

LECTURE 2 :

STRUCTURE AND EXPERIMENTAL CHARACTERIZATION

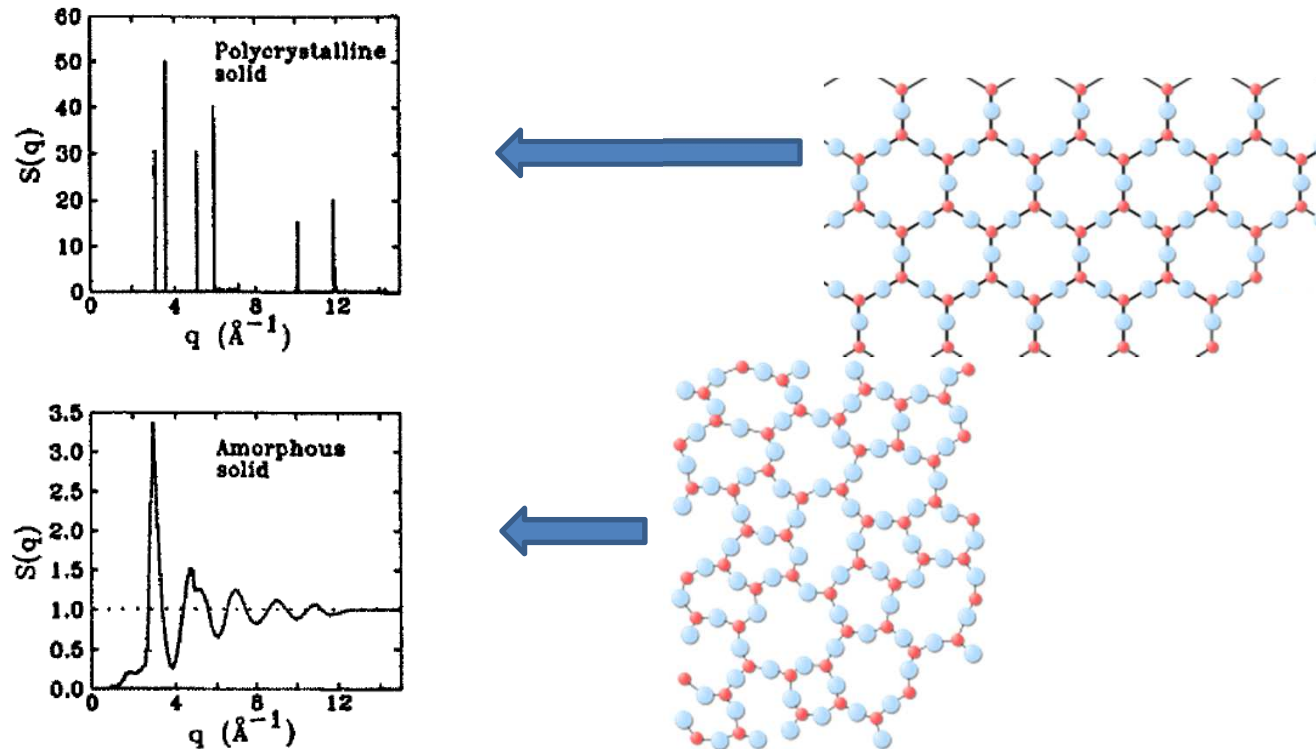
- Order in glasses
- Zachariasen random network theory
- Glass families and glass forming ability
- Experimental tools for structural characterization

A) SHORT, INTERMEDIATE AND LONG RANGE ORDER IN GLASSES

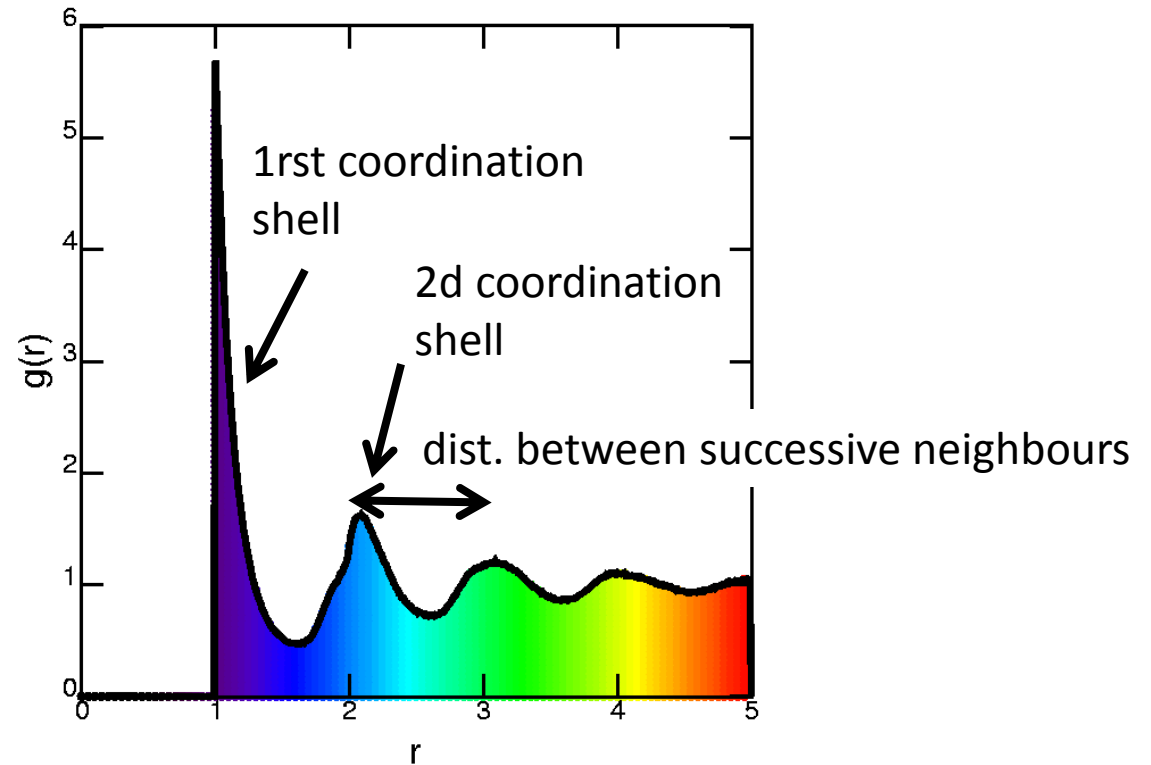
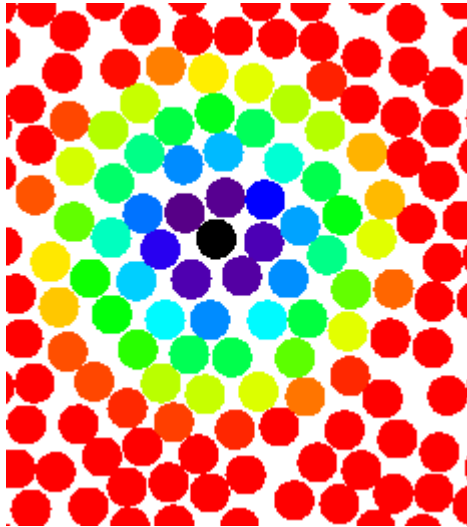
Bragg's Law: conditions for constructive interference, some angle of incident x-rays that will produce intense diffraction peaks associated with the crystalline lattice spacings.

$$n \lambda = 2 d \sin \theta$$

This situation is not met in amorphous systems (glasses) because of the lack of periodic reproduction of an elementary cell. **Broadening of diffraction peaks.**



Pair distribution function $g(r)$ # probability to find another atom at a distance r from a central atom



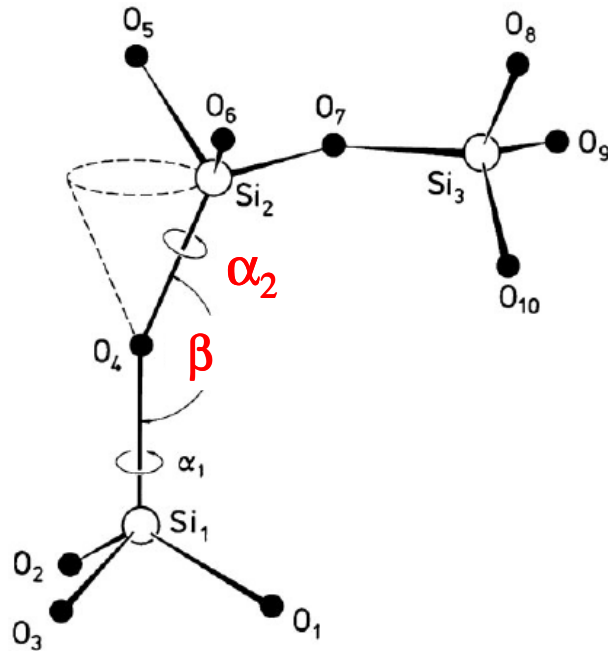
Can something be said beyond the first peak of $g(r)$?

Short range order : first shell of neighbors (coordination number)

Lengthscale \sim atomic bond distance (2-5 Å)

Intermediate range order : the way elementary building blocks arrange together

Intermediate range order : the way elementary building blocks arrange together



Long-range order : beyond 10 Å

Ring statistics

Computer simulations

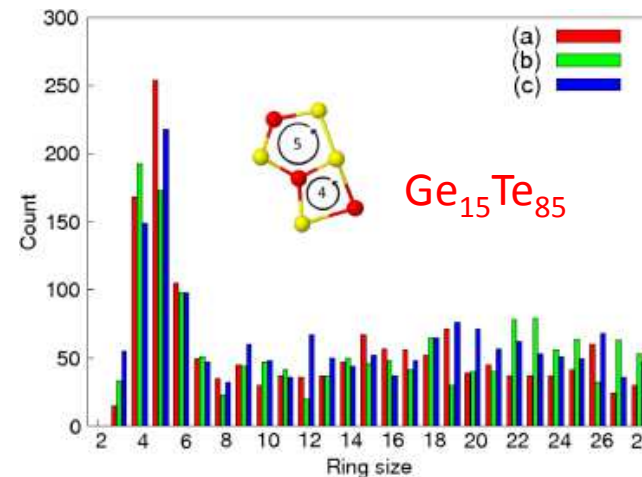
Experiments (Raman, rare systems)

The basic building block of SiO_2 is the $\text{SiO}_{4/2}$ tetrahedron (identical to α -quartz)

Disorder is due to the way the tetrahedra connect together.

Angle β (Si-O-Si) and α_2 (dihedral angle).

Elements of intermediate range order (<10 Å)



Kalikka et al, JPCM 2011

Glasses have random networks with the short range order of corresponding crystals

B) ARE GLASSES CONTINUOUS RANDOM NETWORKS ?

Zachariasen's Random Network Theory (1932)

- Before Zachariasen, the structure of a glass was believed to be comprised of nanocrystals ($\sim 20 \text{ \AA}$ size) given the broadening of the diffraction peaks.

Scherrer equation : monocrystal $\Delta k=0$, polycrystal Δk finite and the size of the grains is $L \propto 1/\Delta k$.

- He noted similar mechanical properties (elastic modulus, etc.) between glasses and crystals and so expected similar structural energies
- Glasses lack the periodic (long range) order of a crystal. Infinite unit cell (no repeating large scale structures). 3D network lacking symmetry and periodicity
- ISOTROPIC: same average packing and properties in all directions. Different from crystals (directions).

Zachariasen's Rules (1932) for Glass formation based on an empirical observation on oxides.

1. No oxygen atom may be linked to more than two cations
2. The cation coordination number CN is small: 3 or 4.
3. Oxygen polyhedra share corners, not edges or faces.
4. For 3D networks, at least three corners must be shared

In general, all four rules should be satisfied for glass formation to occur.

Low coordination numbers, corner-sharing rules imply that glass formation is more likely with open, low density polyhedral structures.

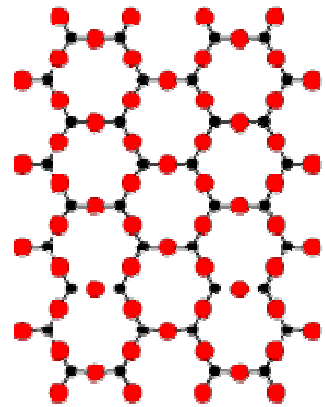
Having stated this, one identifies a certain number of compounds to be either good glass formers (i.e. satisfying the 4 rules) or bad glass formers (do not satisfying at least one of the rules).

Example : SiO_2 , GeO_2 are good glass formers (CN =4)

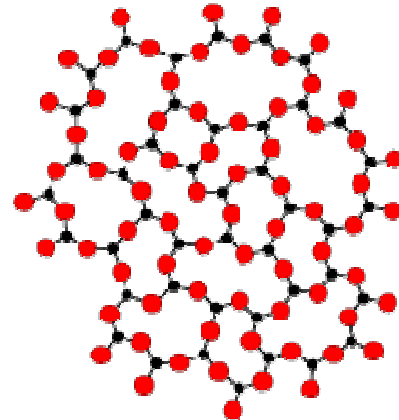
V_2O_5 (CN=5) is not a good glass former (breakdown of rule 2)

MgO (rocksalt structure , CN=6) is not a good glass former (breakdown of rule 2)

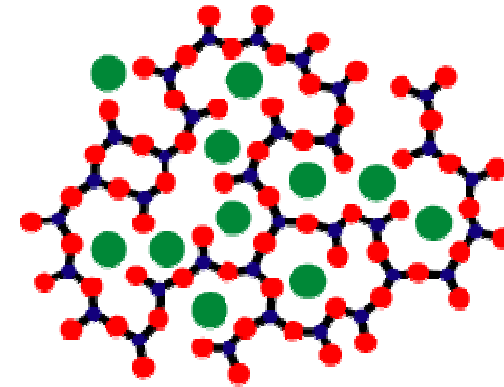
Zachariasen's theory applied and revisited



Crystalline A_2O_3

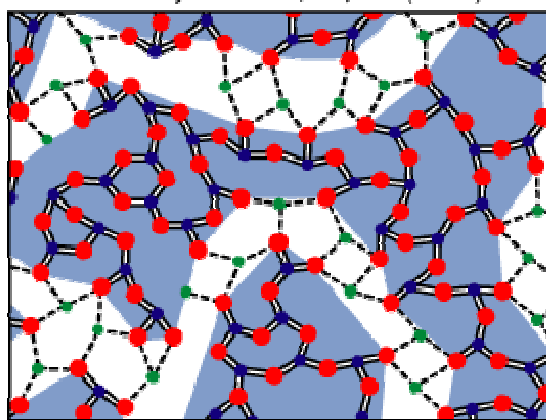


Glassy A_2O_3



Shannon and Prewitt:
ionic radii

Extension to modified oxides
Warren and Bischoff, 1930's



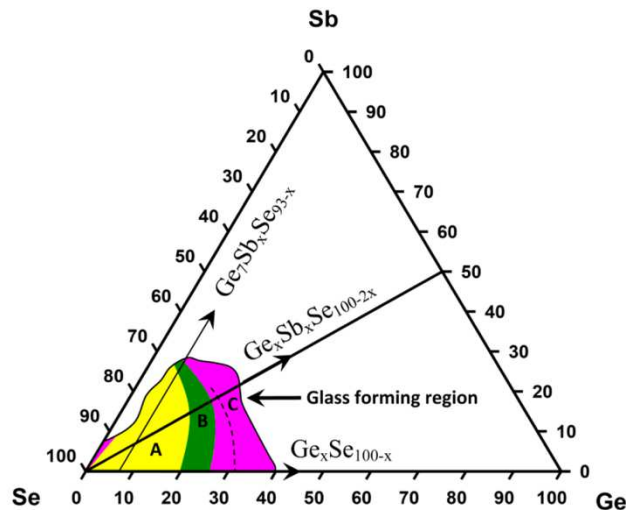
Modified Random Network
Greaves, 1989

C) GLASS FAMILIES AND GLASS FORMING ABILITY

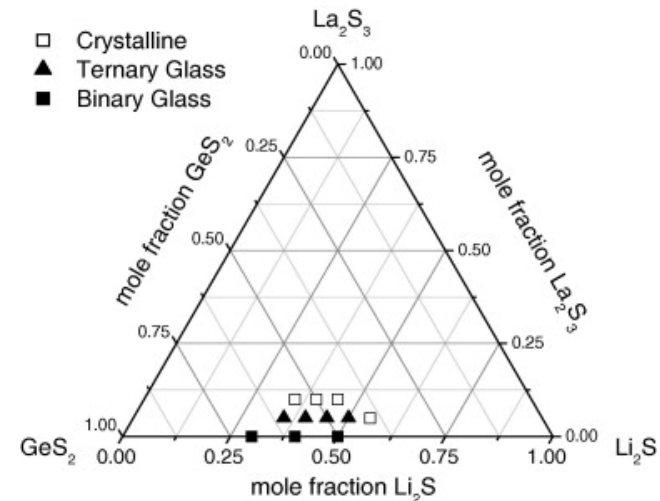
Why do glasses form ?

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

- ❑ Sulfur or selenium based glasses do form quite easily glasses
- ❑ Extensive studies in composition have led to the definition of the glass forming region



Gunasekera et al. JPC B (2013)

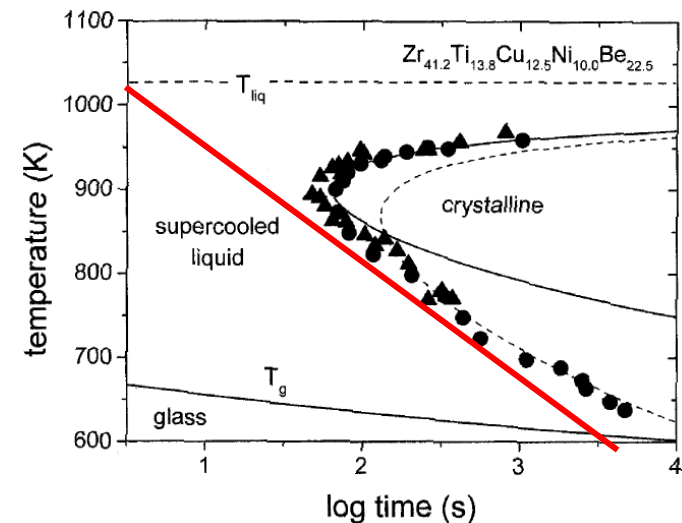


Saienga and Martin, JNCS (2008)

C) GLASS FAMILIES AND GLASS FORMING ABILITY

Why do glasses form ?

- ❑ Competition between crystalline growth and cooling 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?
- ❑ Critical cooling rate R_c =
the nose of the TTT curve



- ❑ See: http://www.lehigh.edu/imi/docs_LL/GCC/Lecture_2_Martin.pdf

R. Busch, JOM (2000)

Why do glasses form ?

- Richet (2006): Glasses form more easily in 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.

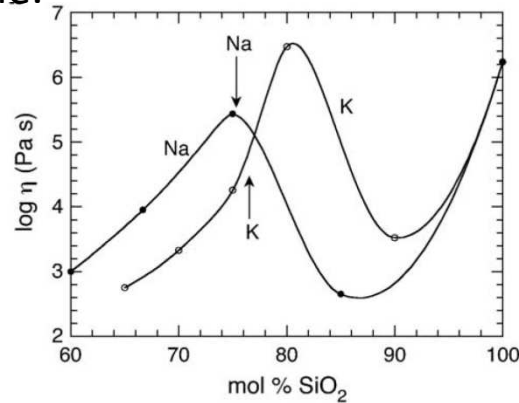


Fig. 7. The combined effects of composition and temperature on viscosity along liquidus branches in alkali silicate systems. (a) Viscosity of sodium silicate melts at 1200 °C (Bockris et al., 1955; Leko et al., 1977). (b) Viscosity of alkali silicate melts along the liquidus branches of Fig. 5. Data from Poole (1948) and Bockris et al. (1955). The arrows indicate the positions of the deepest eutectics of the binary systems.

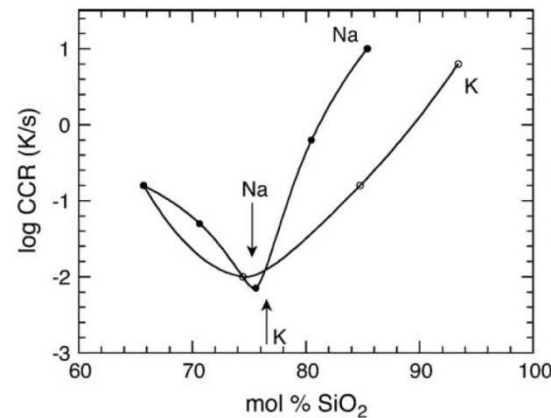
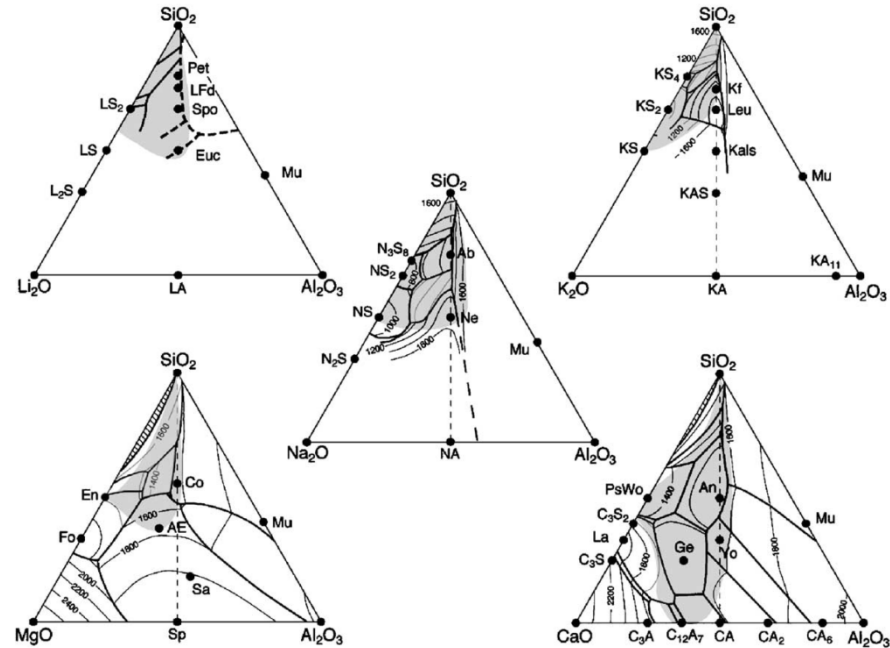


Fig. 6. Critical cooling rates for glass formation in sodium and potassium silicates. Data from Fang et al. (1983) for a crystal fraction of less than 10⁻⁶. The arrows indicate the position of the deepest eutectics of the binary systems shown in Fig. 5.

Richet et al.
Chem. Geol. 2006

C) GLASS FAMILIES AND GLASS FORMING ABILITY

Measuring glass-forming stability from DSC

□ A calorimetric measurement of the glass transition T_g and the recrystallization temperature T_x provides a measure of the stability of a glass.

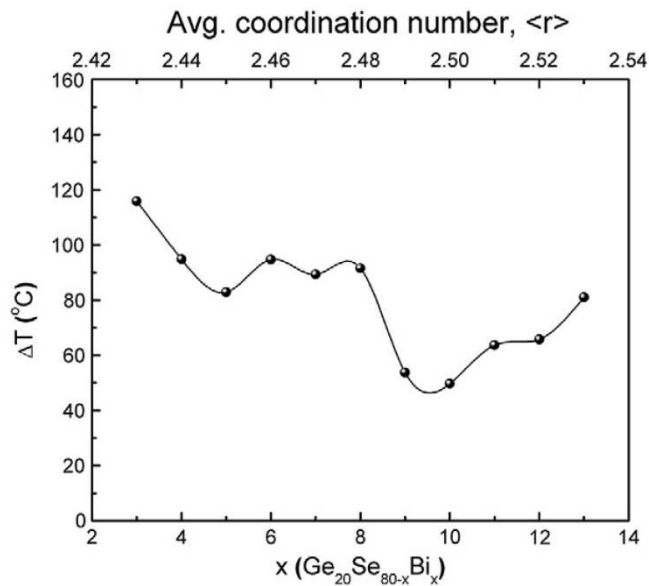
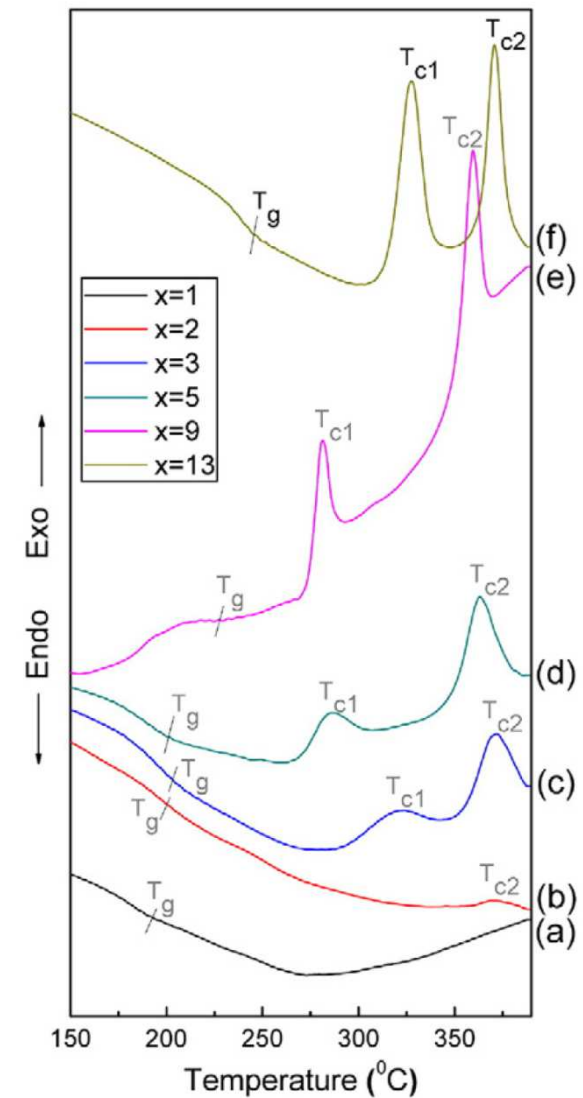


Fig. 4. The variation of thermal stability ($\Delta T = T_{c1} - T_g$) of $\text{Ge}_{20}\text{Se}_{80-x}\text{Bi}_x$ glasses as a function of Bi concentration and average coordination number.

Gunti and Asokan, JNCS 2010



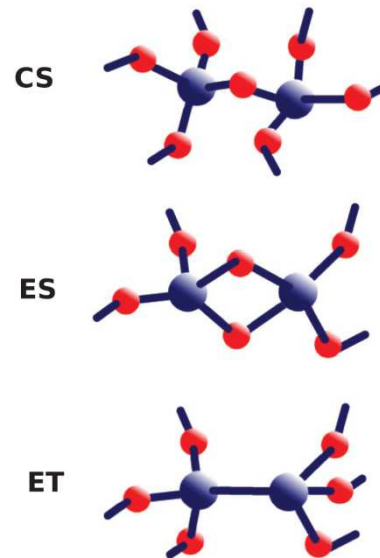
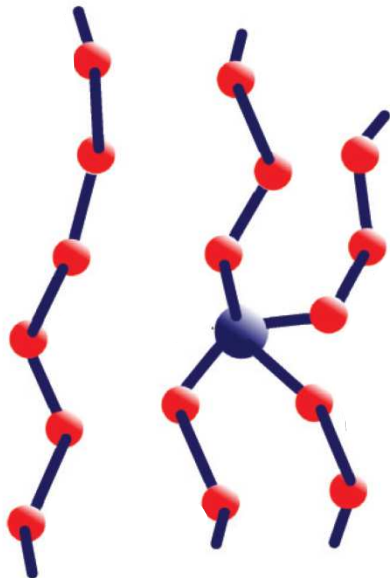
C) GLASS FAMILIES AND GLASS FORMING ABILITY

Glass families: Network formers

❑ **Chalcogenide** network formers: mixing of Group III, IV, V, VII with (S, Se, Te). **Off-stoichiometric glasses.**

e.g. $\text{Si}_x\text{Se}_{1-x}$, P_xS_{1-x} , $\text{Ge}_x\text{Te}_{1-x}$, Ge-As-Se, ...

- ❖ Cross-linking into a base Se ($T_g=316$ K) or S ($T_g=245$ K) glass
- ❖ Variety of connectivity motifs and chemical bonding: corner-sharing (CS), edge-sharing (ES) and homopolar bonding



	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	
6	B Boron 10.811	C Carbon 12.011	N Nitrogen 14.00674	O Oxygen 15.9994	F Fluorine 18.998403
13	Al Aluminum 26.981539	Si Silicon 28.0855	P Phosphorus 30.973762	S Sulfur 32.066	Cl Chlorine 35.4527
31	Ga Gallium 69.732	Ge Germanium 72.64	As Arsenic 74.92159	Se Selenium 78.96	Br Bromine 79.904
49	In Indium 114.818	Sn Tin 118.71	Sb Antimony 121.760	Te Tellurium 127.6	I Iodine 126.90447
81	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.98037	Po Polonium [209]	At Astatine [210]

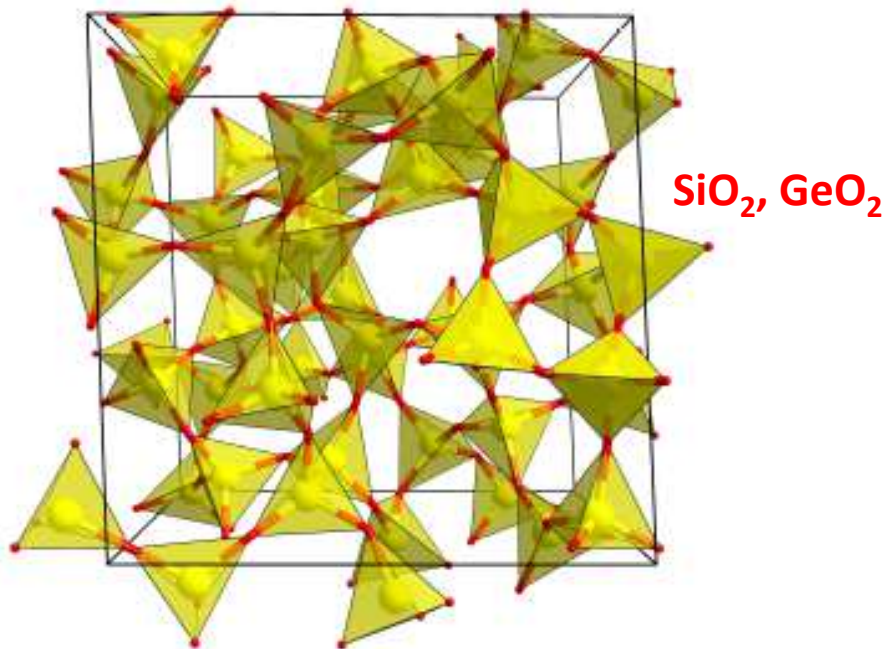
C) GLASS FAMILIES AND GLASS FORMING ABILITY

Glass families: Network formers

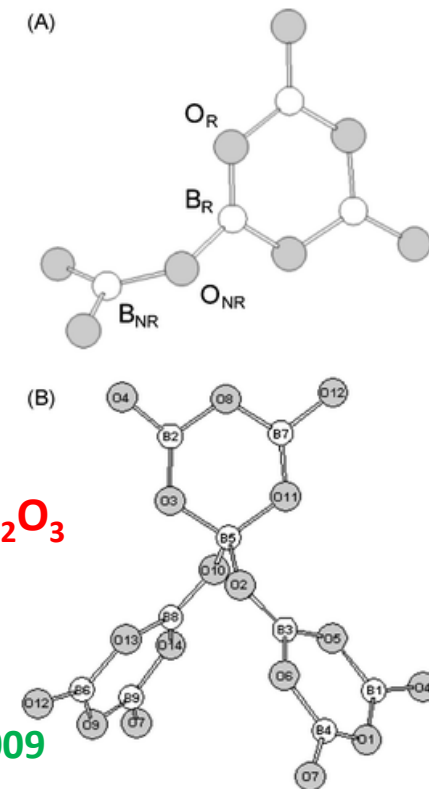
□ **Oxide** network formers at stoichiometric compositions

e.g. SiO_2 (silica), GeO_2 (germania), B_2O_3 , P_2O_5

Corner-sharing (CS) connections of base structural motifs (triangles, tetrahedra).



Th. Charpentier et al. JPC 2009



A. Wong et al. PCCP, 2009

C) GLASS FAMILIES AND GLASS FORMING ABILITY

Glass families: Binary, ternary and multicomponent modified glasses

❑ **Network former** (usually at stoichiometric composition) **and modifiers**

Modifier (alkali or alkaline earth oxide or chalcogenide)

e.g.	SiO_2 - Na_2O - CaO - Al_2O_3 - Fe_2O_3 -...	Magmas
	$(1-x-y)\text{SiO}_2$ - $x\text{Na}_2\text{O}$ - $y\text{CaO}$	Window glass
	$(1-x)\text{GeS}_2$ - $x\text{Li}_2\text{S}$	Solid electrolytes
	60 SiO_2 -36 CaO -4 P_2O_5	Bioglass
	$(1-x)\text{GeSe}_3$ - $x\text{Ag}$	Programmable Memories

❑ Physical/chemical/mechanical/optical/etc. properties heavily depend on the composition.

❑ « *Le nombre de compositions possibles est quasiment infini* »

J.Cl. Lehmann, St. Gobain chair

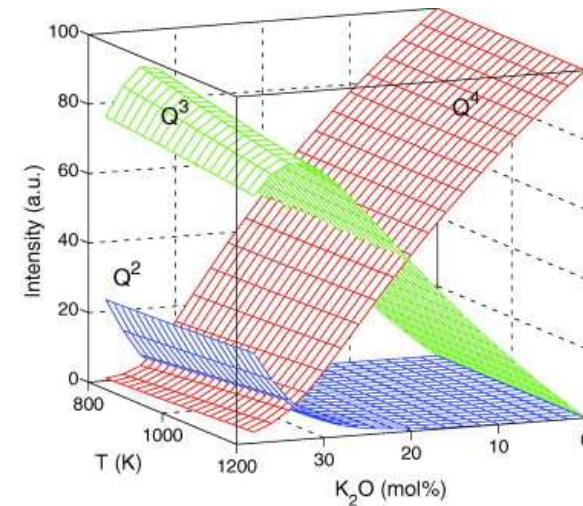
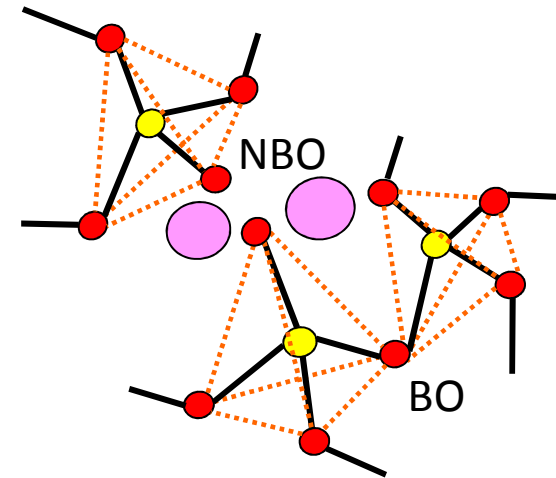
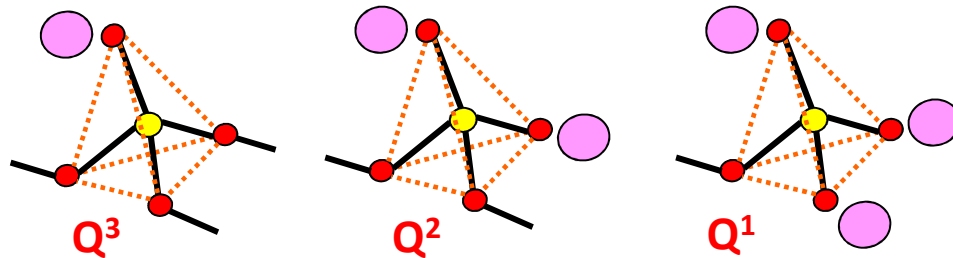
❑ Huge space for improvements, new compositions, new glasses, new studies...

C) GLASS FAMILIES AND GLASS FORMING ABILITY

Glass families: Binary, ternary and multicomponent modified glasses

❑ Effect on structure

- ❖ In **tetrahedral systems**, modifiers (alkali or alkaline earth oxide or chalcogenide) disrupt the basic network former structure and replace bridging oxygens (BO) by non-bridging oxygen (NBO).
- ❖ Analogue in sulphides (BS and NBS).
- ❖ The population Q^n of tetrahedra having $n=4, 3, 2, 1, \dots, 0$ BOs is changing with modifier composition, temperature or pressure.



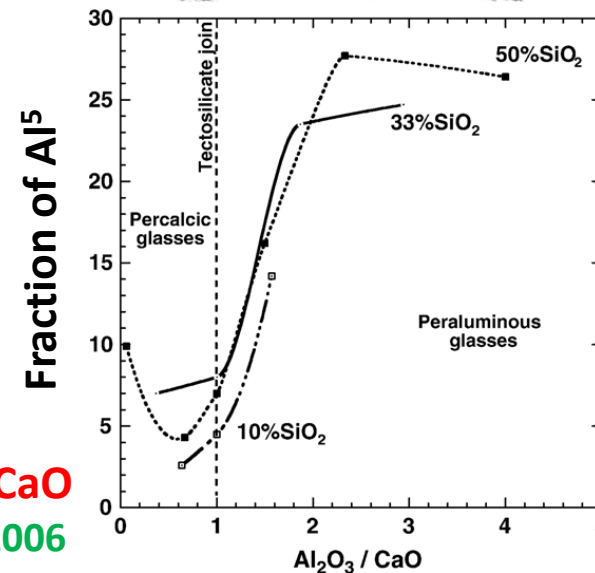
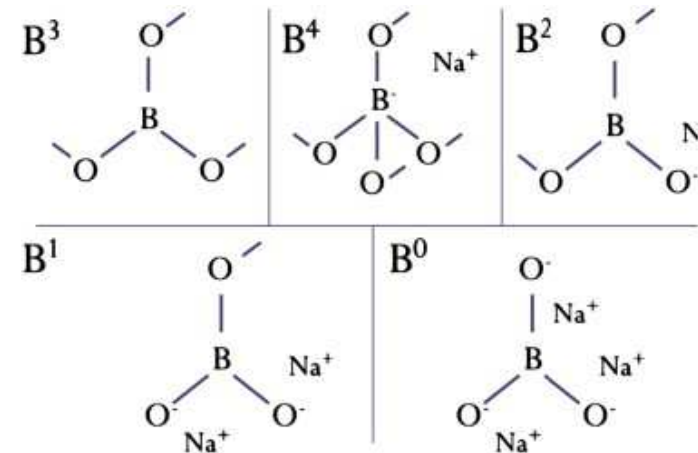
W.J. Malfait et al., JNCS 353, 4029 (2007).

C) GLASS FAMILIES AND GLASS FORMING ABILITY

Glass families: Binary, ternary and multicomponent modified glasses

Charge compensation

- ❖ In other systems (**borates or aluminates**), modifiers can either
 - depolymerize the base network (NBOs)
 - increase the coordination number of some species (B3→ B4 in borates) because of charge compensation.
- ❖ Analogue in sulphides (BS and NBS).
- ❖ The species population also is changing with modifier composition, temperature or pressure.



SiO₂-Al₂O₃-CaO

Neuvillle et al. Chem. Geol. 2006

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Among various methods

- Neutron or X-ray diffraction**

 - access to information on short and intermediate range order
 - access to dynamics (vibrational density of states)

- Raman or infrared spectroscopy**

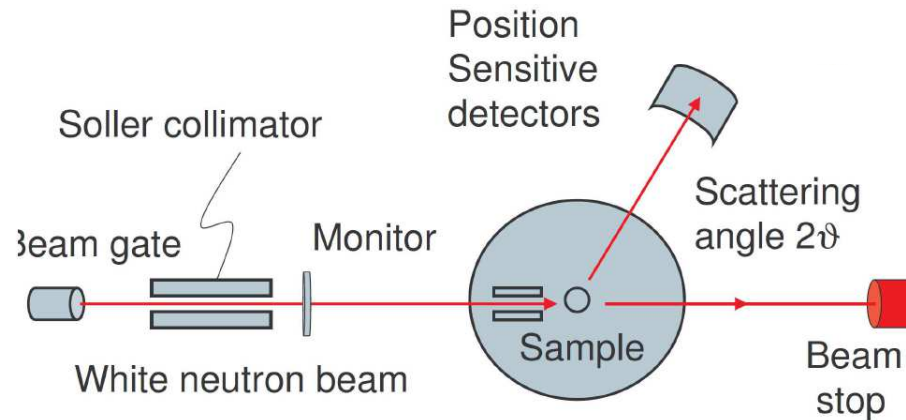
 - access to access to information on vibrational dynamics and structure

- NMR**

 - probe of structure and connectivity

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Neutron or X-ray diffraction



□ Measure of a scattering cross-section given by:

Neutrons:
$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega_{self}} + \frac{d\sigma}{d\Omega_{Inelastic}} + \frac{d\sigma}{d\Omega_{distinct}} \rightarrow F_N(Q)$$

X-ray:
$$\frac{d\sigma}{d\Omega} = \frac{d\sigma}{d\Omega_{self}} + \frac{d\sigma}{d\Omega_{Compton}} + \frac{d\sigma}{d\Omega_{distinct}} \rightarrow I_X(Q)$$

Neutron Nuclear function

$$S_N(Q) - 1 = \frac{F_N(Q)}{\left(\sum_{\alpha} c_{\alpha} b_{\alpha}\right)^2}$$

$$= \frac{1}{\left(\sum_{\alpha} c_{\alpha} b_{\alpha}\right)^2} \sum_{\alpha, \beta} c_{\alpha} b_{\alpha} c_{\beta} b_{\beta} (S_{\alpha\beta}(Q) - 1)$$

Coherent neutron scattering length

Distinct scattering

X-ray pseudo-nuclear function

$$S_X(Q) - 1 = \frac{I_X(Q)}{\left(\sum_{\alpha} c_{\alpha} f_{\alpha}(Q)\right)^2}$$

De-convolute electron cloud

$$= \frac{1}{\left(\sum_{\alpha} c_{\alpha} f_{\alpha}(Q)\right)^2} \sum_{\alpha, \beta} c_{\alpha} f_{\alpha}(Q) c_{\beta} f_{\beta}(Q) (S_{\alpha\beta}(Q) - 1)$$

X-ray form factor

- ❑ An isotopic neutron diffraction experiment will give access to the partials $S_{\alpha\beta}(Q)$ different coherent neutron scattering lengths
- ❑ Anomalous X-ray scattering (change in $f_i(Q)$) will give access to the partials $S_{\alpha\beta}(Q)$

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Neutron or X-ray diffraction: Isotopic substitution

- **Faber-Ziman formalism** : element specific
e.g. formation of skydivers illustrates order on an interlediate length scale

$$\begin{aligned} S_{\text{Red-Red}}(k) \\ S_{\text{Red-Green}}(k) \\ S_{\text{Green-Green}}(k) \end{aligned}$$

« Each diver has simple set of rules for bonding to the next but there is sufficiently flexibility for different patterns of ordering to be created on the scale of a few body lengths. »

Salmon, Nature (2002).

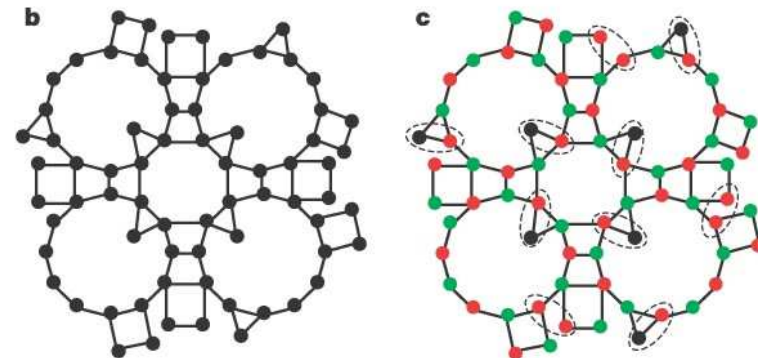
e.g. $S_{\text{GeGe}}(k)$, $S_{\text{Ge-Se}}(k)$ in GeSe_2

- **Bhatia-Thornton formalism** (linear combination of FZ)

$S_{\text{Number-Number}}(k)$ – **topology-b**

$S_{\text{Concentration-concentration}}(k)$ **chemical ordering-c**

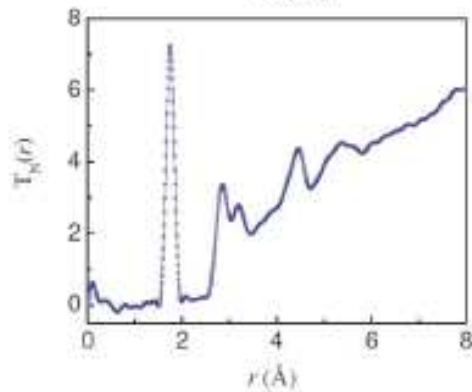
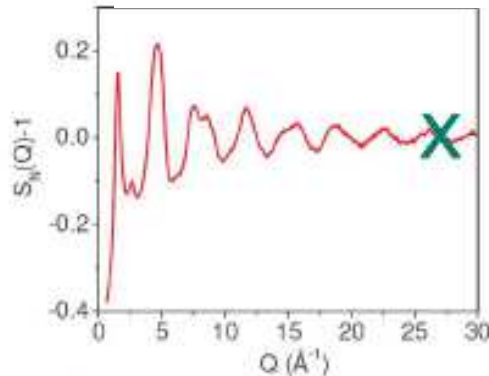
$S_{\text{Number-concentration}}(k)$



D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Neutron or X-ray diffraction: Back to real space

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 n_0 r} \int_0^\infty dk [S_{\alpha\beta}(k) - 1] k \sin(kr)$$

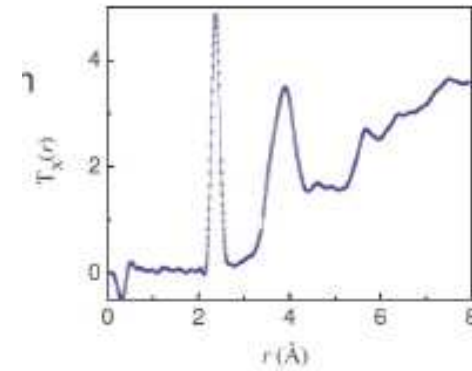
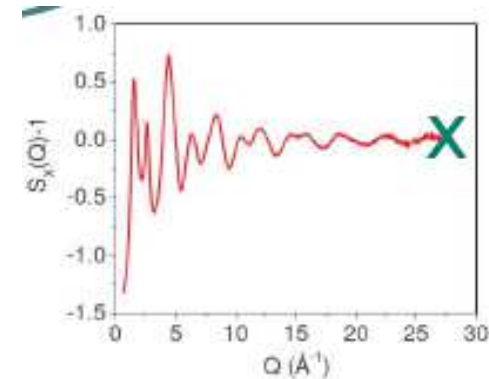


Neutrons

Total distribution function

$$T(r) = 4\pi n_0 r g(r)$$

Access to total or partial functions



X-ray

C. Benmore, Nxschool 2009

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Raman and Infrared spectroscopy

- ❑ **Infrared (IR)** : direct coupling between electric field E and instantaneous dipolar momentum p . Interaction energy given by:

$$W = -\vec{p} \cdot \vec{E}$$

Happens each time the charges are displaced (modification of the dipolar momentum)

- ❑ **Raman** : coupling between E and the atomic polarizability α (ability of the electron cloud to be deformed under the action of E).

- ❖ Induced electric polarisation : $\vec{P} = \vec{\alpha} \vec{E}$
(rank 2 tensor – possible anisotropies)

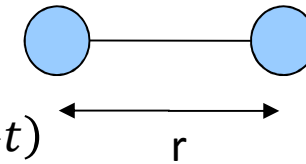
- ❖ Expression of α is modulated by the atomic vibrations (harmonic approximation) $\vec{q} = \vec{q}_0 \cos 2\pi\nu_v t$

- ❖ Incident field : $\vec{E} = \vec{E}_0 \cos 2\pi\nu_0 t$

which creates an induced dipole : $\vec{P} = \vec{\alpha} \vec{E}$

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Raman spectroscopy



□ Assume a vibrational mode such as $\|\vec{q}\| = r - r_{eq} = r_m \cos(2\pi\nu_V t)$

□ Polarisability is given by :

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 q + \frac{1}{2}\left(\frac{\partial^2\alpha}{\partial q^2}\right)_0 q^2 + \dots$$

$$= \alpha_0 + \alpha_1 q + \frac{1}{2}\alpha_2 q^2 + \dots$$

□ At the first order, one can write: $\alpha = \alpha_0 + \alpha_1 q$

and:

$$P = \alpha E = (\alpha_0 + \alpha_1 q) E = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \alpha_1 r_m \cos(2\pi\nu_V t) E_0 \cos(2\pi\nu_0 t)$$

$$P = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \alpha_1 E_0 r_m \cos(2\pi(\nu_0 - \nu_V) t) + \frac{1}{2} \alpha_1 E_0 r_m \cos(2\pi(\nu_0 + \nu_V) t)$$

Rayleigh

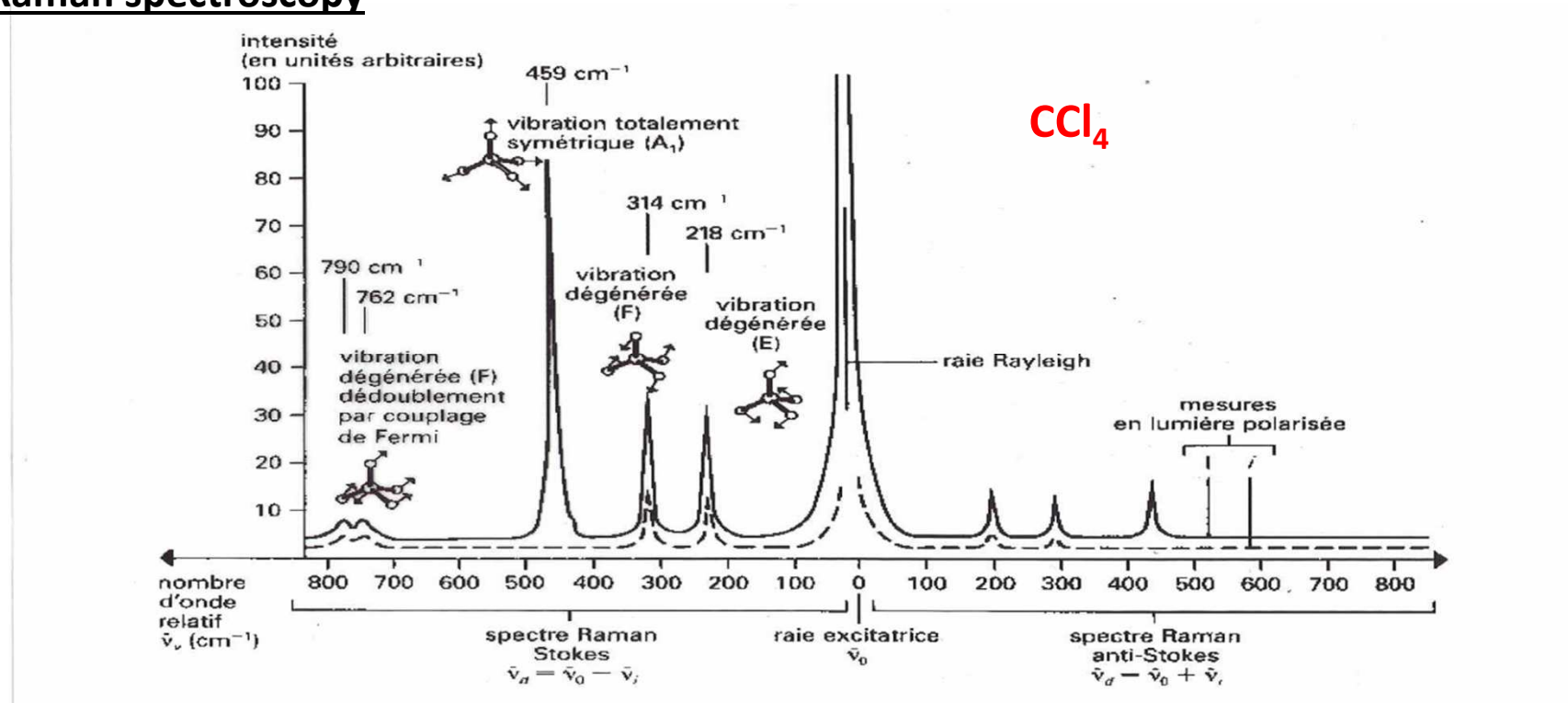
Stokes

Anti-Stokes

Can be extended to higher order

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Raman spectroscopy



Atomic and molecular vibrations (mass and force constants between ions) lead to the Raman spectrum

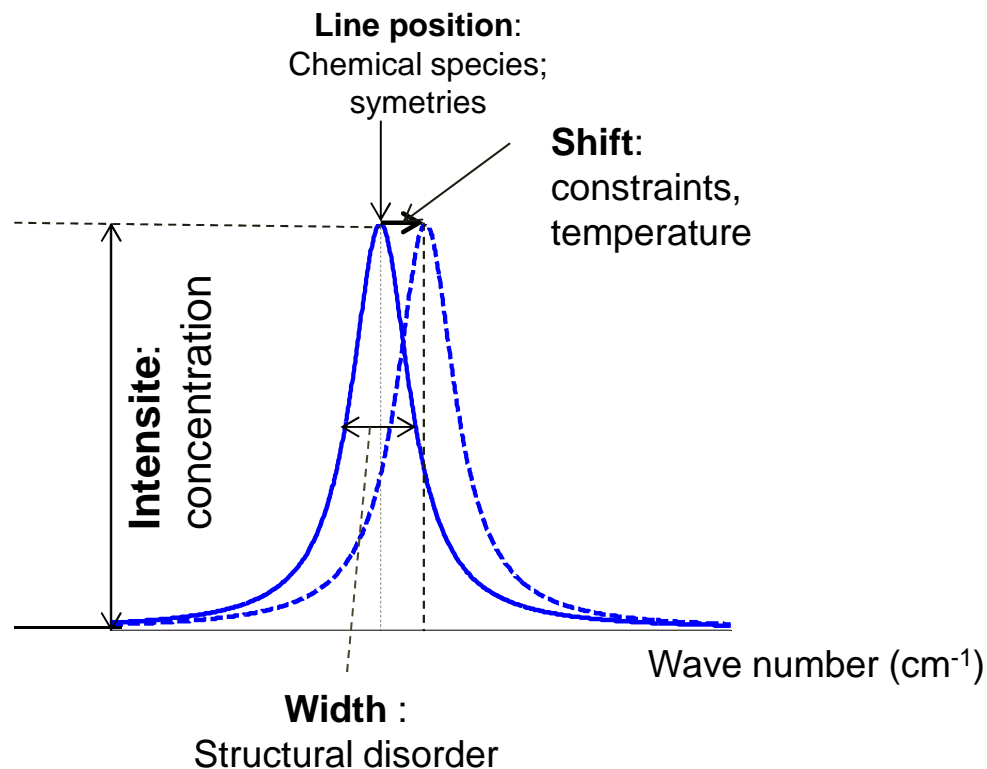
→ *Mass = chemical composition*

→ *Force constant = structure, constraints (bonds, angles)*

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Raman spectroscopy and probe of glass structure

- Raman lines in glasses provide different informations on structure



- Connection with vibrational density of states

$$I_r(\omega) = \frac{C(\omega)g(\omega)}{\omega^2} (n(\omega, T) + 1)$$

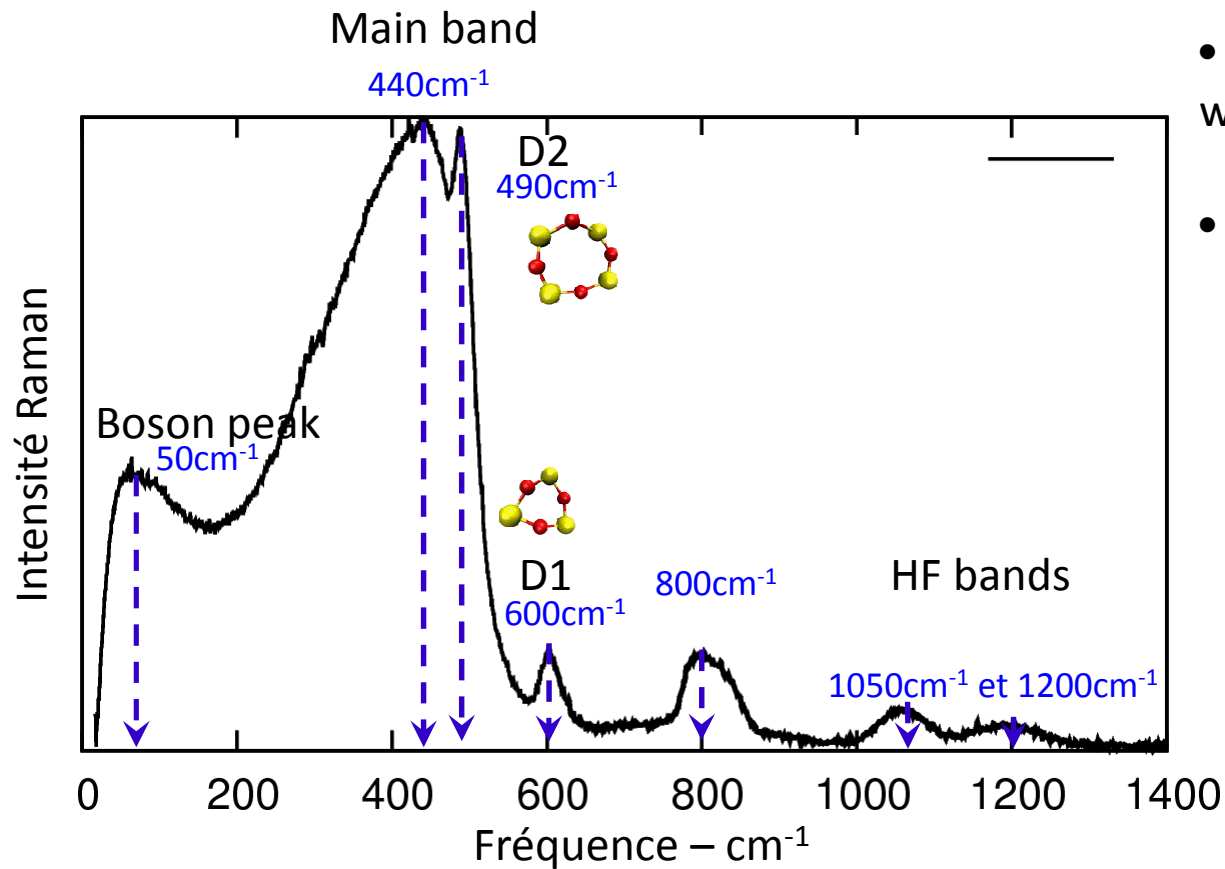
With $C(\omega)$ coupling function and $n(\omega, T)$ the Bose-Einstein statistics (vibrations=bosons)

$$n(\omega) = \frac{1}{e^{\frac{h\omega}{kT}} - 1}$$

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Raman spectroscopy and probe of glass structure

Raman spectra of vitreous SiO_2 (silica)

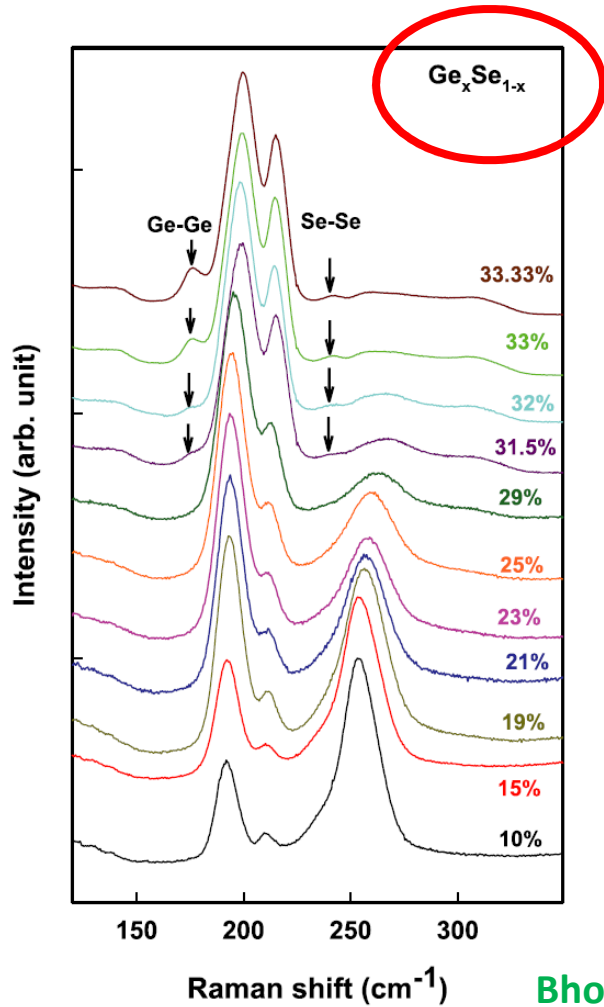


- « Boson peak » at low frequency.
- Main band at 440cm^{-1} together with a shoulder peak D2
- Shoulder at D1 (600cm^{-1}).

T. Deschamps, 2009

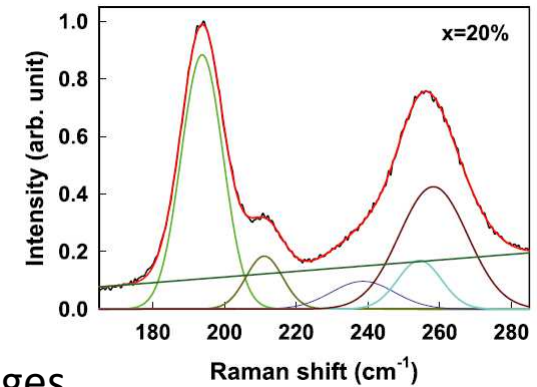
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Raman spectroscopy and probe of glass structure

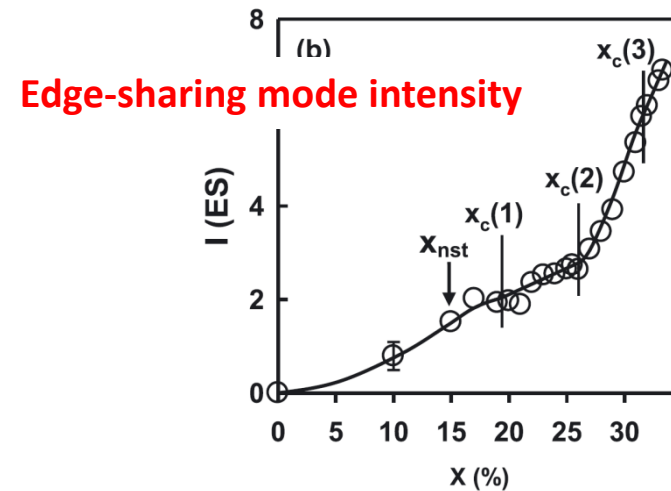


☐ Measure of spectral changes with composition

☐ Gaussian decomposition of the main lines



☐ Analysis of structural changes



D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Nuclear Magnetic Resonance

- ❑ NMR active nuclei possess a magnetic dipole moment
 ^{13}C , ^{31}P , ^{29}Si , ^{77}Se ,...
- ❑ The coupling of this magnetic dipole moment to an applied external magnetic fields as well as the magnetic dipole moments of neighboring nuclei, is used in the solid state NMR experiment to characterize structure and bonding arrangements.
- ❑ Excitation frequency ν_0 of the magnetic field (adapted to match energy differences between magnetic dipole excitations)
- ❑ NM Resonance (Larmor) frequency at $\nu_0 = \gamma B$ with γ gyromagnetic ratio (unique for a given nucleus). Allows to adapt B in order to probe ν_0 for a given isotope.

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Nuclear Magnetic Resonance

- ❑ Resonance frequency is also depending on the magnetic interaction with neighboring atoms (nuclei)
 - ❖ Intramolecular interaction
 - ❖ Intermolecular interaction (dipolar interaction)
 - +electrical (quadrupolar moment, Spin angular momentum > 1/2)

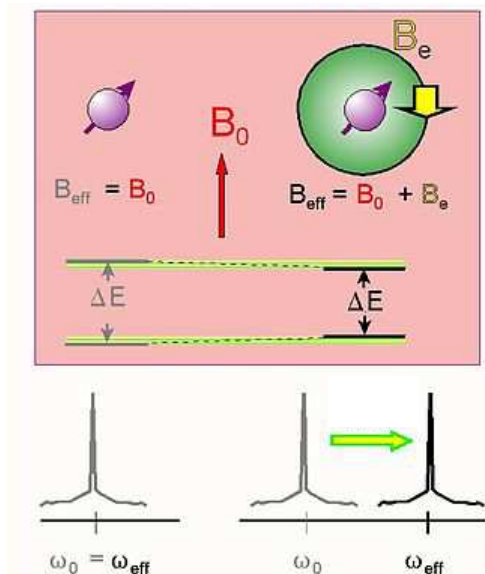
- ❑ Difference in frequency induced by different magnetic/electric atomic environment
Involves an effective screening constant σ (dia- or para-magnetism, etc.)

$$\nu_L = \nu_0(1 - \sigma)$$

- ❑ The « *chemical shift* » δ (in ppm) is defined with respect to an arbitrary reference (crystal, ref. compound).

$$\delta = \frac{\nu_L - \nu_{ref}}{\nu_0} \cdot 10^6$$

- ❑ Evolution of the chemical shift with concentration, temperature, pressure provides information about structure.



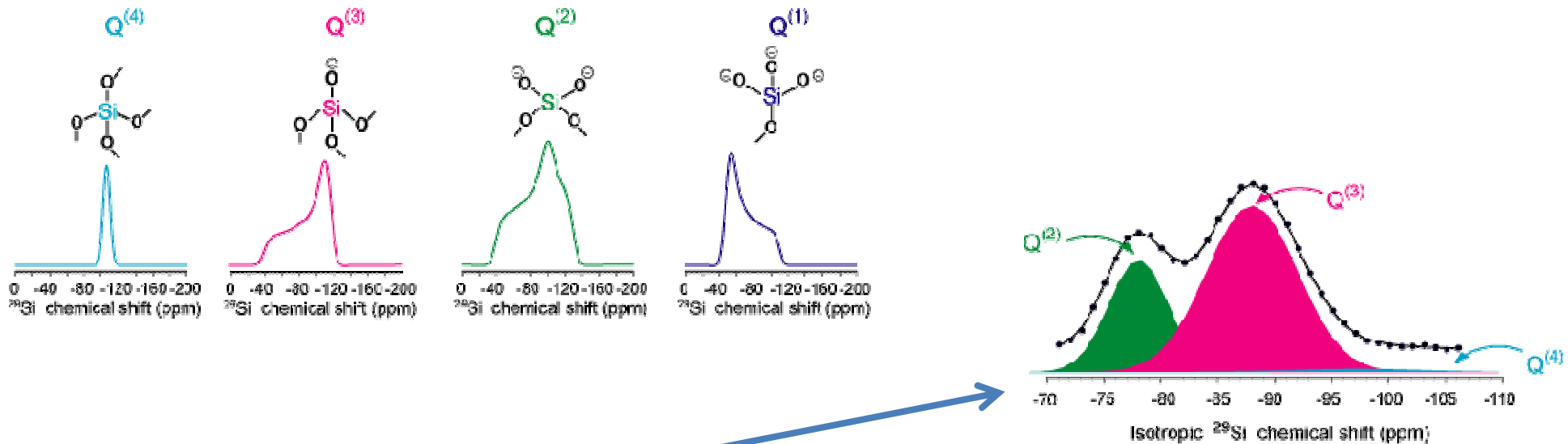
D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Nuclear Magnetic Resonance and structure

1. **In silicates**, identification of specific NMR signals depending on the local structure (e.g. Q^n speciation), and deconvolution (estimation of population)

^{29}Si Solid-State NMR of Silicates

90° Spinning Spectra



2. **Deconvolution of a given spectra** and estimation of the Q^n population

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Nuclear Magnetic Resonance and structure

3. Characterization of structure and evolution with chemical composition

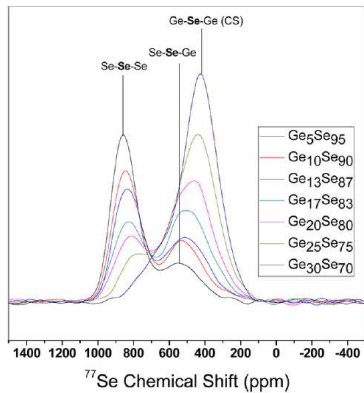


Figure 3. ^{77}Se isotropic NMR spectra of $\text{Ge}_x\text{Se}_{100-x}$ glasses. Average δ_{iso} for the Se–Se–Se, Se–Se–Ge, and CS Ge–Se–Ge sites are shown with vertical lines.

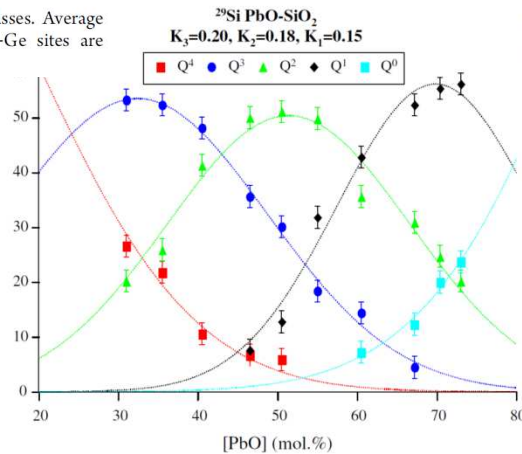


Figure 4. Compositional variation of the relative fraction of Se–Se–Se sites (black squares) is compared with the predictions for the chain crossing model (red circles), the clustering model (blue triangles), and the random network model (green inverted triangles).

Q^n speciation in lead silicates
Massiot et al., JNCS 2008

D) EXPERIMENTAL CHARACTERIZATION OF STRUCTURE

Having more interest in experimental characterization ?

Go to: <http://www.lehigh.edu/imi/GlassStructureCourse.htm>

Conclusion: Before getting started, which theory for which kind of experiments ?

Experiments		Theory			
Technique	Quantity	MD	DFT	Reverse Monte Carlo	Bond models
Neutron X-ray	SRO, MRO S(k), g(r), Partial $g_{ij}(r)$	☺☺☺	☺☺☺	☺☺☺	
	VDOS	☺☺☺	☺☺☺		
EXAFS, XANES	SRO Spectra	☺☺☺	☺☺☺ ☺	☺☺☺	
Anomalous X-ray	SRO, MRO, partial S(k), g(r)	☺☺☺	☺☺☺	☺☺☺	
Vibrational	Raman	☺	☺☺		☺
	Infrared	☺	☺☺		☺
NMR	Speciation, SRO, MRO		☺		☺☺☺
XPS	eDOS, SRO		☺☺		
Dynamics	D/ viscosity	☺☺	☺☺		☺

☺☺☺ = Easy and/or excellent agreement

☺☺ = Medium difficulty and/or fair agreement

☺ = Difficult and/or poor agreement

Home reading

- ❑ 80 years of random networks, M.F. Thorpe and A. Wright, Physica Status Solidi (2013).

[pdf file](#)

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

[pdf file](#)