Advanced Vitreous State - Physical Properties of Glass

Lecture 25: Charge Conduction Properties of Glass:
Ionic Conduction in Glass - Part 1

Relationship to Glass Structure and Composition

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Ionic Conduction in glass

- Glasses can be systematically doped to increase conductivity
  - From near insulating values to those that rival ionic liquids
- Strong glass forming character over wide compositions ranges make them ideal for many composition studies of the ionic conductivity
- Low melting temperatures often make them compatible with many industrial processing techniques such as sputtering and evaporation to produce thin film electrolytes
Formation of Non-Bridging Oxygens

- Modifier $M_2O$ or $MO$ creates two NBOs per $M_2O$ or $MO$ added
- $xNa_2O + (1-x)SiO_2$ creates $2x$ NBOs
- $f_{\text{NBO}} = \frac{\text{NBOs}}{\text{NBOs} + \text{BOs}}$  
  \[f_{\text{NBO}} = \frac{2x}{x + 2(1-x)} = \frac{2x}{2-x}\]
- $f_{\text{BO}} = 1 - f_{\text{NBO}}$
“$Q_i$” Units in Alkali Silicate Glasses

\begin{align*}
Q_4 & \quad Q_3 & \quad Q_2 \\
Q_1 & \quad Q_0
\end{align*}

O \quad Si \quad Na^+
Alkali Ions are “weakly” bound

- “Frame work” cations, Si$^{+4}$, and anions, O$^-$
  - Covalently bonded to the network
  - “Large” bond strength, 100+ kcal/mole
- “Modifying” cations, M$^+$, and anions F$^-$
  - Ionically bonded to the network
  - “Small” bond strength, < 50 kcal/mole
- Alkali cations can be thermally activated
- To break their weak ionic bond
- And move from one alkali cation site to another
- Thermally activated ionic conduction….
Relation of glass structure to ionic conduction

\[ x\text{Na}_2\text{O} + (1-x)\text{SiO}_2 \quad \text{Glass in 2-D} \]
Molecular Dynamics Simulation of Ionic Conduction

- Go to Movie.....
Relation of glass structure to ionic conduction

\[ \Delta E_{\text{act}} = \Delta E_s + \Delta E_c \]

\[ \Delta E_s = \text{Strain Energy} \]

\[ \Delta E_c = \text{Coulomb Energy} \]
Cation Conduction – “Rattle and Jump”

\[ \text{Energy} \]

\[ +\frac{1}{r^n} \]

\[ \Delta E_s \]

\[ \Delta E_c \]

\[ -\frac{e^2}{r} \]

MD Simulations

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Ionic Conduction in Glass – Part 1
Theory of Ionic Conduction in Glass: Simple Models

- \( \sigma = \frac{1}{\rho} \equiv neZ\mu \)
  - \( n \) is the number density
  - \( eZ \) is the charge, +1 most of the time
  - \( \mu \) is the mobility

- **What are the units of \( n \)?**
  - \#/cm\(^3\)

- **What are the units of \( \mu \)?**
  - \((\text{cm/sec})/V = \text{cm/V-sec}\)

- **What are the units of \( \sigma \)?**
  - \((\Omega \text{ cm})^{-1} \equiv \text{S/cm}\)
Theory of Ionic Conduction in Glass: Simple Models

\[ \frac{\lambda z e |E|}{2} \]

\[ \Delta E_{\text{act}} = \frac{\lambda z e |E|}{2} \]

\[ \lambda \]

\[ \lambda / 2 \]
Theory of Ionic Conduction in Glass: Simple Models

\[ \nu^+(T) = \nu_0 \exp\left[ -\frac{\Delta E_{\text{act}} - \lambda ze|E|/2}{RT} \right] \]

\[ \nu^-(T) = \nu_0 \exp\left[ -\frac{\Delta E_{\text{act}} + \lambda ze|E|/2}{RT} \right] \]

\[ \nu_{\text{net}} = \nu^+(T) - \nu^-(T) \]

\[ \nu_{\text{net}} = \nu_0 \exp\left[ -\frac{\Delta E_{\text{act}}}{RT} \right] \left( \exp\left[ \frac{\lambda ze|E|}{2RT} \right] - \exp\left[ -\frac{\lambda ze|E|}{2RT} \right] \right) \]

\[ \nu_{\text{net}} = 2\nu_0 \exp\left[ -\frac{\Delta E_{\text{act}}}{RT} \right] \sinh\left( \frac{\lambda ze|E|}{2RT} \right) \sim \frac{\nu_0 \lambda ze|E|}{RT} \left( \frac{\Delta E_{\text{act}}}{RT} \right) \]
Theory of Ionic Conduction in Glass: Simple Models

\[
\nu_{net} = 2\nu_0 \exp\left[ -\frac{\Delta E_{act}}{RT} \right] \sinh\left( \frac{\lambda ze|E|}{2RT} \right) \sim \frac{\nu_0 \lambda ze|E|}{RT} \exp\left[ -\frac{\Delta E_{act}}{RT} \right]
\]

velocity = \( \nu_{net} \times \lambda = \frac{\nu_0 \lambda^2 ze|E|}{RT} \exp\left[ -\frac{\Delta E_{act}}{RT} \right] \)

mobility = velocity / \( E = \frac{\nu_0 \lambda^2 ze}{RT} \exp\left[ -\frac{\Delta E_{act}}{RT} \right] \)

conductivity = mobility × conductivity × charge

\[
\sigma(T) = \frac{n\nu_0 \lambda^2 (ze)^2}{RT} \exp\left[ -\frac{\Delta E_{act}}{RT} \right] \equiv \frac{\sigma_0}{T} \exp\left[ -\frac{\Delta E_{act}}{RT} \right]
\]
**Theory of Ionic Conduction in Glass: Simple Models**

\[ \Delta E_{\text{act}} = \Delta E_s + \Delta E_c \]

\( \Delta E_s = \text{Strain Energy} \)

\( \Delta E_c = \text{Coulomb Energy} \)

\[ \sigma(T) = \frac{\sigma_0}{T} \exp\left[ -\frac{\Delta E_{\text{act}}}{RT} \right] \]

\[ = \frac{\sigma_0}{T} \exp\left[ -\frac{\Delta E_c + \Delta E_s}{RT} \right] \]

\[ n(T) = n_0 \exp\left[ -\frac{\Delta E_c}{RT} \right] \]

\[ \mu(T) = \frac{\mu_0}{T} \exp\left[ -\frac{\Delta E_s}{RT} \right] \]

\[ \nu_0 \lambda^2 \frac{(ze)^2}{RT} \exp\left[ -\frac{\Delta E_s}{RT} \right] = \]

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Ionic Conduction in Glass – Part 1

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Arrhenius Ionic Conductivity in Glass

The graph shows the Arrhenius plot for various glass compositions, plotting the ionic conductivity ($\sigma_{dc}$) against the inverse temperature ($1000 / T$) on a log-log scale. The temperature range is from 600 to 1200 °C. Different compositions are represented by various lines, with some key compositions labeled:

- $\alpha$-AgI
- RbAg$_{4.5}$
- $\beta$-NaAl$_{11}$O$_{17}$
- 29.8Ag$_2$O-40.4(Agl)$_2$-29.8P$_2$O$_5$
- 28.6Ag$_2$O-42.8(Agl)$_2$-28.6MoO$_3$

Other compositions include:

- LiBO$_2$Cl
- 50Ag$_2$S-5GeS-45GeS$_2$
- 5Li$_2$O-10(LiCl)$_2$-12.5SiO$_2$-12.5B$_2$O$_3$
- 26.9LLO-9(LiCl)$_2$-64.1B$_2$O$_3$
- 25Li$_2$O-25Al$_2$O$_3$-50SiO$_2$
- 25Li$_2$O-78B$_2$O$_3$
- LiNbO$_3$
- ZrO$_2$-9%Y$_2$O$_3$
- Li$_2$O-30Li$_2$O-10LiCl

The graph also indicates the crystalline and glassy regions, with transition temperatures $T_g$ and $T_m$.
Binary Alkali Silicate Glasses

- Addition of Na₂O Increases the ionic conductivity, decreases the electrical resistivity
- Increasing the temperature increases the ionic conductivity, decreases the ionic resistivity
- Ionic conductivity of soda glasses is still very low except for the highest temperatures

Fig. 17.17. Conductivity of glasses in the system Na₂O–SiO₂. From E. Seddon, E. J. Tippett, and W. E. S. Turner, J. Soc. Glass Technol., 16, 950 (1912).
DC ion conductivity in glass

- $x\text{Li}_2\text{O} + (1-x)\text{P}_2\text{O}_5$
- Creation of non-Bridging oxygens
- “Mobile” lithium ions
- The higher the concentration of Li$_2$O, the higher the conductivity
  - Lower resistivity
- Activation energy decreases with Li$_2$O content
Composition Dependence of the Conductivity

- Binary lithium phosphate glasses, Li$_2$O + P$_2$O$_5$, are relative poor ion conductors
- Binary lithium borate glasses, Li$_2$O + B$_2$O$_3$, are slightly better conductors
- Binary lithium silicate glasses, Li$_2$O + SiO$_2$ are slightly better conductors yet.


![Diagrams of Li$_2$O:P$_2$O$_5$, Li$_2$O:B$_2$O$_3$, and Li$_2$O:SiO$_2$]
Salt doped phosphate glasses

- Halide doping strongly increases the conductivity
Effect of Sulfur Substitution

\[ T = 25^\circ C \]

\[ \log_{10}(\sigma_0/cm) \]

\[ X \text{ LiX} \]

\[ E_{act}/\text{kcalmol}^{-1} \]

\[ X \text{ LiX} \]
Salt doped phosphate glasses

- Lil doped LiPO₃ show highest conductivity and lowest activation energy among the halides
- Crystallization at the end of the glass forming limit
Silver Phosphate Glasses

\[
T = 25^\circ C
\]

\[
\log_{10}(\sigma \text{ cm})
\]

\[
X \ AgX
\]

\[
E_{\text{act}} \ (\text{kcal mol}^{-1})
\]

\[
X \ AgX
\]
Other Silver sulfide doped glasses

\[ T = 25^\circ C \]

\[ \log_{10}(\sigma) \text{ cm} \]

\[ \begin{align*}
X_{AgI} & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \\
X_{AgBr} & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \\
X_{AgCl} & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \\
\end{align*} \]

- \( 2Ag_2S:As_2S_3 \)
- \( Ag_2S:As_2S_3 \)
- \( Ag_2O:B_2O_3 \)
- \( AgPS_3 \)
- \( AgPO_3 \)
- \( 2Ag_2S:As_2S_3 \)
- \( Ag_2S:As_2S_3 \)
- \( AgPS_3 \)
- \( AgPO_3 \)
- \( 2Ag_2S:As_2S_3 \)
- \( Ag_2S:As_2S_3 \)
- \( AgPS_3 \)
- \( AgPO_3 \)
Mixed Glassformer Systems

- Phosphate and borate mixed glasses show non-linear “Mixed Glassformer” effect
Short Range Order models of Conduction Energetics

- Anderson-Stuart Model
- Assignment of Coulombic and Strain energy terms, $\Delta E_C + \Delta E_s$
- “Creation” or Concentration versus Migration energy terms, $\Delta E_C + \Delta E_m$
- Coulomb energy term, $\Delta E_C$ attractive force between cation and anion

$$\approx \frac{C_{\text{struct}}}{\varepsilon_\infty} \left[ \frac{-Z_cZ_a e^2}{\lambda / 2} - \frac{-Z_cZ_a e^2}{(r_c + r_a)} \right] = \frac{C_{\text{struct}}}{\varepsilon_\infty} \frac{Z_cZ_a e^2}{(r_c + r_a)} \left[ \frac{1}{\lambda} - \frac{2}{\lambda} \right]$$

$$\lim_{\lambda \to \infty} \Delta E_{\text{act}} \rightarrow \frac{C_{\text{struct}}}{\varepsilon_\infty} \frac{Z_cZ_a e^2}{(r_c + r_a)} = \text{const}.$$
Short Range Order models

- Strain energy term - $\Delta E_s$
- “Work” required to “dilate the network so large cations can migrate

\[
\Delta E_s = \pi G (r_c - r_d)^2 \lambda / 2
\]

- $G$ - Shear modulus
- $r_c$ - Cation radius
- $r_d$ - Interstitial site radius
- $\lambda$ - Jump distance
Thermodynamic Models

- Glass is considered as a solvent into which salt is dissolved.
- If dissolved salt dissociates strongly, then glass is considered a strong electrolyte.
- If dissolved salt dissociate weakly, then glass is considered a weak electrolyte.
- Coulomb energy term calculations suggest that the salts are only weakly dissociated, largest of the two energy terms.
- Migration energy term is taken to be minor and weak function of composition.
- Dissociation constant then determines the number of mobile cations available for conduction, dissociation limited conduction.
Weak Electrolyte model,  

\[
\frac{1}{2}M_2O + \text{SiO}_{4/2} \rightarrow \frac{3}{2}O\text{-Si-O-M}^+ \rightarrow \frac{3}{2}O\text{-Si-O} \ldots \ldots M^+
\]

(Unreacted)  (Reacted but Undissociated)  (Dissociated)

\[
K_{\text{diss}} = a_{M^+} a_{OM^-}/ a_{M_2O}
\]

\[
\sim [M^+][OM^-]/a_{M_2O} = [M^+]^2/ a_{M_2O}
\]

\[
[M^+] \sim K_{\text{diss}}^{1/2} a_{M_2O}^{1/2} \equiv n
\]

\[
\sigma = ze\mu_n = ze\mu K_{\text{diss}}^{1/2} a_{M_2O}^{1/2} \sim C a_{M_2O}^{1/2}
\]

\[
\log K_{\text{diss}} \sim -Ne^2RT/4\pi\varepsilon_\infty \varepsilon_\infty (r_+ + r_-)
\]

As \(r_+, r_-\) increase, \(K_{\text{diss}}\) increases
As \(\varepsilon_\infty\) increases, \(K_{\text{diss}}\) increases
Strong and Weak Electrolyte models

- “Strong electrolyte” model suggests all cations are equally available for conduction.
  - Each cation experiences an energy barrier which governs the rate at which it hops

- “Weak electrolyte” model suggests only those dissociated cations are available for conduction
  - Dissociation creates mobile carriers available for conduction

- SE models suggests that $\Delta E_C + \Delta E_s$ both contribute, one could be larger or smaller than the other

- WE model suggests that $\Delta E_c$ is the dominant term
Intermediate Range Order models

- Models recognize that ion conductivity requires ion motion over relatively long length scales.
- Ions must be able to move from one side of the electrolyte to the other.
- Long range connectivity of the SRO structures favorable to conduction must exist.
- Deep “traps” along the way must be infrequent and not severe.
- Rather, low energy conduction “pathways” are thought to exist which maximize connectivity and minimize energy barriers and traps.
- Cluster pathway model of Greeves ‘85, for example.
Intermediate Range Order models

- Cluster pathway model,
  *Greeves et al ‘85*
AC versus DC ionic conductivity

\[ \omega \tau < 1 \quad \text{and} \quad \omega \tau > 1 \]

\[ \log_{10}(\sigma_{a.c.}) \]

\[ \log_{10}(f/\text{Hz}) \]

D.C. Conductivity

A.C.

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Ionic Conduction in Glass – Part 1
AC ionic conductivity in glass

- Connection to Far-IR vibrational modes,
Intermediate Range Order models

- Percolation Models - Johari et al. ‘87
  - At low dopant concentrations
    - Cations are far separated
    - Mobile species are diluted in a non-conducting host glass
  - At intermediate concentrations
    - Cations begin to approach proximity
    - Preferential conduction paths form
    - Sites percolate
  - At high concentrations
    - Cations are fully connected
    - Conduction pathways are fully developed
Conductivity percolation in AgI + AgPO₃
RMC Modeling of AgI + AgPO$_3$, Swenson et al. ‘98
Intermediate Range Order models

- Microdomain models of conductivity
- Dopant salts such as AgI to oxide glasses, especially AgPO$_3$, are added to increase conductivity
- AgI is itself a FIC crystal above 150°C
- Extrapolations of $\sigma$ to $x$AgI = 1 give $\sim \sigma_{\text{AgI}}(298\text{K})$
- The question then is: Does the AgI create “microdomains” of $\alpha$-AgI giving rise to the high conductivity?
AgI Microdomain model

- Most well known of all glasses is xAgI + (1-x)AgPO₃
- AgPO₃ is a long chain structure of -O-P(O)(OAg)-O repeat units
- Intermediate range structure is for these long chains to intertwine and as such frustrate crystallization
- Added AgI dissolves into this liquid without disrupting the structure of the phosphate chains
- Microdomain model then suggests that this dissolved AgI creates increasingly large clusters of α-AgI between the phosphate chains
AgI Microdomain model
Ionic Conduction in Glass

- **Ohms law**
  - $V = IR$
  - $V = I \rho \frac{t}{A} = I \rho k$
  - $\rho = \frac{1}{\sigma}$
  - $\rho(\Omega \text{cm}), \sigma(\Omega \text{cm})^{-1}$

- **Calculate $\sigma$ for**
  - $I = 1 \, \mu\text{A}$
  - $V = 1 \, \text{V}$
  - $k = 1 \, \text{mm}/1 \, \text{cm}^2$