Glasses for Energy Storage: Advancing the Energy Density and Safety of Batteries

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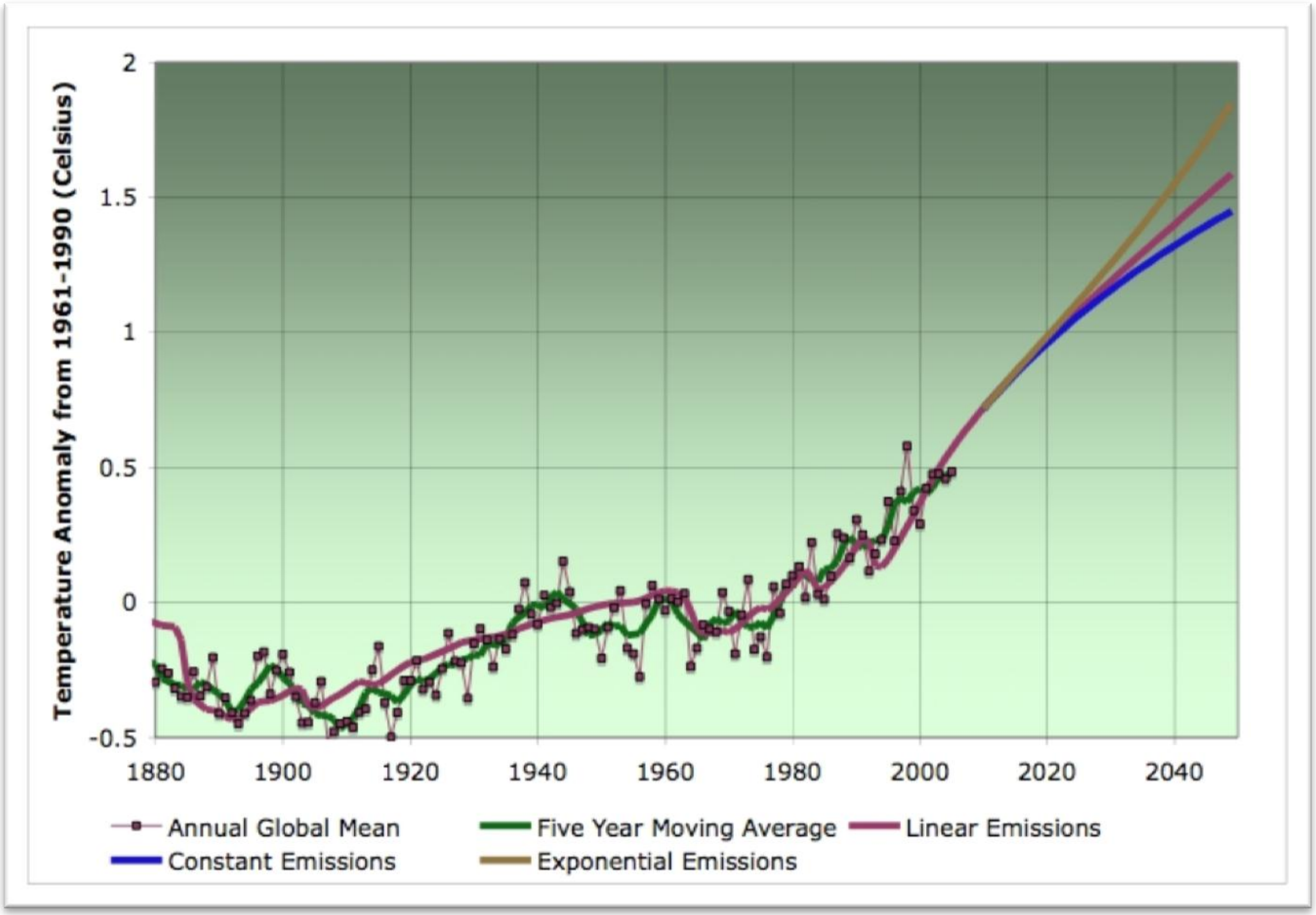
Sandia National Laboratory

The Lithium Battery Opportunity…



Suggests Alternative Zero-Carbon Energy Systems…such as solar…

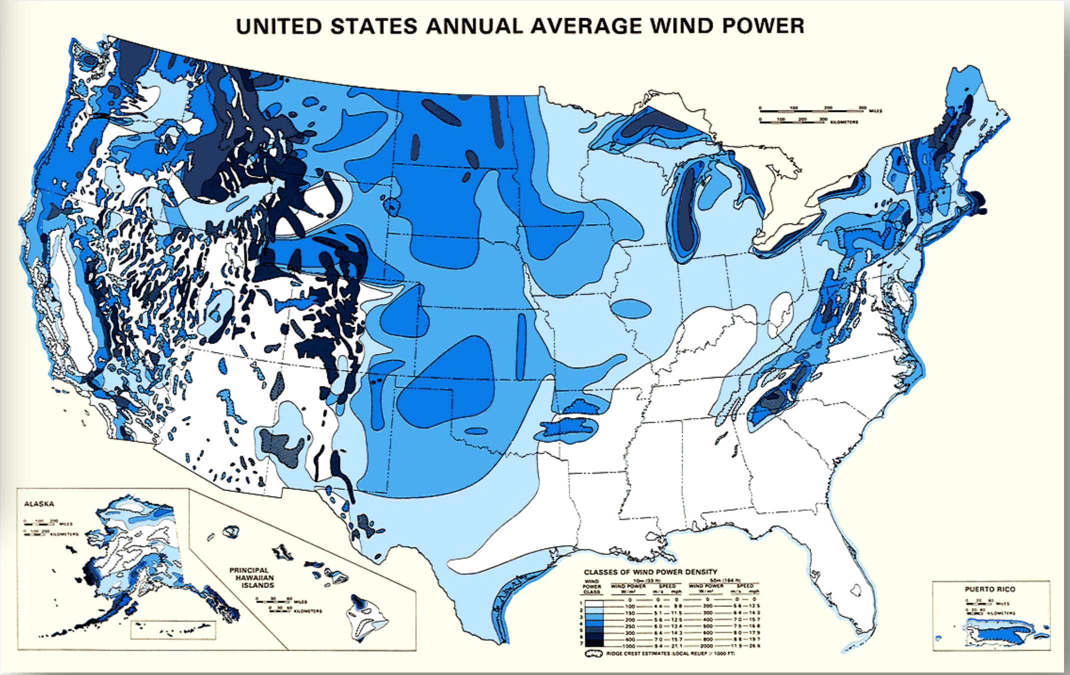
Photovoltaic…

Thermal…

Solar source ~ 6,600 TW/year

World use ~ 16 TW/year

And Wind…


UNITED STATES ANNUAL AVERAGE WIND POWER
ALASKA
PRINCIPAL HAWAIIAN ISLANDS
CLASSES OF WIND POWER DENSITY
PUERTO RICO

However….

- Solar-based energy systems are temporal
- Energy demand is temporal
- Energy storage systems are necessary to balance supply and demand
  - Mechanical – pressure, m·g, hydro…
  - Electrical – capacitors…
  - Chemical – batteries…

Further…

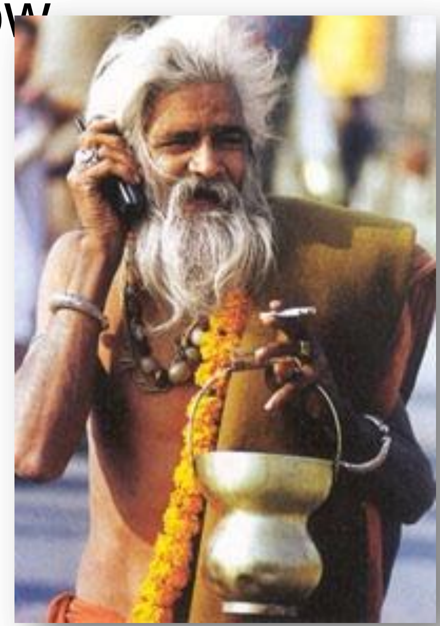
- Portable energy is also required for….
  - Transportation
  - Mechanical work
  - Electronics
  - Health care
  - Food production
  - …

Portable energy systems for transportation…

- Must be developed
- Will be more expensive than oil
- Must be used as efficiently as possible
- Consider the demand…
  - ~8,000 cars and ~150 miles of paved roads in 1900
  - ~600,000,000 passenger cars in 2008
  - ~1,200,000,000 passenger cars expected in 2030
- Will half of all cars be hybrids, plug-ins?
  - 600,000,000+ battery systems?

Portable energy for personal electronics…

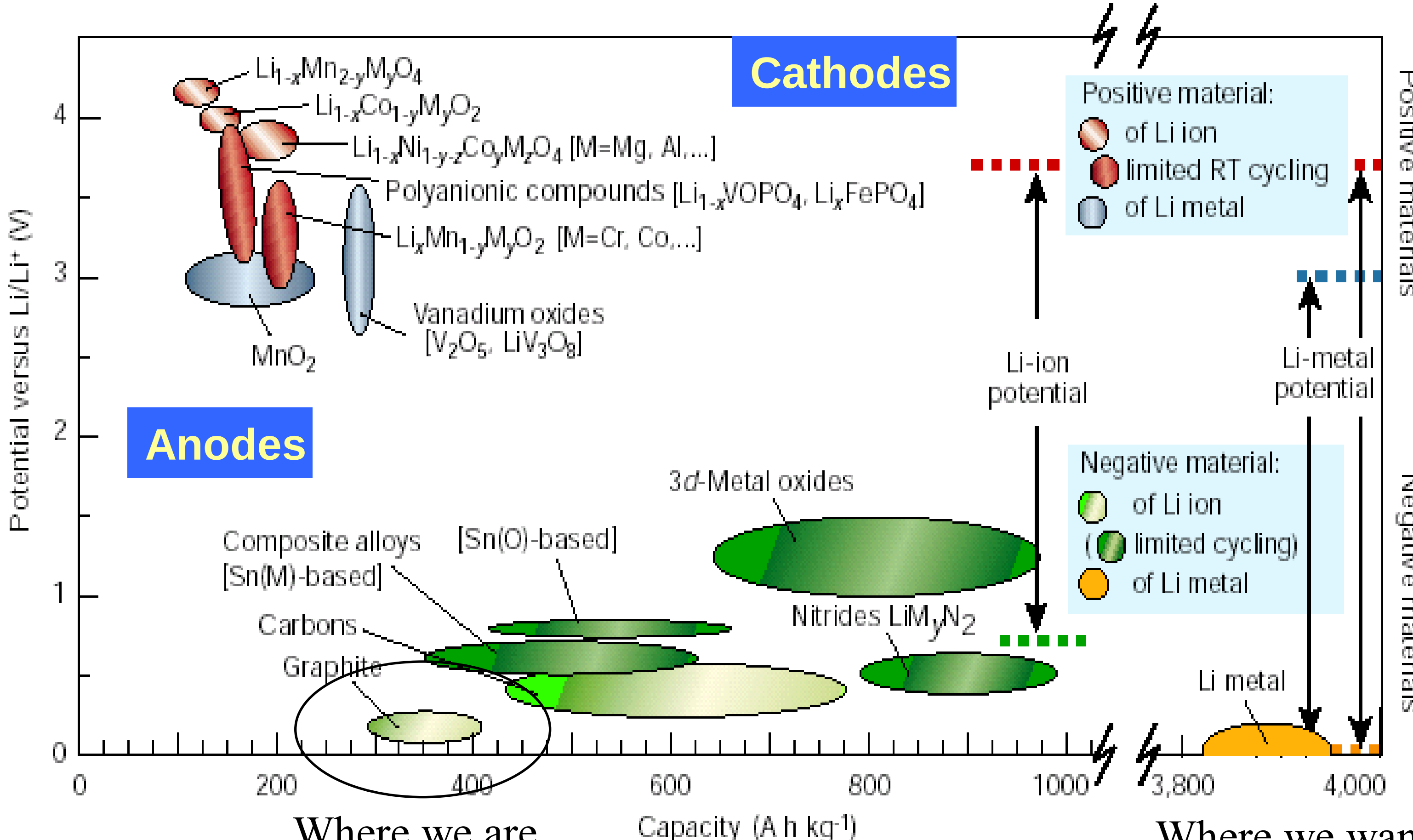
- ~6 Billion people, ~4 billion cell phones in 2008
- In 30 countries, cell phone penetration now exceeds 100%
  - Italy ~ 122%
  - Sweden ~ 110%
- Consider the demand…
  - ~9 Billion people in 2050?
  - ~10 Billion cell phones?
  - ~10+ Billion Lithium batteries?



The paradigm has changed….

But, what's the opportunity…?

Anode and Cathode Combinations Determine the Voltage and Energy Density of Lithium Batteries



Where we are…

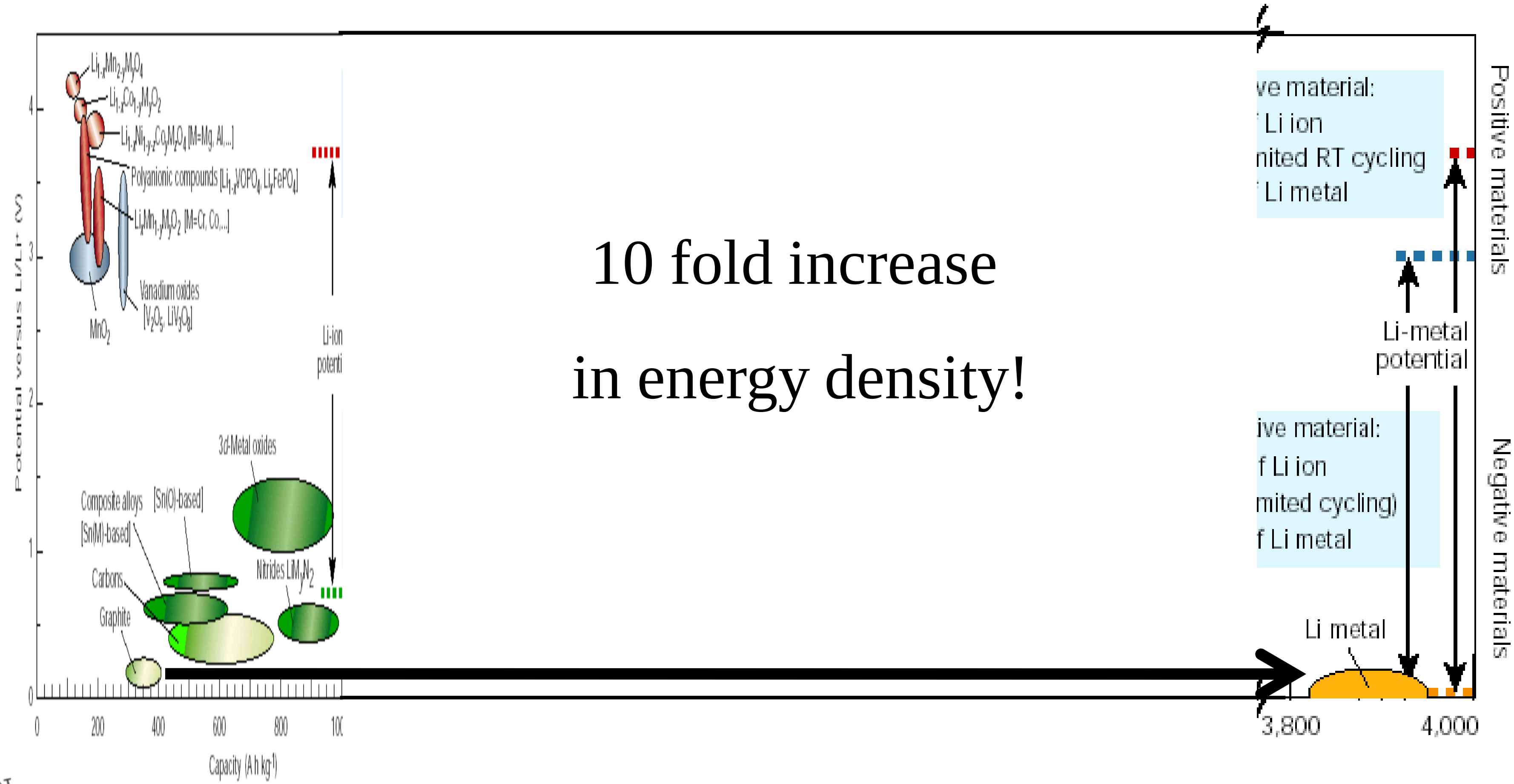
Where we want to go…

J.M. Tarascon, M. Armand, Nature, 414, 15 (2001) 359

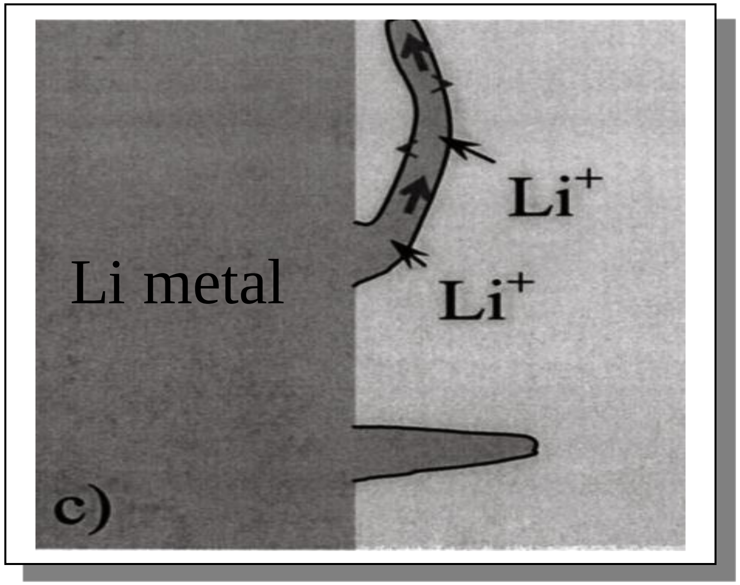
Just for comparison…

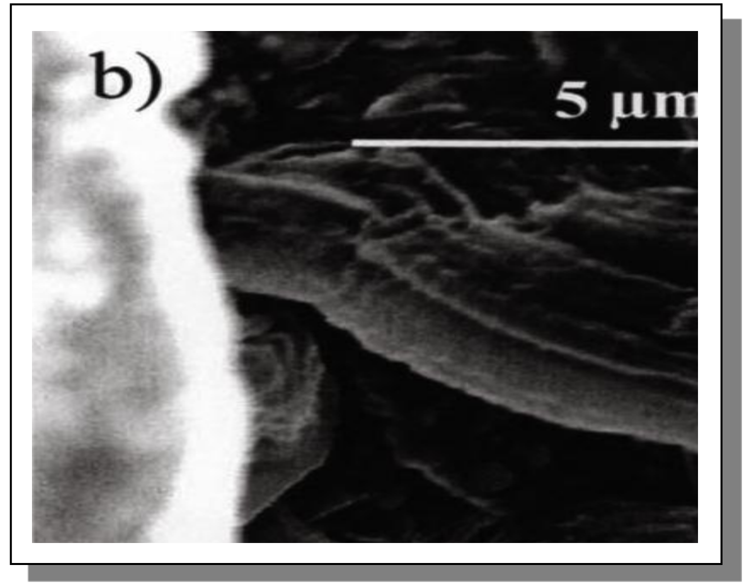
Where we are…

Where we can go…



Lithium Dendrite Formation in Li ion Batteries





Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven “fingers” or dendrites of lithium

Internal dendrites result in short circuits of the battery

M. Dolle et al. Electrochemical and Solid-State Letters, 5(12) (2002)A286

Lithium Dendrite Formation in Li-Ion Batteries

- Cell short circuits lead to over heating and fires

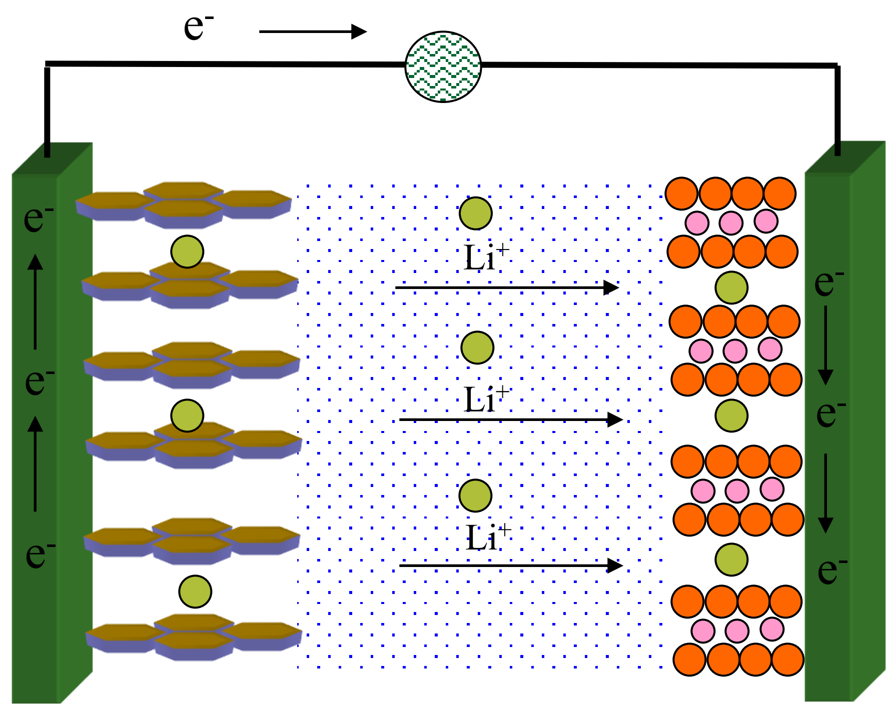
Li-ion Batteries

C_6 is a common anode material for Li-ion batteries

The maximum capacity of graphite (LiC_6): 373 Ah/kg

Good cycle-life

But, Low capacity for new portable devices

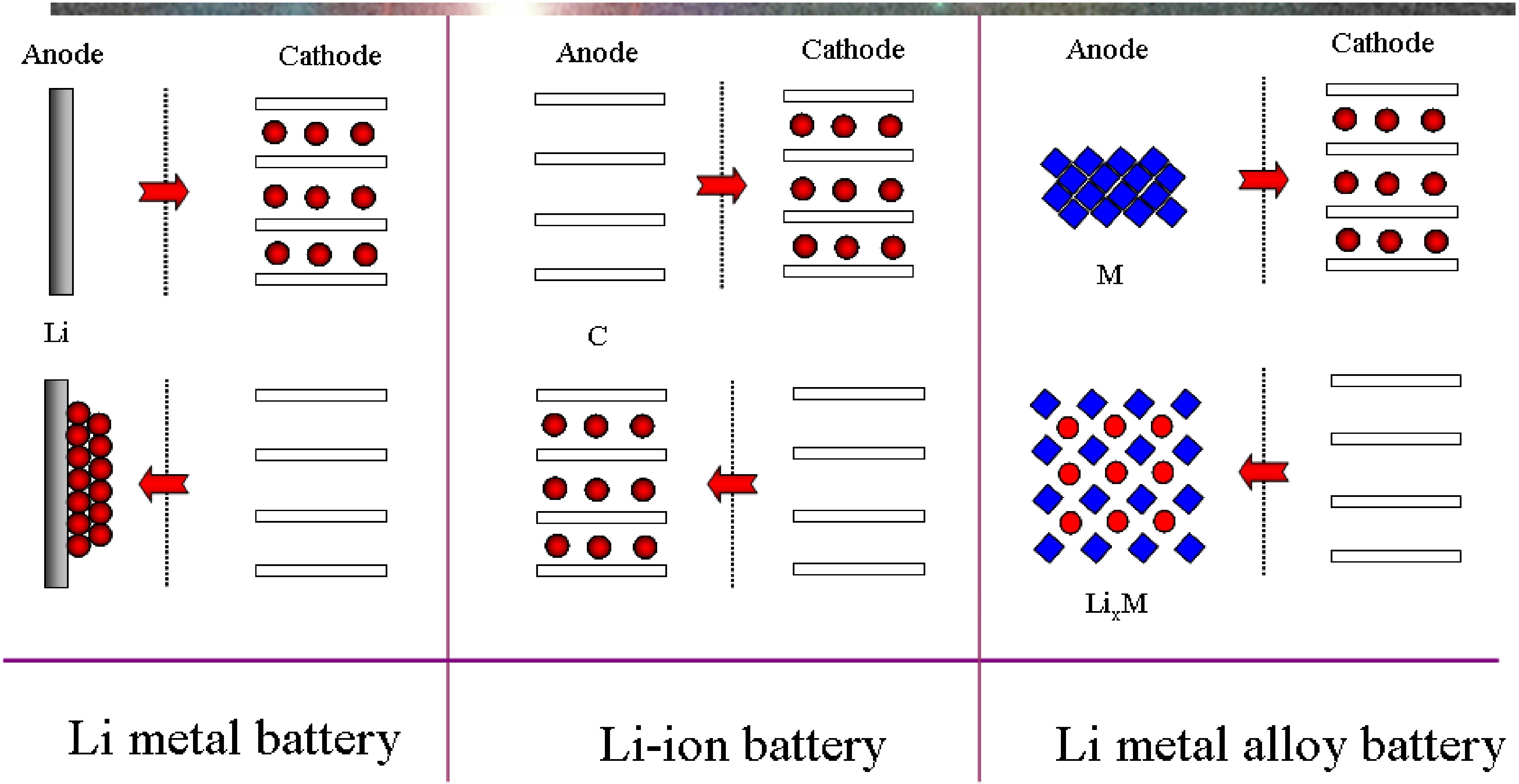


Li_xC_6 Li^+ conducting electrolyte $Li_{1-x}CoO_2$

Anode: $Li_xC_6 \longrightarrow xLi^+ + xe^- + C_6$

Cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow LiCoO_2$

Different Anode and Cathode Combinations



New Lithium Battery Designs - Anode

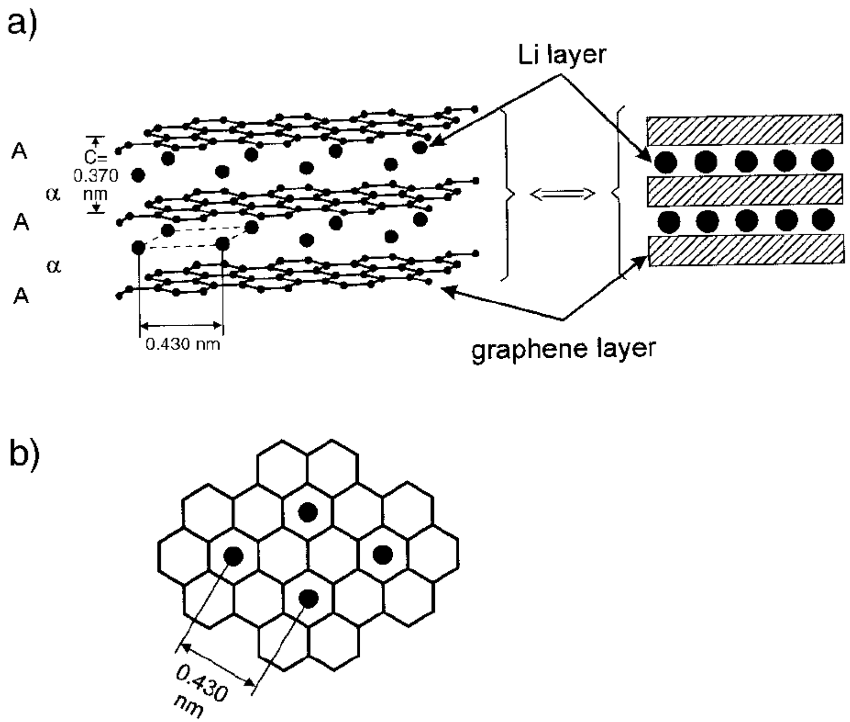
- Higher energy storage in the anode
  - Move closer to unit activity of metallic lithium
  - Yet maintain safety
    - Stability in contact with electrolyte and other battery materials
  - Preference is to manufacture Lithium batteries in the discharged state
    - Does not require handling high activity material
    - Increases shelf life of battery before selling
    - Reduces time and cost of manufacture
    - Increases safety during storage and shipment
    - Increases the lifetime of the battery for the consumer

New Lithium Battery Designs - Anode

- Need a cheap material that will store lithium safely near unit activity that will charge and discharge Li reversibly, ~4000x (~10 years), near 0 V (vs. Li/Li^{+}) at a density near that of Li
- To obtain 50% loss after ~ 10 years, ~4000 cycles, reversibility at each cycle must be >99.98% reversible

Carbons as Negative Insertion Electrodes

- $Li_xC_n \leftrightarrow xLi^+ \; xe^- + C_n$
- x ~ 1, n ~ 6
- C has high e- conductivity
- Cheap
- Plentiful
- Good voltage
- Relatively low capacity, small x



M. Winter, J. Besenhard, M. Spahr, P. Novak, Adv. Mater. 10(1998) 10

New Lithium Battery Designs - Anode

- Metallic alloy anodes
- Metal + xLi → MLi_x
- x can be very large
- $Li_{22}Si_5$ for example
- However, large capacity fade
- Associated with large volume change
- +400% from Si to $Li_{22}Si_5$

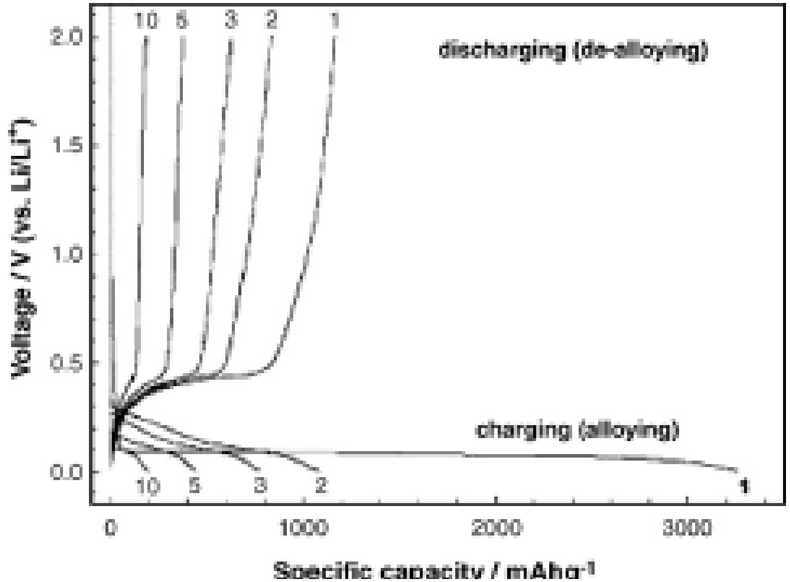


Table 1
Crystal structure, unit cell volume and volume per Si atom for the Li–Si system [10]

Compound and crystal structure	Unit cell volume (Å^3)	Volume per silicon atom (Å^3)
Silicon cubic	160.2	20.0
$Li_{12}Si_7$, ($Li_{1.71}Si$) orthorhombic	243.6	58.0
$Li_{14}Si_6$, ($Li_{1.71}Si$) rhombohedral	308.9	51.5
$Li_{13}Si_4$, ($Li_{3.25}Si$) orthorhombic	538.4	67.3
$Li_{22}Si_5$, ($Li_{4.4}Si$) cubic	659.2	82.4

A.J. Appleby, et al. J Power Sources 163(2007)1003

Nano-Structured Si anode

- Nano-structured Si improves cyclability
- Cycle fade still strong
- 1000 cycles is a design goal

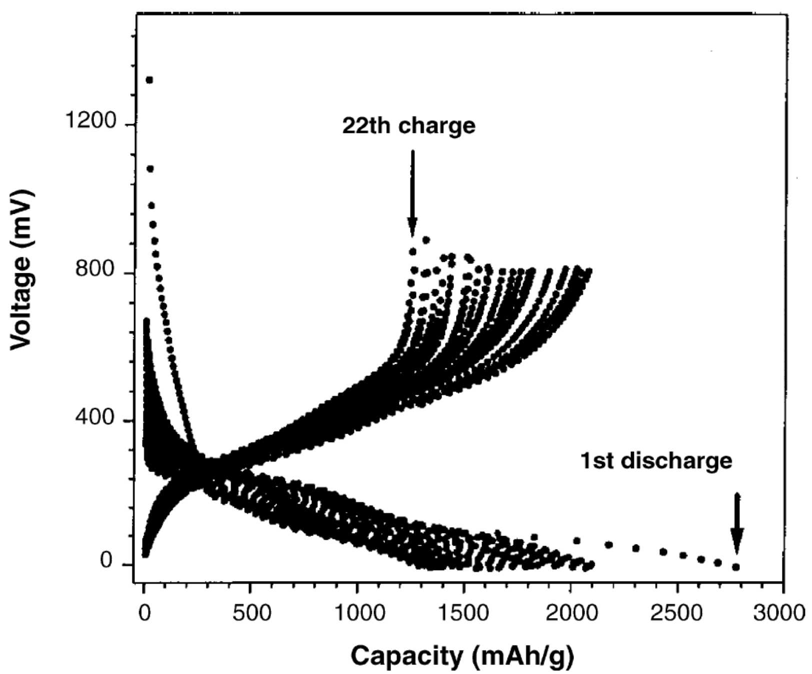


Fig. 5. §§Charge–discharge curves between 0.0 and 0.8 V at 0.1 mA cm^{-2} for nano-Si anode with 4:4:2 weight ratio of nano-Si, carbon black and PVDF binder. Electrolyte: 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1) [22].

1 mAhr/g = 1Ahr/kg

A.J. Appleby, et al. J Power Sources 163(2007)1003

Opportunities for Improved Lithium Batteries

- Cycle life, the number of times the Lithium battery can be discharged and recharged, is often only a few hundred to at most a thousand
  - This leads to lifetimes of only a year or two
- Unbroken paradigm of good cyclability and Lithium activity at the anode
  - Li metal has the highest activity, but the poorest cyclability
  - Li-C has among the lowest activity, Li_6C, but among the highest cyclability
- New materials are needed that can help break this paradigm of low activity, (voltage), but good cyclability

New Anodes for Lithium Batteries

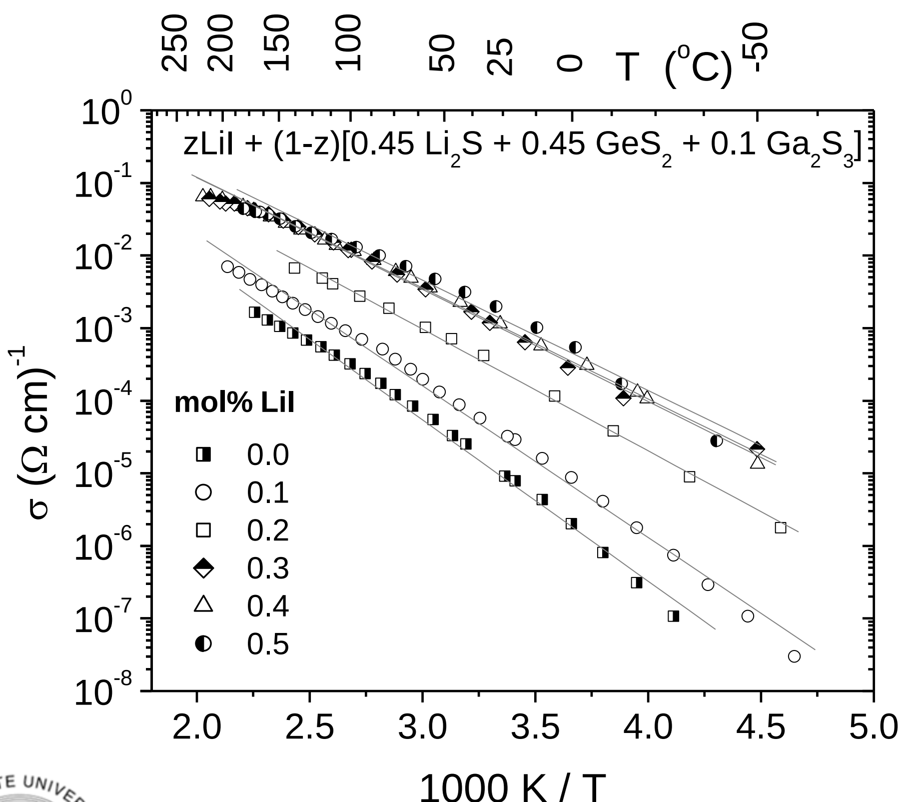
- Needed: An Anode Material which:
  - Conducts Li^+ ions rapidly to insure fast electrode kinetics and charge transfer
  - Has significant fractions of alloying metal, such as Si or Ge, to store large amounts of Li to insure high Li activity and cell voltage
  - Has a relatively low mechanical modulus that will accommodate volume changes during alloying reactions
  - Is chemically stable under highly reducing conditions of the Lithium battery anode
  - Relatively cheap, plentiful, and easily manufactured

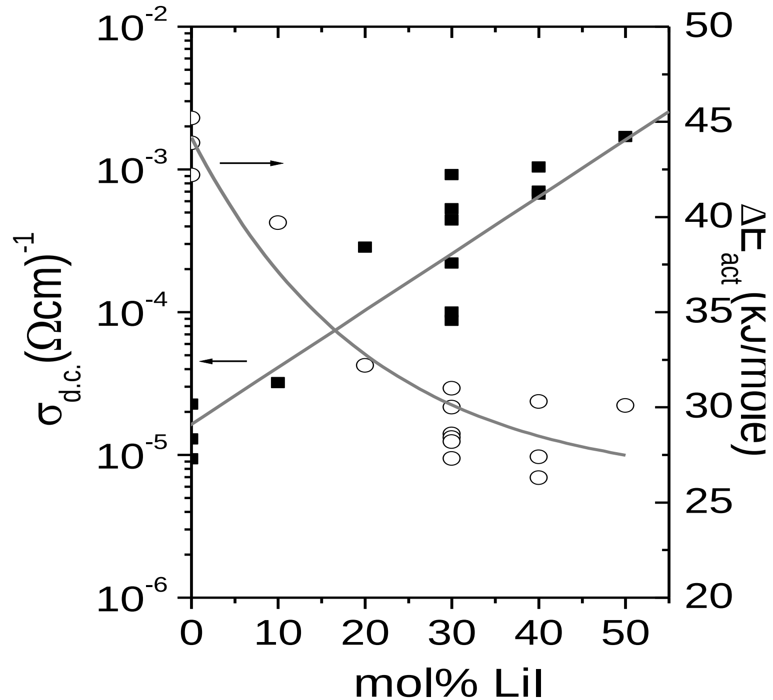
A New Functionality for Glass: Chalcogenide Glasses as High Capacity, High Voltage, High Cyclability, Safe Lithium Battery Anodes

- Idea: Li^+ ion conducting chalcogenide glass anodes
  - Chalcogenide glasses are among the highest of all Li^+ ion conductors known, 10^{-3} $(\Omega cm)^{-1}$ at 25°C
  - Chalcogenide glasses can be readily made using Si and Ge over a continuous range of compositions, ~50 at% to ~ 10 at%
  - Chalcogenide glasses are significantly "softer" than oxide glasses, MPa moduli versus GPa, for example
  - Sulfide glasses while commonly unstable under oxidizing conditions can be quite stable under reducing (Anode) conditions
  - Due to their ease of preparation, glasses can be inexpensively prepared, especially in powder form, using mechanical milling where no melting is required

Fast Ion Conducting Chalcogenide Glasses

- ISU research group has been active for many years developing new chalcogenide glasses as fast ion conductors, primarily as solid electrolyte materials

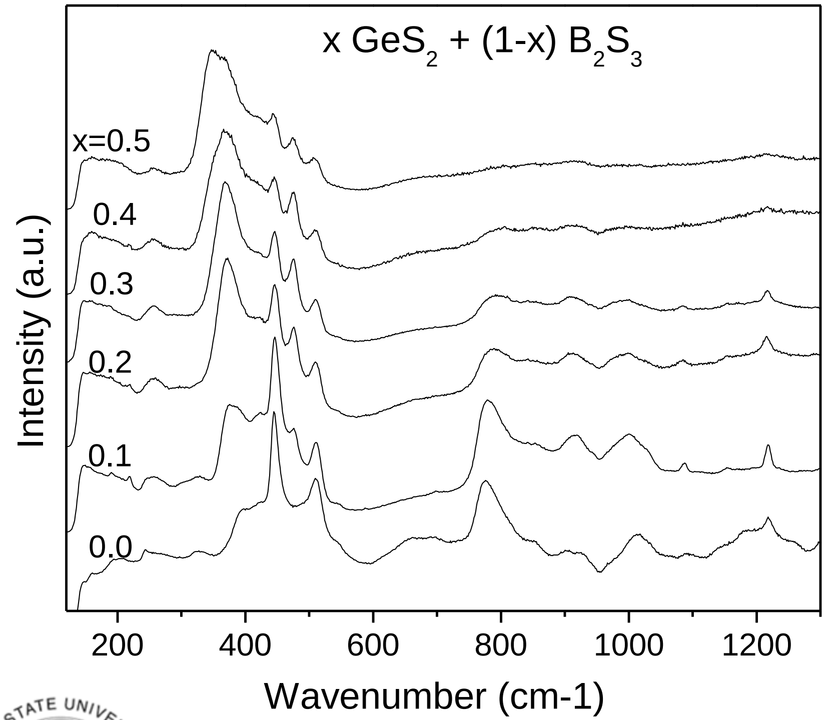


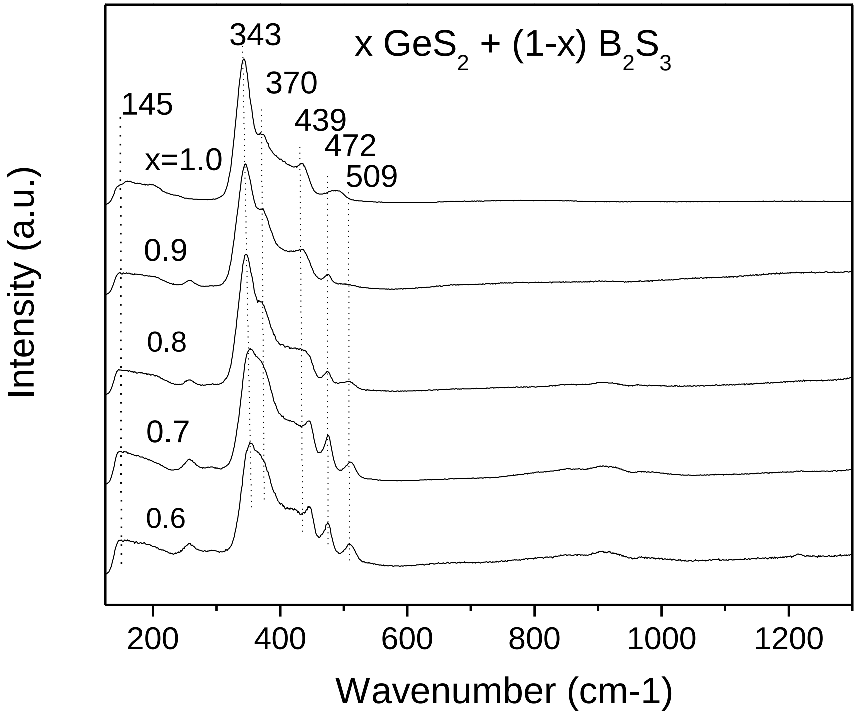


Saienga, J., Martin, S. W., JNCS, 354, 1475 (2008)

$GeS_2 + B_2S_3$ Glass Preparation and Characterization

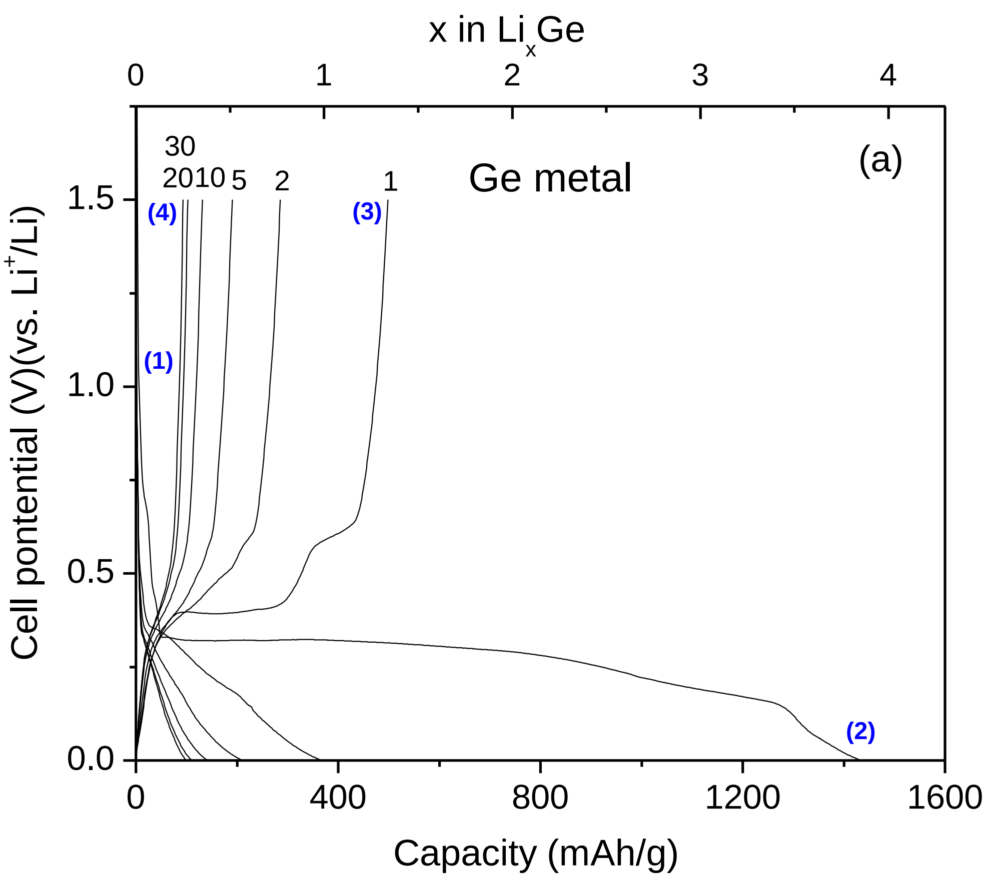
- Ge + 2S → GeS_2 + B_2S_3 → $xGeS_2$ (+1-x)B_2S_3 Glasses
- IR and Raman spectroscopy to examine glass structure
- Density and Tg to examine the physical properties

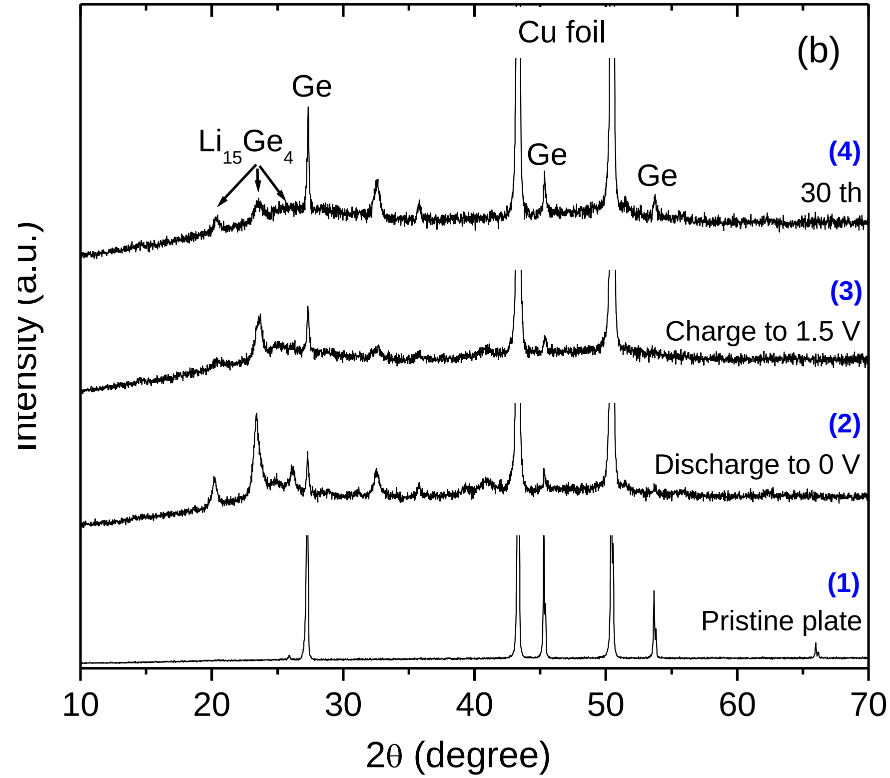




Kim, Y., Martin, S. W., JNCS 351 1973 (2005)

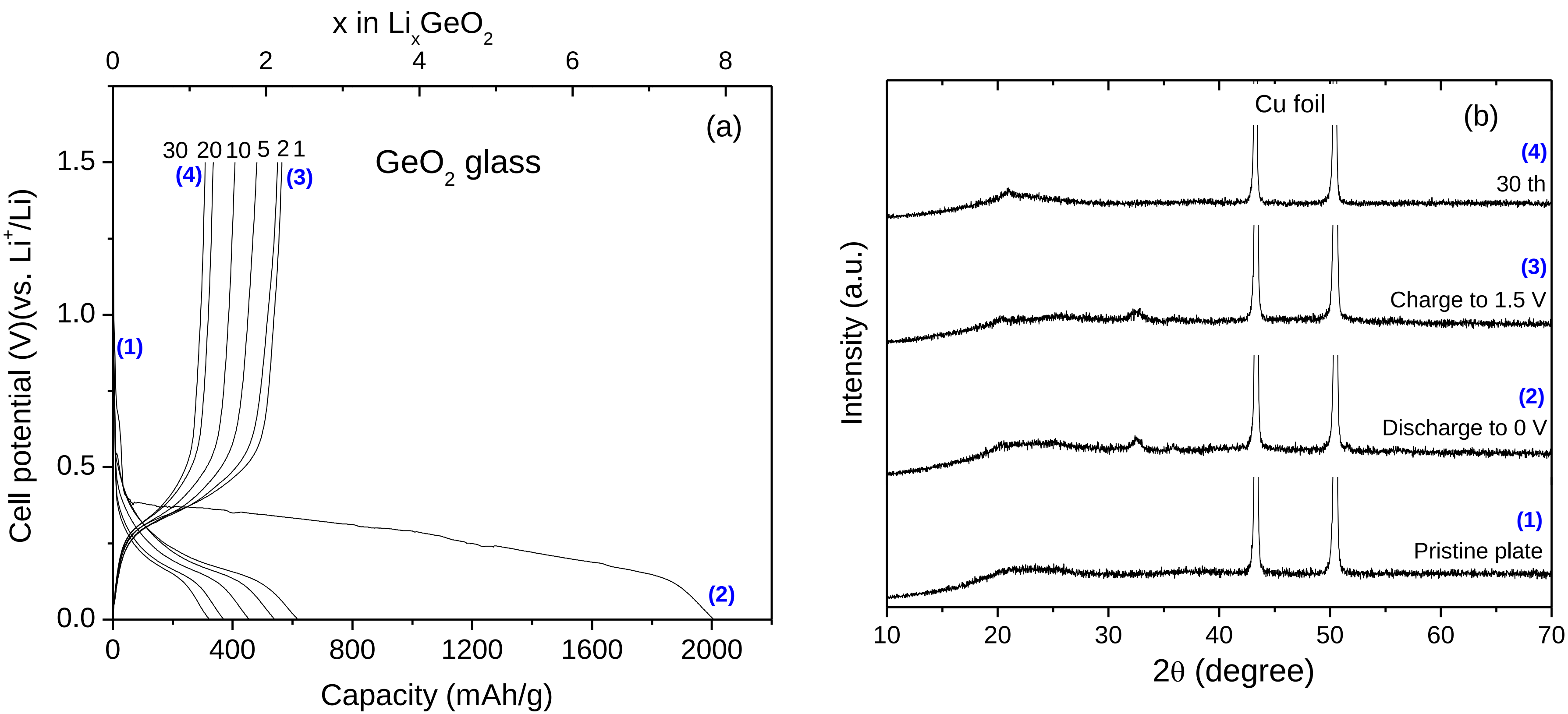
Comparative behavior of pure Ge





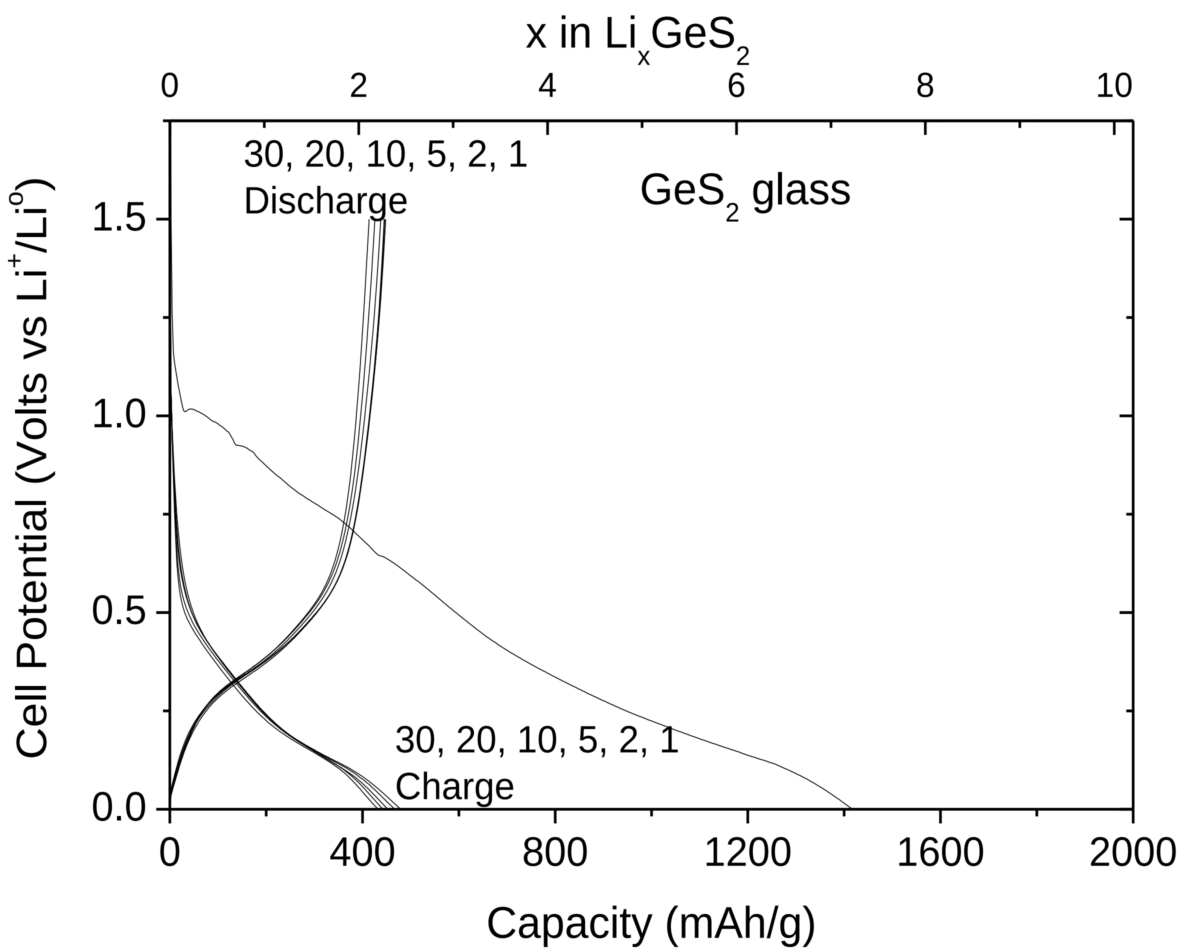
Kim and Martin et al. Electrochimica Acta 53(2008) 5058

Comparative behavior of GeO_2 Glass



Kim and Martin et al. Electrochimica Acta 53(2008) 5058

GeS_2 Glass Li anodes



Kim and Martin et al. Electrochimica Acta 53(2008) 5058

Ge-based Active Material Anodes

- GeS_2 glass based anode has best reversibility

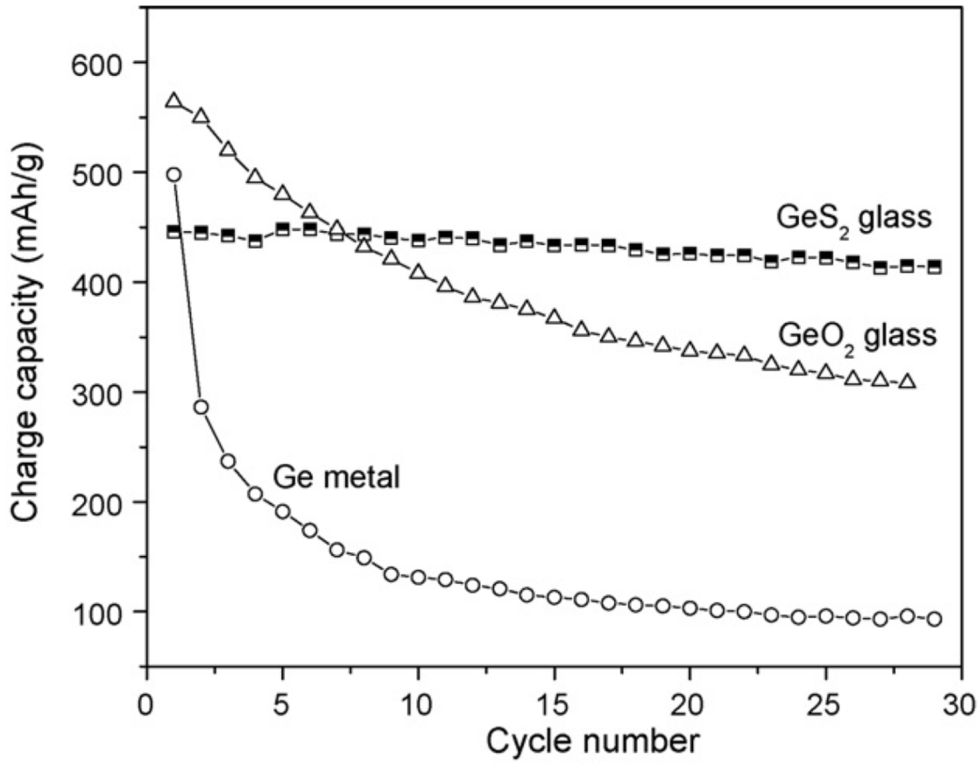


Fig. 5. Cycle-life performance of Ge metal, GeO_2 glass, and GeS_2 glass, respectively. They are operated between 1.5 and 0 V at the rate of 0.1 C.

Kim and Martin et al. Electrochimica Acta 53(2008) 5058

Plausible mechanism of Glassy Anodes

- Reaction steps:

  $x/2GeS_2 + 2xLi \rightarrow xLi_2S + x/2Ge$

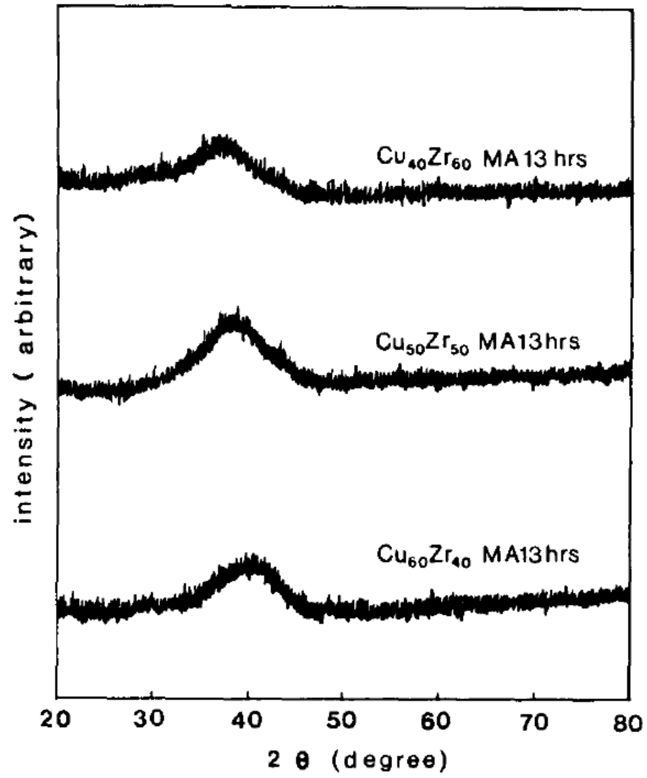
  $Ge + nLi \rightarrow Li_nGe$

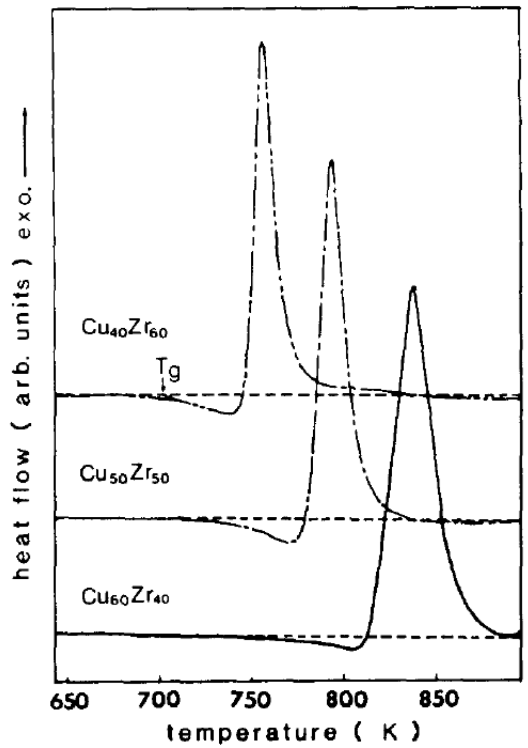
Comparative Structures, Na^+ Ion Conductivities and Glass Transition Studies of Melt Quenched and Mechanically Milled Na_2S + P_2S_5 Glasses

New non-oxide glasses as solid electrolytes for new room temperature Na batteries

Mechanical Alloying to the Amorphous State

- Mechanical Milling, Ball Milling, is a known and common route to the amorphous state for metal alloys
- XRD amorphous Cu –Zr Alloys
- Exhibit Glass Transition and Crystallization behavior



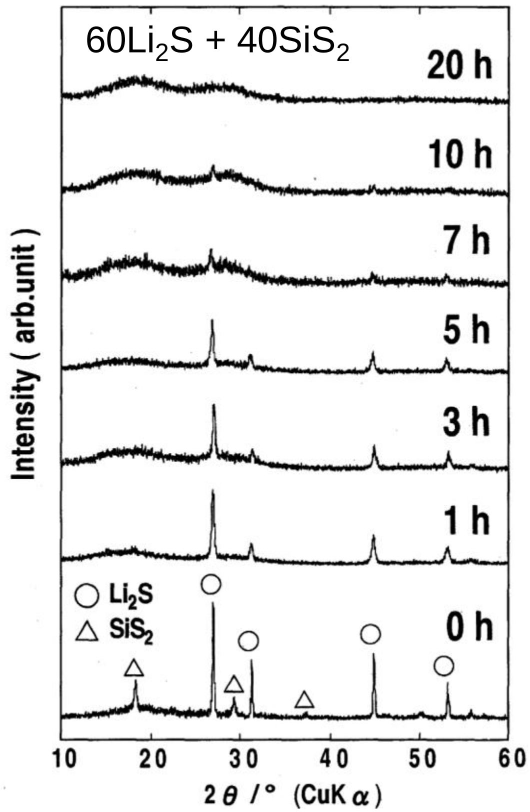


Jang et al., Scripta METALLURGICA 23(1989) 1805-18210

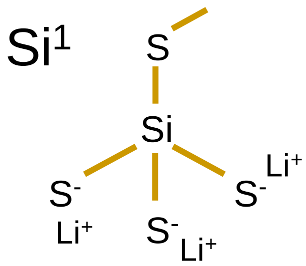
Mechano-Chemical Milling Can Also Occur

- Milling can also lead to the amorphous state and combined with complete chemical reaction of the starting materials.

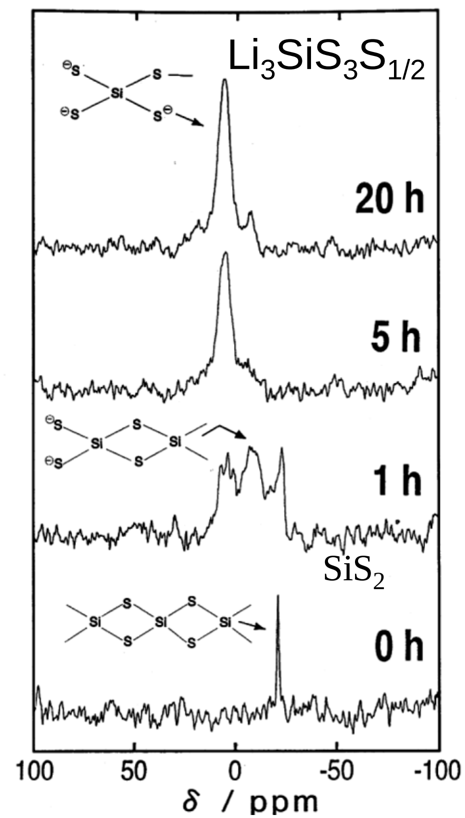
- Formation of XRD amorphous materials



$60Li_2S + 40SiS_2$
→
$3Li_2S + 2SiS_2$
→
$Li_3SiS_3S_{1/2}$



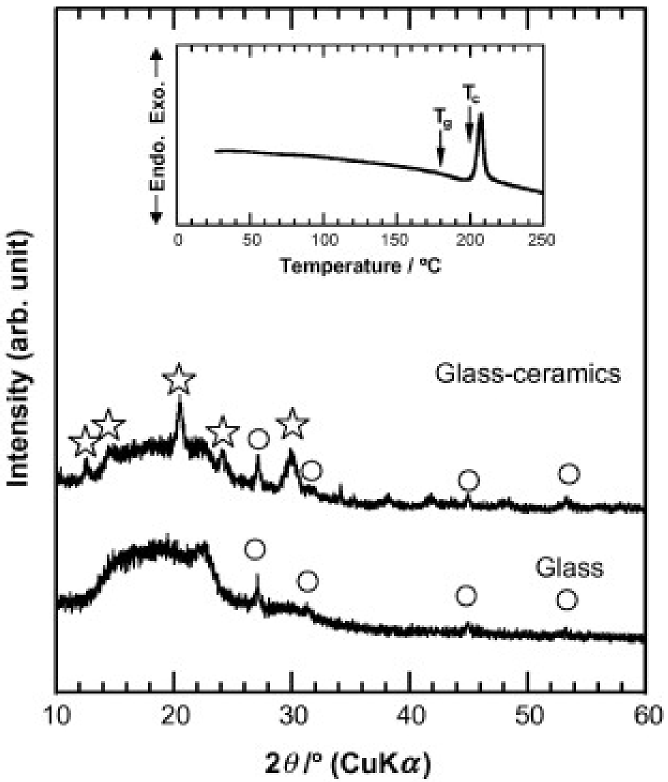
- ^{29}Si MAS-NMR shows the formation of expected chemically reacted structures

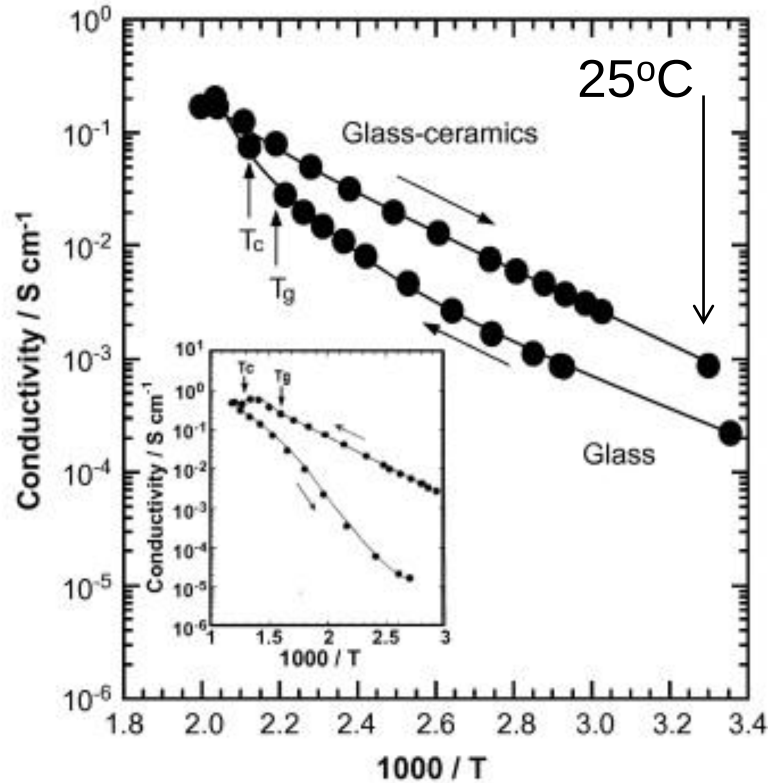


Tatsumisago et al. Journal of the Ceramic Society of Japan 108 [11] 973-978 (2000)

New Amorphous Li^+ ion Conducting Solid Electrolytes

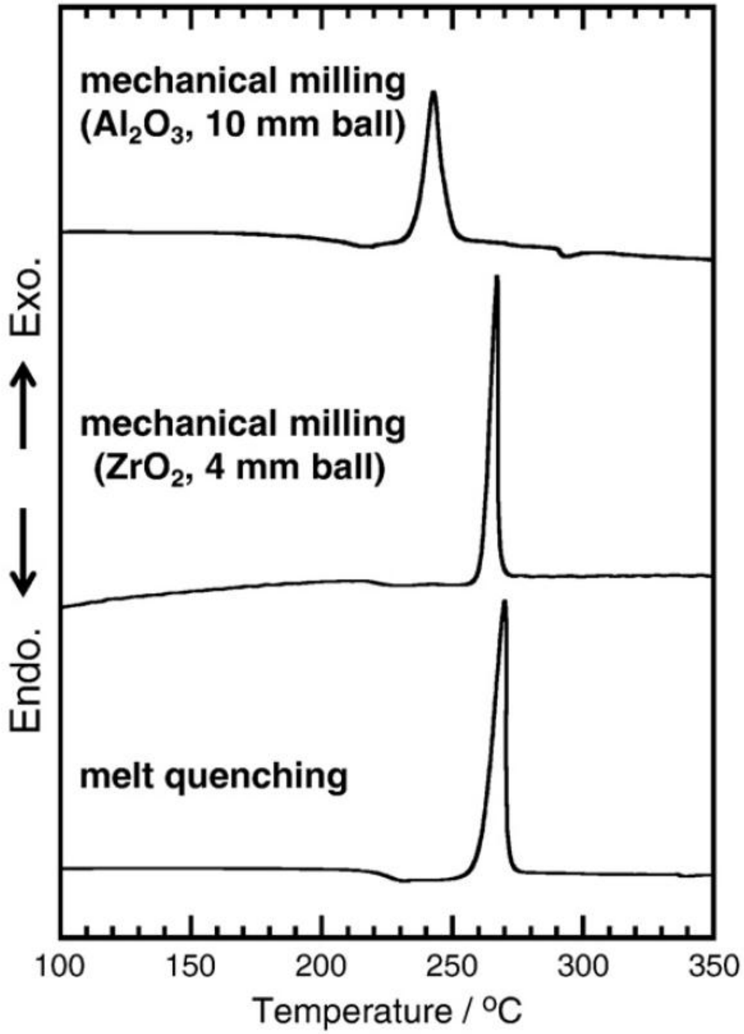
- Mechanically Milled Compositions
  - Are amorphous
  - Can Exhibit very high Li^+ ion conductivities





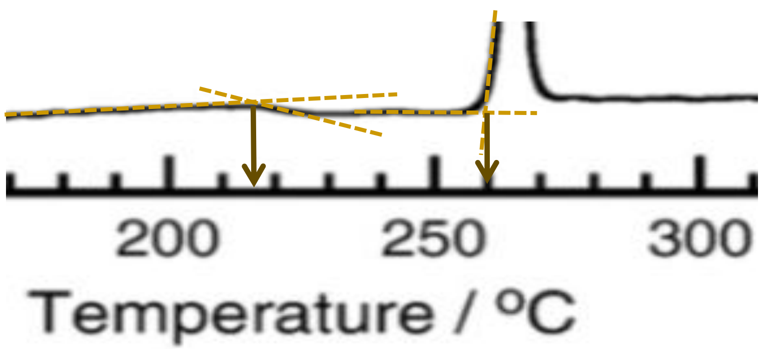
Tatsumisago et al. JNCS 356 (2010) 2670–2673

DSC Scans of Mechanically Milled $Li_2S + P_2S_5$ powders



- Amorphous materials exhibit a glass transition
- Exhibit crystallization behavior quickly above Tg
- Behavior is comparable to melt quenched glass Tg DSC behavior

Tx-Tg ~260-217 °C ~ 33 °C



Tatsumisago et al. JNCS 356 (2010) 2670–2673

Background of the Study….

New Sodium Electrolytes for Energy Storage…

- Lithium based batteries will grow in importance
  - Transportation
  - Mobile electronics
- Demands for lithium will grow
- The world (unfortunately) has few Lithium sources
- To minimize competition among scarce resources
  - Move to Sodium chemistries
  - Less Expensive
  - Nearly Identical Volumetric Energy Densities
  - There are many abundant Sodium sources
- Idea: *Can we develop near room temperature sodium glassy battery electrolytes for safer and cheaper solid state chemistries?*

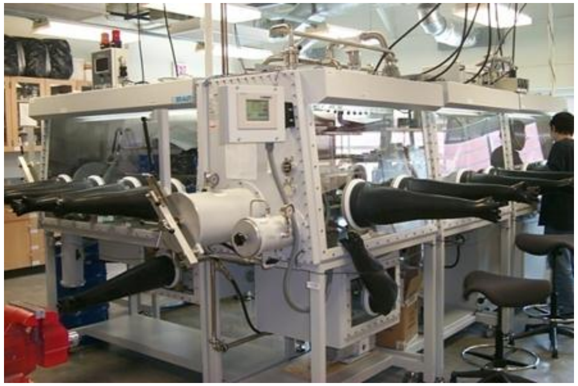
Comparative Studies of Melt Quenched and Mechanically Milled $Na_2S + P_2S_5$ Glasses

Purpose of this study

- Can new highly conducting Na^+ thiophosphate glasses and glass-ceramics be developed?
- What are their structures? Properties? Na^+ ion conductivities?
- Can the DSC/Tg behavior of these mechanically milled amorphous materials be explored more fully?
- Do these glass transitions exhibit kinetic behavior like “normal” melt quenched glasses?

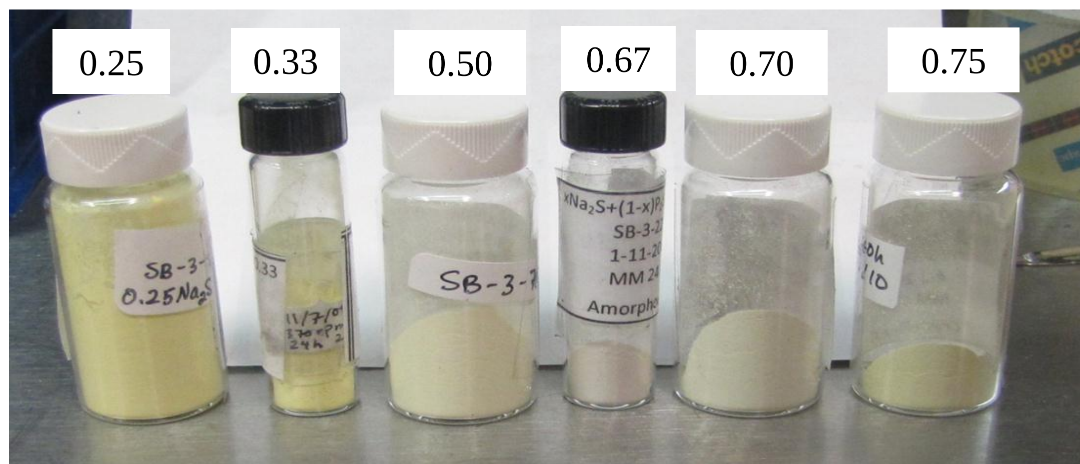
Melt Quenching of $Na_2S + P_2S_5$ Glasses

- Na_2S was prepared by dehydrating $Na_2S{\cdot}9H_2O$ (Aldrich, 99.99%) under vacuum at ~0.1 Pa, 150 °C for 1 h and then 650 °C for 24 h.
- P_2S_5 (Aldrich, 99%) was used as is without further
- $xNa_2S+(1-x)P_2S_5$ compositions were melted in a glovebox (<1 ppm O_2 <1 ppm H_2O). at 650 °C for 15 min and then splat-quenched to room temperature
- Glassy compositions were x-ray amorphous for x=0.50 and 0.67.
- The melt-quenched samples were then annealed ~30 °C below their Tgs for 1 h.
- Sealed tube preparations to extend the glass forming range to lower Na_2S contents are in progress and will be reported separately

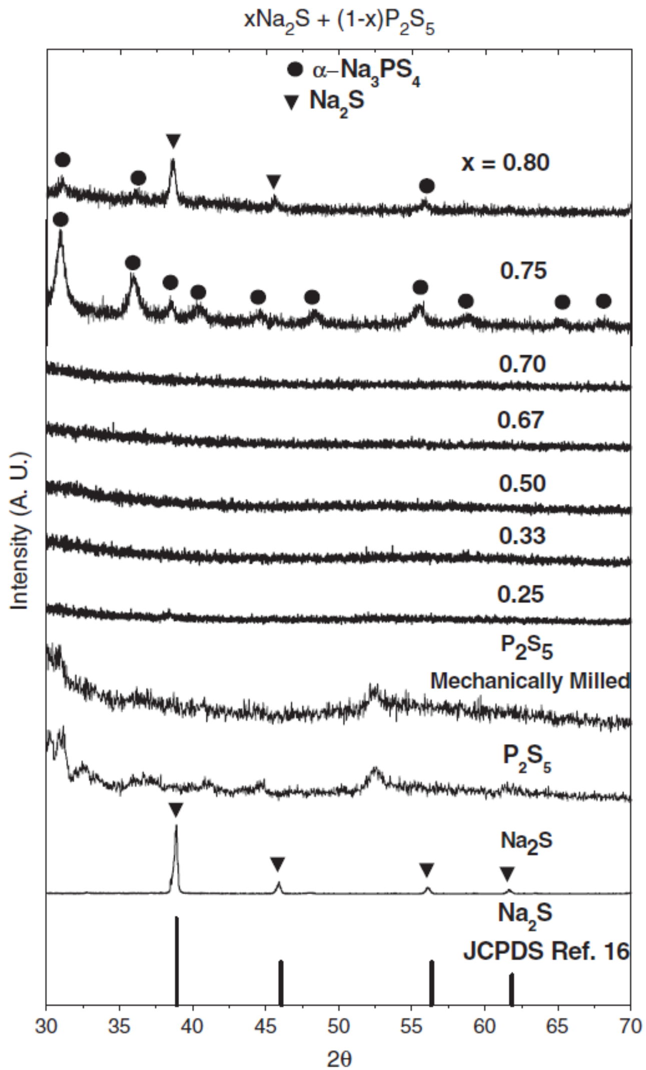


Mechanical Milling of Na_2S + P_2S_5 Amorphous Materials

- Planetary ball mill
- 85 ml Zirconia pot
- 20 zirconia balls, 10 mm diameter
- Powder: 5 g
- Speed: 370 rpm
- Milling time: 24 hrs.
- 6 compositions of $xNa_2S+(1-x)P_2S_5$ from 0.25 to 0.75



X-ray Diffraction of Mechanically Milled Compositions

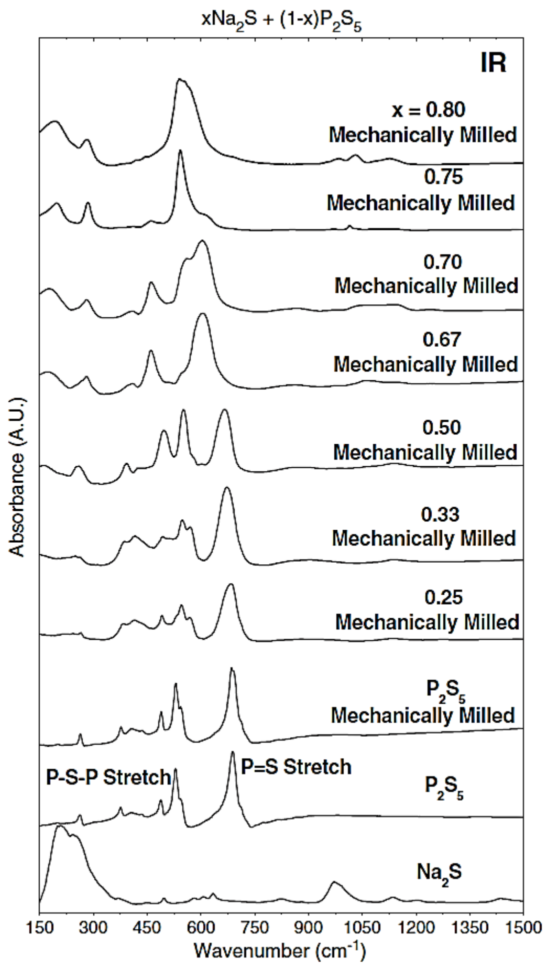


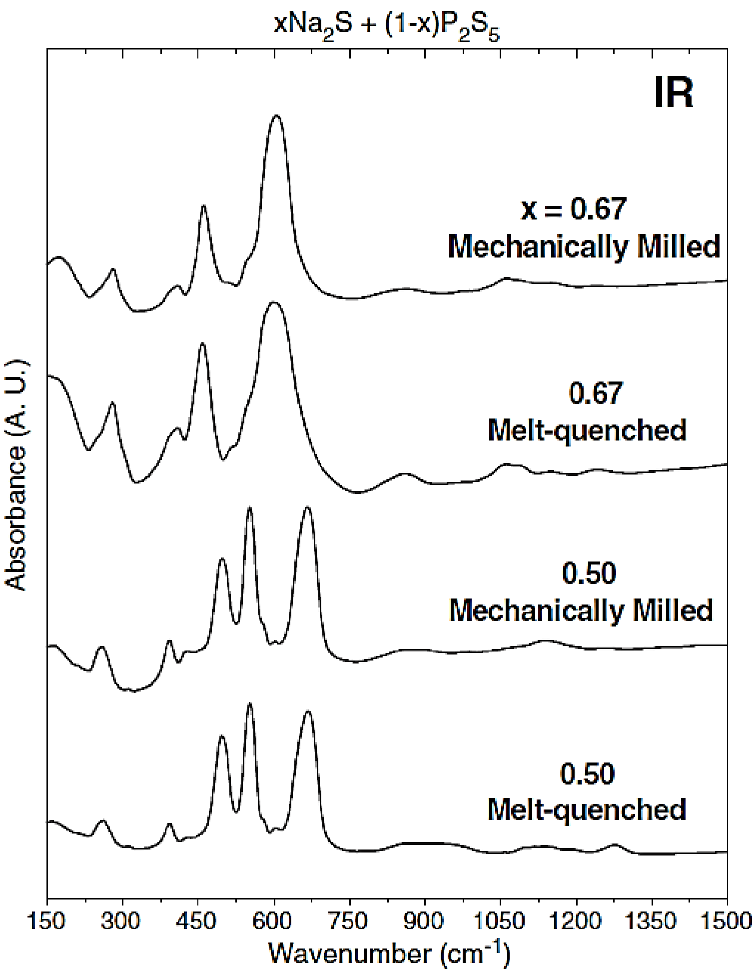
- X-ray amorphous between 0.25 and 0.7
- Unreacted P_2S_5 at low P_2S_5 contents
- Formation of Na_3PS_4 at and above 75% Na_2S contents
- Unreacted Na_2S at highest contents

Berbano, S., Seo, I., Bischoff, C., Schuller, K., Martin, S. W. JNCS, 358 (2012) 93–98

Structural Evolution with Na_2S – IR Spectra

- Progressive formation of terminal Non-Bridging Sulfur Units

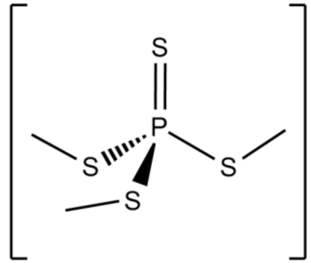




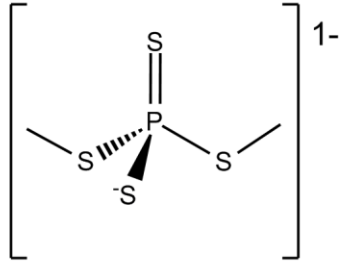
Berbano, S., Seo, I., Bischoff, C., Schuller, K., Martin, S. W., JNCS, 358 (2012) 93–98

Short Range Order Structures in $yNa_2S + (1\text{-}y)P_2S_5$ Glasses

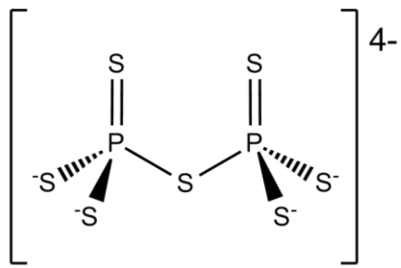
0% < y < 50% — P^3



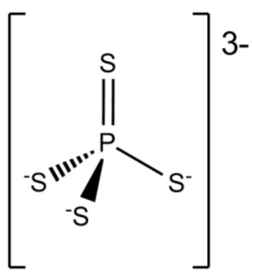
0% < y < 65% — P^2



50% < y < 75% — P^1



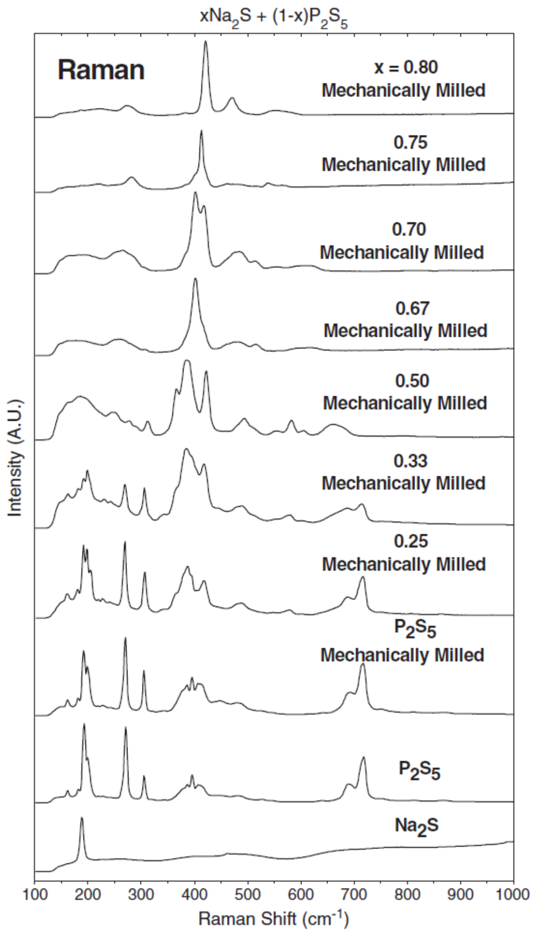
66% < y < 100% — P^0

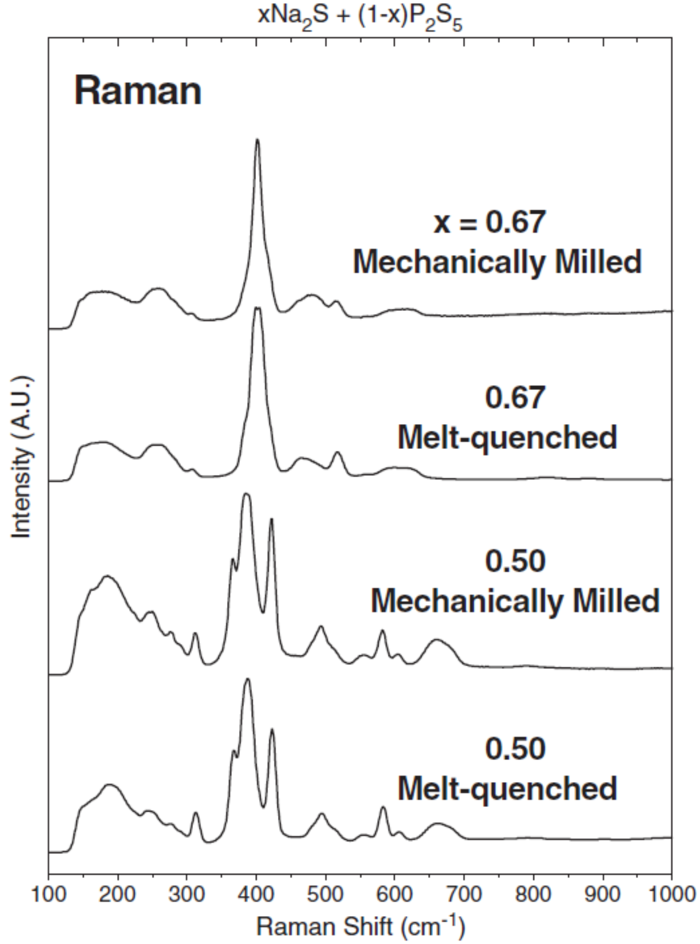


- Progressive formation of non-bridging sulfur units with added Na_2S

Structural Evolution with Na_2S – Raman Spectra

- Spectra of melt-quenched glasses identical to mechanically milled amorphous materials





Berbano, S., Seo, I., Bischoff, C., Schuller, K., Martin, S. W. JNCS, 358 (2012) 93–98

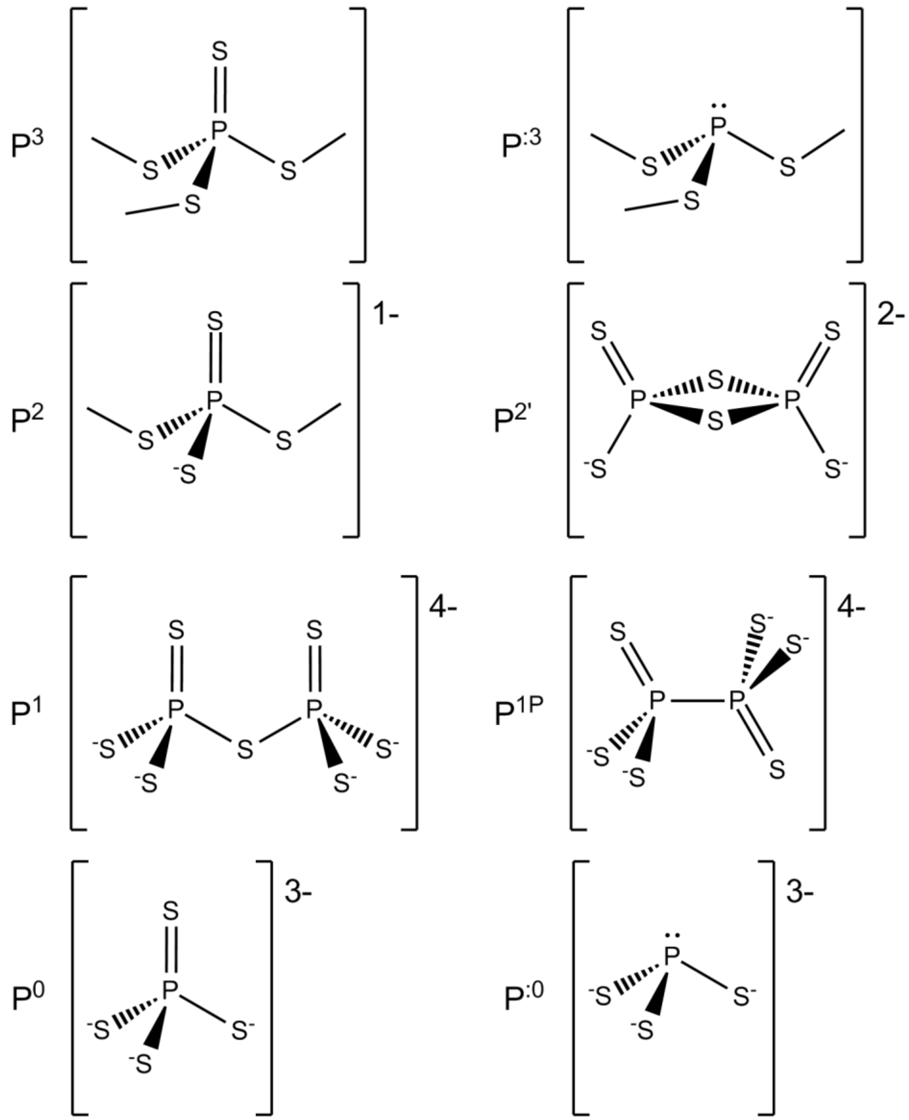
SRO Structures in $Na_2S + P_2S_5$ Glasses

0% < y < 50%

0% < y < 65%

50% < y < 75%

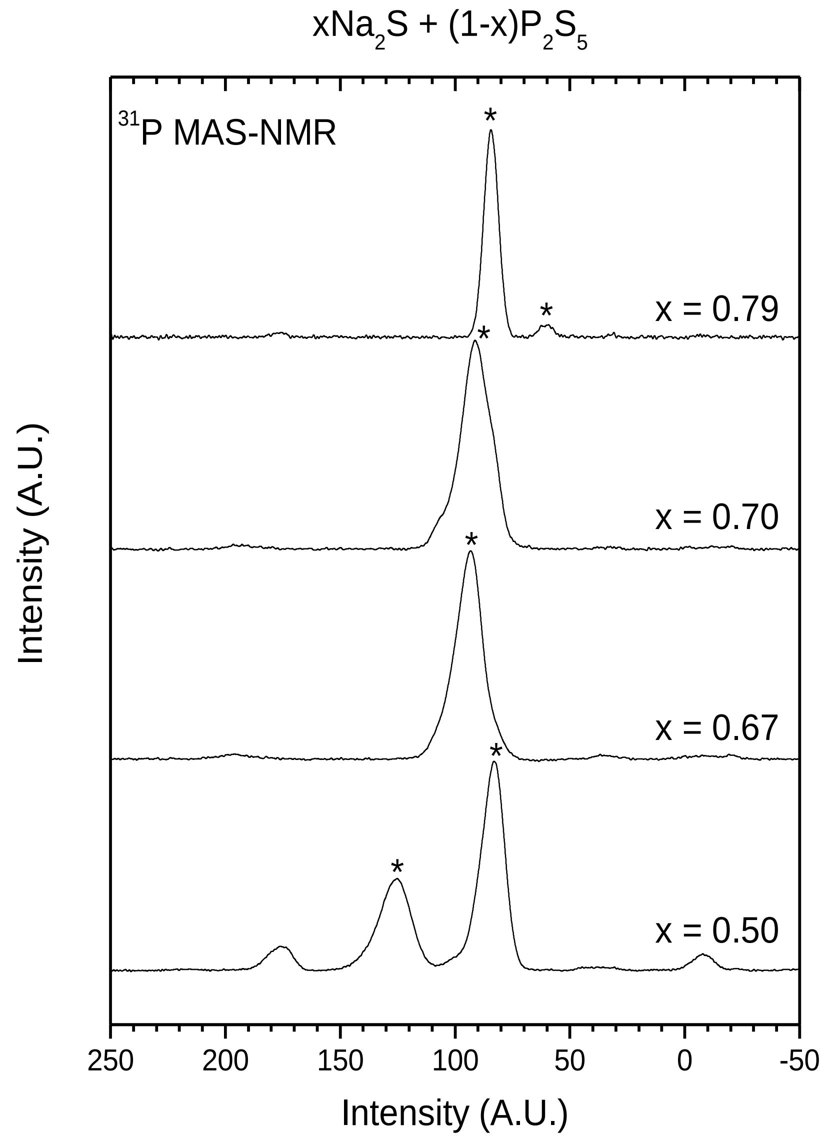
66% < y < 100%



^{31}P MAS-NMR

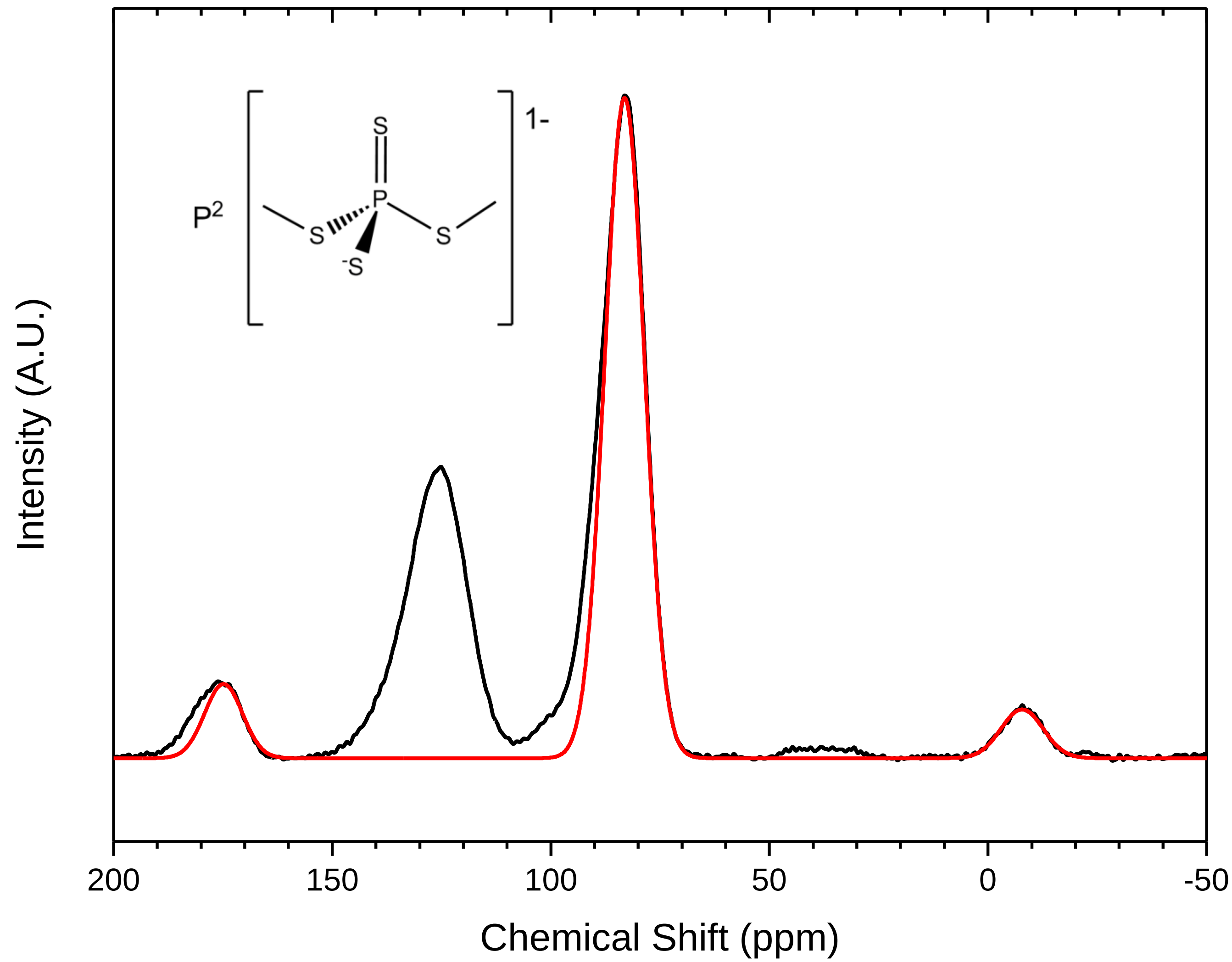
- Spun at 22-25 kHz
- * denotes center band

- x = 0.5 shows two distinct chemical environments
  - P^2 (~83 ppm)
  - $P^{2'}$ (~125 ppm)
- P^{1P} (~105 ppm) is present for all compositions except x = 0.79
- x = 0.79 shows two chemical environments
  - P^0 (~85 ppm)
  - $P^{:0}$ (~60 ppm)



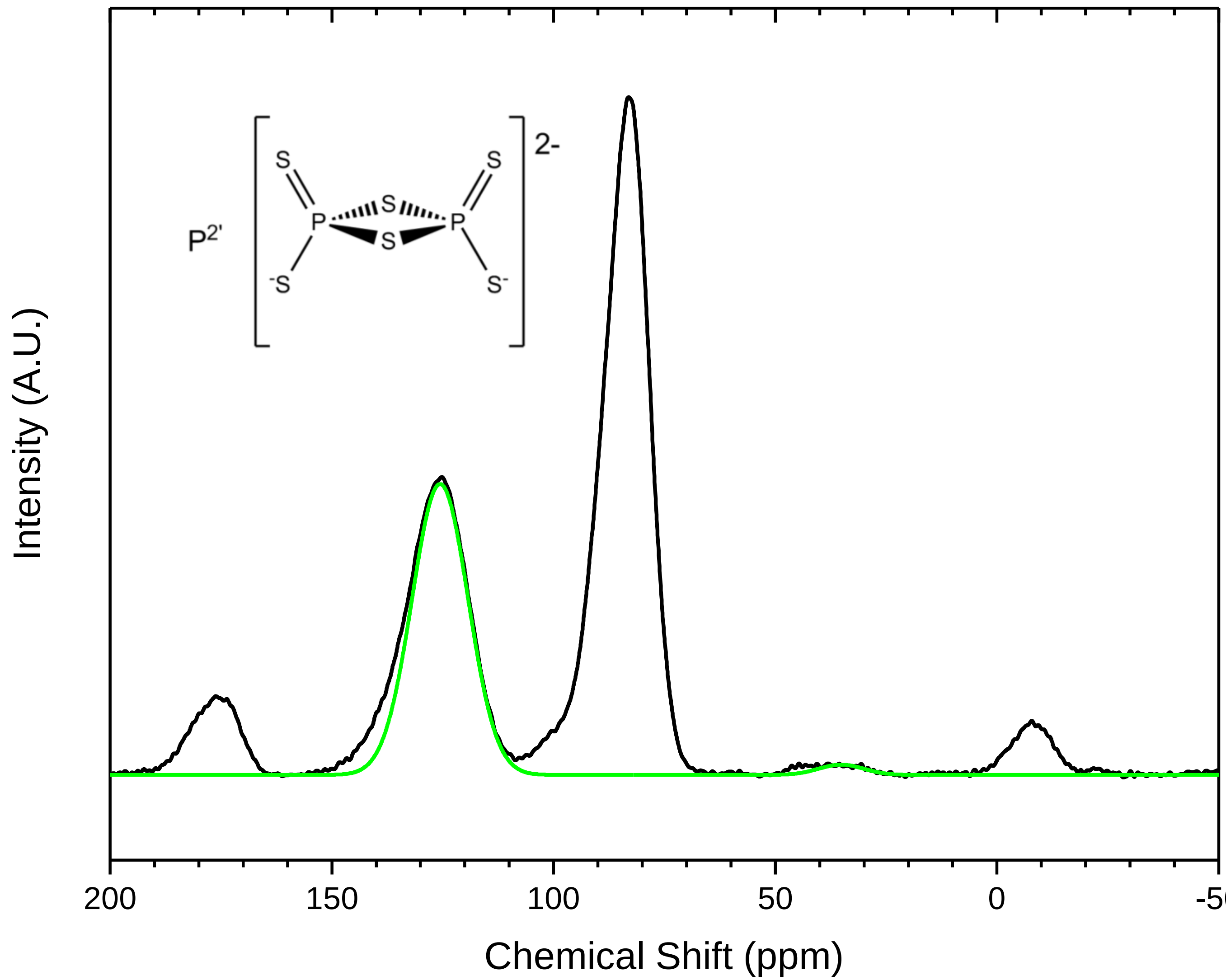
Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

$0.50Na_2S + 0.50P_2S_5$ Spectra deconvolution – P^2 group



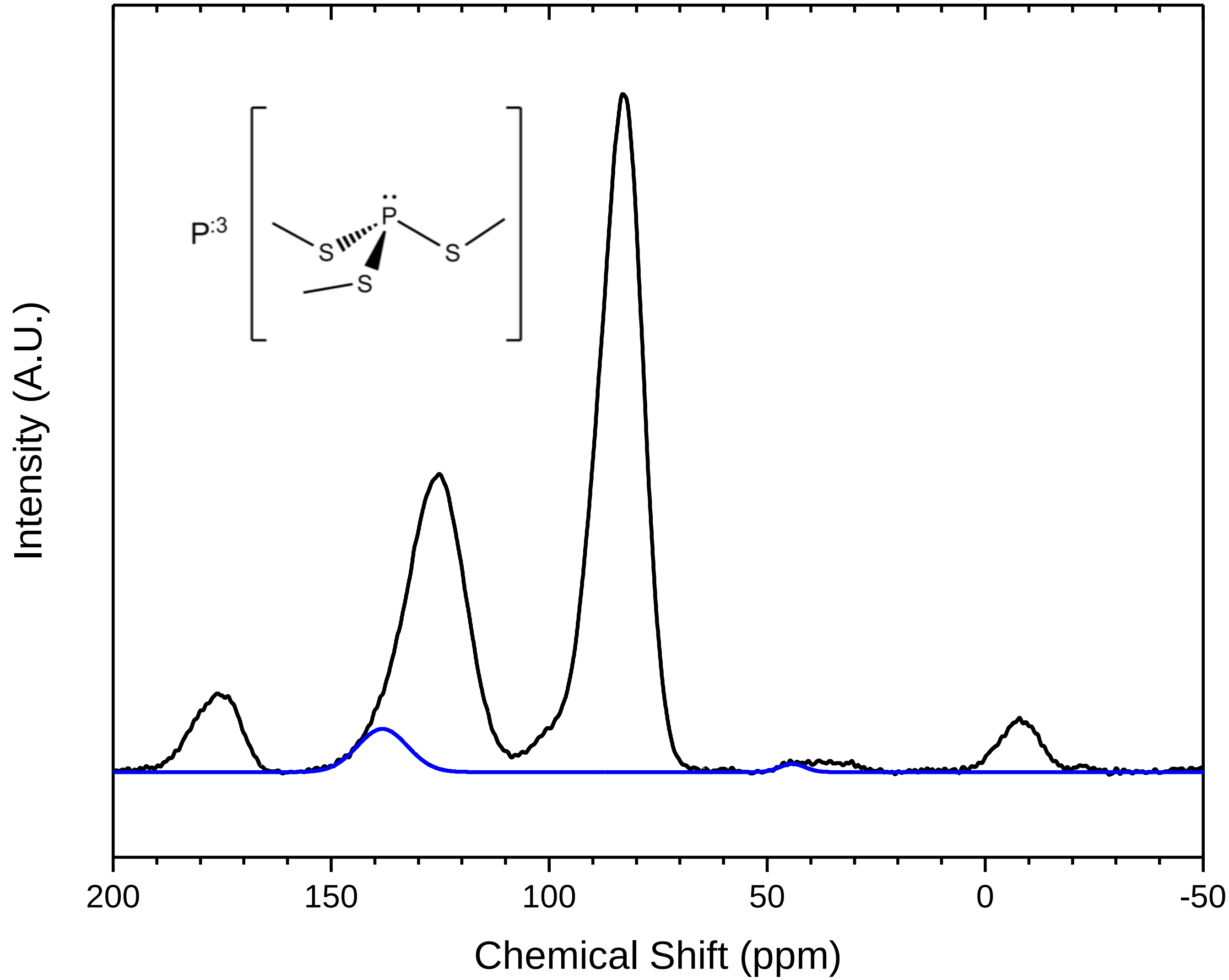
Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

$0.50Na_2S + 0.50P_2S_5$ Spectra deconvolution – $P^{2'}$ group



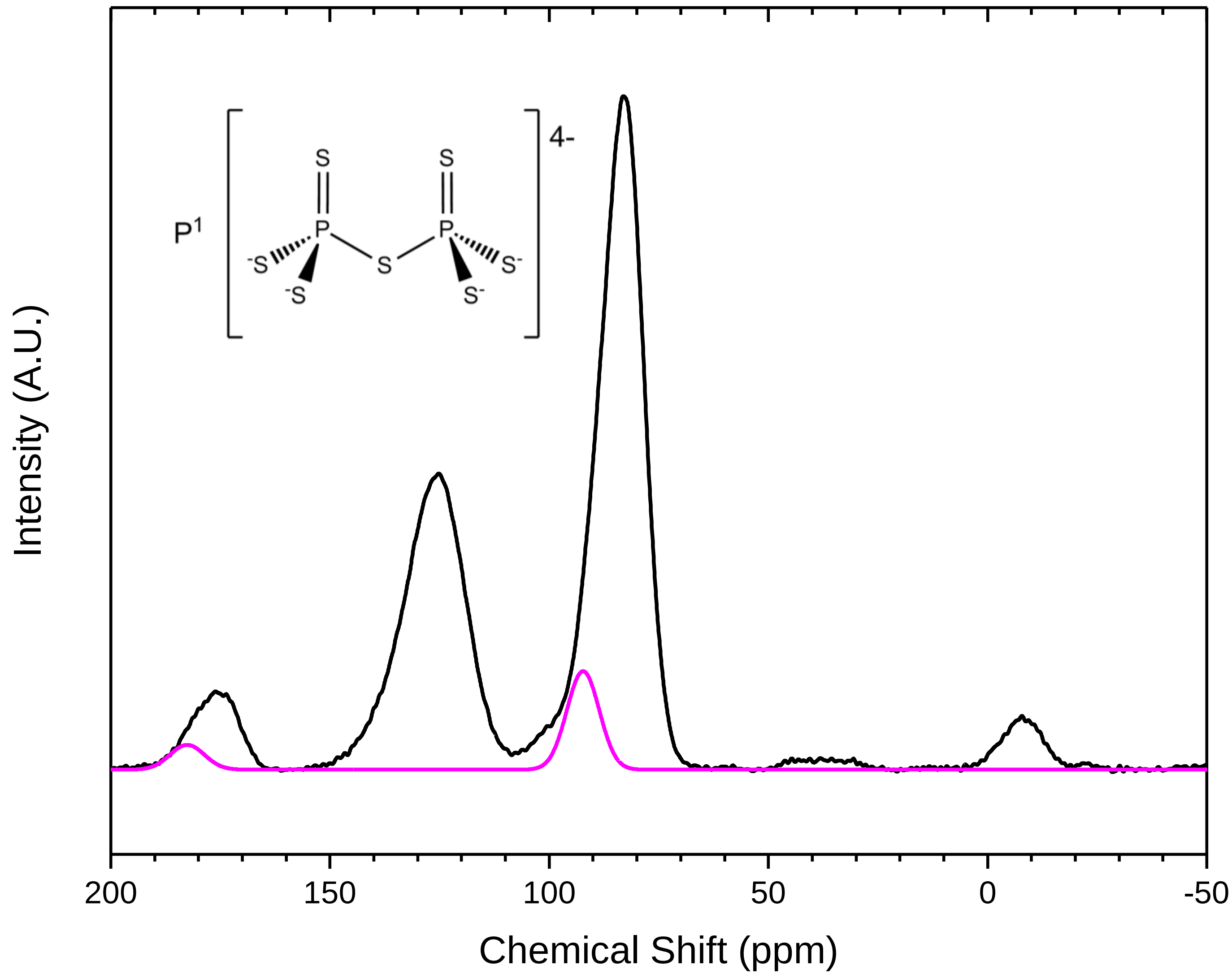
Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

$0.50Na_2S + 0.50P_2S_5$ Spectra deconvolution – $P^{3:}$ group



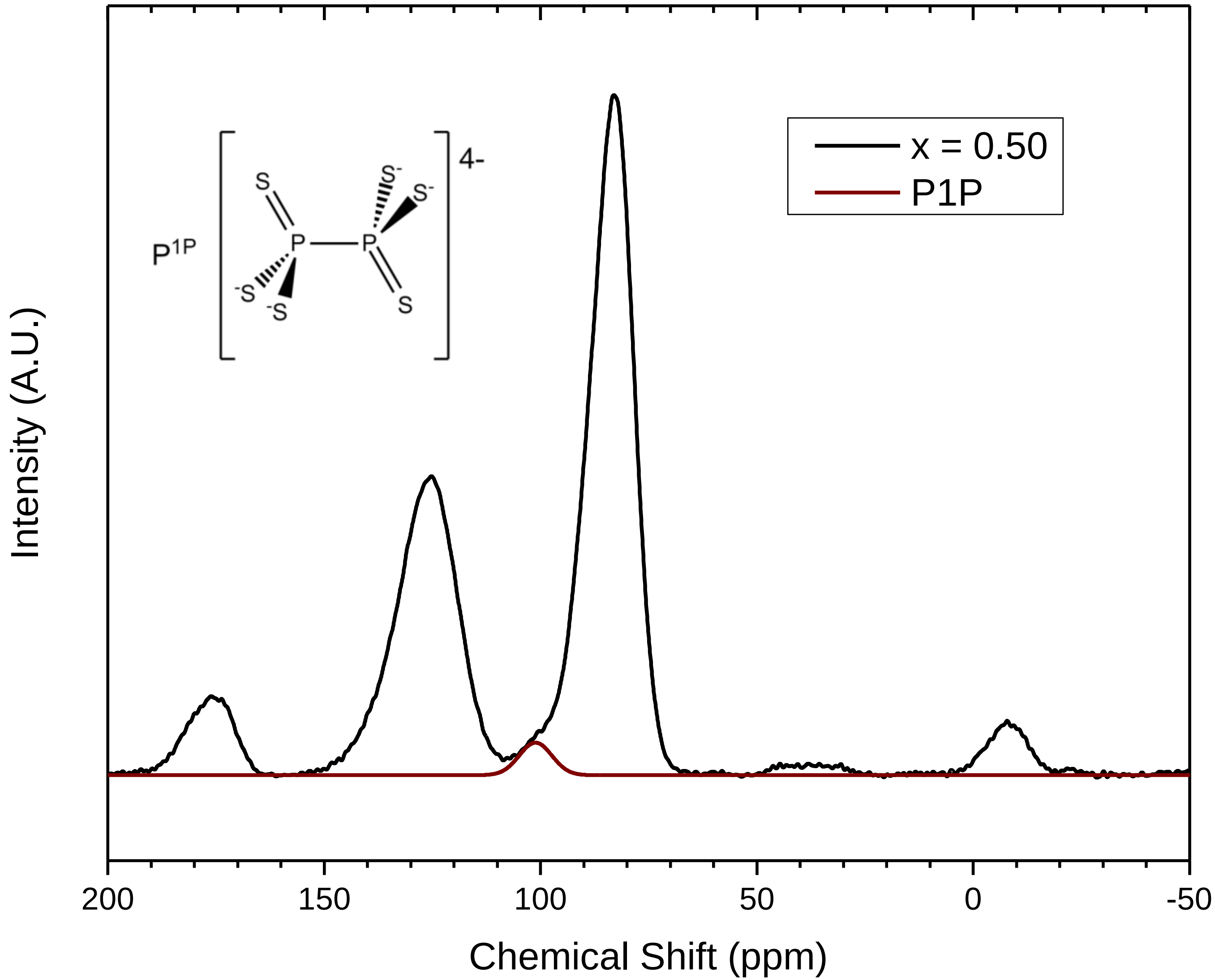
Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

0.50Na_2S + 0.50P_2S_5 Spectra deconvolution – P^1 group



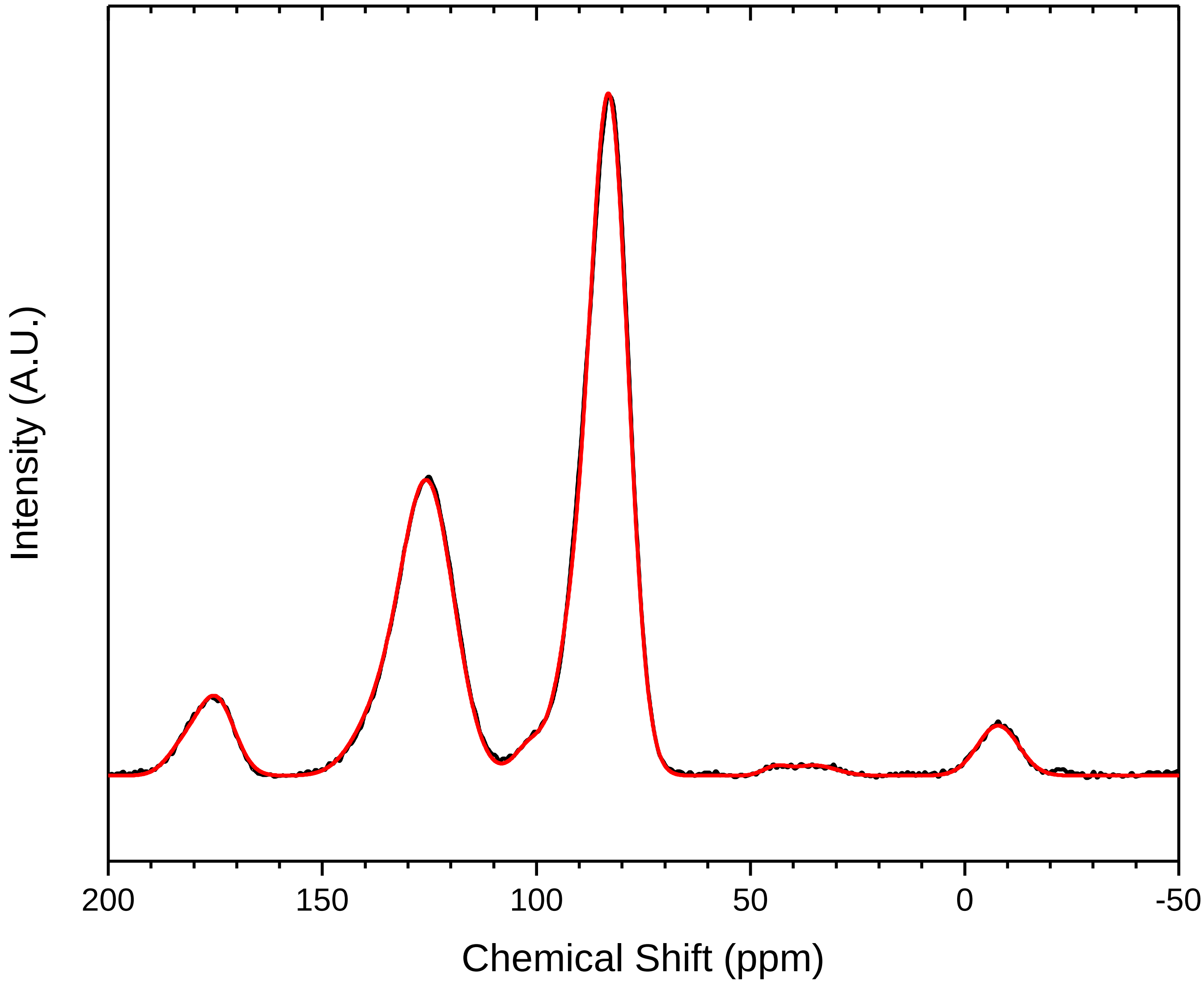
Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

$0.50Na_2S + 0.50P_2S_5$ Spectra deconvolution – P^{1P} group



Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

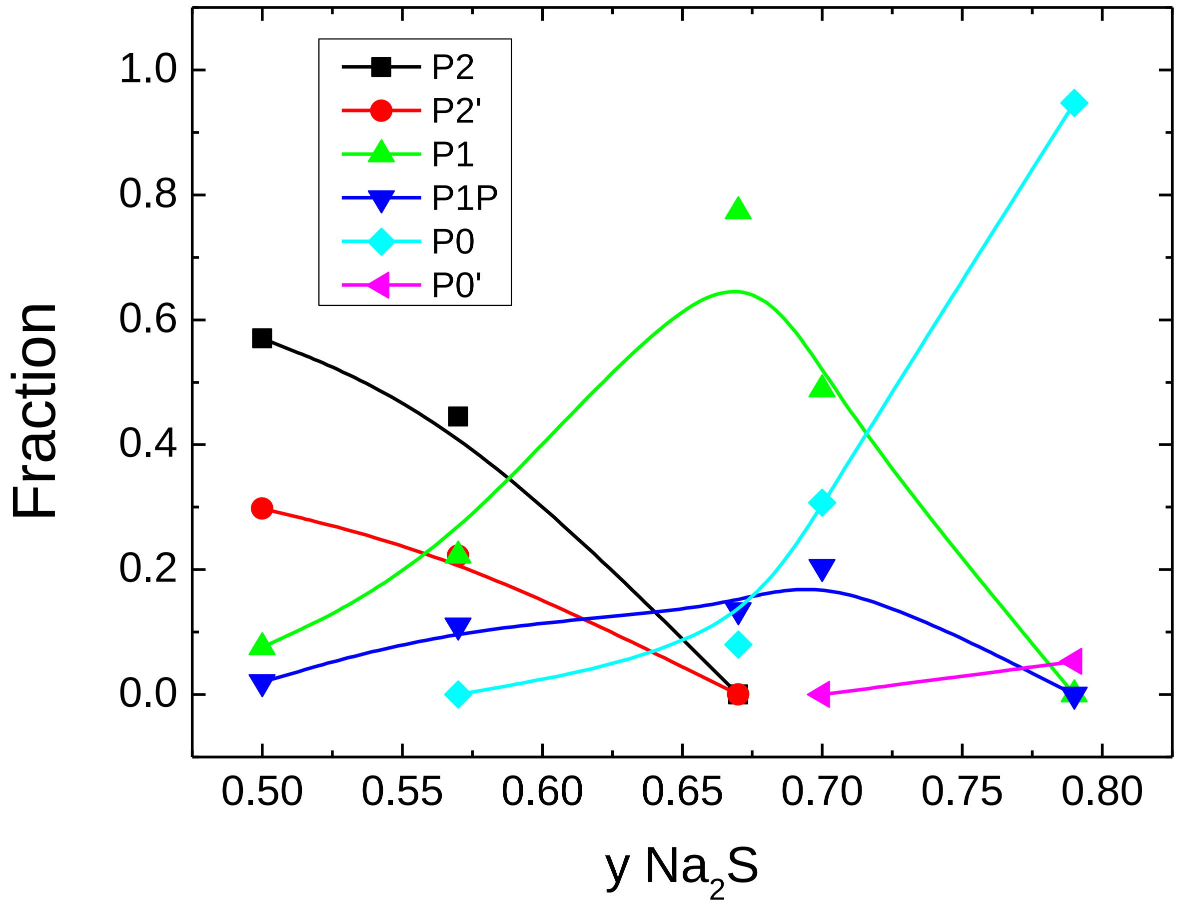
$0.50Na_2S + 0.50P_2S_5$ Spectra Convolution



Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

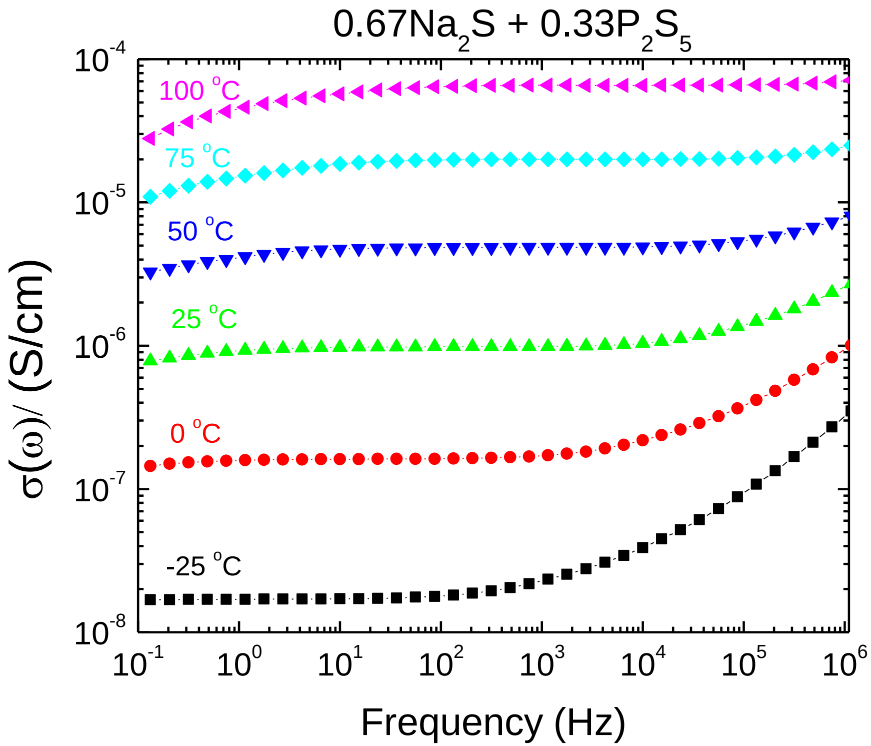
Compositional "Map" of the SRO Structural Groups

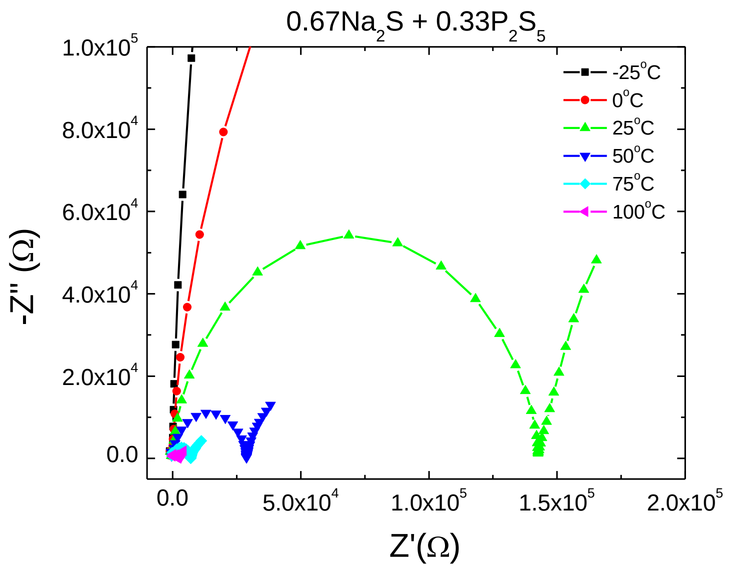
- As Na_2S is added to the glass
- Progressive formation of more "depolymerized" structural groups

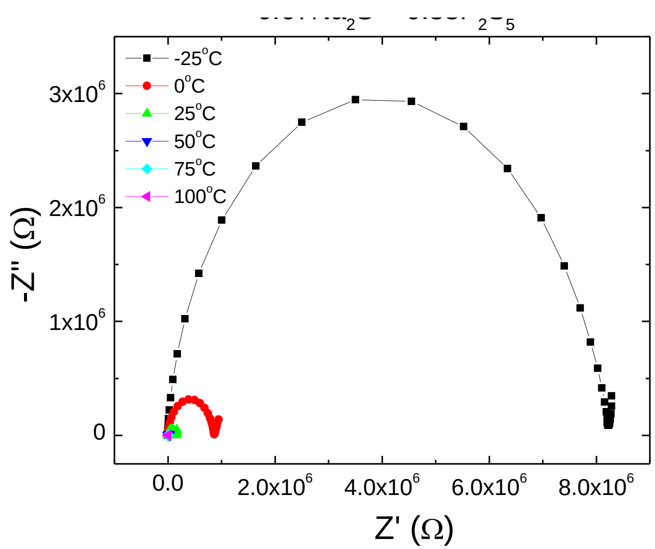


Bischoff, C., Martin, S. W. J. Phys. Chem. B, to be submitted

a.c. Na^+ Ion Conductivity



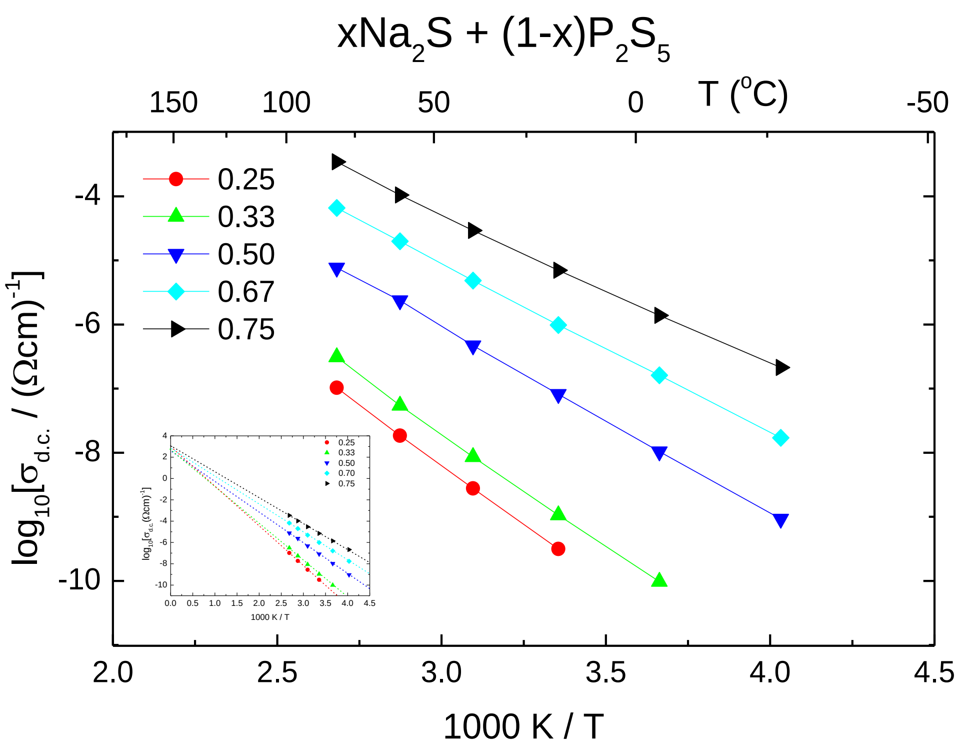


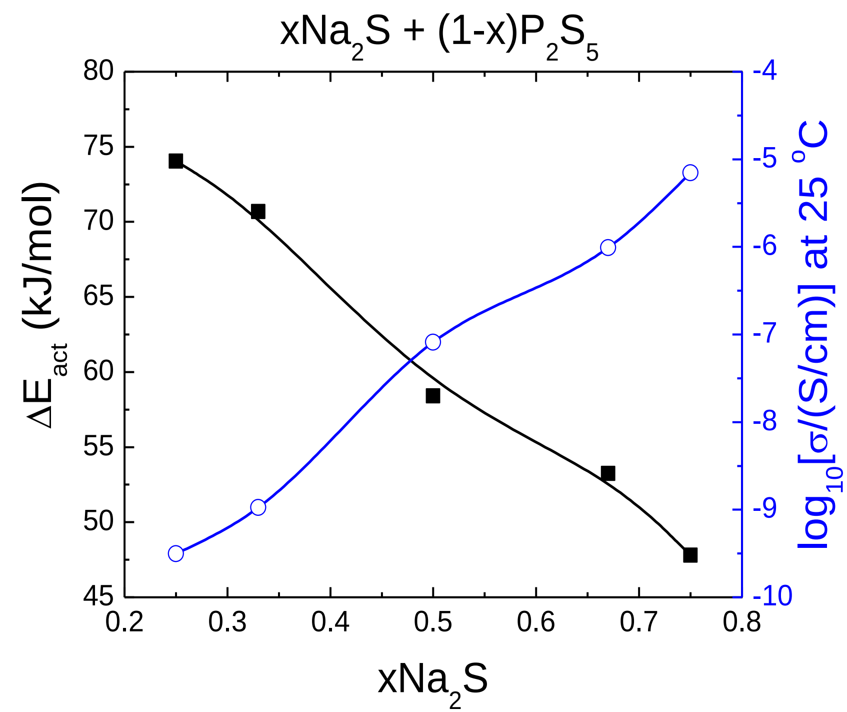


Berbano, S., Bischoff, C., Martin, S. W. JNCS, to be submitted

d.c. Na^+ Ion Conductivity

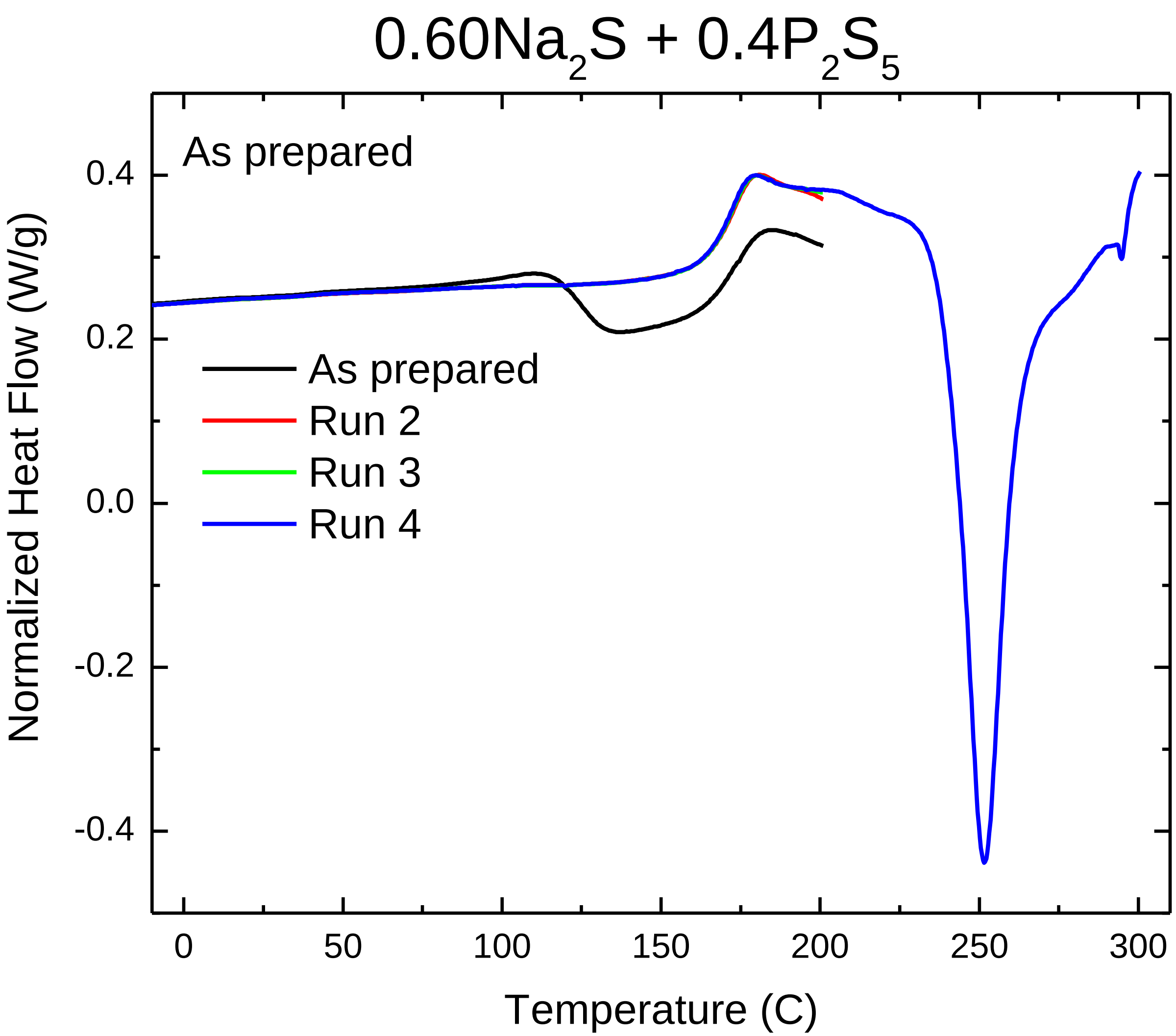
- Maximum Conductivity at Maximum Na_2S content



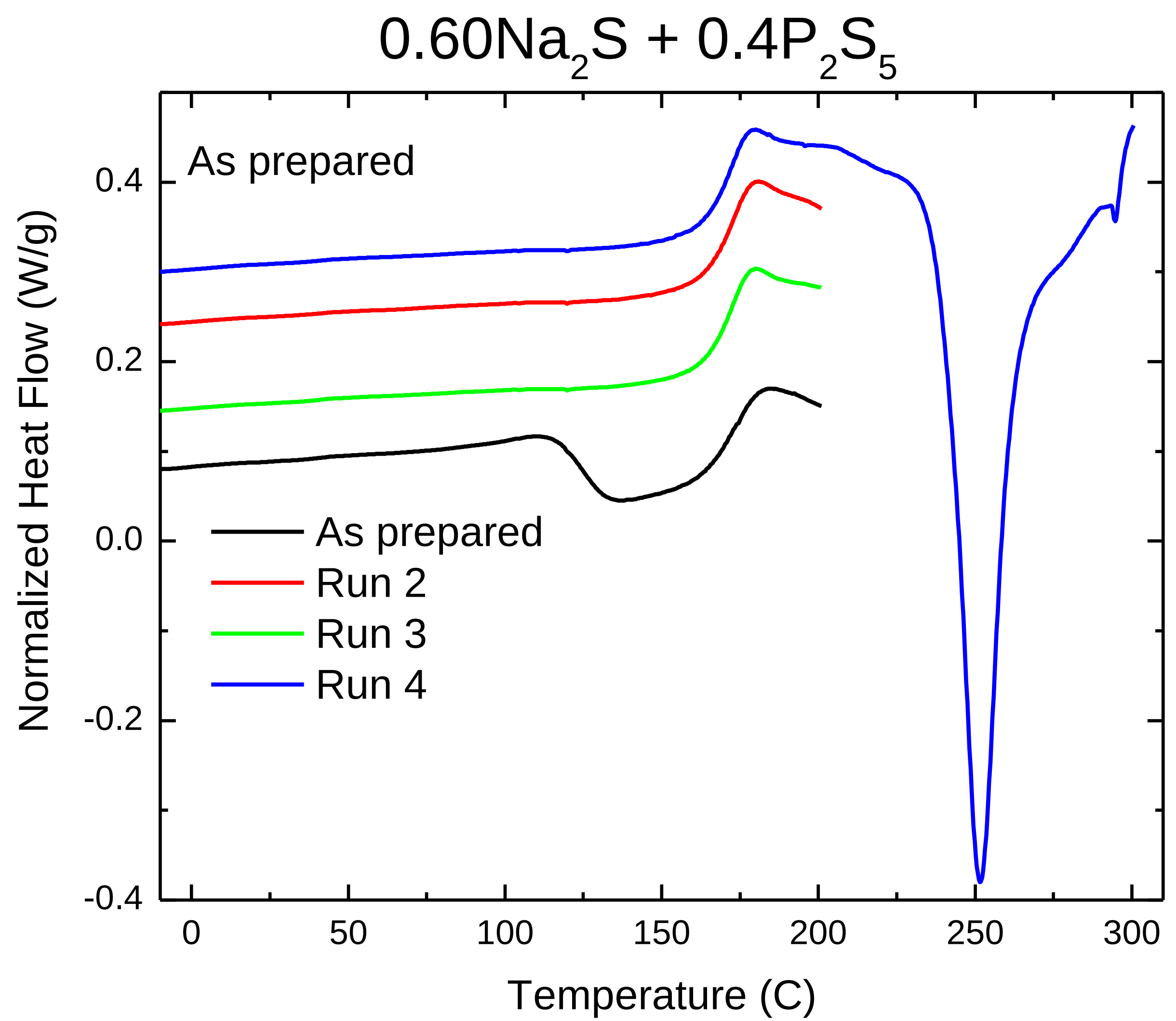


Berbano, S., Bischoff, C., Martin, S. W. JNCS, to be submitted

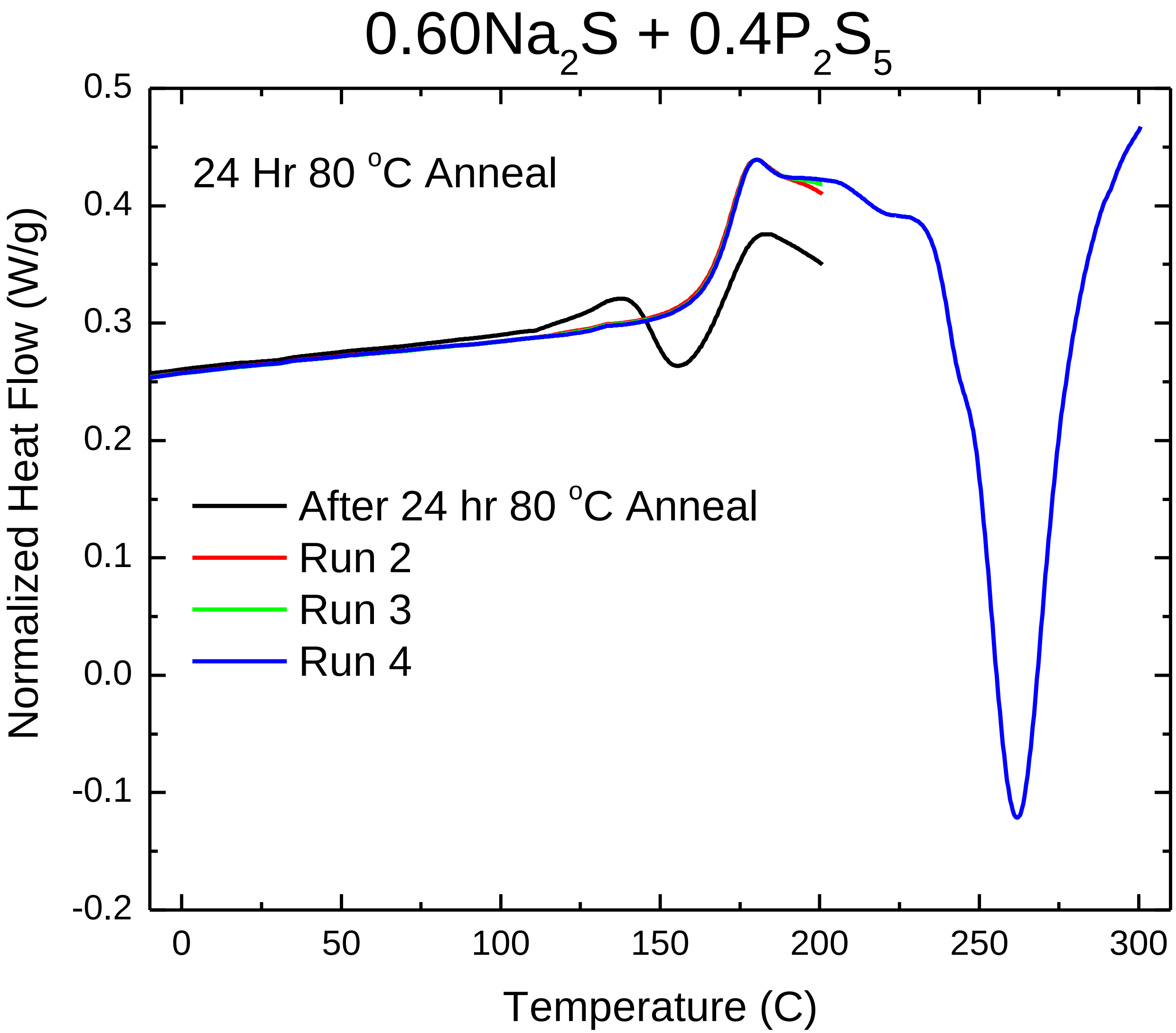
DSC Scans of $Na_2S + P_2S_5$ Amorphous Materials



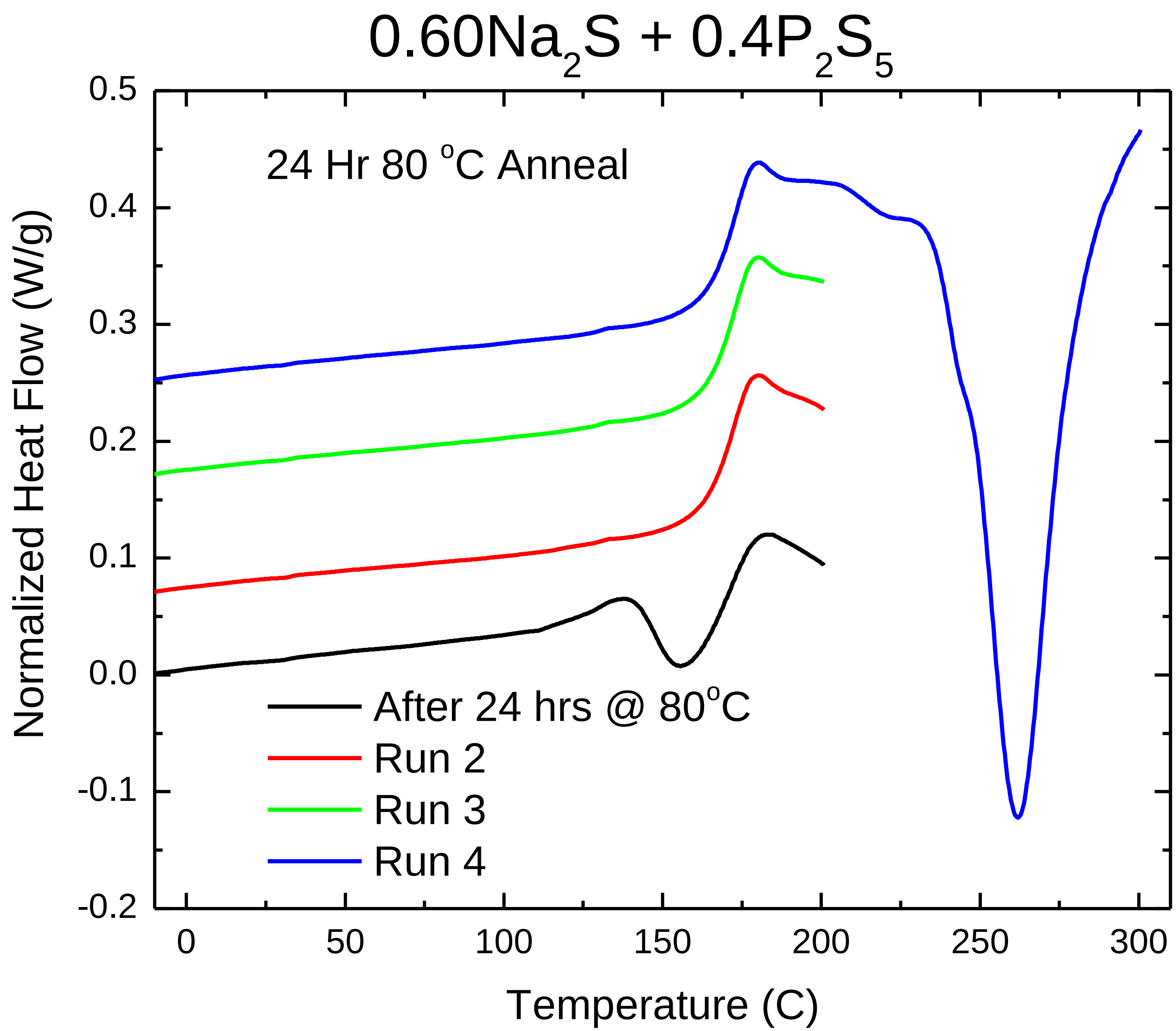
DSC Scans of $Na_2S + P_2S_5$ Amorphous Materials



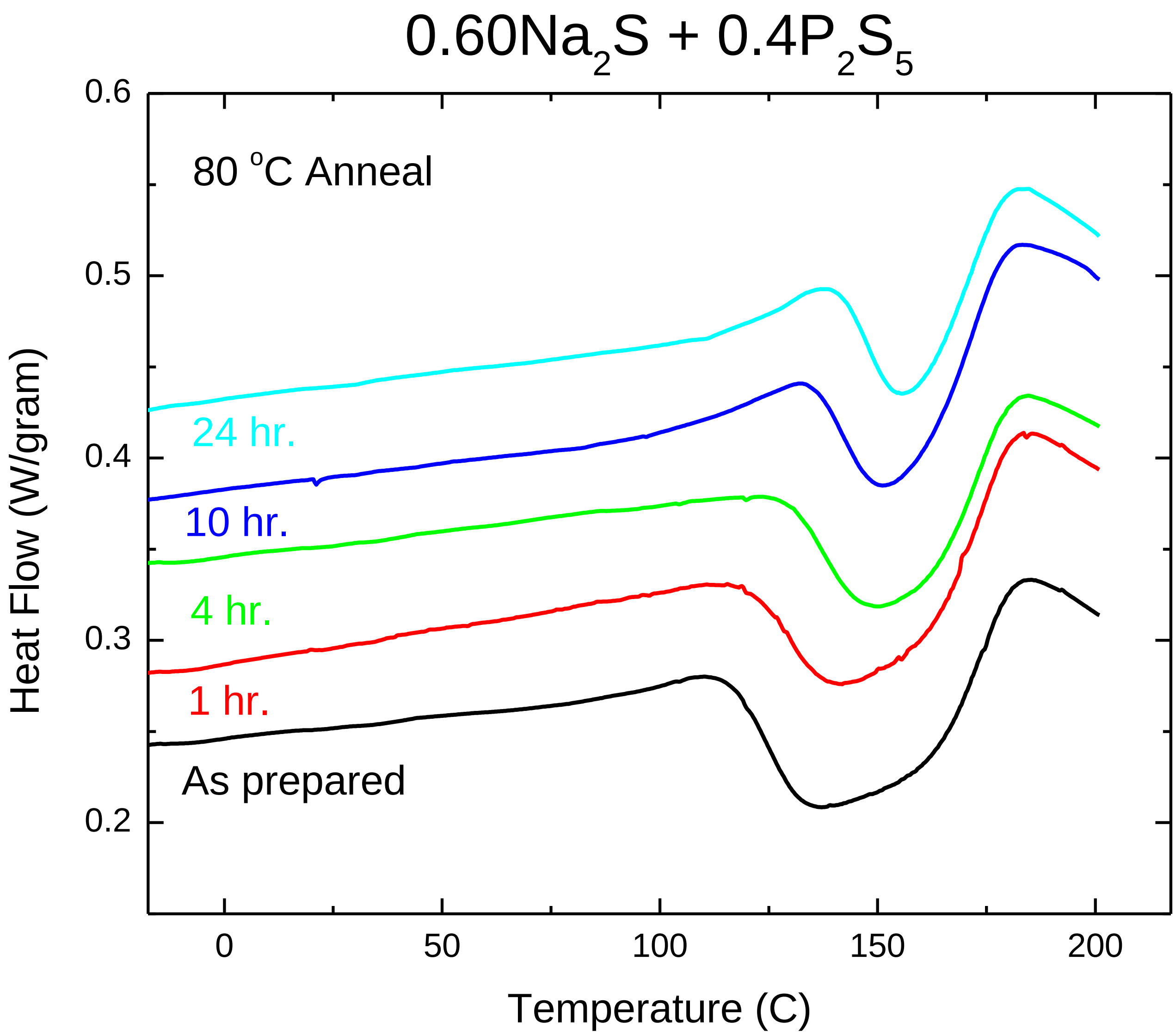
DSC Scans of $Na_2S + P_2S_5$ Amorphous Materials



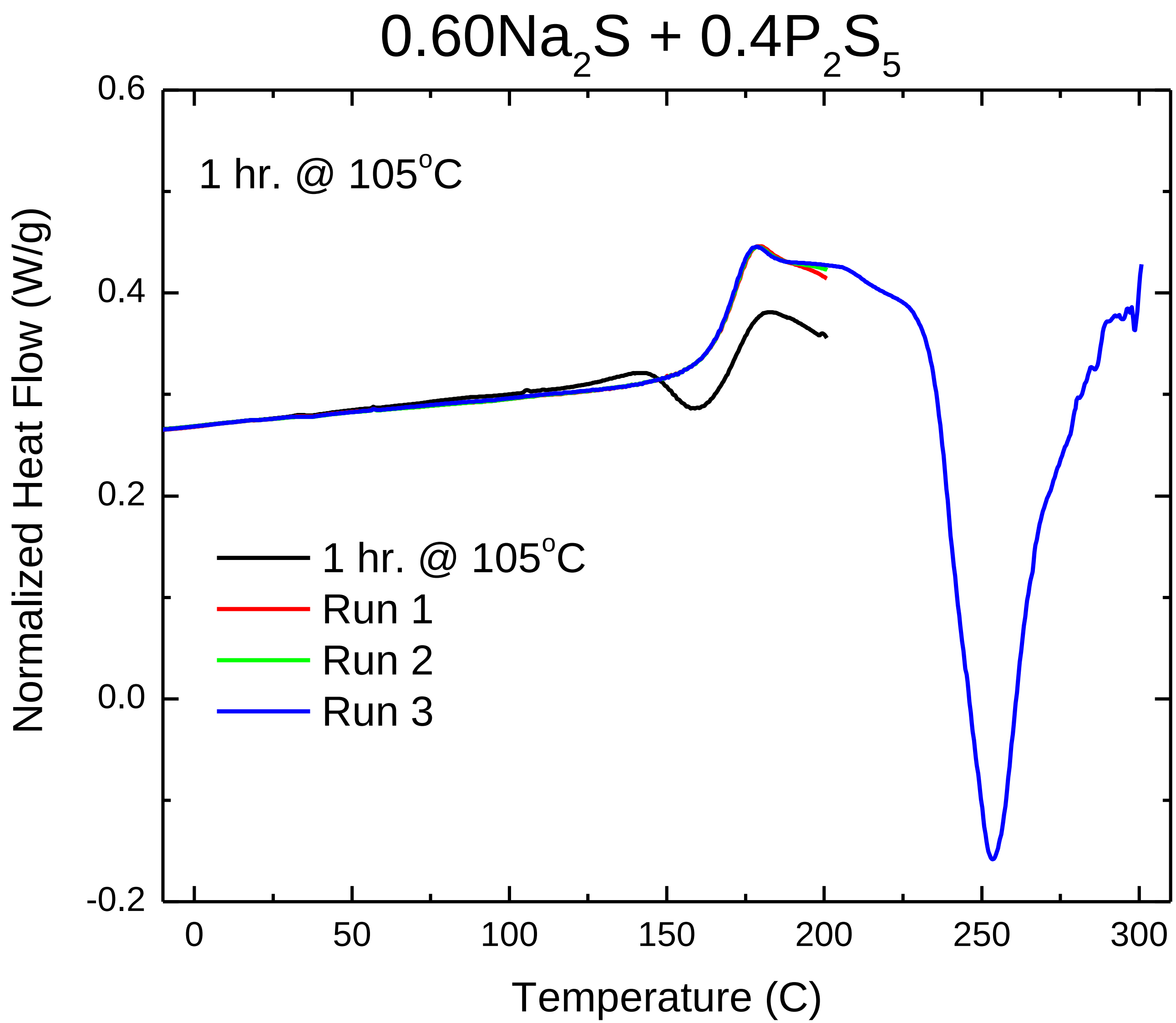
DSC Scans of $Na_2S + P_2S_5$ Amorphous Materials



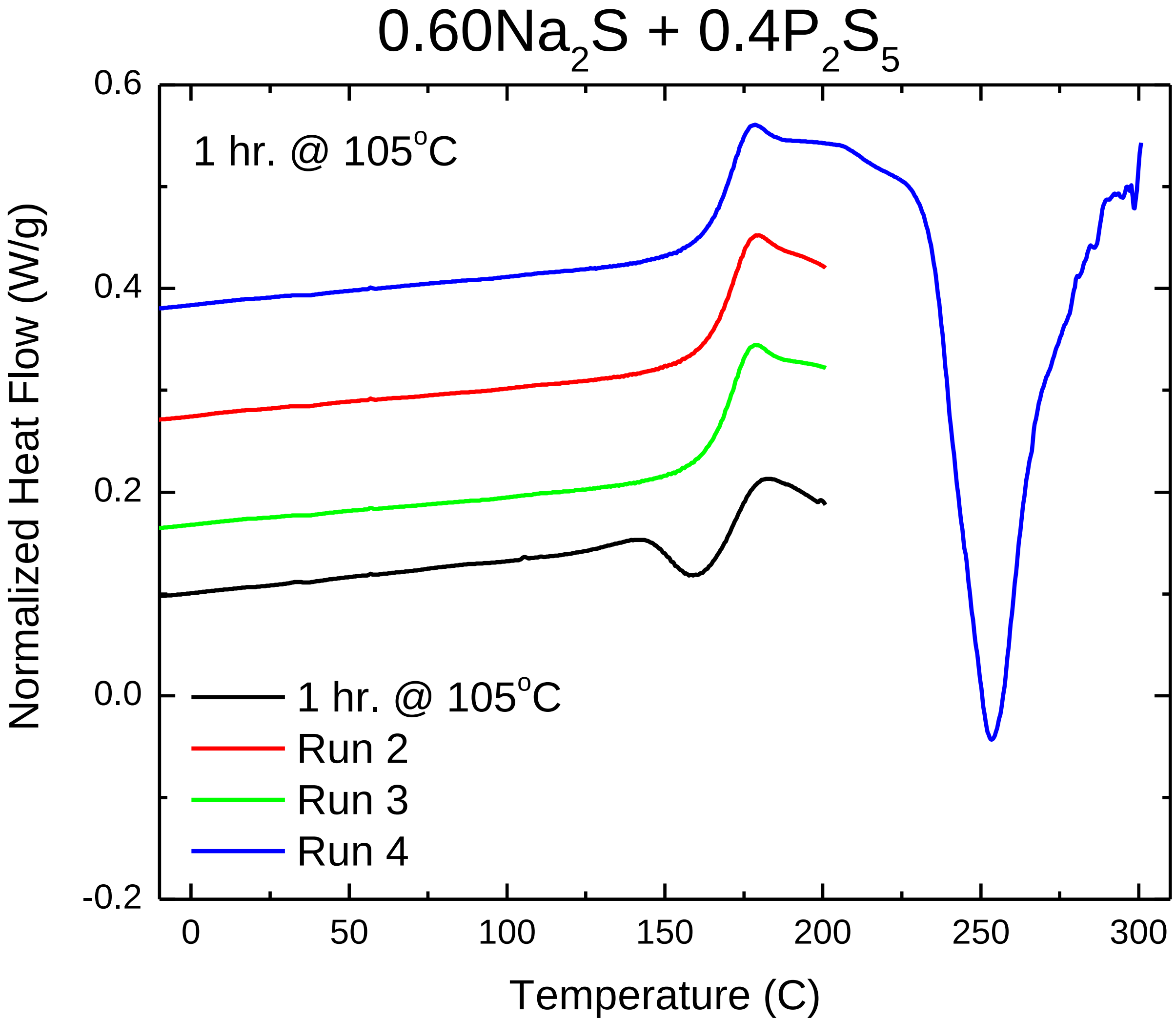
DSC Scans of Annealed $Na_2S + P_2S_5$ Amorphous Materials



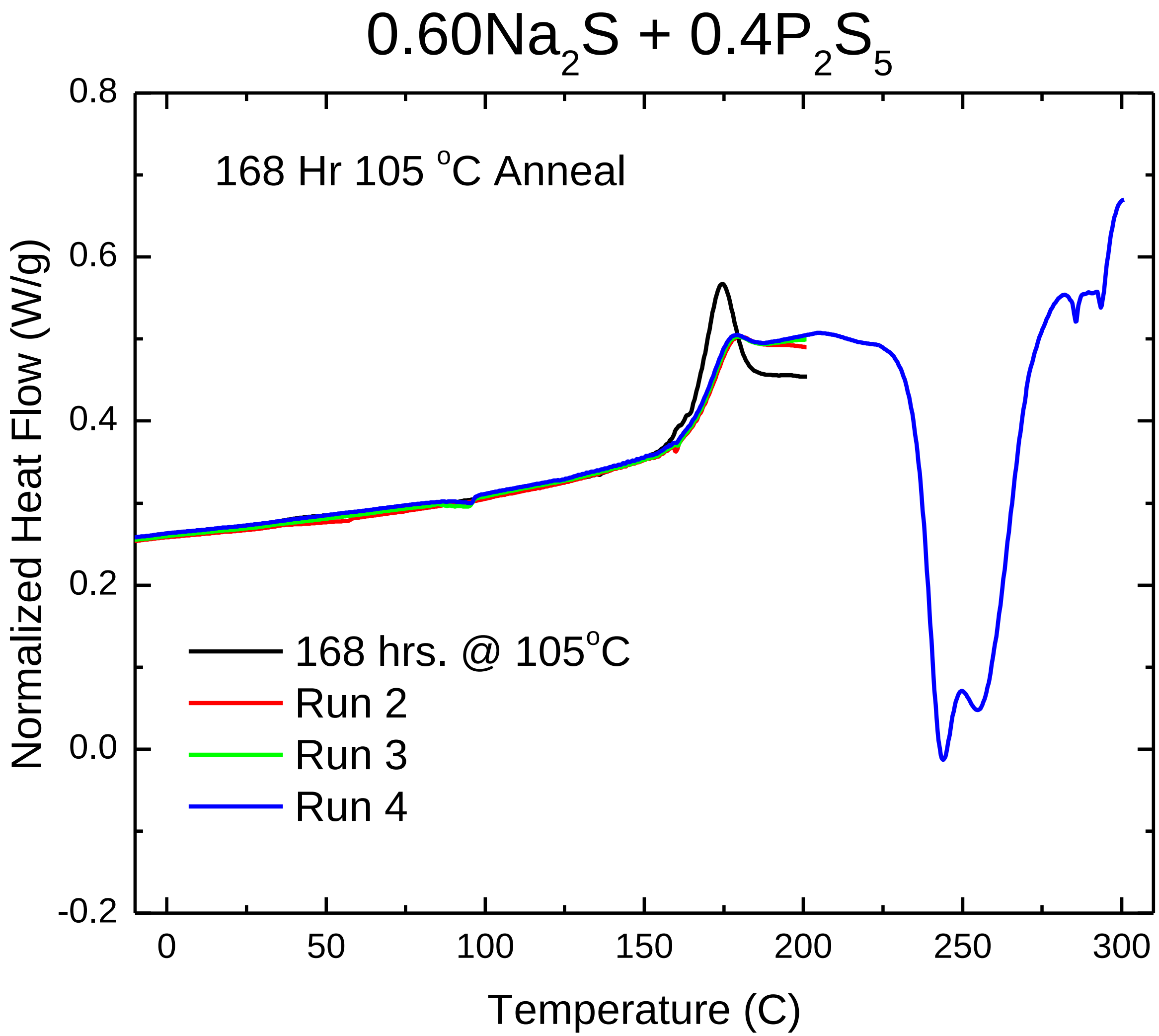
DSC Scans of Annealed $Na_2S + P_2S_5$ Amorphous Materials



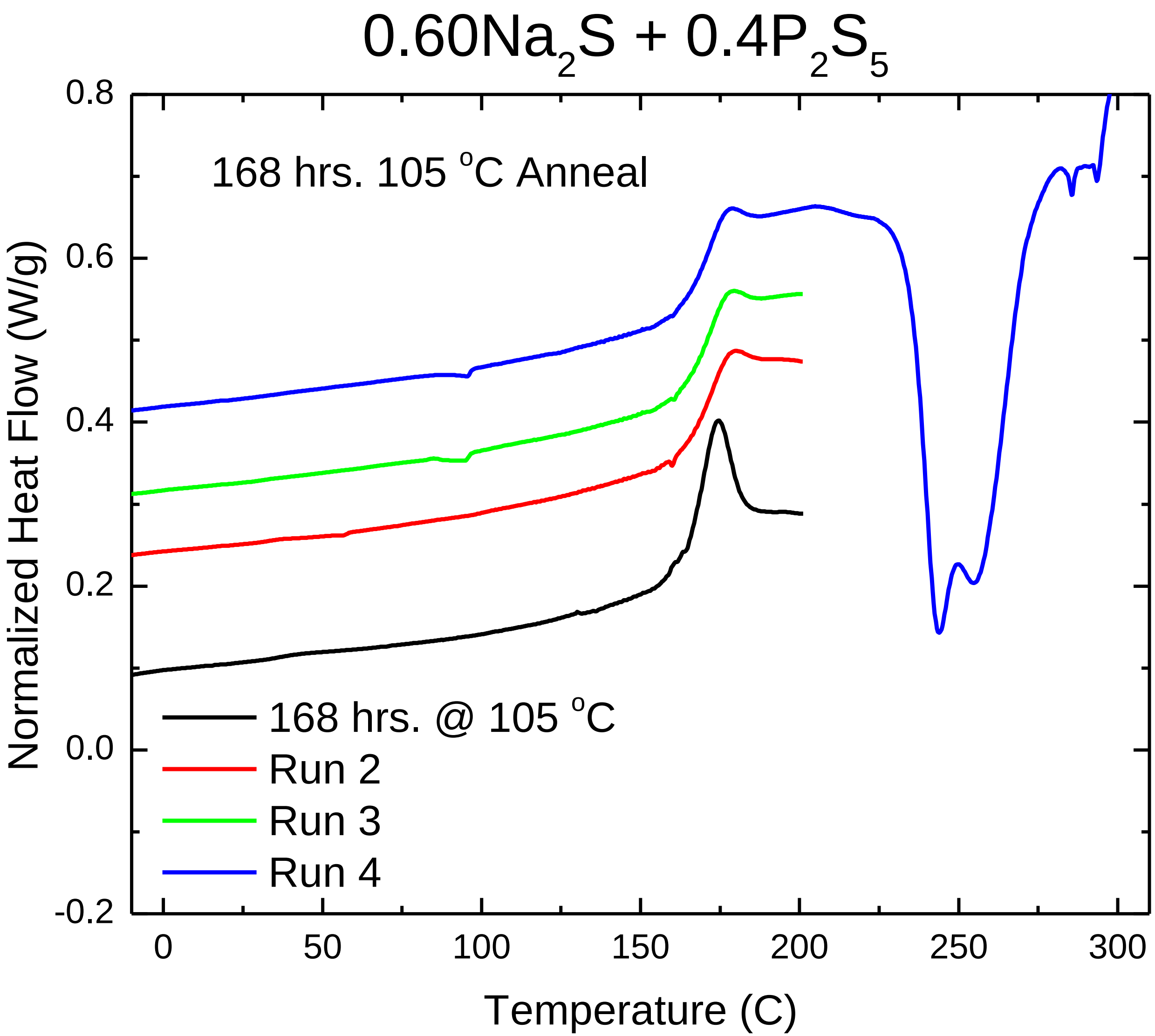
DSC Scans of 1 hr. Annealed $Na_2S + P_2S_5$ Amorphous Materials



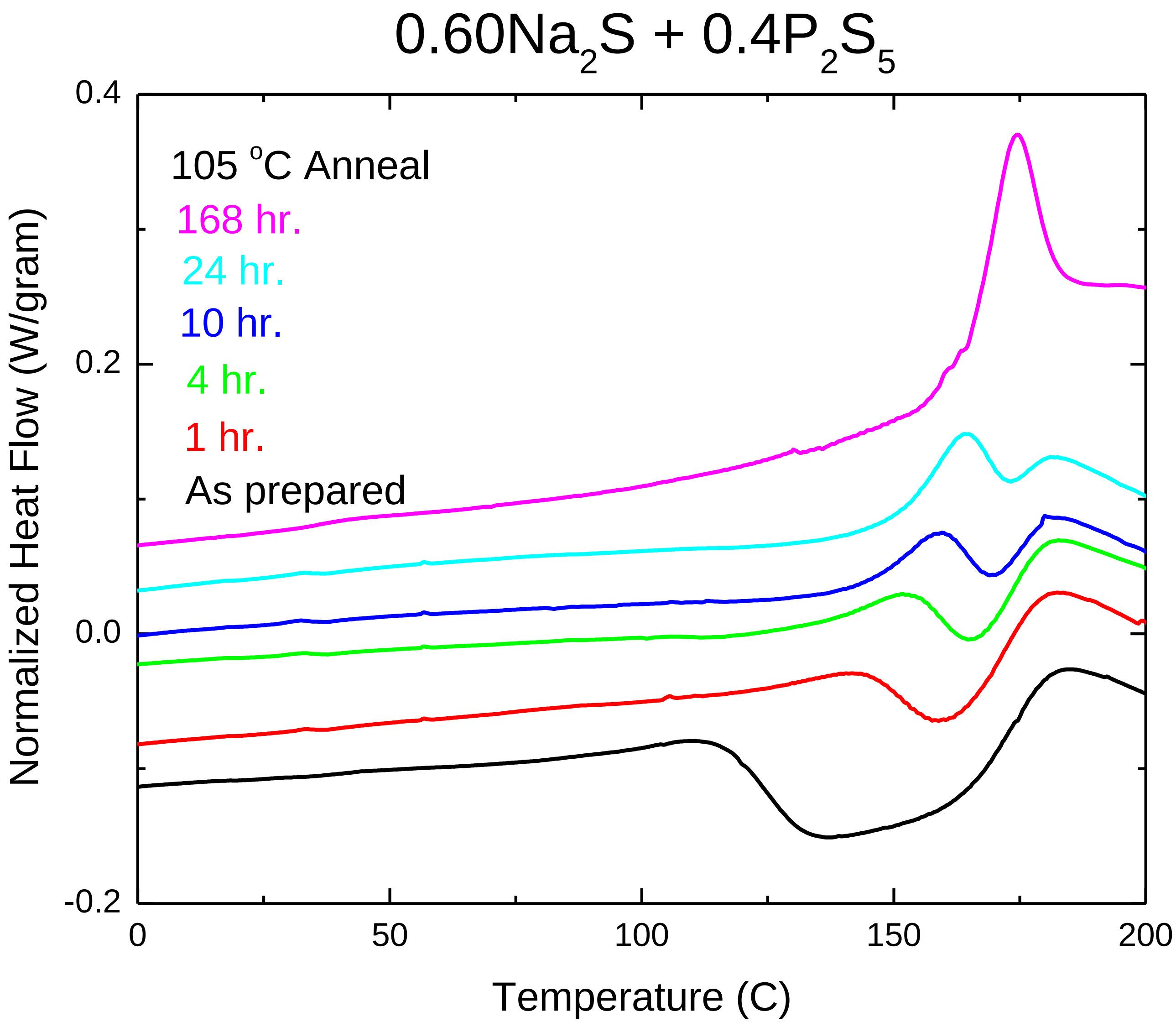
DSC Scans of 168 hr. Annealed $Na_2S + P_2S_5$ Amorphous Materials



DSC Scans of 168 hr. Annealed $Na_2S + P_2S_5$ Amorphous



DSC Scans of 105 °C Annealed $Na_2S + P_2S_5$ Amorphous Materials



Examples of Compression Processed Materials

- PVC powder – cold pressed (compression) at room temperature, annealed at 40 °C, 1 hr.

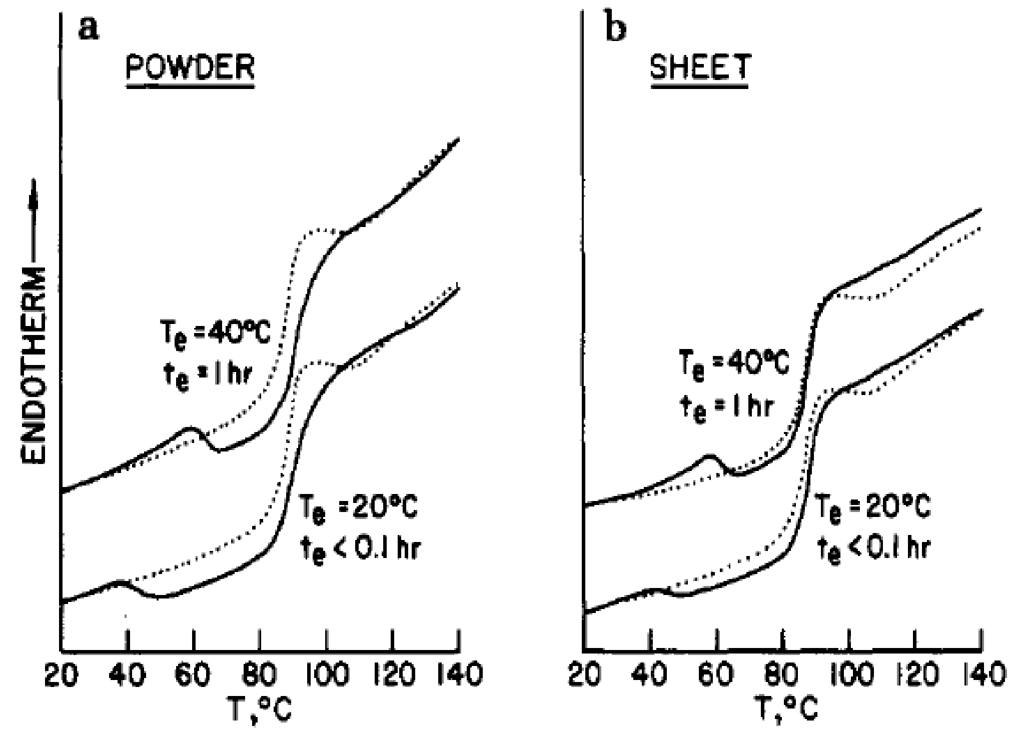


Figure 7. DSC: (a) cold-pressed PVC powder; (b) cold-re-pressed PVC sheet. T_e = 40 °C, t_e = 0 and 1 h.

Berens and Hodge Macromolecules 1982,15, 756-761

PVC powder – cold drawn (tension) at room temperature, annealed at 20 (left) and 40 °C (right)

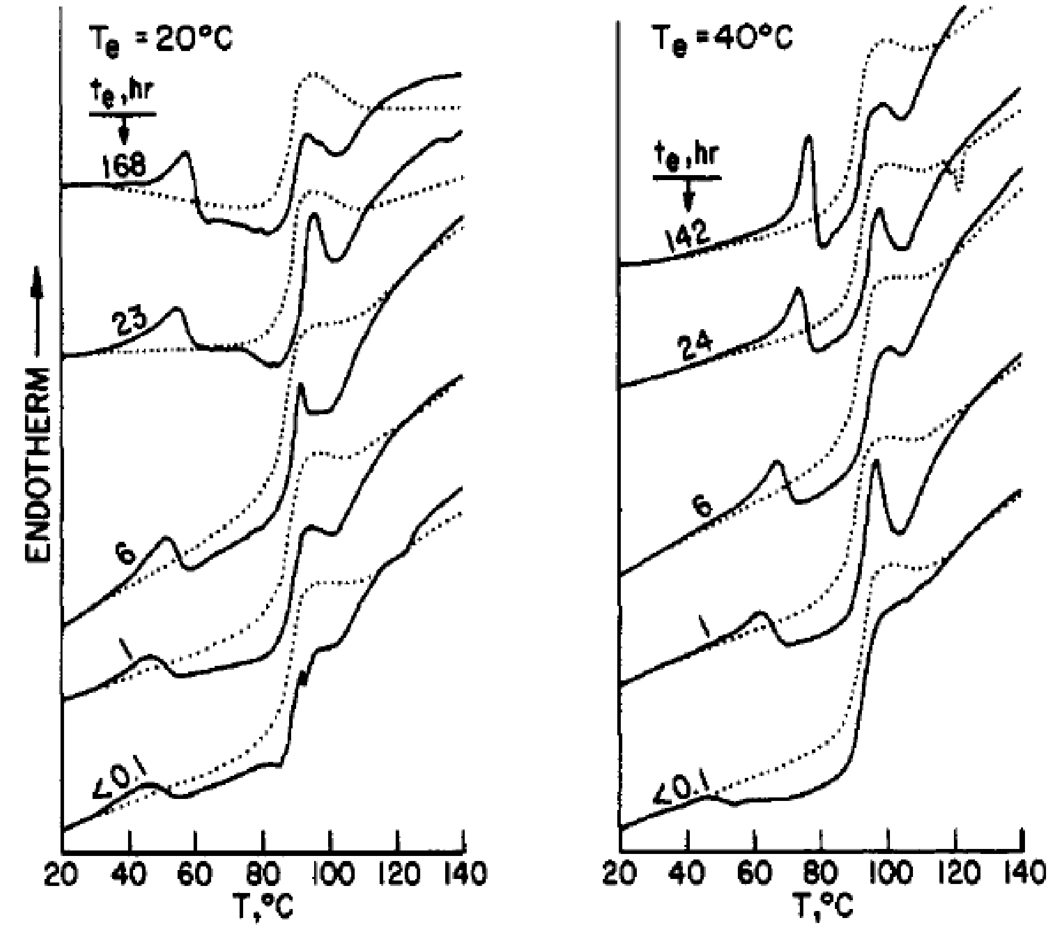


Figure 6. DSC, cold-drawn PVC sheet, varied T_e and t_e.

Berens and Hodge Macromolecules 15 (1982) 756-761

Conclusions and Summary

- Melt Quenched and Mechanically Milled Glasses have similar structures and properties
- $Na_2S + P_2S_5$ glasses have high Na^+ ion conductivity at room temperature
- Are favorable candidates for new solid electrolytes in solid state batteries
- Mechanically milled amorphous materials exhibit glass transition phenomena
- DSC behavior suggests that MM “glasses” have very high fictive temperatures produced by high equivalent cooling rates
- Significant enthalpy relaxation below Tg
- “Compression” based high fictive temperature rather than “tension” based high fictive temperature
- Rescanned glasses exhibit normal Tg behavior with “normal” Tg signatures
- Relaxation is associated with volume expansion rather than volume contraction?
- Expansion relaxation is a different process than contraction relaxation?
- New Polyamorphic State produced by compression to high density structures between MM and MQ produced glasses?

Acknowledgements

- Ian Hodge for helpful discussions
- Connie Moynihan for helpful and enjoyable conversations over many years!
- The GOMers of the GOM group!

Concluding comment…..

It's all we've got …(for now)…..let's take care of it…

168 hrs. Anneal @ 105 °C

ln τ_o = -109, ΔE_{act} = 98 kcal/mole, x=0.40, β= 0.40, Q_c= 2,000, Q_h= 20 C/min, 105 °C, 168 hrs.