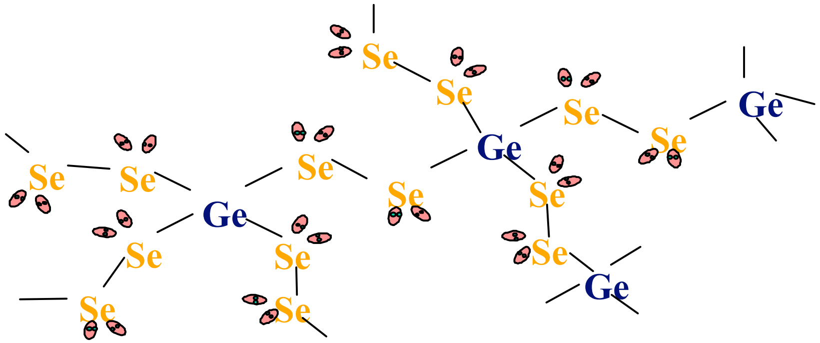
0D: Clusters, litlle short to medium range ordering



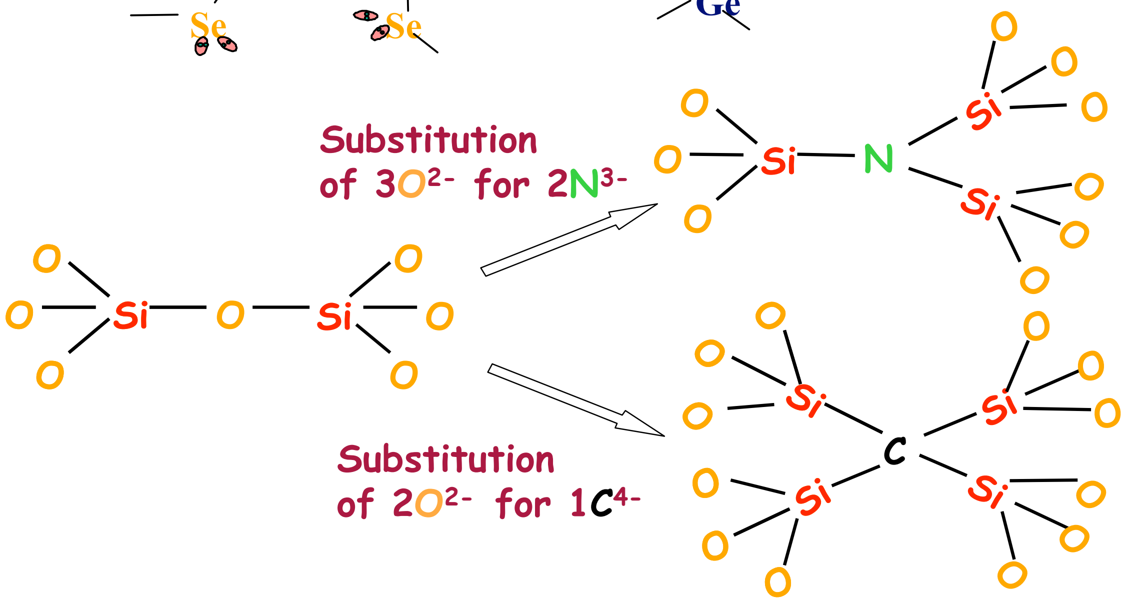
1D: Chains and rings



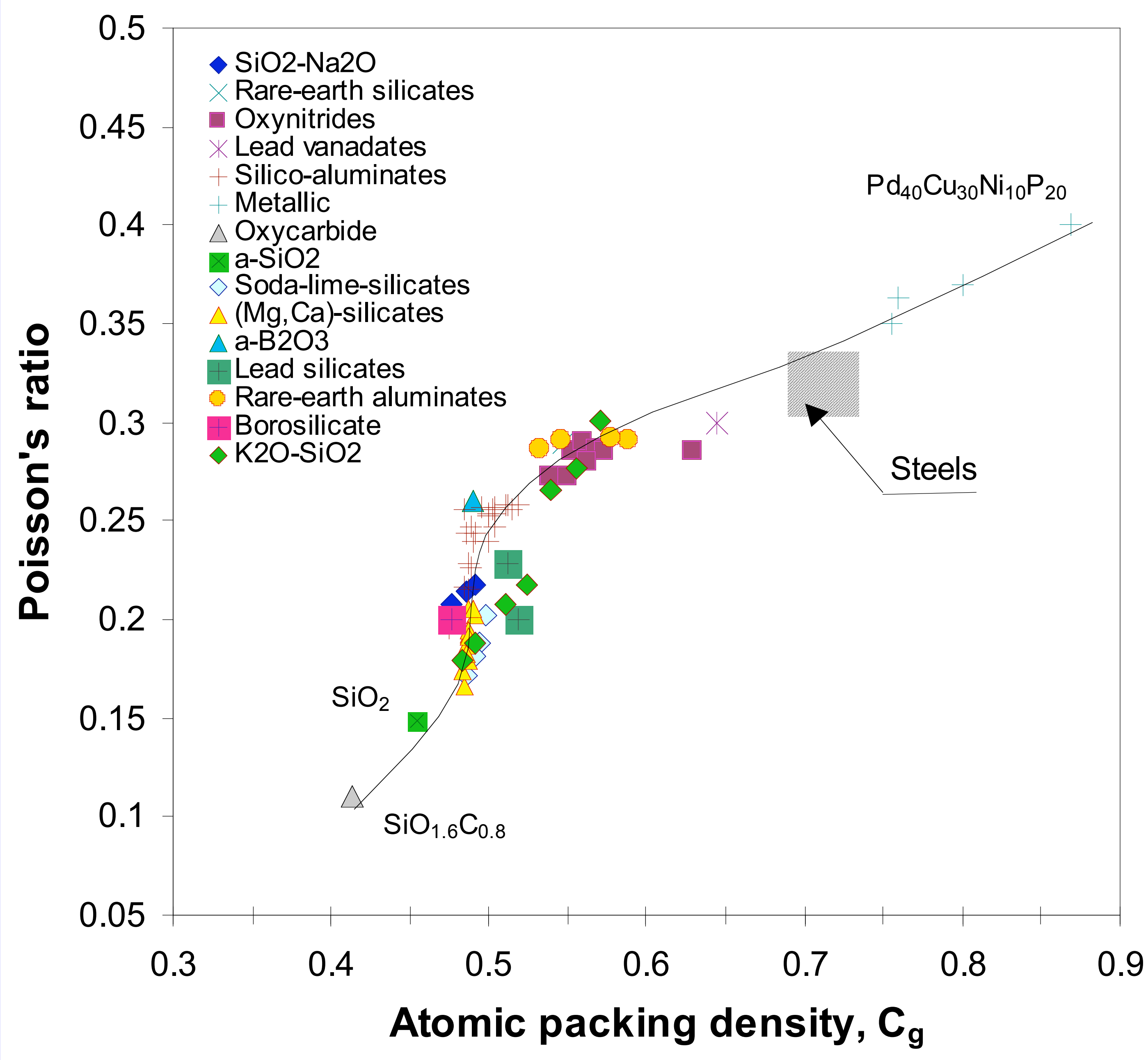
2D: Layers



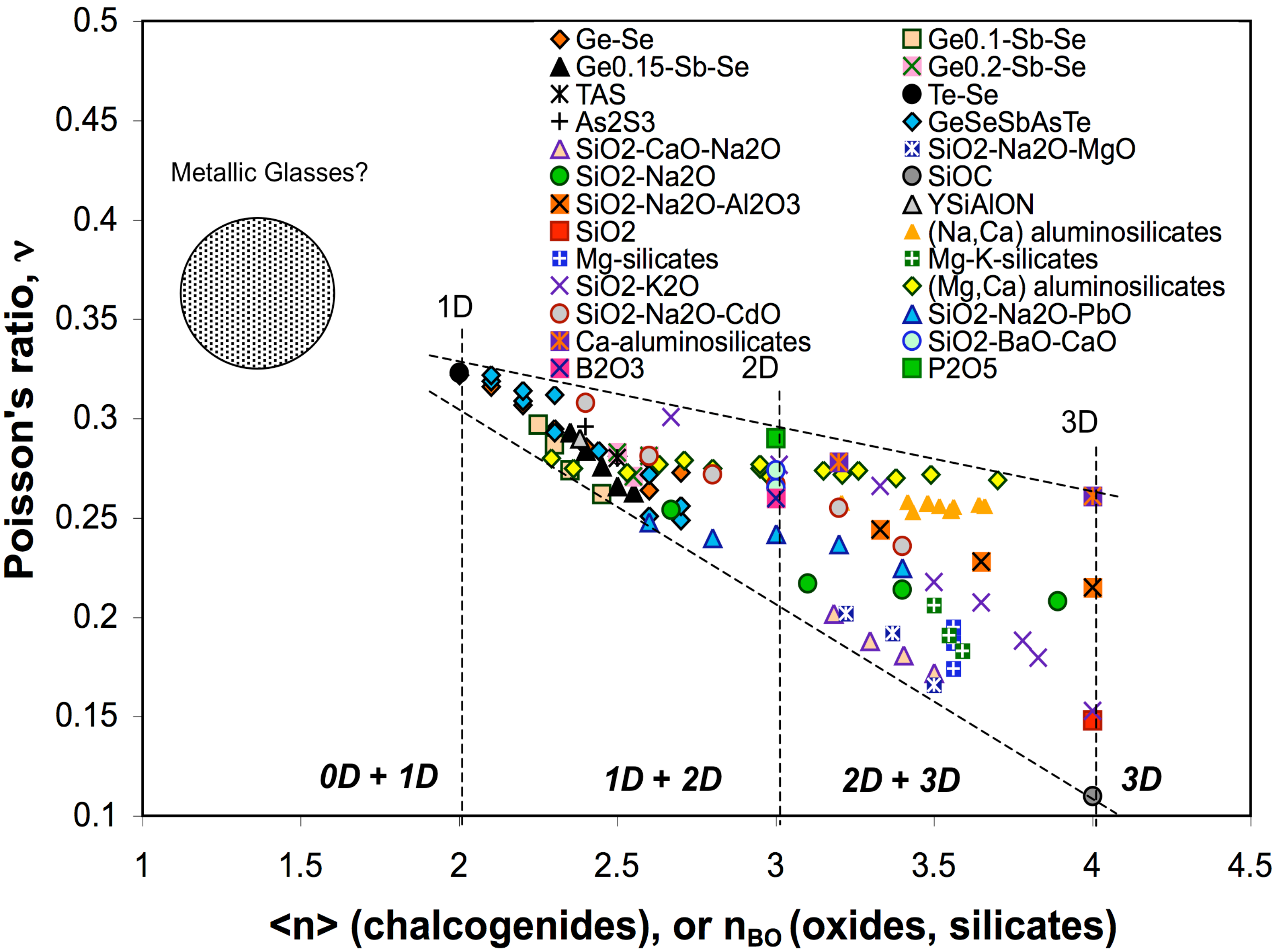
3D: 3D units and crosslinking



Influence of the atomic packing density

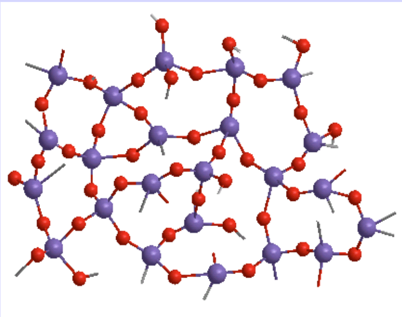


Poisson's ratio and dimensionality



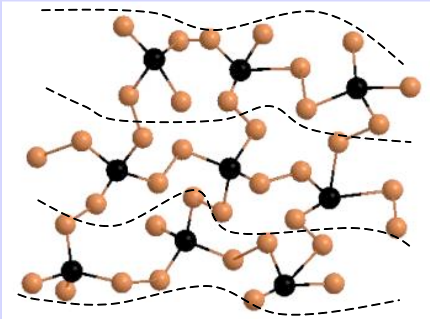
Poisson's ratio and atomic network dimensionality

a-SiO_2



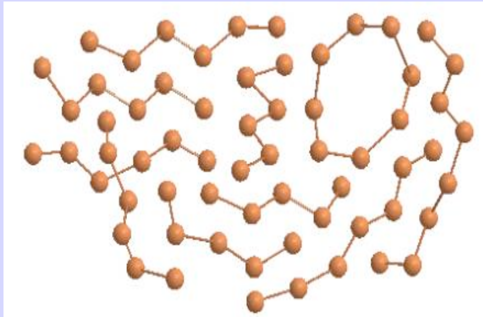
$\nu \approx 0.16$
3D

$GeSe_4$



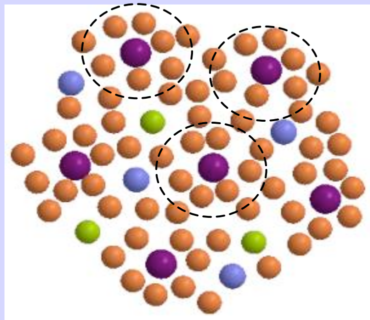
$\nu \approx 0.286$
2D

a-Se

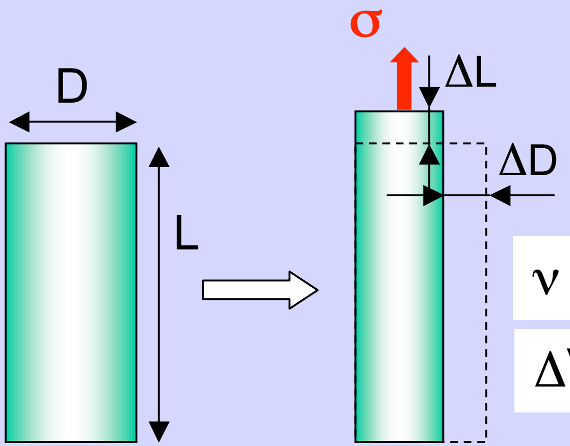


$\nu \approx 0.323$
1D

$Zr_{55}Cu_{30}Al_{10}Ni_5$



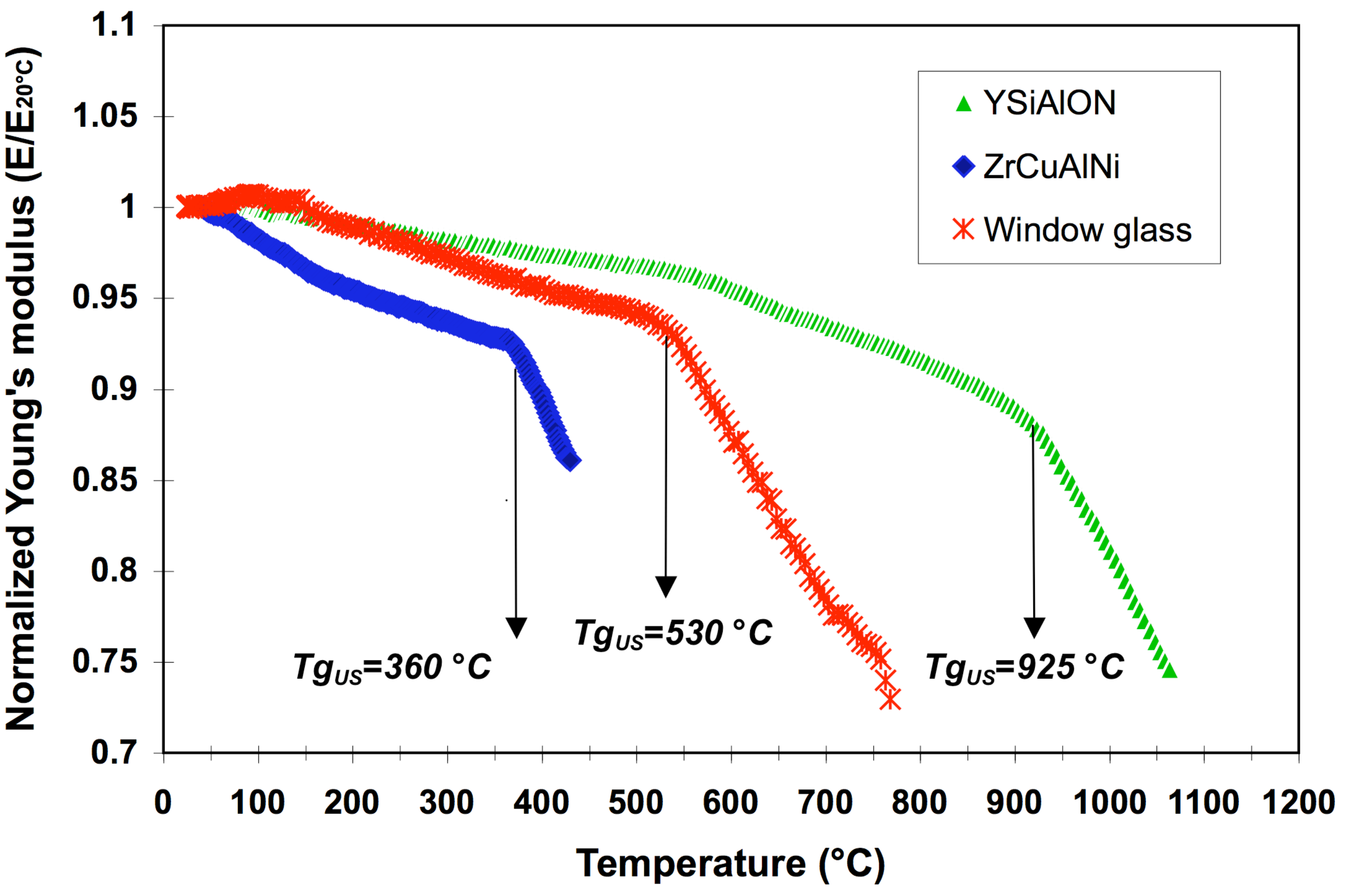
$\nu \approx 0.37$
0D?

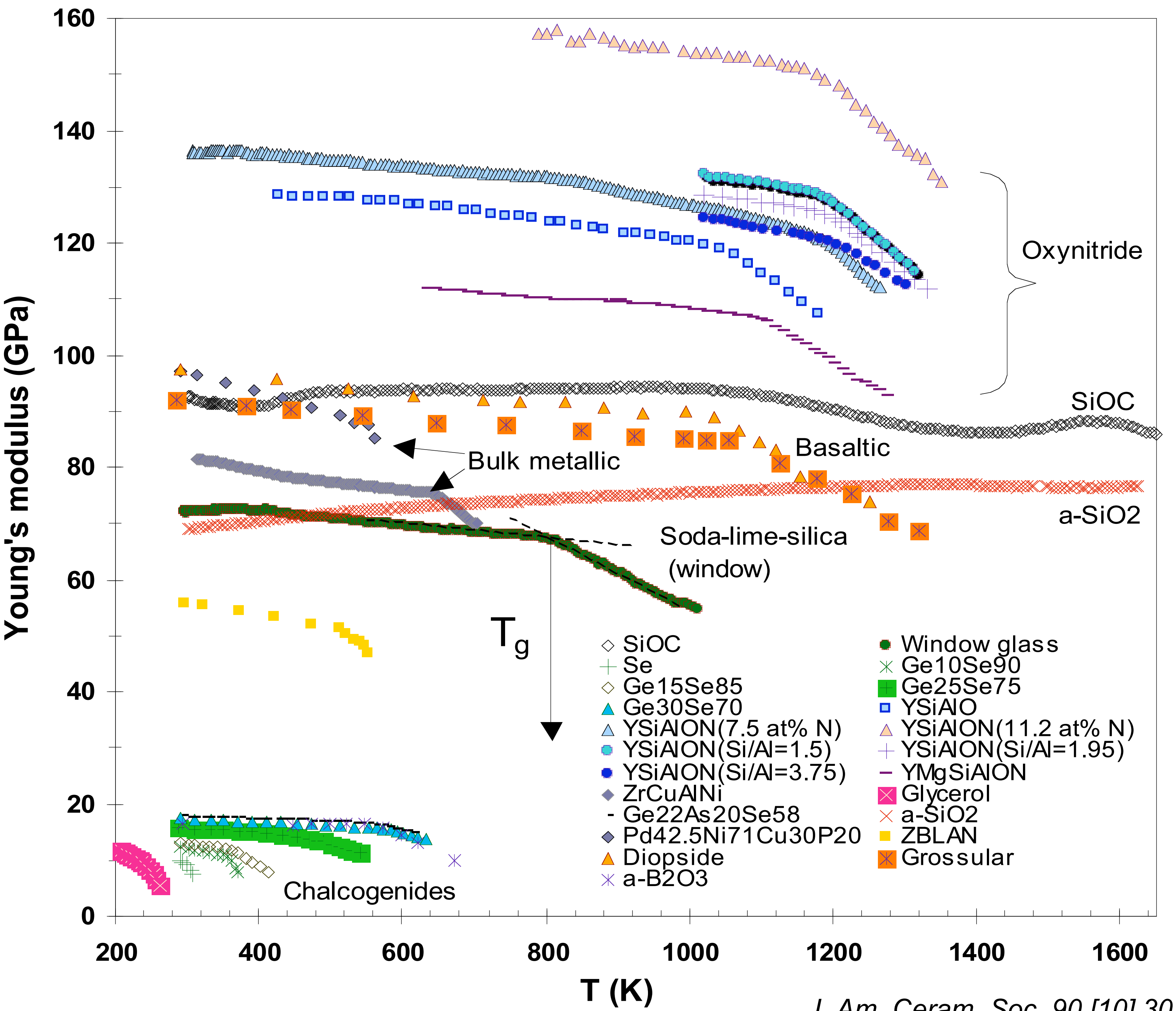


$\nu = -\varepsilon_t/\varepsilon_l = -\, L/D \times \Delta D/\Delta L$

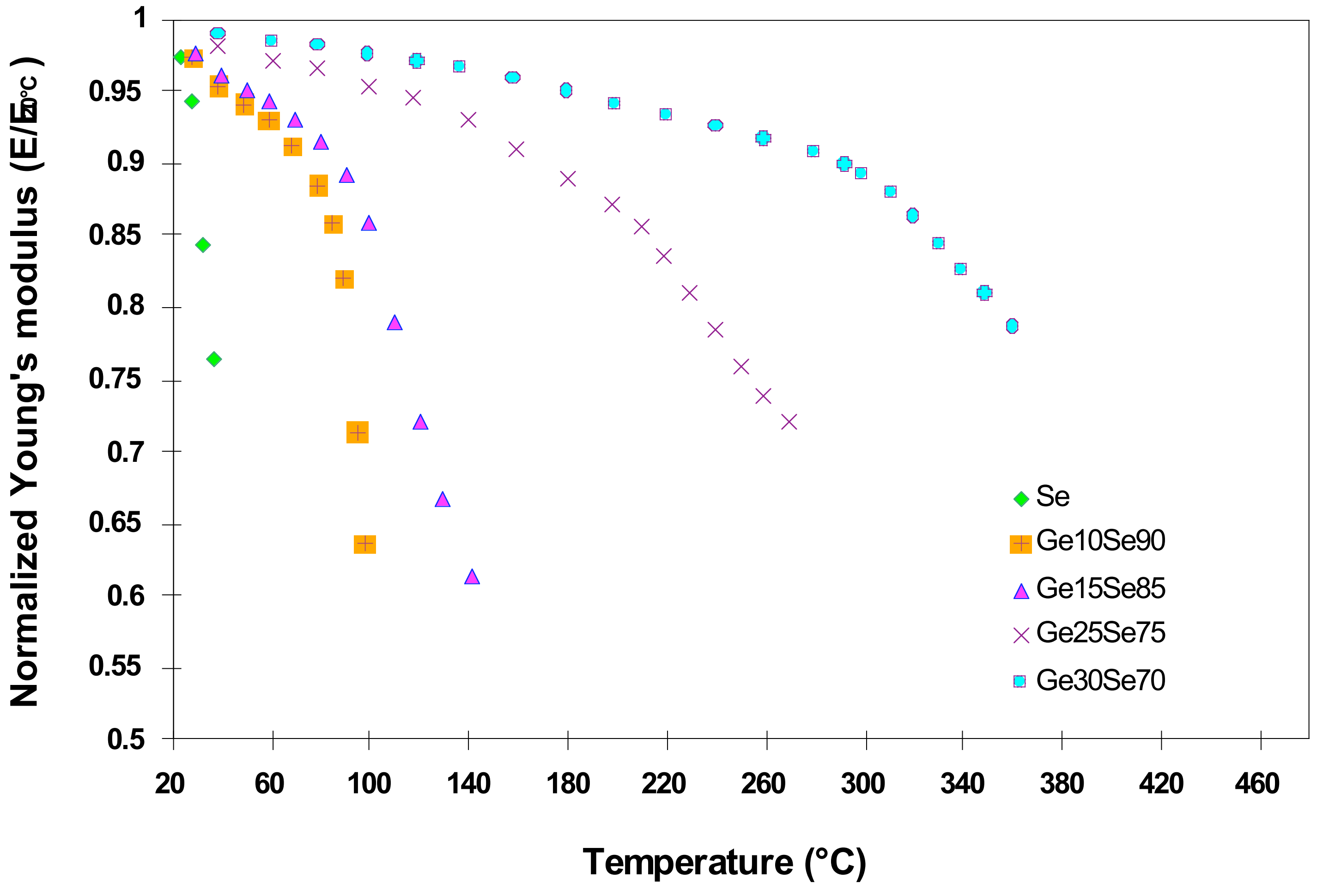
$\Delta V/V = \text{Trace } \varepsilon = (1-2\nu)\sigma/E$

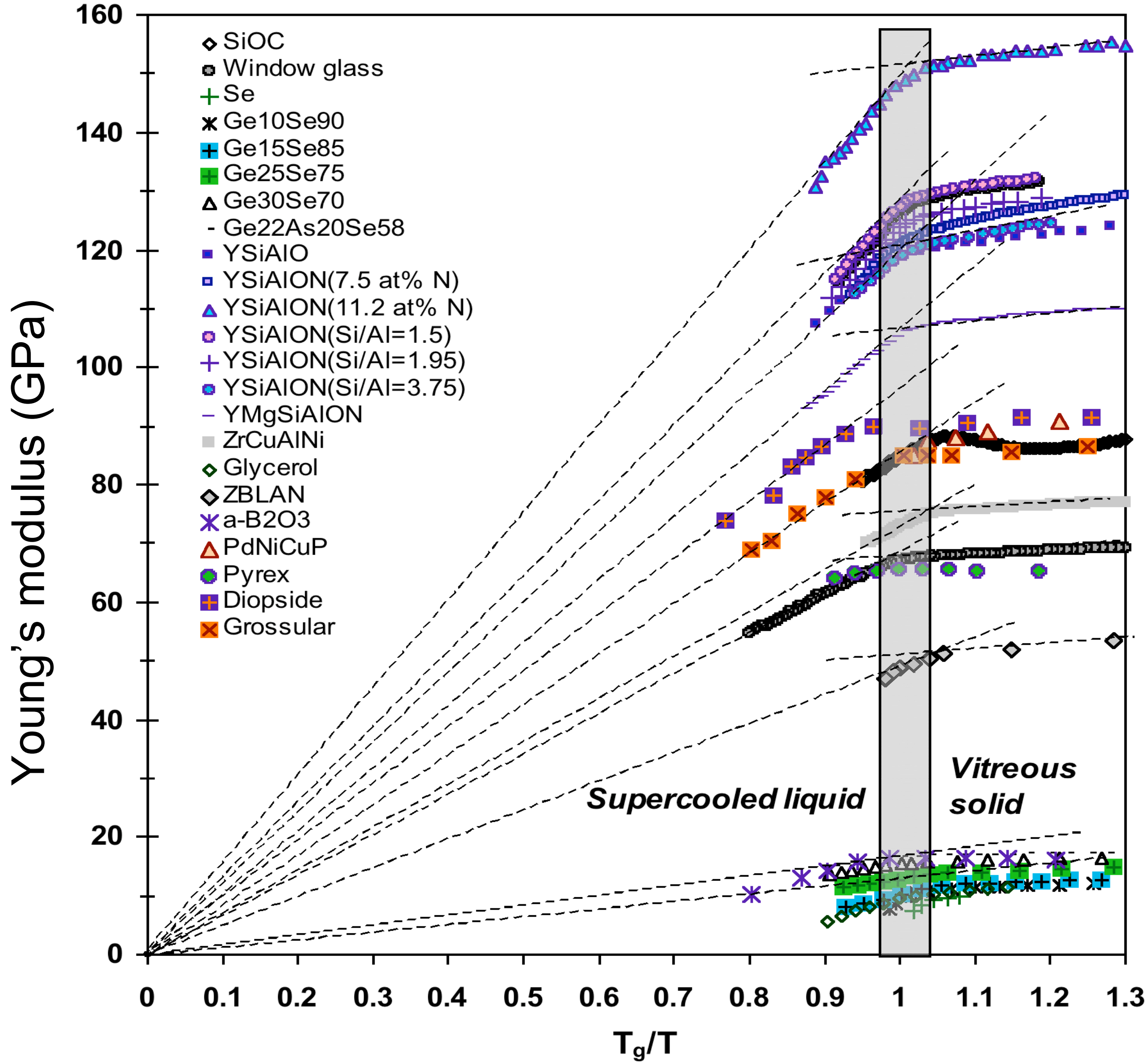
- **HIGH TEMPERATURE ELASTICITY**


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
TgUS=360 °C
TgUS=530 °C
TgUS=925 °C

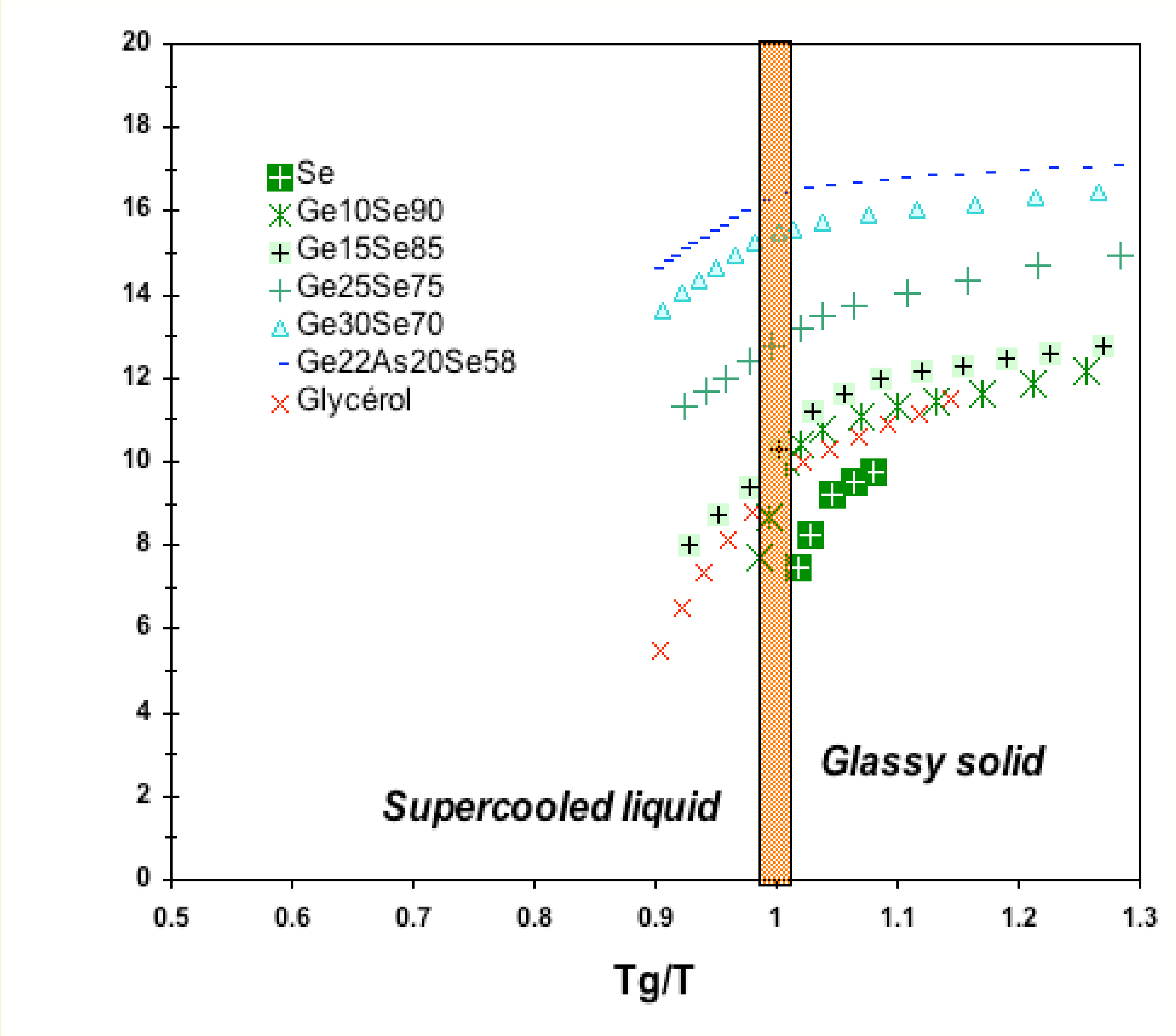


J. Am. Ceram. Soc. 90 [10] 3019-3039 (2007)


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
20
18
16
14
12
10
8
6
4
2
0
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
Tg/T

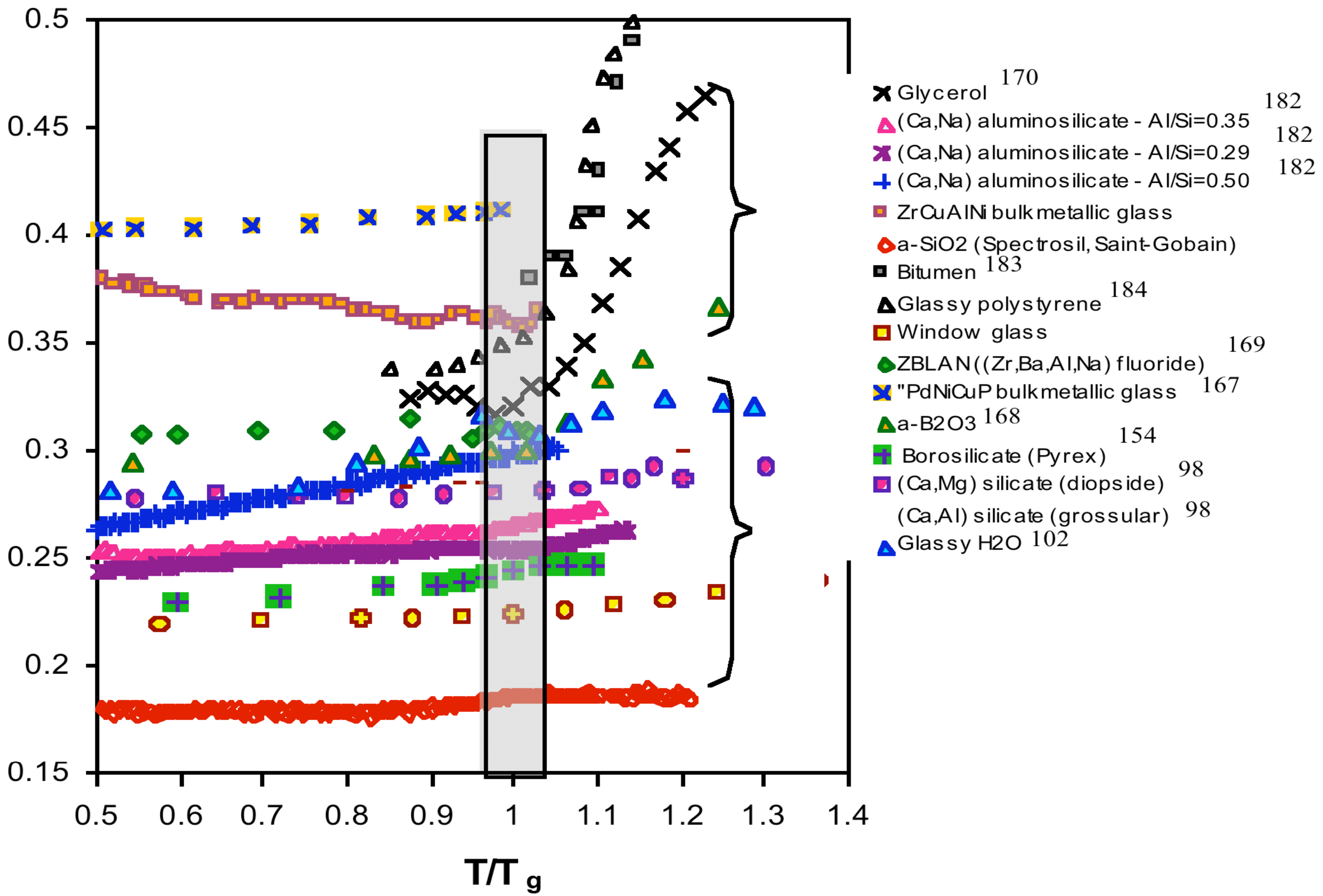
$$\beta = \frac{1}{1 - \frac{T}{E}\frac{\partial E}{\partial T}}$$

« 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)	β (~T_g)[2)]	β[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 (ν) 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