Web Course
Physical Properties of Glass

Glass Transformation-Range Behavior- Odds and Ends

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Outline

- Memory Effect
- Measuring T_g
- Effect of composition and structure on T_g

Properties depend on thermal history

Example: room temperature refractive index after quenching from different equilibrium temperatures. (Soak times >> relaxation times)

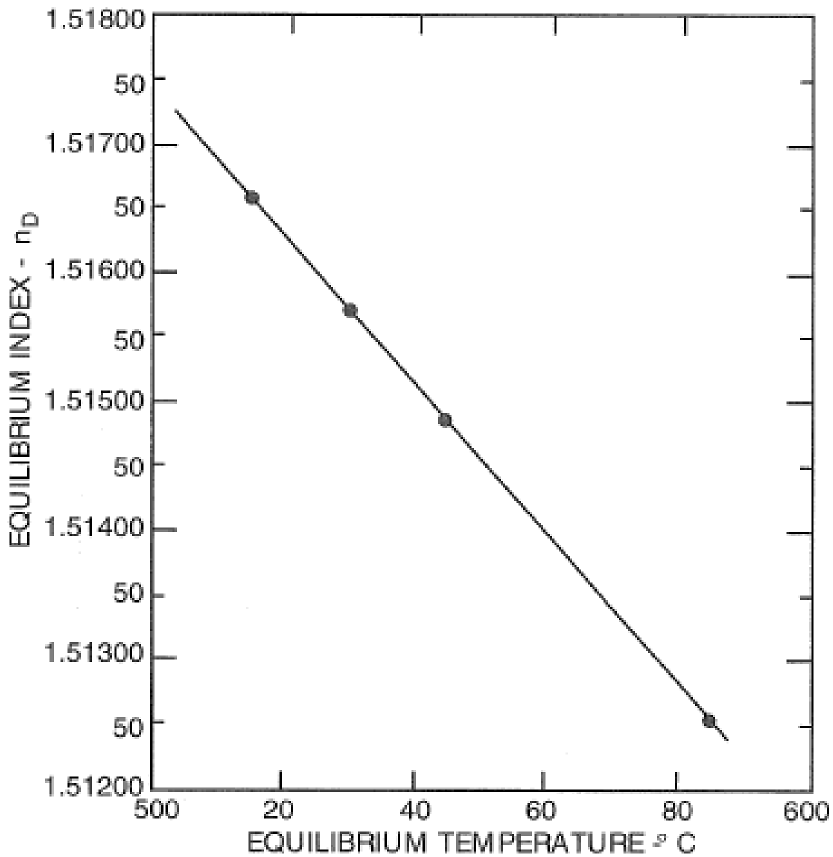
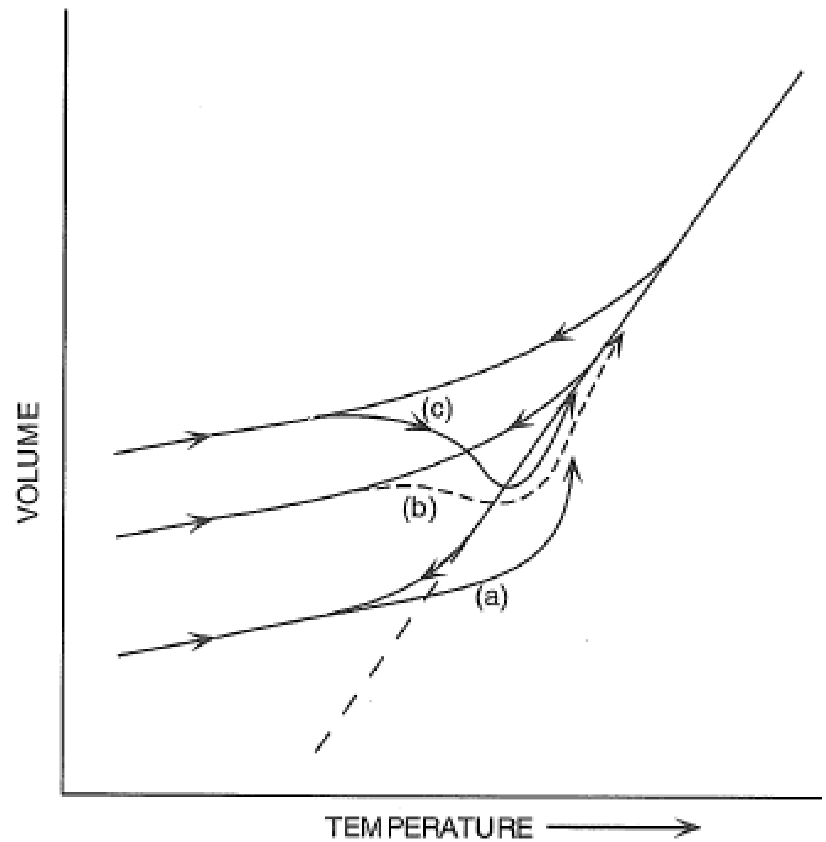


Figure 13-27. Equilibrium room temperature index as a function of temperature for BSC517. (After Spinner and Napolitano[18].)



The 'room temperature' properties of glass depend on thermal history

….. but, just because properties are equivalent, doesn't mean that thermal history and structure are the same…

Ritland (JAcerS, 1956)

- Borosilicate crown glass
- Identical room temperature refractive indices from two thermal histories
  - A: Soaked at 530°C for 24 hrs, then quenched
  - B: Rate cooled at 16°C/hr through the transition range
- On re-heating to 530°C, the glasses follow much different paths to the 'equilibrium'
  - Memory Effect

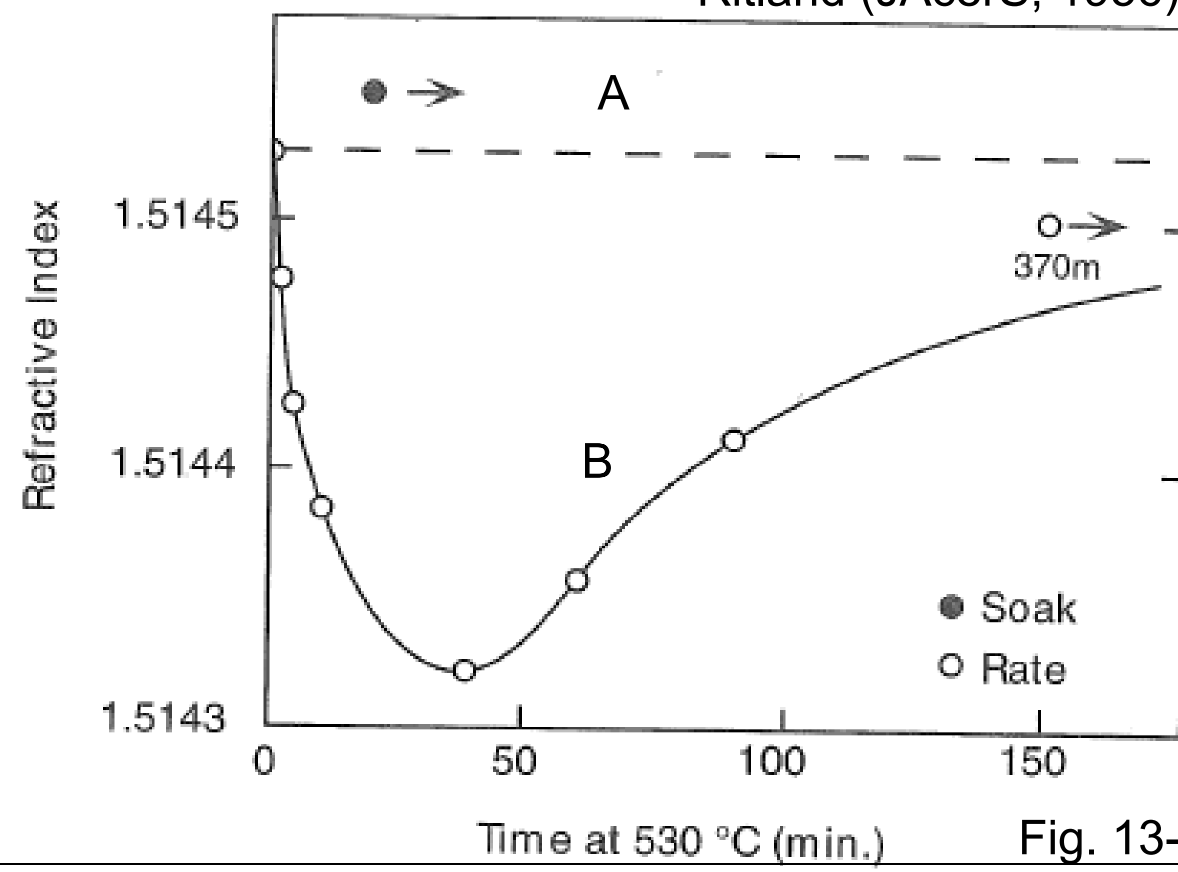
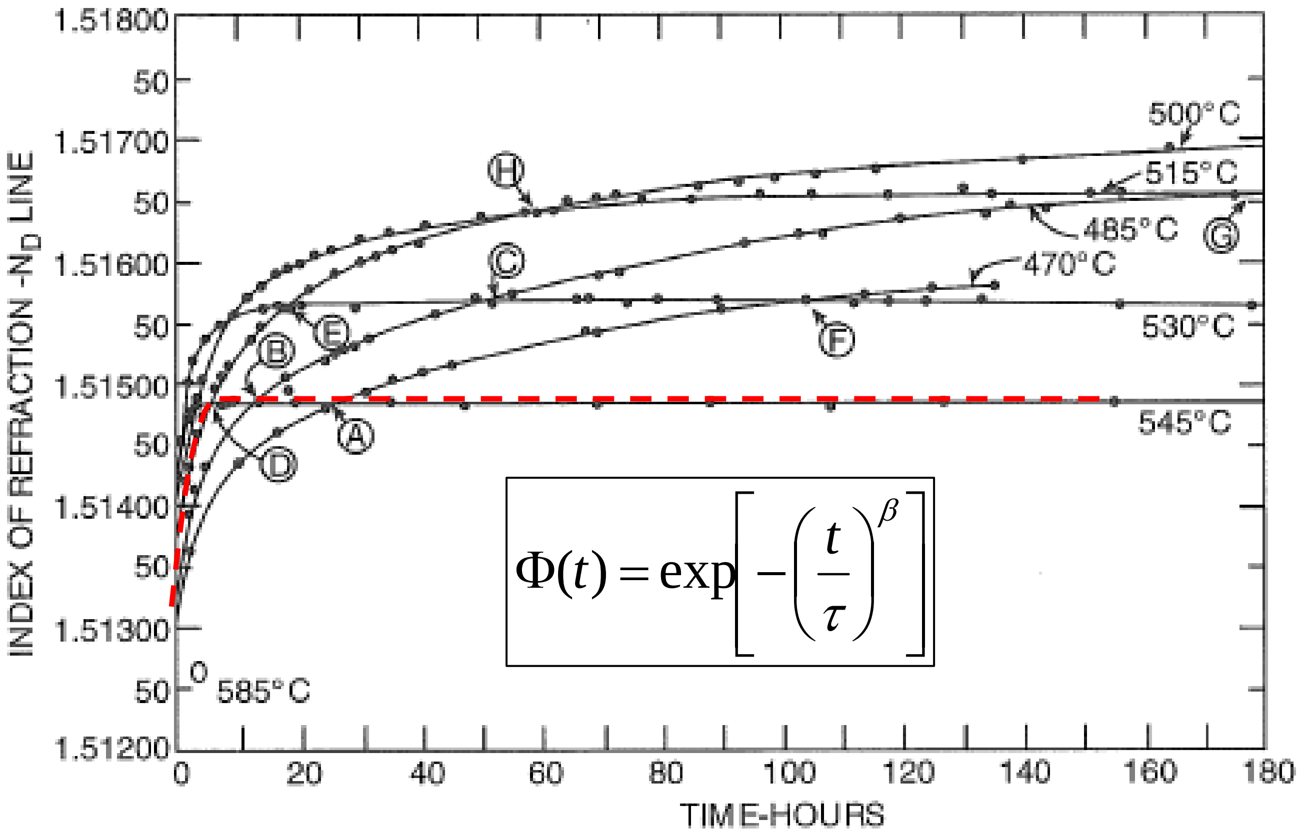


Fig. 13-25

A single fictive temperature is insufficient to describe glass properties and structure

The ‘memory effect’ is a consequence of non-exponential relaxation



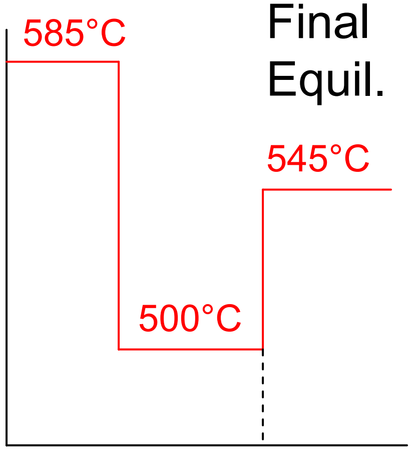
$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$

Figure 13-26. Room temperature refractive index – time ‘approach curves’ for BSC517. (After Spinner and Napolitano[25].)

Samples were initially stabilized at 585°C, quenched to room temp, then ‘up quenched’ to the temperatures indicated

All properties measured at room temperature- “cross-over points” have same properties but different thermal histories

The 'memory effect' depends on fictive temperature history



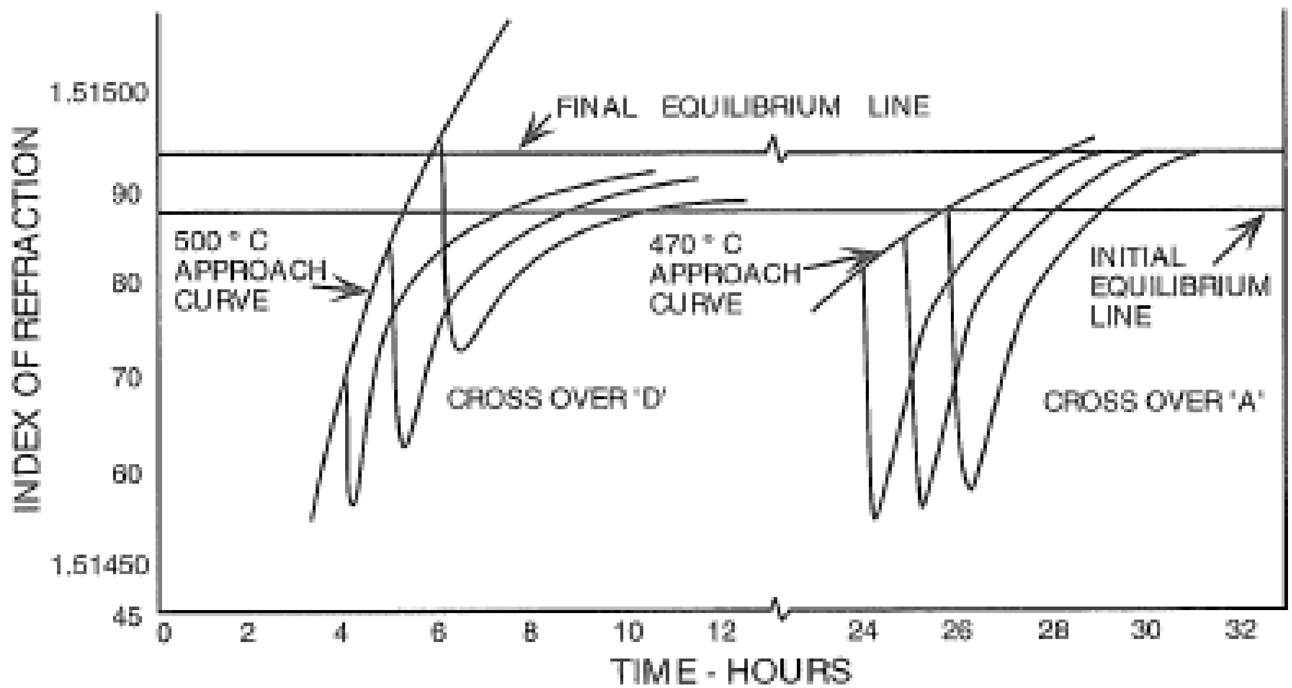


Figure 13-28. Refractive index vs. time at crossovers A and D. (After Spinner and Napolitano[25].)

Glass has a 'memory' of its most recent excursion through the transition range

- Multiple relaxation processes

The Tool-Narayanaswamy model is one way to account for the 'fictive temperature history'

$$\Phi(t) = \sum_i g_i \exp\left[-\int_0^t dt'/\tau_i \right]$$

$$\tau_i = \tau_0 \exp\left[\frac{x\Delta H^*}{RT} + \frac{(1-x)\Delta H^*}{RT_f} \right]$$

Microscopic interpretation:

- Relaxation involves coupled responses of a series of processes with different 'reaction rates'- bond 1 breaks, then bond 2…..
- Different regions within liquid relax at different rates because of structural differences (differences in configurational entropy from μ-region to μ-region)
- Glasses brought to the same point on a V-T diagram by different routes relax differently

Measuring T_g

1. T_g is defined by experimental conditions
2. Relaxation time ≈ experimental time
3. Dependent on thermal history (fictive temperature history)

Measuring Tg

- Changes in enthalpy- DTA, DSC
- Changes in volume- dilatometry, TMA
- Changes in mechanical modulus- DMA
- Changes in transport properties
- Etc.

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Measurement of glass transition temperature by mechanical (DMTA), thermal (DSC and MDSC), water diffusion and density methods: A comparison study

Mohammad Shafiur Rahman *, Insaaf Mohd Al-Marhubi, Abdullah Al-Mahrouqi

The glass transition temperature of………………. Spaghetti!

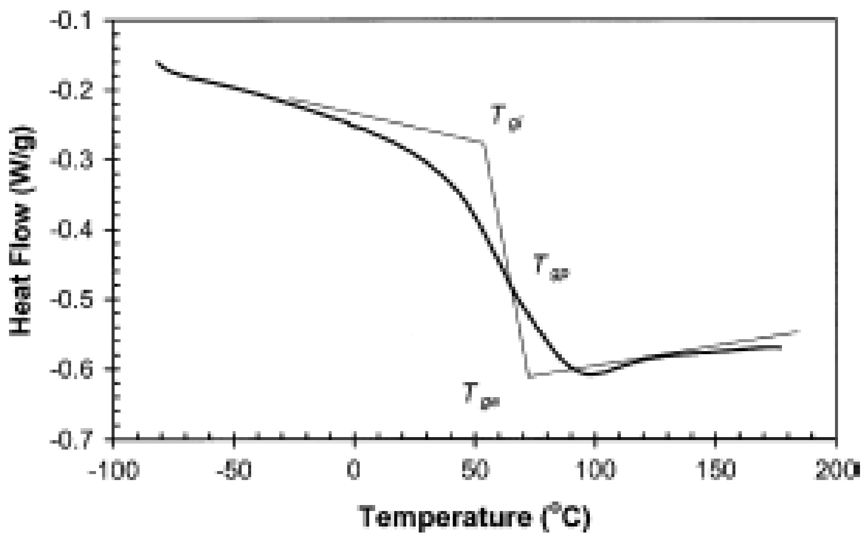

Fig. 4. DSC thermogram at a heating rate of 10 °C/min.

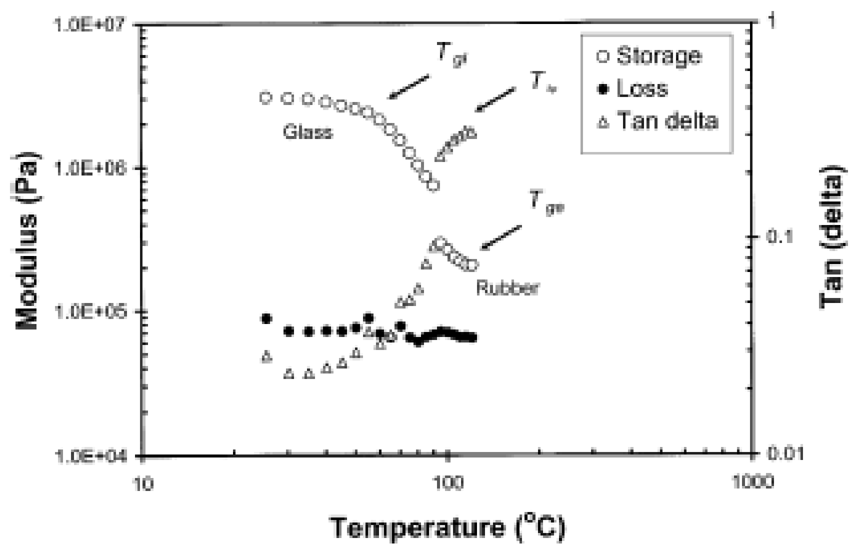

Fig. 2. Storage and loss modulus of spaghetti at 1 Hz and 0.6% compression.

T_g can be determined from the temperature dependence of glass properties

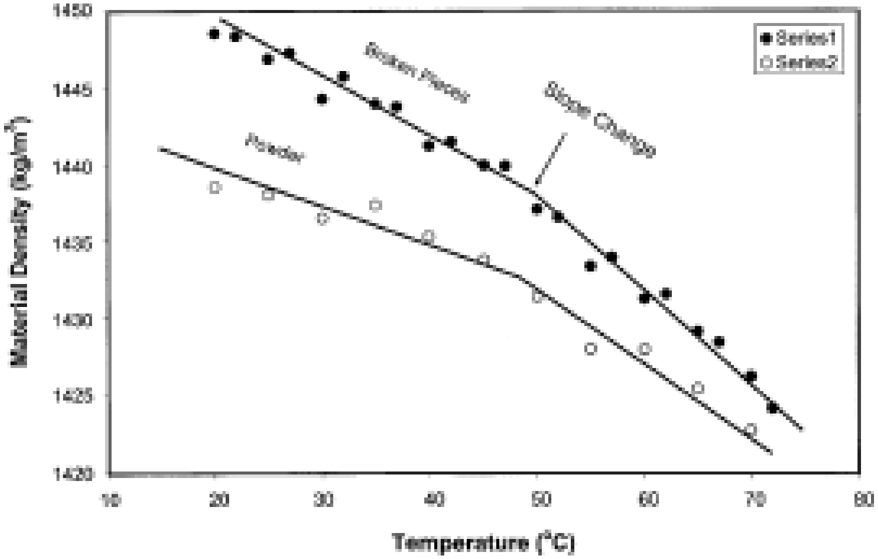

Fig. 14. Material density of spaghetti as a function of temperature (series1: broken sample, series2: powder sample).

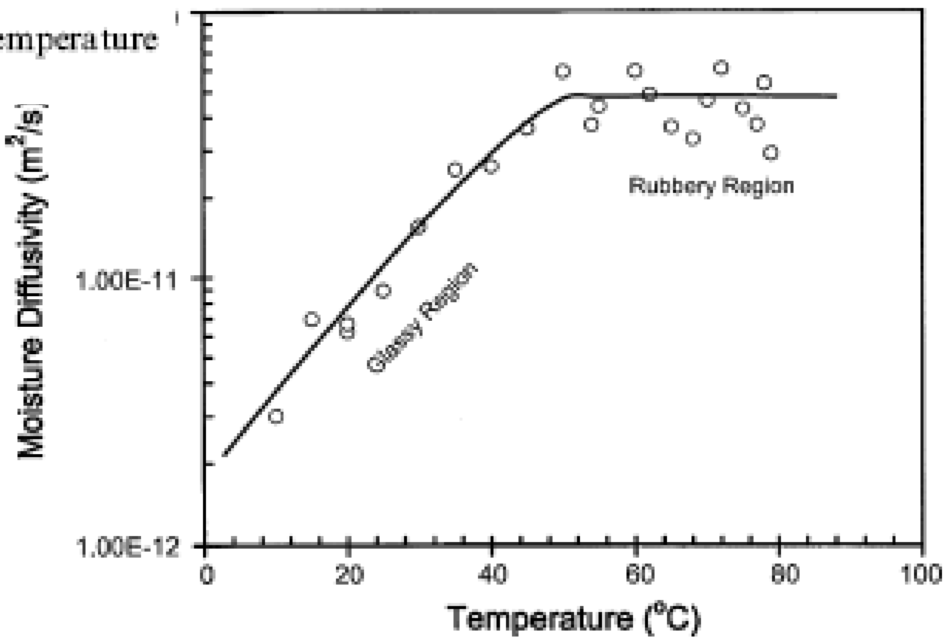

Fig. 13. Moisture diffusivity as a function of drying temperature.

Rahman, et al, Chem Phys Lett (2007)

Density fluctuations in oxide glasses investigated by small-angle X-ray scattering

Claire Levelut,[a]* Rozenn Le Parc,[a] Annelise Faivre,[a] Ralf Brüning,[c]
Bernard Champagnon,[b] Valérie Martinez,[b] Jean-Paul Simon,[d]
Françoise Bley[d] and Jean-Louis Hazemann[e]

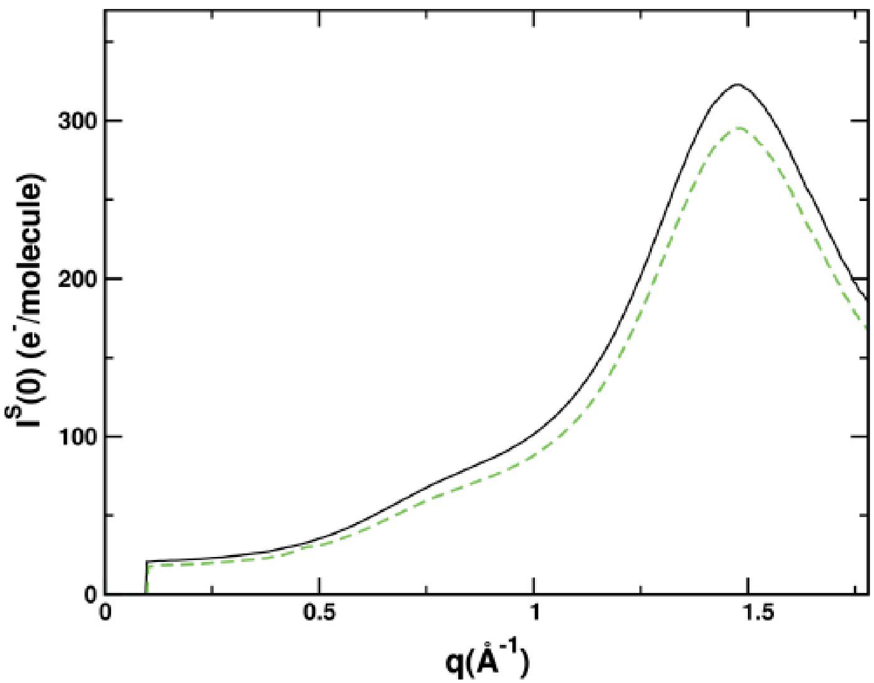

Figure 1
Scattering intensity as a function of modulus of scattering vector in two samples of silica A with different thermal histories: one sample heat-treated at 1523 K (solid line) and one sample heat-treated at 1373 K (dashed line).

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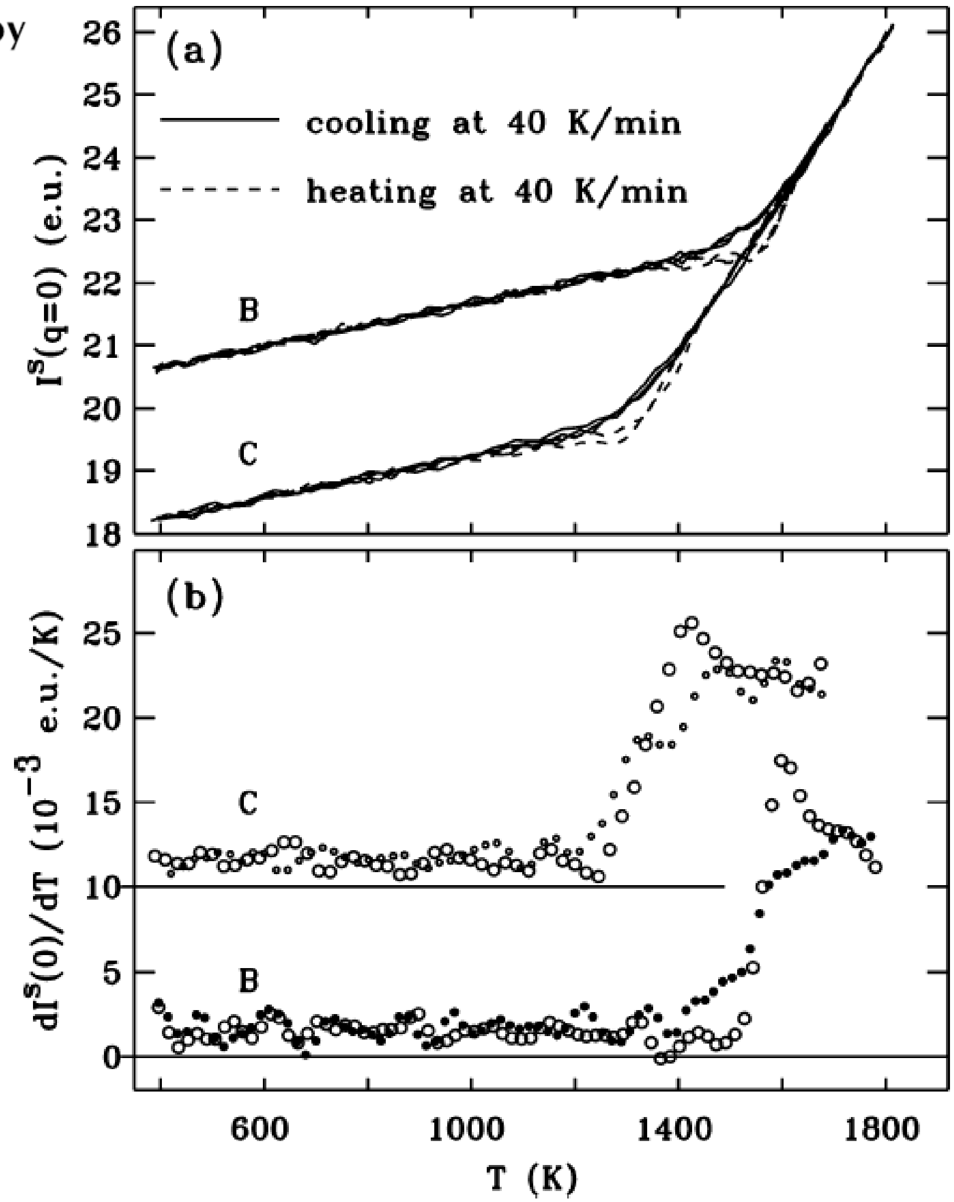
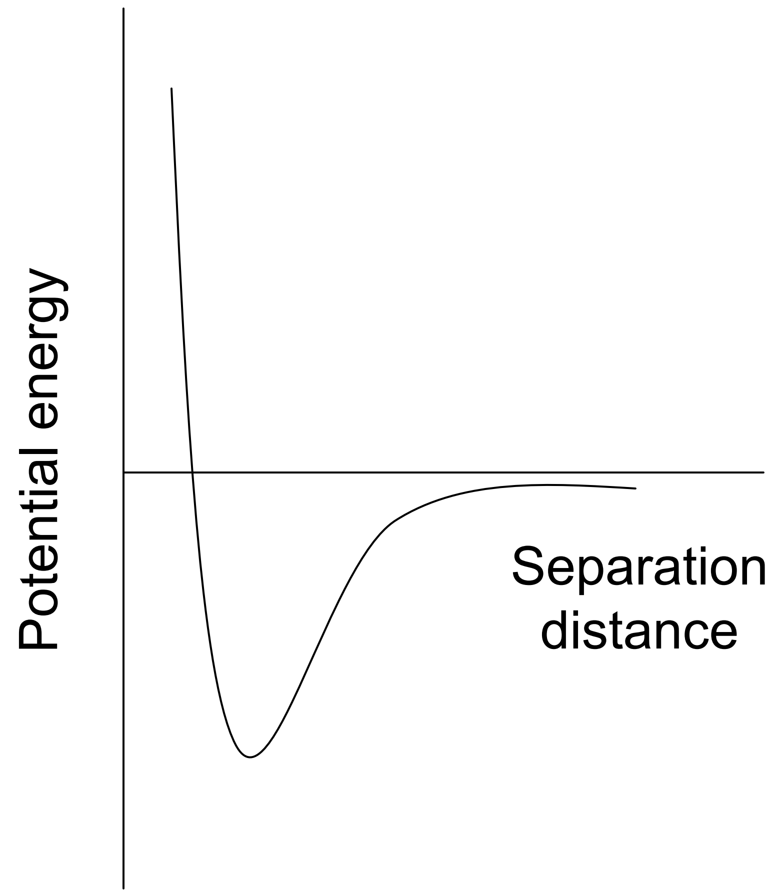


Figure 5
(a) Scattering intensity, measured at 40 K min^{-1} and extrapolated to $q = 0$, as a function of temperature for samples B and C, measured upon heating (dashed lines) and upon cooling (solid lines). (b) Temperature derivatives of $I^S(0)$ data obtained at 40 K min^{-1} for samples B and C. For clarity, sample C is shifted up by 10×10^{-3} e.u. K^{-1}. T_g is found to be 1535 K for sample B ([OH] = 2 p.p.m.) and 1303 K for sample C ([OH] = 900 p.p.m.).

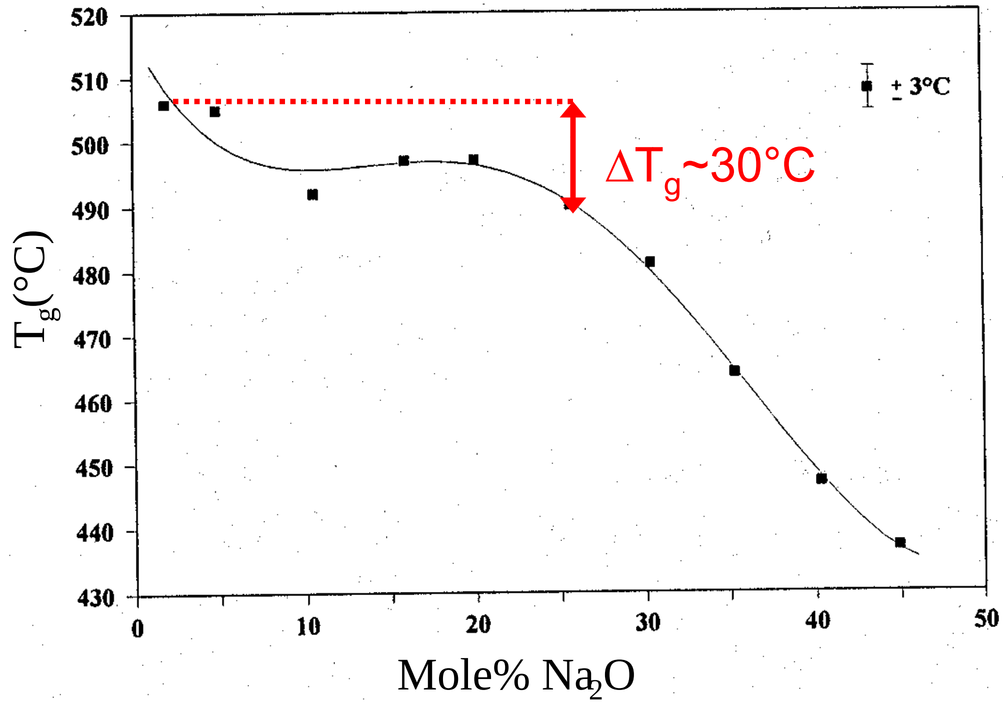
What structural properties affect T_g?

- Deep potential wells
  - Strong network forming bonds
  - More cross-linked networks
    - Greater network coordination number
    - More network bridges
  - Greater modifier field strengths
  - Greater anion coordination
    - $N^{3-} > O^{2-} > F^{-}$

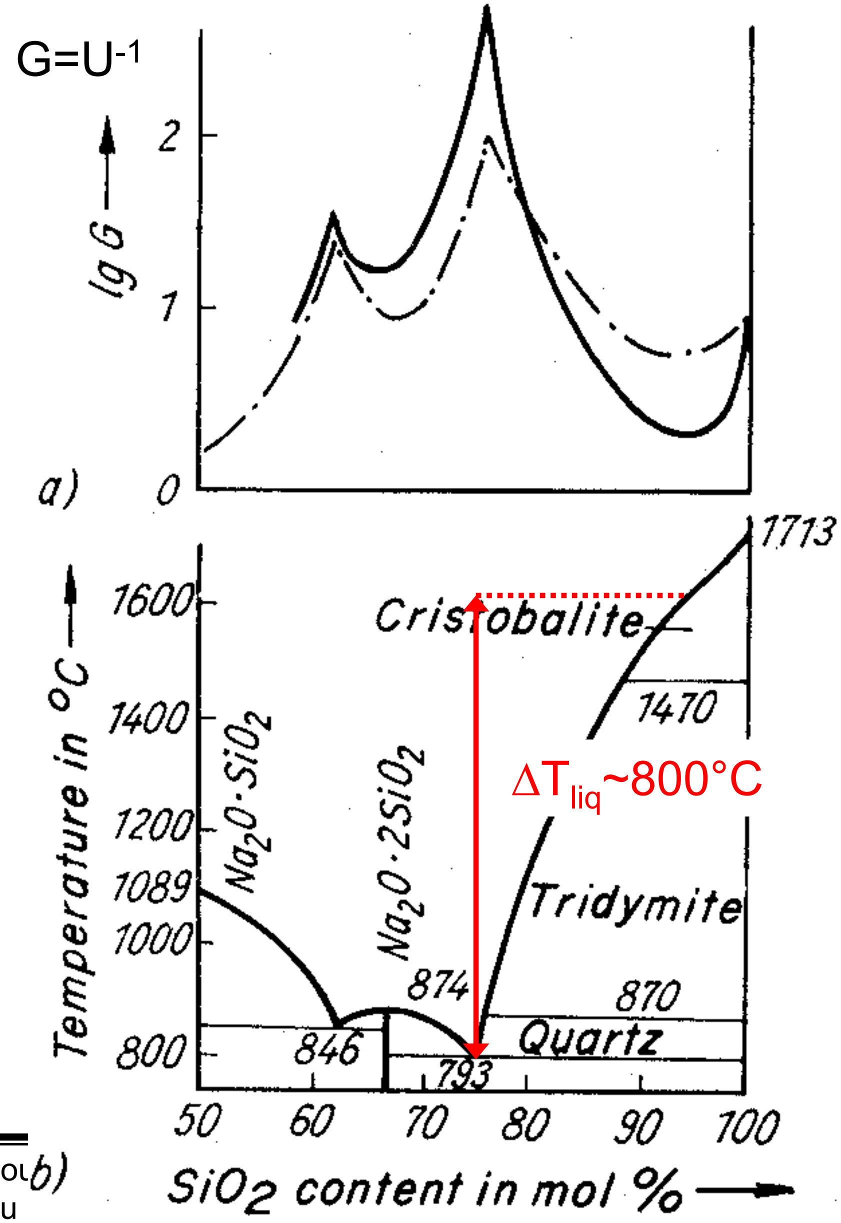


T_g decreases with the addition of modifiers to silica

From Dingwell in *Rev. Mineral.* **32** (1995)



W. Vogel, *Chemistry of Glass*, 1985



T_g/T_{liq} is a maximum (~0.7) at the eutectic

Nitrogen increases T_g

Hampshire et al, JACerS, 1984

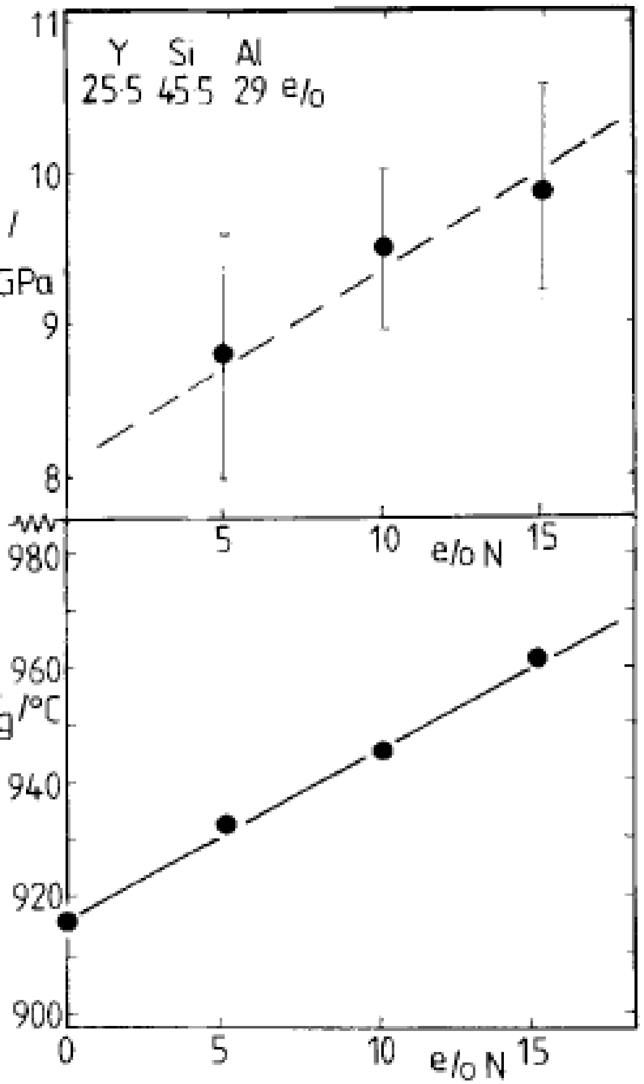
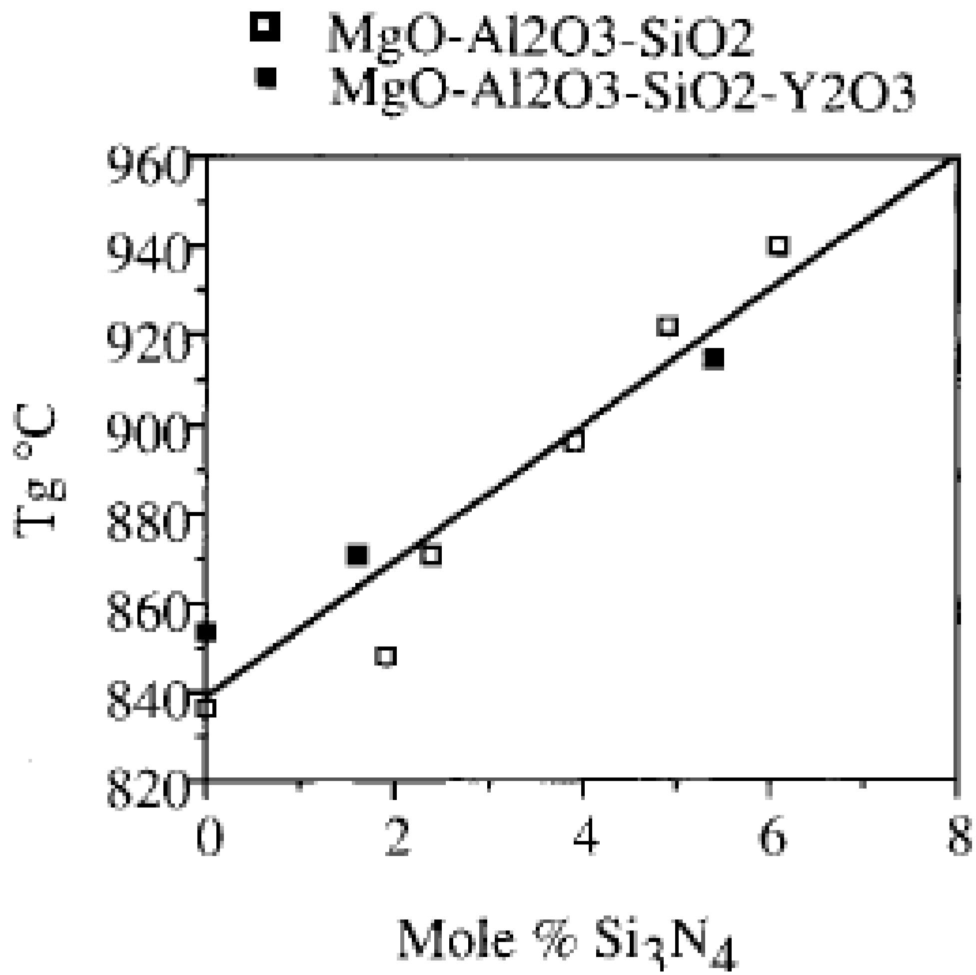


Fig. 1. Hardness and glass transition temperature vs nitrogen content for Y-Si-Al-O-N glasses.



Peterson et al., JACerS, 1995

Adding nitrogen increases the average number of cross-links between glass-forming tetrahedra

$$6\equiv Si-O-Si\equiv +4N$$

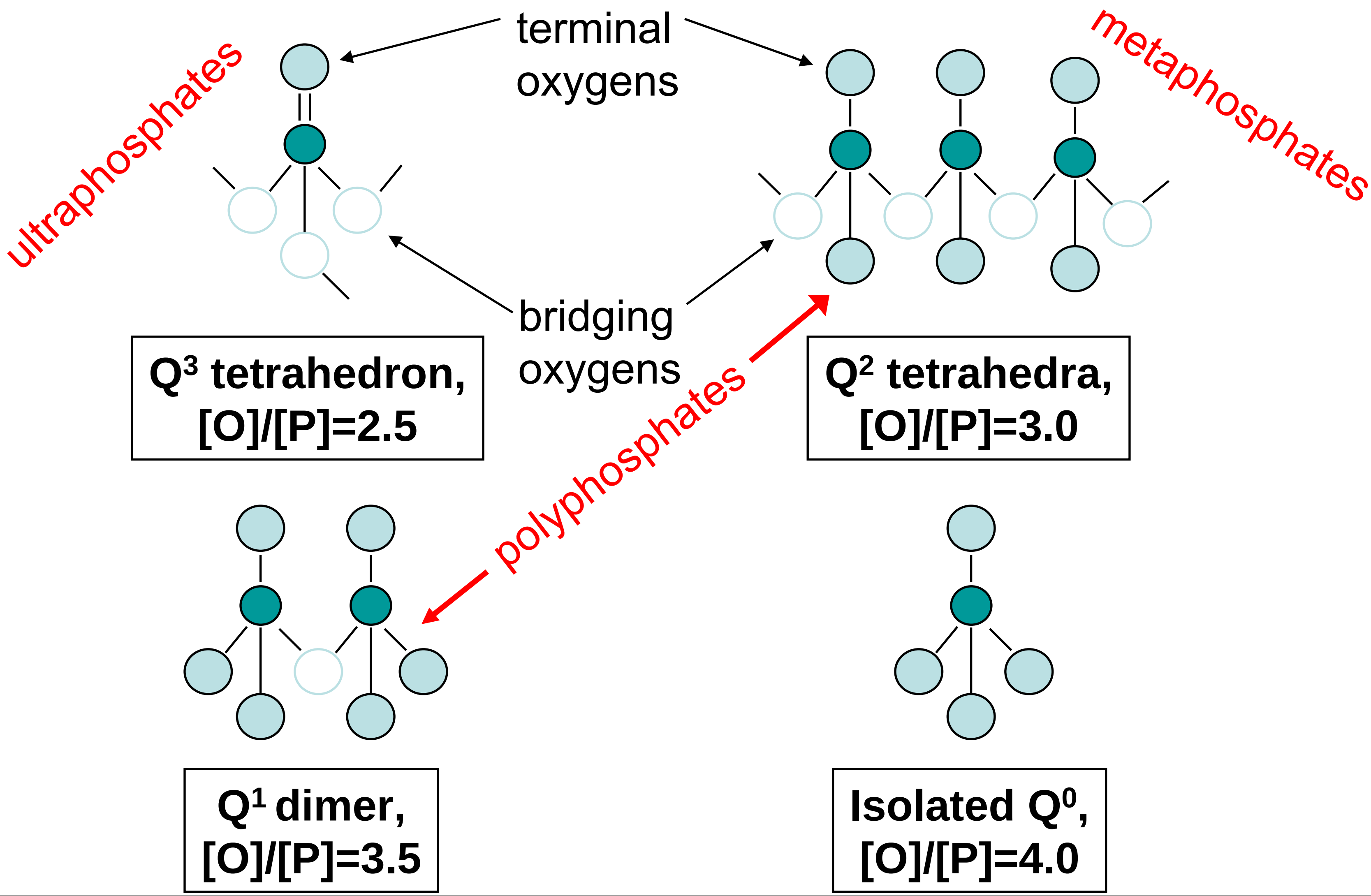
$$\longrightarrow 4\equiv Si-N\begin{matrix} \diagup Si\equiv \\ \\ \diagdown Si\equiv \end{matrix} \quad +6O$$

Composition and structure effects on glass transition temperature-

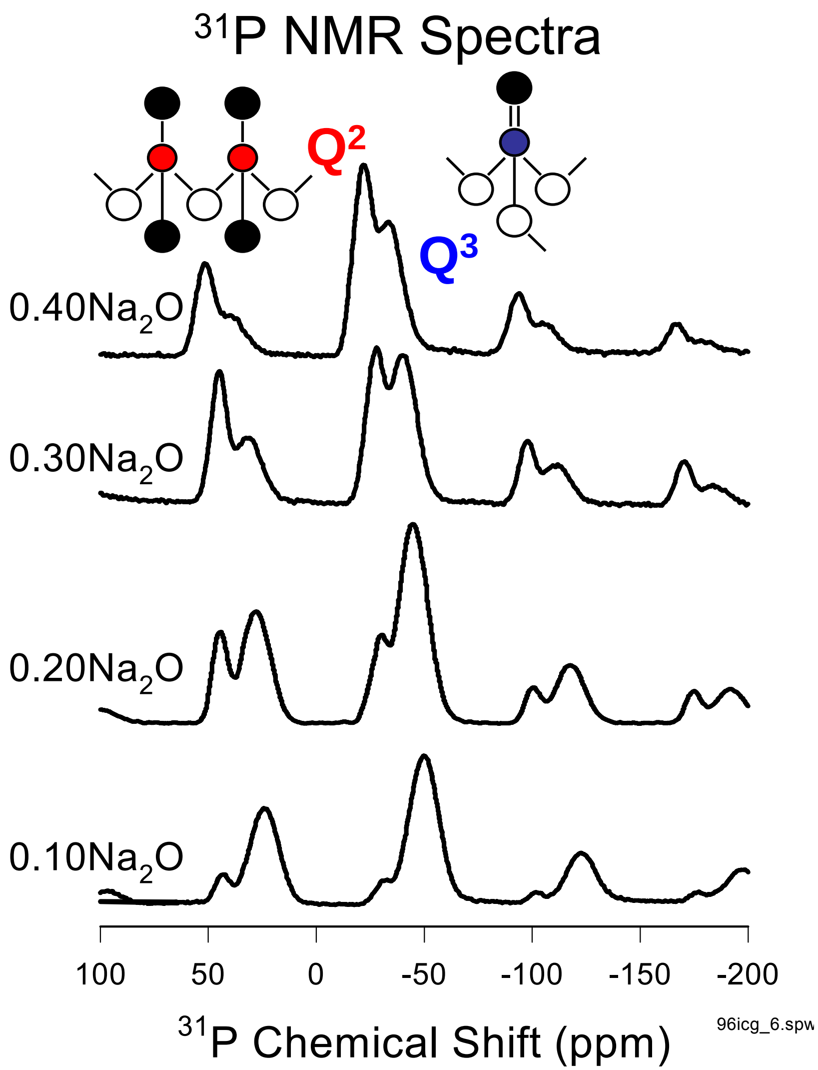
A few case studies

Example 1: Phosphate Glasses

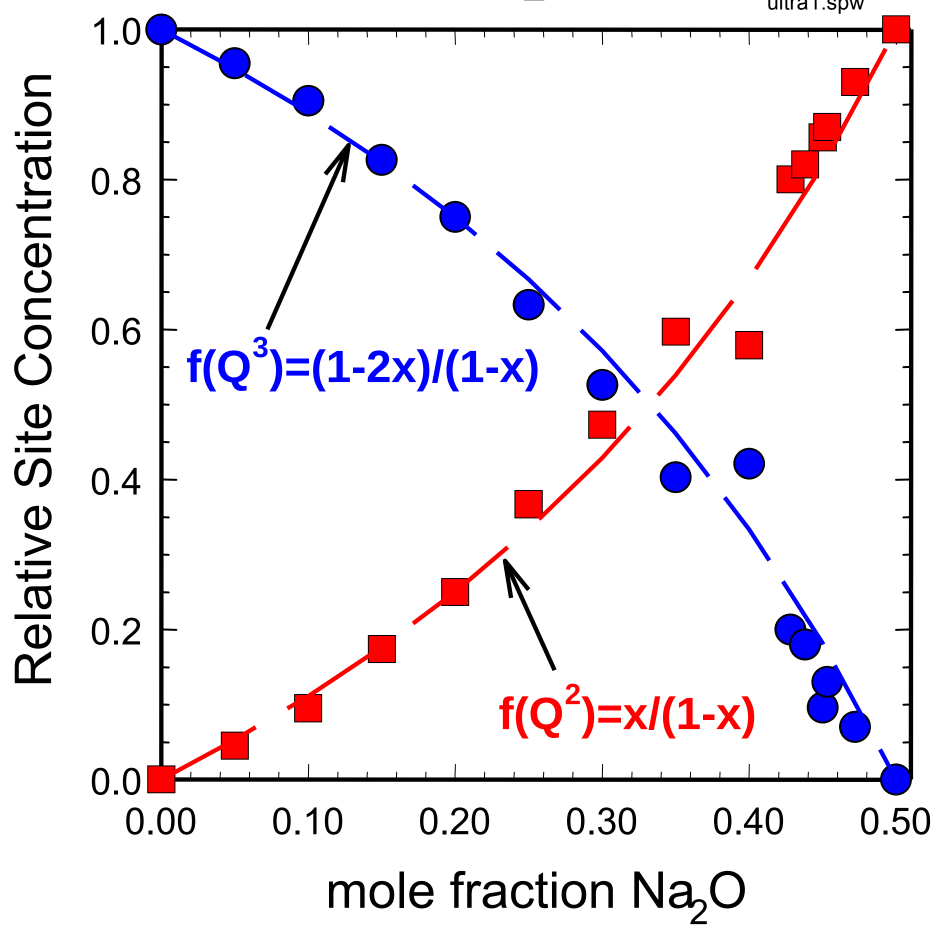
Glass Network Structures Are Based on Phosphate Tetrahedra



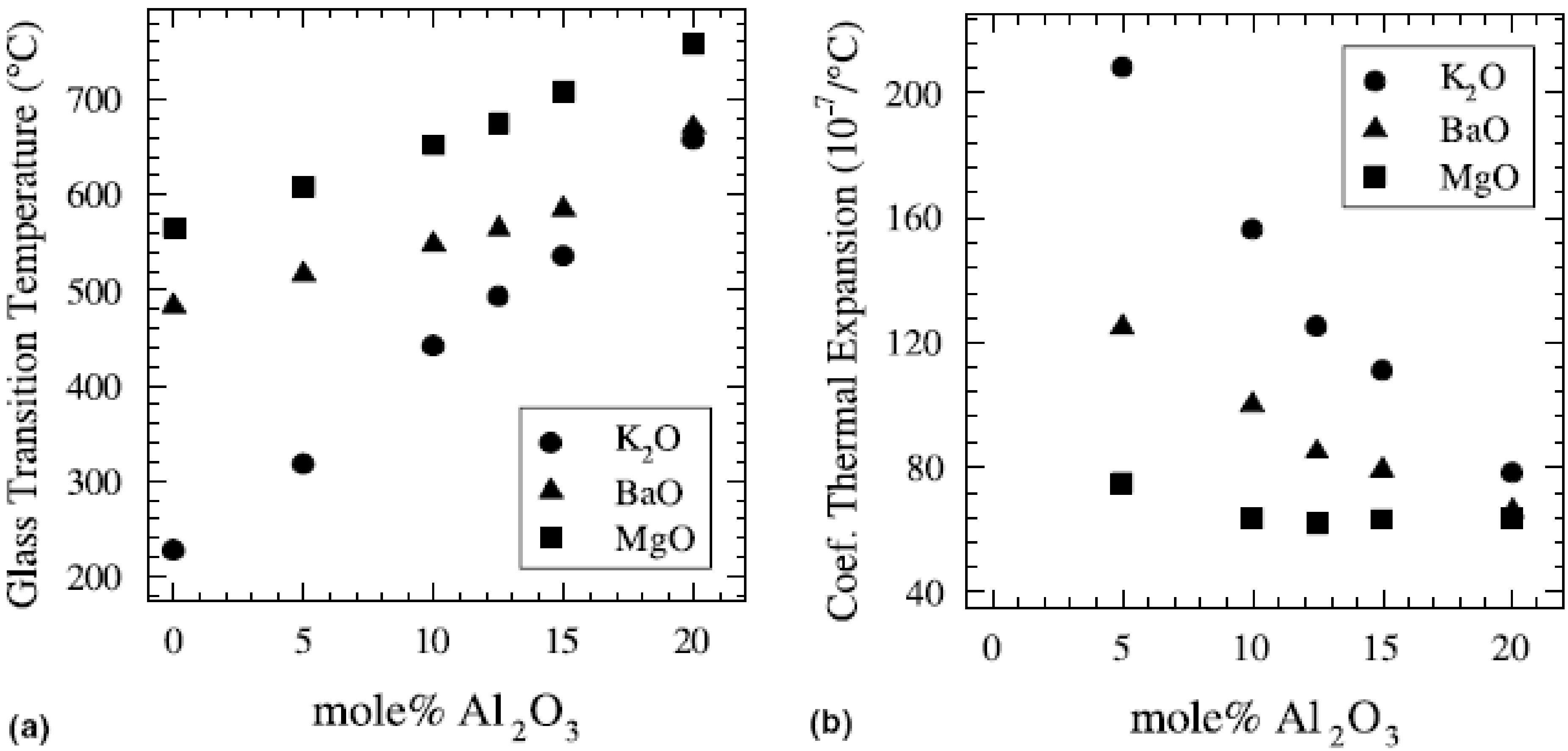
Spectroscopic Studies Reveal Systematic Changes in Network Connectivity



$2Q^3 + Na_2O \rightarrow 2Q^2$

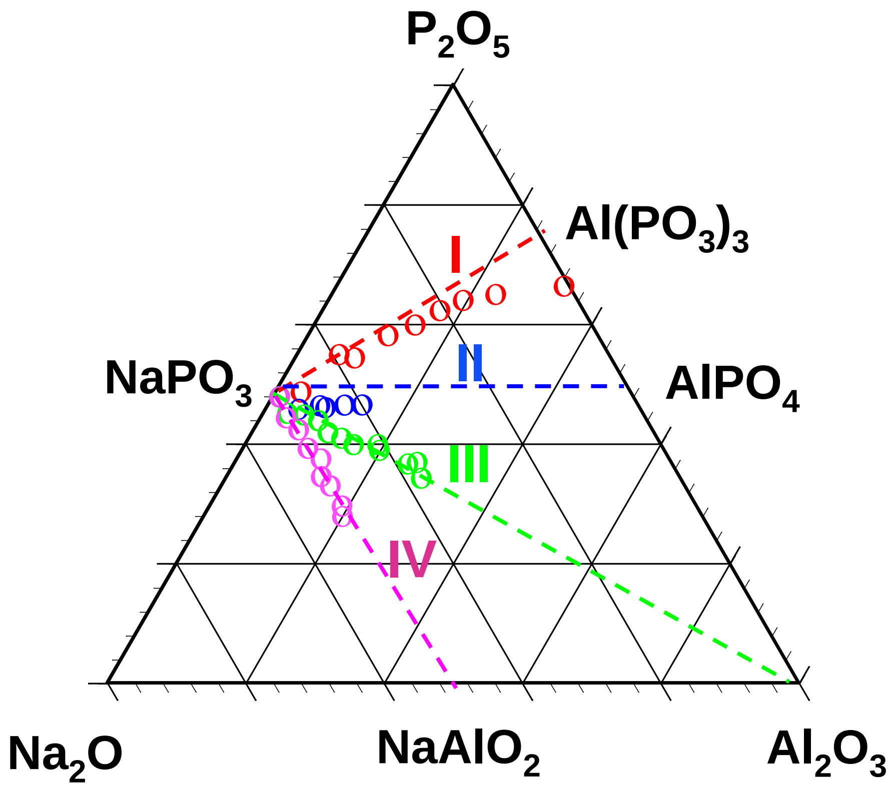


Alumina Additions Affect Metaphosphate Glass Properties

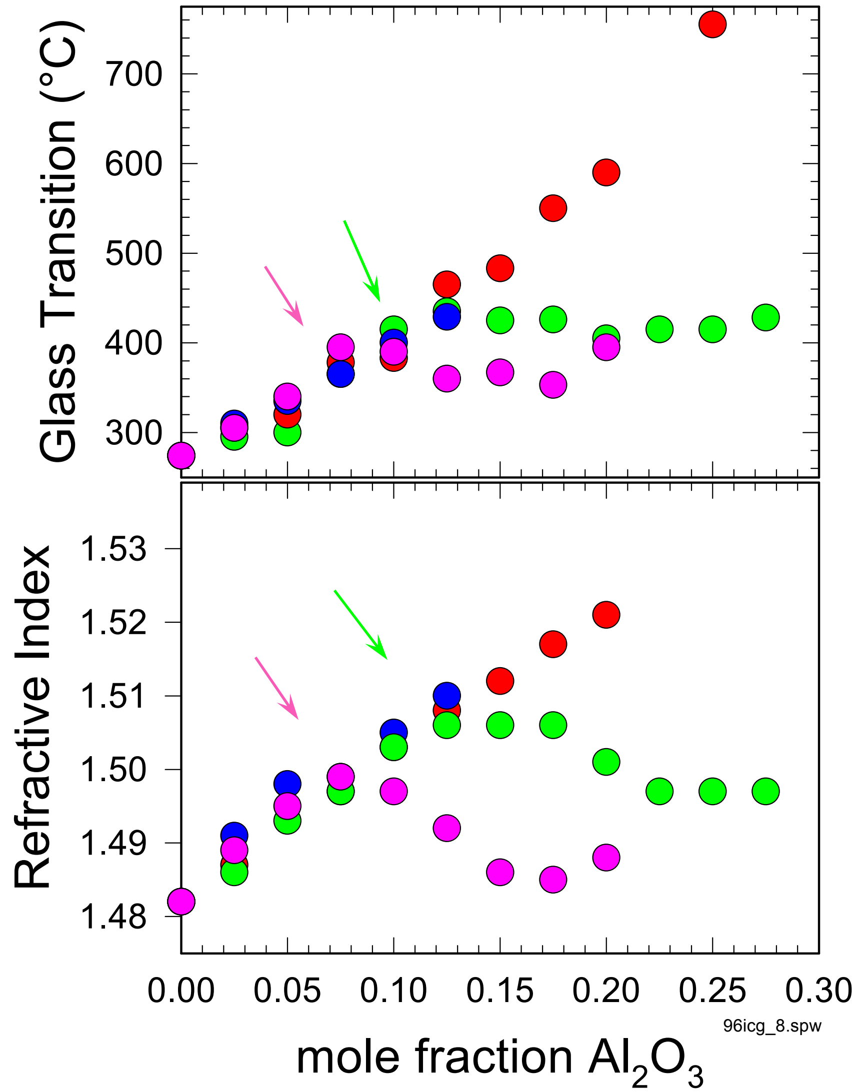


Metwalli, Brow, *JNCS*, **289** 2001

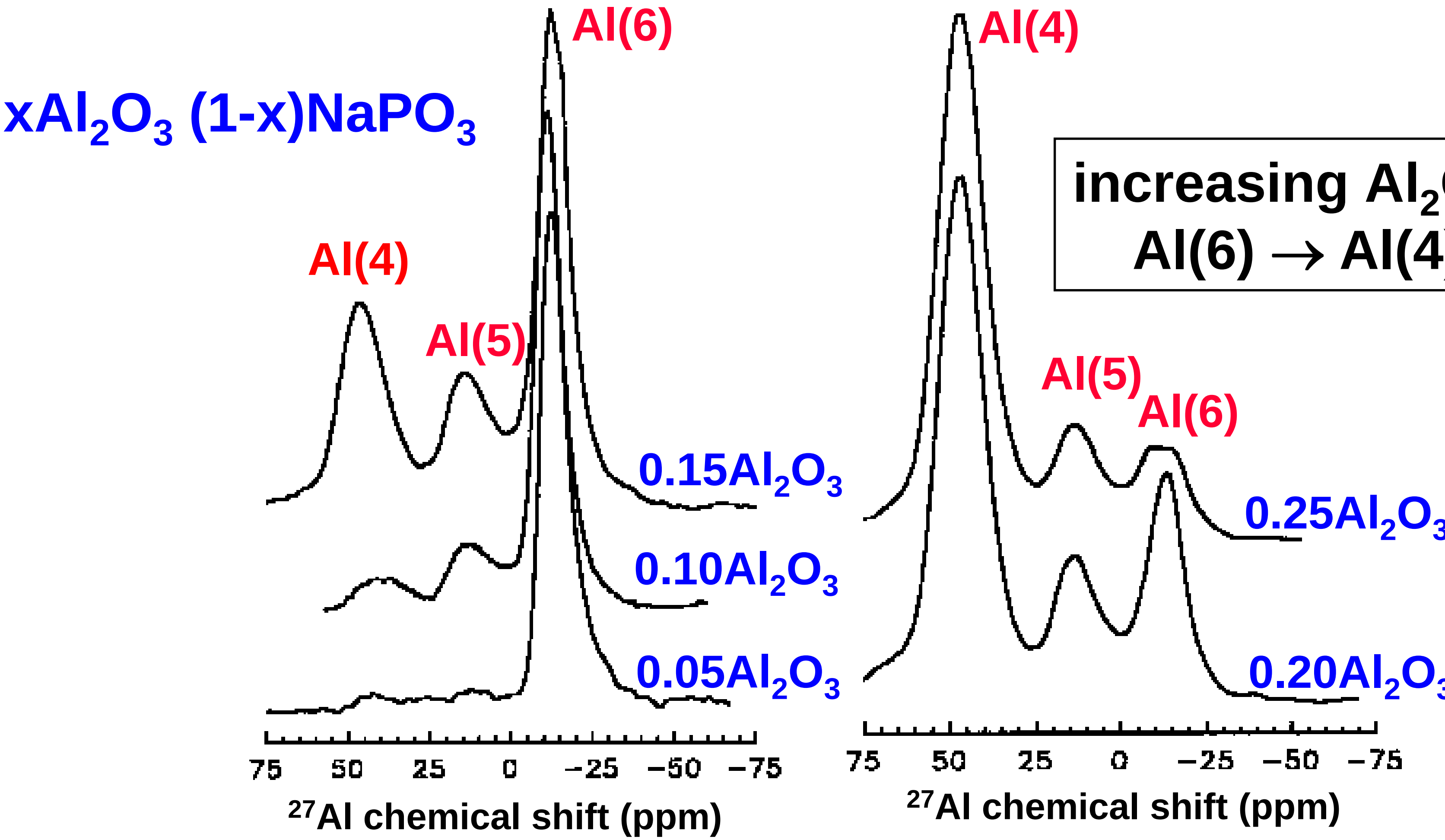
We Have Examined a Variety of Sodium Aluminophosphate Glasses



'basic' compositions exhibit breaks in property trends.



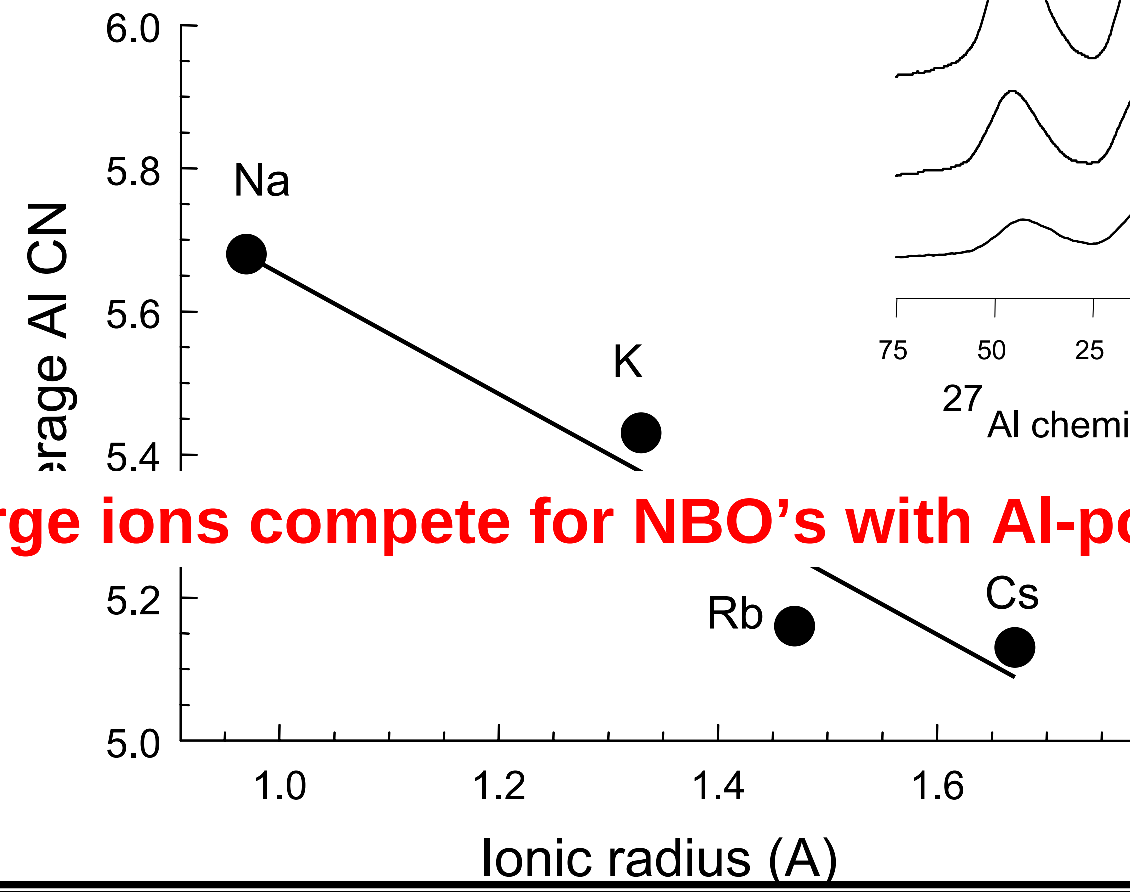
^{27}Al MAS NMR Provides a Structural Explanation for the Composition/Property Behavior

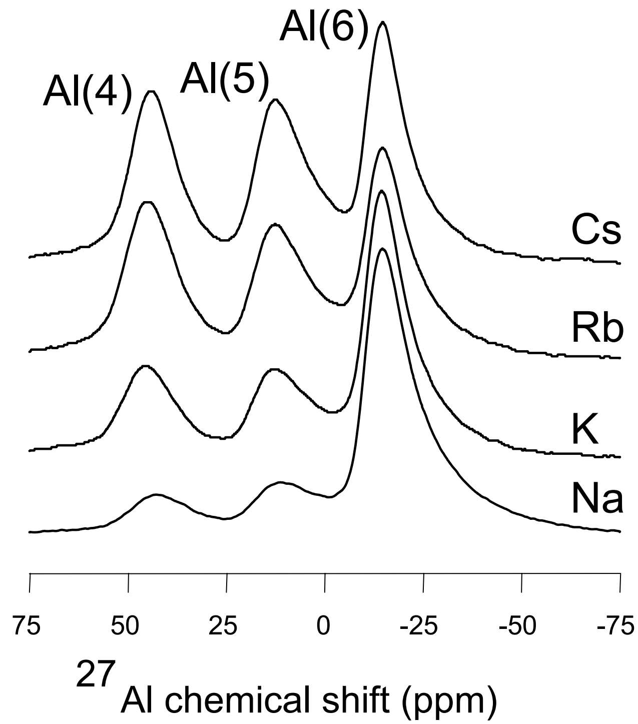


increasing Al_2O_3:
Al(6) → Al(4)

Al-Coordination Depends on the Modifier

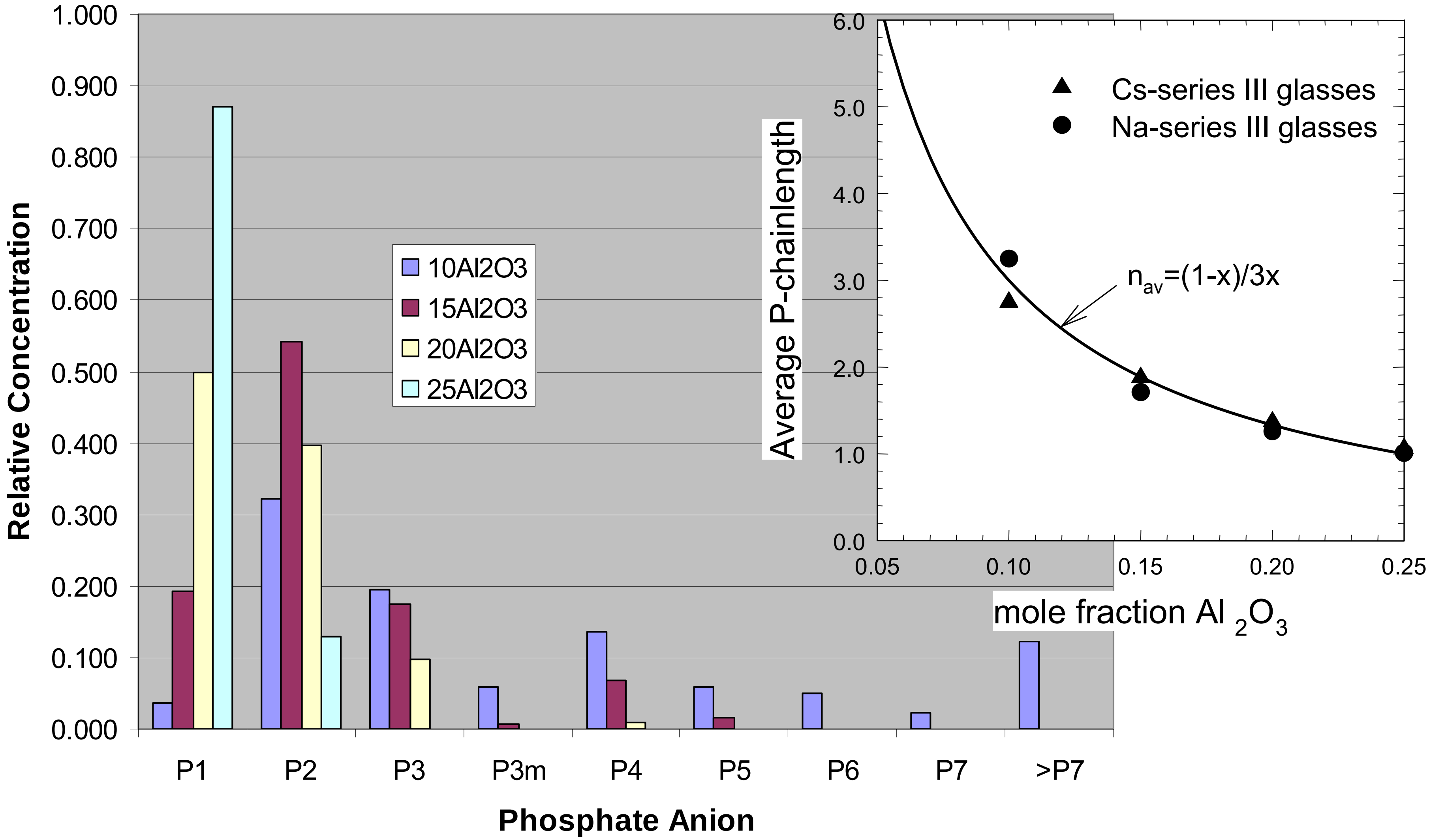
$10Al_2O_3 \cdot 90RPO_3$ glasses



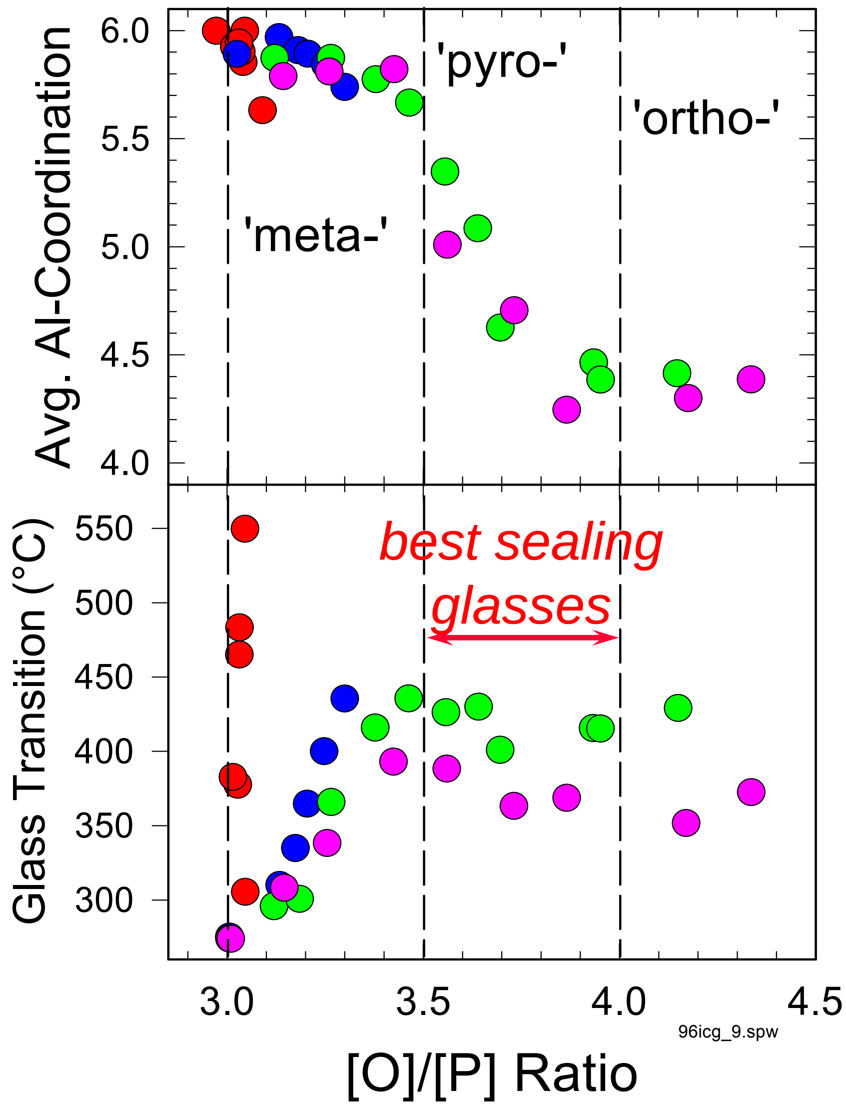


Do large ions compete for NBO's with Al-polyhedra?

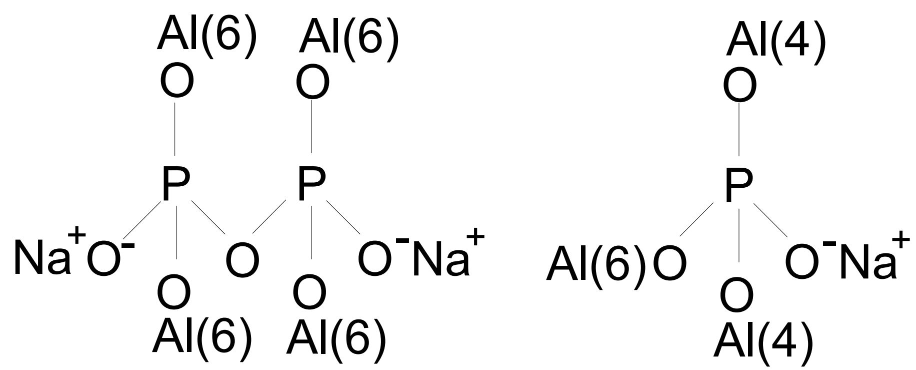
Chromatography Reveals that Alumina Reduces the Average Phosphate Chain-Length



Al-Coordination and Glass Properties Depend on the Phosphate Chain Length

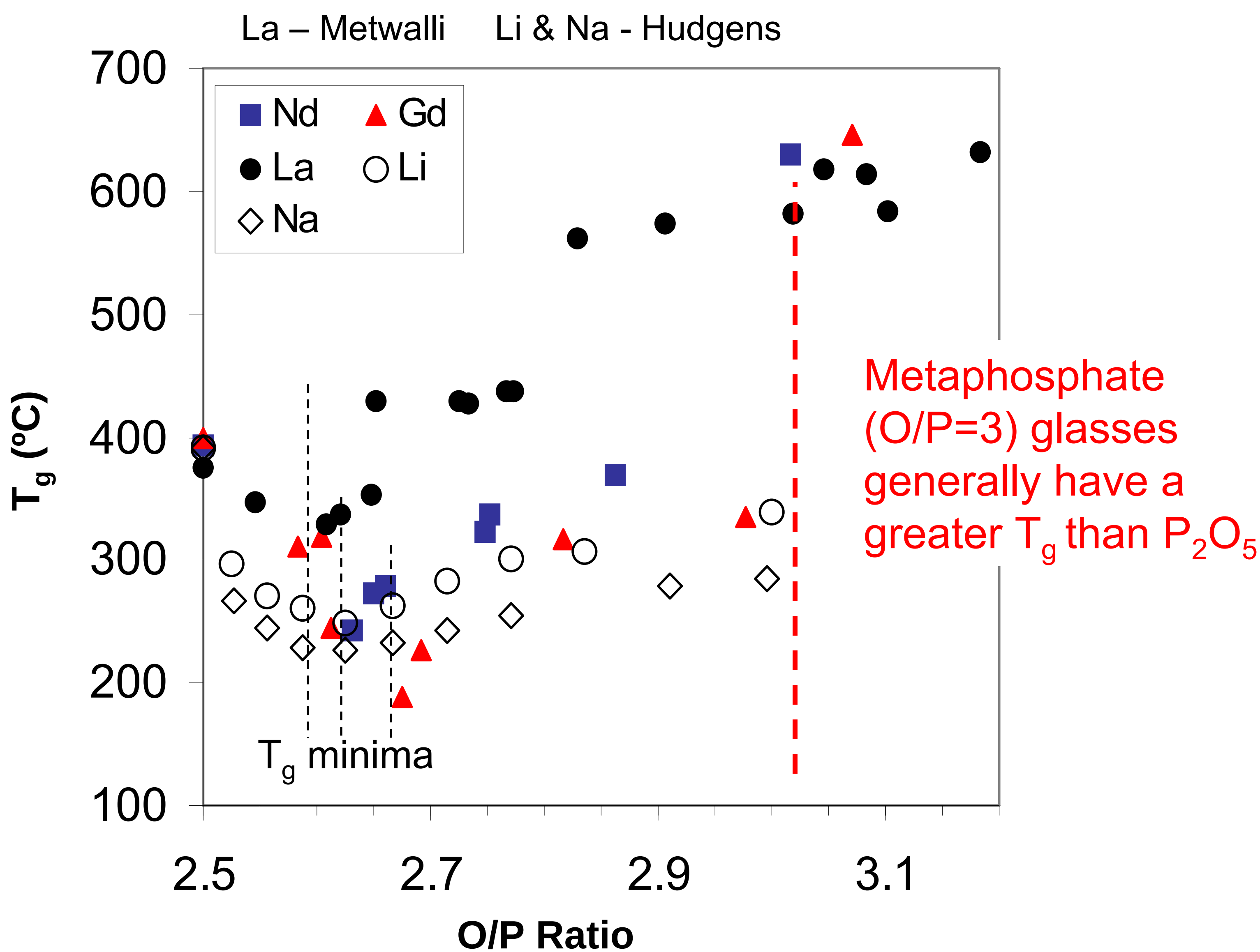


Al coordination changes to maintain a neutral aluminophosphate network

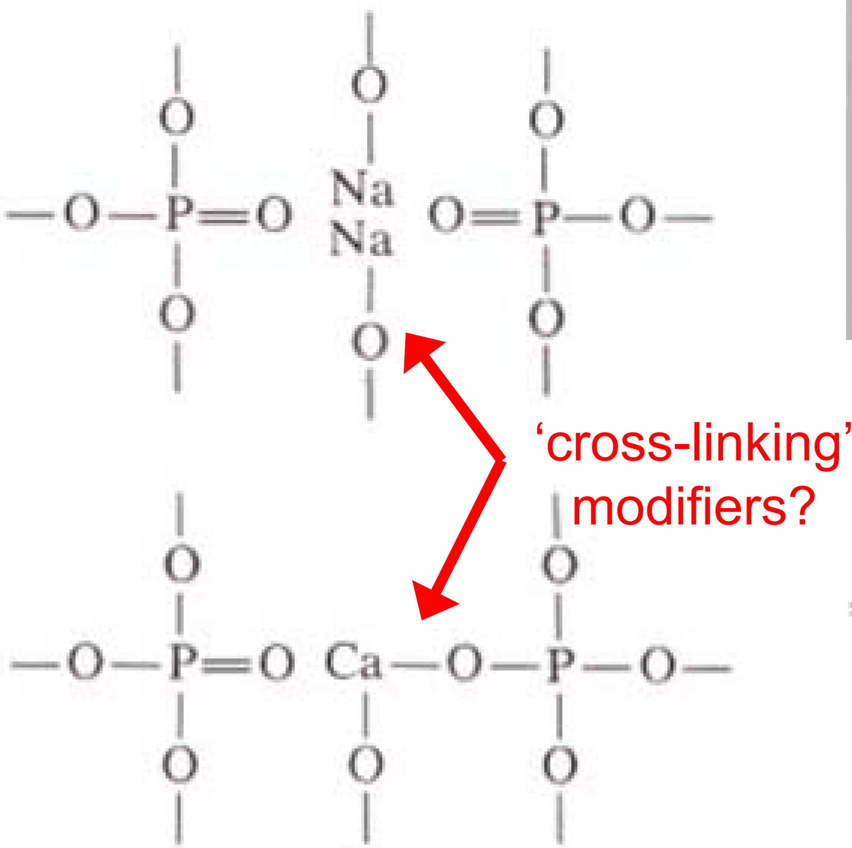


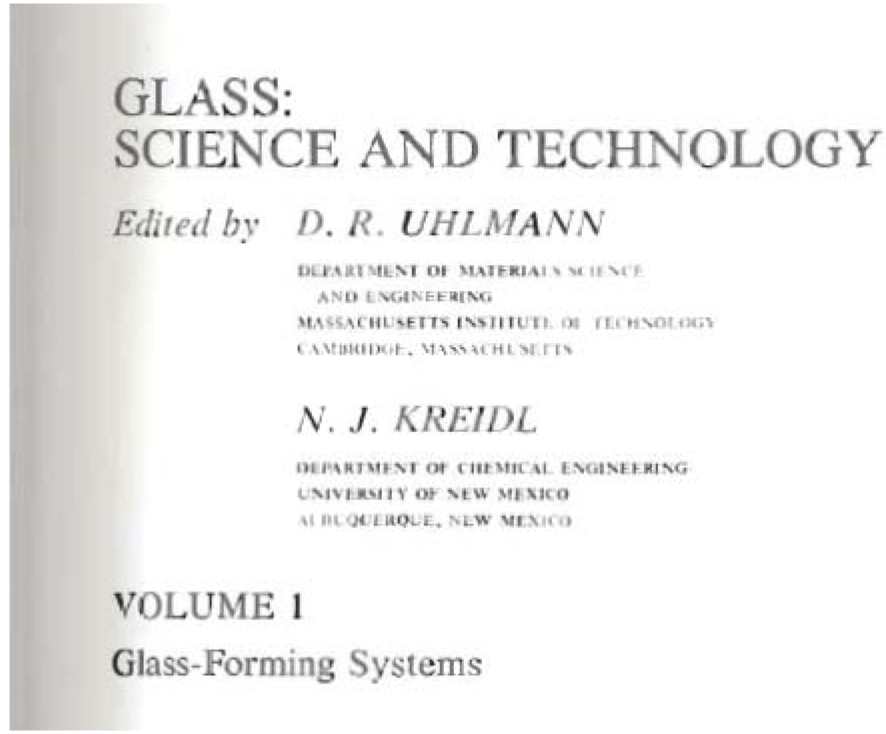
'pyrophosphate' **'orthophosphate'**

Ultraphosphate Glasses Exhibit T_g Minima



Kreidl Recognized the Effects of Modifiers on the Properties of Phosphate Glasses

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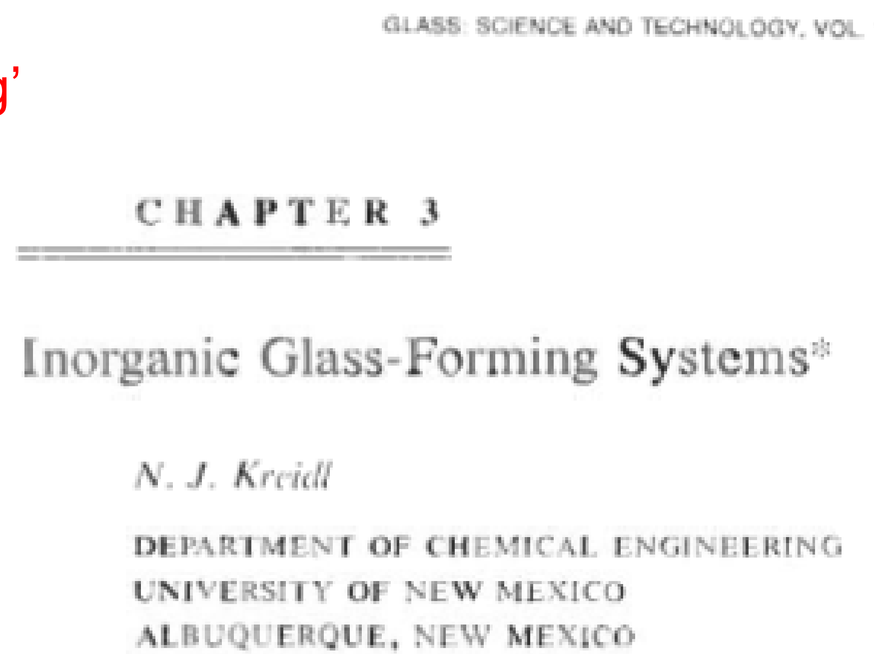
VOLUME 1
Glass-Forming Systems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CHAPTER 3

Inorganic Glass-Forming Systems*

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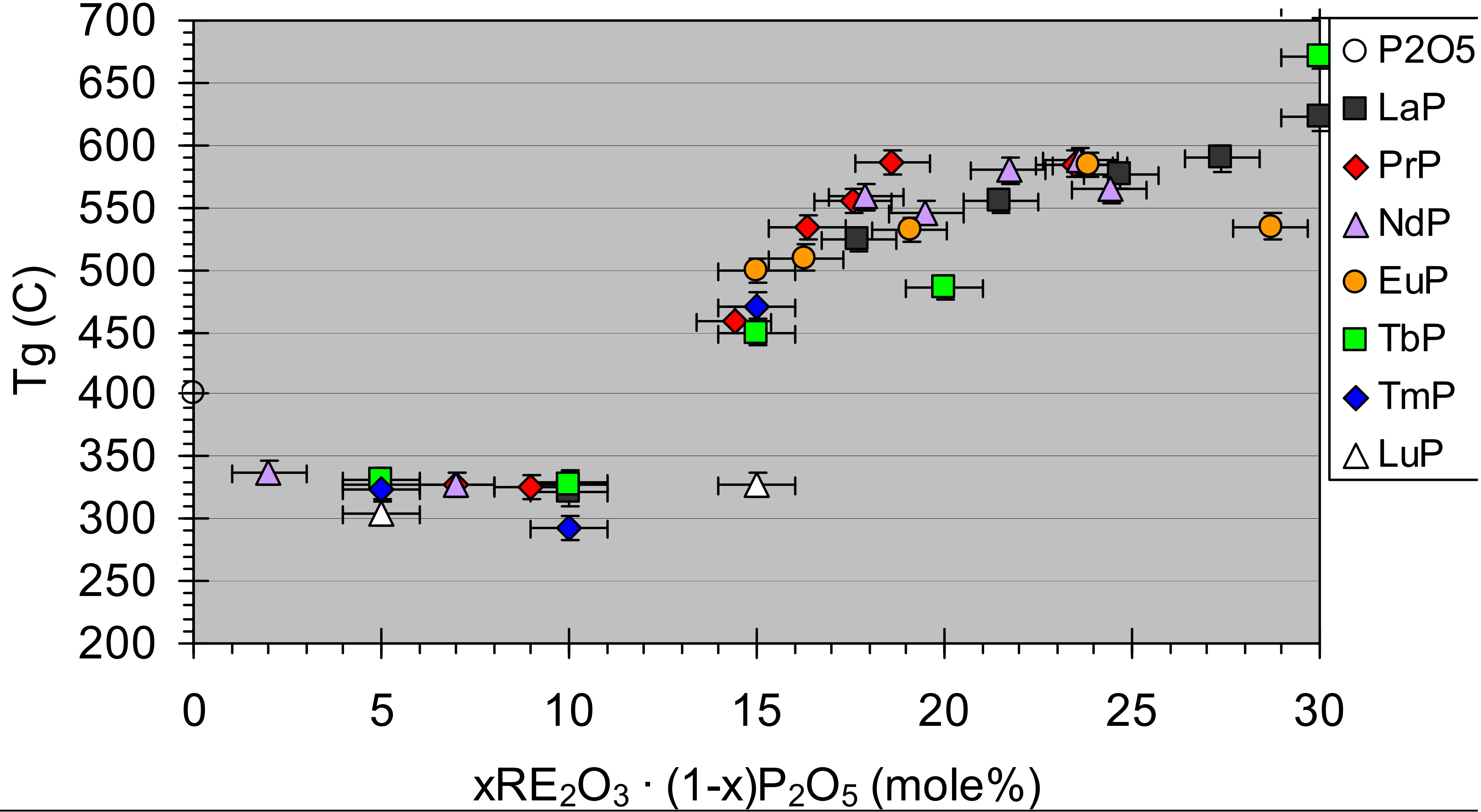
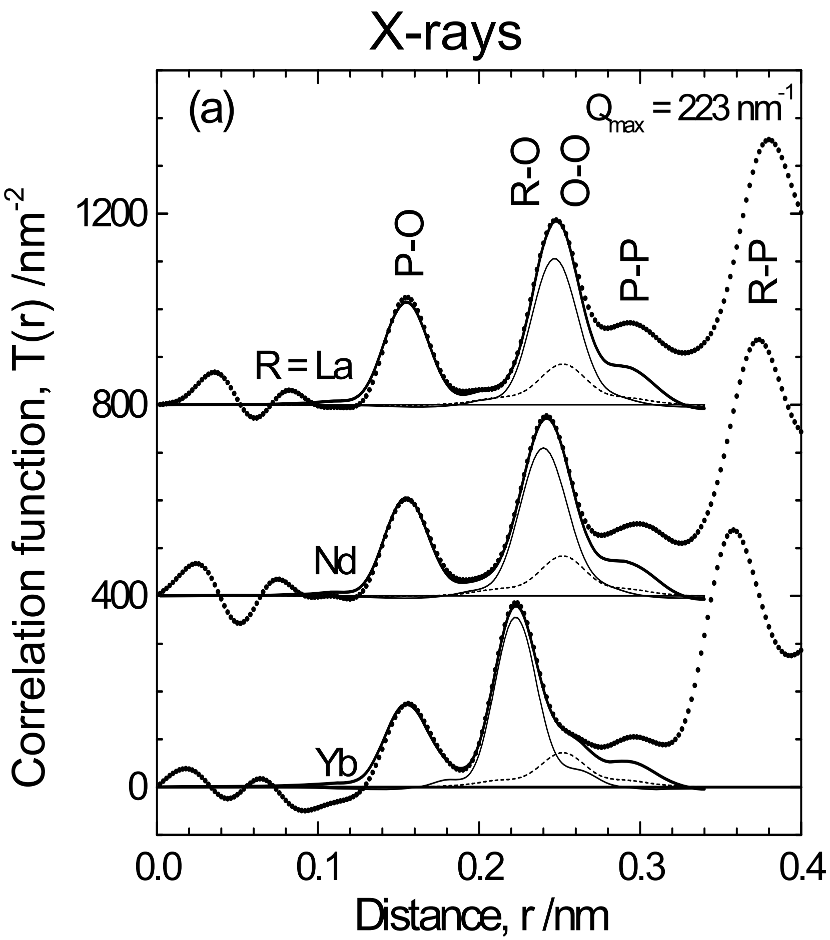
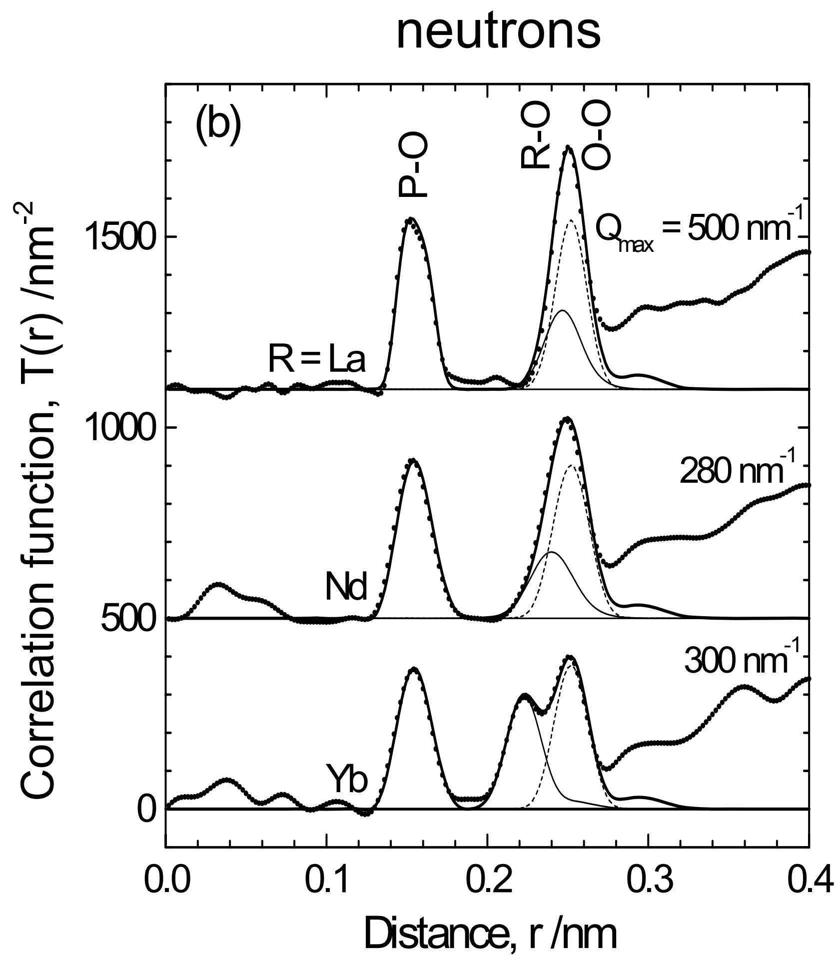
The properties of rare-earth phosphate glasses depend on composition



X-ray and neutron diffraction results are complementary

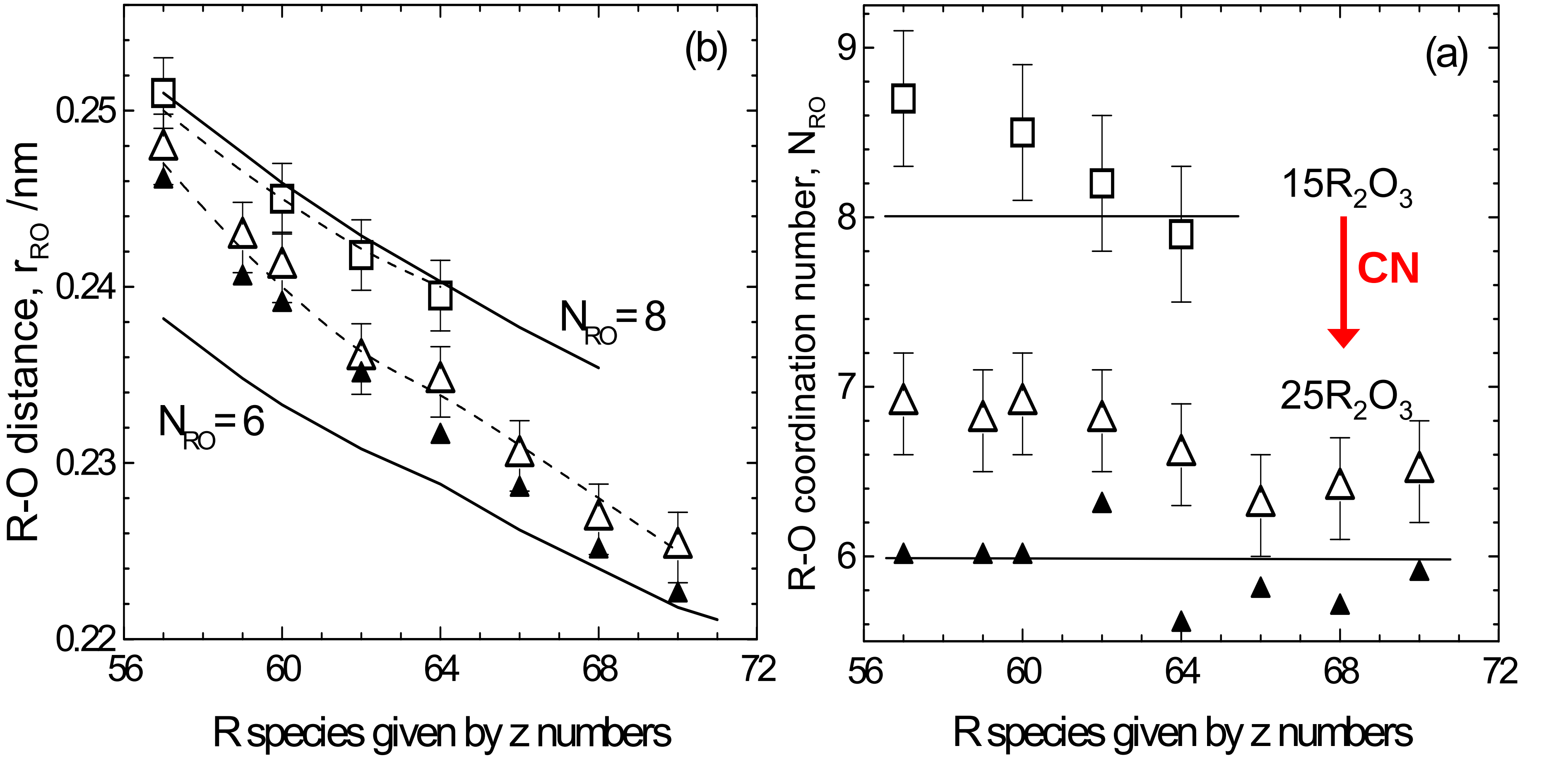




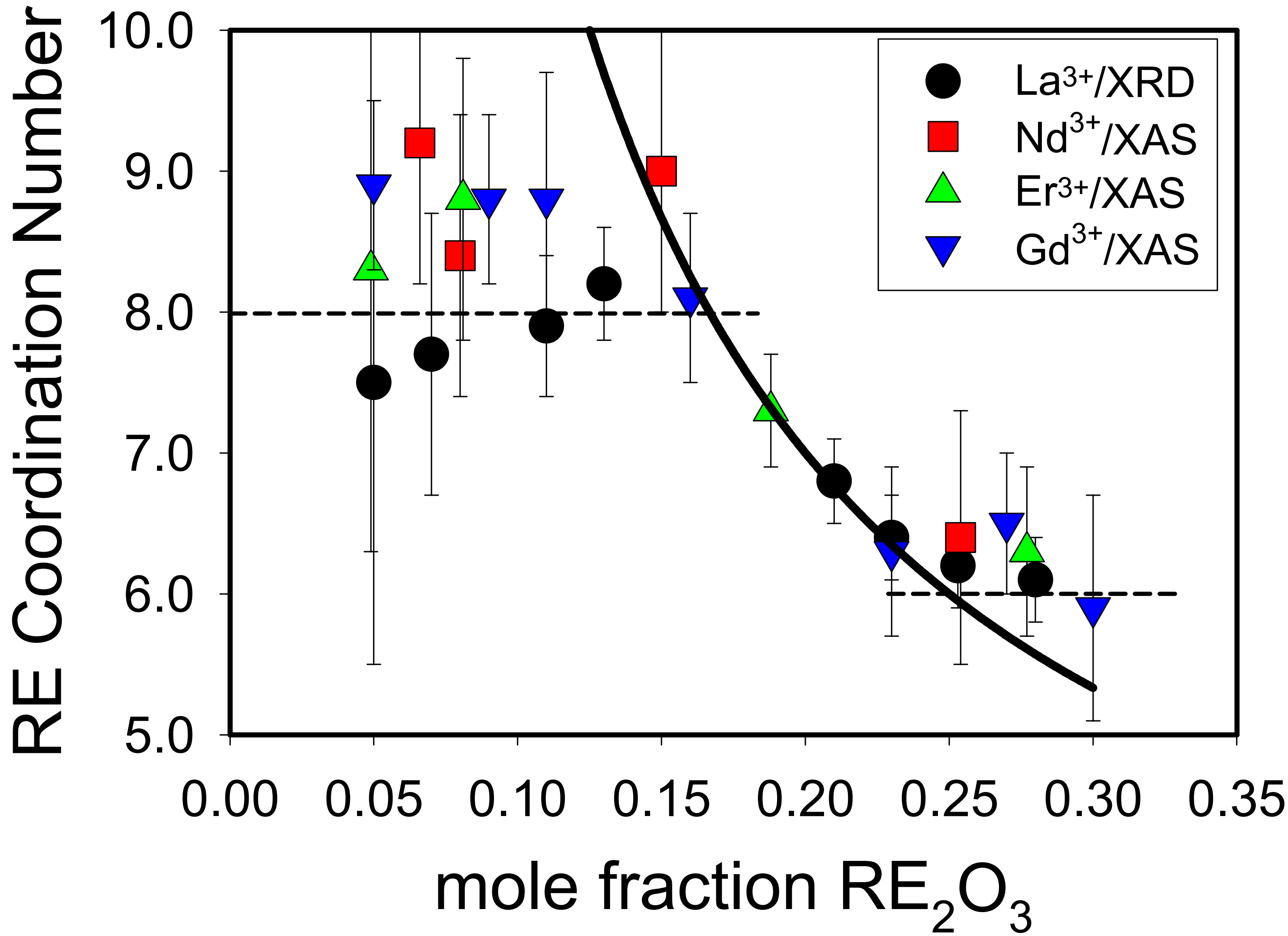
Separation of the R–O and O–O-contributions

N_{PO} with 3.7 - 4.1
P–P, R–P-distances estimated

'Lanthanide contraction' is evident in the rare earth phosphate glasses

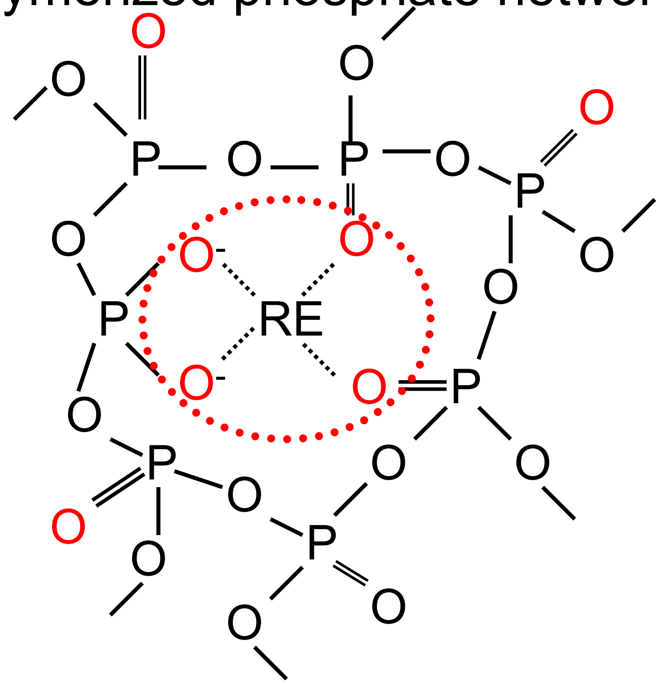


RE CN depends on composition

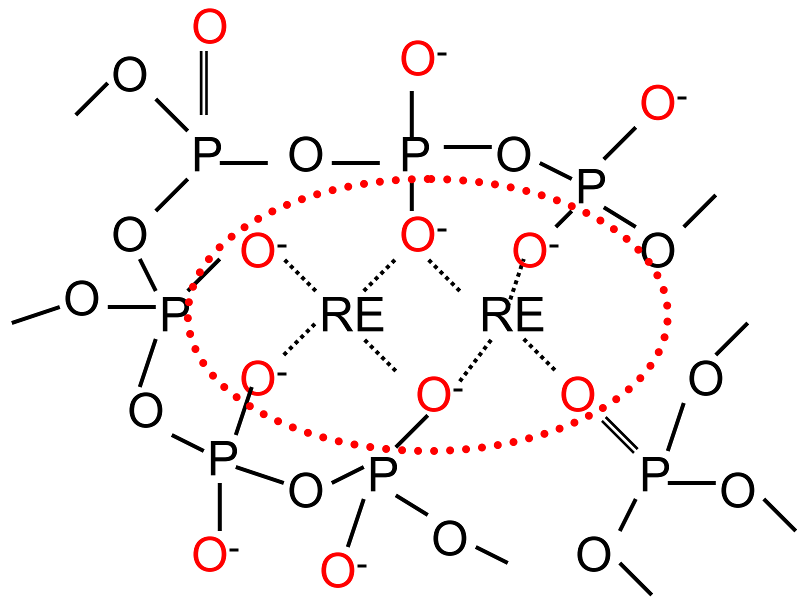


Modifier coordination requirements are satisfied by terminal oxygens

Low RE_2O_3: Isolated RE polyhedra
- [TO]/RE^{3+} > CN(RE^{3+}), (Hoppe, 1996)
- depolymerized phosphate network



High RE_2O_3: Linked RE polyhedra
- [TO]/RE^{3+} < CN(RE^{3+})
- ionic bridges between Q^2-tetrahedra



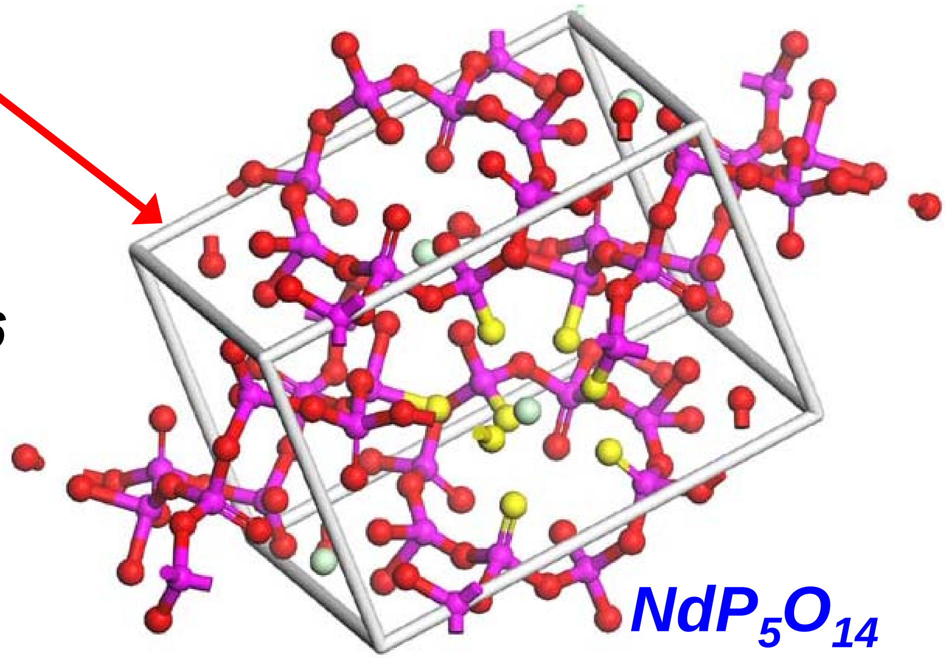
Rules for RE^{3+} incorporation into phosphate glass structures

1. ***RE coordination environments include all terminal oxygens: Q^3 P=O & Q^2 $P\text{-}O^-$***
2. ***RE-O-RE clusters to be avoided***
3. ***RE CN is consistent with Pauling's Rules: Minimum CN~6***

Hoppe (1995): Metal coordination environment depends on the number of terminal oxygens per metal ion.

xRE_2O_3 $(1\text{-}x)P_2O_5$ glasses

$TO/RE^{3+} = (1+2x)/x$

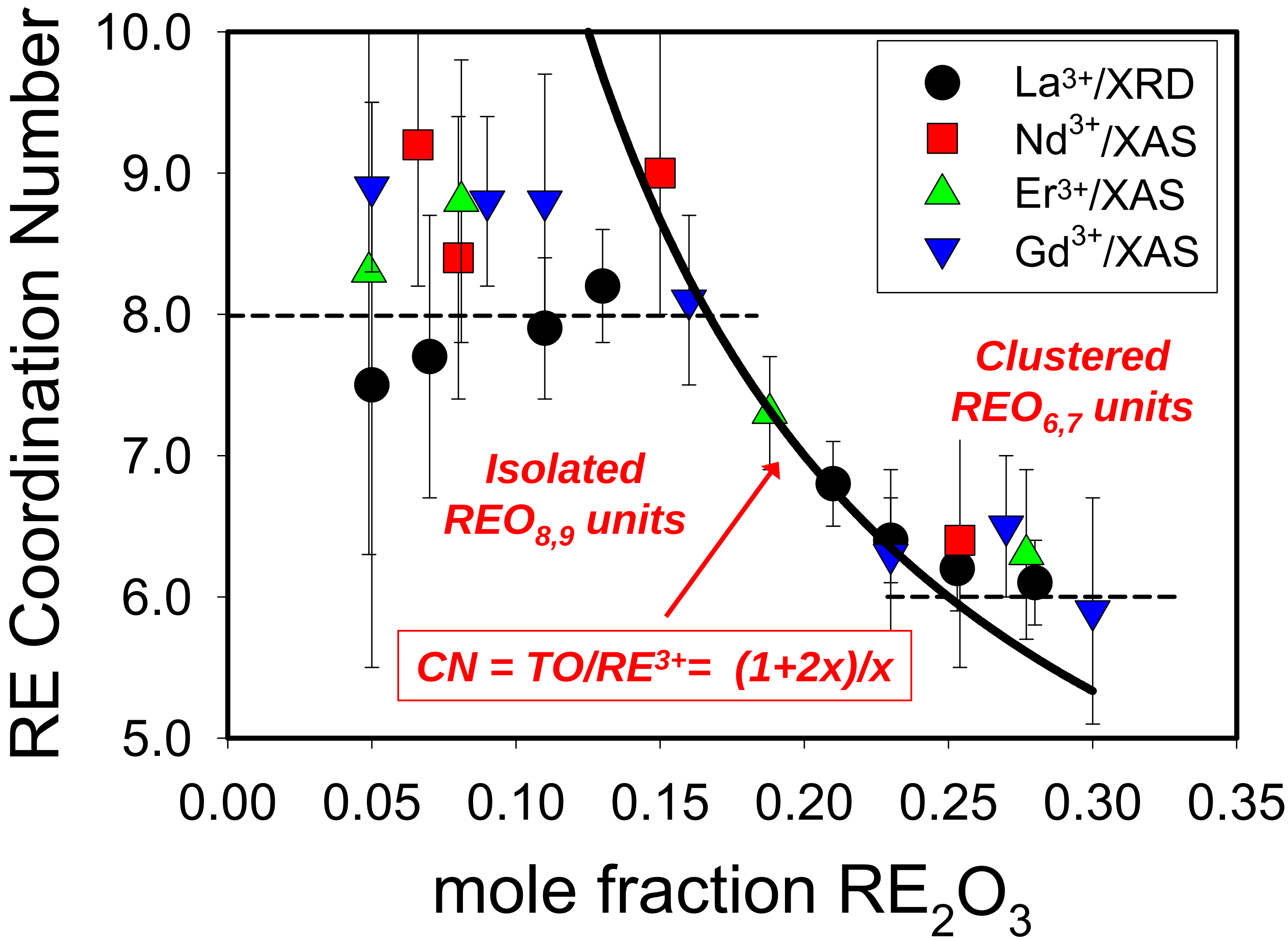


NdP_5O_{14}

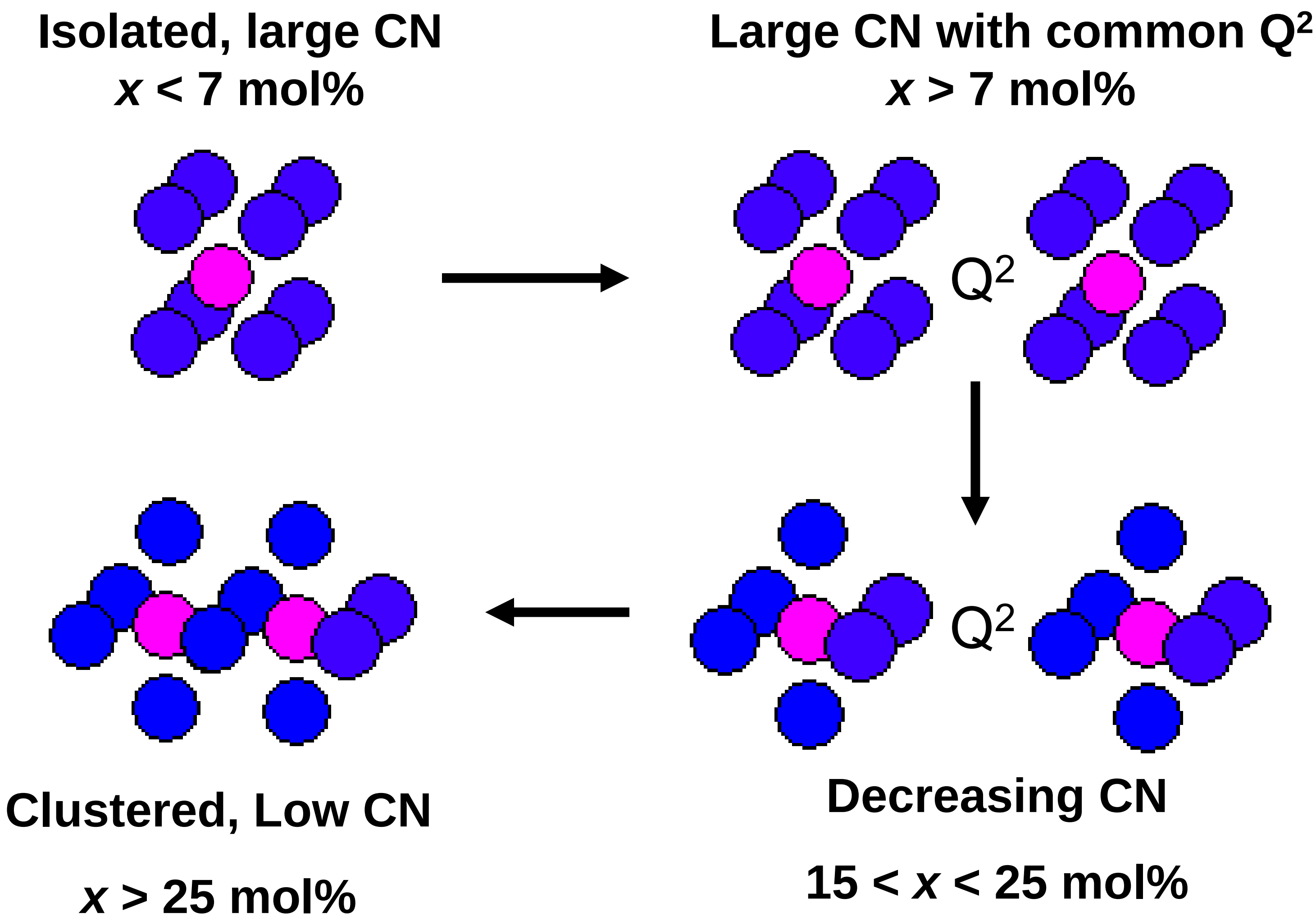
Isolated NdO_8 species

- **P-O-Nd bonds to Q^2 and Q^3 tetrahedra**

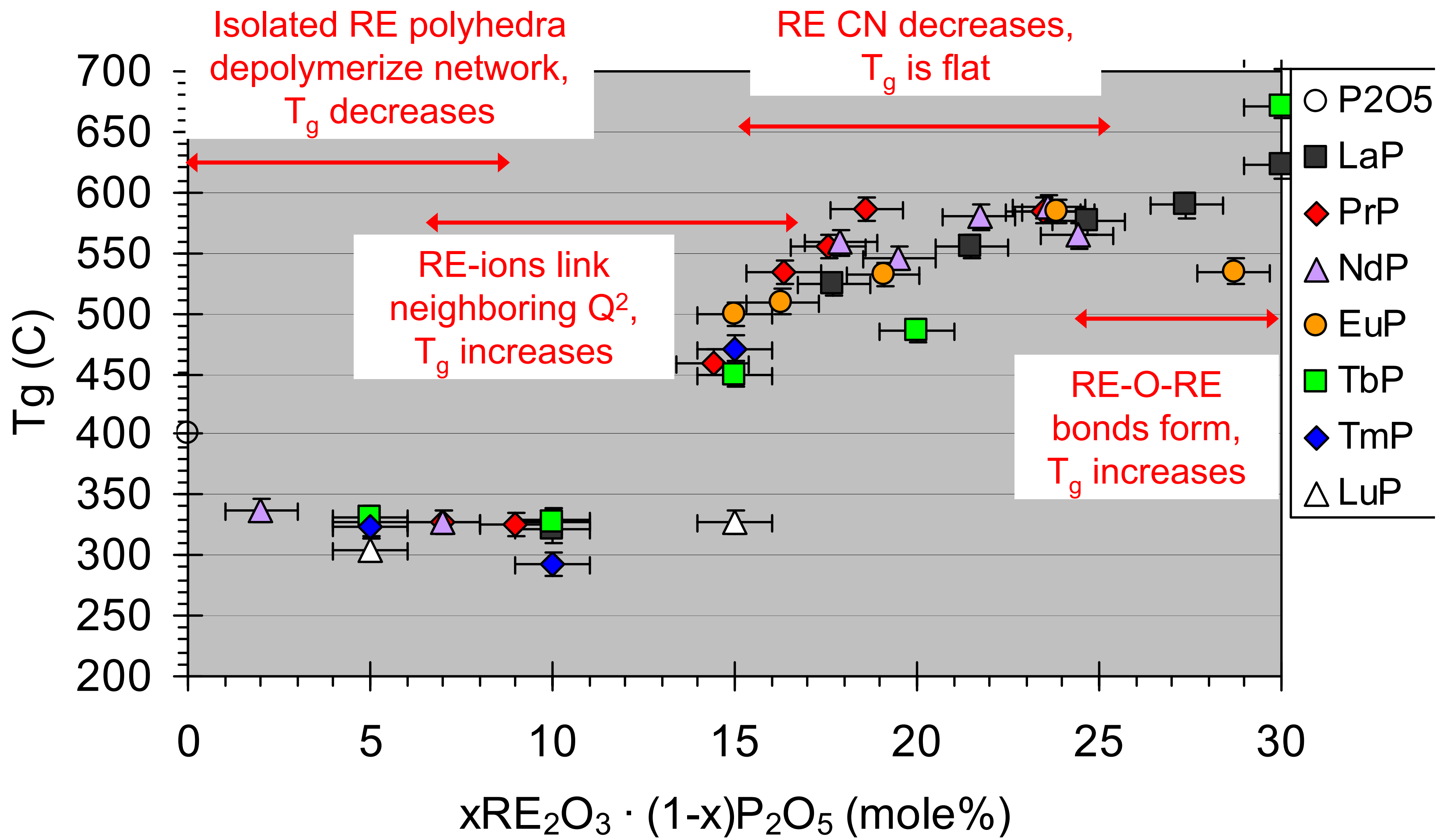
RE CN decreases to avoid RE clusters



Summary of the RE coordination environments in phosphate glasses



The structural model helps explain the effects of composition on T_g



PbO-free low T_g glasses have many possible applications

- Low temperature processing of optical glasses
- Low temperature sealing glasses

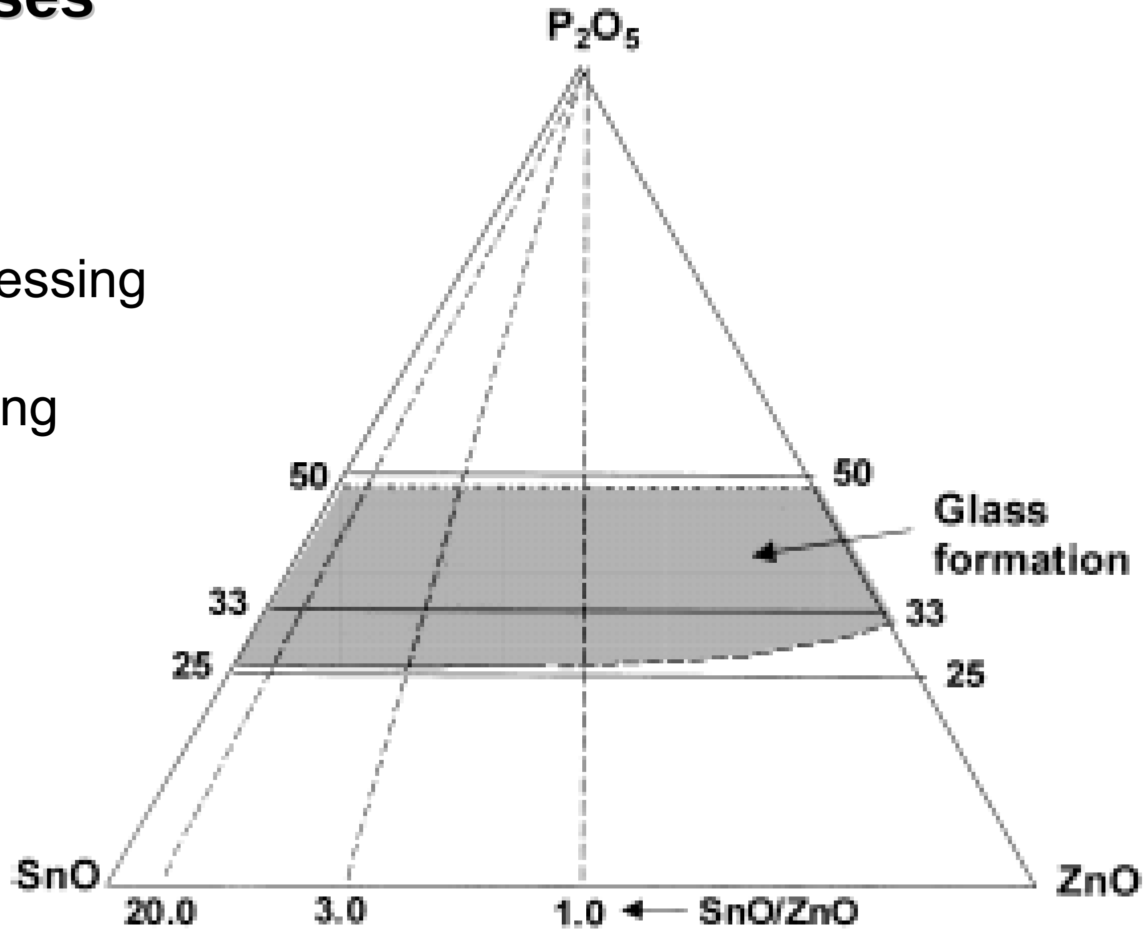


Fig. 1. Glass formation region in SnO–ZnO–P_2O_5 ternary.

Morena, JNCS, 2000

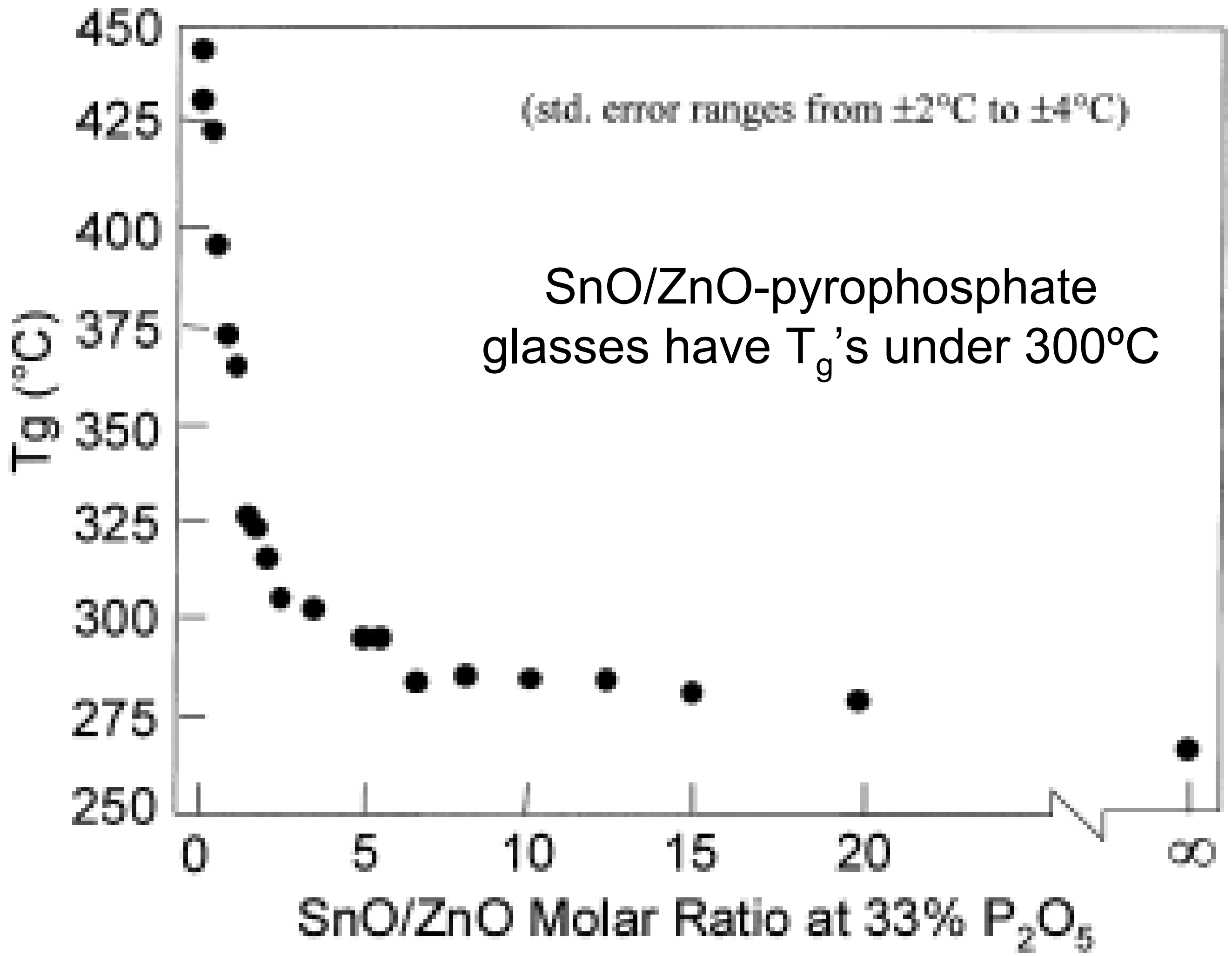
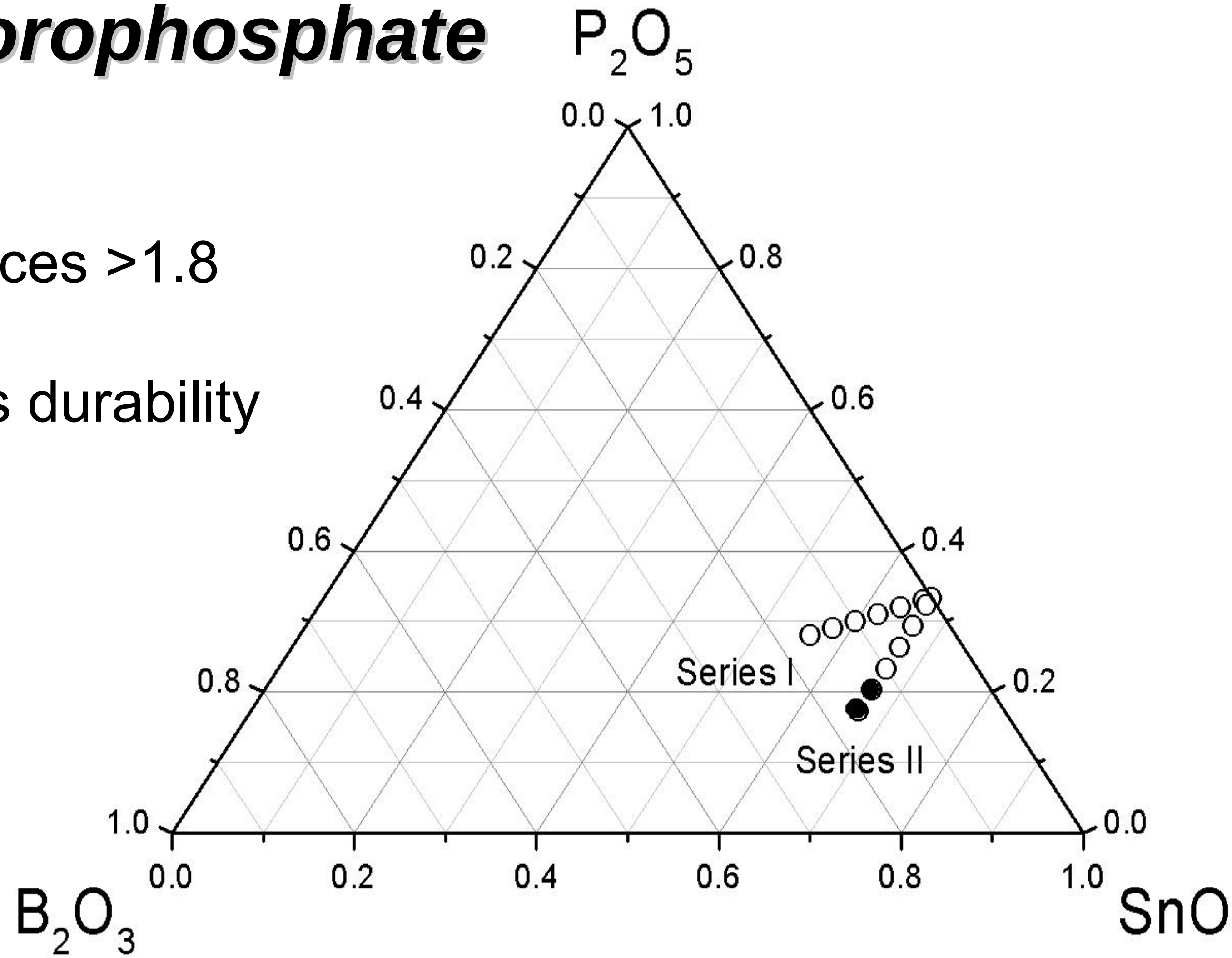


Fig. 2. Glass transition temperature versus SnO/ZnO at 33% P_2O_5.

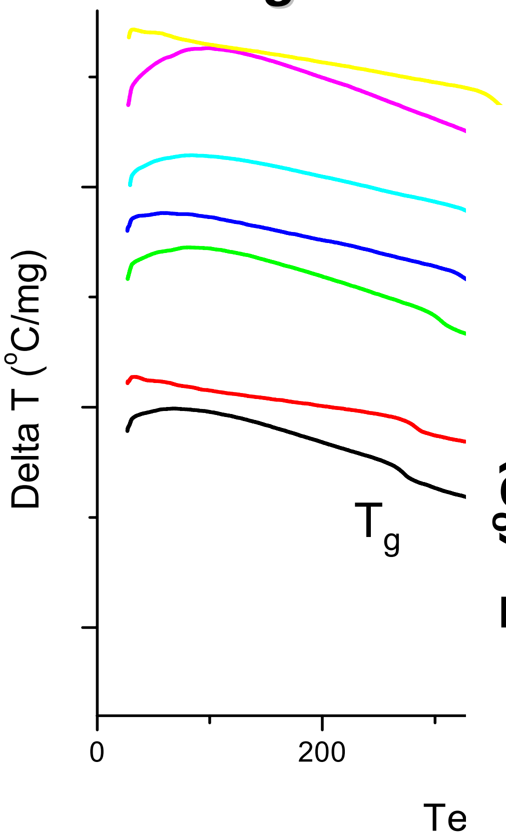
Morena, JNCS, 2000

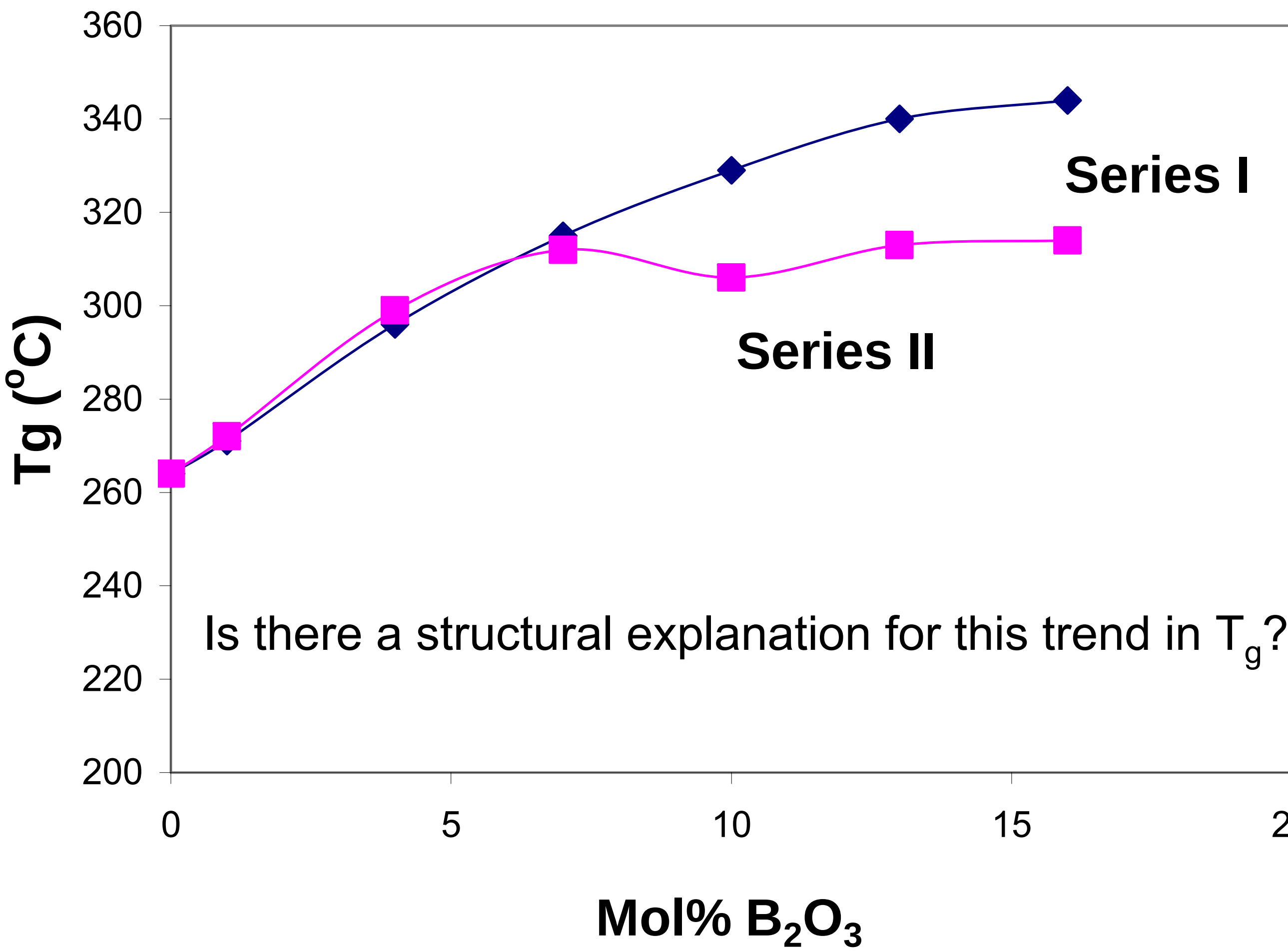
We are evaluating glasses in the Sn-borophosphate system

- Refractive indices >1.8
- T_g<325ºC
- Good aqueous durability

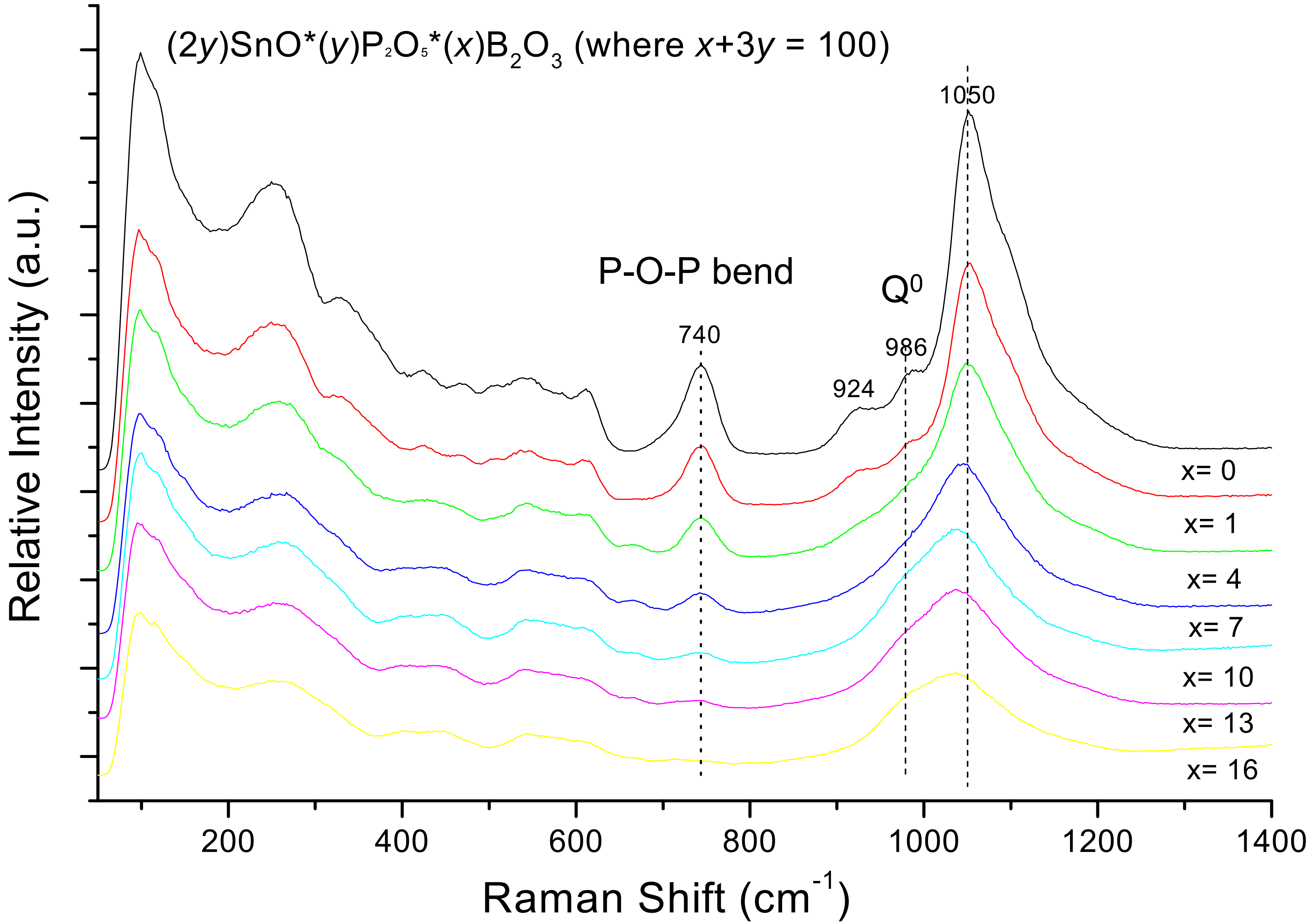


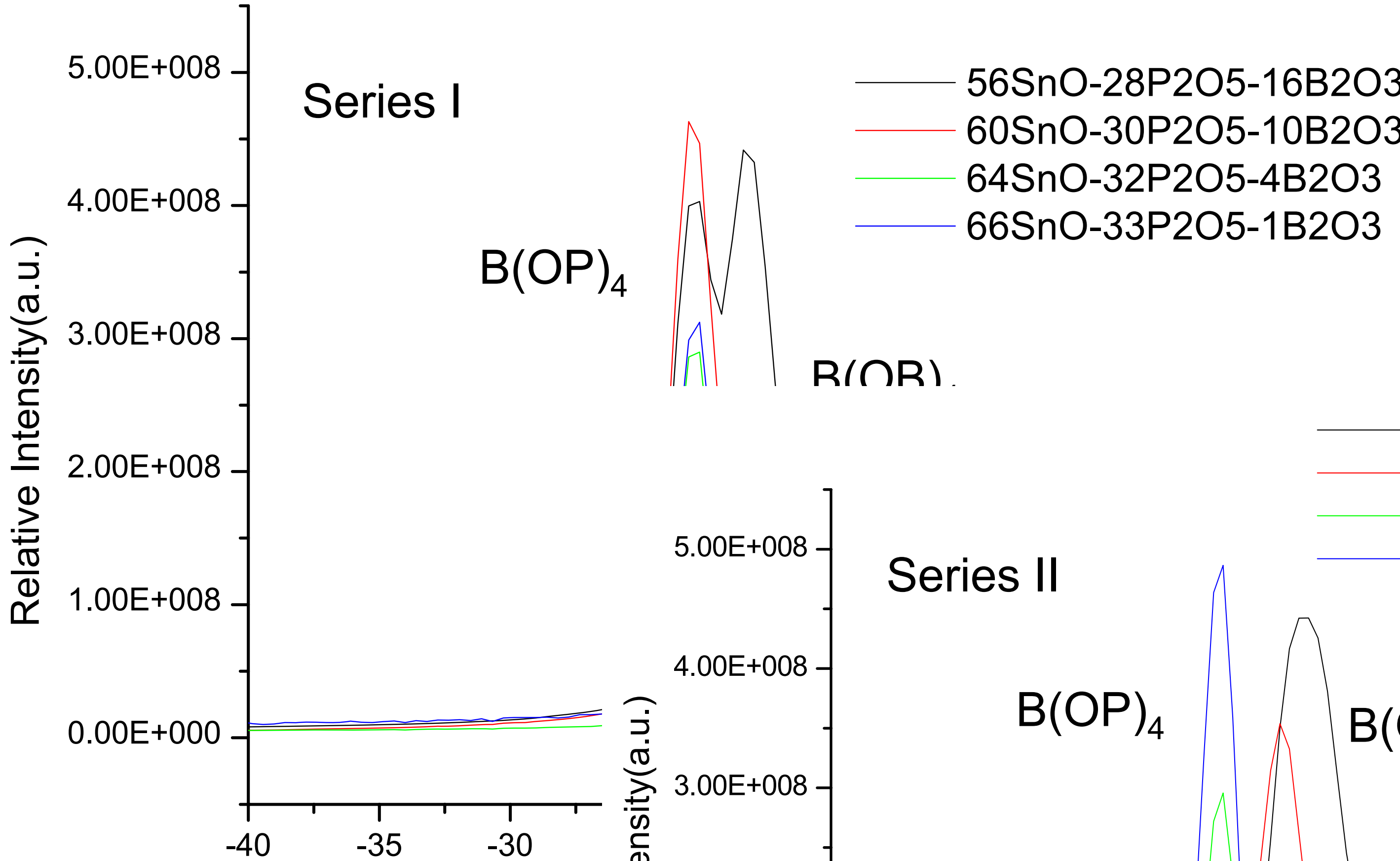
T_g increases with B_2O_3-additions

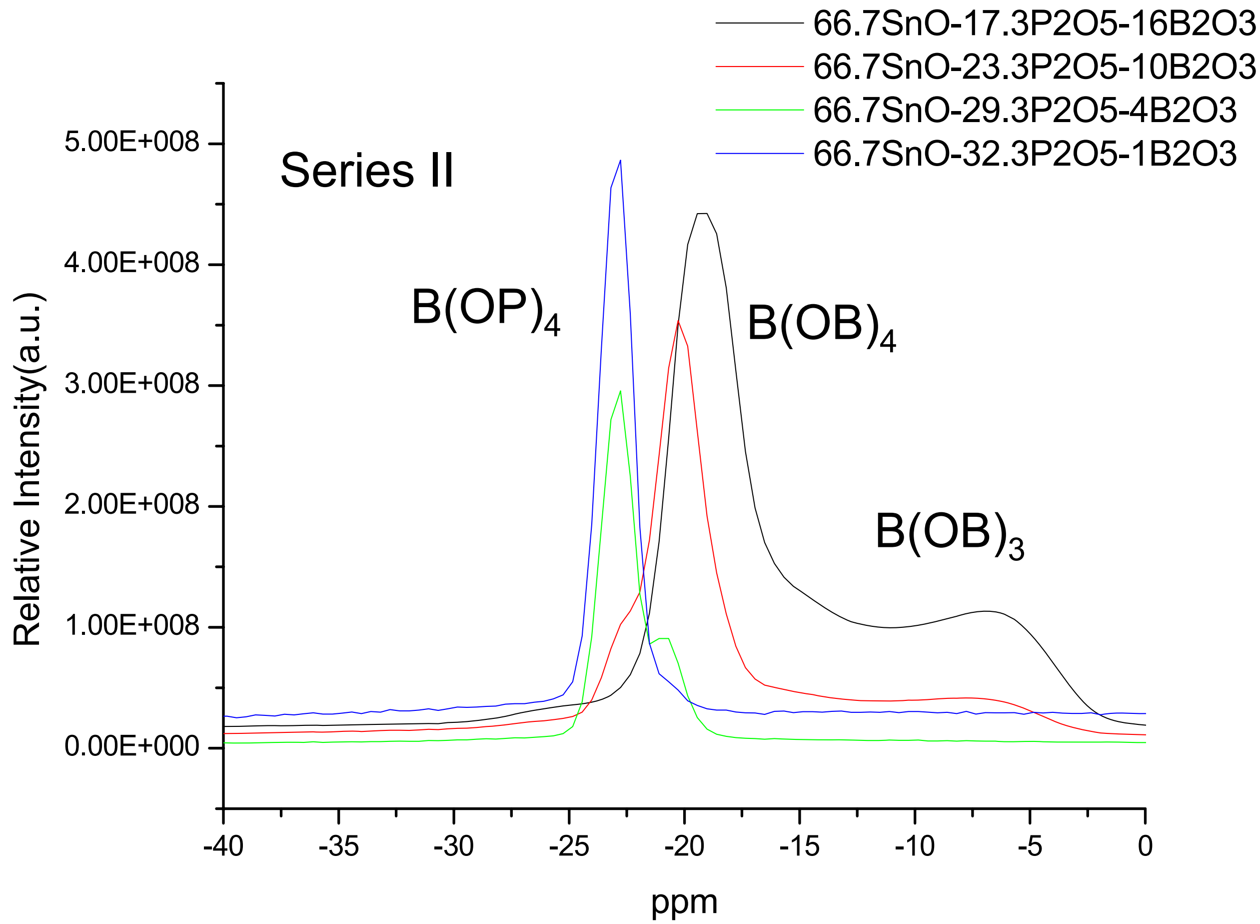




Raman spectra indicate that the phosphate network is depolymerized by borate additions







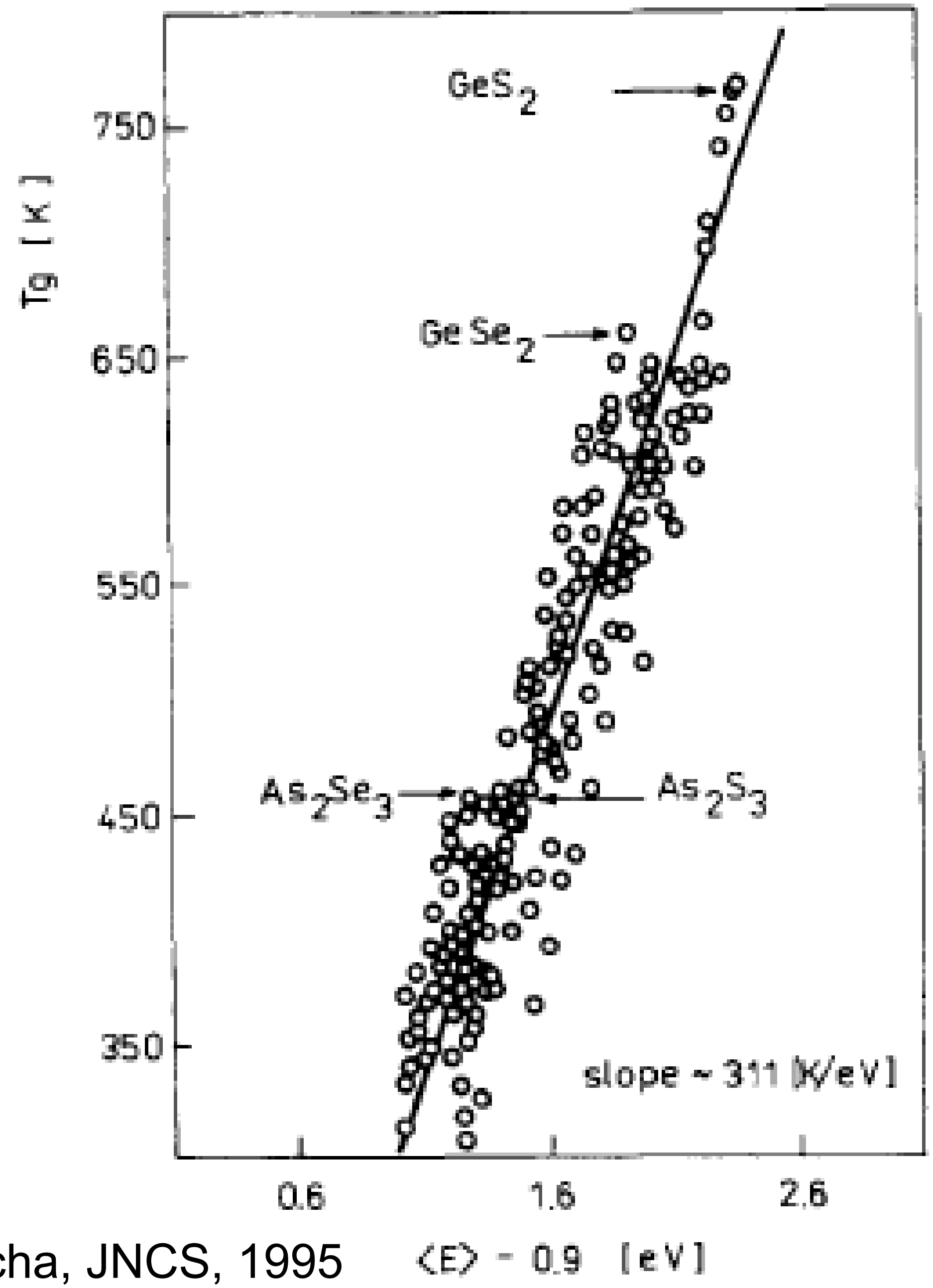
^{11}B NMR provides an explanation for the T_g trends

Example 2: Chalcogenide Glasses

Tg's depend on average bond strength

Heteropolar Pauling bond energies:

As-Te	1.41eV	As-As	1.38eV
As-Se	1.8eV	Sb-Sb	1.31eV
Ge-Se	2.12eV	Ge-Ge	1.63eV….



Tichy and Ticha, JNCS, 1995

The T_g's of covalent chalcogenide glasses depends on average CN

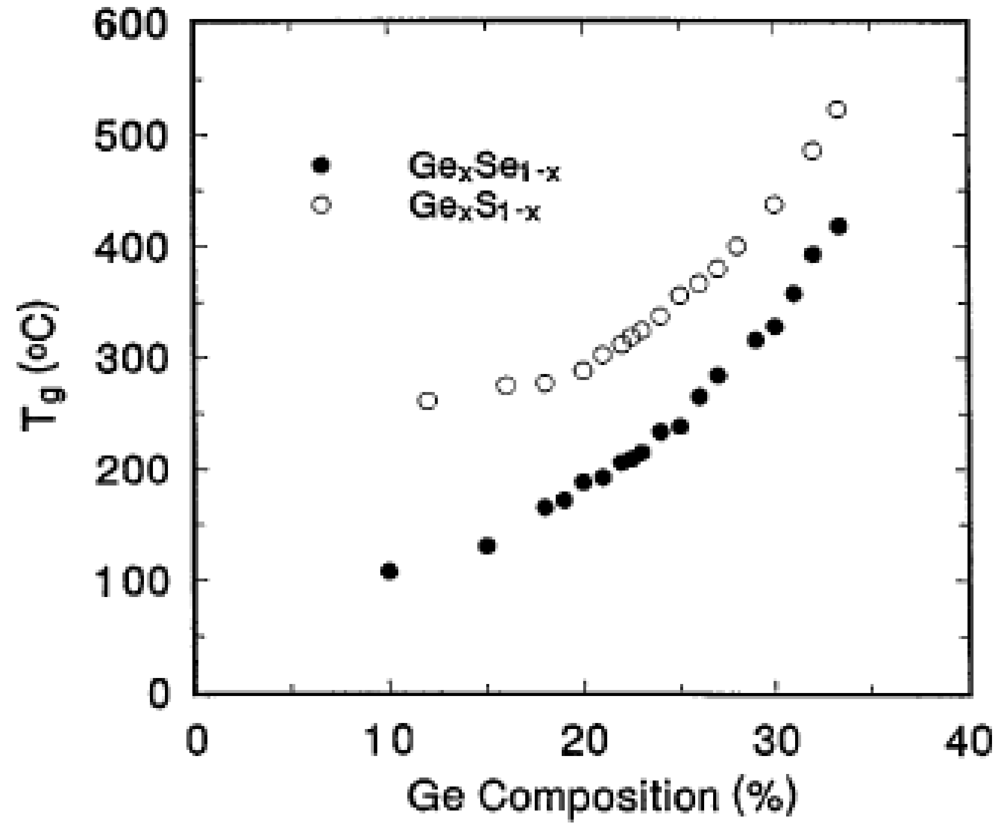


FIG. 1. T_g of Ge_xS_{1-x} glasses (top) from DSC measurements taken at a 20 K/min scan rate, and of Ge_xSe_{1-x} glasses (bottom) from MDSC measurements at a scan rate of 3 K/min and a modulation of ±1 K/100 sec.

$CN = \Sigma x_i \cdot CN_i$

CN(Ge)=4
CN(Se)=2

Increasing CN, increasing T_g

Feng et al, PRL, 1997

Properties are considered with respect structural rigidity

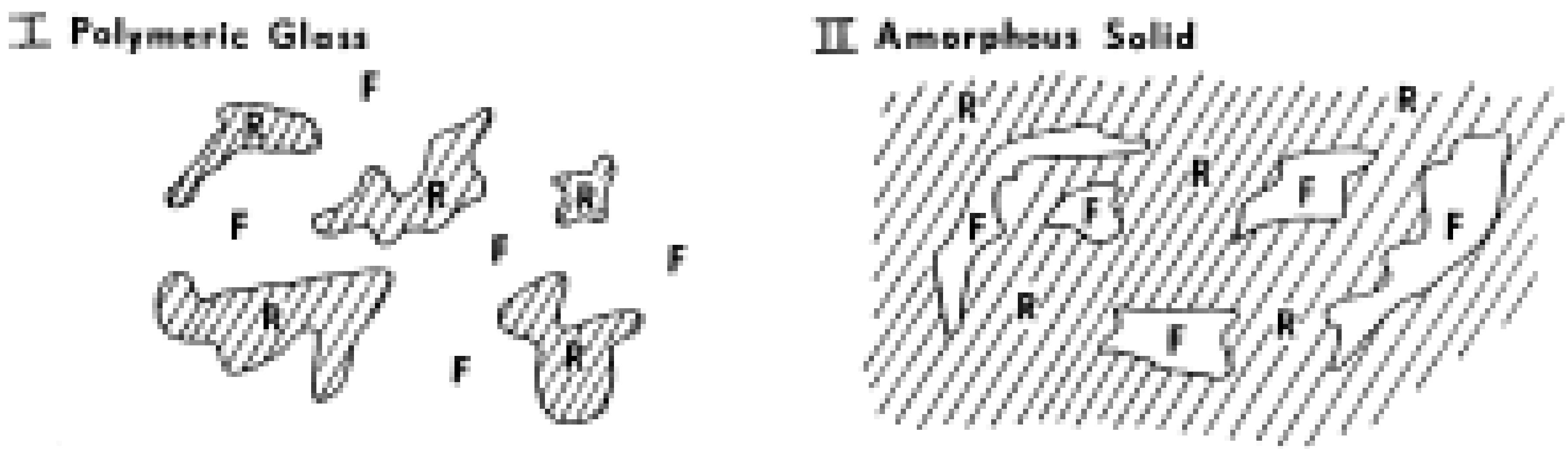


Fig. 1. The Rigid and Floppy regions in polymeric glass and amorphous solid. (After Thorpe [3].)

Average coordination number defines network rigidity

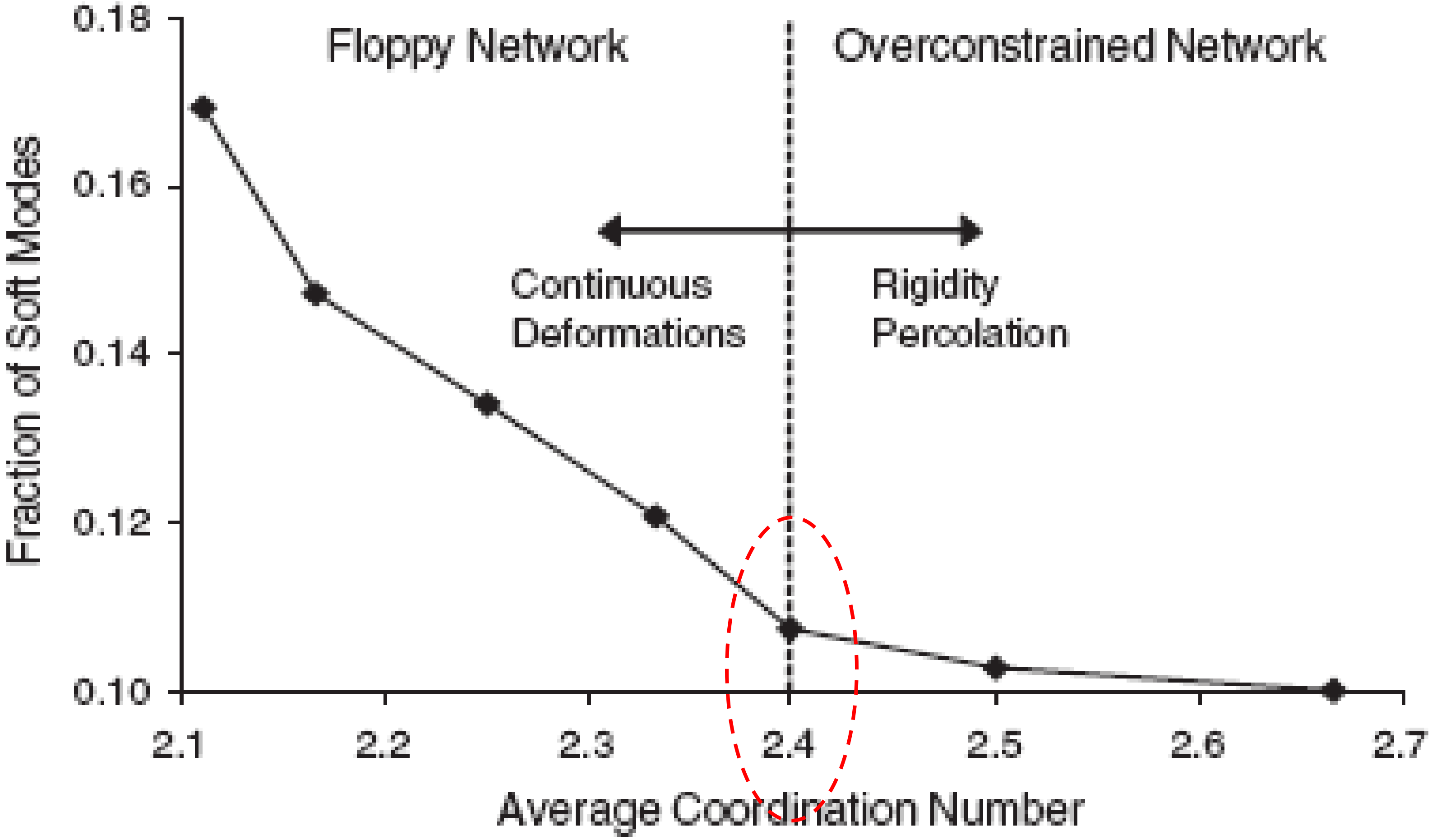


Fig. 2. Fraction of soft modes as a function of average coordination number for bulk germanium–selenium glasses.

Mauro and Varshneya, JACerS, 2007

'Something' happens near <r>=2.4-

Other properties are sensitive to average CN

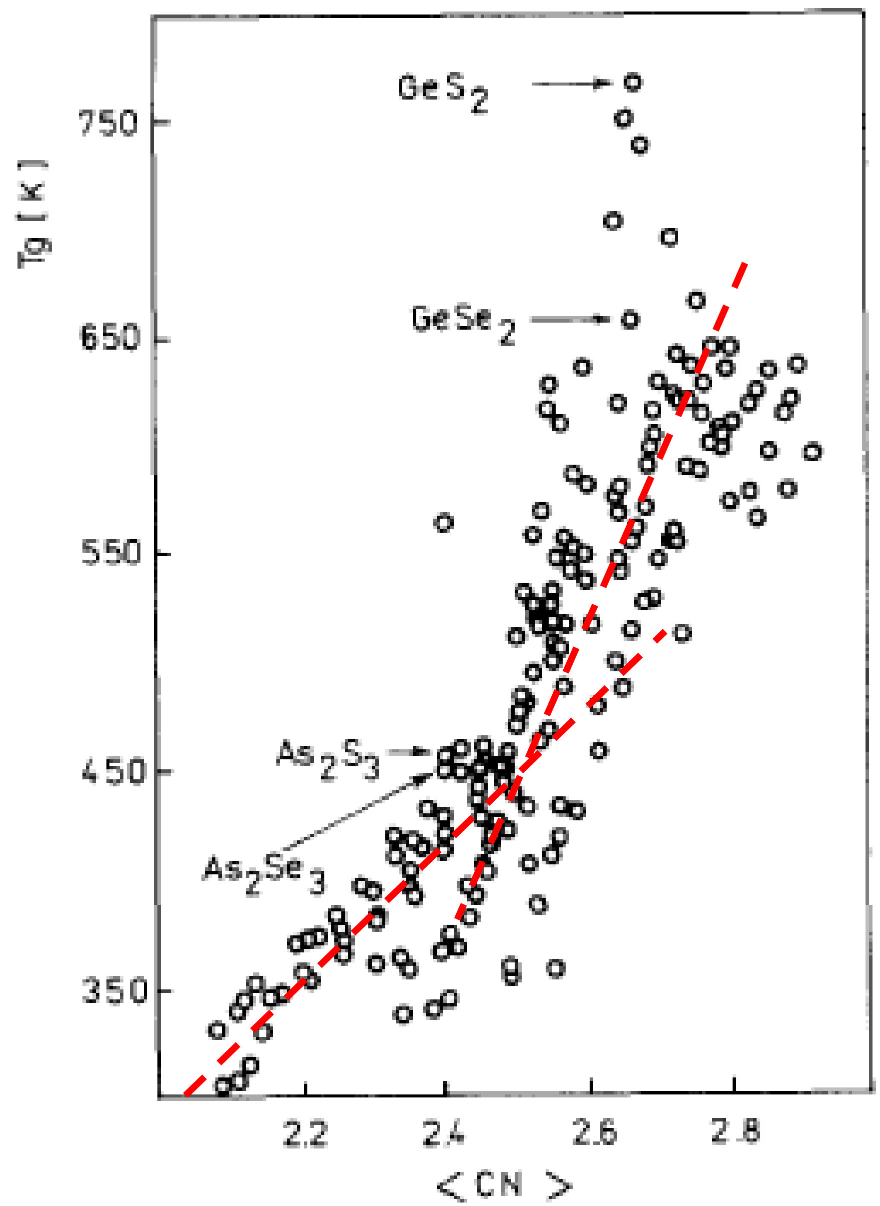


Fig. 2. The variation of T_g with the mean coordination number, ⟨CN⟩. For data sources, see Table 1.

Tichy and Ticha, JNCS, 1995

Summary of the Glass Transition

- Kinetic vs. thermodynamic transition?
- Depends on thermal history and experimental details
- Sensitive to structural details
- Important for many engineering applications

Best Wishes from the Glass Weenies at Missouri S&T!