Introduction to the structure and the structural role of elements in glasses

Laurent Cormier

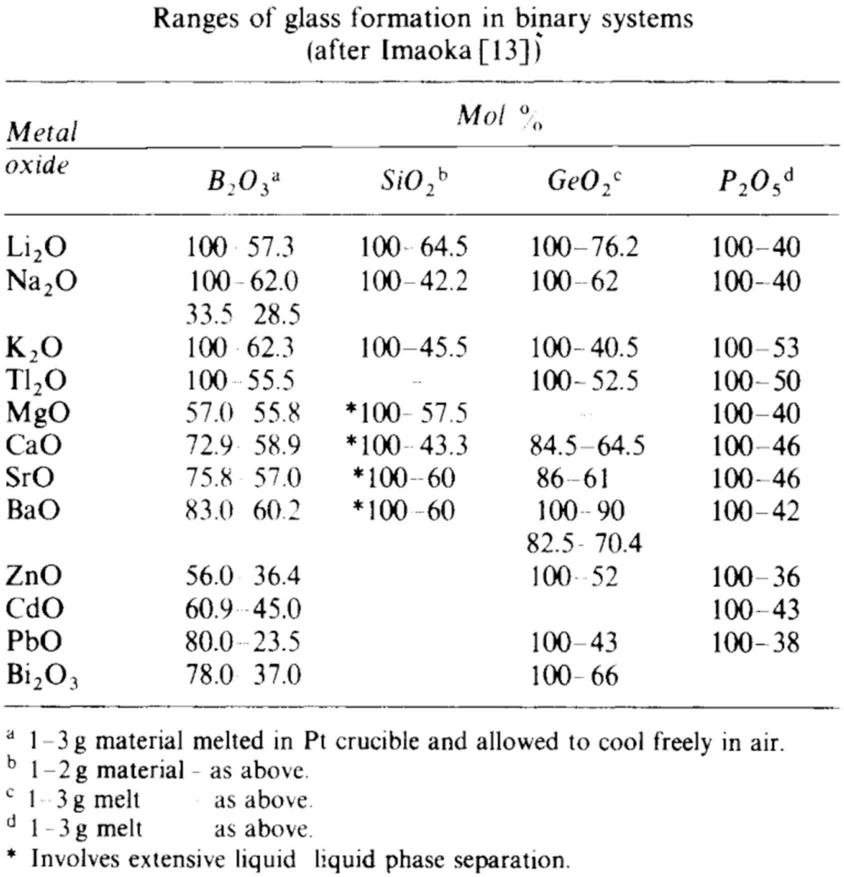
Institut de Minéralogie, Physique des Matériaux et Cosmochimie
Université Pierre et Marie Curie – CNRS
Paris, France
cormier@impmc.upmc.fr

Ecole GDR Verres Cargèse

Glass forming ability (GFA)

In principle almost any substance can be made into a glass by cooling it from the liquid state **if cooled sufficiently fast** to prevent crystallization. In practice, however, it seems useful to make some classification scheme.

No theories able to predict which materials are able to form a glass, and under what conditions



Ranges of glass formation in binary systems
(after Imaoka [13])

Metal oxide	Mol %			
	B_2O_3[a]	SiO_2[b]	GeO_2[c]	P_2O_5[d]
Li_2O	100–57.3	100–64.5	100–76.2	100–40
Na_2O	100–62.0 33.5–28.5	100–42.2	100–62	100–40
K_2O	100–62.3	100–45.5	100–40.5	100–53
Tl_2O	100–55.5	–	100–52.5	100–50
MgO	57.0–55.8	*100–57.5	–	100–40
CaO	72.9–58.9	*100–43.3	84.5–64.5	100–46
SrO	75.8–57.0	*100–60	86–61	100–46
BaO	83.0–60.2	*100–60	100–90 82.5–70.4	100–42
ZnO	56.0–36.4		100–52	100–36
CdO	60.9–45.0			100–43
PbO	80.0–23.5		100–43	100–38
Bi_2O_3	78.0–37.0		100–66	

[a] 1–3 g material melted in Pt crucible and allowed to cool freely in air.
[b] 1–2 g material – as above.
[c] 1–3 g melt as above.
[d] 1–3 g melt as above.
* Involves extensive liquid–liquid phase separation.

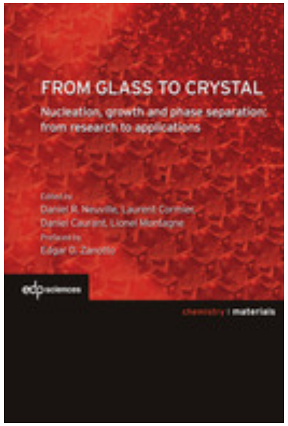
From 'Chemistry of glasses'
Paul (2012)

Glass families and glass forming ability

Glass formation results when

- Liquids are cooled to below T_M (T_L) sufficiently fast to avoid crystallization
  - Nucleation of crystalline seeds are avoided
  - Growth of nuclei into crystallites (crystals) is avoided

⇒ **Kinetic theory** of glass formation (Turnbull and Cohen, 1960)



FROM GLASS TO CRYSTAL
Nucleation, growth and phase separation: from research to applications
Edited by
Daniel R. Neuville, Laurent Cormier,
Daniel Caurant, Lionel Montagne
Prefaced by
Edgar D. Zanotto
edp sciences
chemistry | materials

From glass to crystal -Nucleation, growth and phase separation: from research to applications (2017)
D.R. Neuville, L. Cornier, D. Caurant, L. Montagne

- Liquid is frustrated by internal structure that hinders both events

Glass families and glass forming ability

Competition between crystalline growth and cooling of the melt.

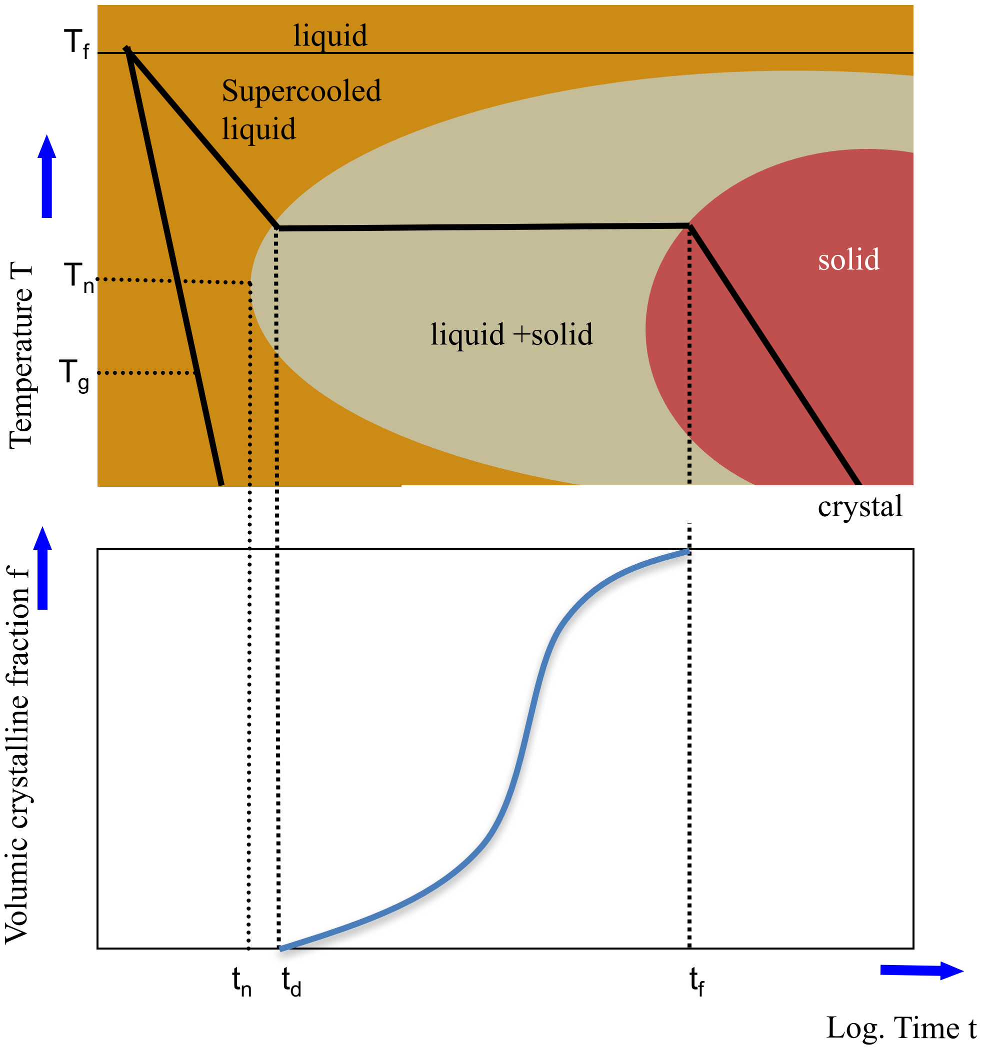
Quantitative estimate through time-temperature-transformation (TTT) curves

How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?

Critical cooling rate R_c = the nose of the TTT curve

$$R_C = \frac{T_f - T_n}{t_n}$$

Good glass formers:
q = dT/dt ~ 10^{-3} K/s
Bad glass formers:
q = dT/dt > 10^{6} K/s



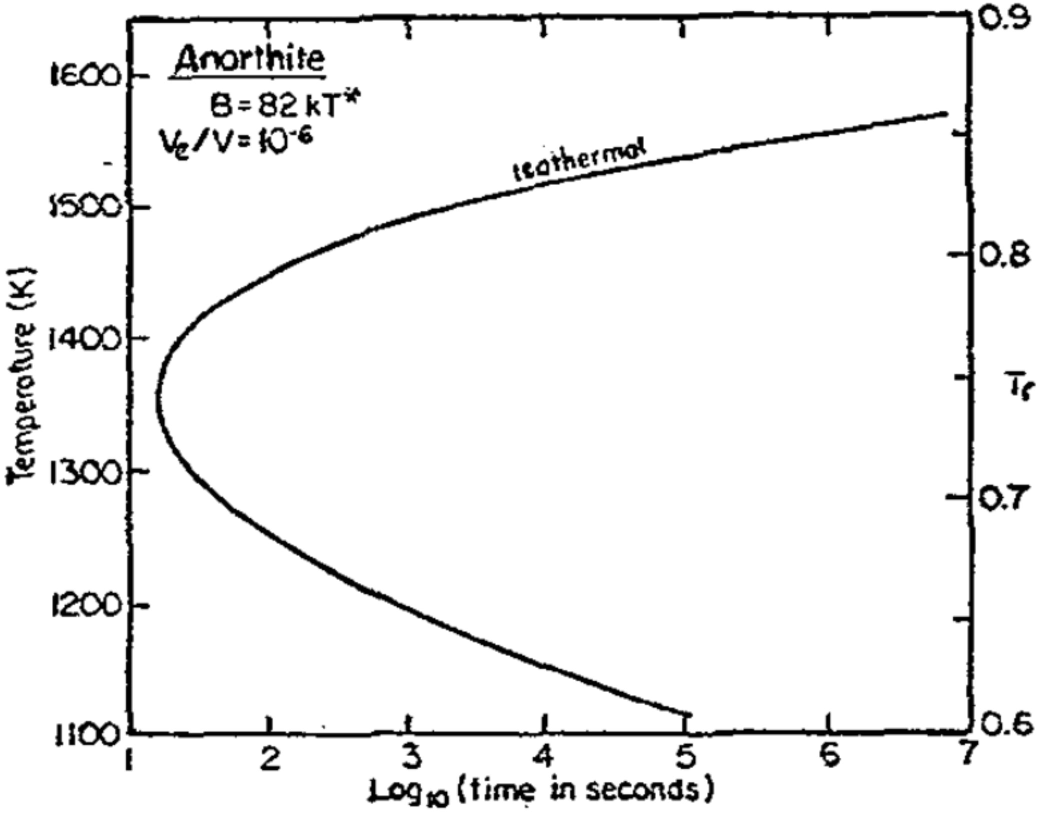
Glass families and glass forming ability

Competition between crystalline growth and cooling of the melt.

Good glass formers:
$q = dT/dt \sim 10^{-3}$ K/s
Bad glass formers:
$q = dT/dt > 10^{6}$ K/s

Quantitative estimate through time-temperature-transformation (TTT) curves

How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?



Uhlmann, J. Phys. Coll., 43 (1982) C9-175-C9-190

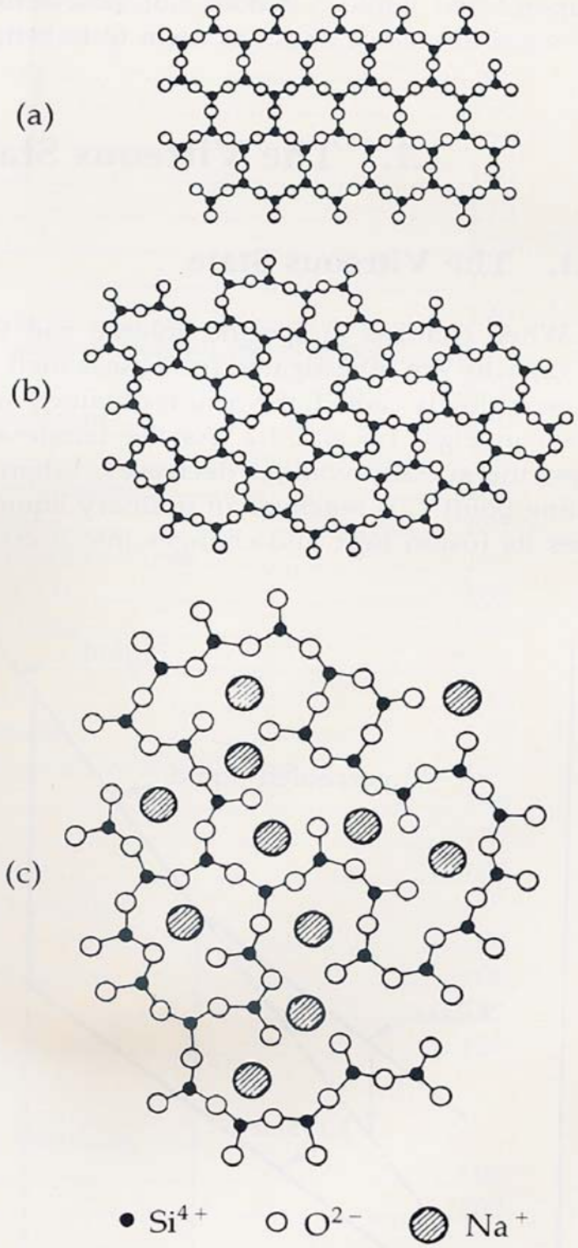
Critical cooling rate R_c = the nose of the TTT curve

$$R_C = \frac{T_f - T_n}{t_n}$$

Glass families and glass forming ability

In a multicomponent material like the SiO_2-Na_2O glass (c), the question of the **region of glass formation** arises:
how much Na_2O can be added to SiO_2, while still keeping the glass forming ability of the system?

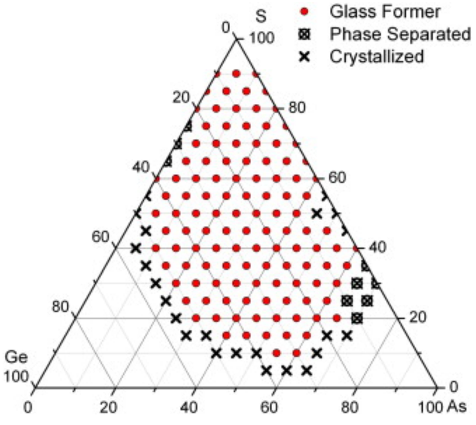
What is the region of glass formation ?



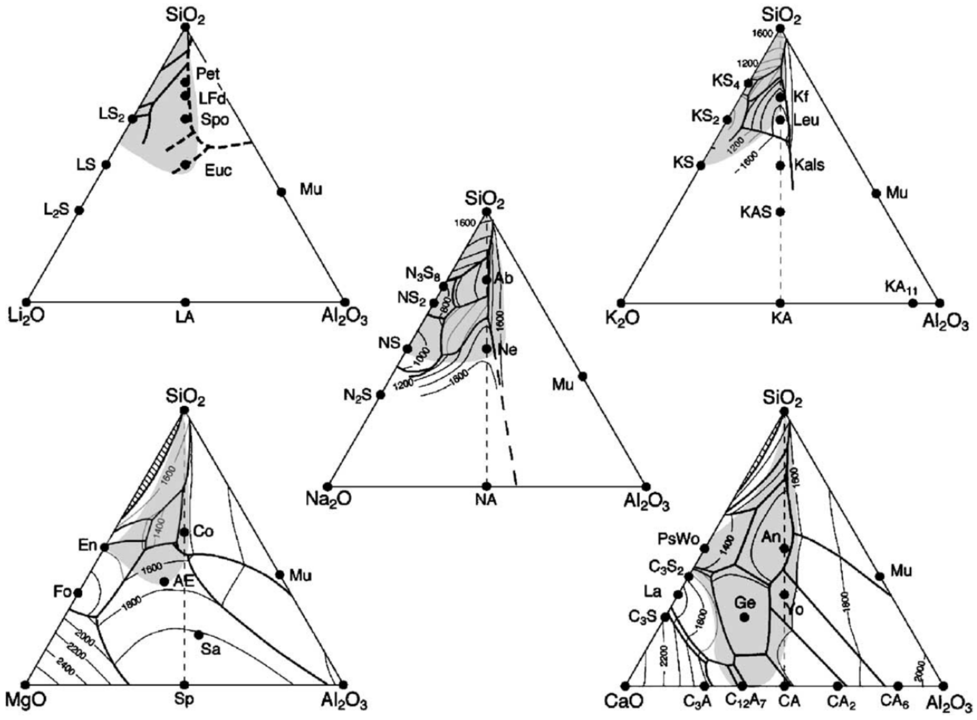
1.3. Network structure of SiO_4^{4+} tetrahedrons: (a) quartz crystal, (b) quartz glass, (c) sodium silicate glass (Ref. 5).

Glass forming region

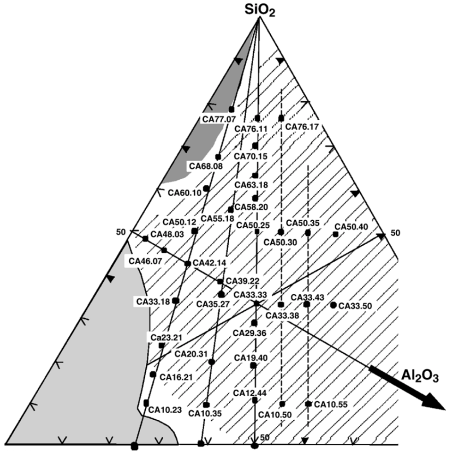
Determination of glass forming region after extensive studies in compositions



Musgrave et al., J. Non-Cryst. Solids, 386 (2014) 61



Richet et al., Chem. Geol. 225 (2006) 388

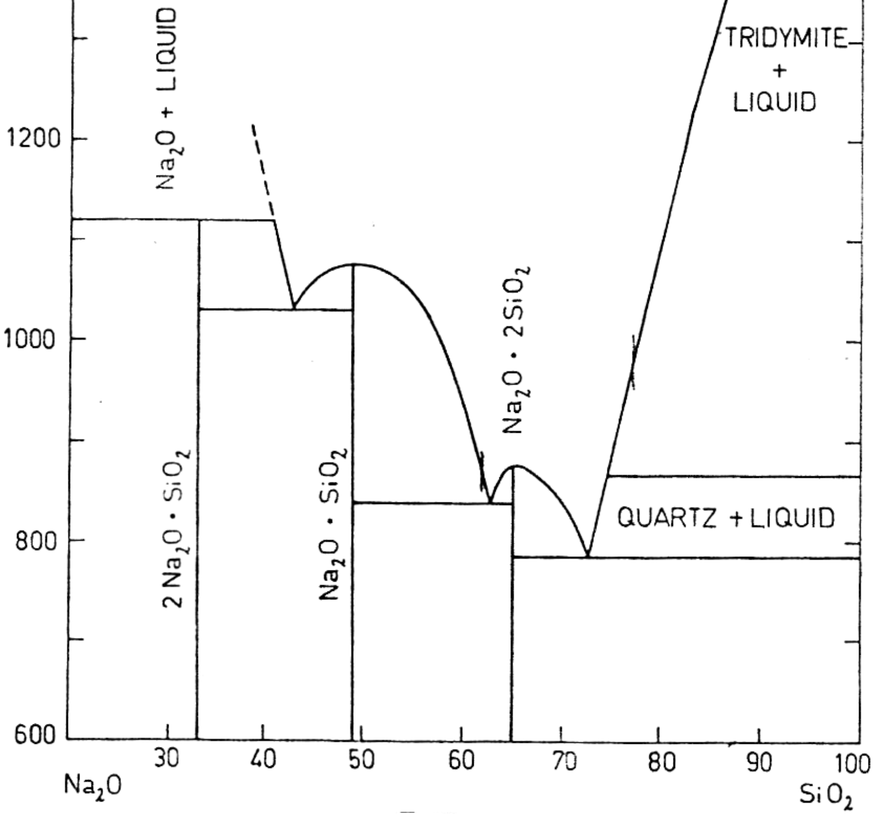


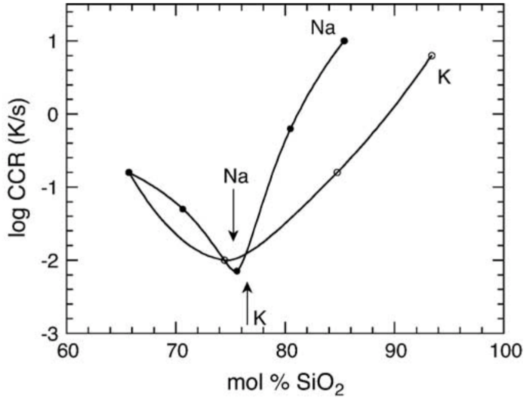
Neuville et al., Chem. Geol. 229 (2006) 173

Glass forming region

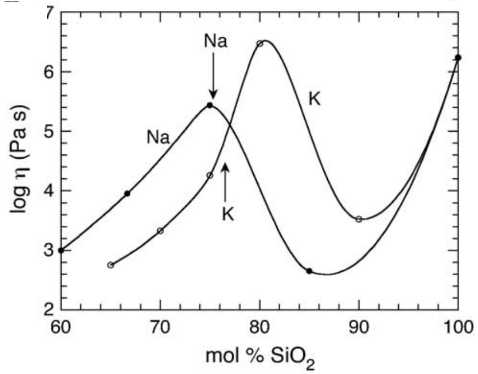
In a phase diagram, glasses are favored near eutectics because these freezing depressions bring the liquid to higher viscosities at lower temperatures

Correlation between critical cooling rate and viscosity along the liquidus branche





Critical cooling rates for glass formation in sodium and potassium silicates. Data from Fang et al. (1983) for a crystal fraction of less than 10^{-6}. The arrows indicate the position of the deepest eutectics of the binary systems shown in Fig. 5.



The combined effects of composition and temperature on viscosity along liquidus branches in alkali silicate systems. (a) Viscosity of sodium silicate melts at 1200 °C (Bockris et al., 1955; Leko et al., 1977). (b) Viscosity of alkali silicate melts along the liquidus branches of Fig. 5. Data from Poole (1948) and Bockris et al. (1955). The arrows indicate the positions of the deepest eutectics of the binary systems.

Richet et al., Chem. Geol. 225 (2006) 388

⇒ Daniel Neuville

Structural approach to glass-forming ability (GFA)

What internal structures promote glass formation?

How can structures be developed that increase the viscosity and frustrate crystallization processes?

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt’s radius ratio
  - Zachariasen’s random network theory

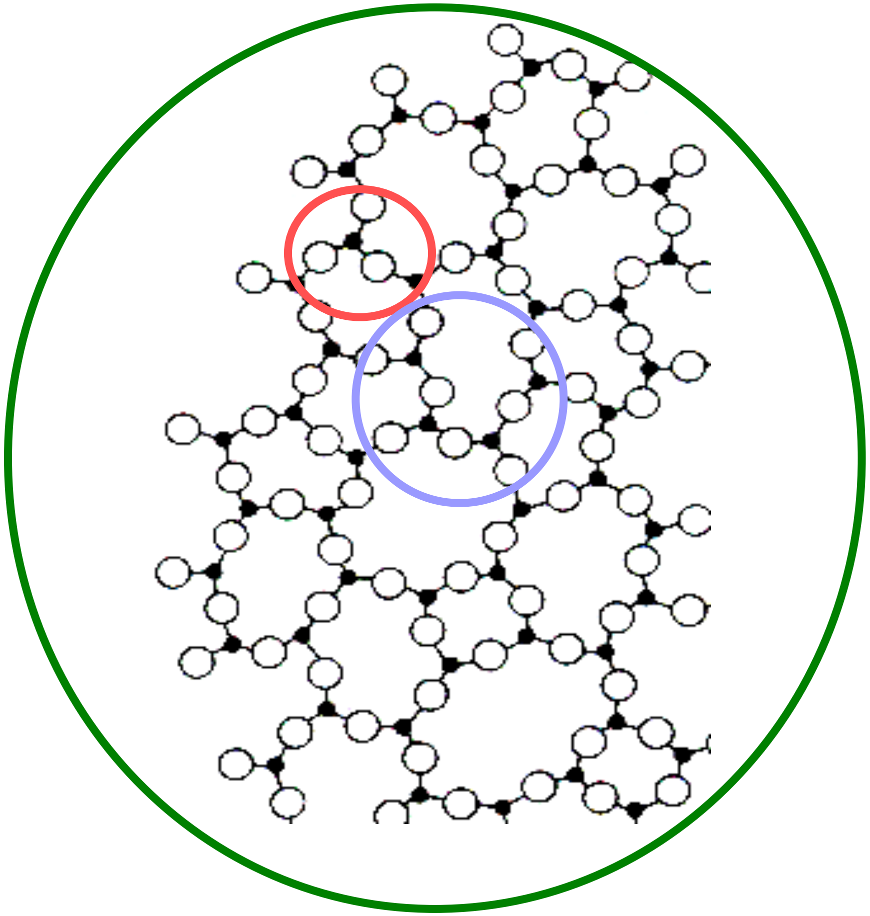
- Based on bond type
  - Smekal’s mixed bonding rule
  - Stanworth’s electronegativity rule

- Based on bond strength
  - Sun’s single bond strength criterion

- Based on field strength
  - Dietzel’s field strength

- Based on Mott’s rule
  - Phillips

Different structural ranges



Short range order (<3 Å):

- coordination, bond length, bond angle
- homopolar (-Se - Se- , -C - C-, -As - As) vs. heteropolar (Si - O, B - O, Ge - S)

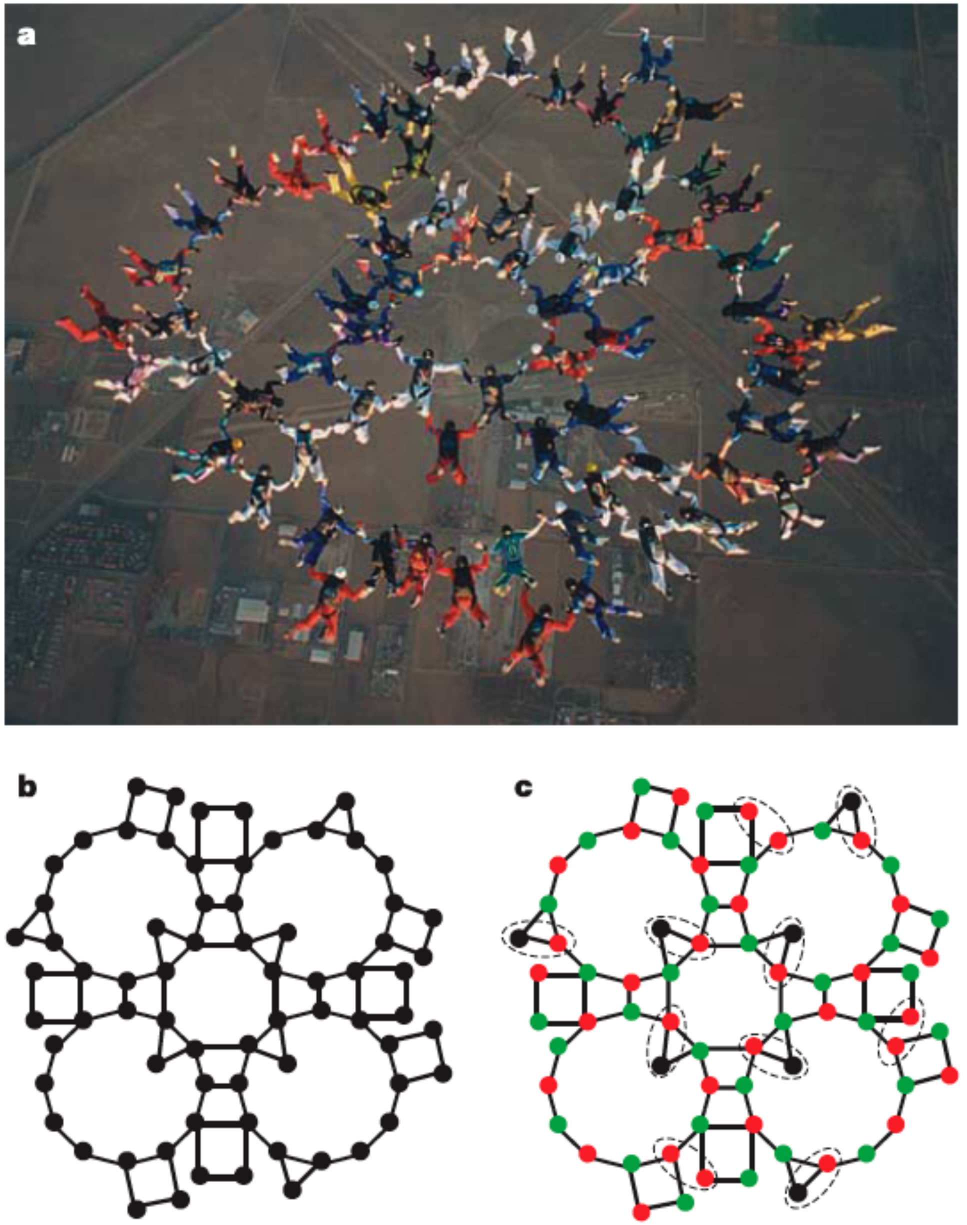
Medium (intermediate) range order (3 – 10 Å typically):

- angles between structural units
- connectivity between structural units (linkages by corner, edge, face)
- dimensionnality, rings

Almost no long range order (no periodicity!) :

- phase separation
- inhomogeneities

Topological and chemical disorder



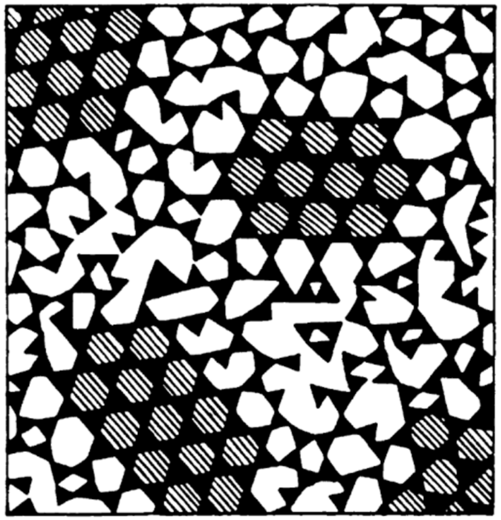
Salmon et al., Nature 435 (2005) 75-78

Structural model

A good structural model should

- explain structure-properties relationships
- describe atomic arrangements at short and medium range
- have general concepts applicable to a large number of systems

Initially, idea of micro-crystallites (quasi-crystals) but it was demonstrated that the size of these crystals is 7-8 Å (size of the unit cell) !



crystallite model of Lebedev

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt's radius ratio
  - Zachariasen's random network theory

- Based on bond type
  - Smekal's mixed bonding rule
  - Stanworth's electronegativity rule

- Based on bond strength
  - Sun's single bond strength criterion

- Based on field strength
  - Dietzel's field strength

- Based on Mott's rule
  - Phillips

Goldschmidt's radius ratio criterion

for a simple oxide of formula M_mO_n (M cation), glass formation is only possible when the ratio of atomic radii, $\boldsymbol{r_a/r_c}$ (where *c* denotes cation, and *a* anion) falls between 0.2 to 0.4

the cation / anion ratio determines how many anions can be packed around a given cation, i.e. the coordination number of the compound. Most crystals with a cation / anion radius ratio of 0.2 to 0.4 have a co-ordination number (CN) of 4 with anions at the corners of a tetrahedron

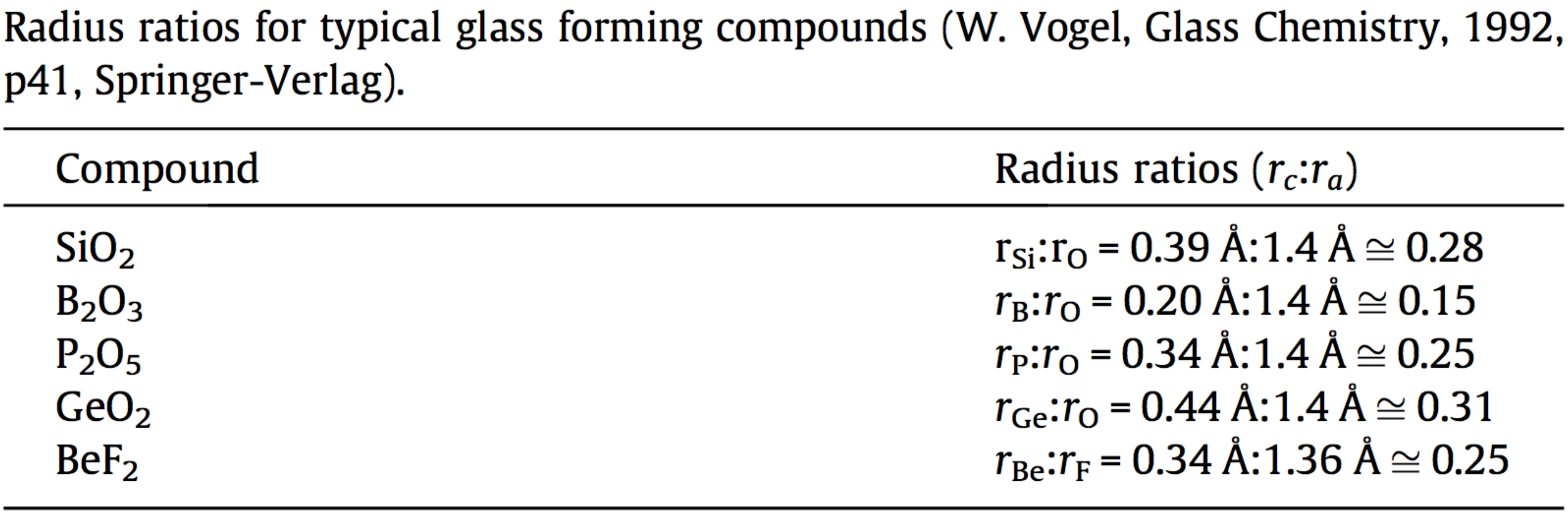
=

tetrahedral arrangement of oxygen ions around a cation M necessary for glass formation

assumed the oxide is purely ionic (not strictly correct as many glass-forming oxides have covalent character, e.g. SiO_2)

Victor M. Goldschmidt (1888-1947)

Goldschmidt’s radius ratio criterion



Radius ratios for typical glass forming compounds (W. Vogel, Glass Chemistry, 1992, p41, Springer-Verlag).

Compound	Radius ratios (r_c:r_a)
SiO_2	$r_{\mathrm{Si}}:r_{\mathrm{O}} = 0.39\,\text{Å}:1.4\,\text{Å} \cong 0.28$
B_2O_3	$r_{\mathrm{B}}:r_{\mathrm{O}} = 0.20\,\text{Å}:1.4\,\text{Å} \cong 0.15$
P_2O_5	$r_{\mathrm{P}}:r_{\mathrm{O}} = 0.34\,\text{Å}:1.4\,\text{Å} \cong 0.25$
GeO_2	$r_{\mathrm{Ge}}:r_{\mathrm{O}} = 0.44\,\text{Å}:1.4\,\text{Å} \cong 0.31$
BeF_2	$r_{\mathrm{Be}}:r_{\mathrm{F}} = 0.34\,\text{Å}:1.36\,\text{Å} \cong 0.25$

condition is fulfilled in the case of SiO_2, B_2O_3, P_2O_5, GeO_2 and BeF_2

BeO with r_{Be}/r_O ~0.221 but does not form a glass

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt’s radius ratio
  - Zachariasen’s random network theory

- Based on bond type
  - Smekal’s mixed bonding rule
  - Stanworth’s electronegativity rule

- Based on bond strength
  - Sun’s single bond strength criterion

- Based on field strength
  - Dietzel’s field strength

- Based on Mott’s rule
  - Phillips

Zachariasen's random network theory

This theory, strictly applicable to oxide glasses only in its original form, sometimes referred to as the *crystallochemical theory*; it led to the model known as the 3-D **continuous random network** (3-D **CRN**) model.

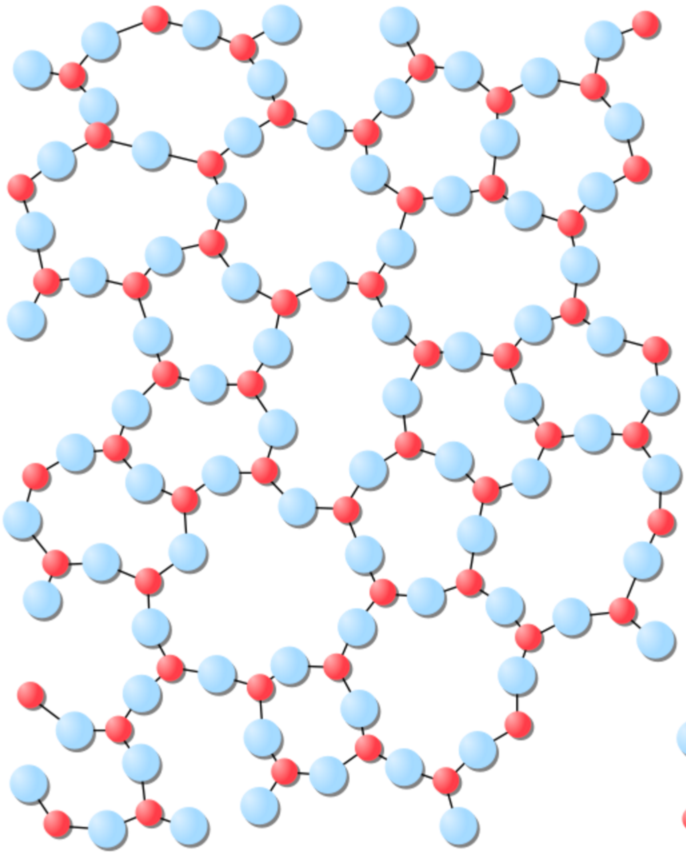
Basic postulates:

- interatomic forces similar in glass and corresponding crystal
- glass is in a slightly higher energy state
- nearest neighbor coordination polyhedra similar in glass and crystal
- nature of interatomic bonds similar in glass and corresponding crystal

William Houlder Zachariasen (1906-1979)

Zachariasen, W.H., The atomic arrangement in glass. J. Am. Chem. Soc., 54 (1932) 3841

Zachariasen's rules for glass formation



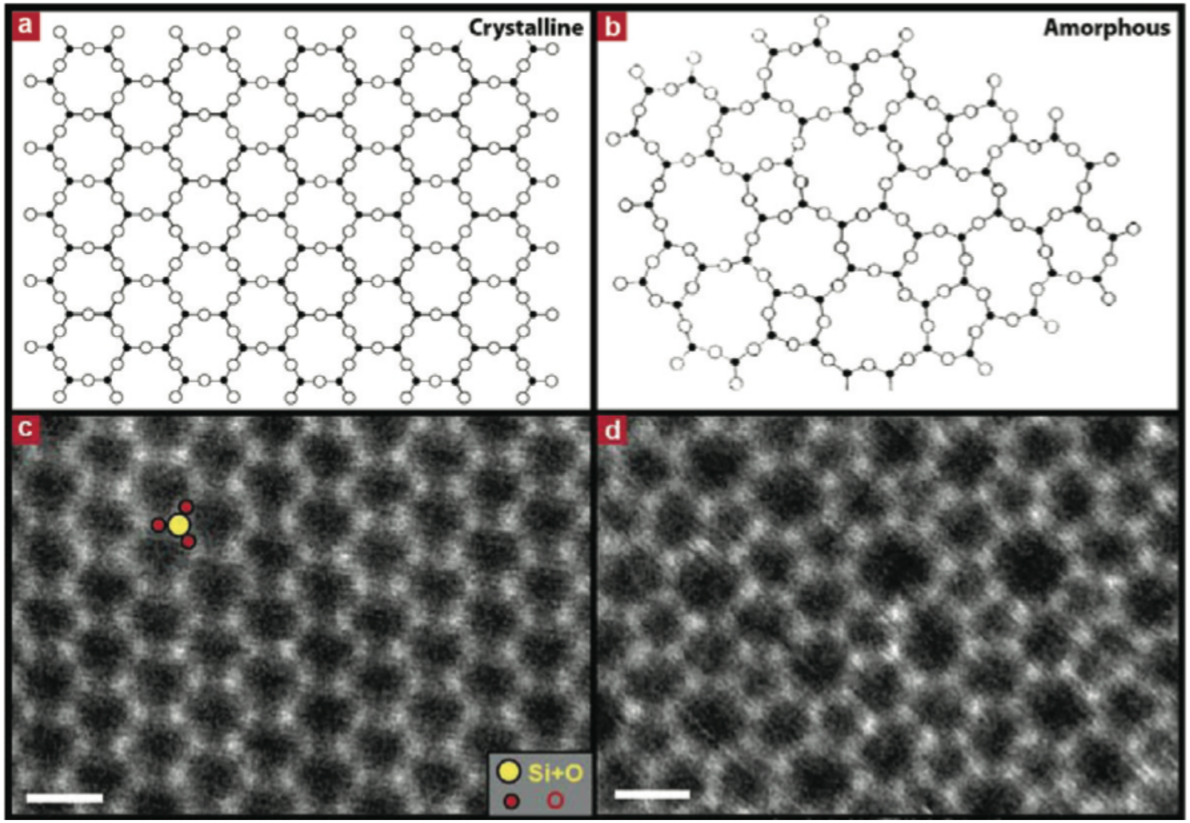
1. Each oxygen atom is linked (bonded) to no more than two glass-forming cations (e.g. Si^{4+});
2. Oxygen coordination number (CN) around glass-forming cation is small: 3 or 4;
3. Cation polyhedra share corners, not edges or faces;
4. The polyhedral structural units form a **3-D continuous random network** in which every polyhedron shares at least 3 corners with its neighbors.

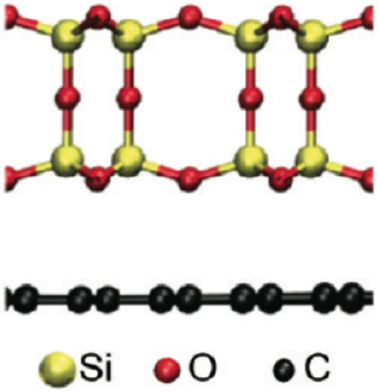
● Network former: Si, Ge, P, B, …
● Oxygen

A_2O_3, AO_2, and A_2O_5 oxides met the above rules => good **glass former**

A_2O, AO, AO_3, A_2O_7, etc., no glasses could be formed

Zachariasen model (1932)





c-SiO_2

a-SiO_2

STEM images

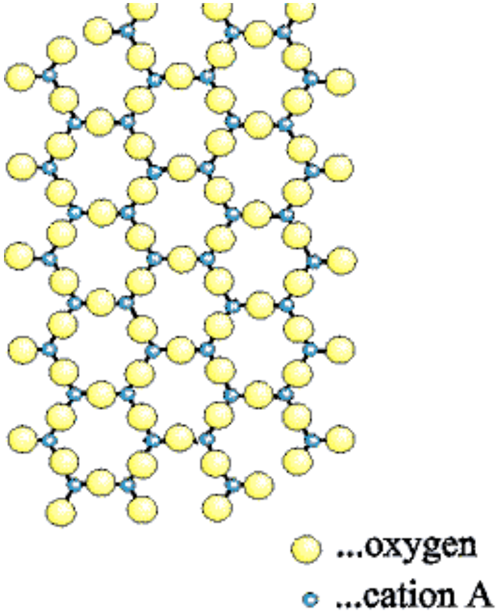
Huang et al., Nano Lett. 12 (2012)1081

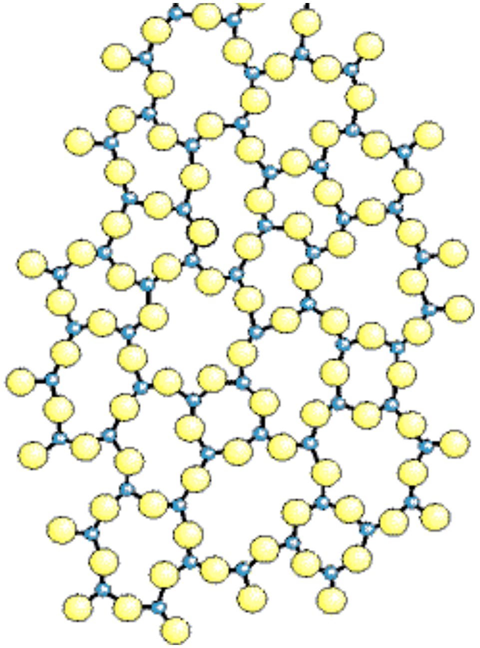
Structural model of covalent glasses

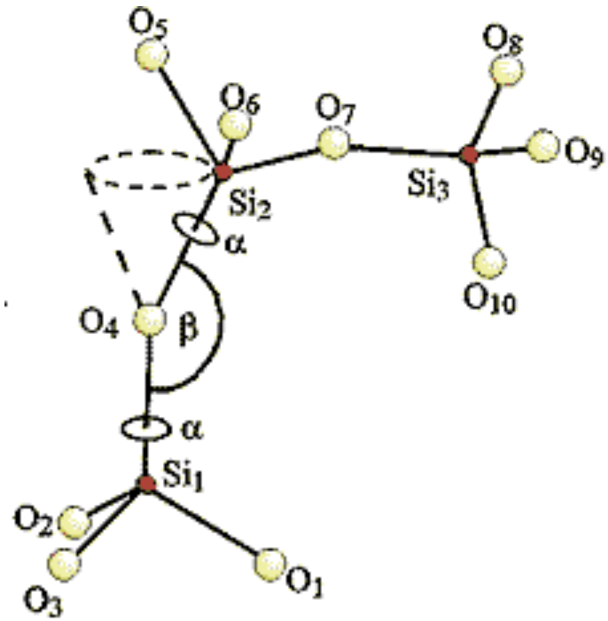
Structural units

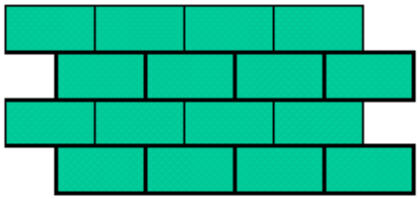
In silicate such as SiO_2: SiO_4 tetrahedra

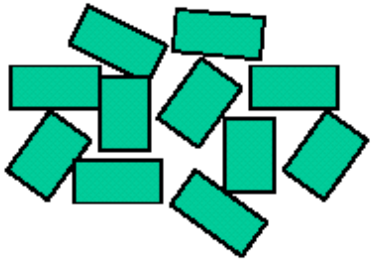
Same basic structural unit for the glass and the crystal





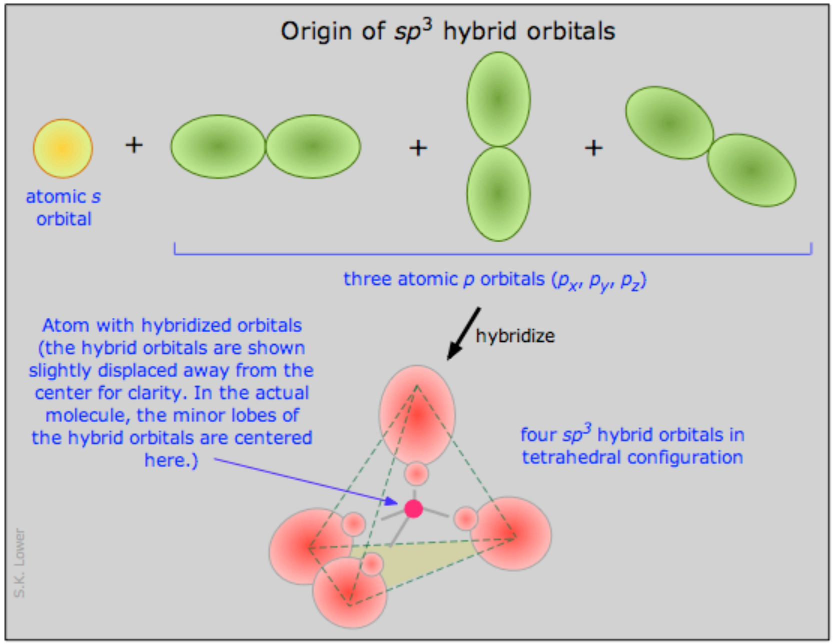




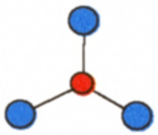


Electronic structure:

Si : (Ne)$3s^2 3p^2$: 4 valence electrons => ions Si^{4+} (can share 4 bonds)
O : (He)$2s^2 2p^4$: 6 valence electrons => ions O^{2-} (can share 2 bonds)

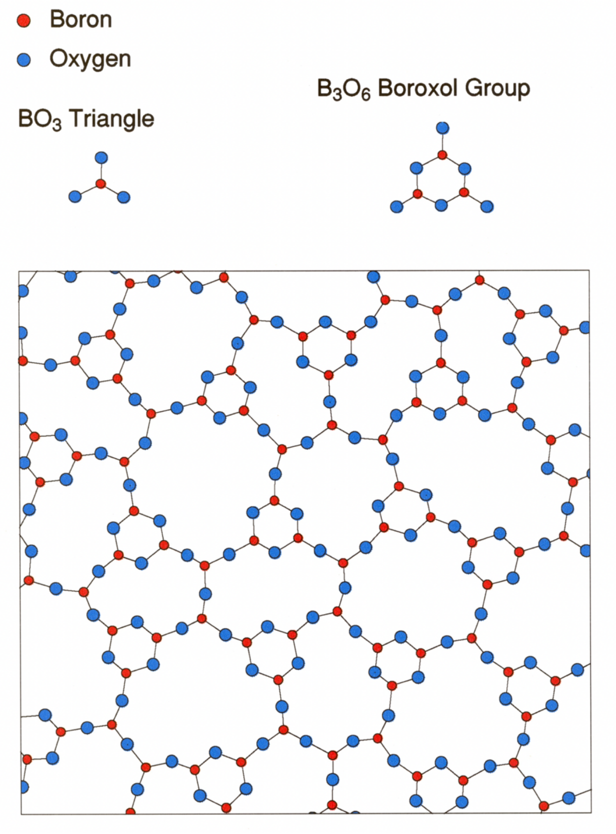


B : (He)$2s^2 2p^1$: 3 valence electron => ions B^{3+} (can share 3 bonds)
O : (He)$2s^2 2p^4$: 6 valence electron => ions O^{2-}(can share 2 bonds)



Borate glass

B_2O_3 not composed primarily of CRN's (continuous random network) of individual BO_4 and BO_3 units. These small units form structural grouping such as boroxol, diborate … that exist in the crystalline compounds of the particular borate system. These larger (but sill quite small) units are then connected randomly to each other to form the glass structure.
Intermediate between the micro-crystallite and the CRN models



About ~75% of B atoms are in boroxol rings

Neutron diffraction: Hannon *et al.*, J. Non-Cryst. Solids 177 (1994) 299
Ab initio simulations: Ferlat et al. Phys. Rev. Lett. 101 (2008) 065504

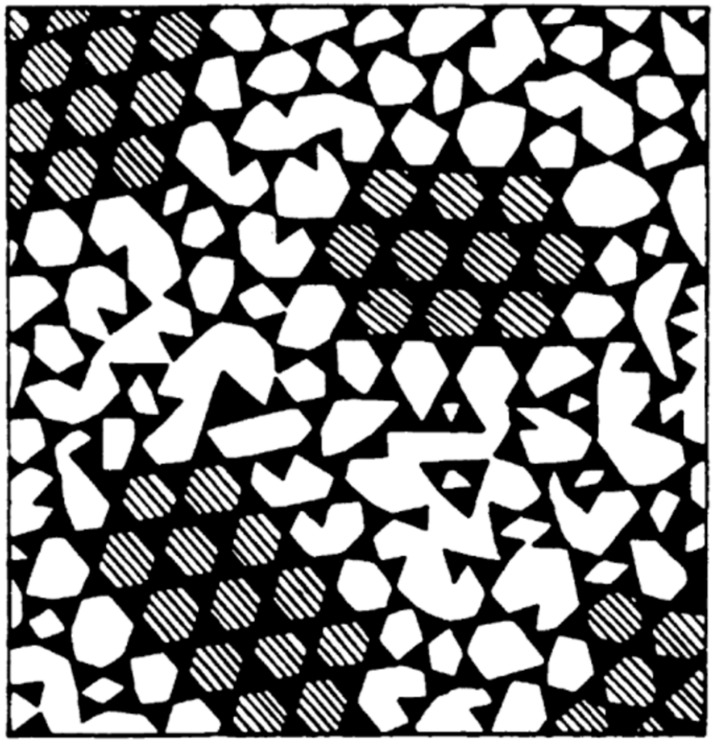
the boroxols allow one to maintain a low-energy structure while keeping a liquidlike density

⇒ **Importance of medium range order in GFA ?**

⇒ Gerald Lelong

Medium range order – inhomogeneities in glasses

Introduce for the first time the notion of inhomogeneities in glasses

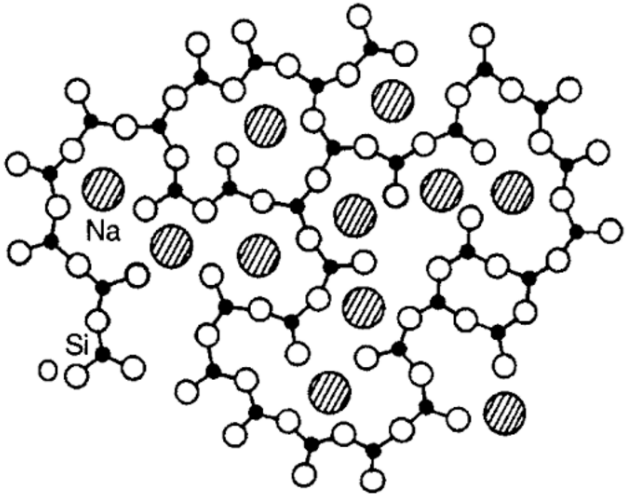


crystallite model of Lebedev

Multicomponent oxide glasses

Zachariasen's rules do not consider at all modified oxides or multicomponent systems, or even non-oxide glasses

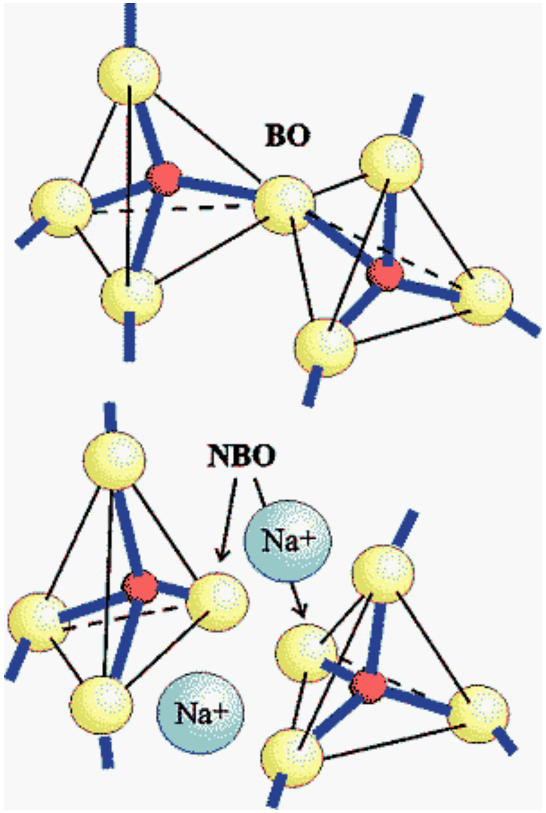
Zachariasen–Warren network theory



Bertram Eugene Warren
1902-1991

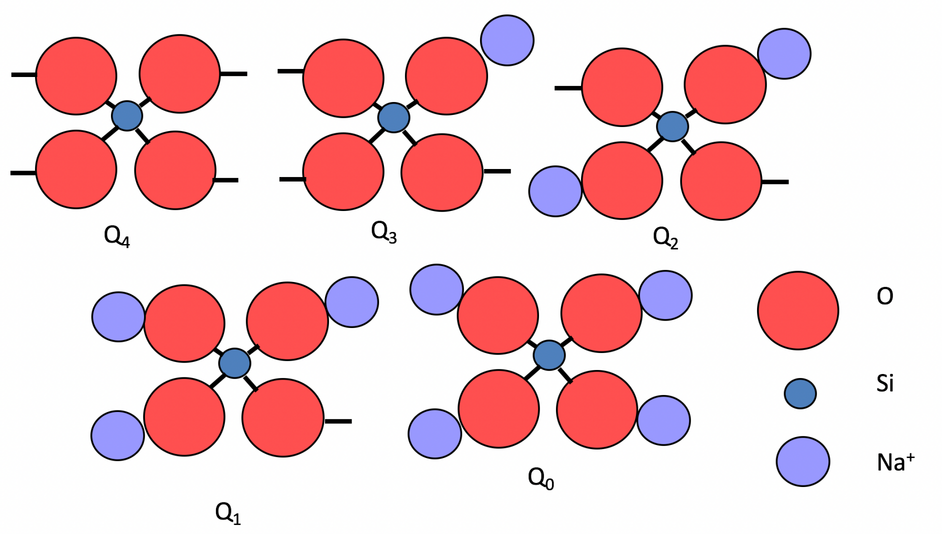
Multicomponent oxide glasses

Alkali silicate glasses



Non-network formers (alkali, alkaline-earth, transition elements) decrease the network connectivity by forming non-bridging oxygens (NBO) (≠ bridging oxygens BO)

⇒ Network modifier



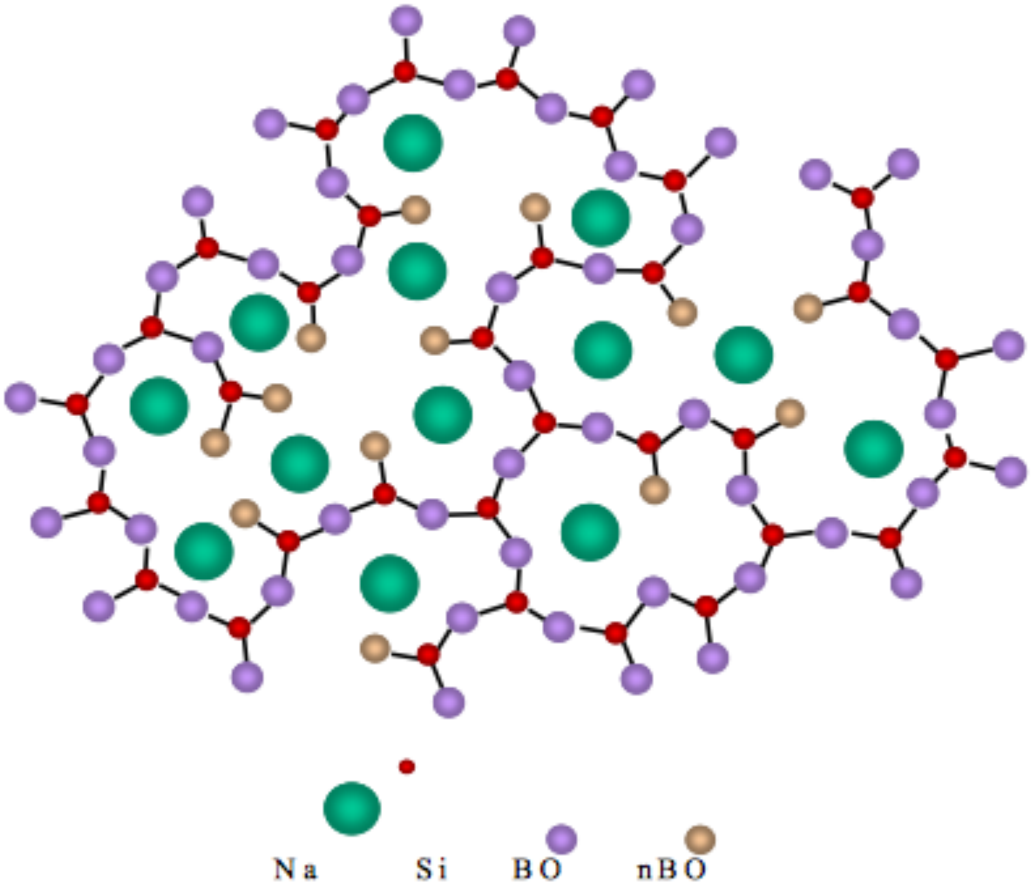
Q_n species

n = number of bridging oxygens by tetrahedra

Multicomponent oxide glasses

Random network

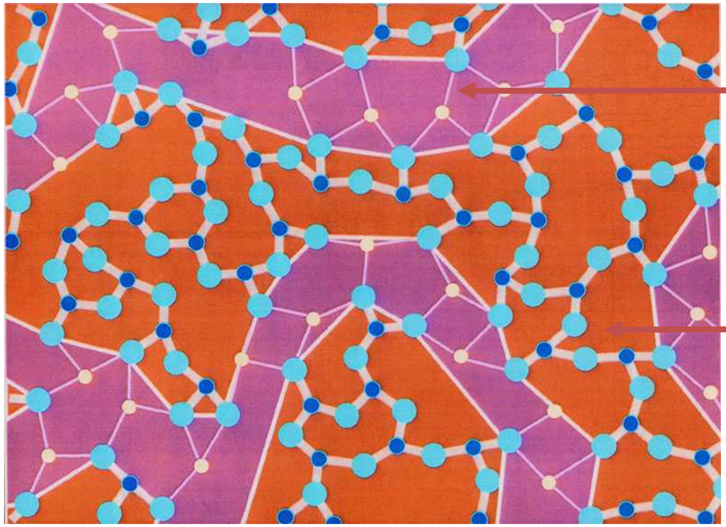
Network modifiers have
- high coordination numbers
- a random distribution in the glass interstices



No information on medium range order

Multicomponent oxide glasses

Modified random network - MRN (Greaves, 1985)



Zones rich with network modifiers

Zones rich with network formers

Relationships with conductivity, alteration etc

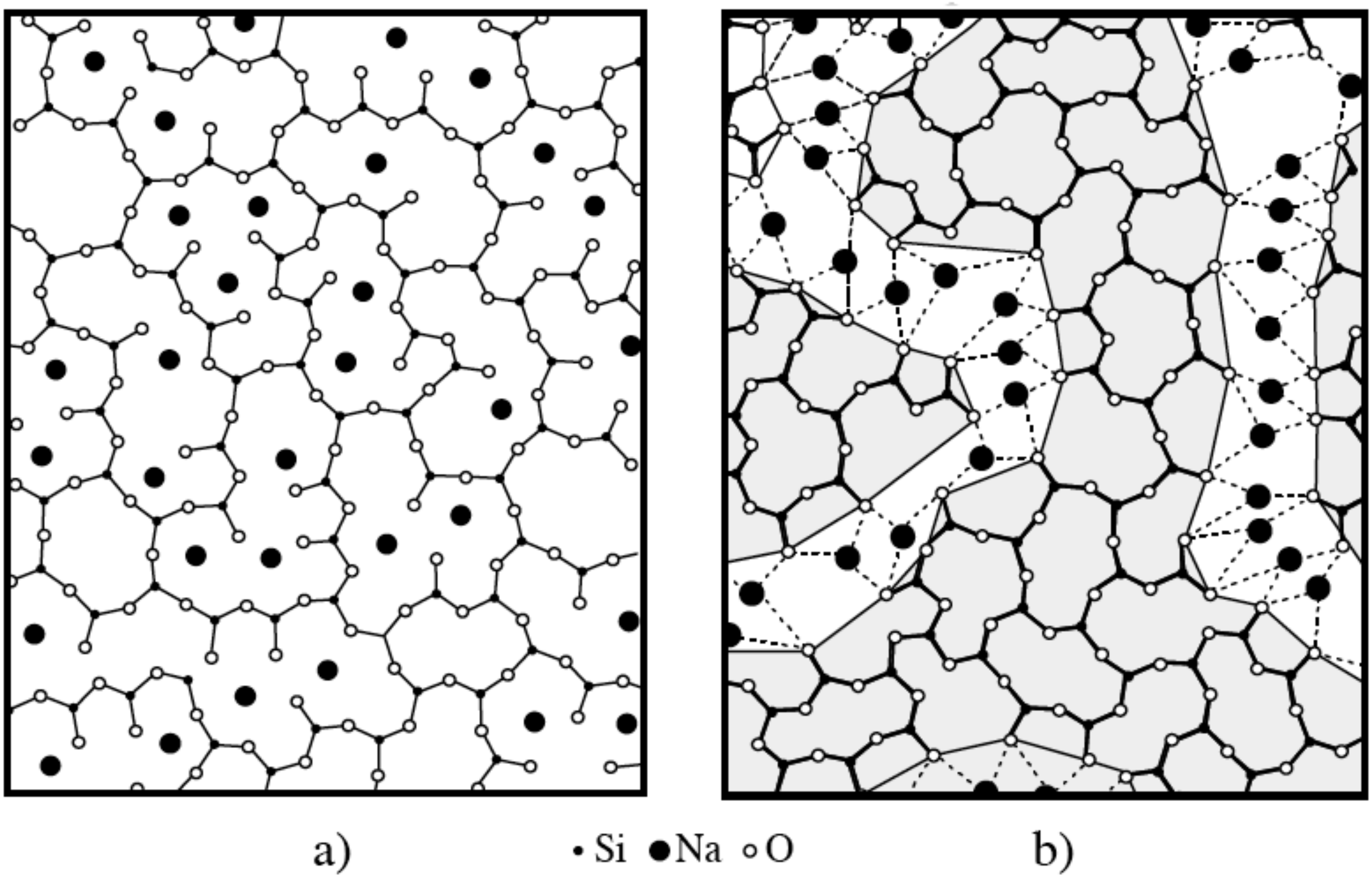


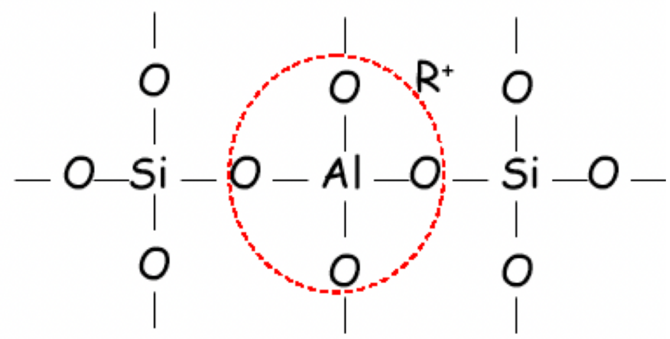
Figure 4-2: Représentation bi-dimensionnelle d'un réseau silicaté a) d'après le modèle CRN (Continuous Random Network) de Zachariasen, 1932, b) d'après le modèle MRN (Modified Random Network) de Greaves et al., 1981.

Aluminosilicate glasses

Al substitute to Si in tetrahedral position

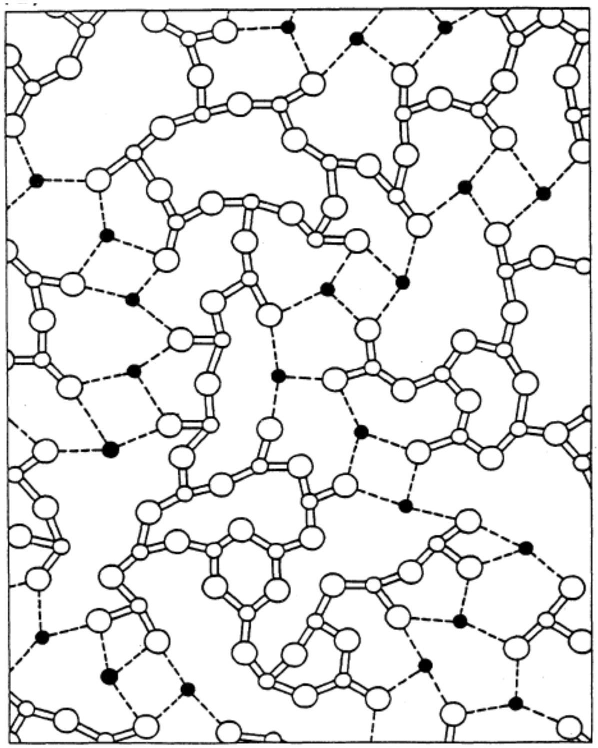
Al : (Ne)$3s^2 3p^1$: 3 valence electrons => ions Al^{3+}

$(AlO_4)^-$ charge electroneutrality ensures by the presence of alkali or alkaline earth

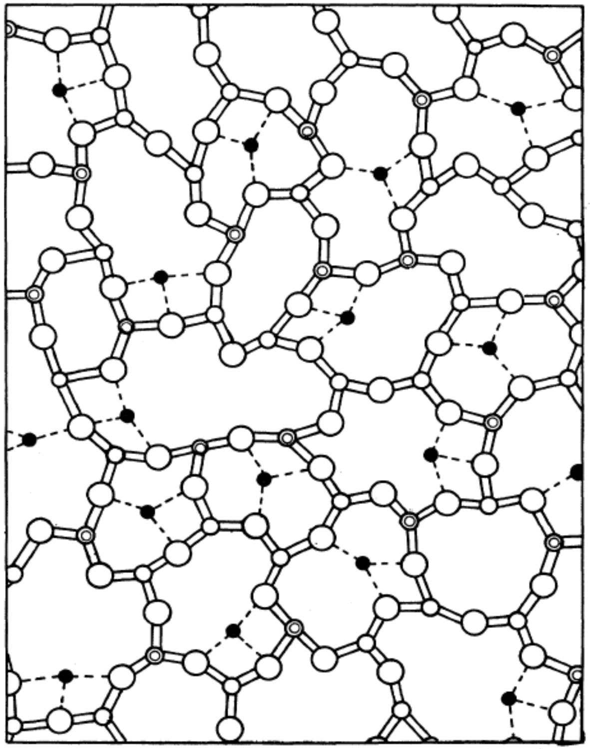


Similar for $(BO_4)^-$

Role of non-network forming cations



Cations connected to NBO
associated to the negative
charge of O^-
= network modifier

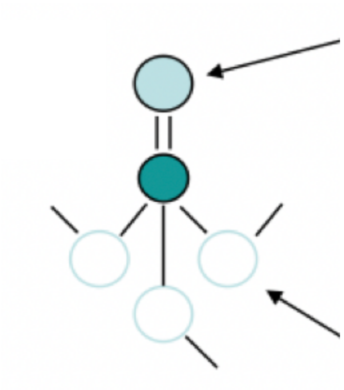


Cations connected to BO
And acting as charge compensator
near $(AlO_4)^-$, $(BO_4)^-$ …
= charge compensator

Phosphate glasses

P in tetrahedral position

P : (Ne)$3s^2 3p^3$: 5 valence electron => ions P^{5+}



Terminal oxygen

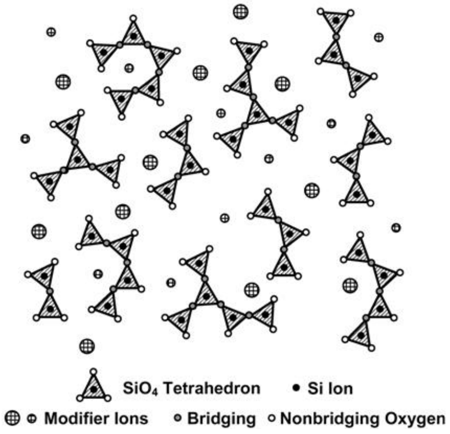
Bridging oxygen

Oxygen position in glass structure:
- bridging oxygen
- non-bridging oxygen
- terminal oxygen

⇒ Francisco Munoz & Lionel Montagne

Invert glasses

Y = NBO/T = Nbre d’O pontant par tétraèdre (Y=6-200/p with p the mol% of SiO_2)



SiO_2	Y=4	3D network
$R_2O\text{-}2SiO_2$	Y=3	
$R_2O\text{-}SiO_2$	Y=2 (metasilicate = SiO_4 chains)	

After Zachariasen’s hypothesis, glasses with Y<3 are not possible

For Y<2, it is named invert glass

Importance of free oxygens in those compositions

Free-oxygen : oxygen not bonded to any network-former

Oxygen position in glass structure:

- bridging oxygen
- non-bridging oxygen
- terminal oxygen
- free oxygen

⇒ Louis Hennet
⇒ Grant Henderson

Trap & Stevels, Phys. Chem. Glasses, 1 (1960) 181

Glasses with non glass formers

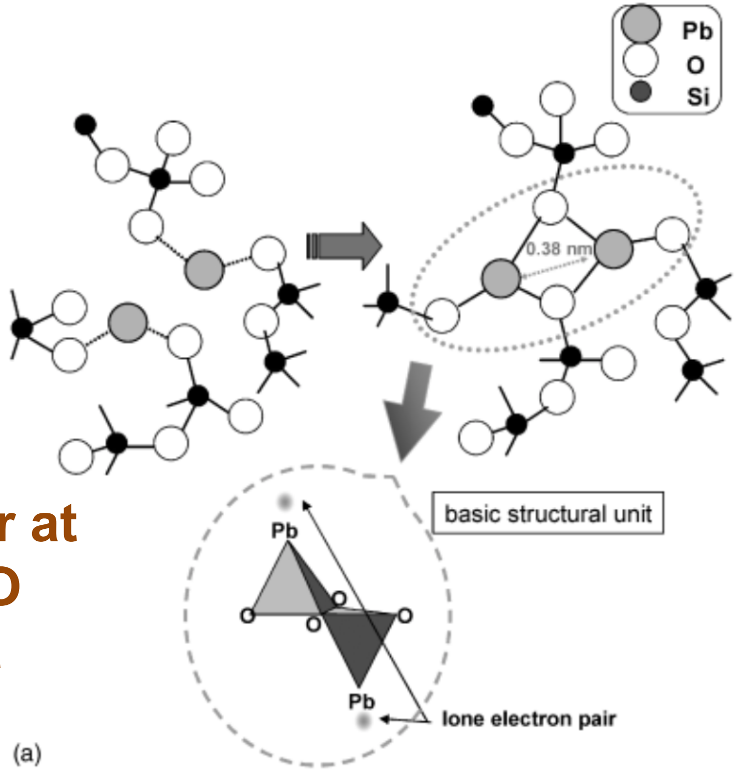
Neither R_2O or TiO_2 can form a glass individually
But possibility to form R_2O-TiO_2 glasses
$(1-x)R_2O$-$xTiO_2$ with x=34-75 mol% and R=K, Rb, Cs

In particular orthotitanate : $2R_2O$-TiO_2

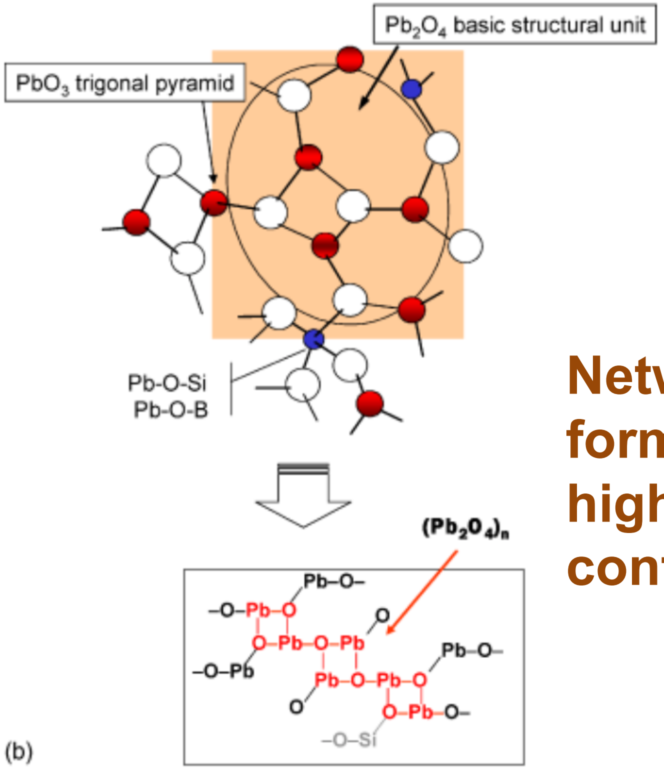
Which one is the glass former ?

Network former or modifier ? The case of Pb^{2+}

xPbO (100 x)SiO_2
x = 90, 67, 50, 33, 25



Modifier at low PbO content



Netwok former at high PbO content

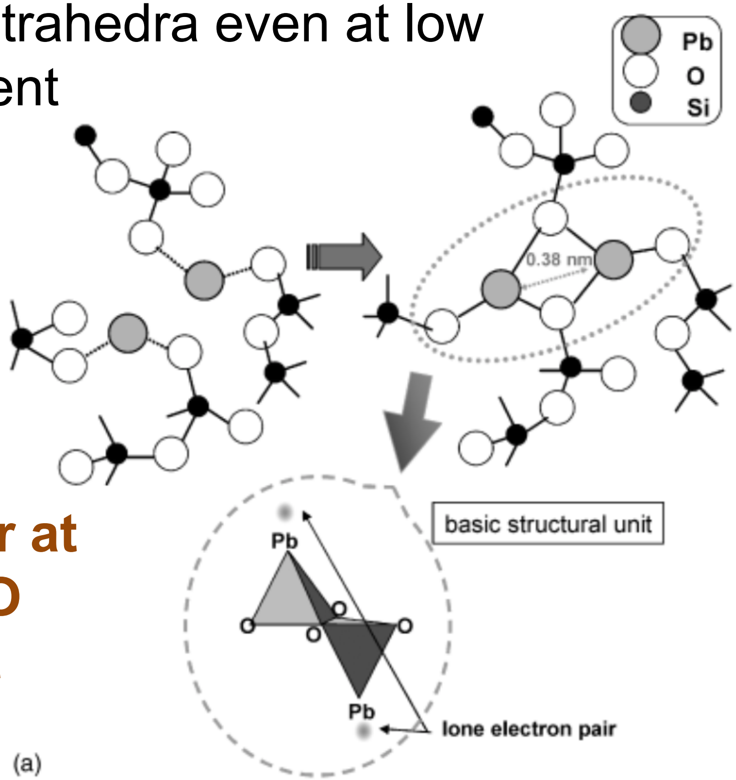
40-60 mol% PbO

Takahashi et al., J. Am. Ceram. Soc., 88 (2005) 1591

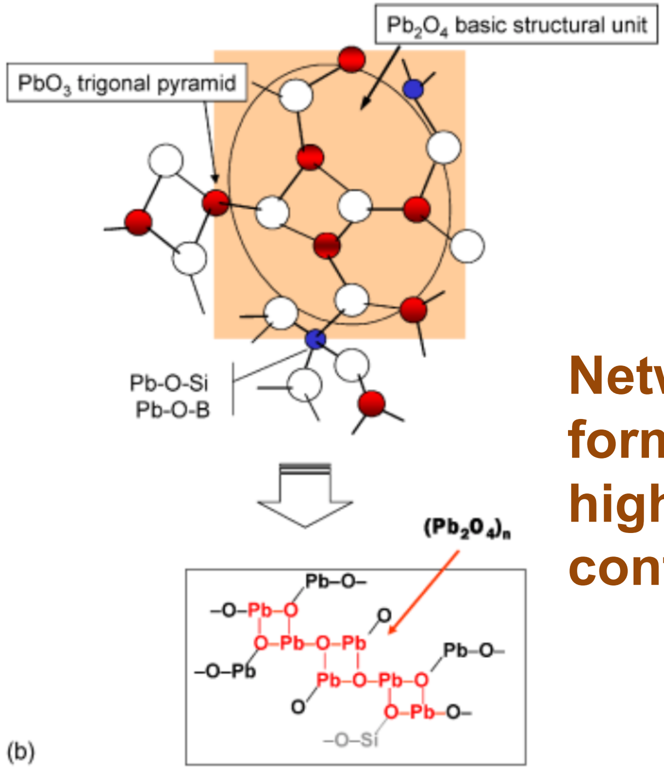
Network former or modifier ? The case of Pb^{2+}

Low PbO content

- PbO_3+_3 unit is dominant
- Pb_2O_4 units participate in the glass network constructed by SiO_4 tetrahedra even at low PbO content



Modifier at low PbO content

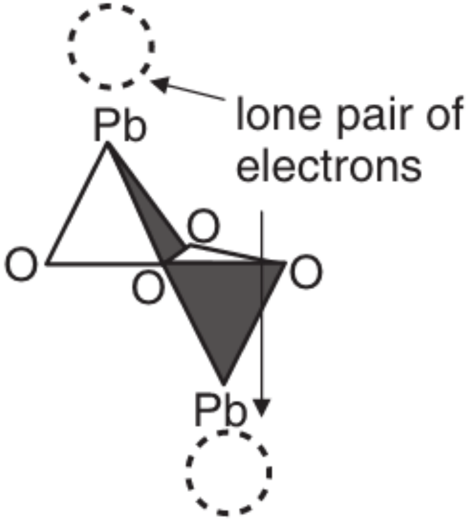


Netwok former at high PbO content

High PbO content

PbO acts as a network former consisting of PbO_3 trigonal pyramids

Case of Pb



High PbO content

PbO acts as a network former consisting of PbO_3 trigonal pyramids

PbO_3 trigonal pyramids are linked to each other by edge sharing to form Pb–O–Pb network => Pb_2O_4 units

$6p^2$ Ion Pb^{2+}

Pb atom tends to have small coordination numbers differing from other divalent elements

$\Rightarrow$ reason that PbO is a good glass forming material ?

Limitations of Zachariasen's rules

- apply only to oxide glasses

- there are several exceptions to the rules, such as:
  - non-oxide glasses (e.g. fluoride and metallic glasses)
  - some oxides ruled out by Zachariasen, such as Al-lime can in fact form glasses
  - chain-like glass structures (e.g., metaphosphate glasses)

Strong points of Zachariasen's model

- predicts the existence of the main oxide **glass formers** (SiO_2, GeO_2, B_2O_3, P_2O_5, ...) and **glass modifiers** (Na_2O, CaO, ...)
- suggests the existence of bridging oxygen (**BO**) and non-bridging oxygen (**NBO**) species

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt's radius ratio
  - Zachariasen's random network theory

- Based on bond type
  - Smekal's mixed bonding rule
  - Stanworth's electronegativity rule

- Based on bond strength
  - Sun's single bond strength criterion

- Based on field strength
  - Dietzel's field strength

- Based on Mott's rule
  - Phillips

Smekal's mixing bond

Pure covalent bonds incompatible with random arrangement (sharply defined bond-lengths and bond-angles)
Purely ionic or metallic bonds lack any directional characteristics

$\Rightarrow$ Presence of 'mixed' chemical bonding necessary

- inorganic compounds, e.g. SiO_2, B_2O_3, where the A-O bonds are partly covalent and partly ionic
- Elements (S, Se) having chain structures with covalent bonds within the chain and van der Waal's forces between the chains
- organic compounds containing large molecules with covalent bonds within the molecule and van der Waal's forces between them

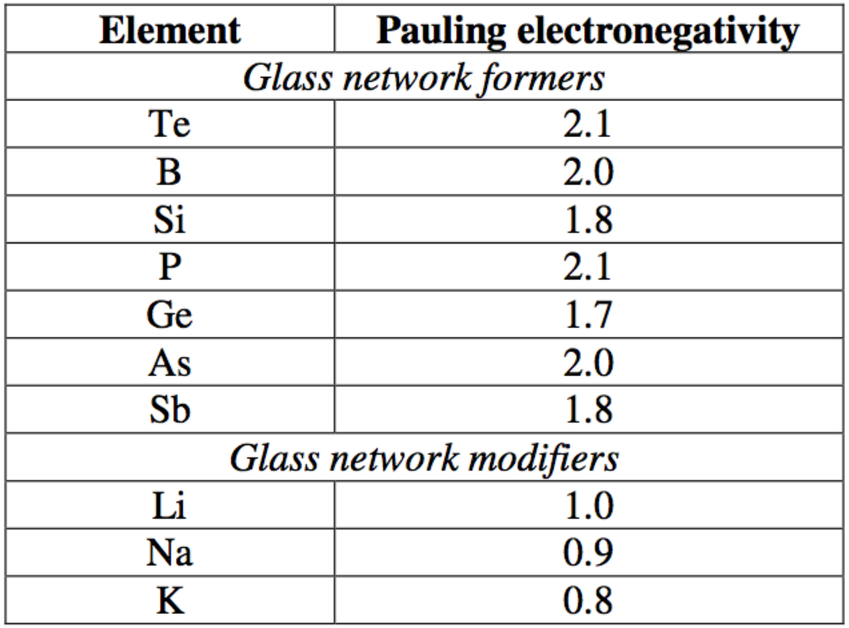
Smekal, J. Soc. Glass. Technol. 35 (1951) 411

Adolf Gustaf Smekal (1895–1959)

Stanworth’s electronegativity criterion

the electronegativity of the cations, of which the oxides are glass-forming, fall within a certain range between 1.90 and 2.20

Electronegativities of good glass forming oxides and network modifiers



Element	**Pauling electronegativity**
Glass network formers	
Te	2.1
B	2.0
Si	1.8
P	2.1
Ge	1.7
As	2.0
Sb	1.8
Glass network modifiers	
Li	1.0
Na	0.9
K	0.8

Stanworth, J. *Soc. Glass Technol.* 36 (1952) 217

Stanworth’s electronegativity criterion

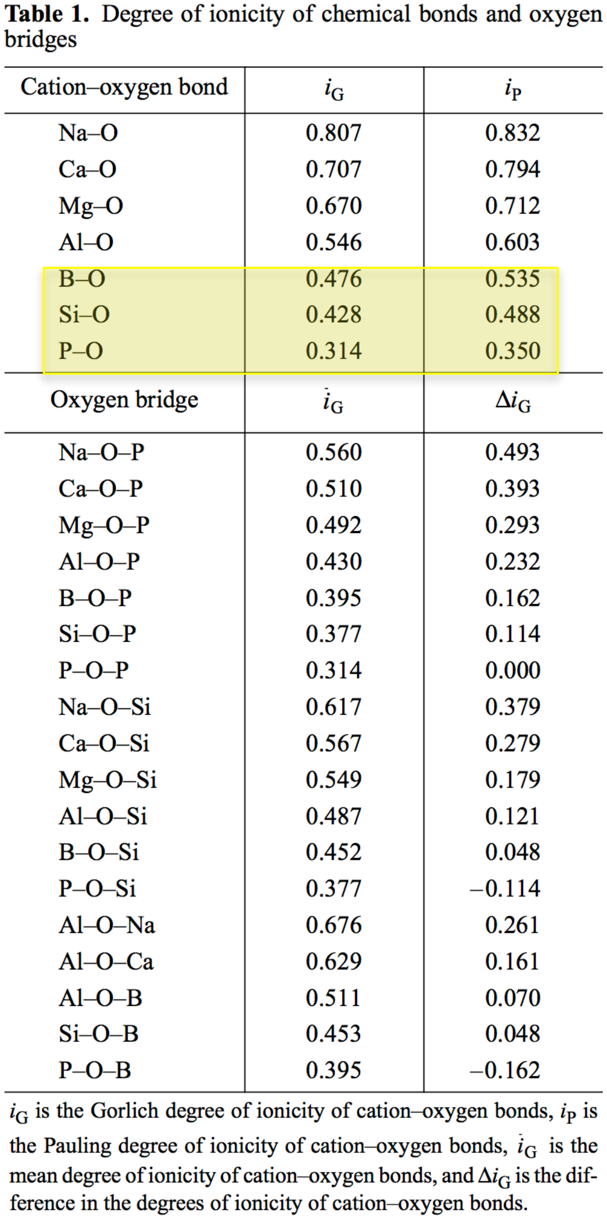


Table 1. Degree of ionicity of chemical bonds and oxygen bridges

Cation–oxygen bond	i_G	i_P
Na–O	0.807	0.832
Ca–O	0.707	0.794
Mg–O	0.670	0.712
Al–O	0.546	0.603
B–O	0.476	0.535
Si–O	0.428	0.488
P–O	0.314	0.350

Oxygen bridge	$\bar{i}_G$	Δi_G
Na–O–P	0.560	0.493
Ca–O–P	0.510	0.393
Mg–O–P	0.492	0.293
Al–O–P	0.430	0.232
B–O–P	0.395	0.162
Si–O–P	0.377	0.114
P–O–P	0.314	0.000
Na–O–Si	0.617	0.379
Ca–O–Si	0.567	0.279
Mg–O–Si	0.549	0.179
Al–O–Si	0.487	0.121
B–O–Si	0.452	0.048
P–O–Si	0.377	−0.114
Al–O–Na	0.676	0.261
Al–O–Ca	0.629	0.161
Al–O–B	0.511	0.070
Si–O–B	0.453	0.048
P–O–B	0.395	−0.162

i_G is the Gorlich degree of ionicity of cation–oxygen bonds, i_P is the Pauling degree of ionicity of cation–oxygen bonds, $\bar{i}_G$ is the mean degree of ionicity of cation–oxygen bonds, and Δi_G is the difference in the degrees of ionicity of cation–oxygen bonds.

Stoch, Glass Phys. Chem. 27 (2001) 167

Mixed bond :

Si-O : ionic character of ~45%

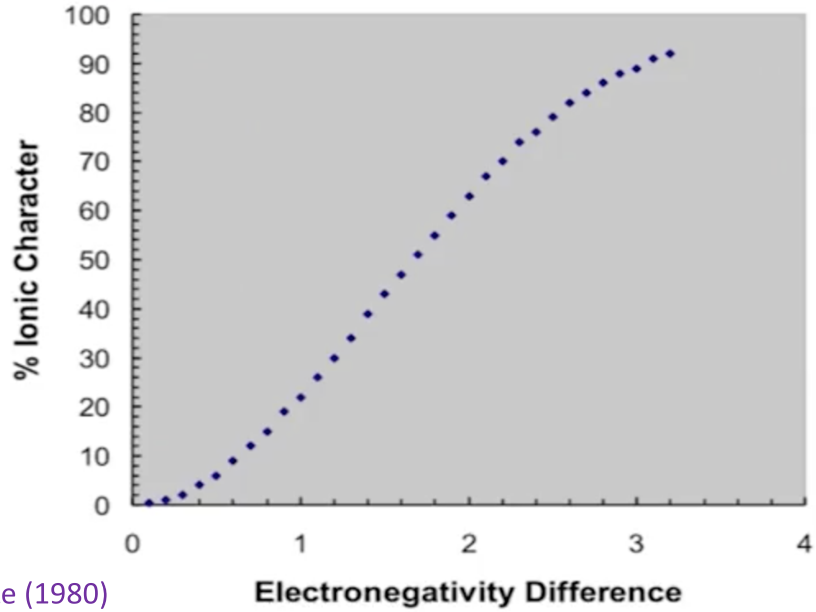
Similar for other network formers

But

Be-F : 75% ionic character but BeF_2 form a glass

Ge-Se : 12% ionic character but GeS_2 form a glass

As-S : 5% ionic character but As_2S_3 form a glass

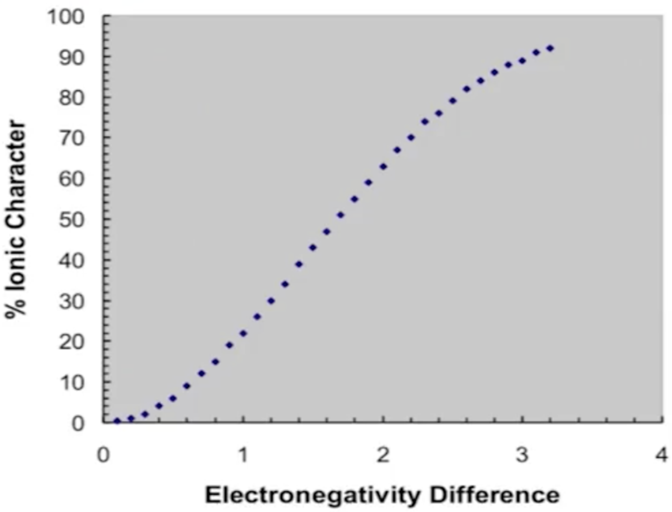


From ’Le verre’ Scholze (1980)

Stanworth's electronegativity criterion

TABLE 8. Electronegativities of some anion formers.

Element	Electronegativity
O	3.5
S	2.5
Se	2.4
Te	2.1
F	4.0
Cl	3.0
Br	2.8
J	2.4



From 'Le verre' Scholze (1980)

Mixed bond :
Si-O : ionic character of ~45%
Similar for other network formers

But
Be-F : 75% ionic character but BeF_2 form a glass
Ge-Se : 12% ionic character but GeS_2 form a glass
As-S : 5% ionic character but As_2S_3 form a glass

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number

– Goldschmidt’s radius ratio

– Zachariasen’s random network theory

- Based on bond type

– Smekal’s mixed bonding rule

– Stanworth’s electronegativity rule

- Based on bond strength

– Sun’s single bond strength criterion

- Based on field strength

– Dietzel’s field strength

- Based on Mott’s rule

– Phillips

Sun’s bond strength model

Glass formation is brought about by both

- Connectivity of bridge bonds
- Strong bonds between atoms (ions)

Sun classified oxide according to their bond strengths

- Glass formers form strong bonds to oxygen – rigid network ,high viscosity
- Modifiers form weak bonds to oxygen - disrupt, modify network
- Intermediates form intermediate bonds to oxygen – can’t form glasses on their own, but aid with other oxides to form glasses

Sun's bond strength model

Sun's criterion: energy criterion
- Establishes a correlation between **glass forming tendency** and the **bond energies** of elements with the anion atom in the glass

Dissociation energy of oxides into gaseous elements:

$$E_d^{MOx} = |1/m\Delta H^o_f (M_mO_n,c) - \Delta H^o_f (M,g) - n/m\Delta H^o_f (O,g)|$$

E_d refers to a mol of M in $MO_{n/m}$.

$E_b = E_d$ / CN is called the **single bond strength**

The basic idea behind this model is that, when a melt is quenched to form a glass, the stronger the M-O bonds, the more difficult are the structural rearrangements necessary for crystallization and, hence, the easier is glass formation

Sun, J. Am. Ceram. Soc. 30 (1947) 277

Sun's bond strength model

The higher the bond strength, the better the glass former

- Single bond strength > 80kcal/mol => network former
  - Greater than 80 kcal/mole bond strength with oxygen
    - B_2O_3, SiO_2, Geo_2, P_2O_5, Al_2O_5….

- Single bond strength < 60kcal/mol => network modifier
  - Less than 60 kcal/mole bond strength with oxygen
    - Li_2O, Na_2O, K_2O, MgO, CaO….

- Single bond strength 60 ≤ strength ≥ 80 => intermediate
  - Between 60 to 80 kcal/mol bond strength with oxygen
    - TiO_2, ZnO, PbO….

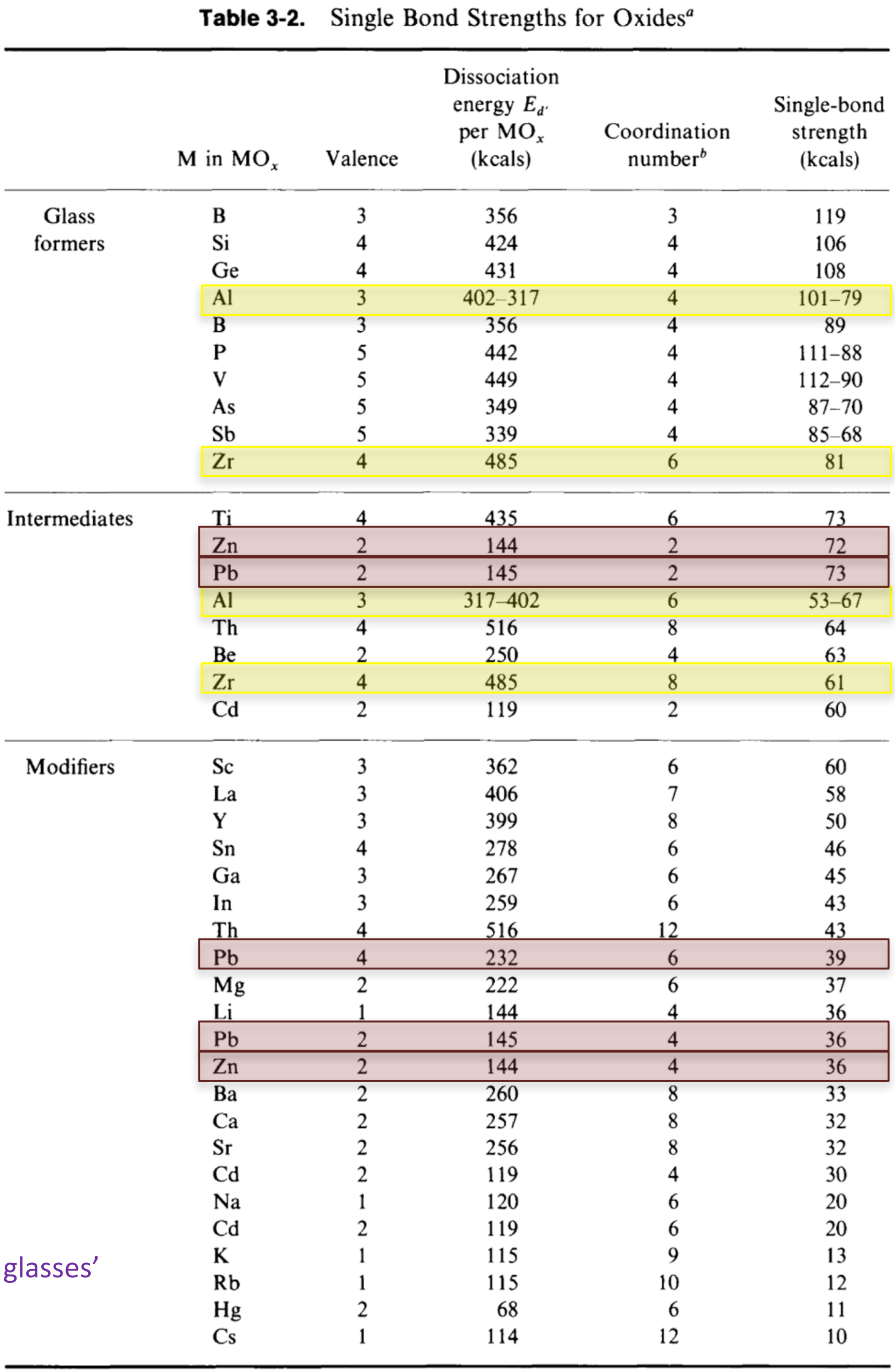


Table 3-2. Single Bond Strengths for Oxides[a]

	M in MO_x	Valence	Dissociation energy $E_{d'}$ per MO_x (kcals)	Coordination number[b]	Single-bond strength (kcals)
Glass formers	B	3	356	3	119
	Si	4	424	4	106
	Ge	4	431	4	108
	Al	3	402–317	4	101–79
	B	3	356	4	89
	P	5	442	4	111–88
	V	5	449	4	112–90
	As	5	349	4	87–70
	Sb	5	339	4	85–68
	Zr	4	485	6	81
Intermediates	Ti	4	435	6	73
	Zn	2	144	2	72
	Pb	2	145	2	73
	Al	3	317–402	6	53–67
	Th	4	516	8	64
	Be	2	250	4	63
	Zr	4	485	8	61
	Cd	2	119	2	60
Modifiers	Sc	3	362	6	60
	La	3	406	7	58
	Y	3	399	8	50
	Sn	4	278	6	46
	Ga	3	267	6	45
	In	3	259	6	43
	Th	4	516	12	43
	Pb	4	232	6	39
	Mg	2	222	6	37
	Li	1	144	4	36
	Pb	2	145	4	36
	Zn	2	144	4	36
	Ba	2	260	8	33
	Ca	2	257	8	32
	Sr	2	256	8	32
	Cd	2	119	4	30
	Na	1	120	6	20
	Cd	2	119	6	20
	K	1	115	9	13
	Rb	1	115	10	12
	Hg	2	68	6	11
	Cs	1	114	12	10

From ’Fundamentals of inorganic glasses’
Varshneya (2013)

Case of Al^{3+}

Al_2O_3 satisfied Zachariasen's criteria but Al_2O_3 does not form a glass

According to Sun's criteria

E_d = 317-402 kcals

CN =4	$79 < E_{Sun} < 101$kcal mol^{-1}	network former
CN =5	$63 < E_{Sun} < 80$kcal mol^{-1}	?
CN =6	$53 < E_{Sun} < 67$kcal mol^{-1}	modifier ?

No Al_2O_3 glass can be formed

But formation of $3CaO\text{-}2Al_2O_3$ glass

⇒ Louis Hennet

Limitations of Sun’s criteria

- Exclusion of the chalcogenide glasses

Bond strength ~40kcal.mol along the chains (covalent bond) and less between the chains (van der Waals forces)

Strong points of Sun’s criteria

- Introduce the notion of intermediate

Structural role

Cations in the glass were catagorized according to their role in the glass network

Network former

- Can form a glass network alone
- Strong directional bonding
- Example: Si^{4+}, B^{3+}, P^{5+}, Ge^{4+}, As^{3+}, Be^{2+}, with CN of 3 or 4

Network modifier

- Break the linkages between network formers
- More ionic bonding
- Example: Na^{+}, K^{+}, Ca^{2+}, Ba^{2+}, with CN ≥ 6

Intermediates (conditional network former)

- May reinforce (CN = 4) or further loosen the network further (CN 6 to 8)
- Can substitute to a network former but cannot form a glass per se
- Example: Al_2O_3, TiO_2, Ga_2O_3, As_2O_3, Sb_2O_3, Bi_2O_3, TeO_2, V_2O_5, MoO_3, WO_3

Structural role

Structural role of constituents; in view of Coulombic interaction

An interesting intermediate class of oxide including TeO_2, MoO_3, Bi_2O_3, Al_2O_3, Ga_2O_3 and V_2O_5 do not by themselves form glasses but will do so when mixed with other (modifier) oxides

Rawson's criteria

- Ratio of the bond strength to the energy available at the freezing point (~3/2 T_m)

- Glass formation is better correlated with E_b/T_m, where T_m is the melting temperature, and $E_b/T_m > 0.05$ for glass forming systems
- The higher the value, the lower the probability for bonds to break at Tm, and hence the higher the tendency for glass formation

- Point out the significance of the liquidus temperature

$\Rightarrow$ eutectic favors glass formation

Vitrification if high bond strength with a liquidus temperature with the lowest possible melting temperature

SiO_2 : E_b = 106 kcals mol^{-1} Tm=1600°C E_b/Tm = 0.066
ZrO_2 : E_b = 81 kcals mol^{-1} Tm=2715°C E_b/Tm = 0.030 => cannot form glass due to its high melting point
B_2O_3 : E_b = 119 kcals mol^{-1} Tm=450°C E_b/Tm = 0.264 => never crystallizes

Rawson, Proc. IV Internat. Congr. on Glass (1956)

Extension of Rawson's criteria

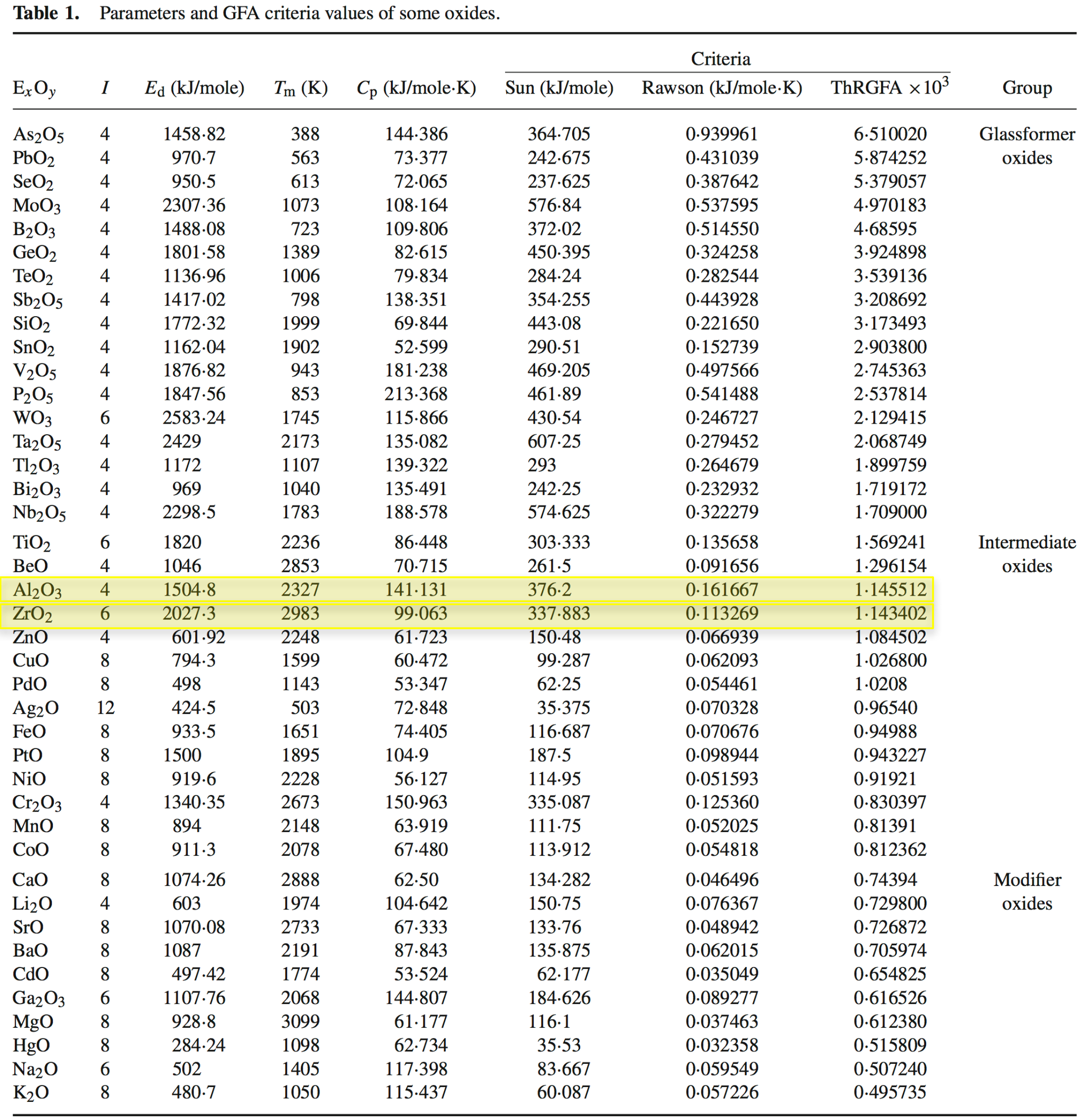


Table 1. Parameters and GFA criteria values of some oxides.

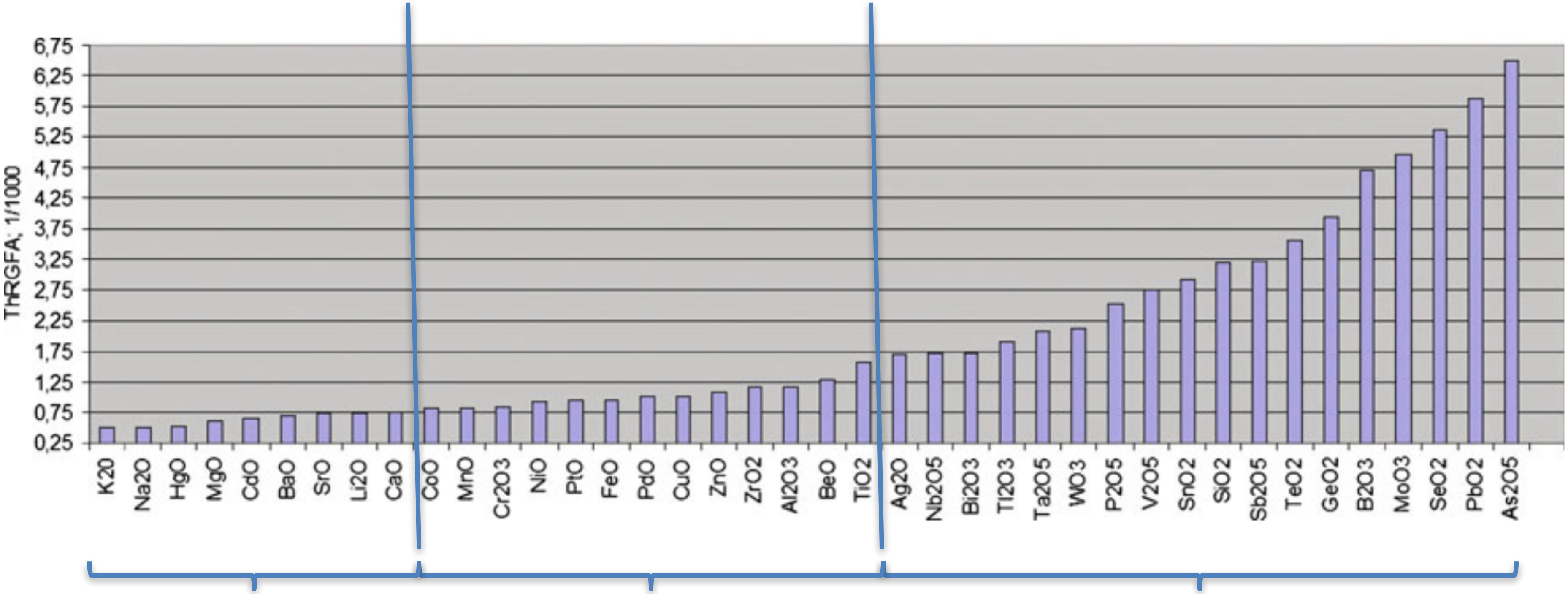
E_xO_y	I	E_d (kJ/mole)	T_m (K)	C_p (kJ/mole·K)	Criteria Sun (kJ/mole)	 Rawson (kJ/mole·K)	 ThRGFA $\times 10^3$	Group
As_2O_5	4	1458·82	388	144·386	364·705	0·939961	6·510020	Glassformer oxides
PbO_2	4	970·7	563	73·377	242·675	0·431039	5·874252	
SeO_2	4	950·5	613	72·065	237·625	0·387642	5·379057	
MoO_3	4	2307·36	1073	108·164	576·84	0·537595	4·970183	
B_2O_3	4	1488·08	723	109·806	372·02	0·514550	4·68595	
GeO_2	4	1801·58	1389	82·615	450·395	0·324258	3·924898	
TeO_2	4	1136·96	1006	79·834	284·24	0·282544	3·539136	
Sb_2O_5	4	1417·02	798	138·351	354·255	0·443928	3·208692	
SiO_2	4	1772·32	1999	69·844	443·08	0·221650	3·173493	
SnO_2	4	1162·04	1902	52·599	290·51	0·152739	2·903800	
V_2O_5	4	1876·82	943	181·238	469·205	0·497566	2·745363	
P_2O_5	4	1847·56	853	213·368	461·89	0·541488	2·537814	
WO_3	6	2583·24	1745	115·866	430·54	0·246727	2·129415	
Ta_2O_5	4	2429	2173	135·082	607·25	0·279452	2·068749	
Tl_2O_3	4	1172	1107	139·322	293	0·264679	1·899759	
Bi_2O_3	4	969	1040	135·491	242·25	0·232932	1·719172	
Nb_2O_5	4	2298·5	1783	188·578	574·625	0·322279	1·709000	
TiO_2	6	1820	2236	86·448	303·333	0·135658	1·569241	Intermediate oxides
BeO	4	1046	2853	70·715	261·5	0·091656	1·296154	
Al_2O_3	4	1504·8	2327	141·131	376·2	0·161667	1·145512	
ZrO_2	6	2027·3	2983	99·063	337·883	0·113269	1·143402	
ZnO	4	601·92	2248	61·723	150·48	0·066939	1·084502	
CuO	8	794·3	1599	60·472	99·287	0·062093	1·026800	
PdO	8	498	1143	53·347	62·25	0·054461	1·0208	
Ag_2O	12	424·5	503	72·848	35·375	0·070328	0·96540	
FeO	8	933·5	1651	74·405	116·687	0·070676	0·94988	
PtO	8	1500	1895	104·9	187·5	0·098944	0·943227	
NiO	8	919·6	2228	56·127	114·95	0·051593	0·91921	
Cr_2O_3	4	1340·35	2673	150·963	335·087	0·125360	0·830397	
MnO	8	894	2148	63·919	111·75	0·052025	0·81391	
CoO	8	911·3	2078	67·480	113·912	0·054818	0·812362	
CaO	8	1074·26	2888	62·50	134·282	0·046496	0·74394	Modifier oxides
Li_2O	4	603	1974	104·642	150·75	0·076367	0·729800	
SrO	8	1070·08	2733	67·333	133·76	0·048942	0·726872	
BaO	8	1087	2191	87·843	135·875	0·062015	0·705974	
CdO	8	497·42	1774	53·524	62·177	0·035049	0·654825	
Ga_2O_3	6	1107·76	2068	144·807	184·626	0·089277	0·616526	
MgO	8	928·8	3099	61·177	116·1	0·037463	0·612380	
HgO	8	284·24	1098	62·734	35·53	0·032358	0·515809	
Na_2O	6	502	1405	117·398	83·667	0·059549	0·507240	
K_2O	8	480·7	1050	115·437	60·087	0·057226	0·495735	

$$\text{ThRGFA} = E_{Sun}/(T_m.C_p)$$

Boubata Bull. Mater. Sci. 36(2013)457

Extension of Rawson's criteria

$ThRGFA = E_{Sun}/(T_m.C_p)$



Modifier

Intermediate

Former

Boubata Bull. Mater. Sci. 36(2013)457

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt's radius ratio
  - Zachariasen's random network theory

- Based on bond type
  - Smekal's mixed bonding rule
  - Stanworth's electronegativity rule

- Based on bond strength
  - Sun's single bond strength criterion

- Based on field strength
  - Dietzel's field strength

- Based on Mott's rule
  - Phillips

Dietzeld and field strength criteria

Sun classifies Al as both a network former and an intermediate

- Al_2O_3 does not form glass at normal quenching rates
- More factors are important than just bond strength
  - Small cations with high charge – network formers
  - Large cations with small charges – modifiers
  - Medium size cations with medium charge - intermediates

Dietzeld and field strength criteria

By extending Goldschmidt's original consideration of glass formation to radius and charge of the constituent atoms / ions, Dietzel classified elements according to their field strength, F_s

This considers the forces (attraction / repulsion) between cations and anions in the glass

$F_s = Z_C / (r_c + r_a)^2$

r = ionic radius of the cation (c) or anion (a)

$F_s = Z_C / a^2$

Z_C = valence of the cation

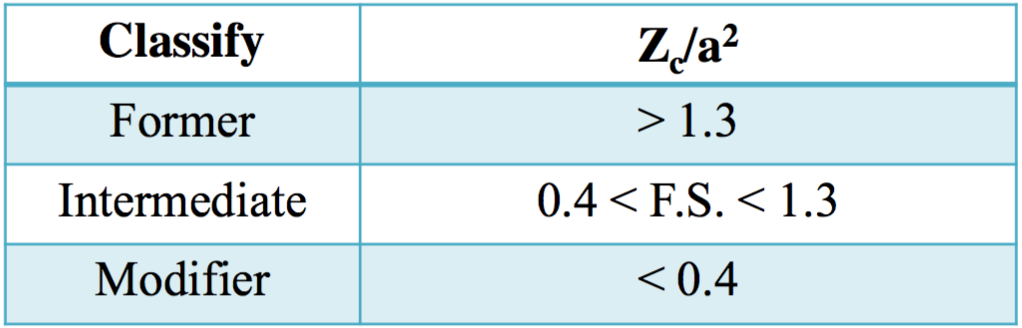
a is the distance between cation and oxygen

Dietzel, Glastechn. Ber. 22, (1948) 41

Dietzeld and field strength criteria

$F_s = Z_C / a^2$

Z_C = valence of the cation
a is the distance between cation and oxygen



Classify	Z_c/a^2
Former	> 1.3
Intermediate	$0.4 < F.S. < 1.3$
Modifier	< 0.4

High field strength (for C it is 2.4) => covalent bonds, difficulty to form a glass

Intermediate field strength (1-2) => mixed bonds, can form glasses

Low field strength => ionic bonds, do not form glasses

Dietzeld and field strength criteria

Mixing two network forming elements

On cooling a binary melt with cations of approximately the same field strength, phase separation or crystallization of the pure oxide phases is normally seen (e.g. SiO_2-P_2O_5, SiO_2-B_2O_3, B_2O_3-P_2O_5).

Field strength of two cations approximately equal => demixing occurs

To form a single stable crystalline compound normally requires $\Delta F_s > 0.3$

As ΔF_s increases, so does the number of possible stable compounds, and the tendency to form a glass. For a binary system, glass formation is likely for $\Delta F_s > 1.33$

this theory can usefully categorize glass forming ability in conventional systems, but not universally

Vogel "Glass chemistry" (1994)

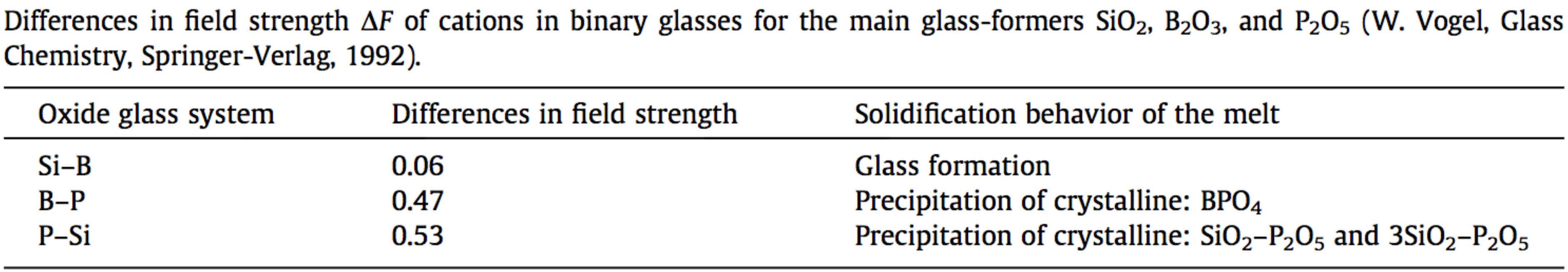
Dietzeld and field strength criteria

Mixing two network forming elements

SiO_2, B_2O_3, and P_2O_5 the best glass-formers (Zachariasen–Warren conditions for glass formation also met for any of their combinations)

But
SiO_2–B_2O_3 melts solidify as glasses at any proportion (with some region of immiscibility)
SiO_2–P_2O_5 and B_2O_3–P_2O_5 melts solidify to crystalline solids for most proportions, or upon rapid quenching, form phase-separated glasses

differences in field strength ΔF_s => crystalline solidification of the B_2O_3–P_2O_5 and SiO_2–P_2O_5 systems



Differences in field strength ΔF of cations in binary glasses for the main glass-formers SiO_2, B_2O_3, and P_2O_5 (W. Vogel, Glass Chemistry, Springer-Verlag, 1992).

Oxide glass system	Differences in field strength	Solidification behavior of the melt
Si–B	0.06	Glass formation
B–P	0.47	Precipitation of crystalline: BPO_4
P–Si	0.53	Precipitation of crystalline: SiO_2–P_2O_5 and $3SiO_2$–P_2O_5

Vogel “Glass chemistry” (1994)

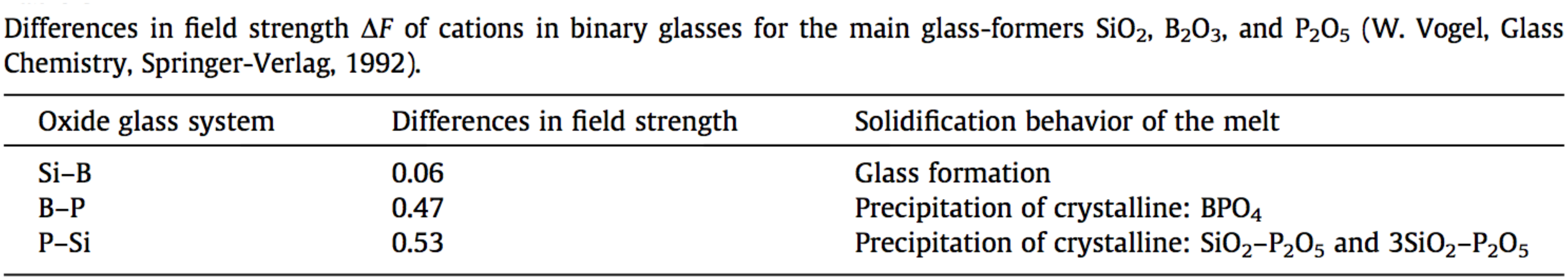
Dietzeld and field strength criteria

Mixing two network forming elements

$SiO_2–B_2O_3$

Si^{4+} (in SiO_4) $F_s = 1.57$
B^{3+} (in B_2O_3) $F_s = 1.63$

Small difference in field strength : tendency for the division of the O^{2-} ions between the two competing cations => formation of immiscible glasses



Differences in field strength ΔF of cations in binary glasses for the main glass-formers SiO_2, B_2O_3, and P_2O_5 (W. Vogel, Glass Chemistry, Springer-Verlag, 1992).

Oxide glass system	Differences in field strength	Solidification behavior of the melt
Si–B	0.06	Glass formation
B–P	0.47	Precipitation of crystalline: BPO_4
P–Si	0.53	Precipitation of crystalline: $SiO_2–P_2O_5$ and $3SiO_2–P_2O_5$

Vogel "Glass chemistry" (1994)

⇒ Thibault Charpentier

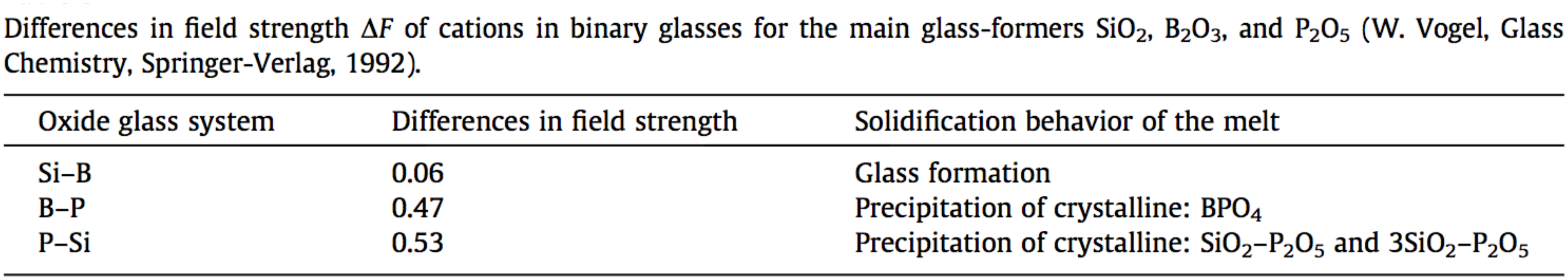
Dietzeld and field strength criteria

SiO_2–P_2O_5

Si^{4+} (in SiO_4) $F_s = 1.57$
P^{5+} (in PO_4) $F_s = 2.1$

P higher field strength => favor the formation of PO_4 tetrahedra
Si cannot compete with P to maintain SiO_4 tetrahedra => SiO_6 octahedra

P often promote phase separation due to its high field strength



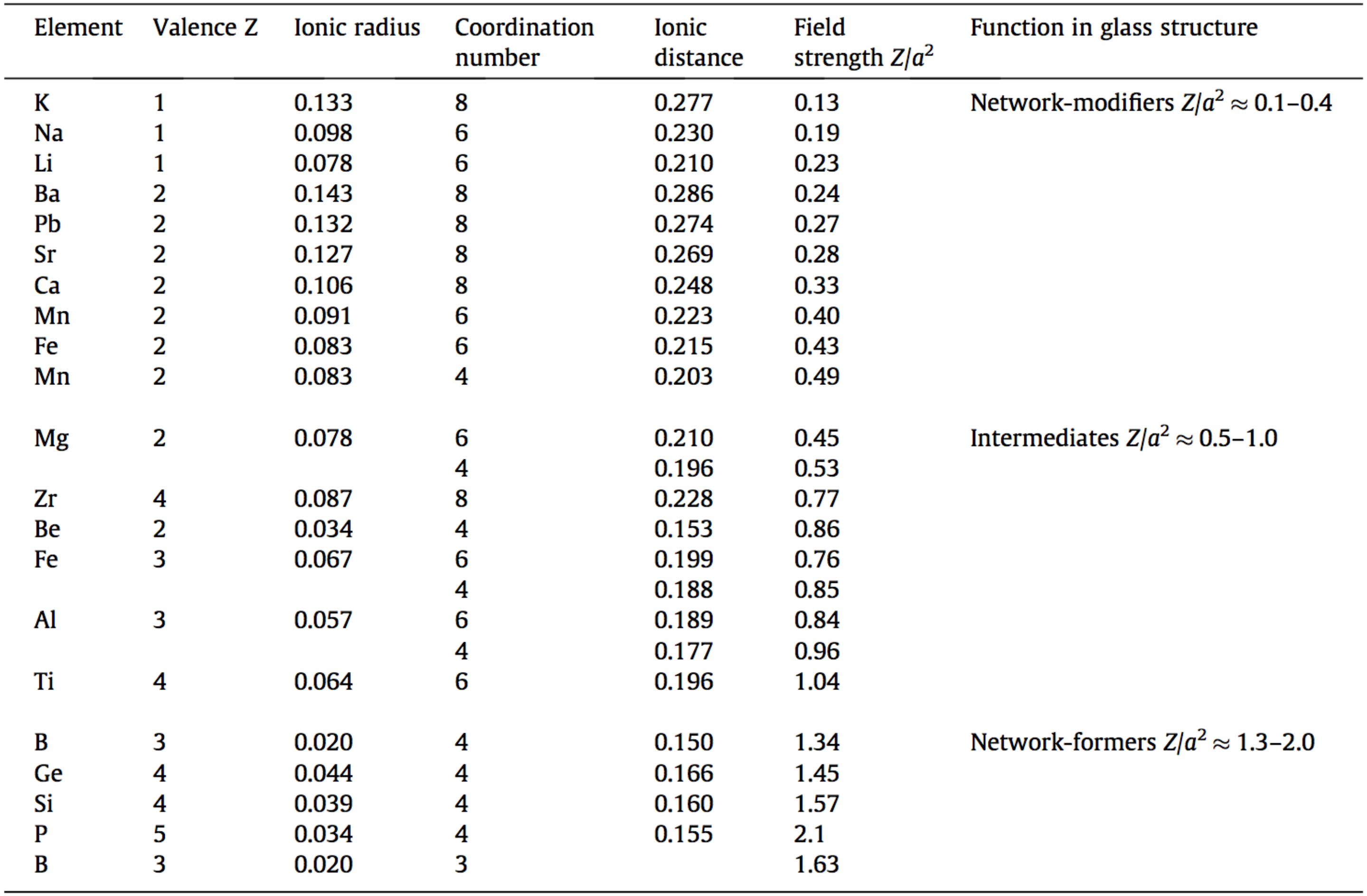
Differences in field strength ΔF of cations in binary glasses for the main glass-formers SiO_2, B_2O_3, and P_2O_5 (W. Vogel, Glass Chemistry, Springer-Verlag, 1992).

Oxide glass system	Differences in field strength	Solidification behavior of the melt
Si–B	0.06	Glass formation
B–P	0.47	Precipitation of crystalline: BPO_4
P–Si	0.53	Precipitation of crystalline: SiO_2–P_2O_5 and $3SiO_2$–P_2O_5

Dietzeld and field strength criteria

Zachariasen’s classification of ions as network-formers, network-modifiers, or intermediates correlates well with Dietzel’s field strength values

Classification of cations according to Dietzel’s field strength (W. Vogel, Glass Chemistry, Springer-Verlag, 1992).



Element	Valence Z	Ionic radius	Coordination number	Ionic distance	Field strength Z/a^2	Function in glass structure
K	1	0.133	8	0.277	0.13	Network-modifiers $Z/a^2 \approx 0.1–0.4$
Na	1	0.098	6	0.230	0.19	
Li	1	0.078	6	0.210	0.23	
Ba	2	0.143	8	0.286	0.24	
Pb	2	0.132	8	0.274	0.27	
Sr	2	0.127	8	0.269	0.28	
Ca	2	0.106	8	0.248	0.33	
Mn	2	0.091	6	0.223	0.40	
Fe	2	0.083	6	0.215	0.43	
Mn	2	0.083	4	0.203	0.49	
Mg	2	0.078	6	0.210	0.45	Intermediates $Z/a^2 \approx 0.5–1.0$
			4	0.196	0.53	
Zr	4	0.087	8	0.228	0.77	
Be	2	0.034	4	0.153	0.86	
Fe	3	0.067	6	0.199	0.76	
			4	0.188	0.85	
Al	3	0.057	6	0.189	0.84	
			4	0.177	0.96	
Ti	4	0.064	6	0.196	1.04	
B	3	0.020	4	0.150	1.34	Network-formers $Z/a^2 \approx 1.3–2.0$
Ge	4	0.044	4	0.166	1.45	
Si	4	0.039	4	0.160	1.57	
P	5	0.034	4	0.155	2.1	
B	3	0.020	3		1.63	

Structural approach to glass formation

Several models encompass most of the relevant aspects which are known to lead to glass formation:

- Based on coordination number
  - Goldschmidt’s radius ratio
  - Zachariasen’s random network theory

- Based on bond type
  - Smekal’s mixed bonding rule
  - Stanworth’s electronegativity rule

- Based on bond strength
  - Sun’s single bond strength criterion

- Based on field strength
  - Dietzel’s field strength

- Based on Mott’s rule
  - Phillips

Topological constraints hypothesis

Glass forming ability discussed by Phillips (1979) in term of a constraint model.

Most inorganic covalently bonded glasses have low values of atomic coordination number. An atom which has all covalent bonds satisfied, obeys the (8-N) rule (Mott's rule) i.e. Se has N_c=2, Ar has N_c=3, Si has N_c=4, etc

For a binary alloy A_xB_{1-x}, the average coordination (m):

$$m = x\ N_c(A) + (1-x)\ N_c(B)$$

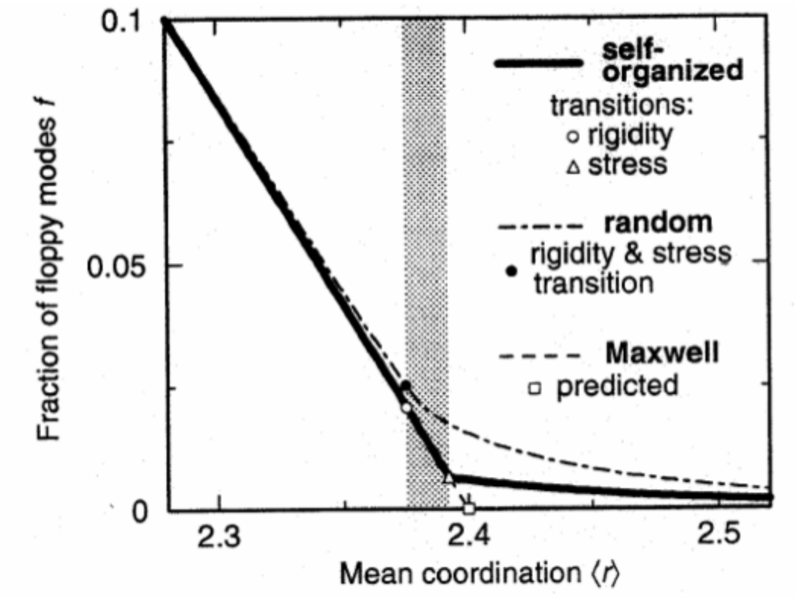
Ex :

$\langle m \rangle As_2Se_3 = 2.4$

$\langle m \rangle SiO_2 = 2.67$

Topological constraints hypothesis

Phillips theory: the glass-forming tendency is maximized when the number of constraints is equal to the number of degrees of freedom, N_d. (usually $N_d = 3$, 3D) => overconstrained (rigid) materials (a-Si,…) ≠ underconstrained (floppy) materials

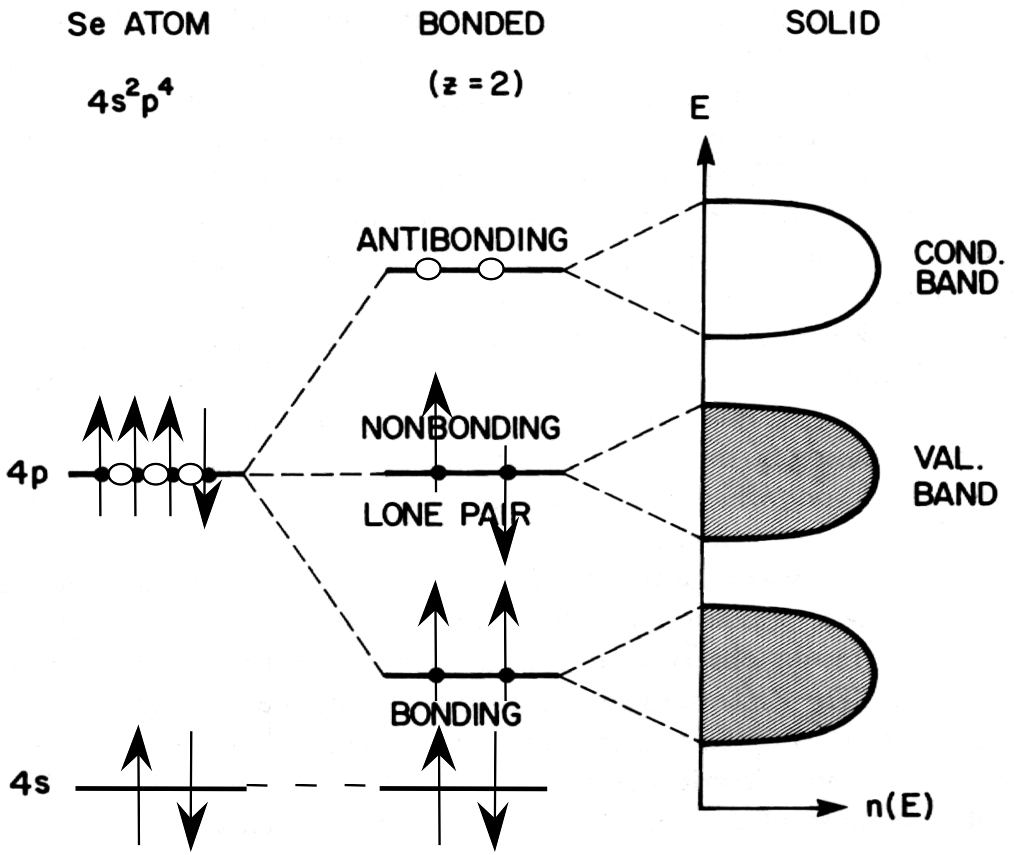


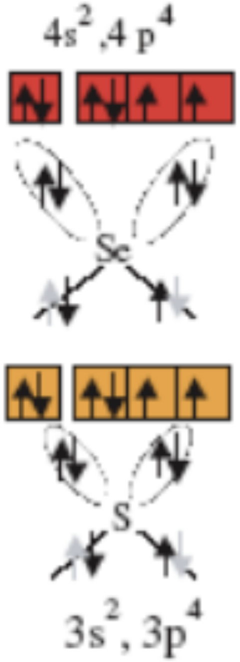
Source of figure: M. F. Thorpe, M. V. Chubynsky in Properties and Applications of Amorphous Materials, Ed. M. F. Thorpe, L. Tichy, Kluwer Academic Press, Dordrecht, p. 61, 2001.

⇒ Matthieu Micoulaut

Structure of chalcogenide glasses

a-S $3s^2 3p^4$
a-Se $4s^2 4p^4$
a-Te $5s^2 5p^4$



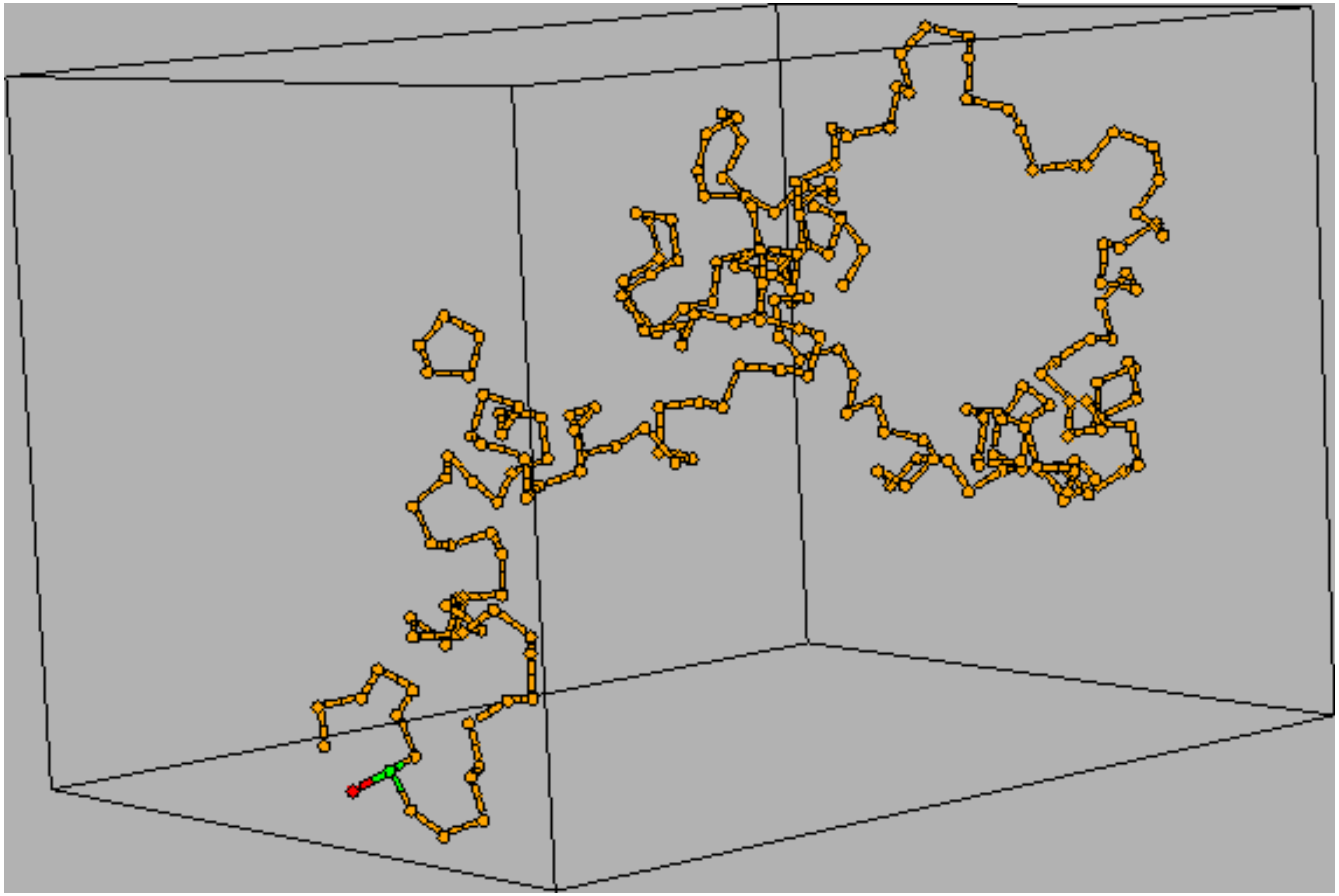


Electronic structure of a-Se
Energy band gap 1.7eV

Valence : lone pair electrons + bonding orbitals
lone pair electrons ➪ specific « defects »

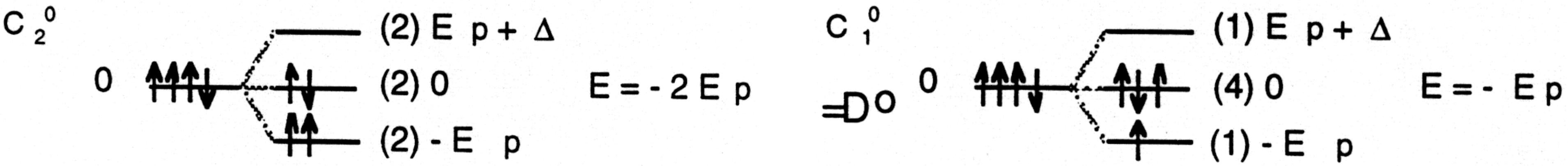
Structure of chalcogenide glasses

Chains or non-connected rings

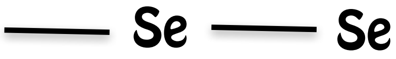


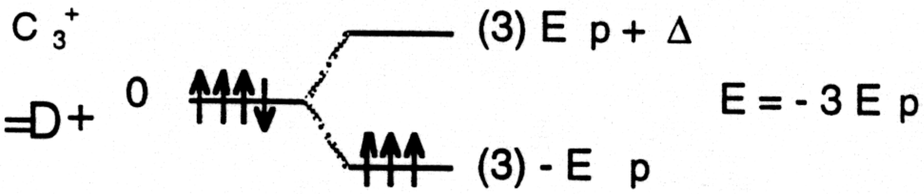
Modèle structural de a-Se

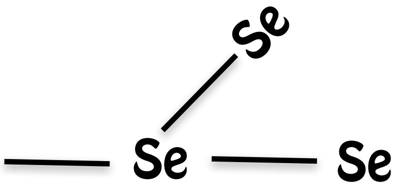
Structure of chalcogenide glasses



Electronic configuration of a-Se and end-of-chain defect



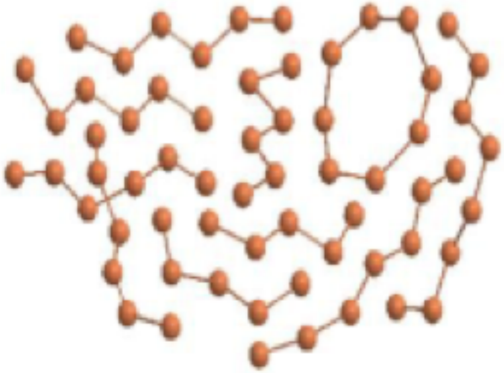


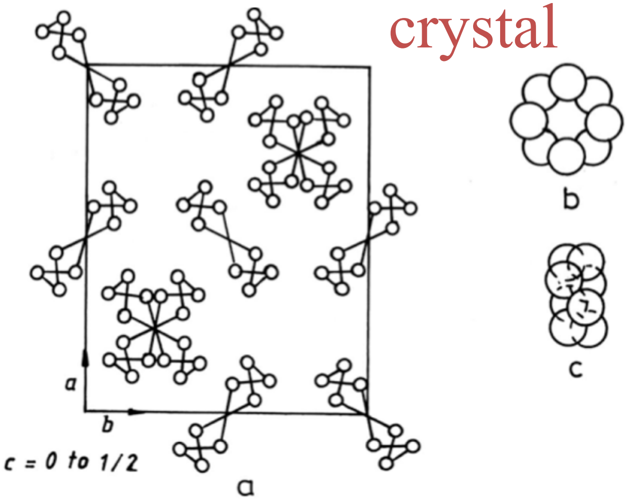


Rebuilding of end-of-chain defect

Structure of chalcogenide glasses

a-S $3s^2 3p^4$
a-Se $4s^2 4p^4$
a-Te $5s^2 5p^4$





crystal

Figure 1.2. The unit cell of the orthorhombic sulphur (S_α).
a the ring packing b, c. front view and side view of the S_8 ring.

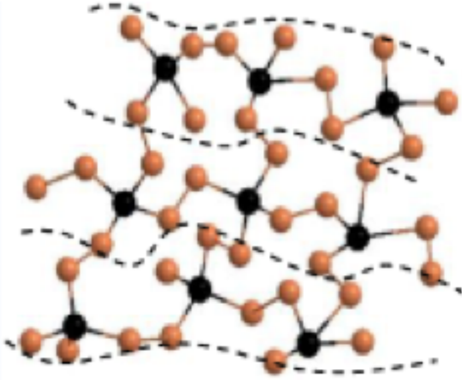
Structure of chalcogenide glasses

System Ge-S or Ge-Se

➪ GeS$_4$ units

GeS$_4$ tetrahedra linking S chains

GeS$_4$



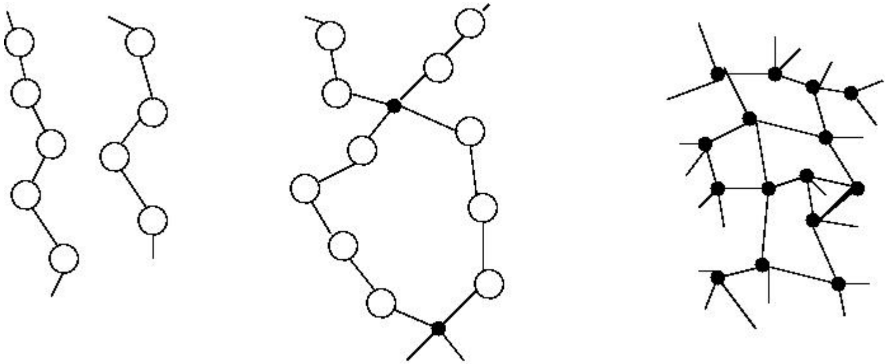
S
chains,
rings

➪

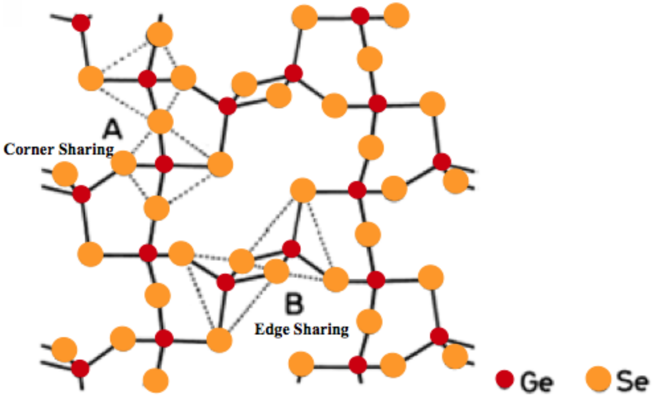
Ge$_x$Se$_{1-x}$
GeS$_4$ are
connecting chains

➪

Ge
All Ge are in 4-fold
coordination (iso-
structural to a-Si)



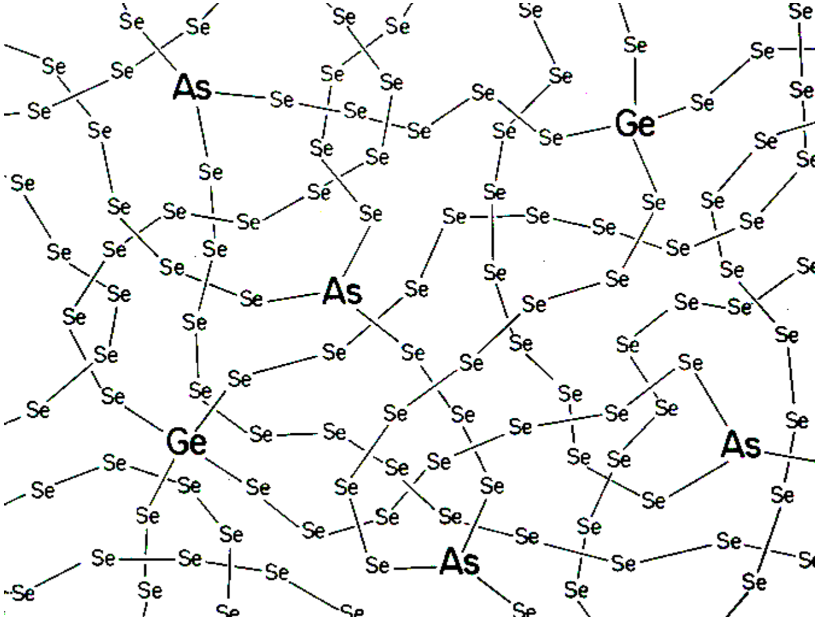
Tetrahedra can shares
corners and edges≠silicates



Glass GeSe $_2$

Structure of chalcogenide glasses

System As-S or As-Se



As_2S_3

cristal

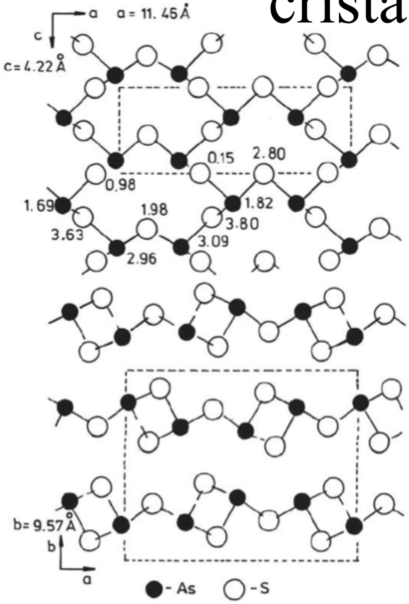


Figure 1.13. The structure of orpiment (As_2S_3) viewed in two projections. (the figures indicate the position of the atoms above the plane of the paper)

- Modifiers ?

⇒ Annie Pradel
⇒ Bruno Bureau
⇒ Eugene Bychkov

Notion of network former applicable to all kind of glasses ?

Possible to define network former or modifier in

- metallic glasses ?
- organic glasses ?

Structure of metallic glasses

Consider packing of dense spheres

Most compact configuration for spheres which are all identical in a 3D-space (cfc, hc)
$\Rightarrow$ compacity 0.74

Proposed by J. Kepler in 1611, this results was demonstrated only in 1998 by T. Hales

Compacity is the ratio between the volume of particules within the cell and the volume of the cell. It is the degree of filling of the space

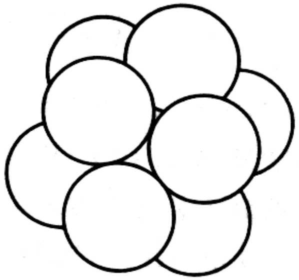
cfc, hc	C=0.74
cc	C=0.68

Structure of metallic glasses

And for a disordered stacking ?

Colloidal
Granular medium
Sand pile or peas

Principle : hard sphere dense random packing



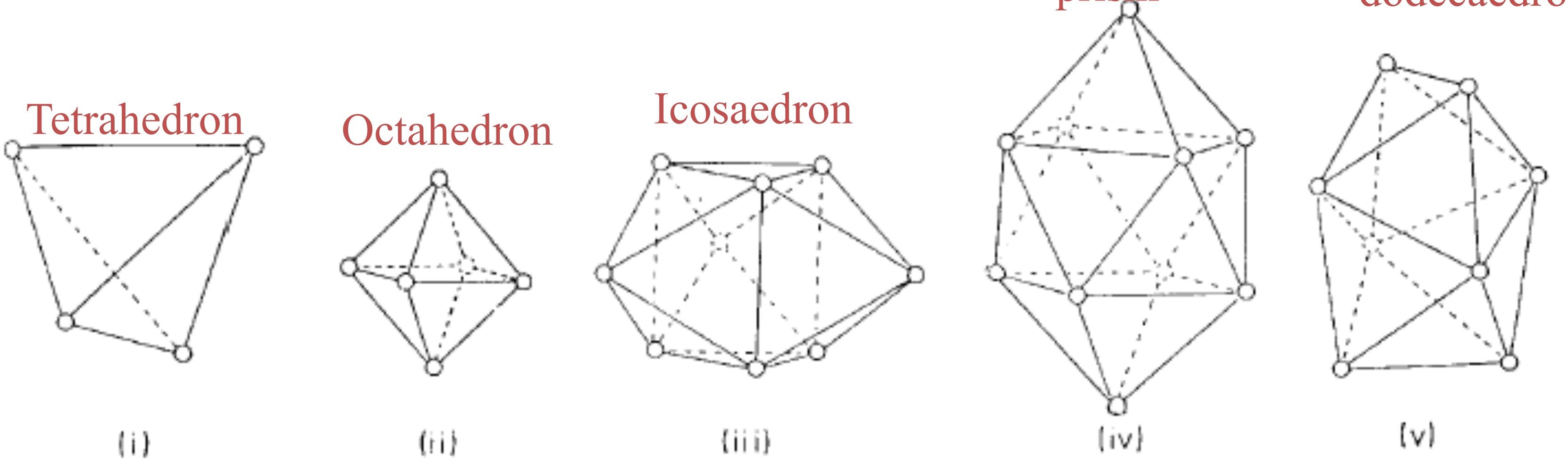
Packing ratio: 0.636

⇒ random packing of spheres
⇒ Importance of free volume
⇒ metallic glasses: minimization of free volume

Structure of metallic glasses

⇒ dense random packing of spheres

Canonical cavities of Bernal



Tetrahedron

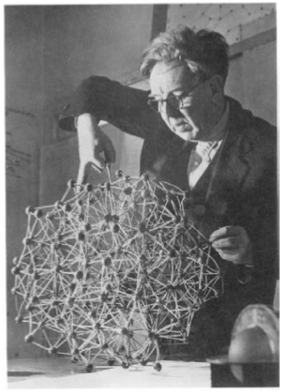
Octahedron

Icosaedron

Archimedes anti-prism

Tetragonal dodecaedron

Local arrangements for a model of dense random packing



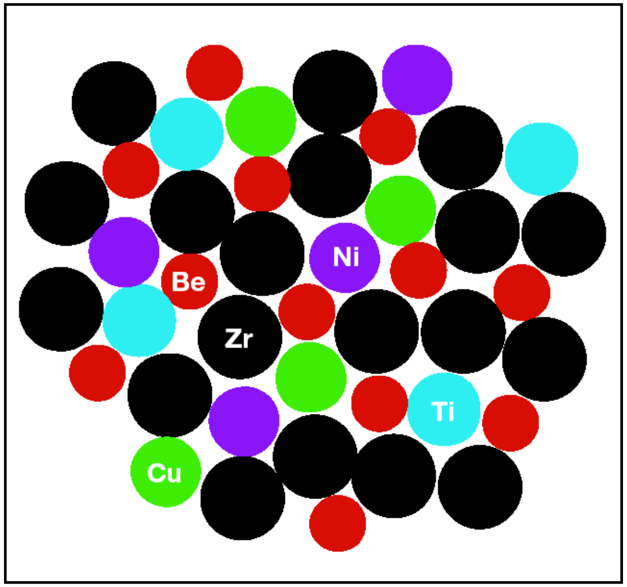
John Desmond Bernal (1901-1971)

Structure of metallic glasses

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

Mixing various elements with different sizes

Metal (Fe,Ni,Al,Cr,Pd)
Metalloids (P,Si,B,Ge)



Tang et al., Nature 402, 160 (1999)

Principle of confusion

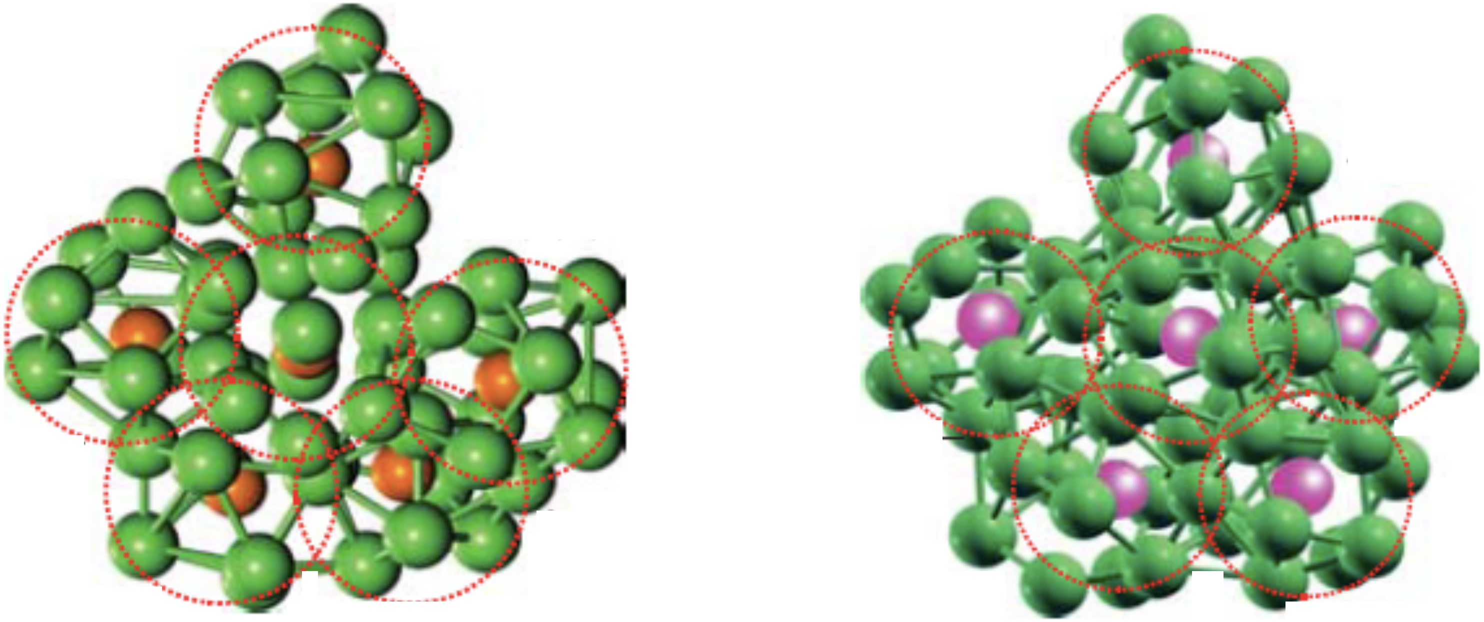
A more complicated chemical composition translate into a greater number of compounds that could nucleate and, thus, in mutual competition such that crystal nucleation and growth is frustrated and does not take place on sufficiently rapid cooling

From 'Silicate glasses and melts: properties and structure'
Mysen & Richet (2005)

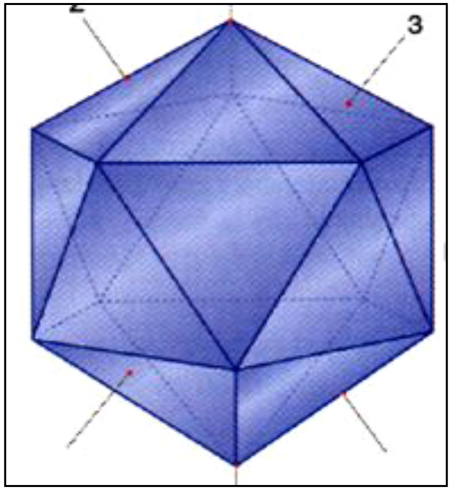
Structure of metallic glasses

+ medium range order (2006)

Stacking of blocks with 5-fold symmetry



Sheng et al., Nature 439, 419(2006)



icosaedron

Miracle, Nature Materials 2004
Yavari, Nature Materials 2005
Sheng et al, Nature 2006
Yavari, Nature 2006

⇒ Lindsey Greer

Structure of metallic glasses

Energetic Stability: Clusters

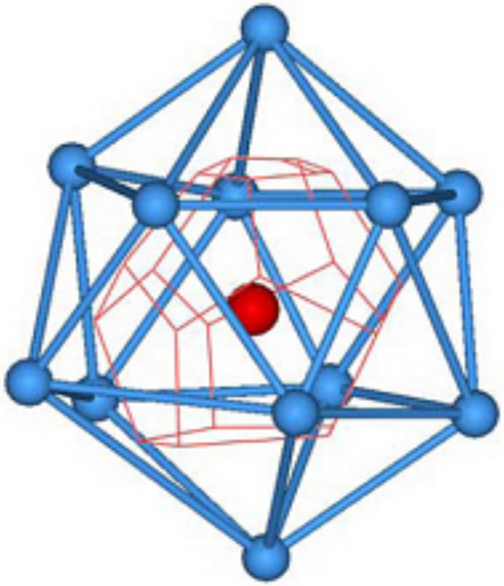
clusters lead to energetic stability

prevalence of efficiently-packed clusters (low free volume and energy) that do not have symmetry suitable for crystal formation explain the stability of supercooled liquids

icosahedrally-coordinated atomic clusters are the probable clusters for pure liquids

⇒ The Zachariasen's rule do not applied

⇒ Possible to talk of network former ?



Structures of polymers

chains packed in a regular way => crystal

Both amorphous and crystalline areas can exist in the same polymer

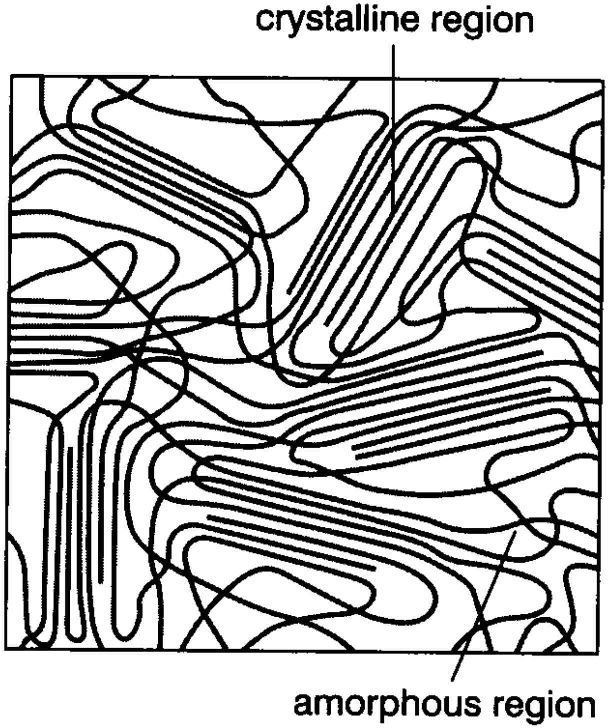
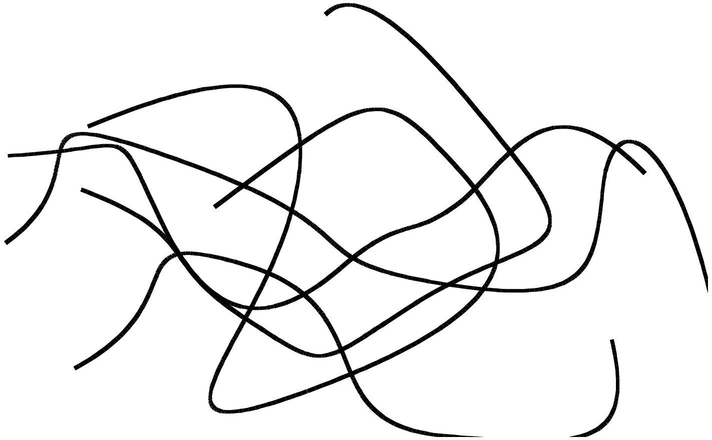


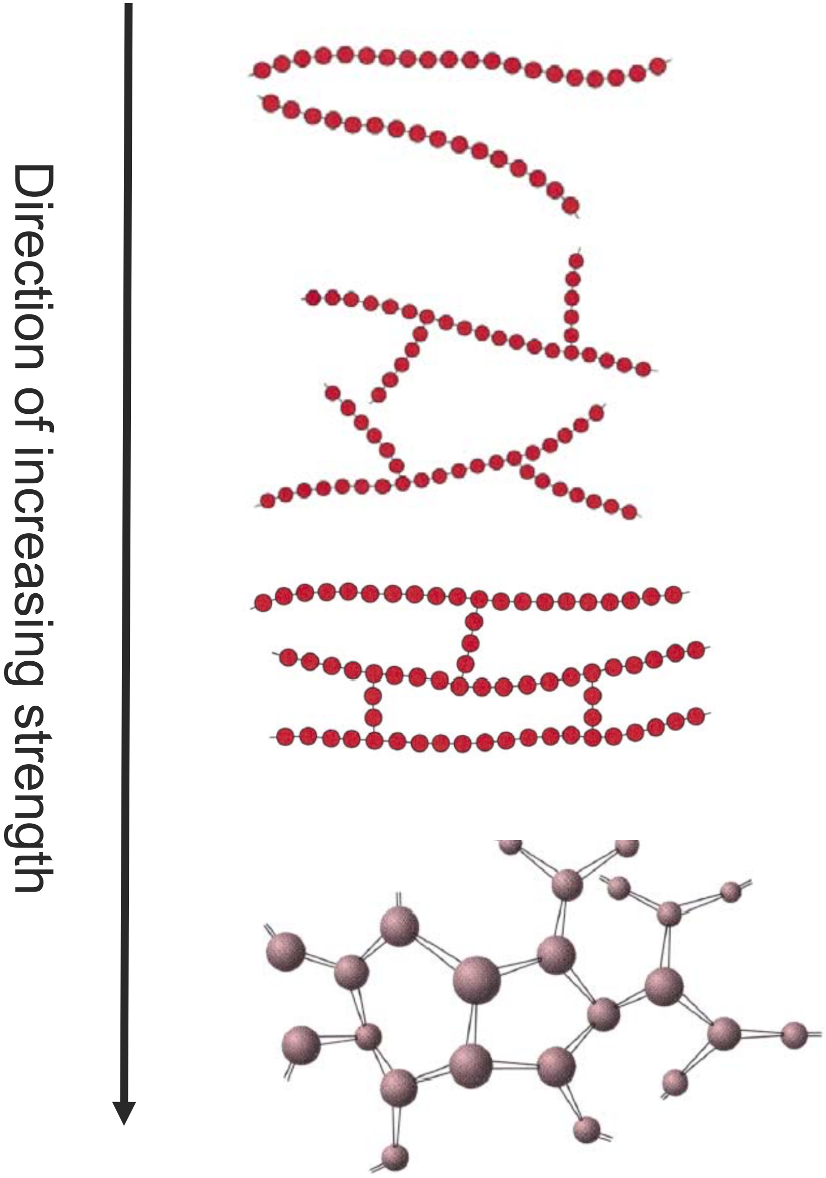
Figure 32 Crystalline and amorphous regions of a polymer.

Chain entanglement: Long polymer chains get entangled with each other

= random coil model
Modèle de pelote aléatoire



Structures des polymères



(a) Linear structure : van der Waals bonding between chains

(b) Branched structure : Chain packing efficiency is reduced compared to linear polymers - lower density

(c) Cross-linked structure : Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains

(d) Polymerized structure : Three active covalent bonds - Highly cross-linked

3 main structural atomic models for non-crystalline solids

- **Random Network**

Continuous random network → ioni-covalent glasses SiO_2
Modified random network → ioni-covalent glasses $Na_2O\text{-}SiO_2$

- **Random Close Packing**

Empilement aléatoire compacte → metallic glasses

- **Random Coil Model**

Modèle de pelote aléatoire → polymeric organic glasses

References

http://www.lehigh.edu/imi/teched/OPG/lecture2.html

https://www.lehigh.edu/imi/teched/GlassCSC/Lecture_2_Martin.pdf

https://www.lehigh.edu/imi/teched/AtModel/Lecture_2_Micoulaut_Atomistics_Glass_Course.pdf

http://web.mst.edu/~brow/pdf_structure1.pdf

www.eng.uokufa.edu.iq/staff/sawsandh/Polymers.ppt

www.phy.bme.hu/Kristalyos_es_amorf.../Introduction.ppt