Lecture 13 - Ionics applications 2: Composition Dependence of Ionic Conduction in Chalcogenide Glasses

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Ion Conduction in Glass: Coulombically or Structurally Constrained?

- Oxide glasses, ΔE_{act} ~100 kcal/mole
- Sulfide glasses, ΔE_{act} ~10 kcal/mole
- $\Delta E_{act} = \Delta E_s + \Delta E_c$
- Are alkali cations coulombically, ΔE_c , constrained?
  - Weak Electrolytes like HOAc, k_A ~ 1 x 10^{-5} ?
  - Cations are only weakly dissociated
- Are alkali cations structurally, ΔE_s, constrained?
  - Strong electrolytes like NaCl?
  - Completely dissociated, Na^+ Cl^- ?

Models of the Activation Energy

- Both activation energies appear to be non-zero and contribute to the total activation energy
- Anderson-Stuart[1] model calculation

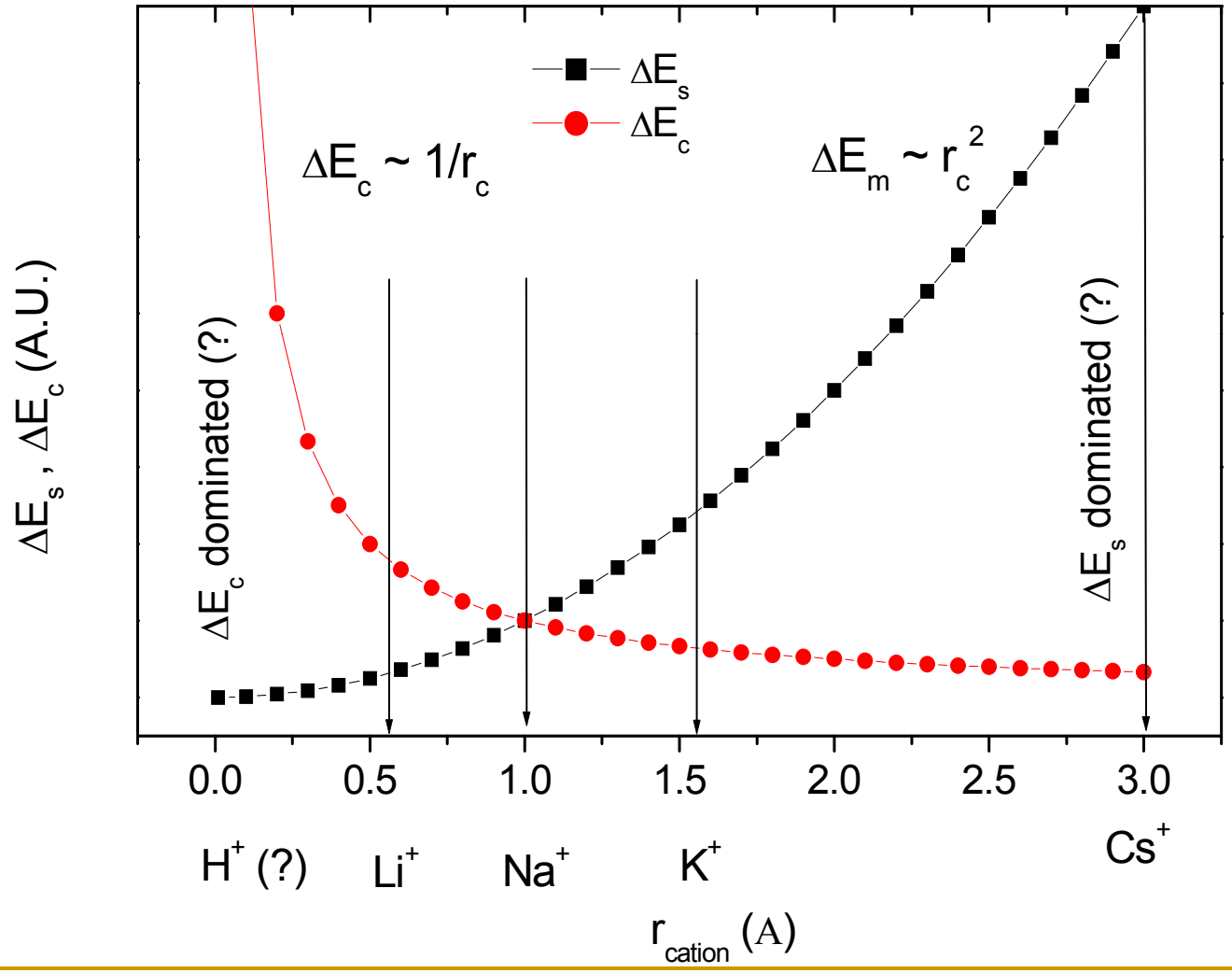
$$\Delta E_C \approx \frac{C_{struct.} Z_c Z_a e^2}{\varepsilon_\infty}\left[\frac{1}{(r_c + r_a)} - \frac{2}{\lambda}\right] \qquad \Delta E_S \approx \pi G (r_c - r_d)^2 \lambda / 2$$

x Na_2O + (1-x)SiO_2	ΔE_s (calc) kcal/mole	ΔE_c (calc) kcal/mole	ΔE_{act}(calc) kcal/mole	ΔE_{act}[2] kcal/mole
11.8	11.7	66.9	78.6	68.1
19.2	10.9	62.3	73.2	63.7
29.7	10.0	56.1	66.1	59.7

- Calculation shows that the ΔE_c term is the larger of the two energy barriers.
- Coulombically constrained?

[1] Anderson, Stuart, J. Amer. Cer. Soc., 1954
[2] SciGlass 5.5, Average of many glasses

Alkali Radii Dependence of Strain and Coulomb Activation Energies

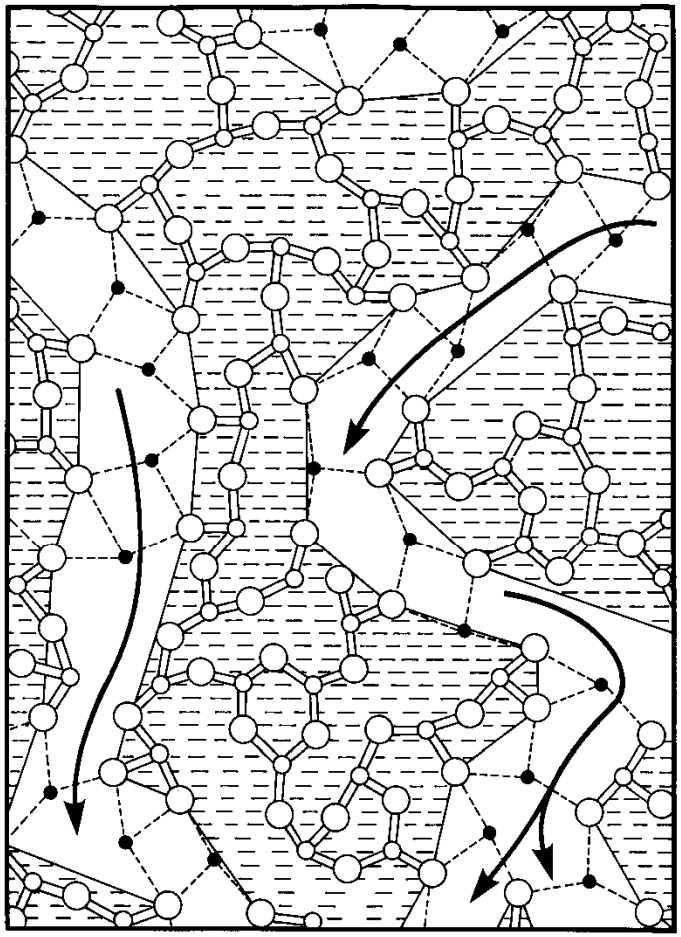


Intermediate Range Order models

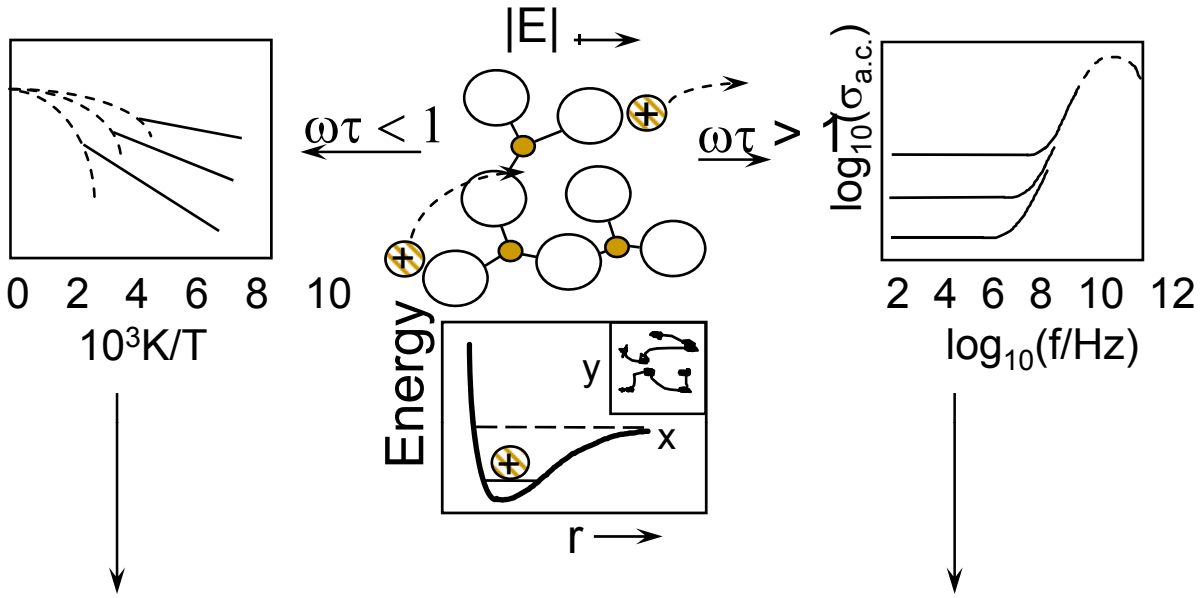
- Models recognize that ion conductivity requires ion motion over relatively long length scales
- Ions must be able to move from one side of the electrolyte to the other
- Long range connectivity of the SRO structures favorable to conduction must exist
- Deep “traps” along the way must be infrequent 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



D.C. Conductivity

Charles - Polarization/Diffusion

Anderson/Stuart - Coulomb & Strain Energies

Moynihan/Macedo - Debeye & Faulkenhagen Theory

Ravaine/Souquet - Weak Electrolyte

Malugani- AgI Micro domains

A.C. Conductivity

Jonscher - Universal Response

Ngai - Coupling Theory

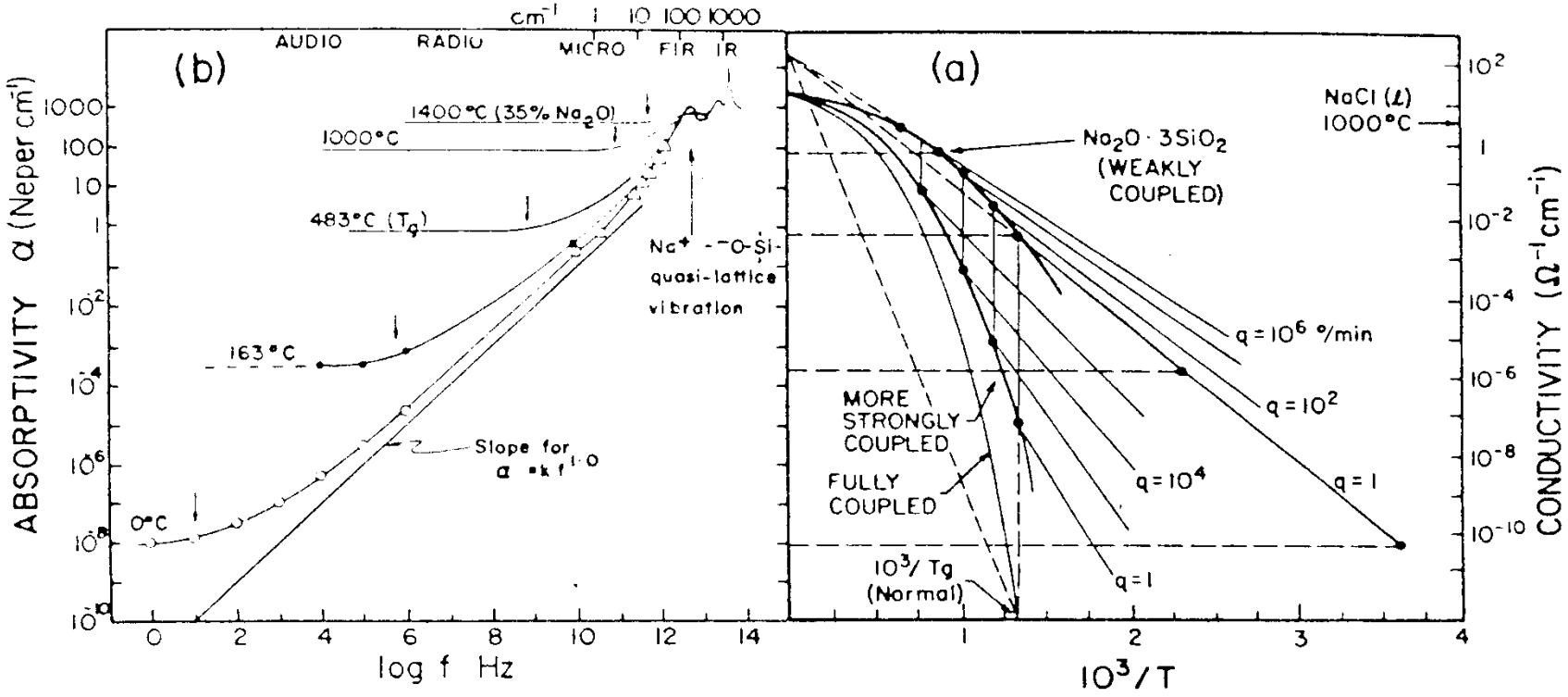
Moynihan - Modulus

Dyre - Power Law

Funke - Jump Relaxation

AC ionic Conductivity in Glass

- Connection to Far-IR vibrational modes *Angell '83*



Fast Ion (M^+) Conducting Glasses

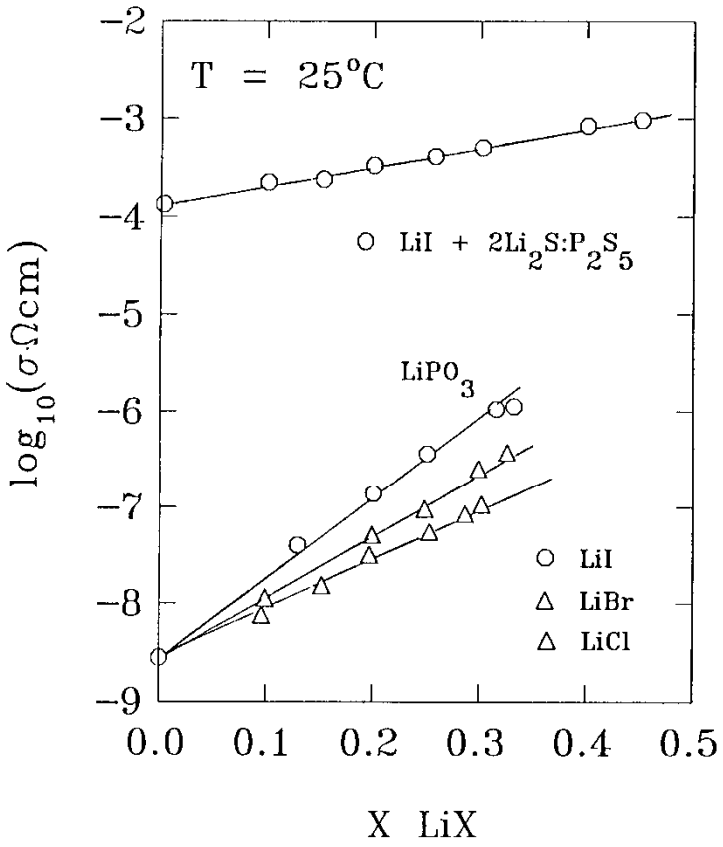
- Typical glass compositions
  - Alkali salt + + glass former + additives

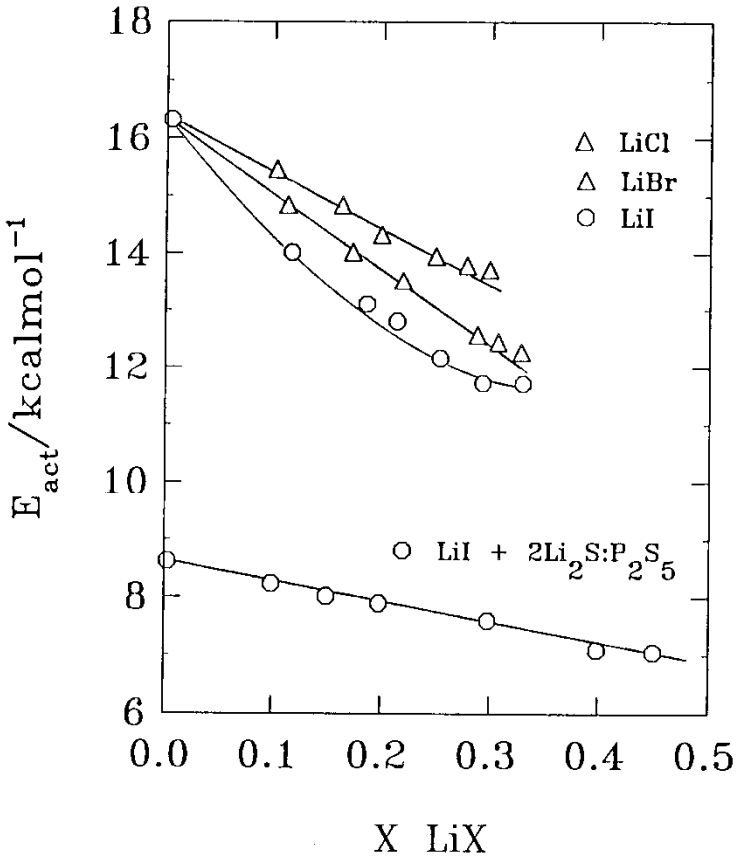
Alkali modifier

Mobile cations | Glass structure | Chemical/mechanical/ electrochemical durability

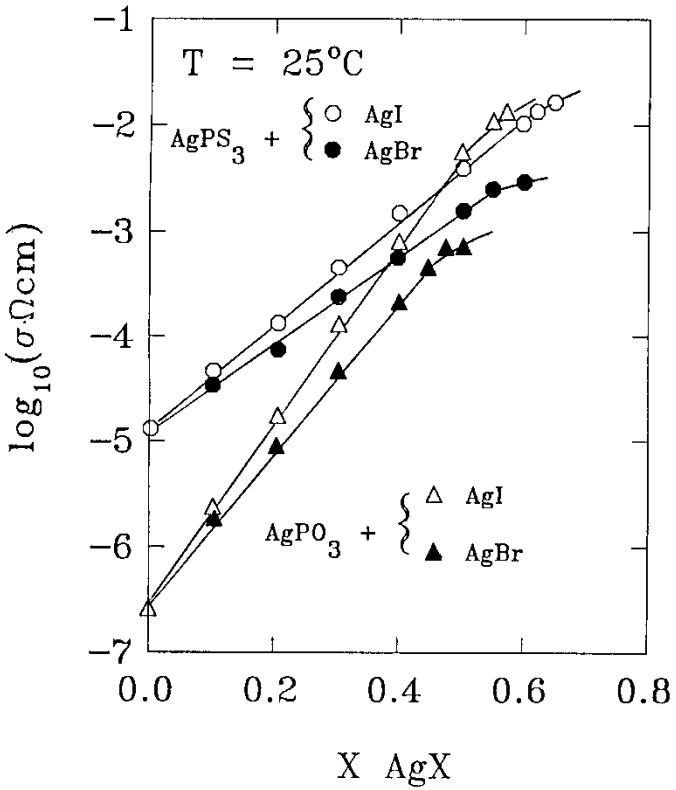
  - $MX + M_2O + G_nO_m + A_pO_q + \ldots$
    - $NaCl + Na_2O + B_2O_3 + Al_2O_3$
  - $MX + M_2S + G_nS_m + A_pS_q + \ldots$
    - $LiI + Li_2S + SiS_2, B_2S_3, GeS_2 \ldots$
    - $LiI + Li_2S + GeS_2 + Ga_2S_3, La_2S_3, ZrS_2 \ldots$

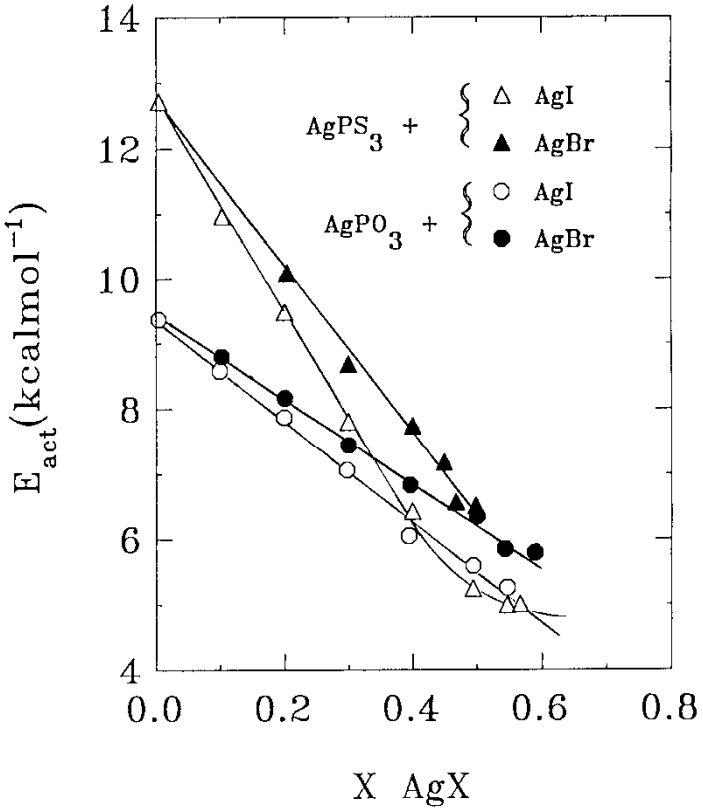
Salt Doped Thiophosphate Glasses



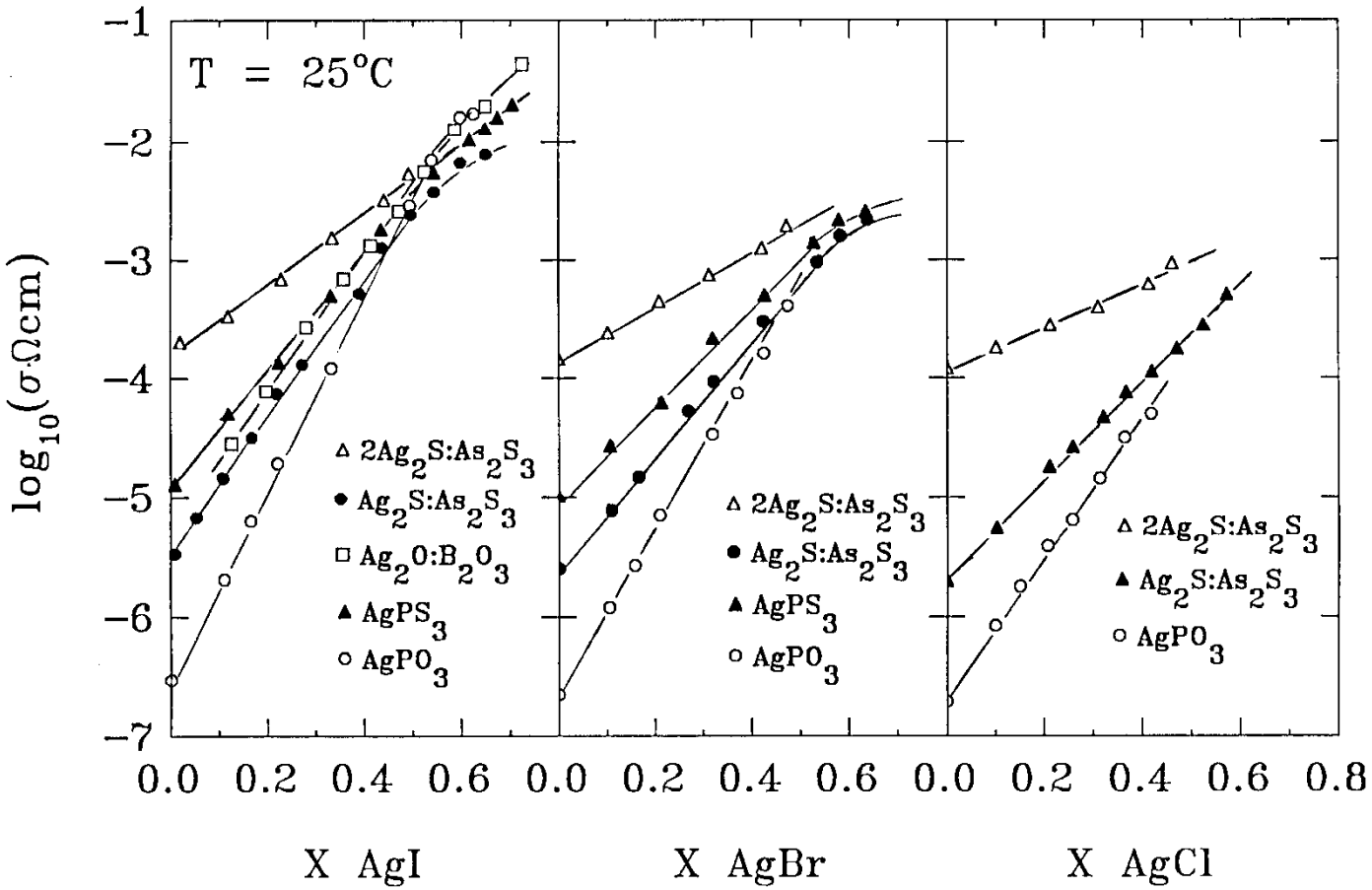


Salt doped Silver Phosphate Glasses





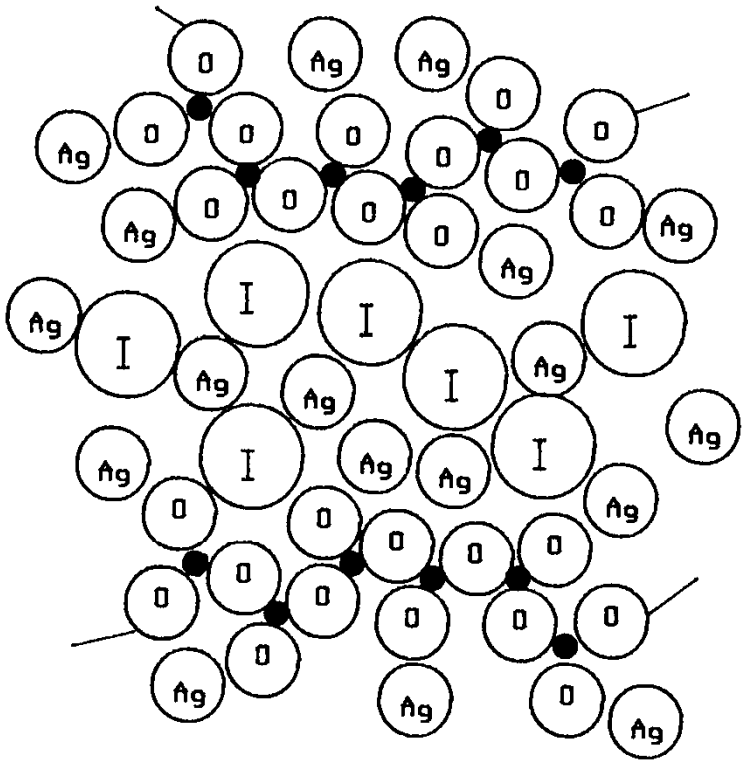
Salt Doped Silver Sulfide Glasses



AgI Micro-Domain Model

- Most well known of all glasses is xAgI + (1-x)$AgPS_3$
- $AgPS_3$ is a long chain structure of -S-P(S)(SAg)-S 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 Micro-Domain Model



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^{o}C
- Extrapolations of σ to xAgI = 1 give ~ σ_{AgI}(298K)
- The question then is: Does the AgI create "microdomains" of α-AgI giving rise to the high conductivity?

Fast Ion Conduction in Glass

- So what have we learned?

- **Chemistry controls Structure and Structure controls conduction**
  - Sulfide glasses exhibit orders of magnitude higher conductivity than oxide glasses
  - Salt doping strongly increases conductivity
  - Conduction appears to be controlled by both charge (coulombic) and volume (strain) energy factors
    - Coulomb constraint appears to be more significant, hence the S^- anion weakens coulomb energy barrier for the smaller cations
  - Glass structural units control the energy barriers
    - Structural units can be determined (IR, Raman, NMR, XRD, ND)
  - Smaller cations appear to be charge constrained whereas larger cations appear to be volume constrained
  - Optimized mixed glassformer glasses hold promise of being both highly conducting, yet more chemically stable

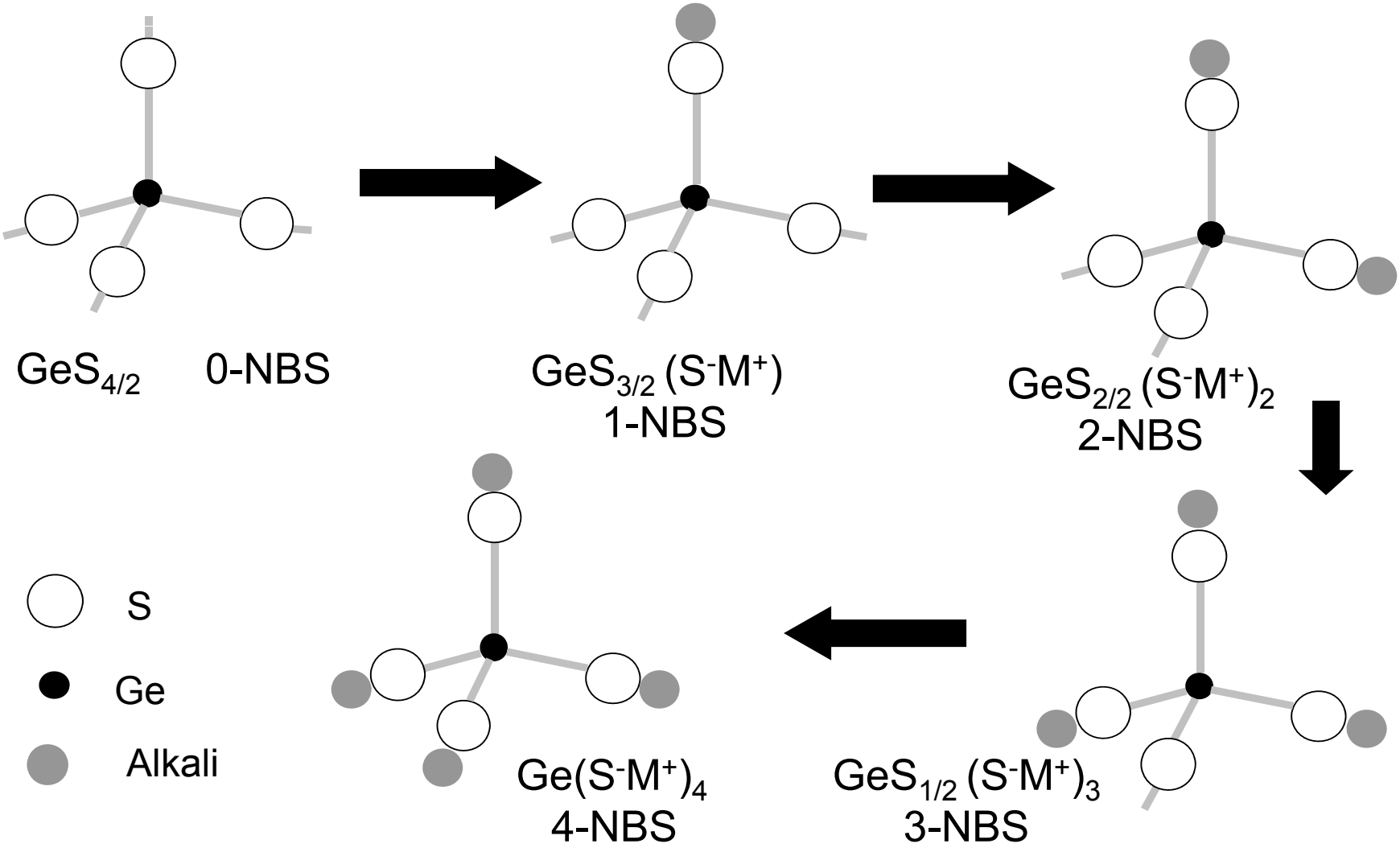
Effect of Cation Radius on the Ionic Conductivity

- Study cation radius effect on conductivity and activation energy
  - $yMI+(1-y)[xM_2S+(1-x)(0.1Ga_2S_3+0.9GeS_2)]$ glasses

M	Radius (Å)	x	y
Li	0.76	0.3, 0.4, 0.5	0-0.3
Na	1.02	0.2, 0.3, 0.4, 0.5, 0.6, 0.67	0-0.2
K	1.38	0.3, 0.4	0, 0.1
Cs	1.67	0.3, 0.4	0, 0.1

- Correlate structure and property
  - Characterize these glasses with Raman and Impedance Spectroscopies
- Examine dependence of conductivity on cation radius
  - Small cations, charge density constrained?
  - Large cations, volume constrained?

Structural Units in $M_2S + GeS_2$ glasses

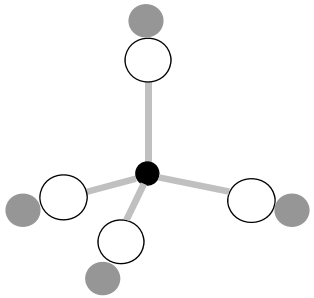


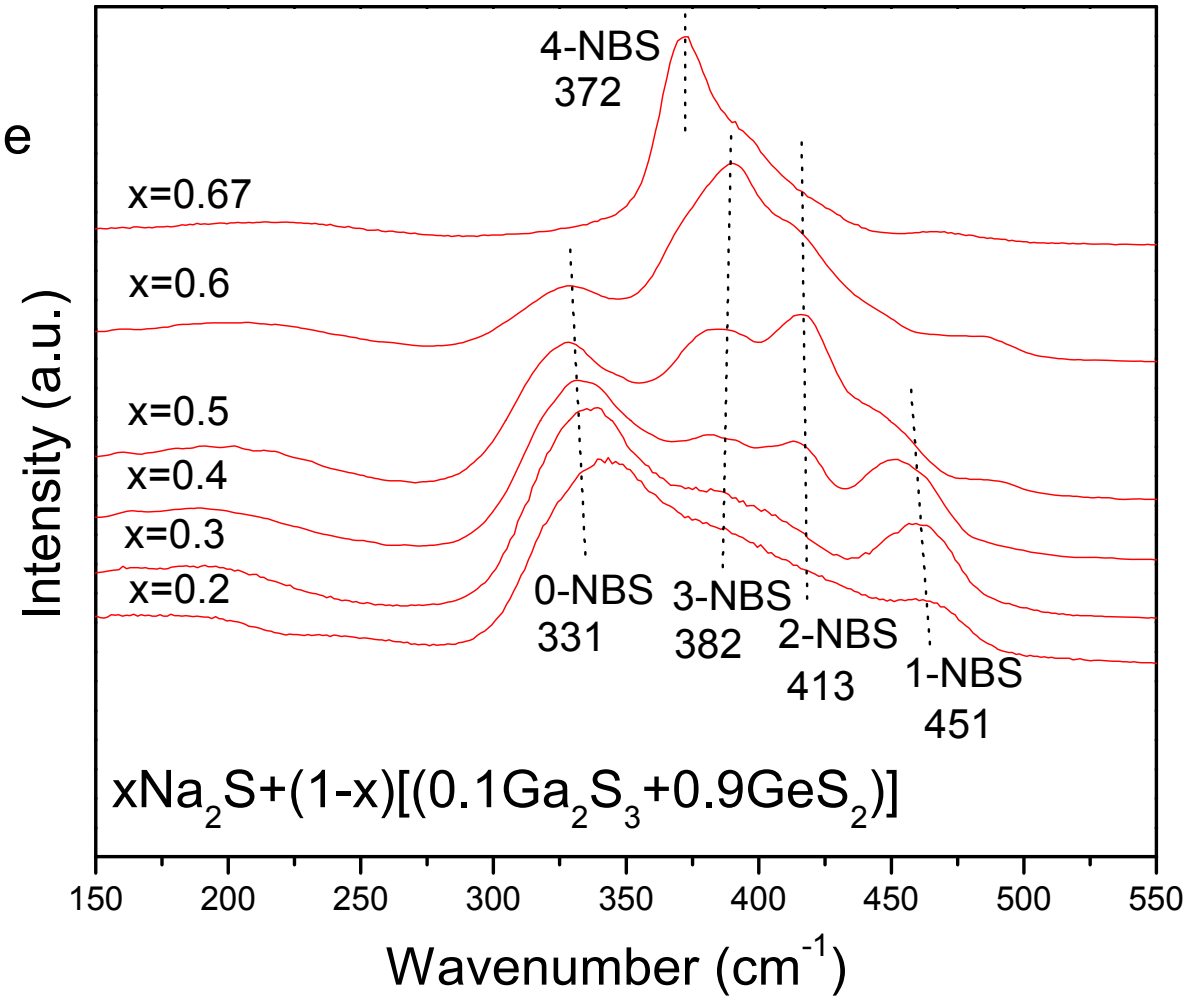
Raman spectra of Na_2S doped glass

With more extensive glass forming range, the trend of formation of non-bridging sulfur is obvious

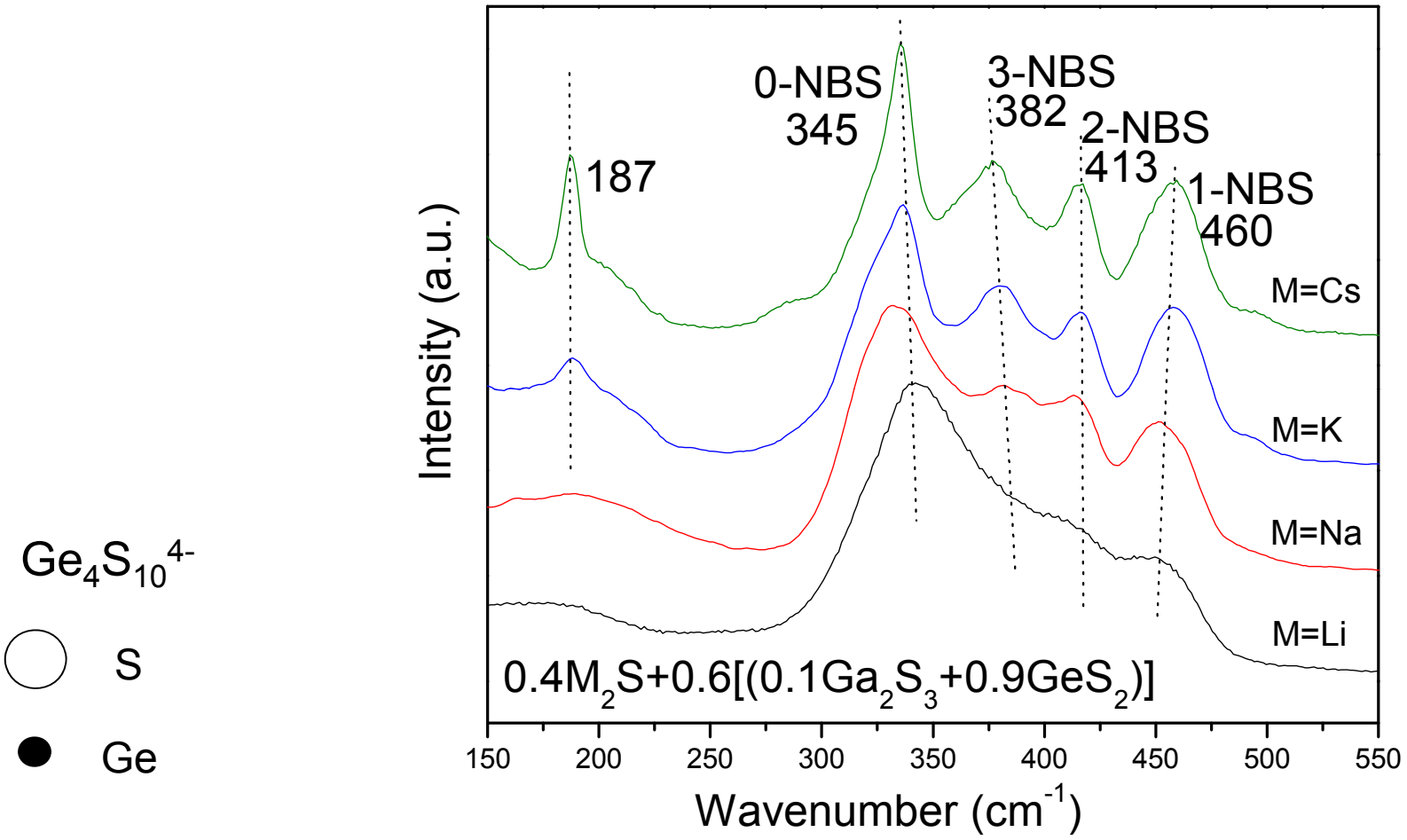
At 0.67Na_2S,

4-NBS forms

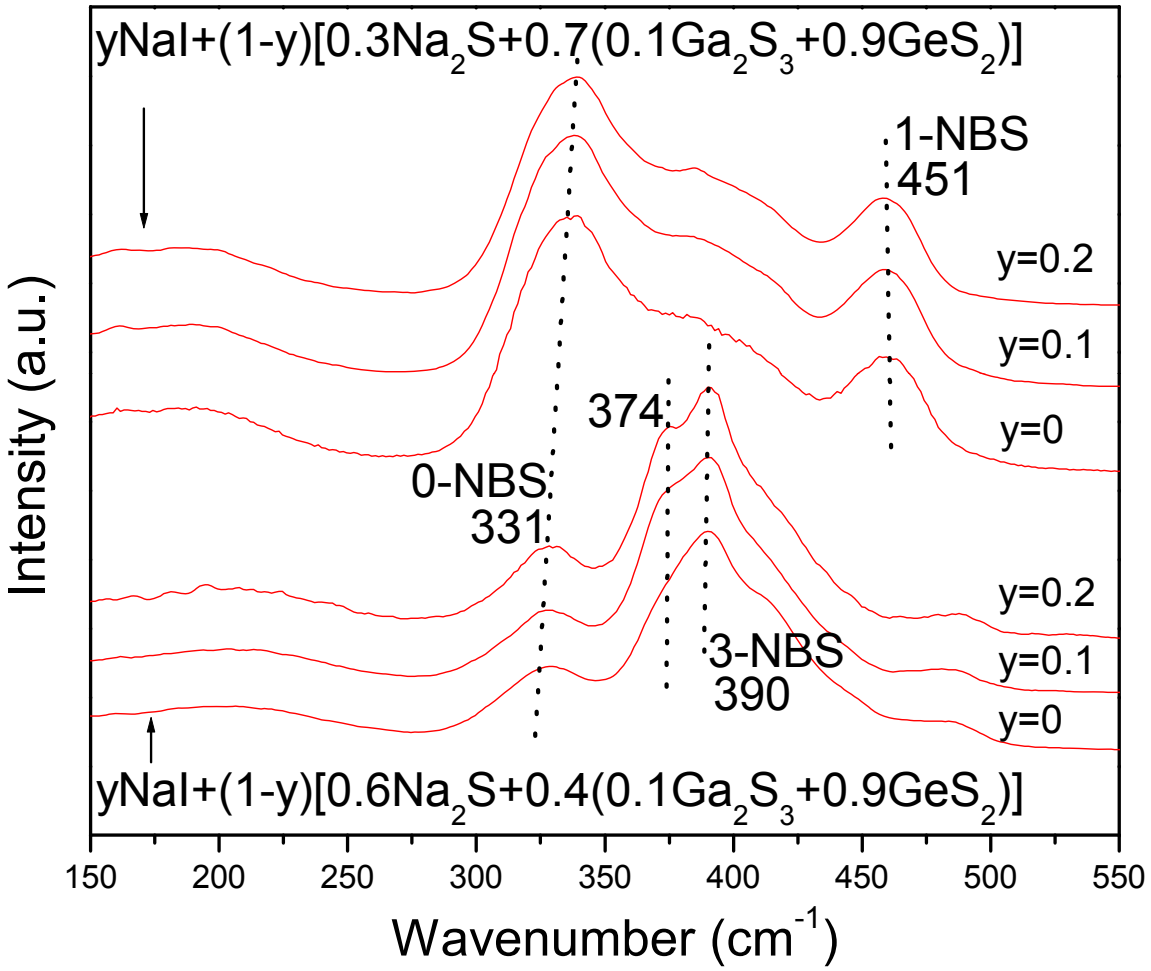




Raman Spectra of M_2S doped glasses



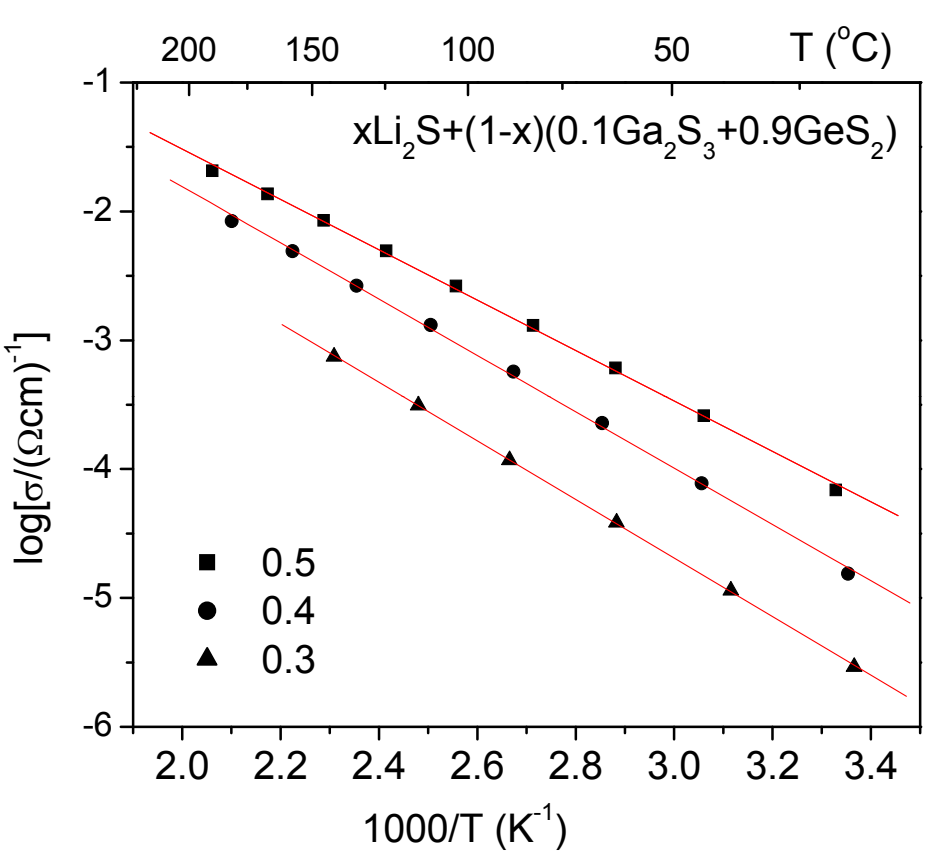
Raman Spectra of NaI doped glasses

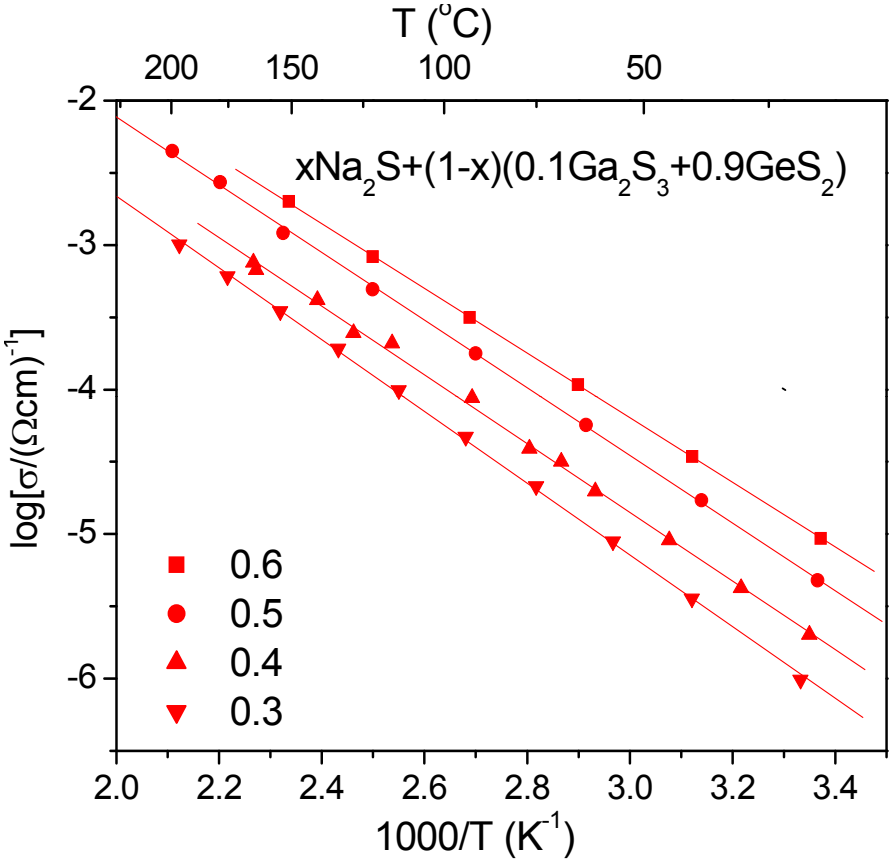


Usually, alkali Iodide (MI) resides in the interstitials of glass structure network and causes no change of structure

At $0.6Na_2S$, 390 cm^{-1} peak splits into two peaks, suggesting that NaI enters into structural network

Alkali Sulfide (M_2S) Effect on Conductivity



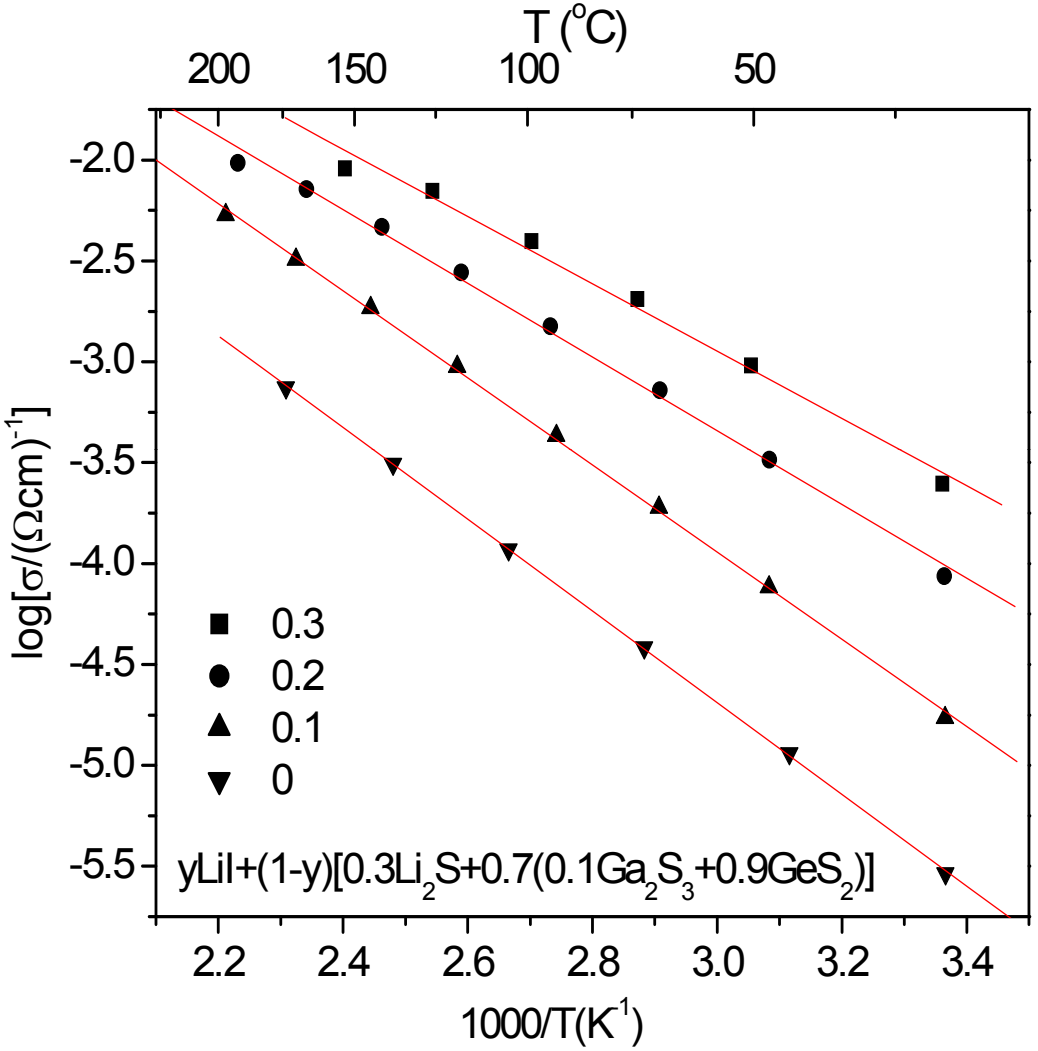


With addition of alkali sulfide, non-bridging sulfurs (NBS) form and the alkali ions dissociate from NBS, improving the ionic conductivity

Effect of LiI on Conductivity

LiI resides in the interstitials of glass structure network.

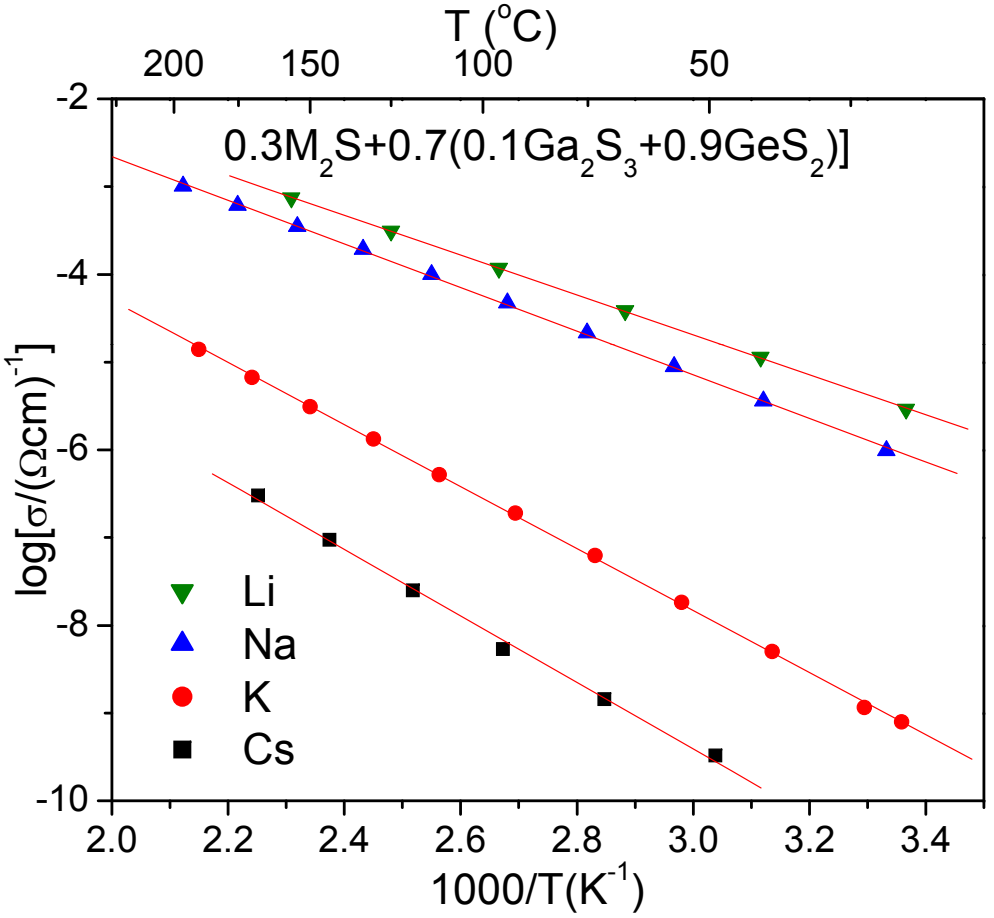
Due to the large I^- radius, it dilates the glass structure and make the Li^+ easily move and improve the conductivity



Effect of Alkali Radius on Conductivity

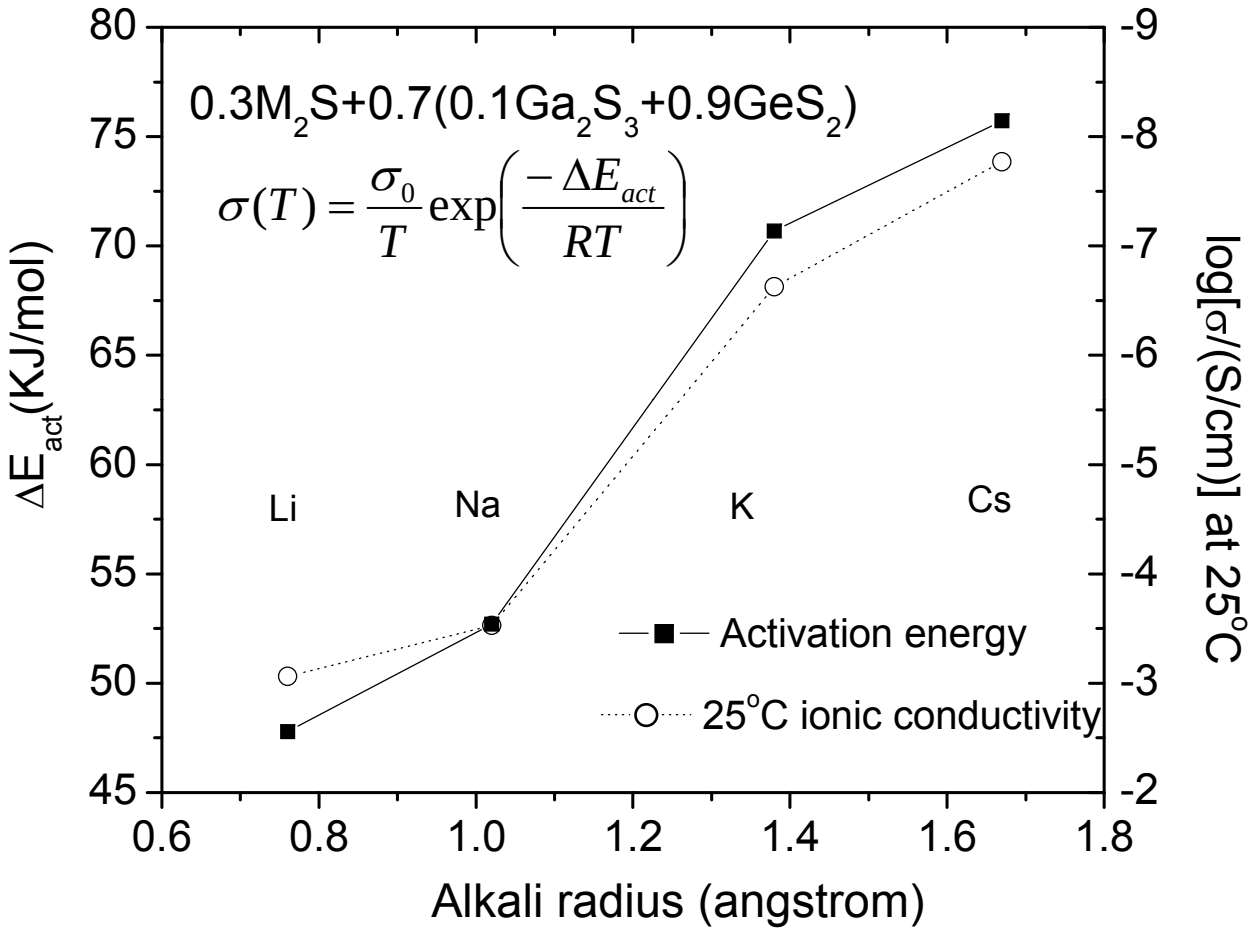
M	Radius (Å)
Li	0.76
Na	1.02
K	1.38
Cs	1.67

Large conductivity difference between Li_2S, Na_2S and K_2S, Cs_2S glasses due to the radius difference



Alkali radius dependence of activation energy

Large activation energy difference between Na_2S and K_2S glasses due to the radius difference



Calculation of the activation energies

$$\Delta E_{act} = \Delta E_c + \Delta E_s$$

$$\Delta E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_\infty}\left(\frac{1}{R_{M-S}} - \frac{1}{R_{M-M}}\right)$$

Modified Anderson-Stuart model

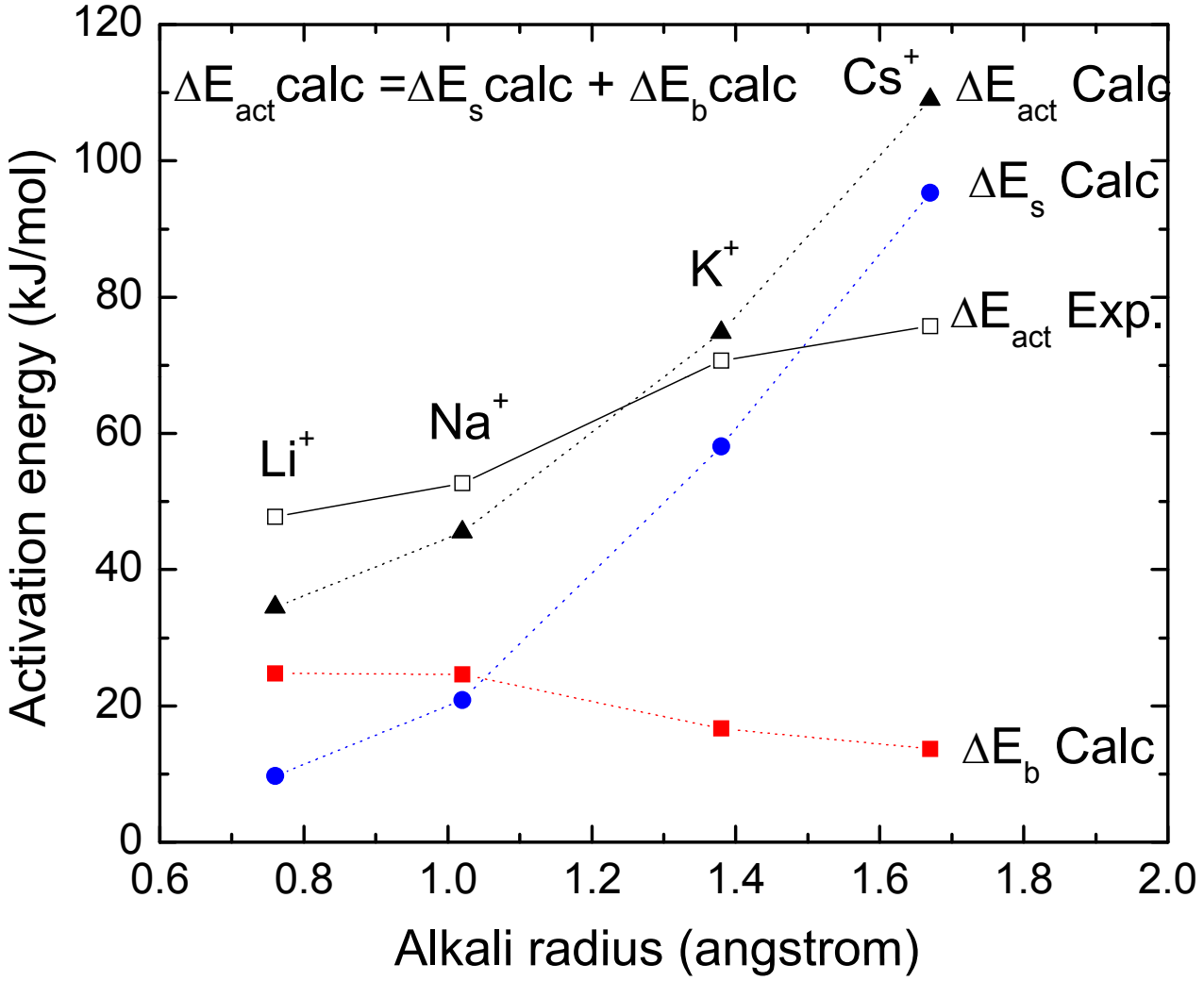
$$\Delta E_s = \pi \cdot G\left(r - r_D\right)^2 (\lambda / 2)$$

- G= 10^{10} (N/m^2)
- r_D= 0.3 Å
- ε_∞= 10
- R_{M-S} = radius of alkali ion,$r_{M,}$ + radius of sulfur, r_S
- R_{M-M} =λ = jump distance between equivalent alkali sites near non-bridging sulfurs

Greaves et al., Physical Review B 52 (9) , (1995) 6358

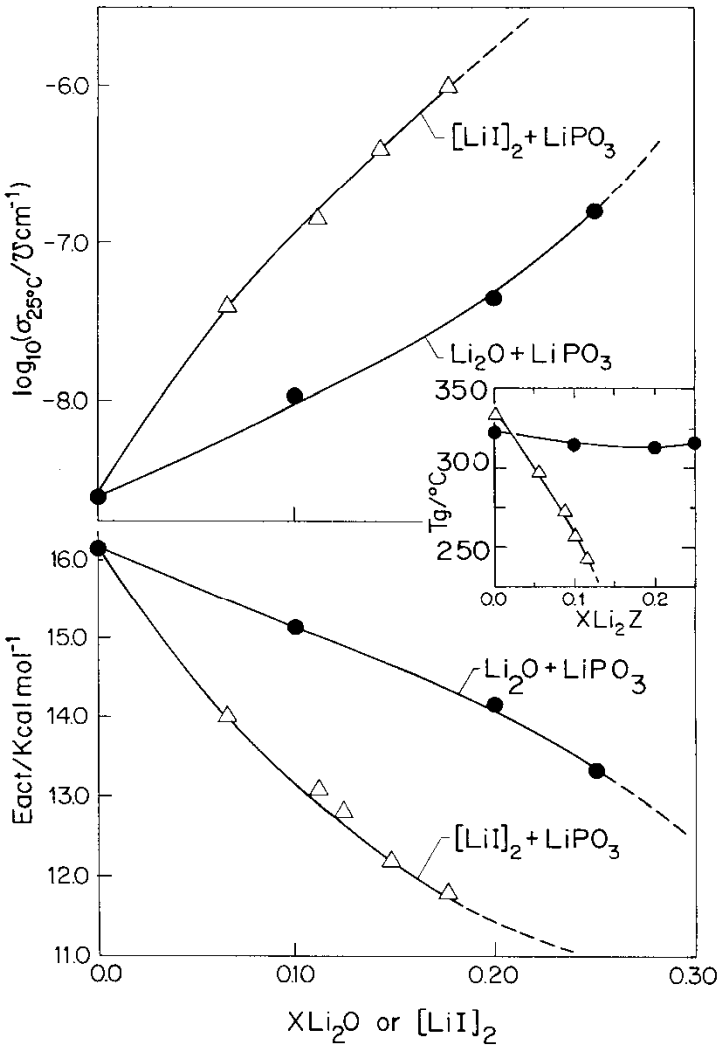
McElfresh et al.,Journal of the American Ceramic Society 69 (10) , (1986) C-237

Comparison of the activation energies



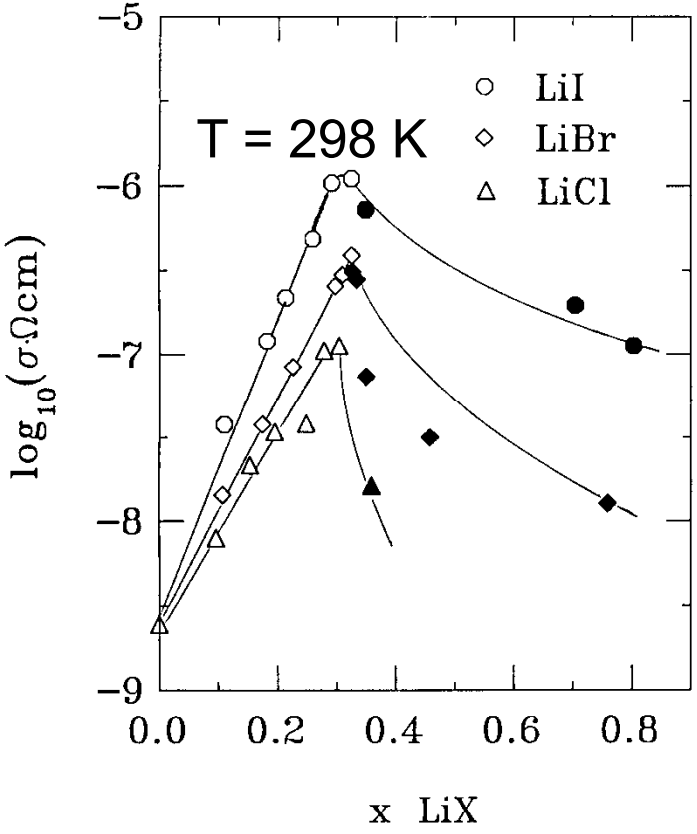
Salt Doping of Glass Strongly Decreases Tg

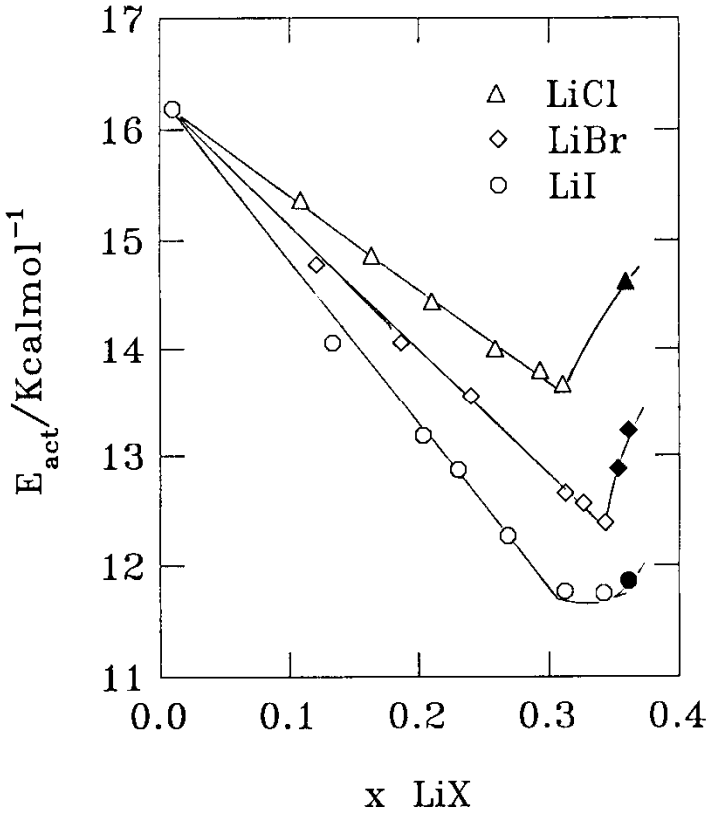
- Modifying oxide (M_2O) is necessary for high ionic conductivity
- Halide salt doping further strongly increases the ionic conductivity
- Both additives, while necessary for high ionic conductivity, strongly decrease the Tg (highest operating temperature) of the glass



Salt Doped Phosphate glasses

- LiI doped $LiPO_3$ show highest conductivity, lowest Tg, and lowest activation energy among the halides



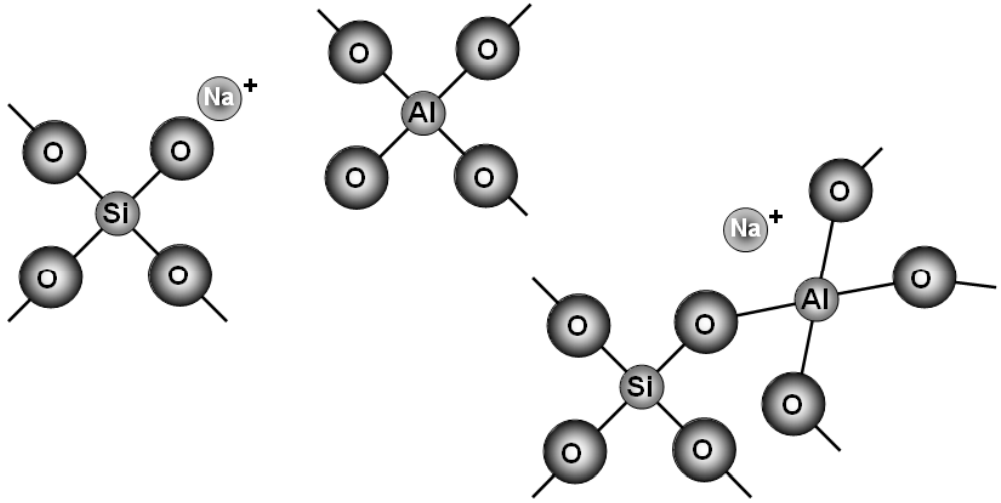


High Conductivity – Low Tg Paradigm?

- To date it has been observed that the glasses with the highest ionic conductivity
  - Have the highest modifying cation concentration
  - Have the highest dopant salt concentration
  - Have the lowest Tg
  - Are at the “end” of the glass forming region
  - Are therefore the most thermally unstable of the glasses in these series
- Can this paradigm of High Conductivity and Low Tg be broken through new glass chemistries?

Effect of Glass Intermediates on Structure

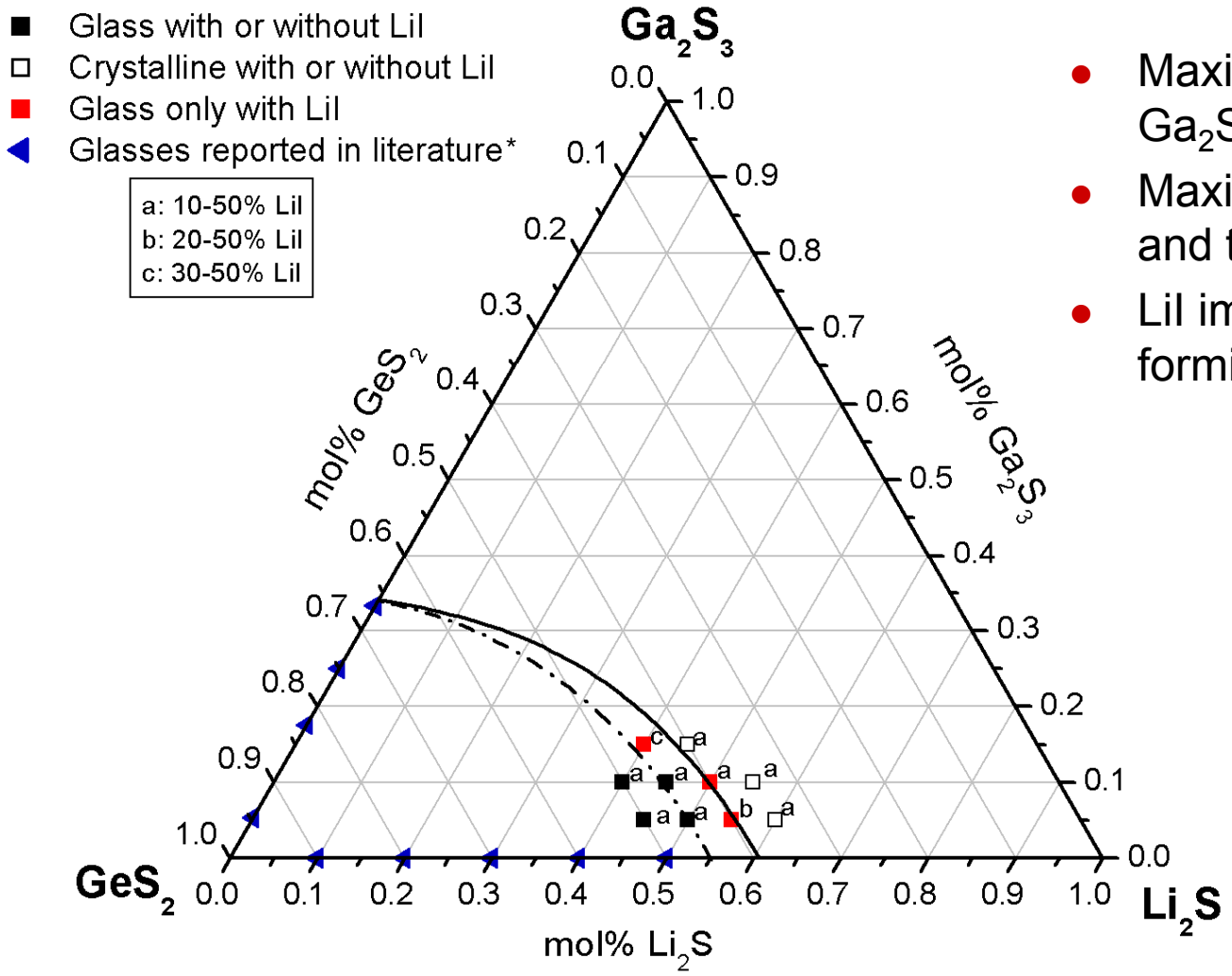
- Improvement in thermal stability through the elimination of non-bridging oxygens (NBOs)
  - NBOs created by addition of alkali ions (Li^+)
  - NBOs are necessary for ionic conduction
- Addition of Al_2O_3 (and other M_2O_3)
  - Trivalent cations eliminate NBOs units in silicate glasses
  - AlO_4^- units also increase the ionic conductivity



Hypothesis

- Maintain High Ionic Conductivity
  - Li_2S (and LiI) are sources of conducting Li^+ ions
- Improve Thermal Stability
  - Through the addition of high melting refractory sulfides
  - Ga_2S_3 should eliminate non-bridging sulfurs and keep the glass network connected
  - Al_2S_3 is very chemically reactive (Al_2O_3 very stable)
- Improve Chemical Stability
  - GeS_2 is more chemically stable glass former

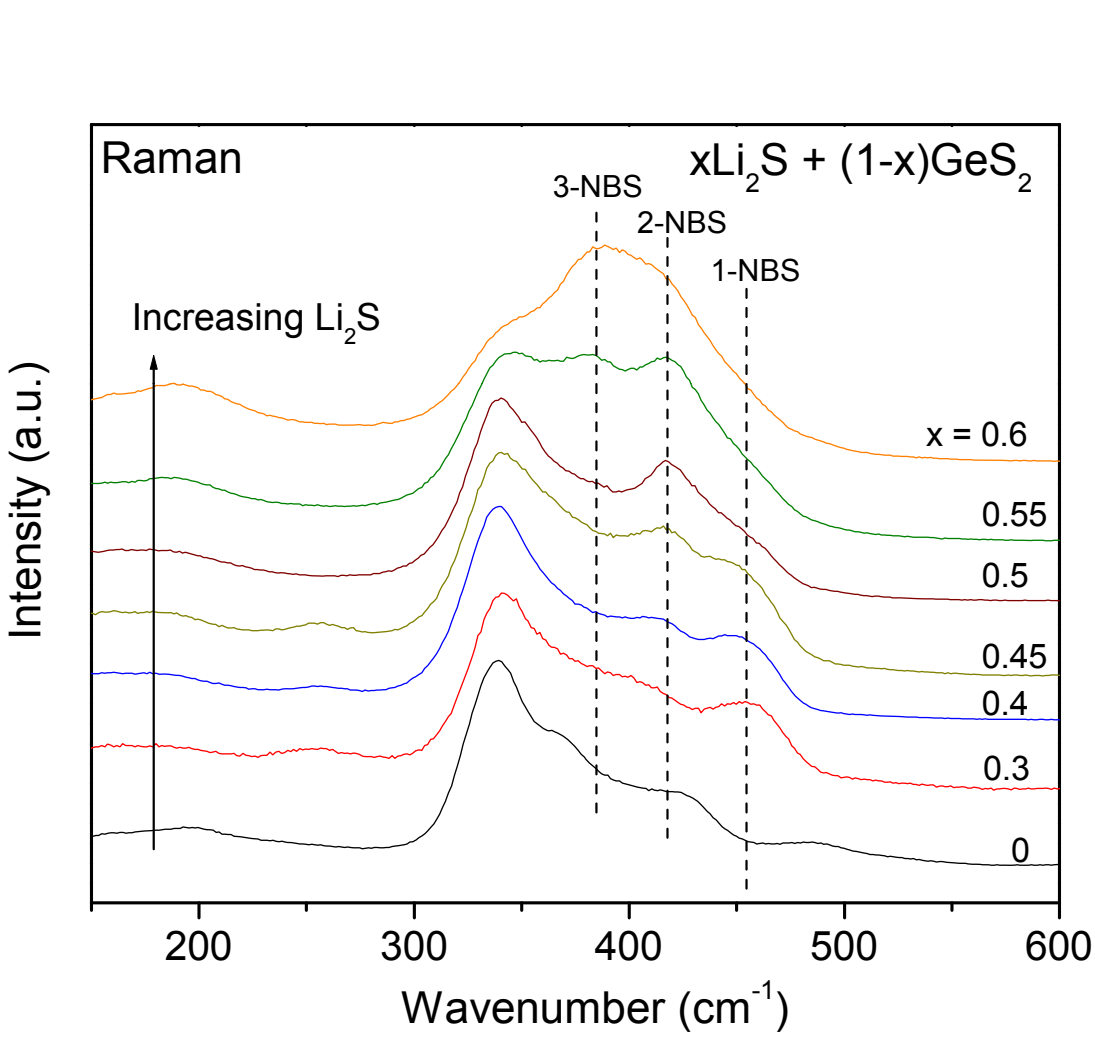
$LiI + Li_2S + GeS_2 + Ga_2S_3$ Glasses

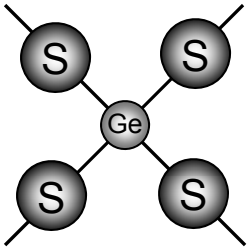


- Maximize Li_2S and Ga_2S_3 concentrations
- Maximize conductivity and thermal stability
- LiI improves glass forming ability

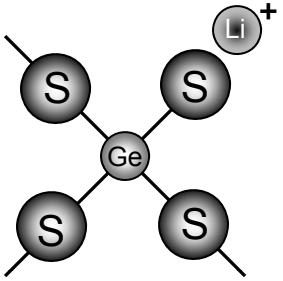
* From Souquet (SSI) 1981 and Yamashita (SSI) 2003

Raman of Spectra of $Li_2S + GeS_2$ Glasses

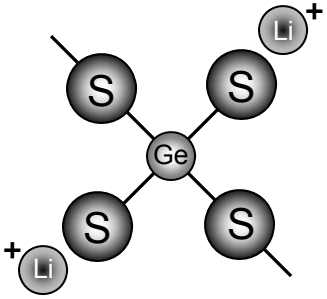




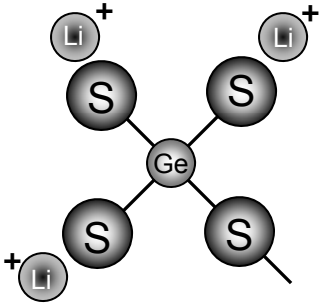
~342 cm^{-1}



~454 cm^{-1}



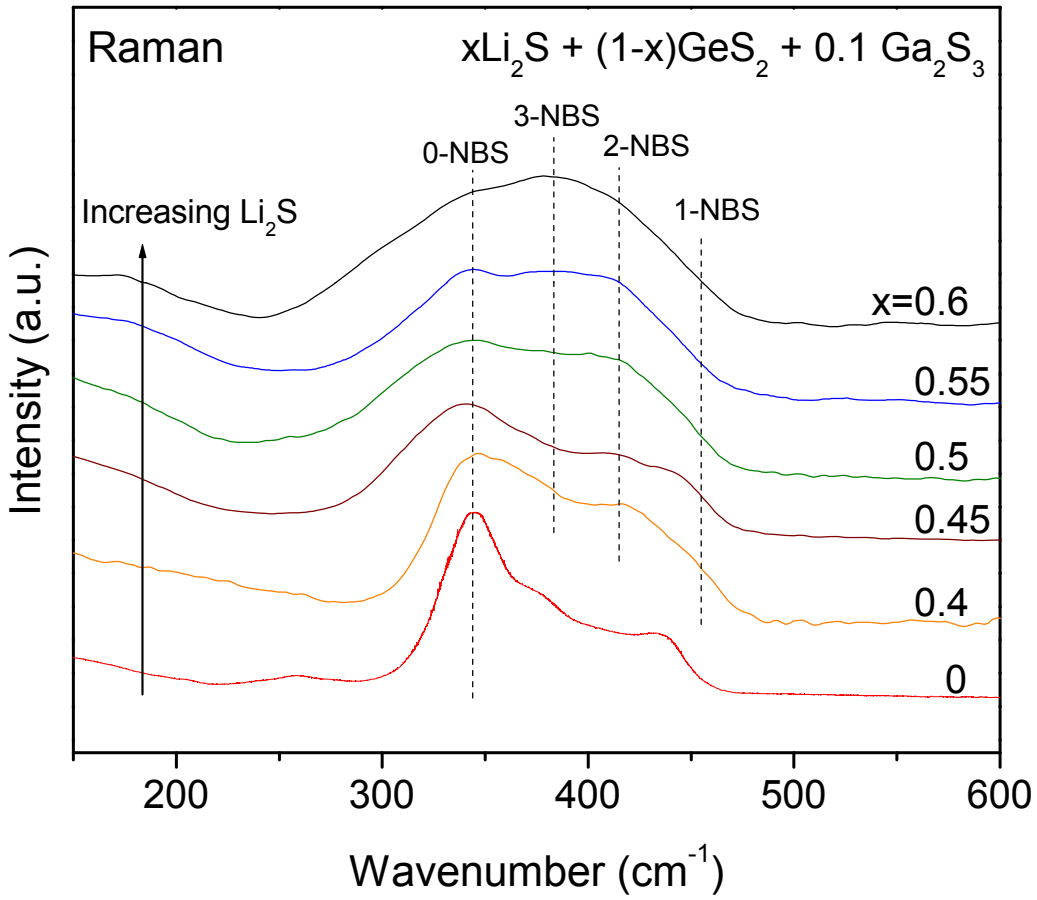
~415 cm^{-1}



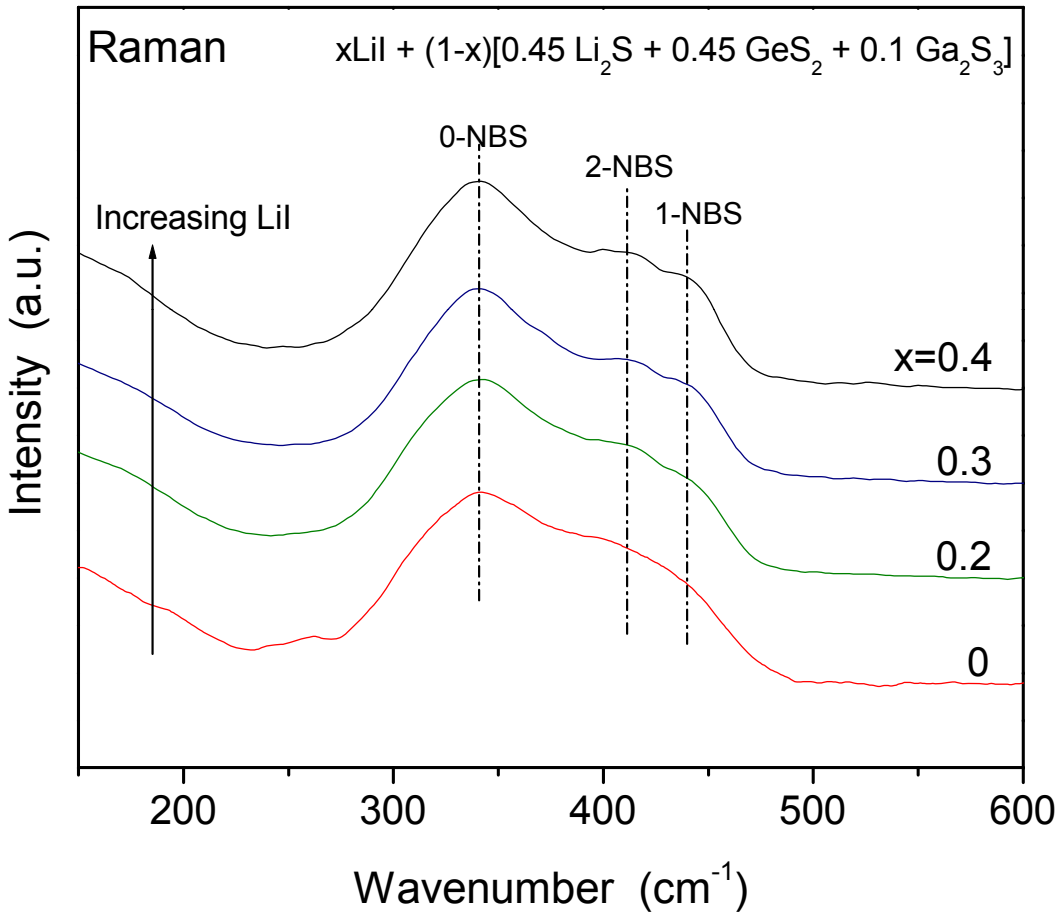
~385 cm^{-1}

Raman Spectra of $Li_2S + Ga_2S_3 + GeS_2$ Glasses

- Addition of Li_2S creates non-bridging sulfurs
  - ~ 454 cm^{-1}: 1 - NBS
  - ~ 415 cm^{-1} : 2 - NBS
  - ~ 385 cm^{-1} : 3 – NBS
- Li_2S is source of NBS and Li^+ ions
- Binary $GeS_2 + Ga_2S_3$
  - ~ 440 cm^{-1} : vibration of corner-shared MS_4
  - ~ 374 cm^{-1} : vibration of edge-shared MS_4



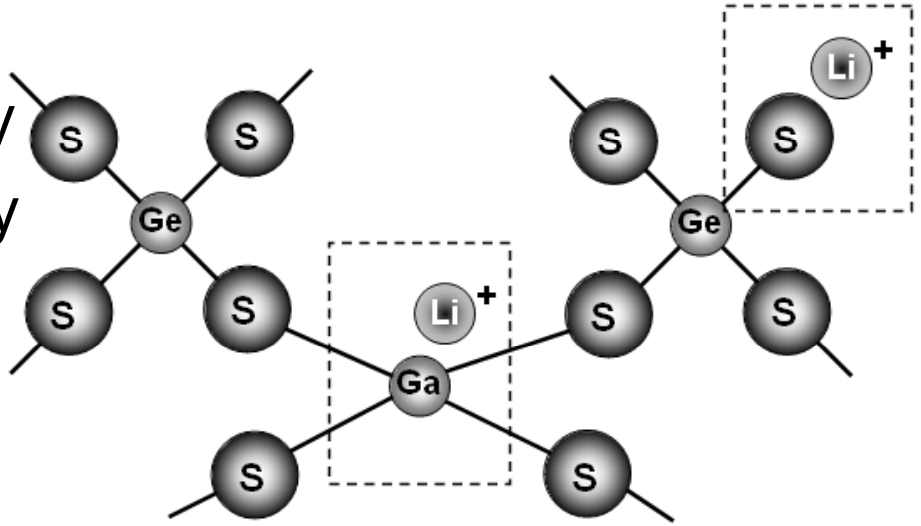
Raman Spectra of LiI +Li + Ga + GeS_2 Glasses



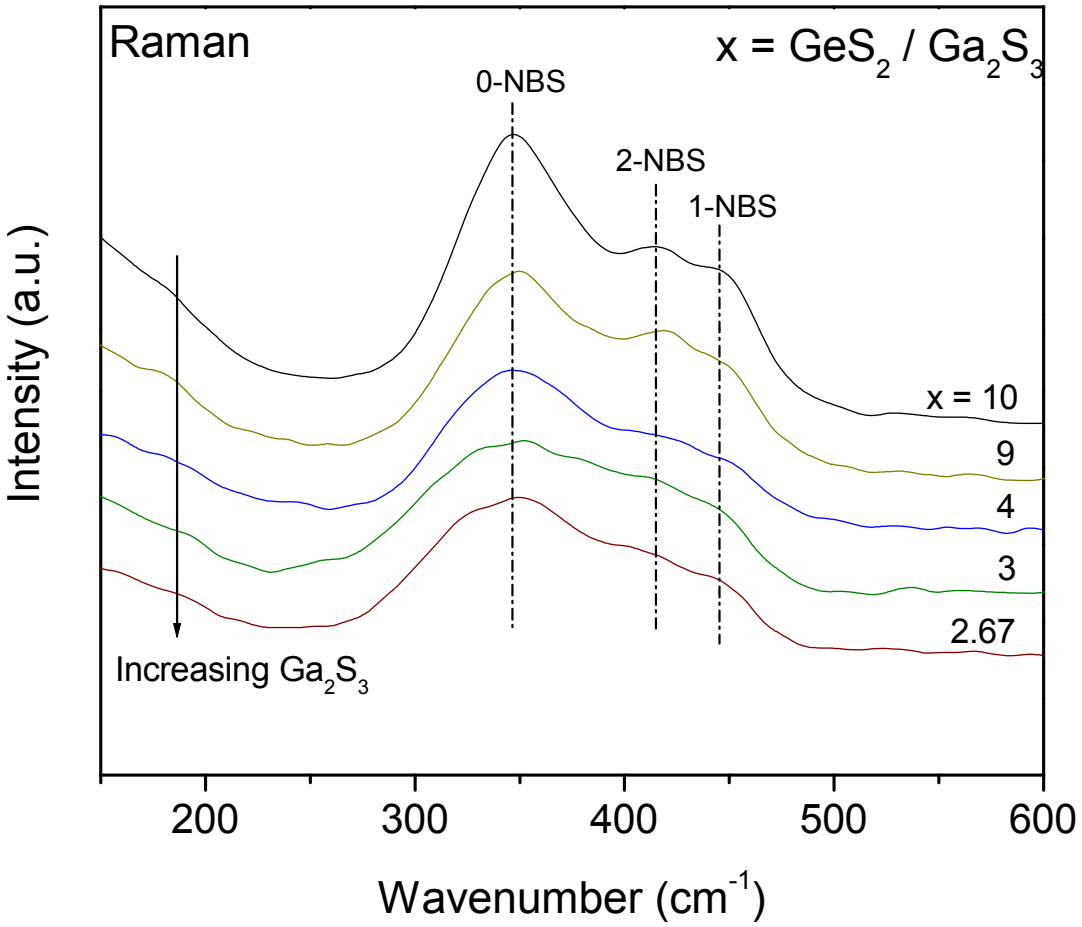
- LiI does not become a structural member of the glass network
- Resides in the interstitials (gaps) of the network
- Little or no change in spectra
- Mobility is high for Li^+ ions associated with I^- anions

Elimination of NBS through Ga_2S_3

- Ga_2S_3 should eliminate NBS
- Li^+ ions are weakly associated with $[GaS_4]^-$
- Elimination of NBS
  - Keeps glass network connected
  - Increases the Tg
  - Improves the conductivity
  - Improves thermal stability

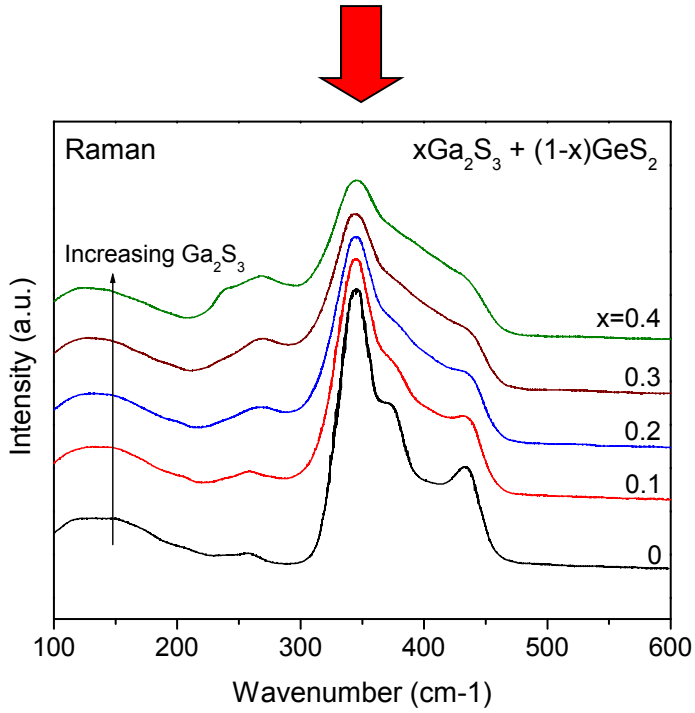


Effect of Ga_2S_3 on the Glass Structure



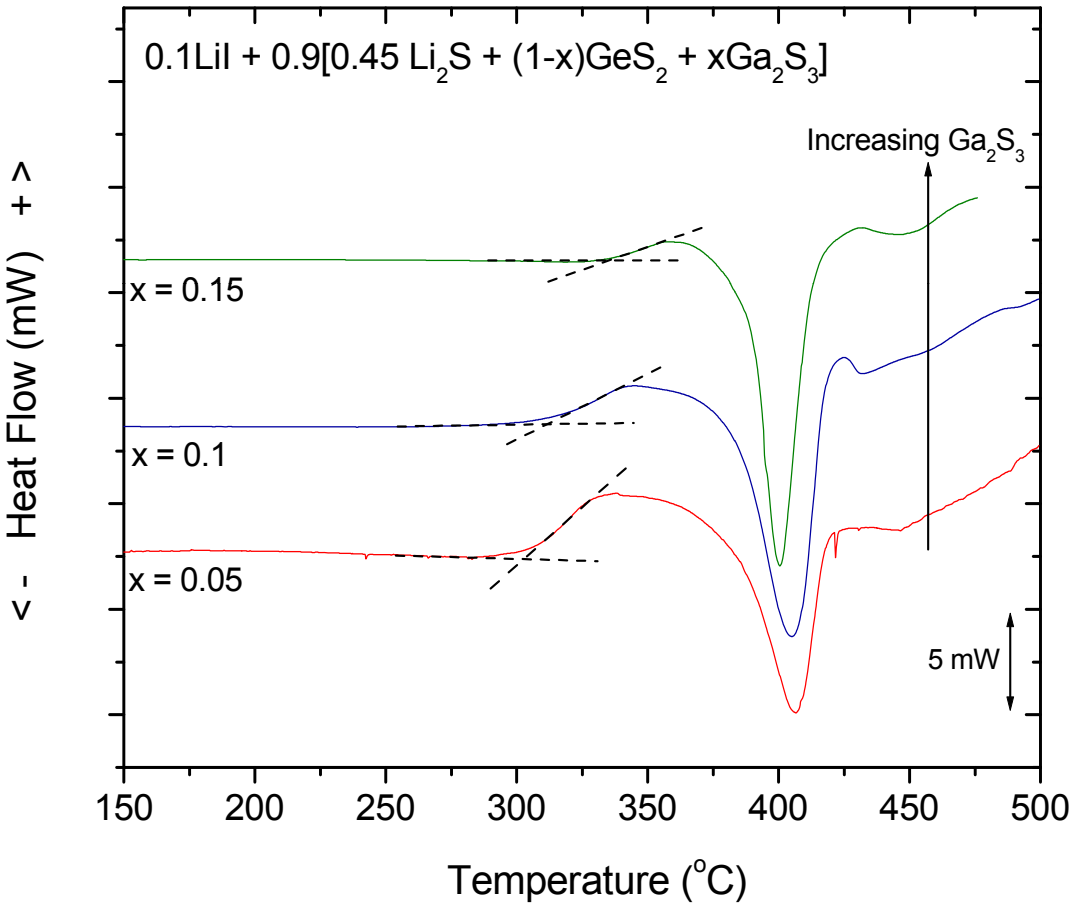
Raman Spectroscopy

- ~ 370 cm^{-1}: edge-shared tetrahedra
- ~ 434 cm^{-1}: corner-shared tetrahedra



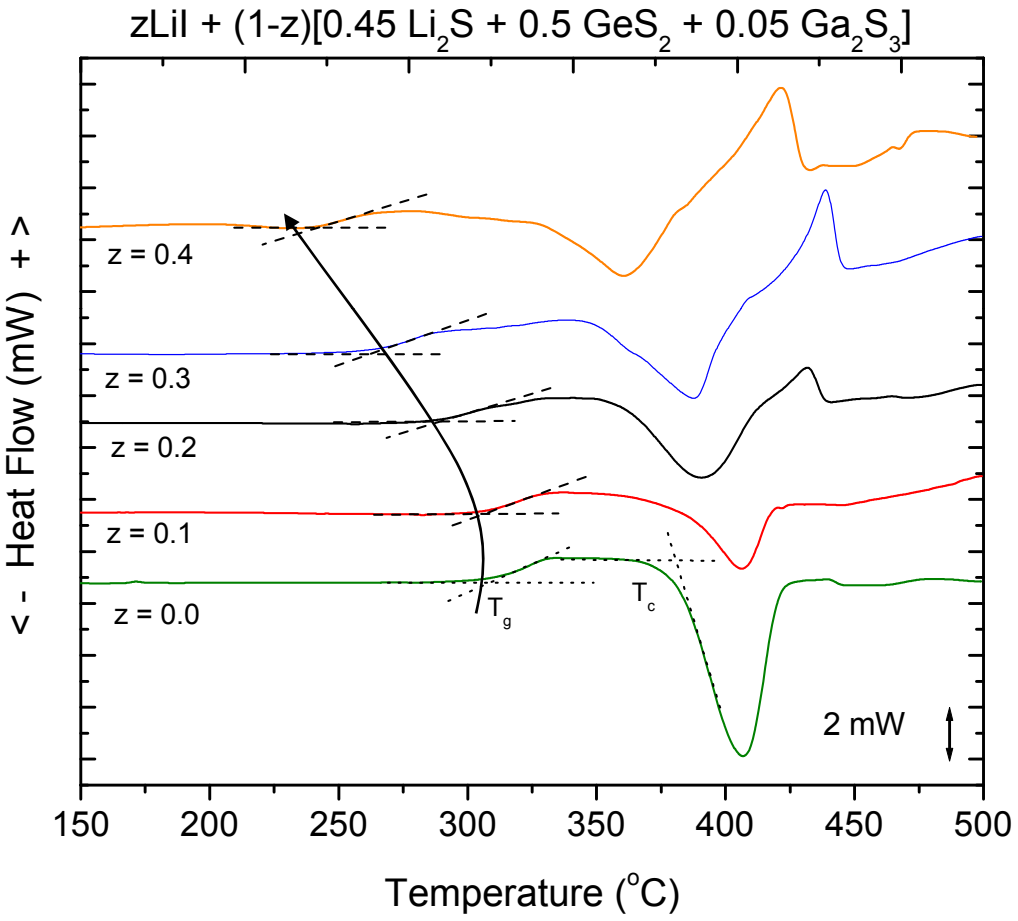
Contribution of Ga_2S_3 on T_g

- Ga_2S_3 is a high melting refractory material
- Eliminates NBS
  - Keeps the glass network connected
- Increasing Ga_2S_3 increases T_g

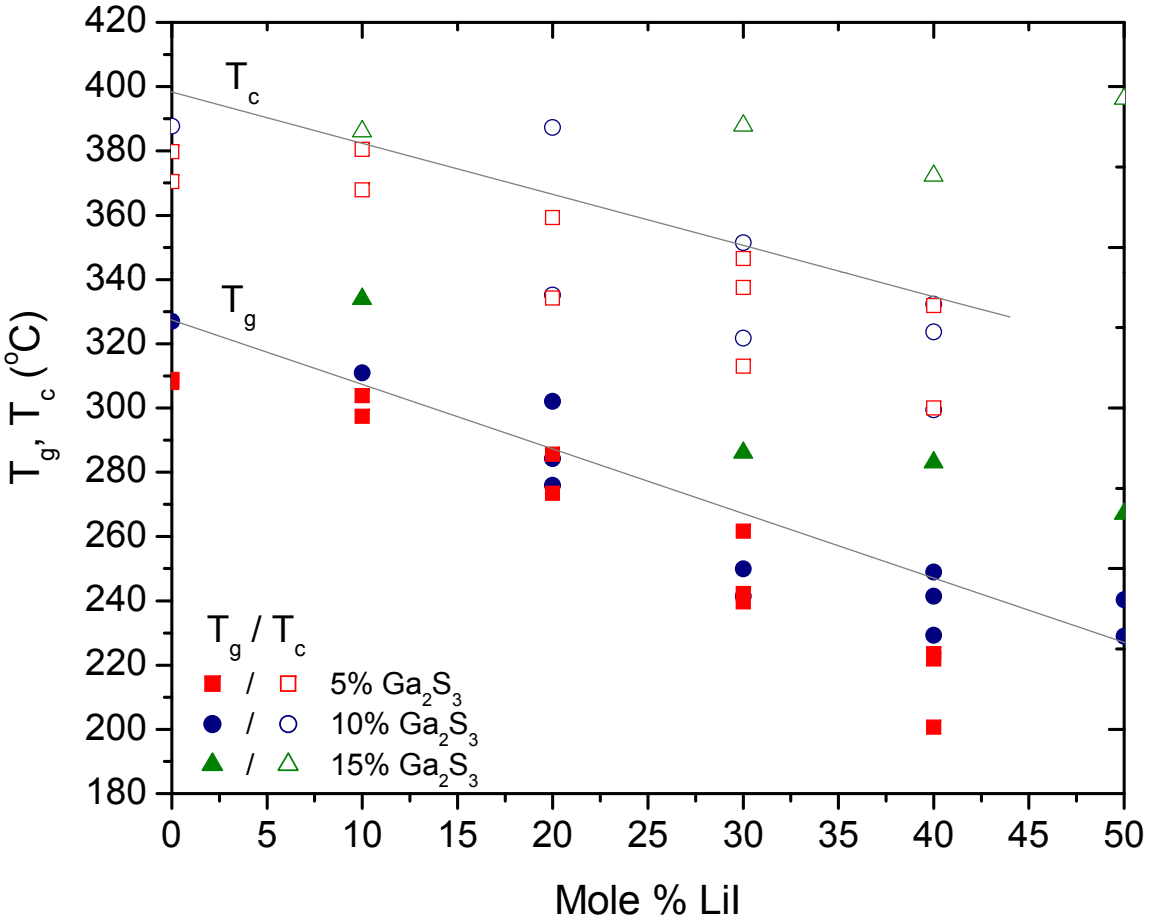


Effect of LiI Concentration on Tg

- Addition of LiI decreases the T_g and T_c
- LiI crystallizes out of the glass and melts ~425°C
- Is not a structural member of the glass network
  - Similar to a solution
- Does disrupt the network
  - Alters bond lengths and angles



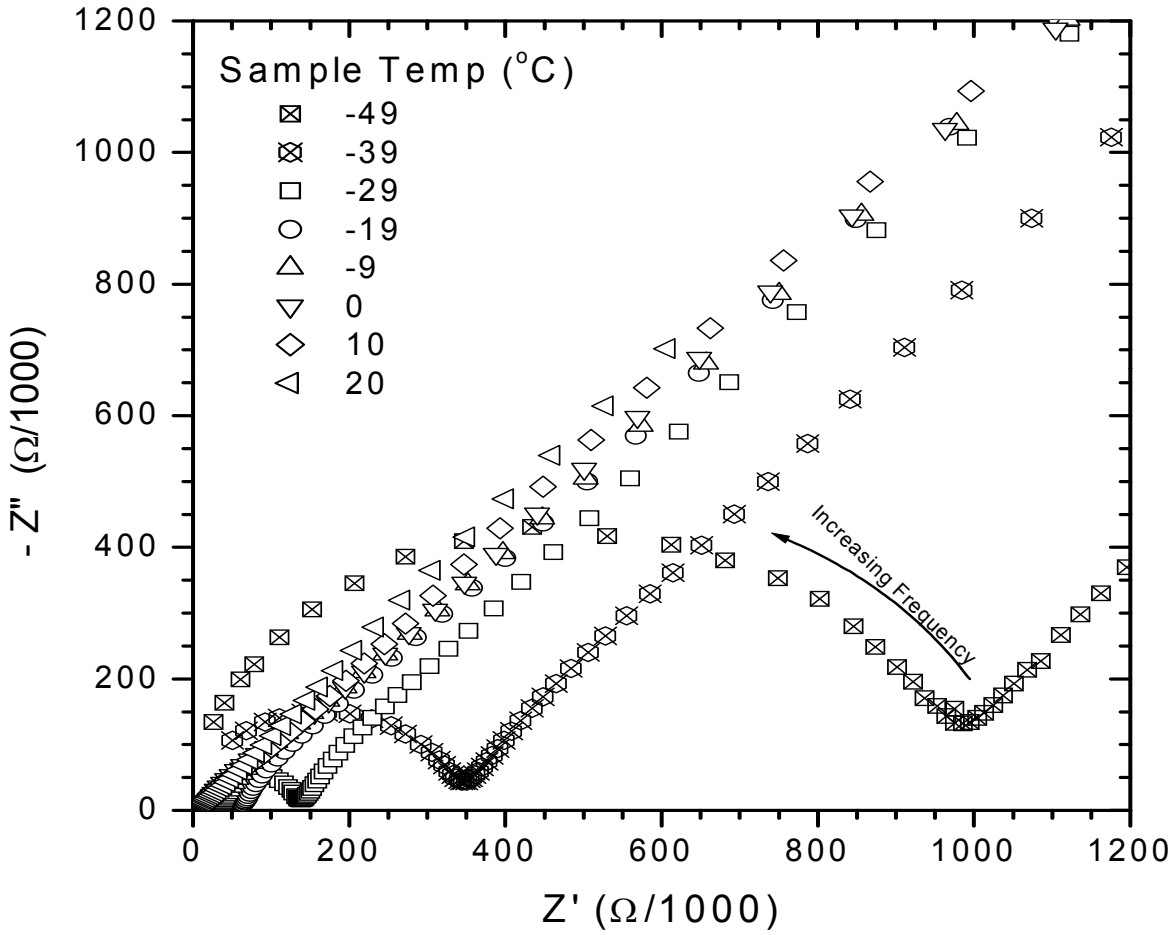
Tg and Tc values for Ternary Glasses



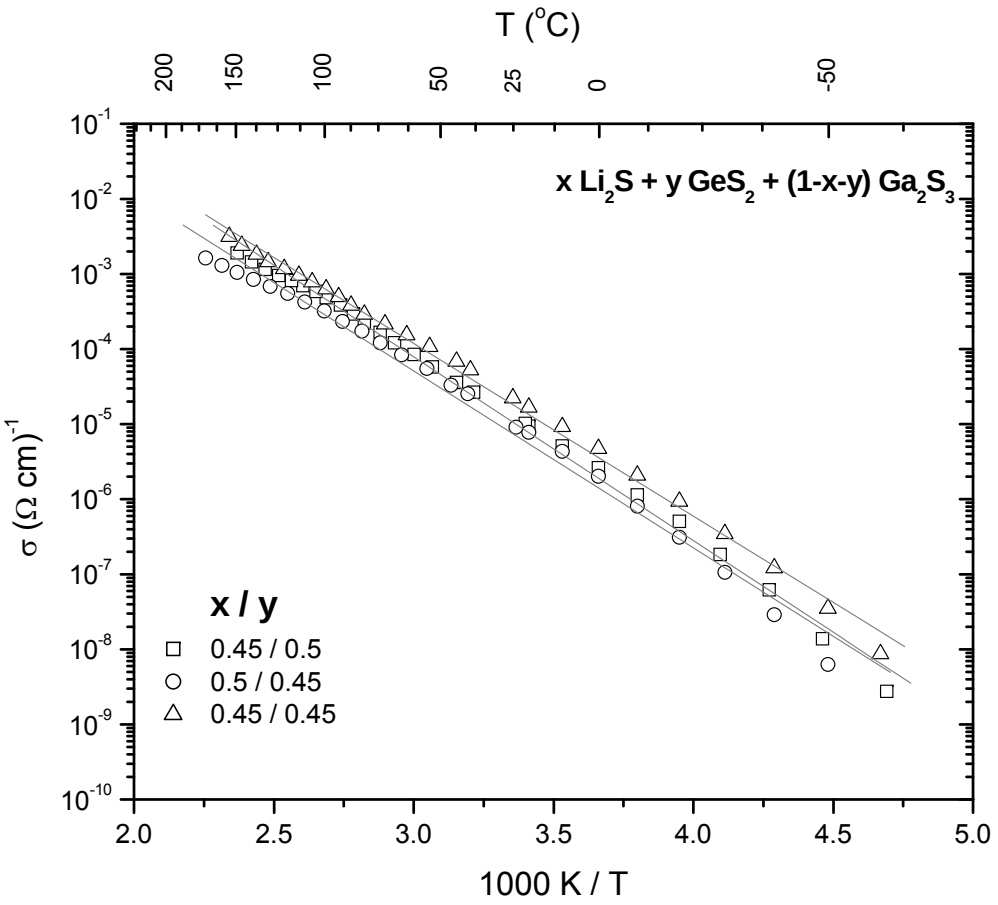
- Ga_2S_3 increases the T_g and T_c
- LiI lowers softening point
  - Improves the glass forming ability
  - Improves stability towards crystallization (T_c-T_g)

5% Ga_2S_3	~ 300°C
10% Ga_2S_3	~ 315°C
15% Ga_2S_3	~ 335°C

Li^+ conductivity of Li-Ga-Ge- Sulfide Glasses



Temperature dependence of the Conductivity



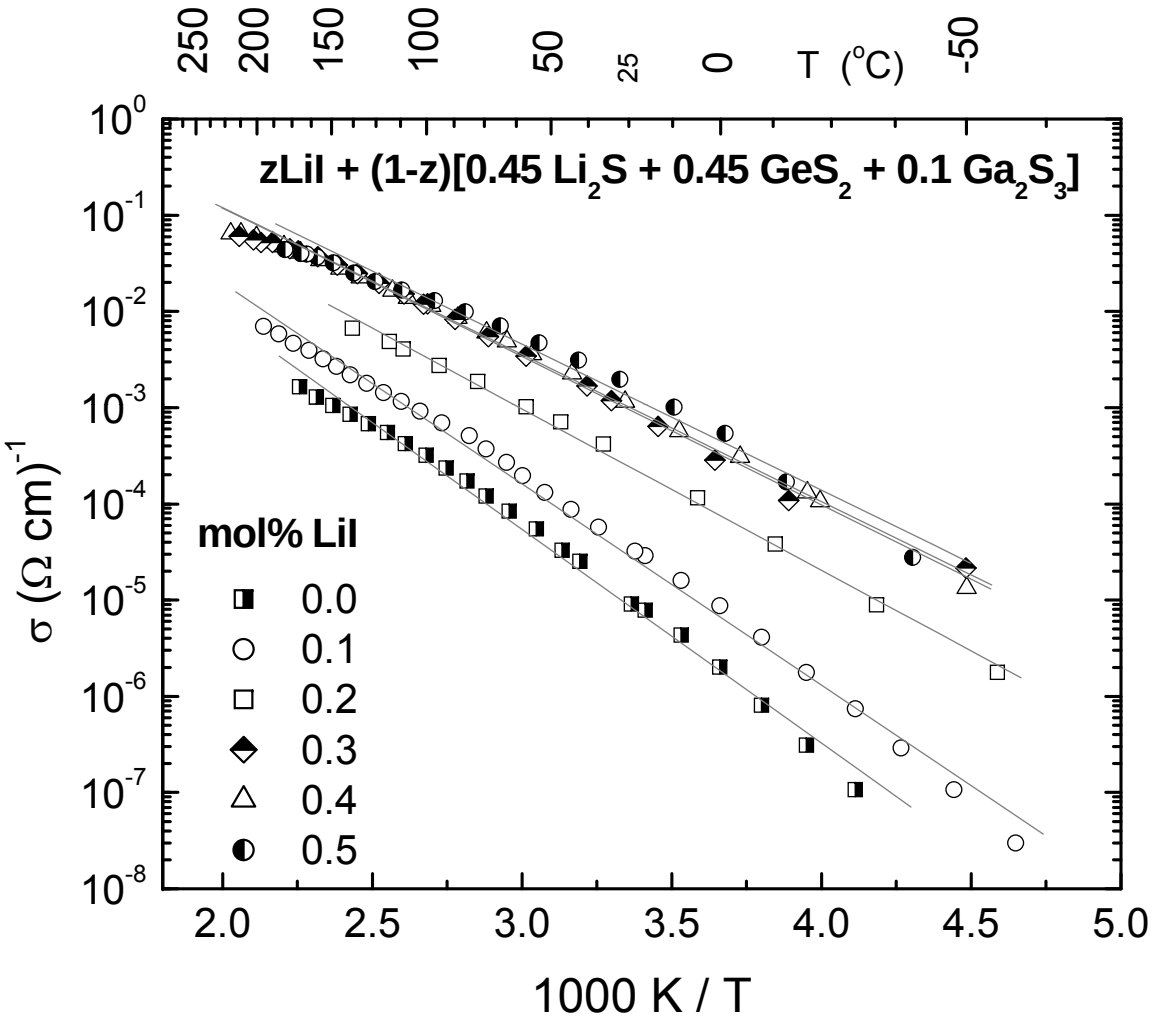
Room Temp Conductivity

0% LiI ~10^{-5} $(\Omega\ cm)^{-1}$

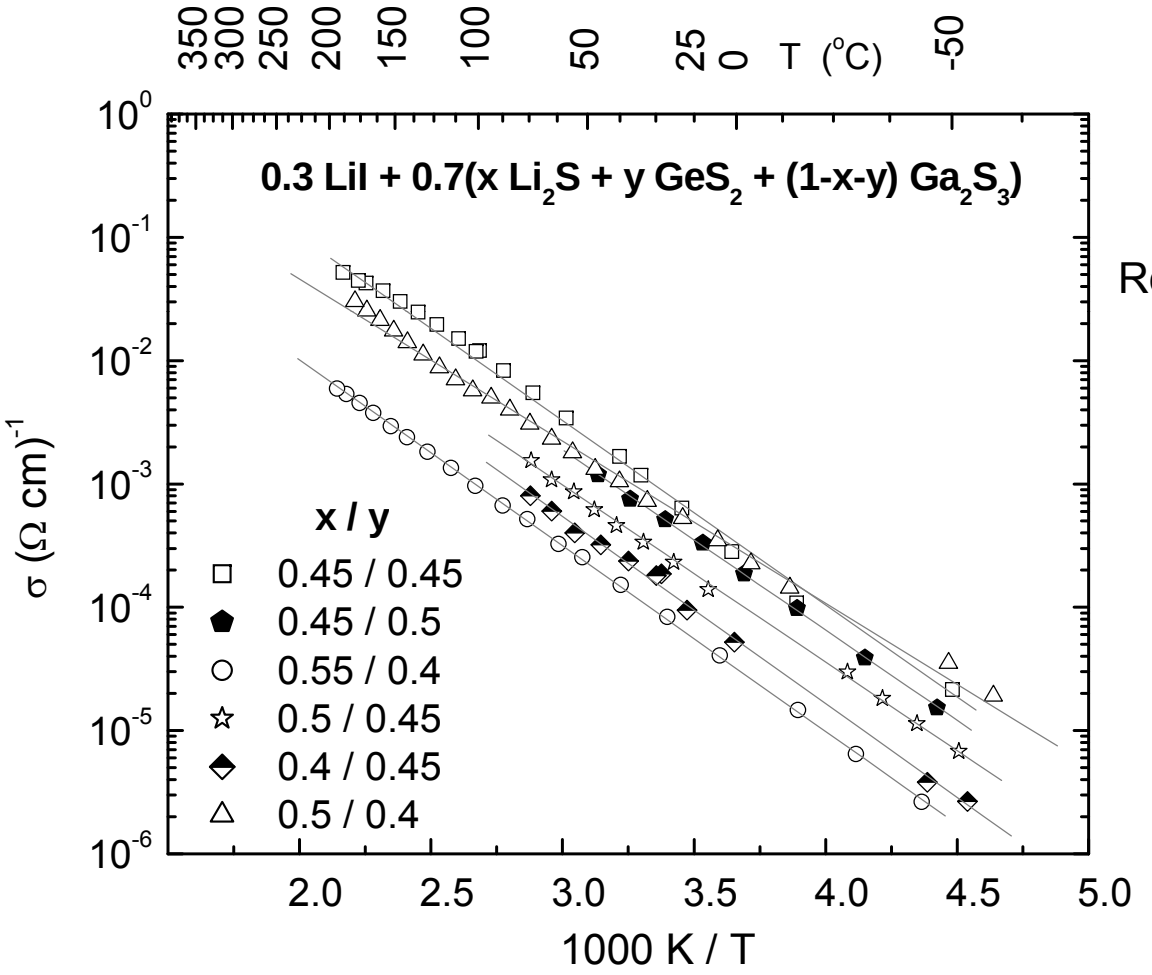
30% LiI ~10^{-3} $(\Omega\ cm)^{-1}$

50% LiI >10^{-3} $(\Omega\ cm)^{-1}$

Composition Dependence of the Conductivity – Effect of LiI



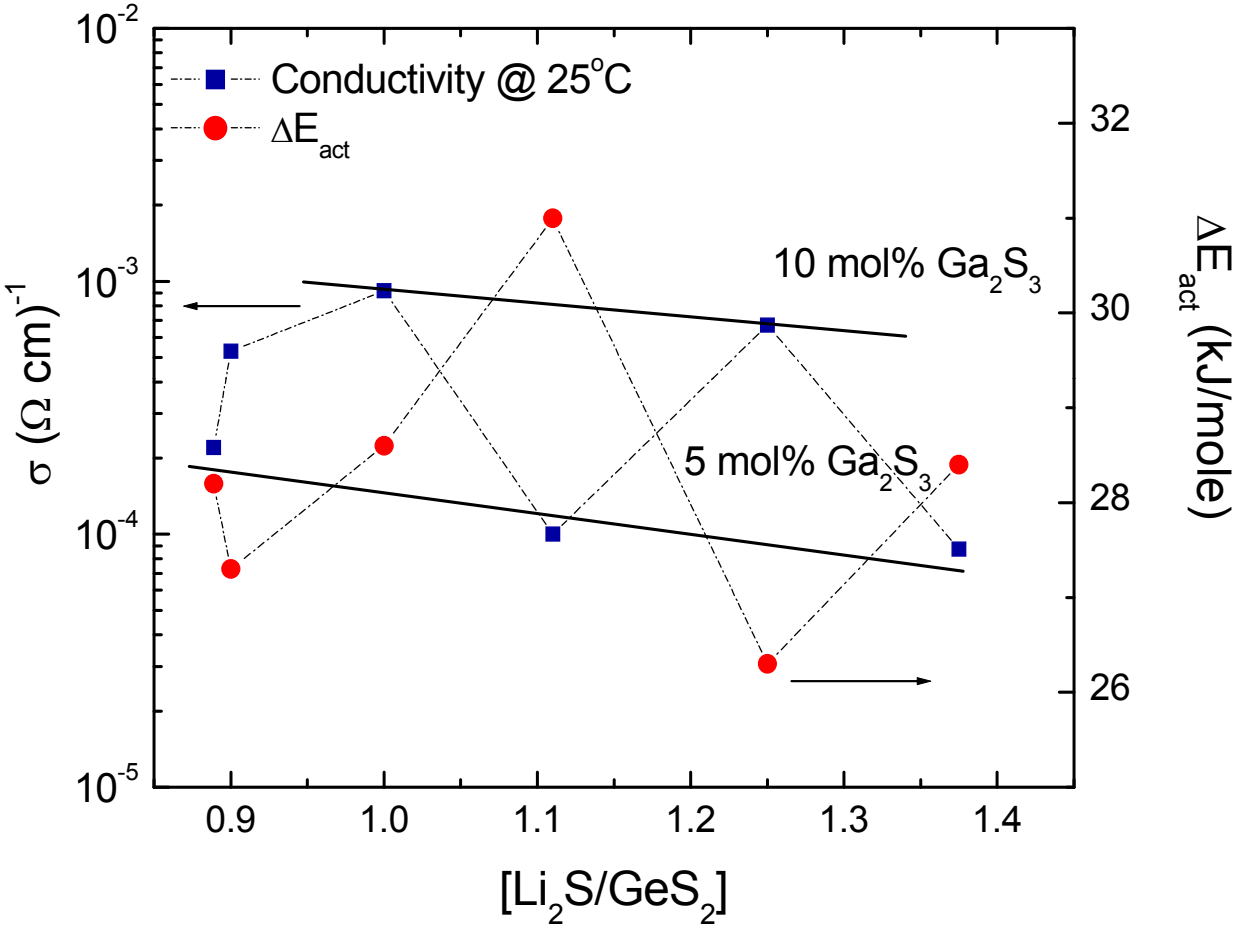
Composition Dependence of the Conductivity



Room Temp Conductivity

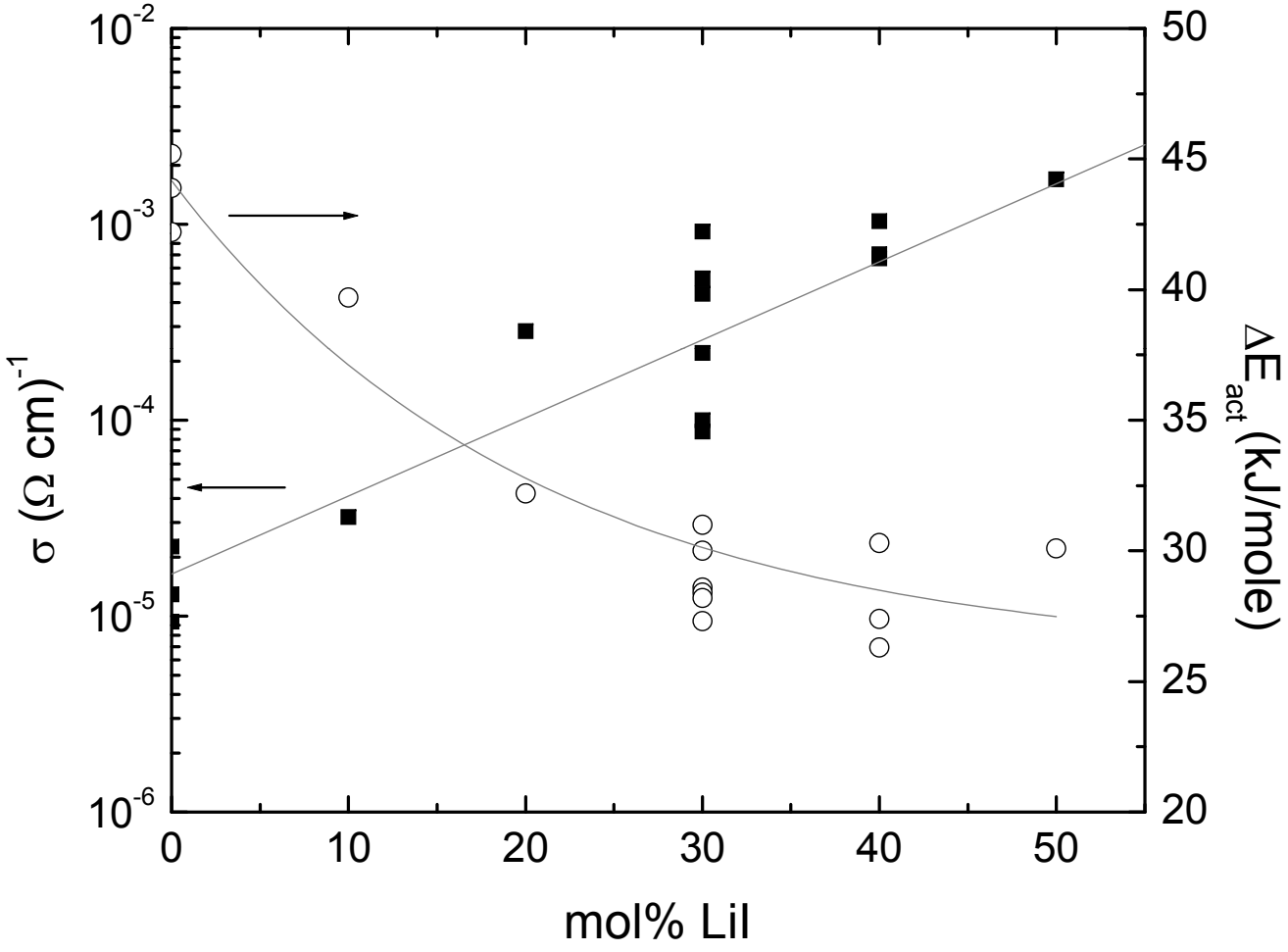
40% Li_2S	~10^{-4} $(\Omega\ cm)^{-1}$
45% Li_2S	~10^{-3} $(\Omega\ cm)^{-1}$
50% Li_2S	10^{-3} - 10^{-4} $(\Omega\ cm)^{-1}$
55% Li_2S	~10^{-5} $(\Omega\ cm)^{-1}$

Composition Dependence of the Activation Energies

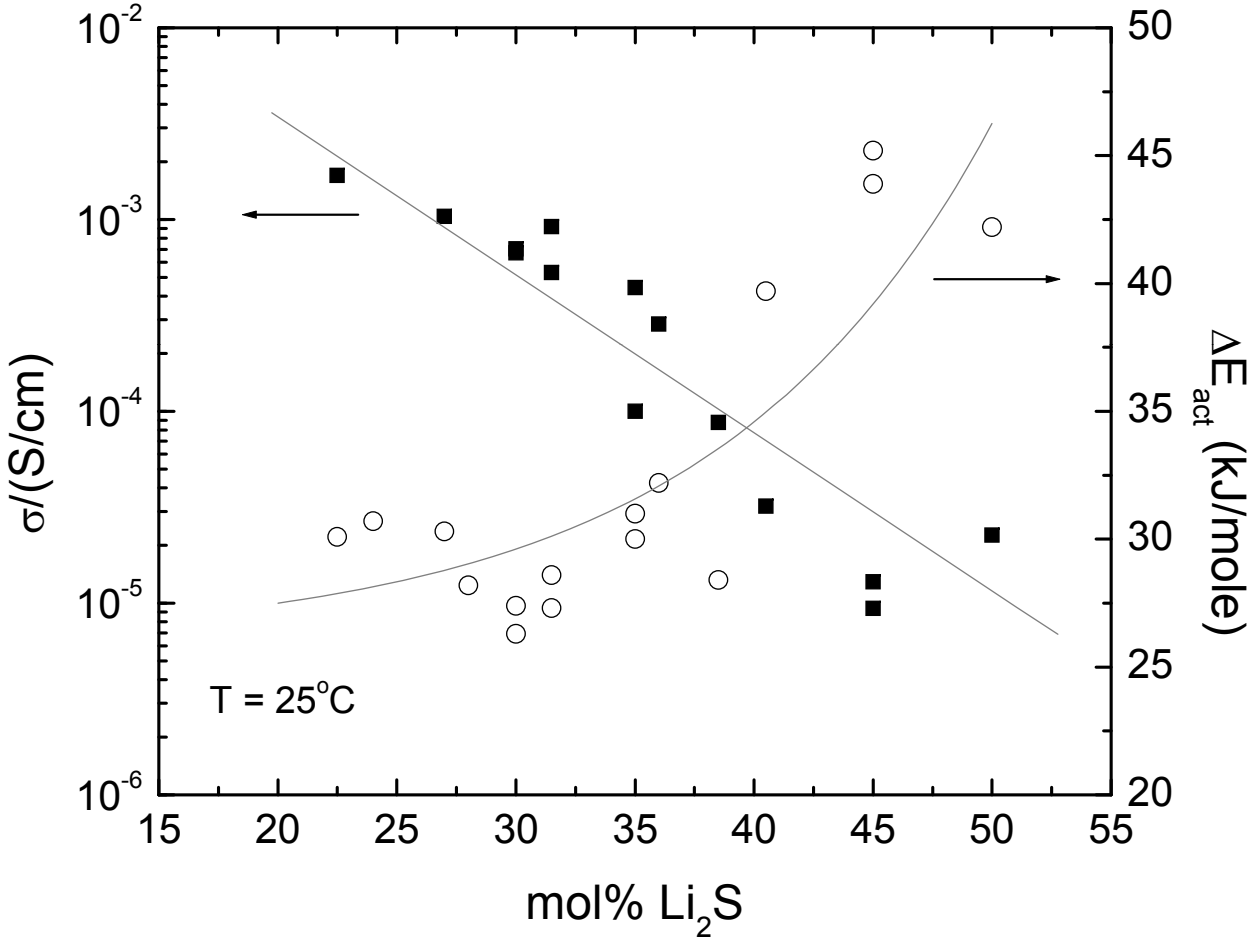


- Highest conductivity values have 10 mol% Ga_2S_3
- Higher conductivity attributed to the elimination of NBS

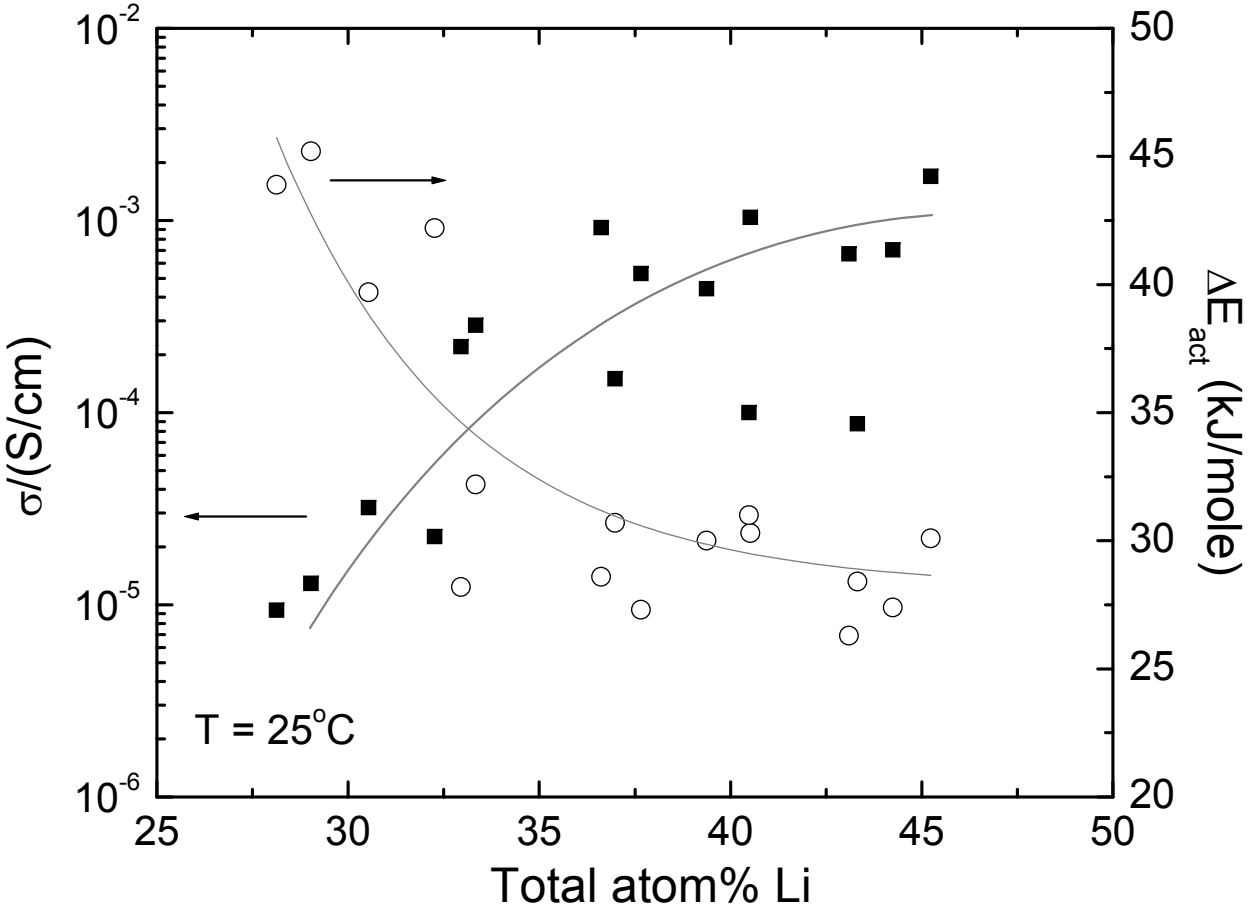
Effect of LiI Concentration



Effect of Li_2S Concentration



Effect of Li Concentration



Effect of Ga_2S_3 Contributions

- Eliminated non-bridging sulfur units
- Improved the thermal stability
- Improvement in conductivity

LiI	Ga_2S_3		
	5%	10%	15%
10%	300°C	311°C	333°C
40%	200°C	250°C	267°C

With 30% LiI at 25°C

5% Ga_2S_3 ~ 10^{-4} $(\Omega\ cm)^{-1}$

10% Ga_2S_3 ~ 10^{-3} $(\Omega\ cm)^{-1}$

Fast Ion Conduction in Glass

- So what have we learned?

- **Chemistry controls Structure and Structure controls conduction**
  - Sulfide glasses exhibit orders of magnitude higher conductivity than oxide glasses
  - Salt doping strongly increases conductivity
  - Conduction appears to be controlled by both charge (coulombic) and volume (strain) energy factors
    - Coulomb constraint appears to be more significant, hence the S^- anion weakens coulomb energy barrier for the smaller cations
  - Glass structural units control the energy barriers
    - Structural units can be determined (IR, Raman, NMR, XRD, ND)
  - Smaller cations appear to be charge constrained whereas larger cations appear to be volume constrained
  - Optimized oxy-sulfide glasses hold promise of being both highly conducting, yet more chemically stable