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

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Structure and 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.

Glass structure corresponds to the disordered structure of the supercooled liquid at the glass transition temperature

Understanding the structure enables the design of new materials with **tailored properties**, optimizing their **glass-forming ability** for diverse applications

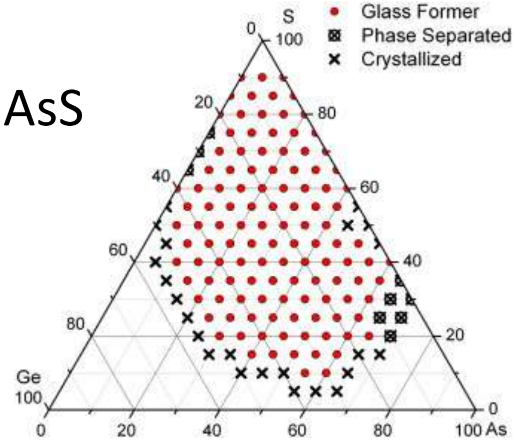
No theories able to predict which materials are able to form a glass, and under what conditions

What is the region of glass formation ?

Glass forming region

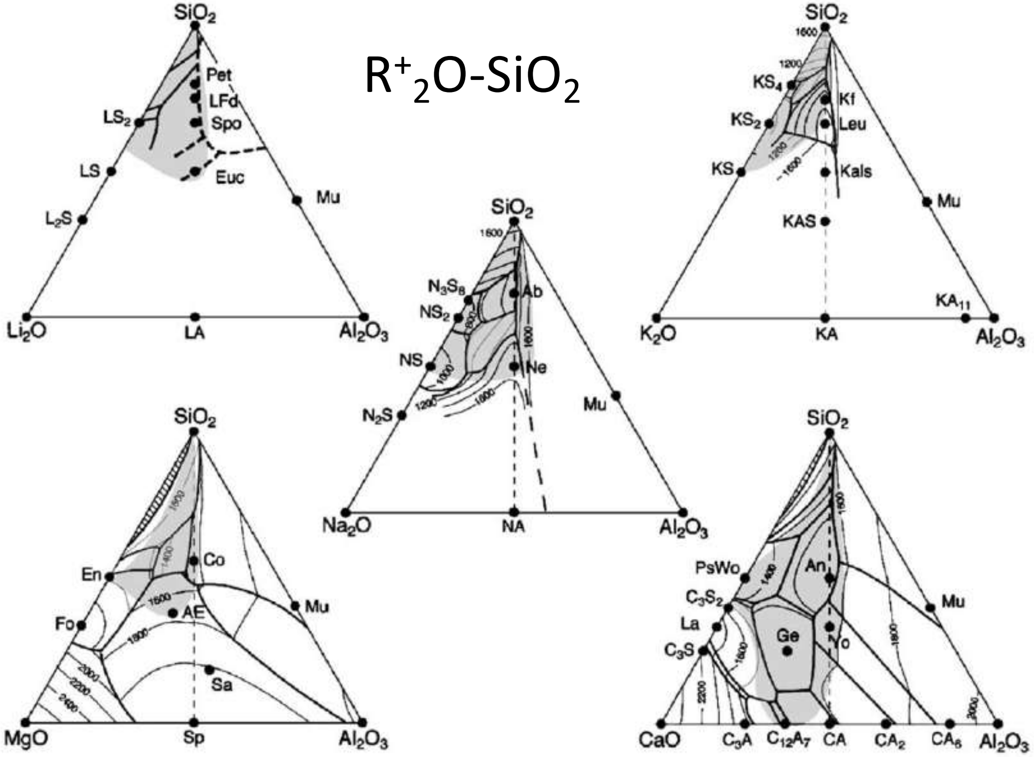
Determination of glass forming region after extensive studies in compositions

GeAsS

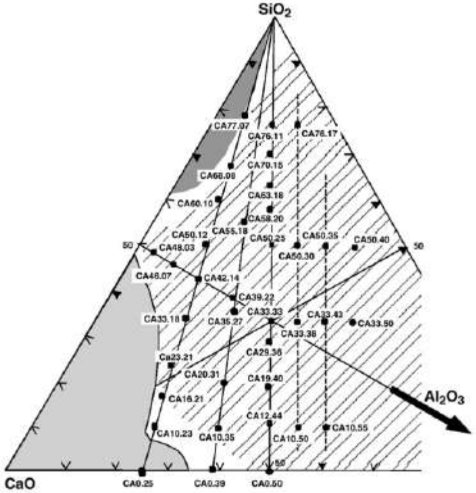


Musgrave et al., J. Non-Cryst. Solids, 386 (2014) 61

$R^+{}_2O$-SiO_2

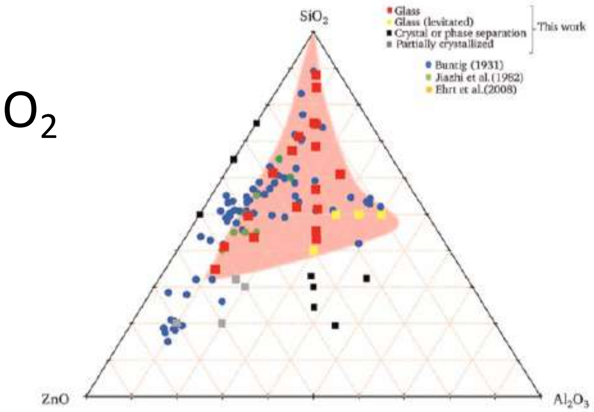


Richet et al., Chem. Geol. 225 (2006) 388



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

$R^{2+}O$-SiO_2

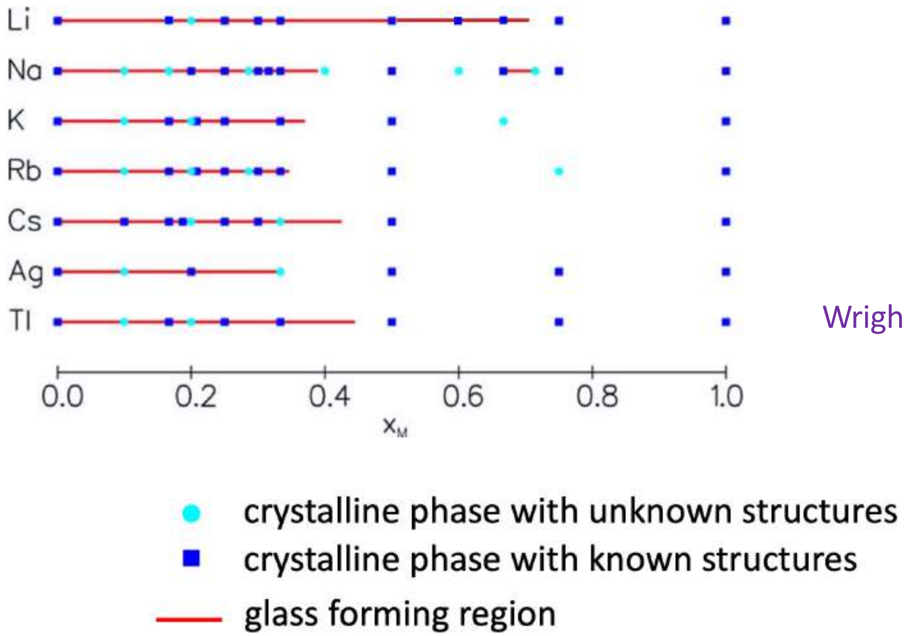


Cormier et al., J. Non-Cryst. Solids 555 (2021) 120609

Glass forming region

Determination of glass forming region
after extensive studies in compositions

R_2O-B_2O_3

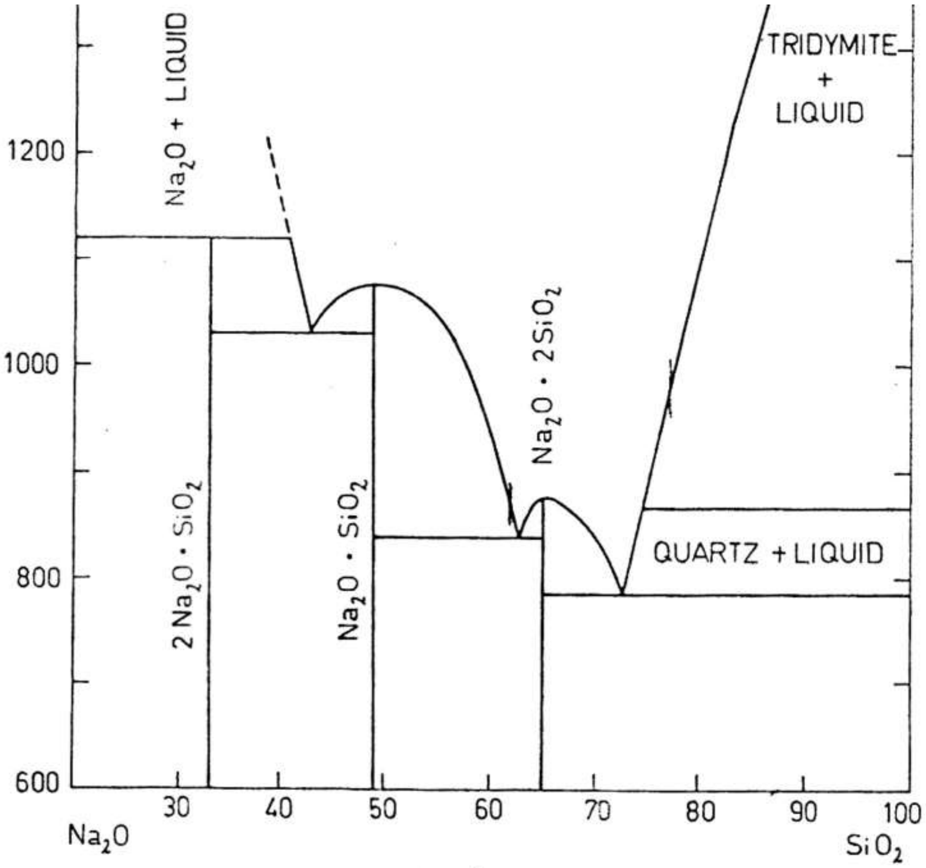


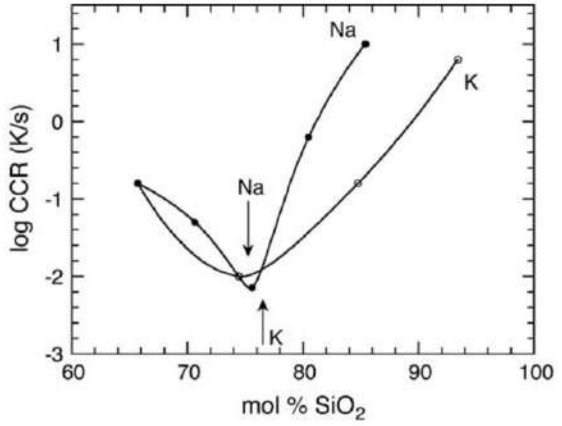
Wright, Phys. Chem. Glasses 6 (2015) 45

Glass forming region

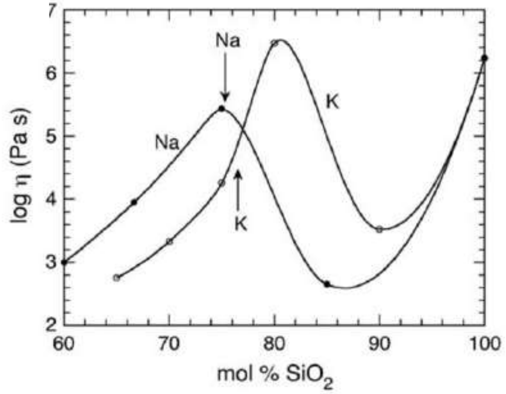
In a phase diagram, glasses are favored near eutectics because these freezing depressions bring the liquid to higher viscosities at lower temperatures

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

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

⇒ Laurent Cormier
USTV School - Cargese - 2017

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)

$F_s = Z_C / a^2$

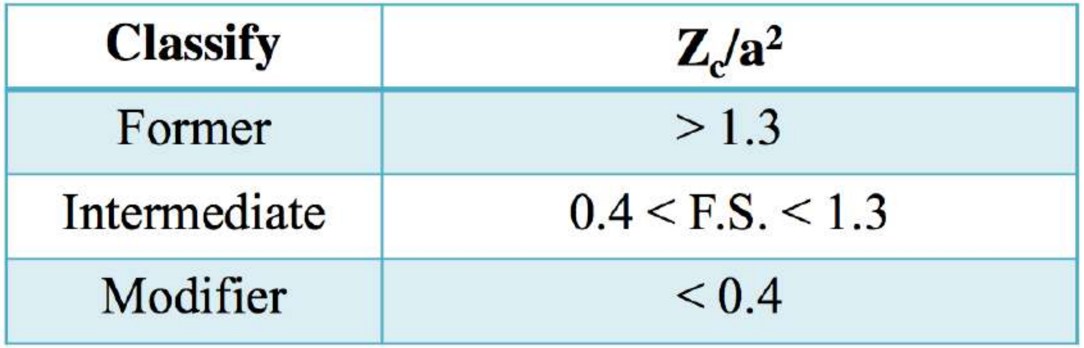
Z_C = valence of the cation
a is the distance between cation and oxygen

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

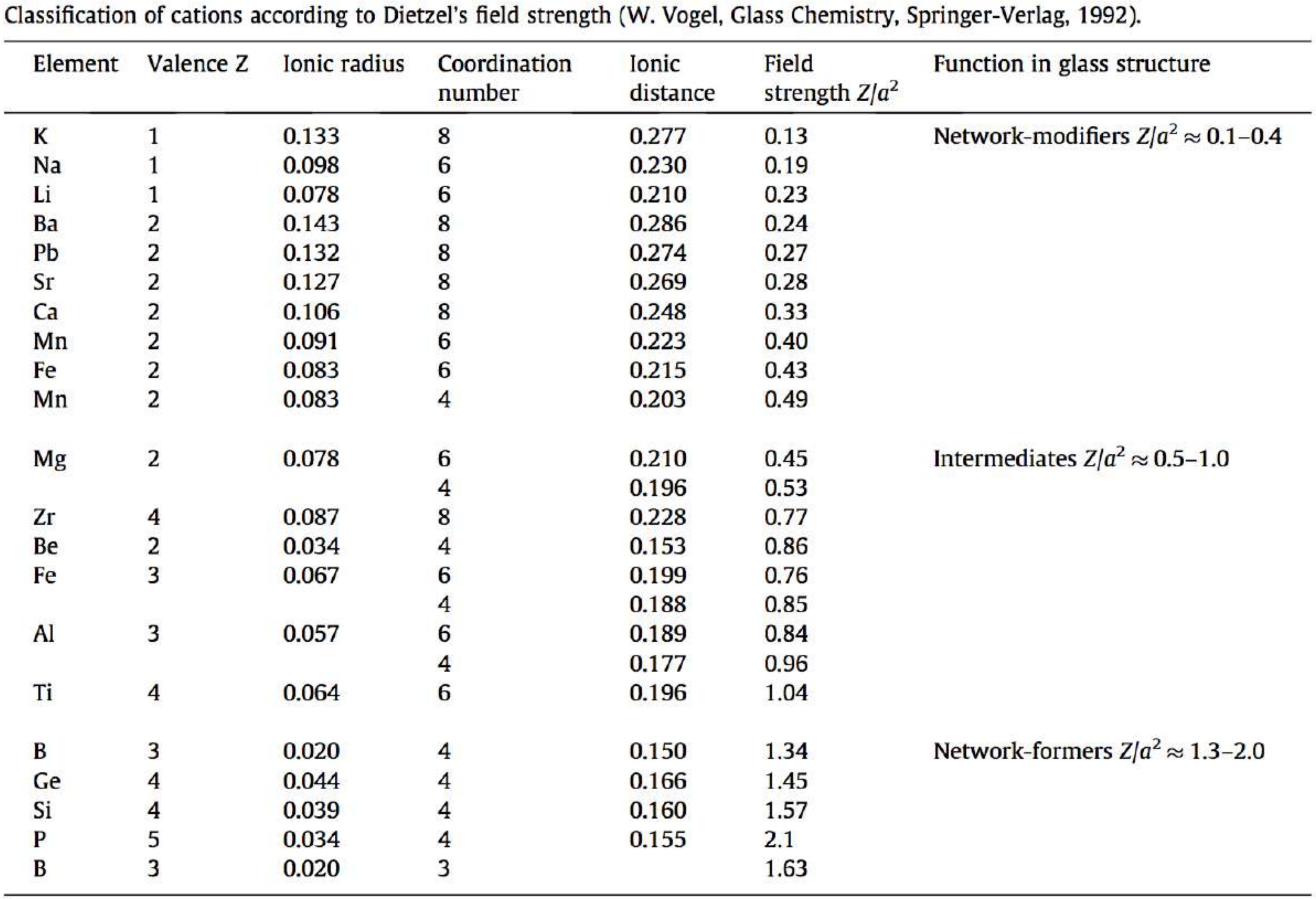
High field strength (for C it is 2.4) => covalent bonds, difficulty to form a glass

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

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

Dietzeld and field strength criteria

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 role

Cations in the glass were categorized 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

Dietzeld and field strength criteria

Mixing two network forming elements

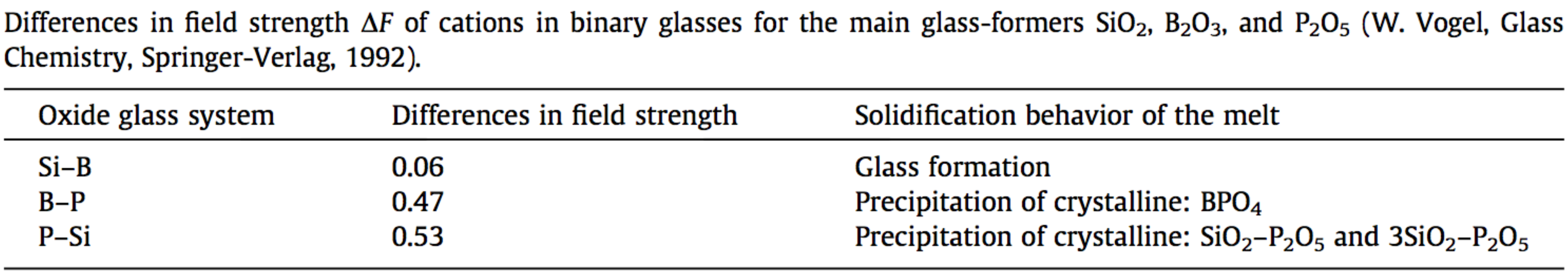
SiO_2, B_2O_3, and P_2O_5 the best glass-formers (Zachariasen–Warren conditions for glass formation also met for any of their combinations)

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)

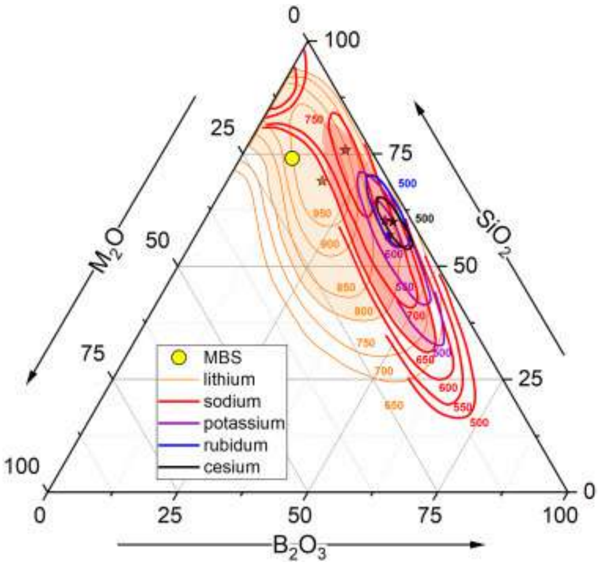
Dietzeld and field strength criteria

Mixing two network forming elements

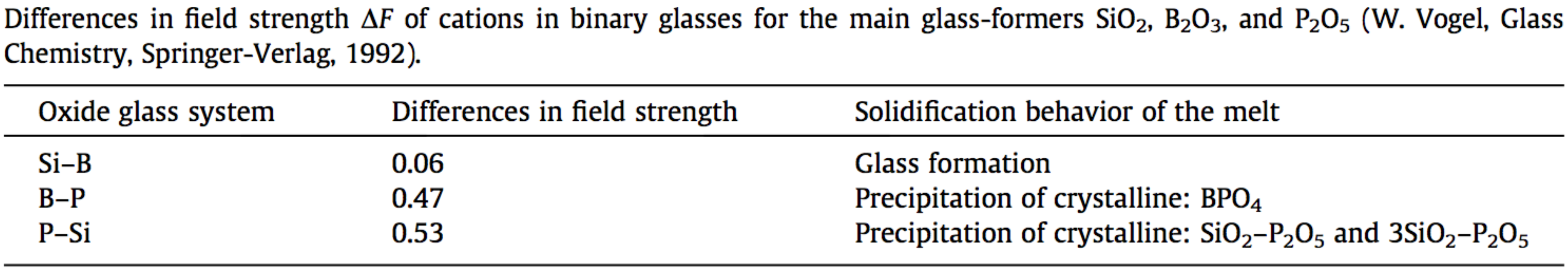
SiO_2–B_2O_3

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



Topper J.Non-Cryst. Solids X 17 (2023) 100161



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Vogel “Glass chemistry” (1994)

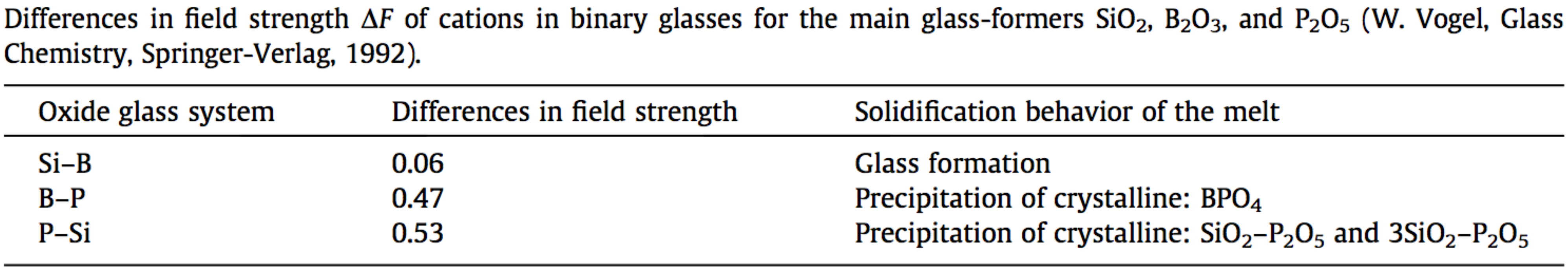
Dietzeld and field strength criteria

$SiO_2–P_2O_5$

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



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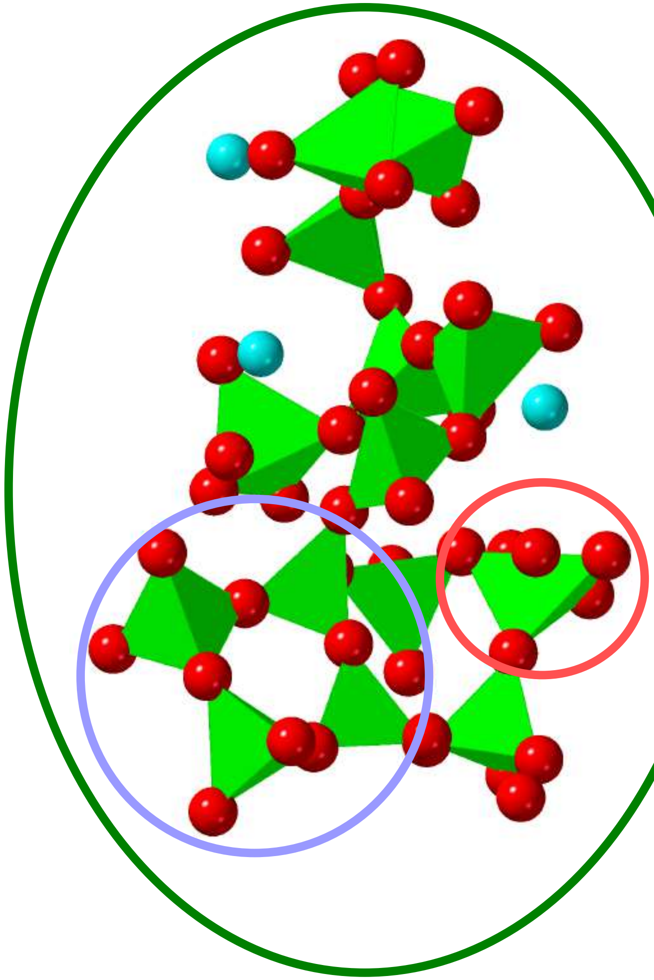
Different structural ranges



Short range structure (<3 Å):

- – coordination, bond lengths, bonding angles
- – linkages homo (-Se - Se- , -C - C-, -As - As) vs. heteropolar (Si - O, B - O, Ge - S)

Medium range structure (3-15 Å):

- – angles between structural units
- – connectivity between structural units(corner-, edge-sharing…)
- – dimensionnality, rings
- – heterogeneities

Long range structure, almost absent (no periodicity!) :

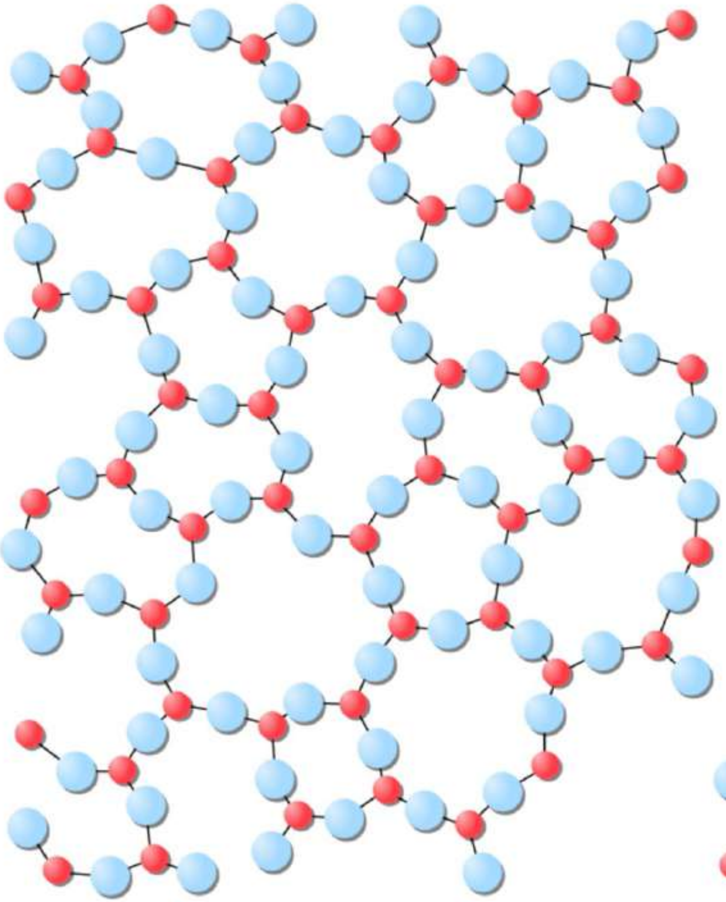
- – phase separation

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

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

William Houlder Zachariasen
(1906-1979)

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

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

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

Chalcogenide glass formers

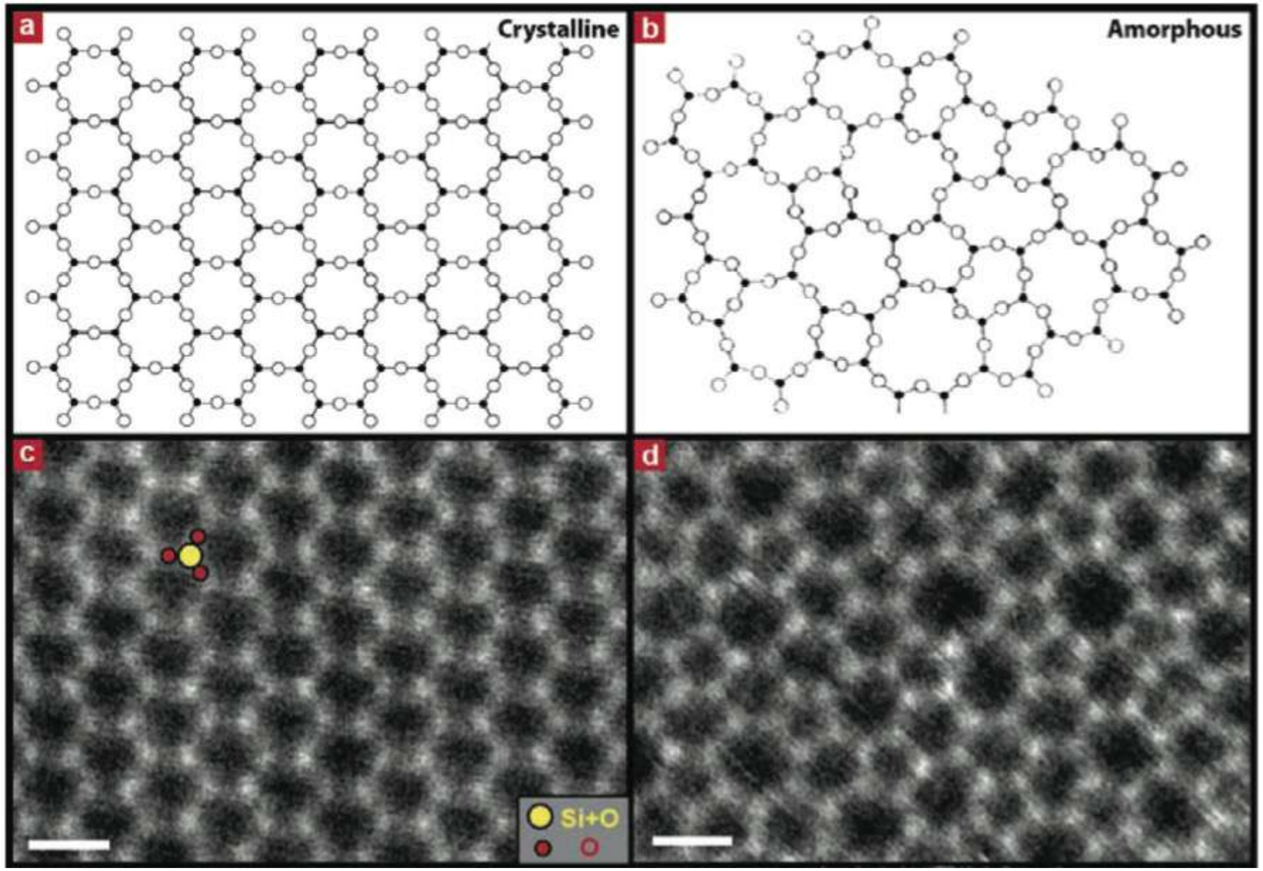
Zachariasen enounced 4 rules to define what is a glass former (in oxides)
Rule # 3 : **constituting polyhedra should share only corners !**

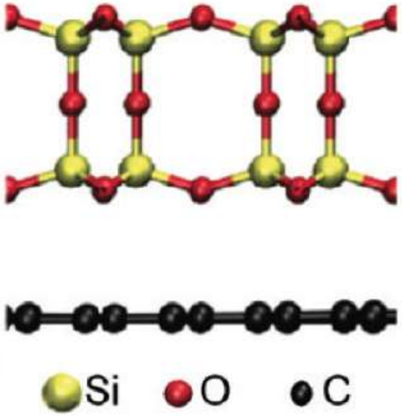
Co-existence of corner-sharing tetrahedra and edge-sharing tetrahedra
Predominance of edge-sharing Td for $SiS(e)_2$
Predominance of corner-sharing Td for GeS(e)2

As a matter of fact, GeS_2 can be obtained rather easily (air quenching);
$SiS(e)_2$ require fast quenching

Smekal model : **co-existence of different types of forces**
Van der Waals + covalent

Zachariasen's random network (1932)





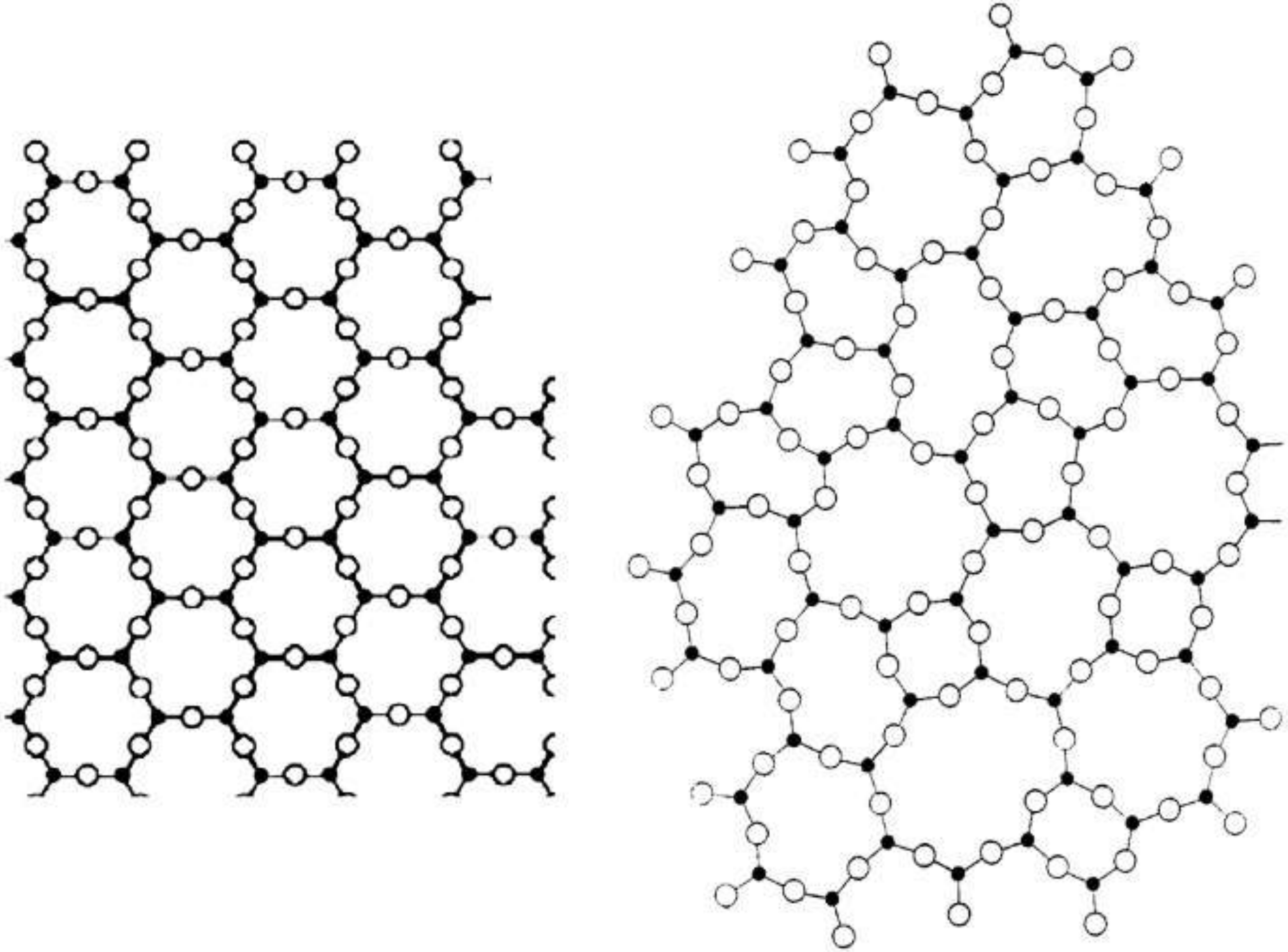
c-SiO_2

a-SiO_2

STEM images

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

Free volume



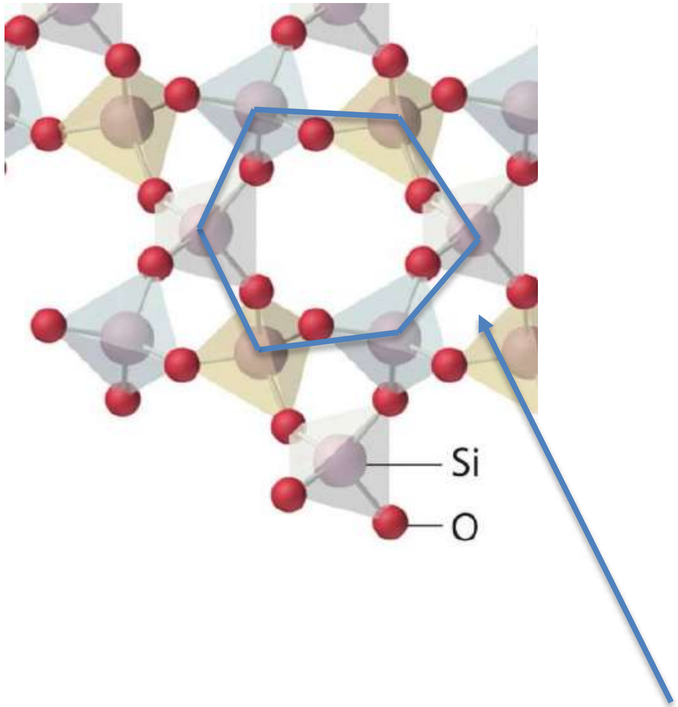
Same number of atoms occupies different volume => different densities

Neuville & Cormier Mat. Techn. 110 (2022) 404

Structure of silica glass

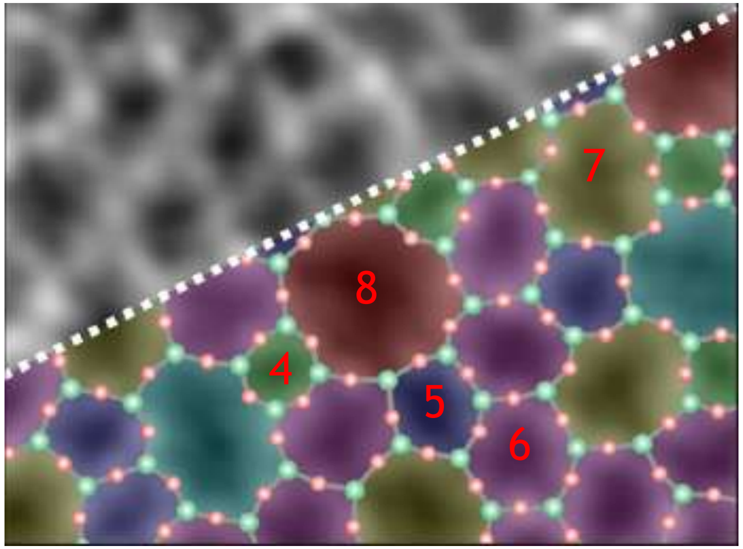
Silica glass

Amorphous material
Random network of SiO_4 tetrahedron



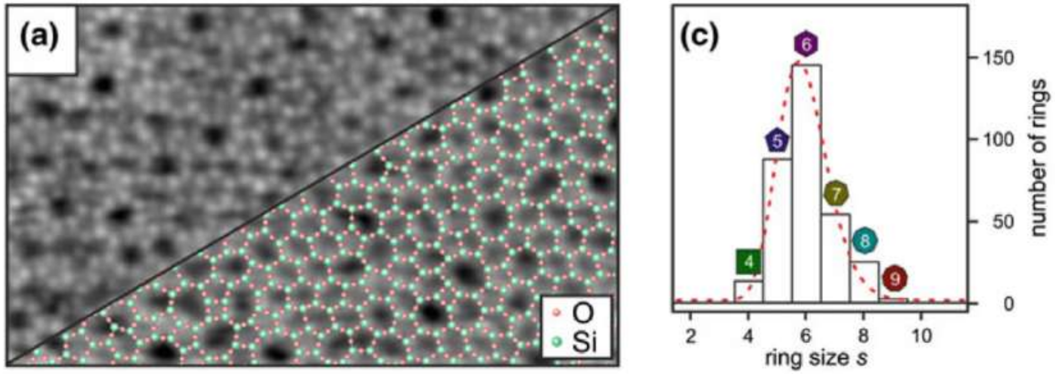
6-membered ring of SiO_4 tetrahedra

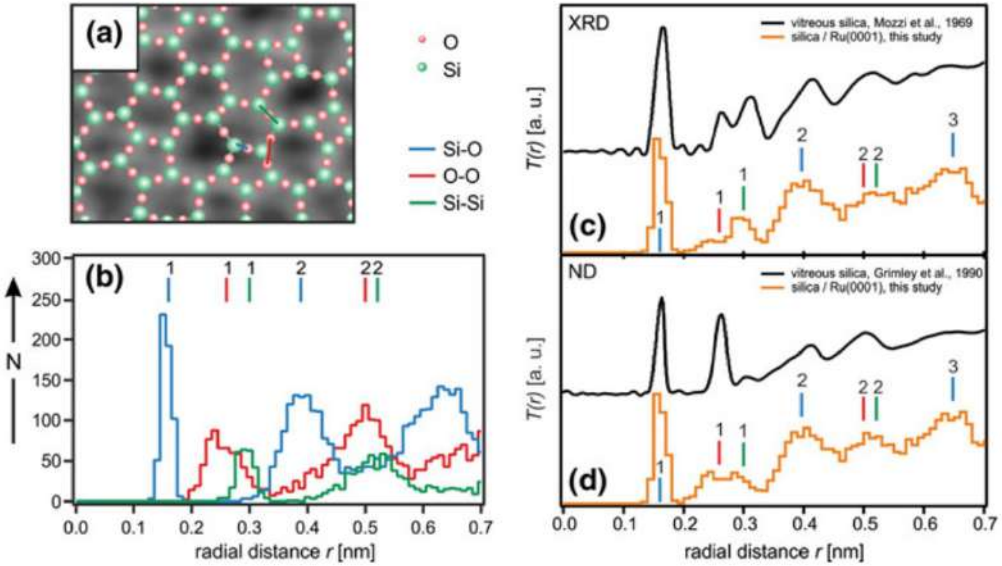
Rings of different size



Lichtenstein et al., J. Phys. Chem. C 116 (2012) 20426

Structure of 2D silica glass



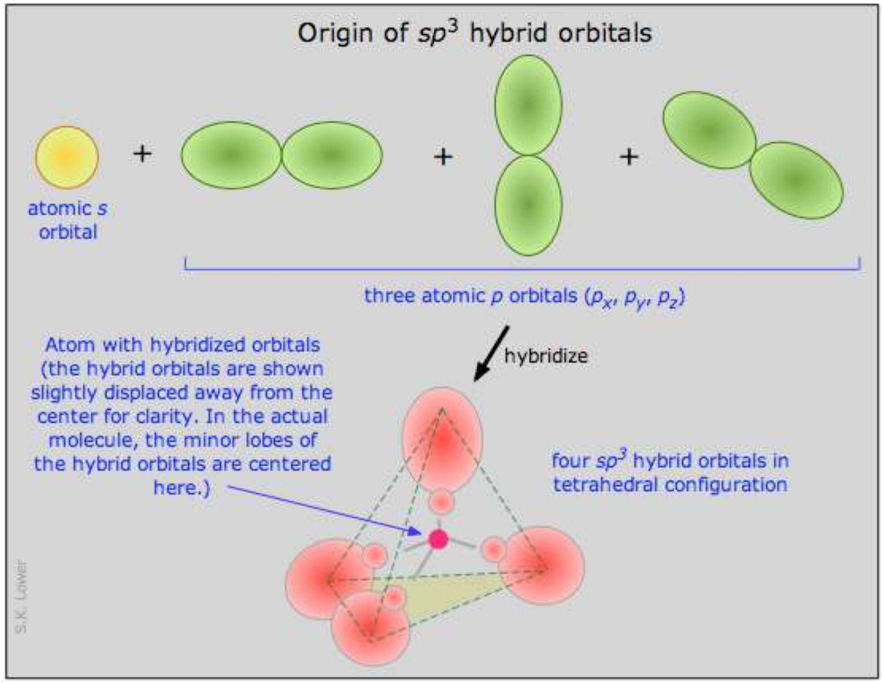


Büchner et al. (2015) 325

Electronic structure

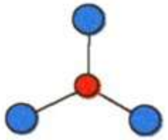
Si : (Ne)$3s^2 3p^2$: 4 valence electrons => ions Si^{4+} (can share 4 bonds)

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)

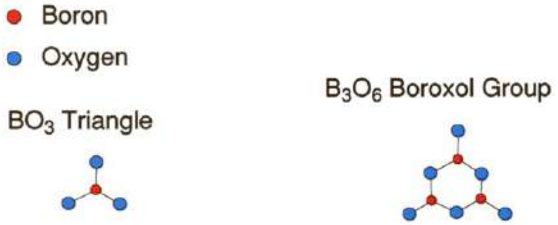
O : (He)$2s^2 2p^4$: 6 valence electron => ions O^{2-}(can share 2 bonds)



Borate glass

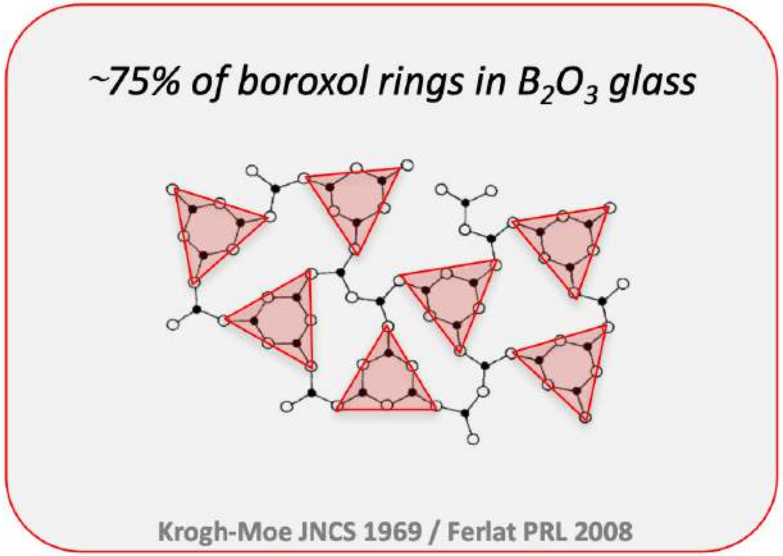
B_2O_3 composed primarily of CRN's of BO_3 units forming boroxol rings.

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



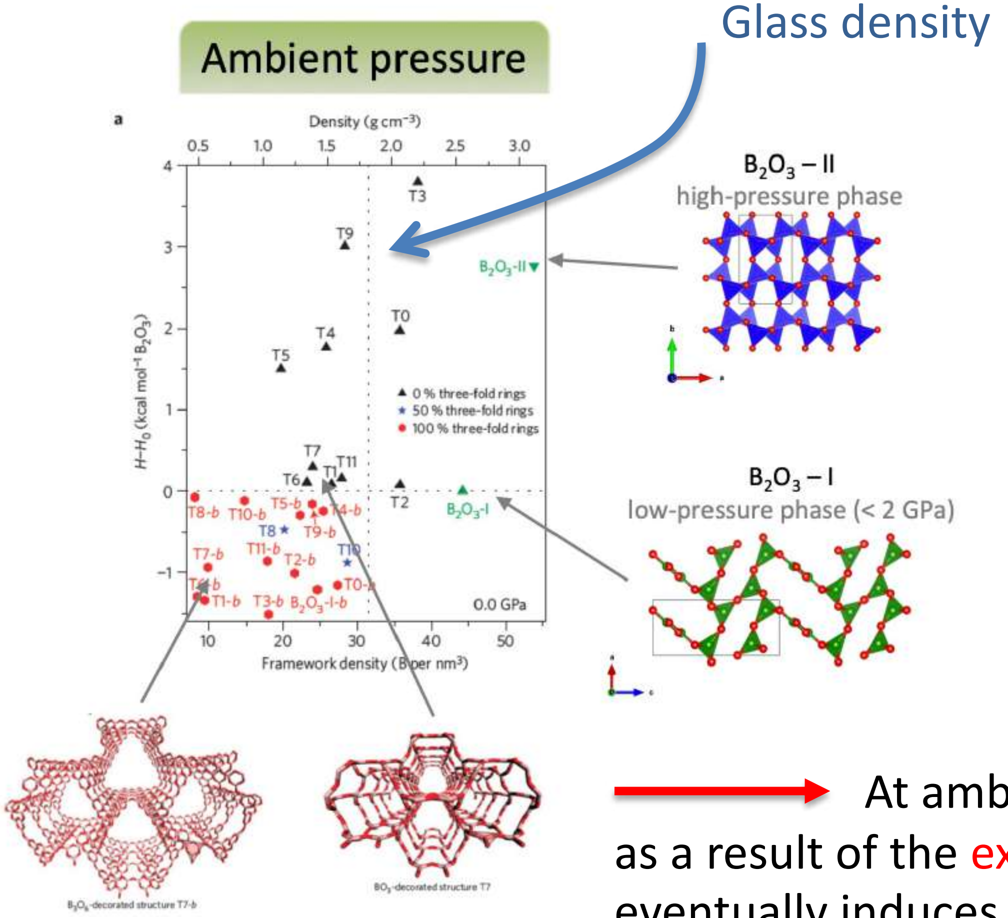
~75% of boroxol rings in B_2O_3 glass

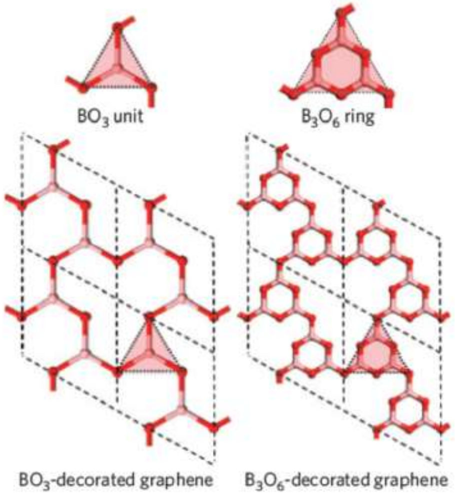
Krogh-Moe JNCS 1969 / Ferlat PRL 2008

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

Borate glass

☐ Predictions of crystalline B_2O_3 forms





→ At ambient pressure, the crystallization is avoided as a result of the existence of several competing phases that eventually induces the system amorphization.

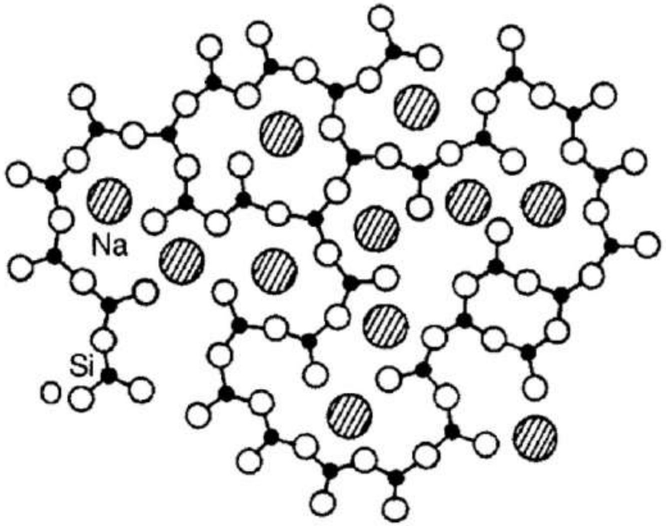
the boroxols allow one to maintain a low-energy structure while keeping a liquid-like density

Ferlat et al. Nature 11 (2012) 925

Multicomponent oxide glasses

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

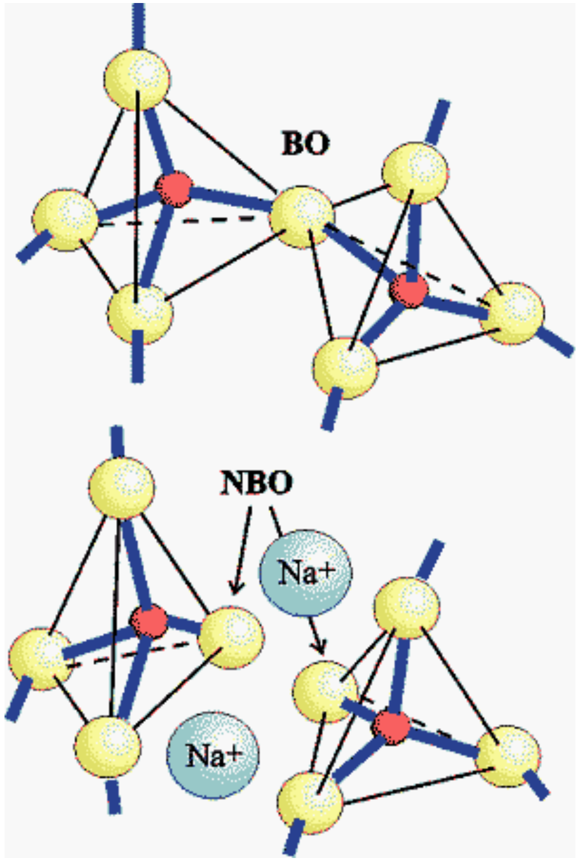
Zachariasen–Warren network theory



Bertram Eugene Warren
1902-1991

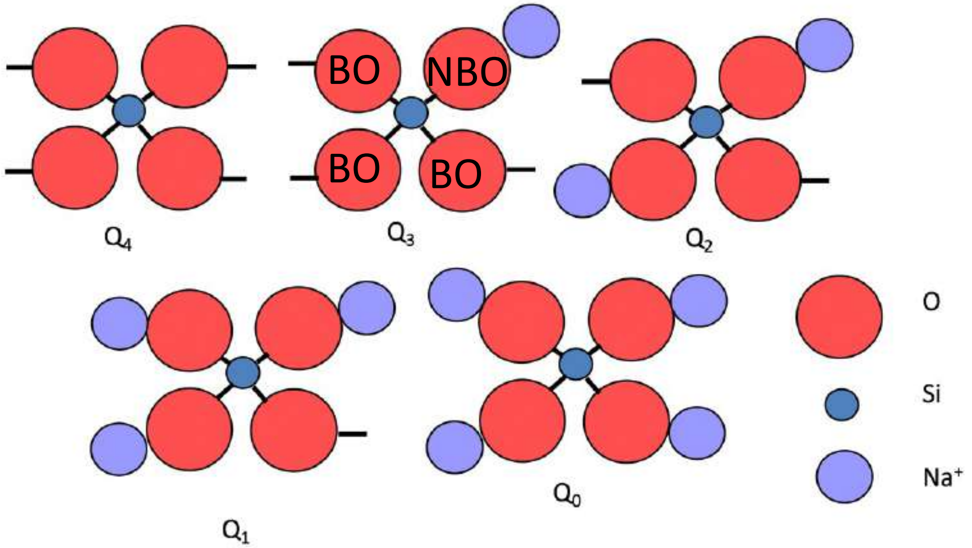
Multicomponent oxide glasses

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 chalcogenide glasses

$SiS(e)_2$

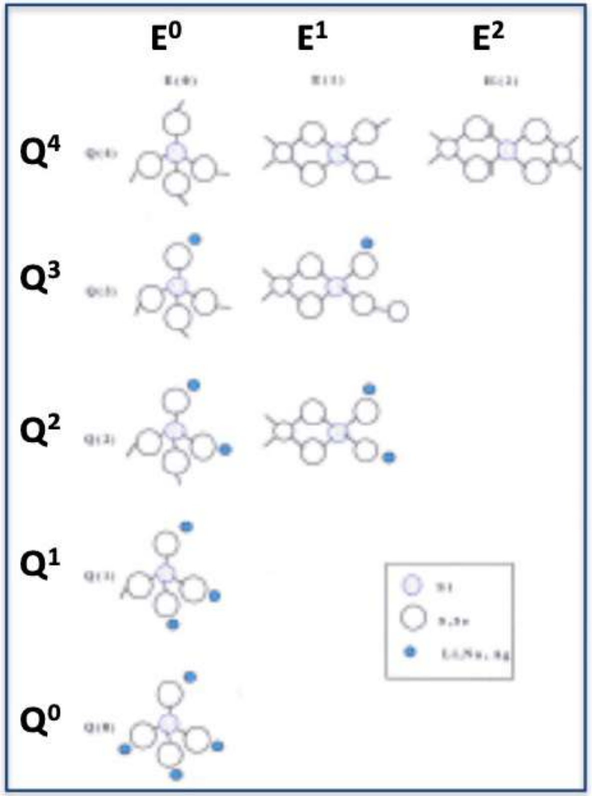
+

$M_2S(e)$

M = Li, Na, Ag

Creation of non bridging sulfur

E^nQ^n Entities



⇒ Annie Pradel
USTV School - Cargese - 2017

Chalcogenide glasses different from oxide glasses

Presence of edge-sharing Td

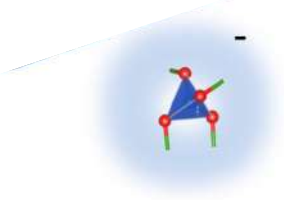
But also many similarities

Bridging vs non-bridging chalcogens

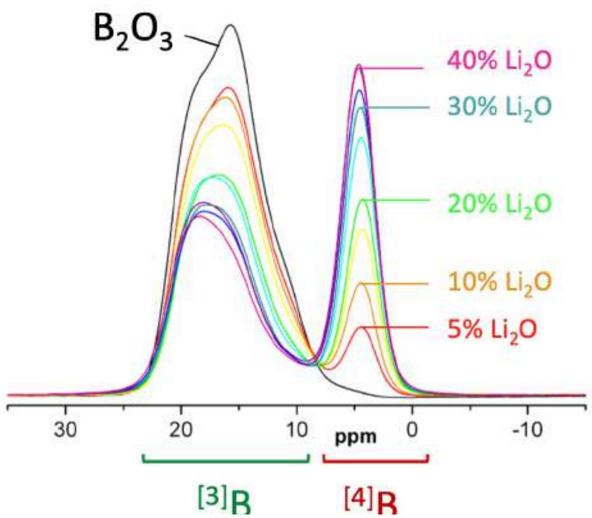
Mixed glass former effect Mixed alkali effect

Multicomponent borate glasses

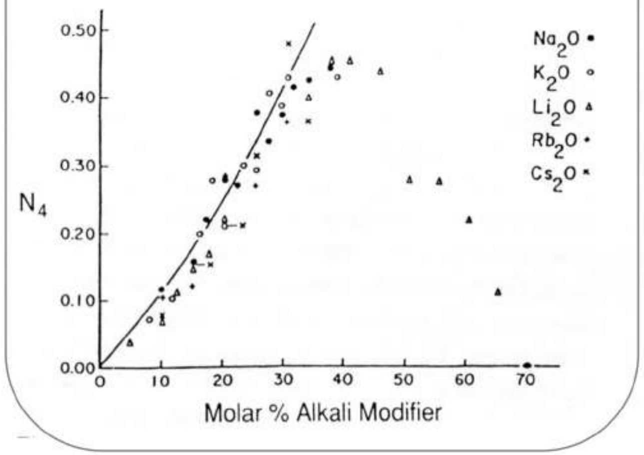
- ☐ By adding alkali oxide into B_2O_3 : $^{[3]}B \longrightarrow {}^{[4]}B$ conversion

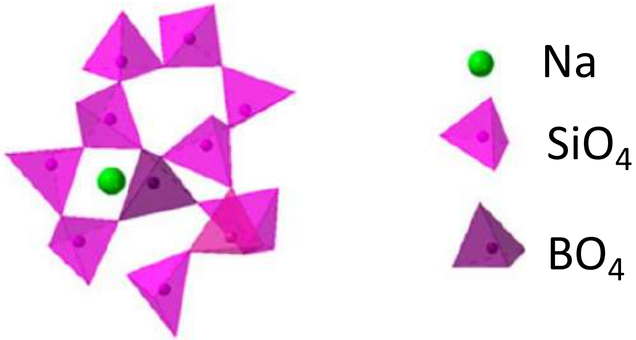


$^{[11]}B$ NMR



Proportion of $^{[4]}B$



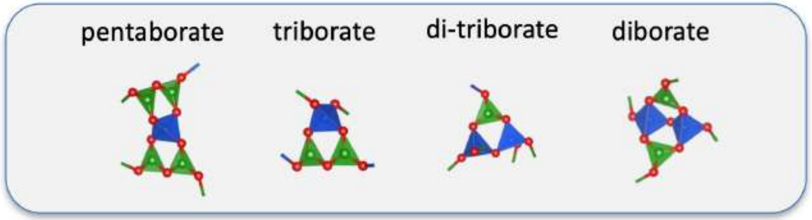


Bray and O'Keefe – PCG (1963)
Zhong et al. JNCS 111, 67 (1989)

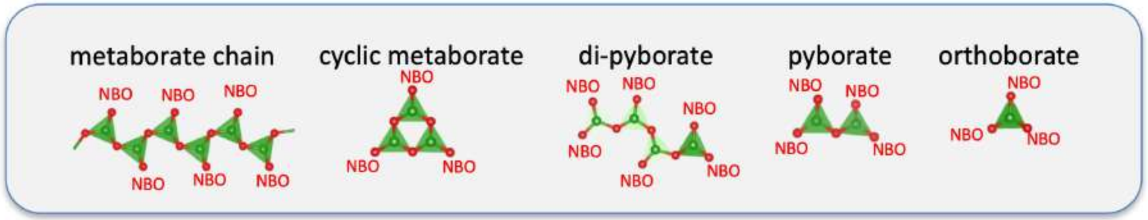
Na becomes a charge compensator

Multicomponent borate glasses

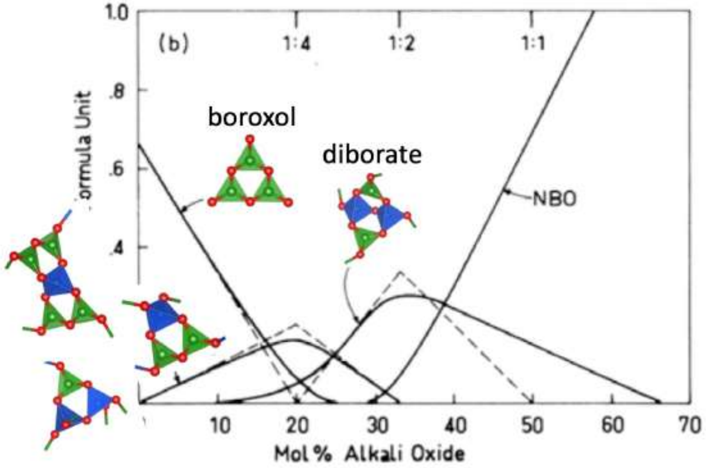
☐ Examples of units containing $^{[3]}B$ and $^{[4]}B$



☐ Examples of units containing only $^{[3]}B$



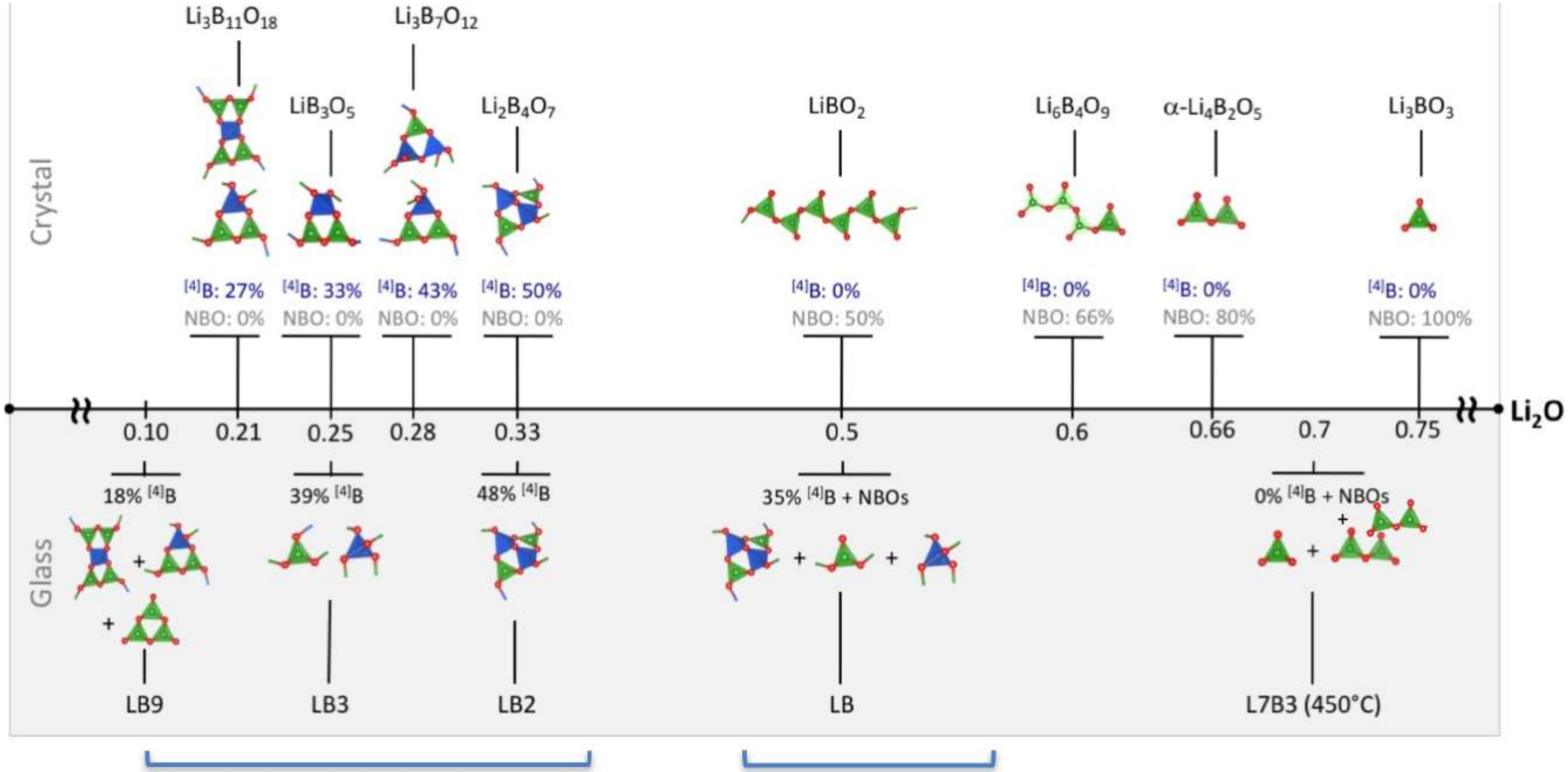
☐ Krogh-Moe in 1962 predicted the distribution of superstructural units in sodium borate glasses as a function of Na_2O content.



Individual BO_4 and BO_3 units forming 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

Multicomponent borate glasses



Similarities glass ⟷cristal at the local scale

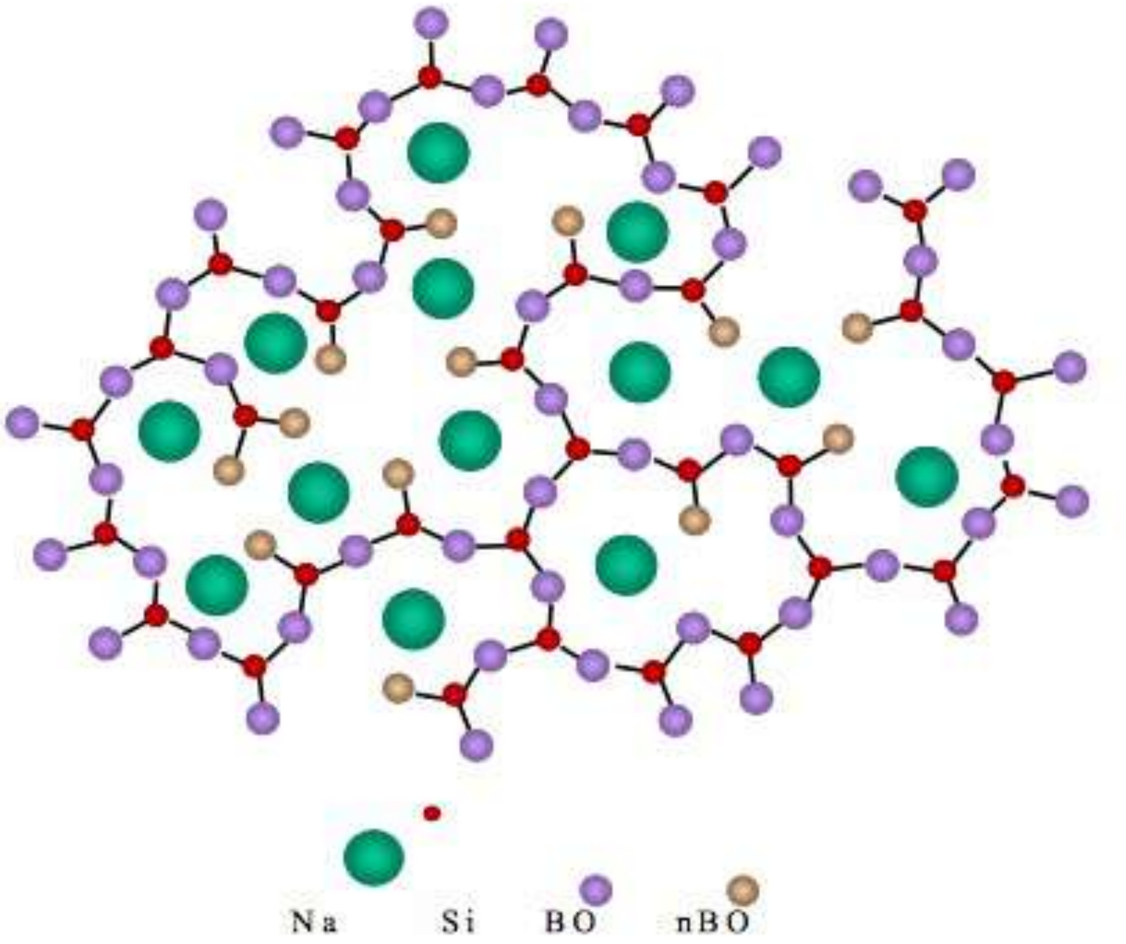
Discrepancies in the local structure of glass & cristal

Lelong et al. J. Non-Cryst. Solids 472 (2017) 1

Multicomponent oxide glasses

Random network

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

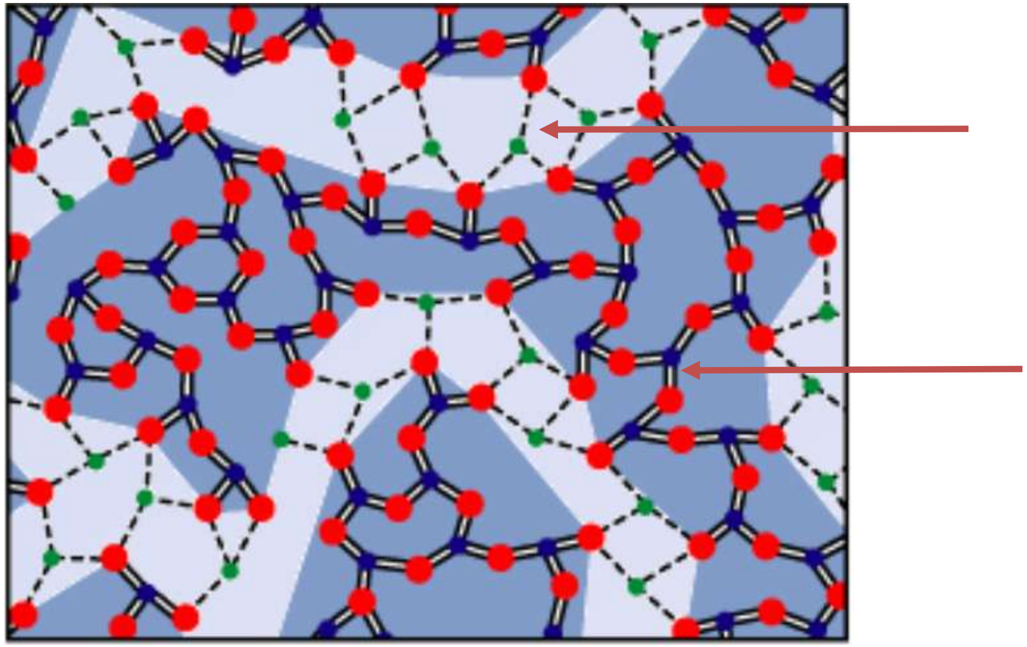


No information on medium range order

Structural models of covalent glasses

Modified random network model (Greaves, 1985)
=> Extension of the Zachariasen’s model with regions rich in network formers and regions rich in modifiers

Deduced from EXAFS, neutron scattering data



Regions rich in modifiers

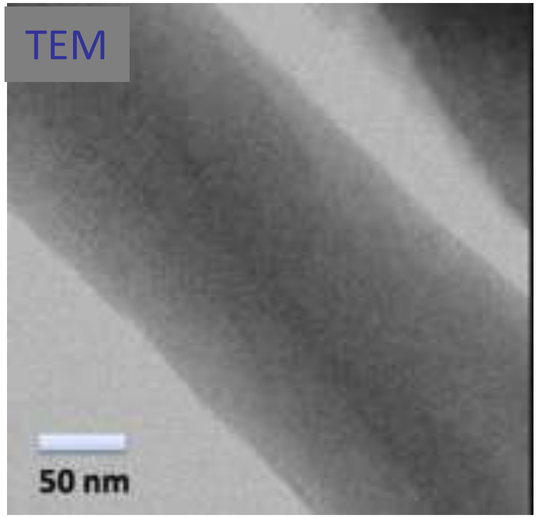
Regions rich in network formers

Relationships with conduction properties, alteration...

Glass may have heterogeneities (at the nanometer scale)

Homogeneity of glass

Electron microscopy



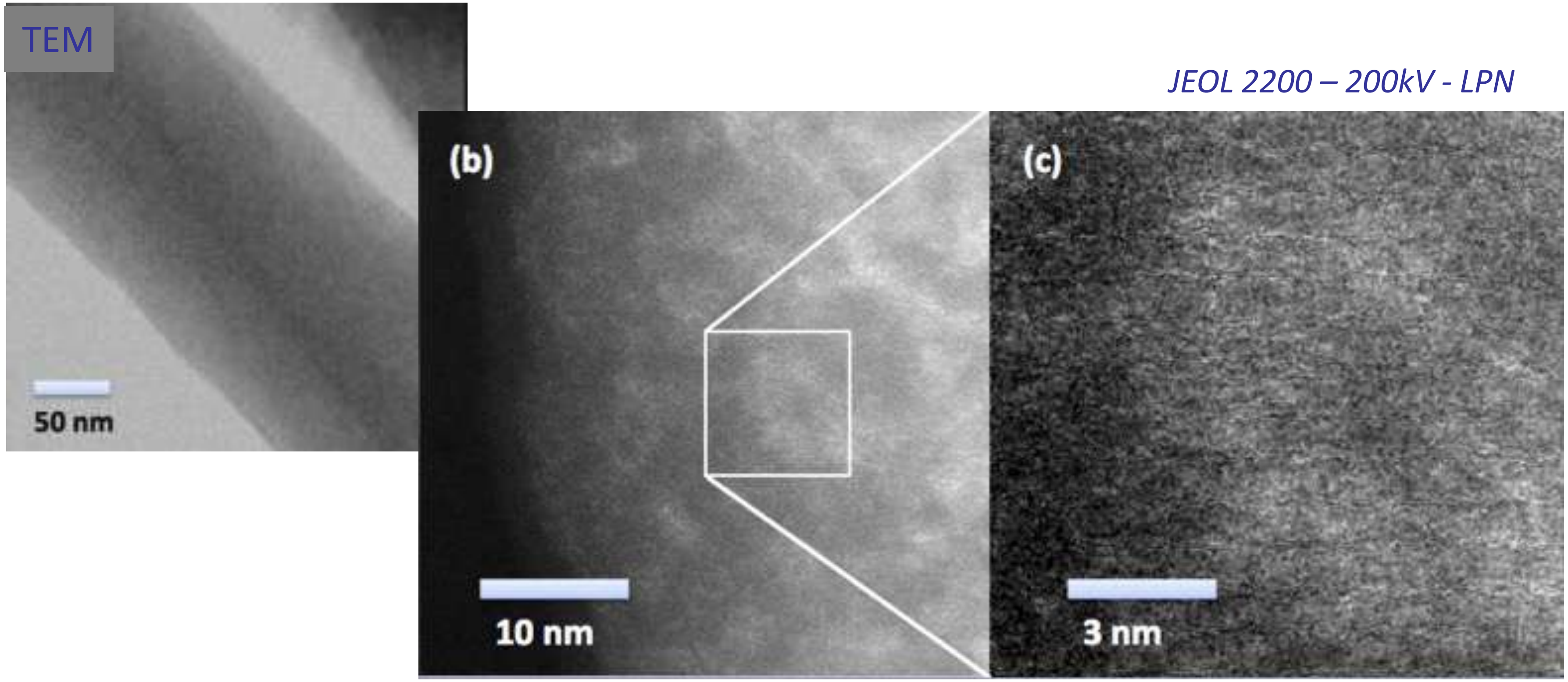
- Isotropy

- homogeneity ?

Nanoheterogeneities in glasses

Glass $MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}ZrO_2$

Electron microscopy HAADF ➪ **chemical resolution**

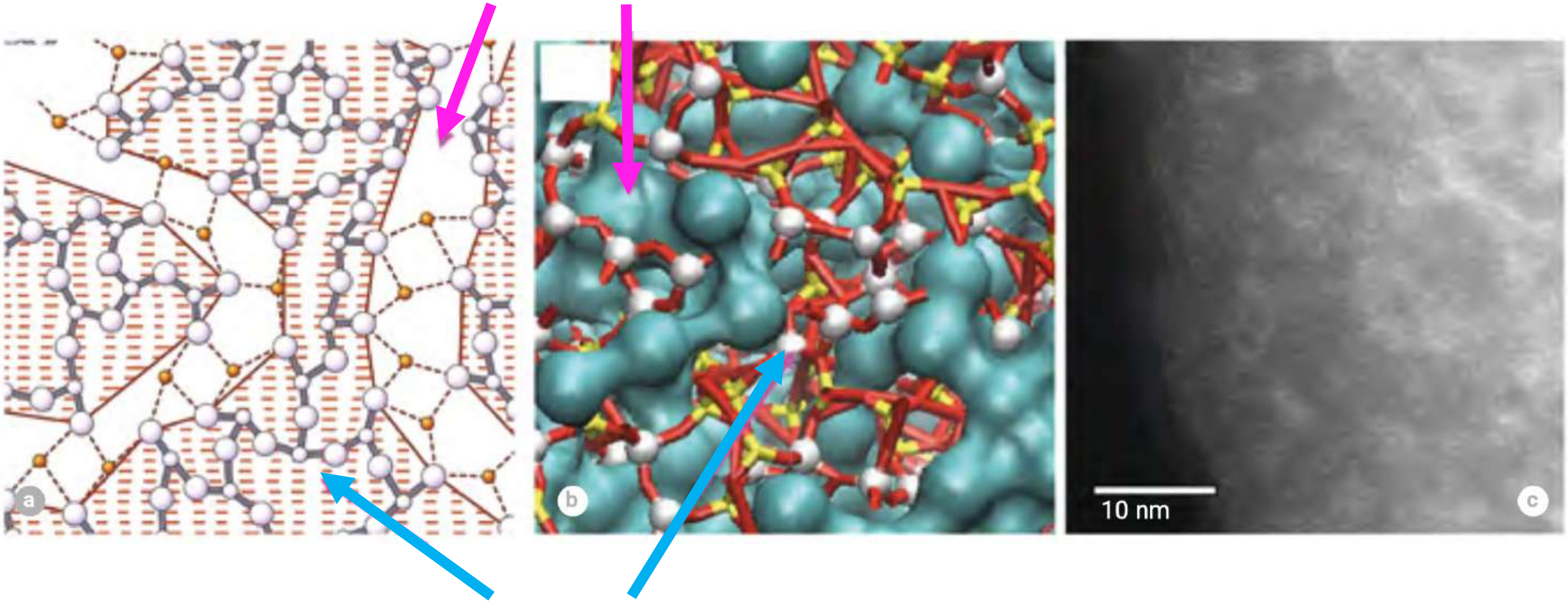


JEOL 2200 – 200kV - LPN

White regions = Zr-rich regions
➪ non-homogeneous distribution of Zr
➪ similarities with Greaves's model

Dargaud et al. Appl. Phys. Lett. 99 (2011) 21904

Nanoheterogeneities in glasses



Regions rich in modifiers

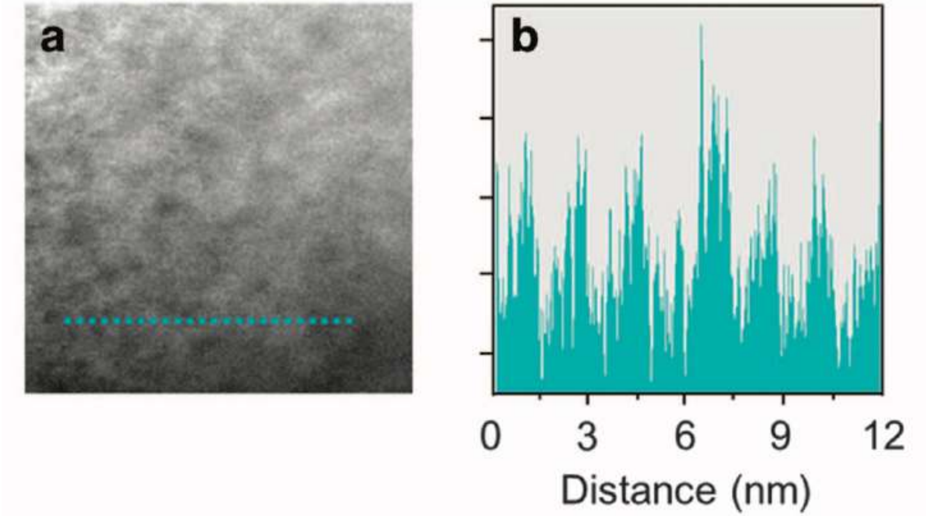
Regions rich in network formers

White regions = Zr-rich regions
➪ non-homogeneous distribution of Zr
➪ similarities with Greaves’s model

Cormier & Neuville Reflets de la Physique 74 (2022) 22

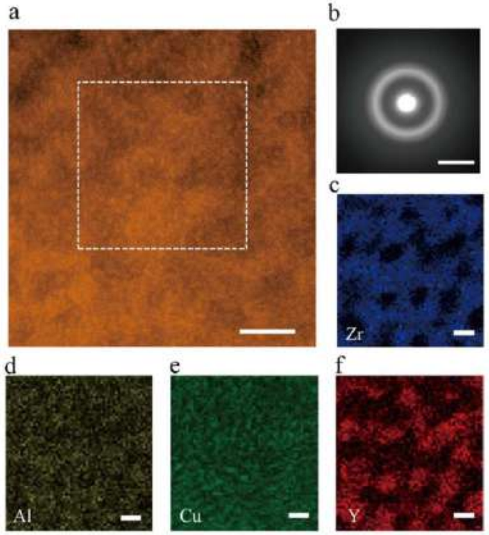
Nanoscopic order in glasses

Electron microscopy in HAADF mode



Mesoscale structure in the host Li_2O-Ta_2O_5-Al_2O_3-SiO_2 glass

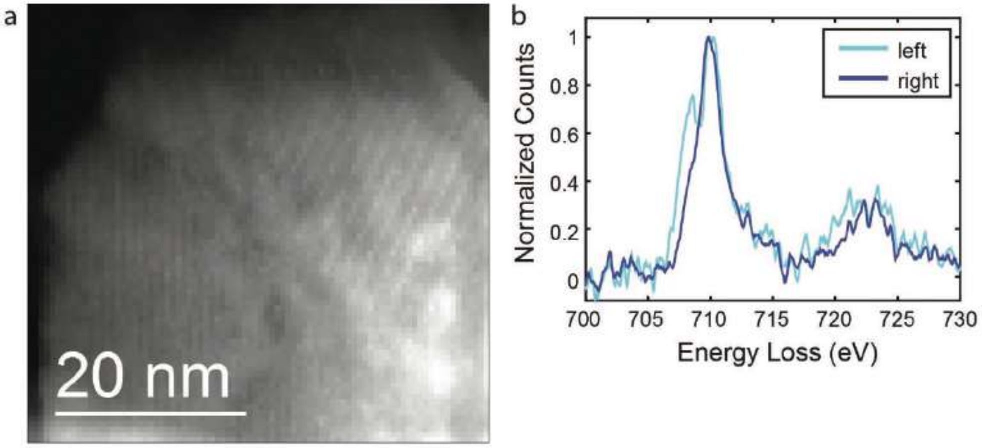
Yu et al. Asia Materials 8(2016)e318



ZrCuAlY alloy
chemically inhomogeneous

spinodal decomposition

Jiao et al., Chem. Materials 29(2017)4478



Submicrometer-scale spatial heterogeneity in **iron silicate** glasses

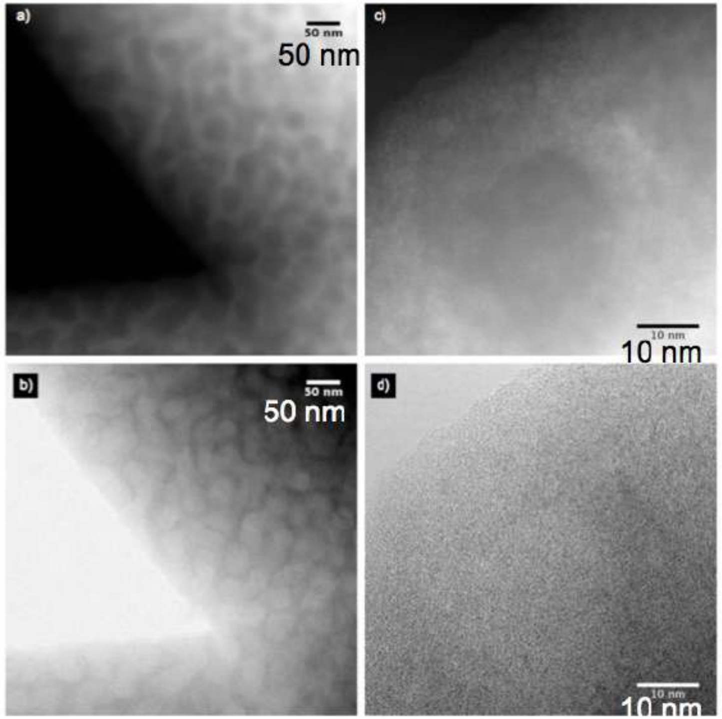
Burgess et al., Ameri. Mineral. 101(2016)2677

Amorphous-amorphous separation (A-A)

Glass MAS+Zr+Zn

➪ Macroscopic A-A separation

STEM
HAADF



STEM

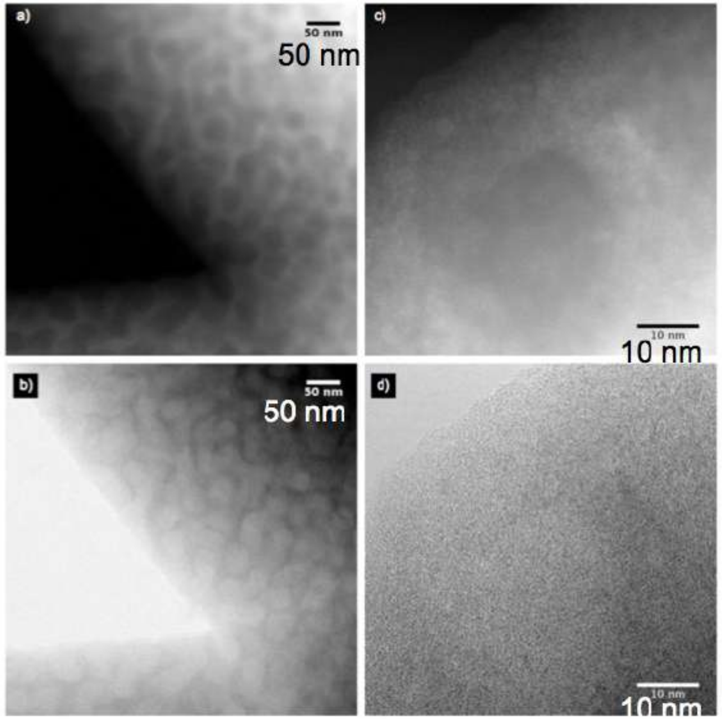
Dargaud et al., JNCS 358, 1257 (2012)

Amorphous-amorphous separation (A-A) and heterogeneities

Glass MAS+Zr+Zn

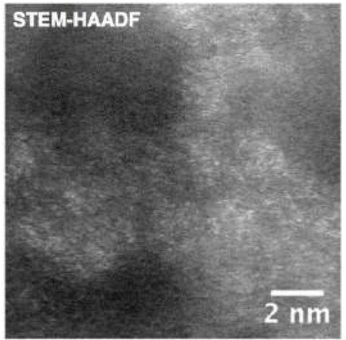
➪ Macroscopic A-A separation

STEM HAADF

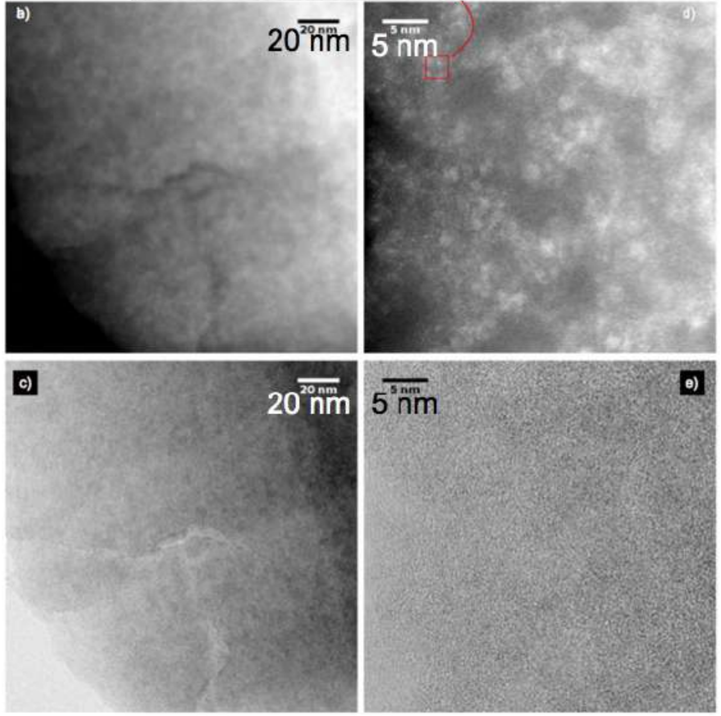


STEM

Dargaud et al., JNCS 358, 1257 (2012)



➪ No macroscopic A-A separation



STEM HAADF

STEM

➪ Heterogeneities visible even without macroscopic A-A separation

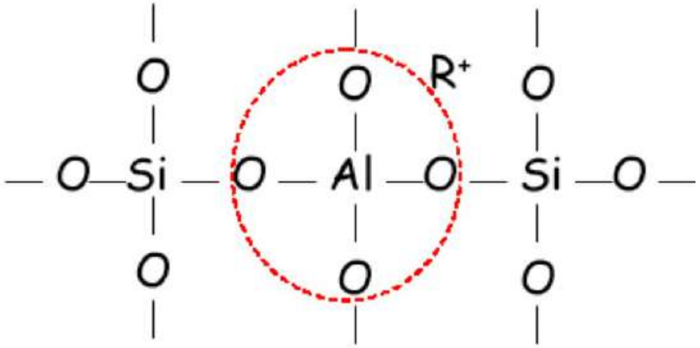
➪ At which scale is there an A-A separation?

Aluminosilicate glasses

Al substitute to Si in tetrahedral position

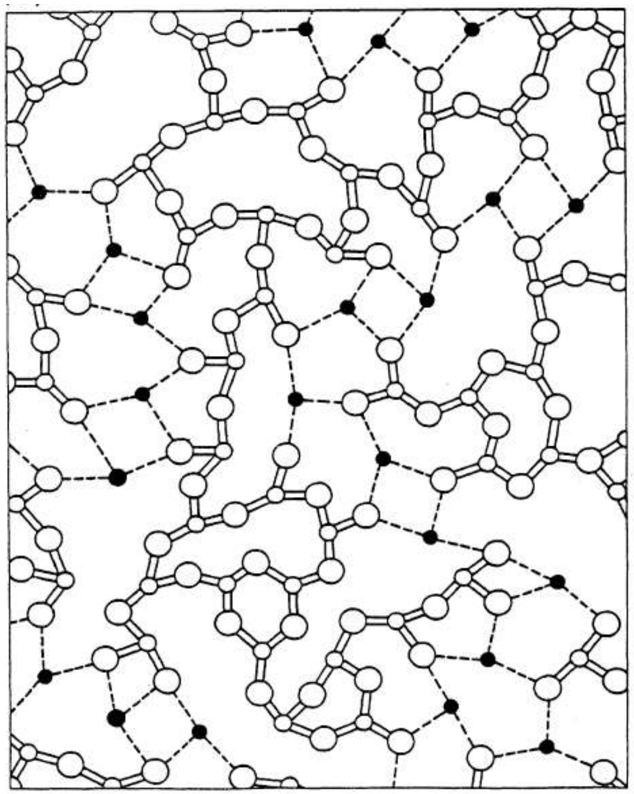
Al : (Ne)$3s^2 3p^1$: 3 valence electrons => ions Al^{3+}

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



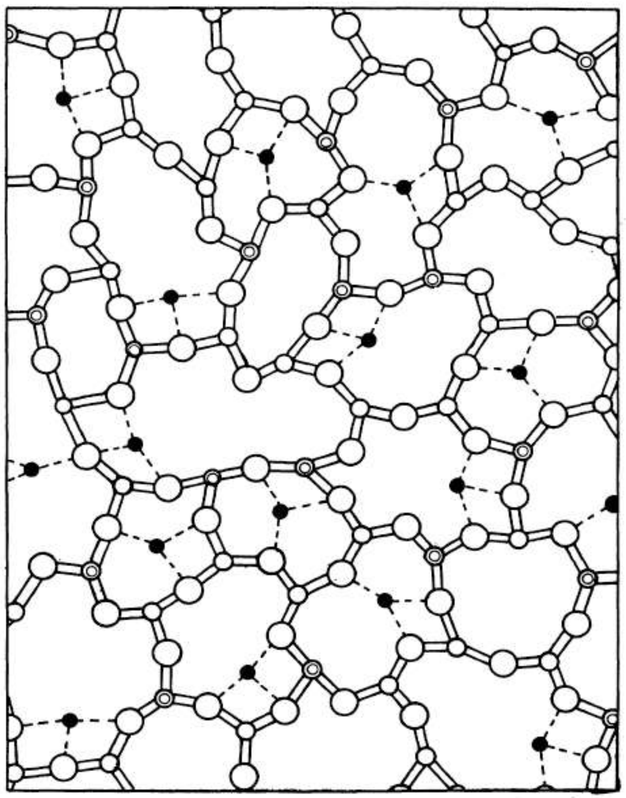
Similar for $(BO_4)^-$

Role of non-network forming cations



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

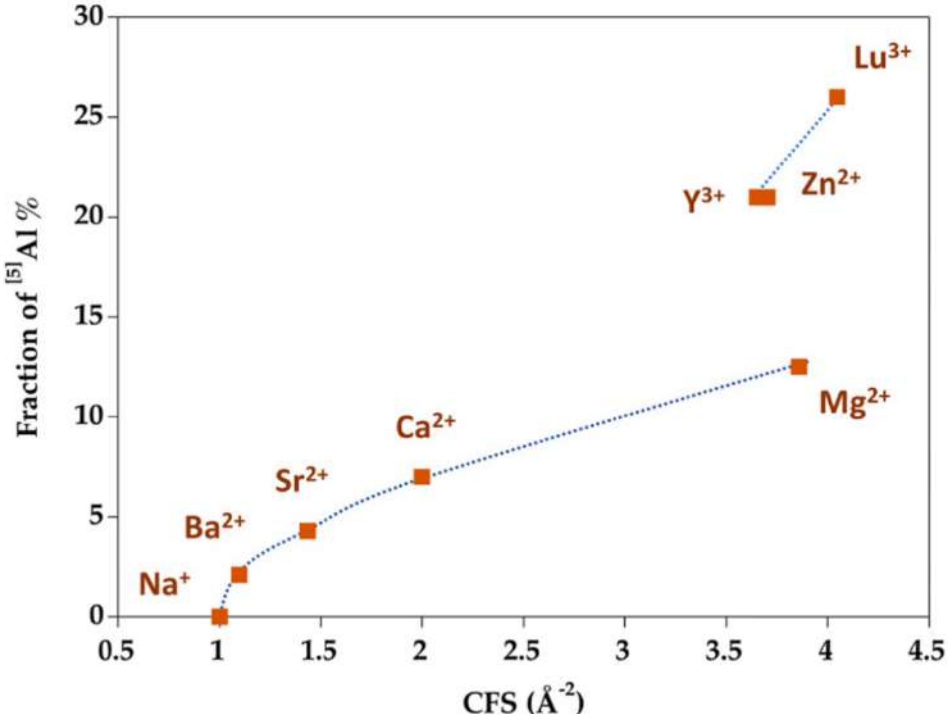
= network modifier



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

= charge compensator

Aluminosilicate glasses

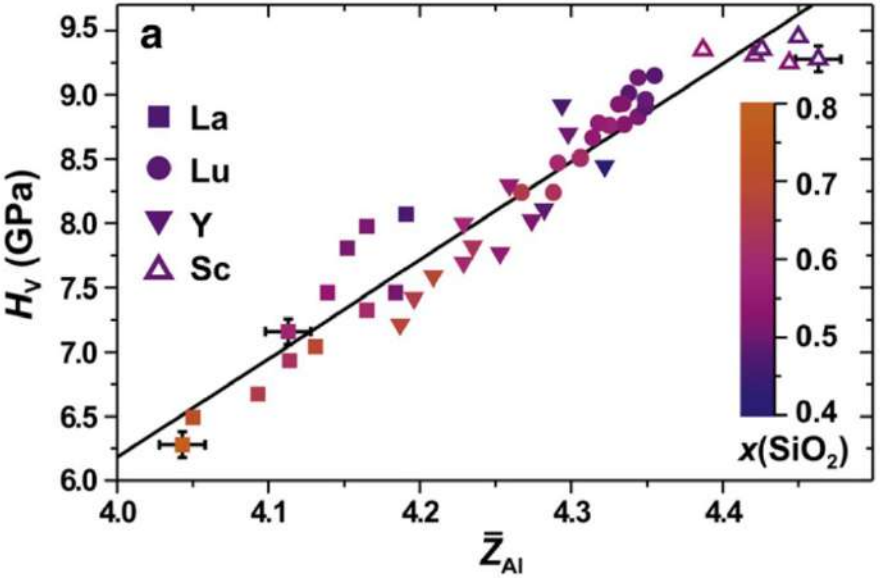


- Proportion of $^{[5]}$Al depends on cation field strength

$F_s = Z_C / a^2$

Z_C = valence of the cation

a is the distance between cation and oxygen

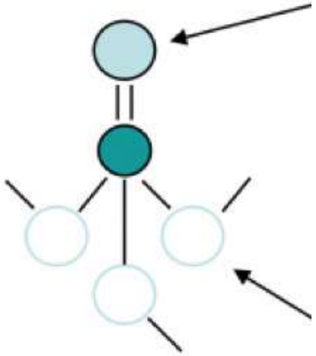


- Proportion of $^{[5]}$Al affects properties (ex : mechanical properties)
- Competition for charge compensator between Al and B …

Phosphate glasses

P in tetrahedral position

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



Terminal oxygen

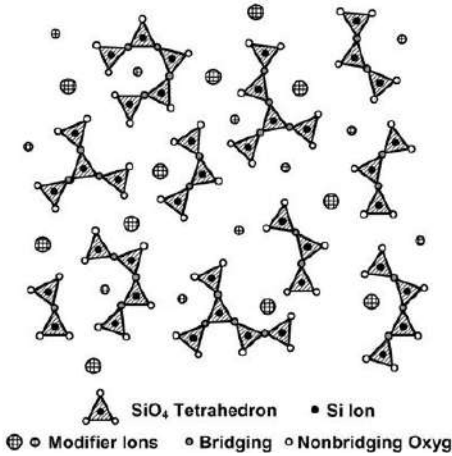
Bridging oxygen

Oxygen position in glass structure:

- bridging oxygen
- non-bridging oxygen
- terminal oxygen

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-$2SiO_2$	Y=3	
R_2O-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

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

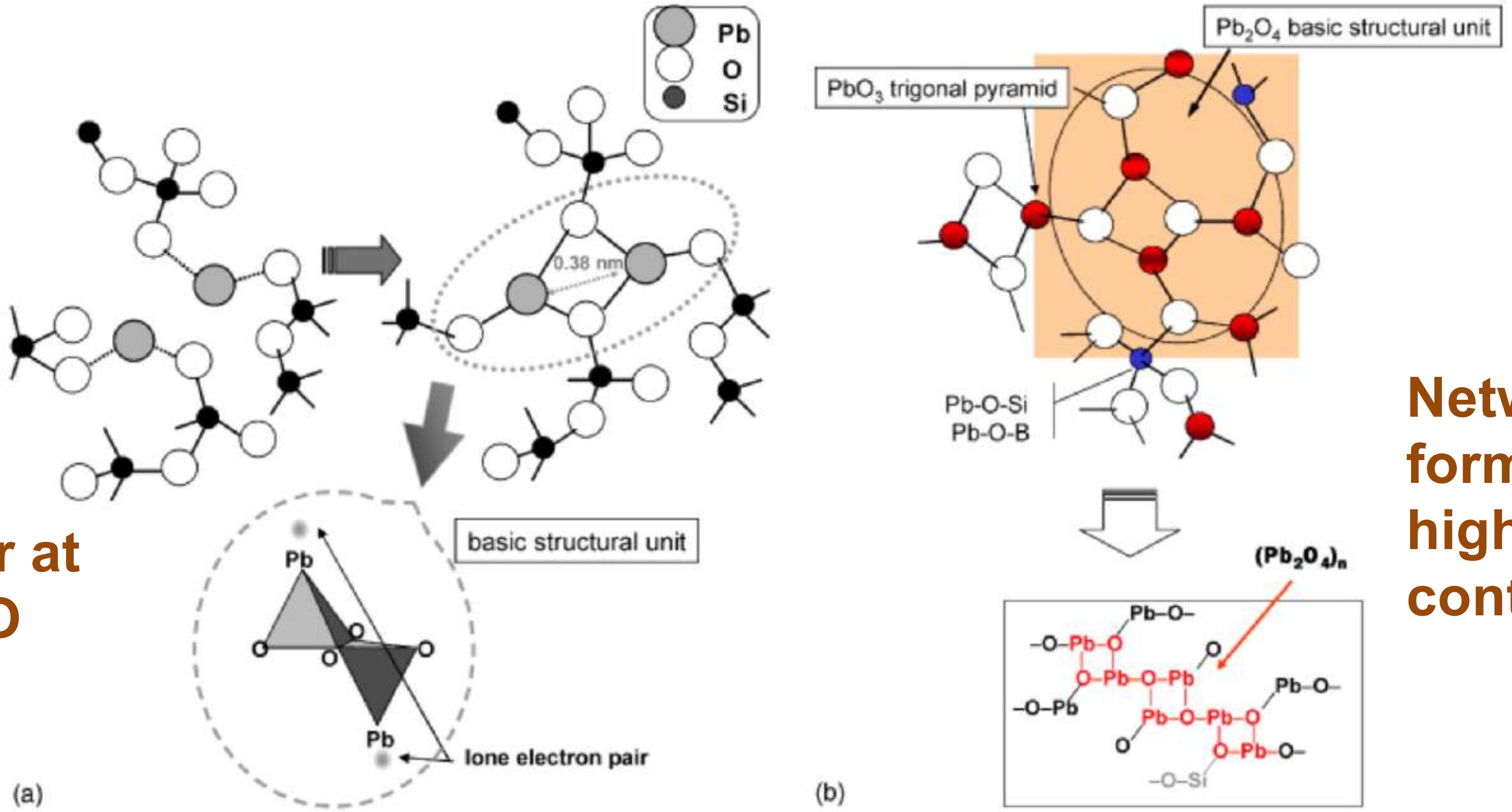
In particular orthotitanate : 2R_2O-TiO_2

Also calcium aluminate : 61CaO-39Al_2O_3

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



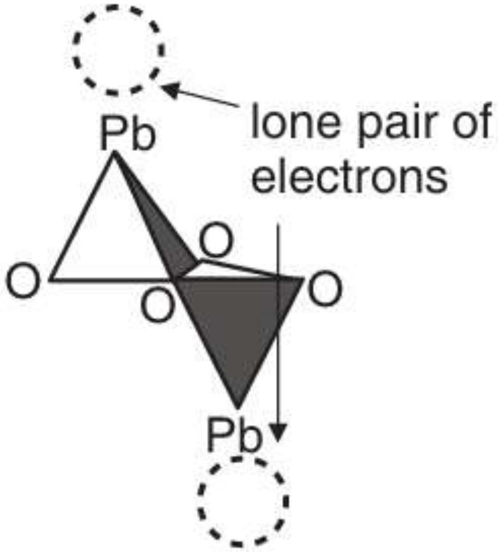
Modifier at low PbO content

Network former at high PbO content

40-60 mol% PbO

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

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 ?

Structure of metallic glasses

Energetic Stability: Clusters

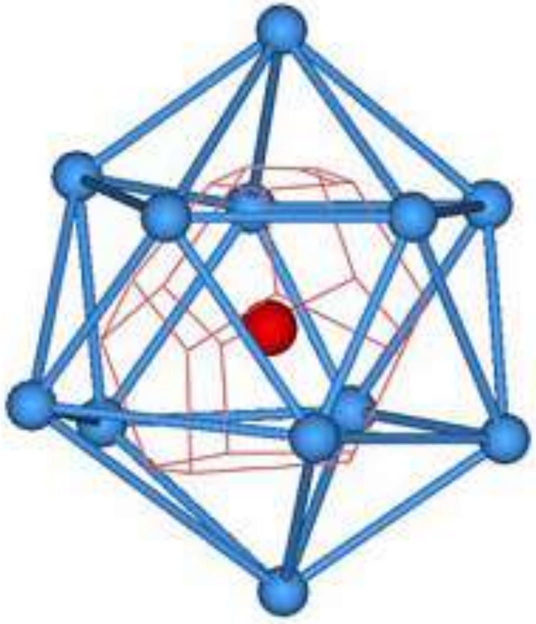
clusters lead to energetic stability

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 ?

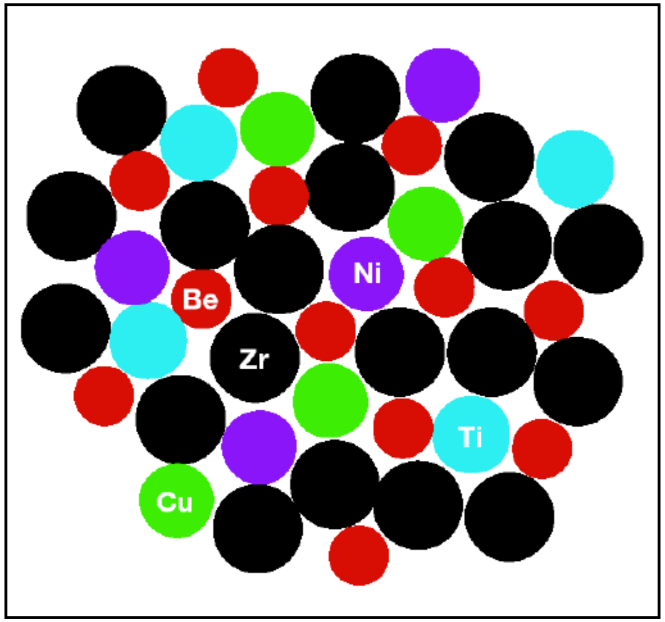


Structure of metallic glasses

Principle : hard sphere dense random packing

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

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



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

Mixing various elements with different sizes

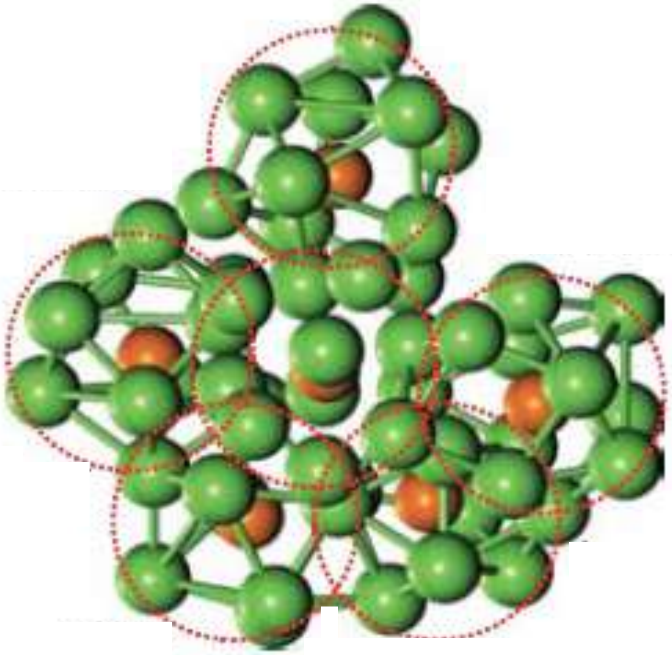
Metal (Fe,Ni,Al,Cr,Pd)
Metalloids (P,Si,B,Ge)

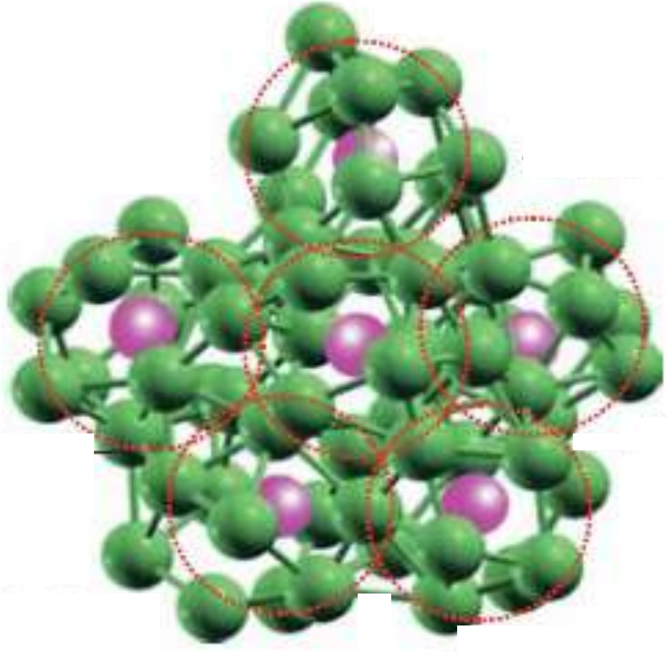
From ’Silicate glasses and melts: properties and structure’
Mysen & Richet (2005)

Structure of metallic glasses

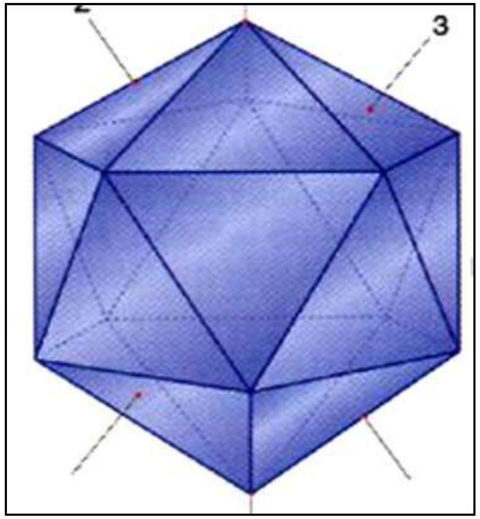
\+ medium range order (2006)

Stacking of blocks with 5-fold symmetry





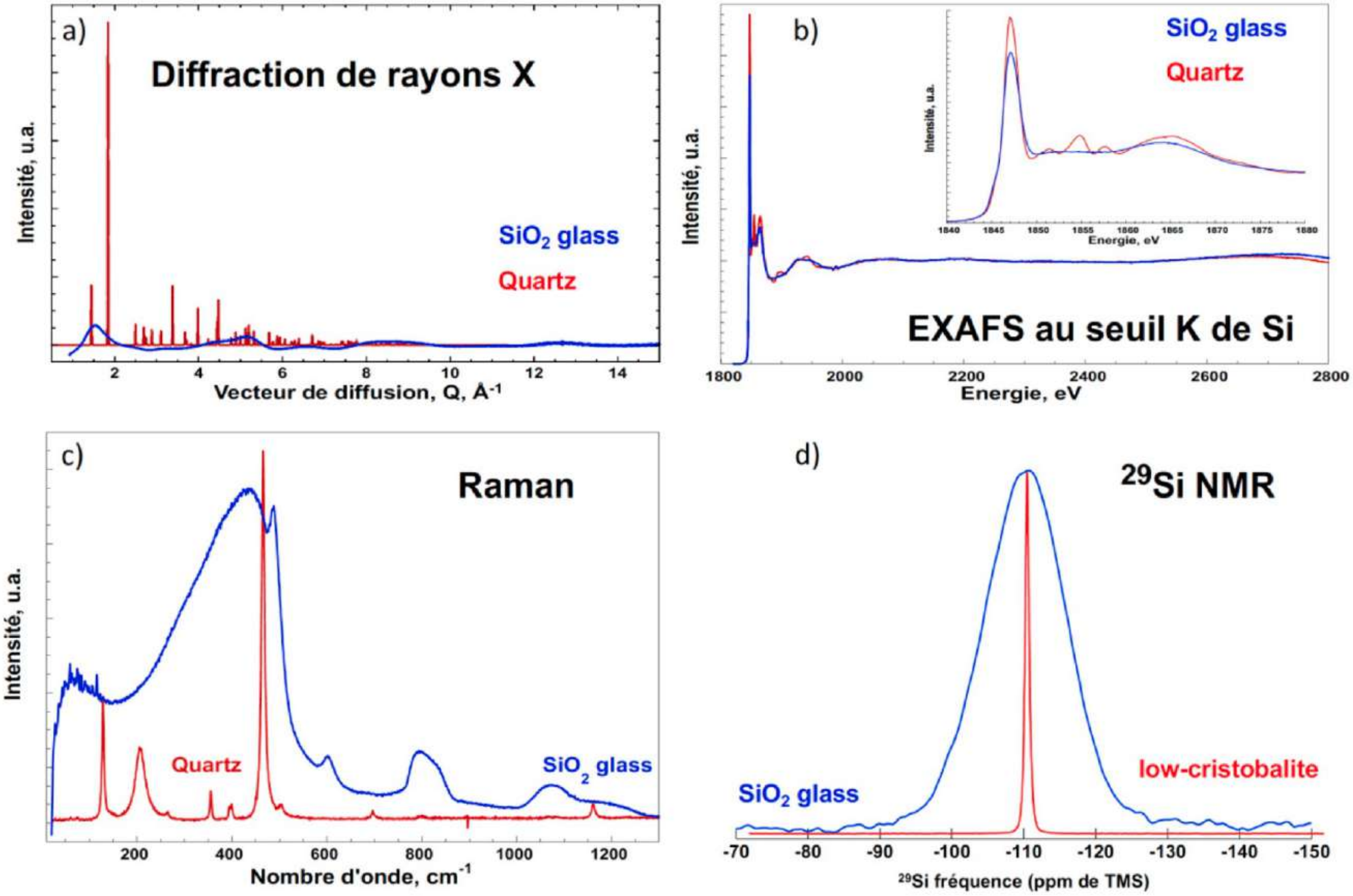
Sheng et al., Nature 439, 419(2006)



icosaedron

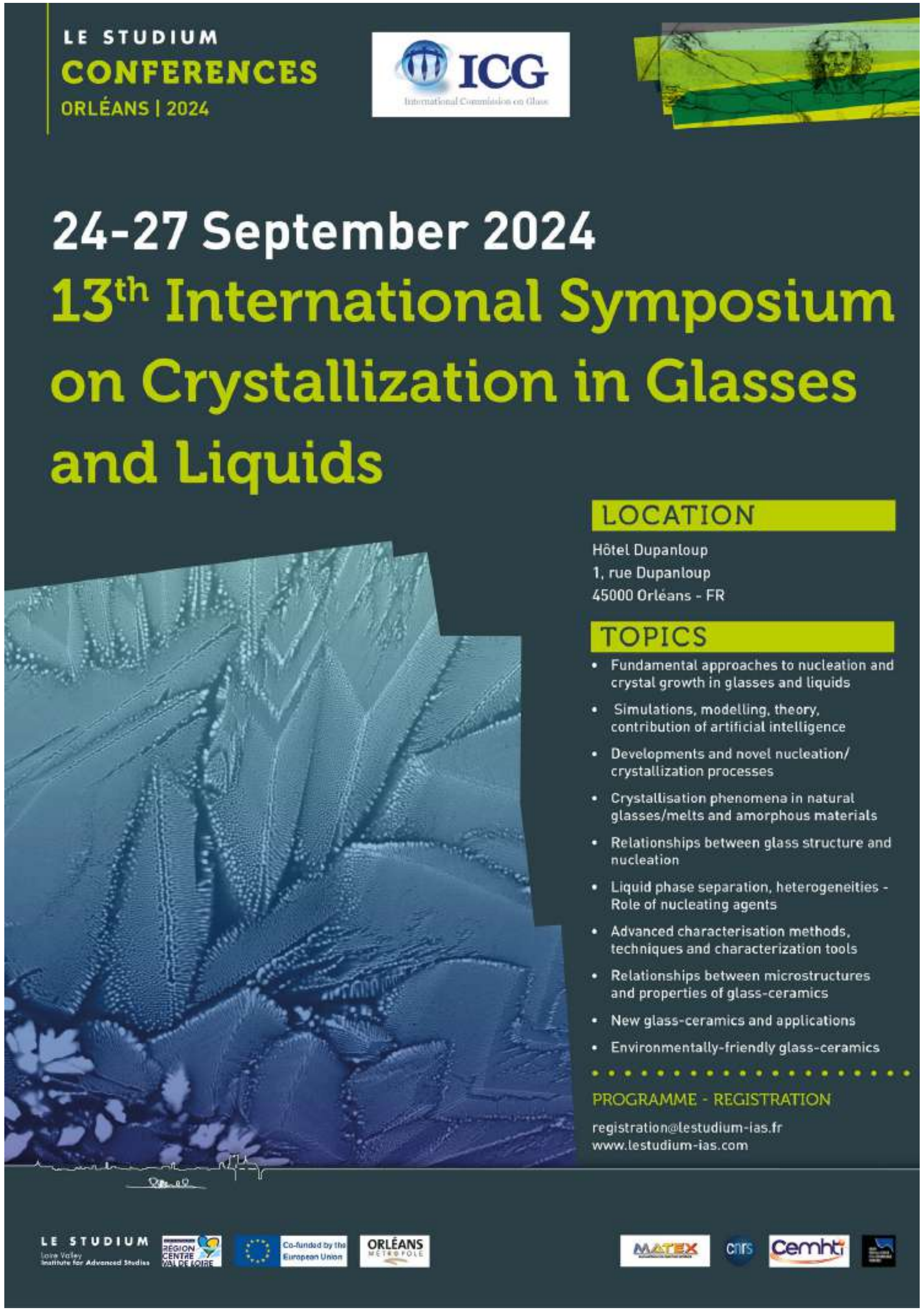
Miracle, Nature Materials 2004
Yavari, Nature Materials 2005
Sheng et al, Nature 2006
Yavari, Nature 2006

How to determine the structure ?



How to determine the structure ?

		Local order	Medium range order	Nanoscale	Redox	Elements	Chemically selective	Sensitivity
Diffraction - Wide & small angle	Neutron	X	X	X		All		Few percents
	+ isotopic substitution	X	X	X		Difference in neutron scattering length	X	Few percents
	X-ray	X	X	X		≥ Li		Few percents
	+ Anomalous scattering	X	X	X		≥ Fe	X	Few percents
XANES (synchrotron /lab) **EELS (electron microscope)**		X			X	All elements ≥ Li	X	10 ppm to few percents
EXAFS (synchrotron /lab)		X	(X)			All elements ≥ Li	X	100 ppm to few percents
Raman		X	X			Active modes		Few percents
IR		X	X			Active modes		Few percents
Mössbauer		X			X	Typically Fe, Sn, Sb	X	Few percents, isotopic enrichment
Optical absorption spectroscopy		X			X	Transition metal - Rare-earths Plasmon resonance		ppm to few percents
NMR		X	X			Some elements Isotope with non-zero spin		Few percents, isotopic enrichment
EPR		X			X	Unpaired radicals or free radicals (Ex : Fe, Cu, defects)		ppm to few percents
Electron microscope				X				



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- Simulations, modelling, theory, contribution of artificial intelligence
- Developments and novel nucleation/ crystallization processes
- Crystallisation phenomena in natural glasses/melts and amorphous materials
- Relationships between glass structure and nucleation
- Liquid phase separation, heterogeneities - Role of nucleating agents
- Advanced characterisation methods, techniques and characterization tools
- Relationships between microstructures and properties of glass-ceramics
- New glass-ceramics and applications
- Environmentally-friendly glass-ceramics

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References

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