Web Course
Physical Properties of Glass

Glass Transformation-Range Behavior- Odds and Ends

Richard K. Brow
Missouri University of Science & Technology
Department of Materials Science & Engineering
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...

• 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

A single fictive temperature is insufficient to describe glass properties and structure
The ‘memory effect’ is a consequence of non-exponential relaxation.

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.

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

Figure 13-26. Room temperature refractive index – time ‘approach curves’ for BSC517. (After Spinner and Napolitano\(^{(25)}\).)
The ‘memory effect’ depends on fictive temperature history

Glass has a ‘memory’ of its most recent excursion through the transition range
• Multiple relaxation processes

Figure 13-28. Refractive index vs. time at crossovers A and D. (After Spinner and Napolitano\(^{25}\).)
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 \(\mu\)-region to \(\mu\)-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 $\approx$ 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.
Measurement of glass transition temperature by mechanical (DMTA), thermal (DSC and MDSC), water diffusion and density methods: A comparison study

Mohammad Shafiu Nur Rahman *, Insaf Mohd Al-Marhabi, 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

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

Claire Levelut, Rozenn Le Parc, Annelise Faivre, Ralf Brüning, Bernard Champagnon, Valérie Martinez, Jean-Paul Simon, Françoise Bley and Jean-Louis Hazemann

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 1525 K (solid line) and one sample heat-treated at 1373 K (dashed line).

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 $I^2(0)$ data obtained at 40 K min$^{-1}$ for samples B and C. For clarity, sample C is shifted up by $10 \times 10^{-3}$ e.u. K$^{-1}$. $T_g$ is found to be 1535 K for sample B ($[\text{OH}] = 2$ p.p.m.) and 1303 K for sample C ($[\text{OH}] = 900$ 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


$\Delta T_g \sim 30^\circ C$

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

W. Vogel, *Chemistry of Glass*, 1985

Δ$T_{liq} \sim 800^\circ C$
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

\[ 6\equiv \text{Si} - \text{O} - \text{Si} \equiv +4\text{N} \]

\[ \rightarrow 4\equiv \text{Si} - \text{N} +6\text{O} \]
Composition and structure effects on glass transition temperature-

A few case studies
Example 1: Phosphate Glasses
Glass Network Structures Are Based on Phosphate Tetrahedra

- **Q³ tetrahedron**, \([O]/[P]=2.5\)
- **Q² tetrahedra**, \([O]/[P]=3.0\)
- **Q¹ dimer**, \([O]/[P]=3.5\)
- **Isolated Q⁰**, \([O]/[P]=4.0\)

- Terminal oxygens
- Bridging oxygens
- Ultraphosphates
- Metaphosphates
- Polyphosphates
Spectroscopic Studies Reveal Systematic Changes in Network Connectivity

\[ f(Q^3) = \frac{1-2x}{1-x} \]

\[ f(Q^2) = \frac{x}{1-x} \]

\[ 2Q^3 + Na_2O \rightarrow 2Q^2 \]
Alumina Additions Affect Metaphosphate Glass Properties

(a) Glass Transition Temperature (°C) vs. mole% $\text{Al}_2\text{O}_3$

(b) Coefficient of Thermal Expansion ($10^{-6}/°C$) vs. mole% $\text{Al}_2\text{O}_3$

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

$x\text{Al}_2\text{O}_3 (1-x)\text{NaPO}_3$

Increasing $\text{Al}_2\text{O}_3$: $\text{Al}(6) \rightarrow \text{Al}(4)$
Al-Coordination Depends on the Modifier

10Al$_2$O$_3$•90RPO$_3$ glasses

Do large ions compete for NBO’s with Al-polyhedra?
Chromatography Reveals that Alumina Reduces the Average Phosphate Chain-Length

Chromatography Reveals that Alumina Reduces the Average Phosphate Chain-Length

Phosphate Anion

Relative Concentration

Average P-chainlength

10Al2O3 15Al2O3 20Al2O3 25Al2O3

mole fraction Al₂O₃

n̅ₐᵥ=(1-x)/3x

Cs-series III glasses
Na-series III glasses

Adv Vitreous State/Glass Properties
Richard K. Brow/Missouri S&T
brow@mst.edu
Web-based Course
Glass Transformation 2-25
Al-Coordination and Glass Properties Depend on the Phosphate Chain Length

Al coordination changes to maintain a neutral aluminophosphate network

- **'pyro-':** Al coordination changes to maintain a neutral aluminophosphate network
- **'meta-':**
- **'ortho-':**

Best sealing glasses

[Diagram showing the relationship between Al coordination and glass properties with [O]/[P] ratio and glass transition temperature.]

- **[O]/[P] Ratio:** 3.0, 3.5, 4.0, 4.5
- **Glass Transition (°C):** 300, 350, 400, 450, 500, 550
- **Avg. Al-Coordination:** 4.0, 4.5, 5.0, 5.5, 6.0

The diagram illustrates how the Al coordination changes as the [O]/[P] ratio increases, affecting the glass transition temperature and the best sealing glasses.
Ultraphosphate Glasses Exhibit $T_g$ Minima

Metaphosphate (O/P=3) glasses generally have a greater $T_g$ than $P_2O_5$. 

La – Metwalli  
Li & Na - Hudgens

Nd $\quad$ Gd
$\bullet$ La  $\bigcirc$ Li
$\bigdiamond$ Na

$T_g$ (°C) vs. O/P Ratio
Kreidl Recognized the Effects of Modifiers on the Properties of Phosphate Glasses

'cross-linking' modifiers?
The properties of rare-earth phosphate glasses depend on composition.
**X-ray and neutron diffraction results are complementary**

**X-rays**

- **Q\_max = 223 nm\(^{-1}\)**
- **R = La**
- **Nd**
- **Yb**

**Correlation function, T(r) /nm\(^{-2}\)**

**Distance, r /nm**

- **0.0**
- **0.1**
- **0.2**
- **0.3**
- **0.4**

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

**Neutrons**

- **Q\_max = 500 nm\(^{-1}\)**
- **R = La**
- **Nd**
- **Yb**

**Correlation function, T(r) /nm\(^{-2}\)**

**Distance, r /nm**

- **0.0**
- **0.1**
- **0.2**
- **0.3**
- **0.4**

\(N_{PO}\) with 3.7 - 4.1

P–P, R–P-distances estimated

X-ray and neutron diffraction results are complementary.
‘Lanthanide contraction’ is evident in the rare earth phosphate glasses
RE CN depends on composition

![Graph showing RE Coordination Number (CN) vs. mole fraction of RE₂O₃. The CN depends on the composition.

- Black circles: La³⁺/XRD
- Red squares: Nd³⁺/XAS
- Green triangles: Er³⁺/XAS
- Blue triangles: Gd³⁺/XAS

The CN decreases as the mole fraction of RE₂O₃ increases./key
**Modifier coordination requirements are satisfied by terminal oxygens**

Low RE$_2$O$_3$: Isolated RE polyhedra
- [TO]/RE$^{3+}$ > CN(RE$^{3+}$), (Hoppe, 1996)
- depolymerized phosphate network

High RE$_2$O$_3$: Linked RE polyhedra
- [TO]/RE$^{3+}$ < CN(RE$^{3+}$)
- ionic bridges between Q$^2$-tetrahedra

---

Adv Vitreous State/Glass Properties  Richard K. Brow/Missouri S&T  Web-based Course
FS08  brow@mst.edu  Glass Transformation 2-33
Rules for RE$^{3+}$ incorporation into phosphate glass structures

1. RE coordination environments include all terminal oxygens:
   \[ Q^3 P=O \text{ and } Q^2 P-O^- \]
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.

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

\[ \text{TO/RE}^{3+} = \frac{(1+2x)}{x} \]

Isolated NdO$_8$ species
- P-O-Nd bonds to Q$^2$ and Q$^3$ tetrahedra
**RE CN decreases to avoid RE clusters**

\[ CN = \frac{TO}{RE^{3+}} = \frac{1+2x}{x} \]

![Graph showing the relationship between mole fraction of RE₂O₃ and RE coordination number.](image)

- Isolated REO₈,₉ units
- Clustered REO₆,₇ units

**Co-ordinated by Richard K. Brow/ Missouri S&T**

brow@mst.edu

**Adv Vitreous State/Glass Properties**

FS08

**Web-based Course**

Glass Transformation 2-35
Summary of the RE coordination environments in phosphate glasses

- **Isolated, large CN**
  - $x < 7$ mol\%

- **Large CN with common Q$^2$**
  - $x > 7$ mol\%

- **Clustered, Low CN**
  - $x > 25$ mol\%

- **Decreasing CN**
  - $15 < x < 25$ mol\%
The structural model helps explain the effects of composition on $T_g$.

- Isolated RE polyhedra depolymerize network, $T_g$ decreases.
- RE ions link neighboring Q2, $T_g$ increases.
- RE-CN decreases, $T_g$ is flat
- RE-O-RE bonds form, $T_g$ increases.
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\(_2\)O\(_5\) ternary.

Morena, JNCS, 2000
SnO/ZnO-pyrophosphate glasses have T_g's under 300°C.
We are evaluating glasses in the Sn-borophosphate system

- Refractive indices >1.8
- $T_g < 325^\circ C$
- Good aqueous durability
$T_g$ increases with $B_2O_3$-additions

Is there a structural explanation for this trend in $T_g$?
Raman spectra indicate that the phosphate network is depolymerized by borate additions.

\[(2y)\text{SnO}^* (y)\text{P}_2\text{O}_5^* (x)\text{B}_2\text{O}_3 \text{ (where } x+3y = 100)\]
$^{11}B$ NMR provides an explanation for the $T_g$ trends.

Series I

- 56SnO-28P2O5-16B2O3
- 60SnO-30P2O5-10B2O3
- 64SnO-32P2O5-4B2O3
- 66SnO-33P2O5-1B2O3

Series II

- 66.7SnO-17.3P2O5-16B2O3
- 66.7SnO-23.3P2O5-10B2O3
- 66.7SnO-29.3P2O5-4B2O3
- 66.7SnO-32.3P2O5-1B2O3
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

$$\text{CN} = \sum x_i \cdot \text{CN}_i$$

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

Increasing CN, increasing $T_g$

Feng et al, PRL, 1997

FIG. 1. $T_g$ of $Ge_xSe_{1-x}$ 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 $\pm 1$ K/100 sec.
Properties are considered with respect to 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

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