Exploring Modified *Closo*-Borate Electrolytes in All-Solid-State Batteries

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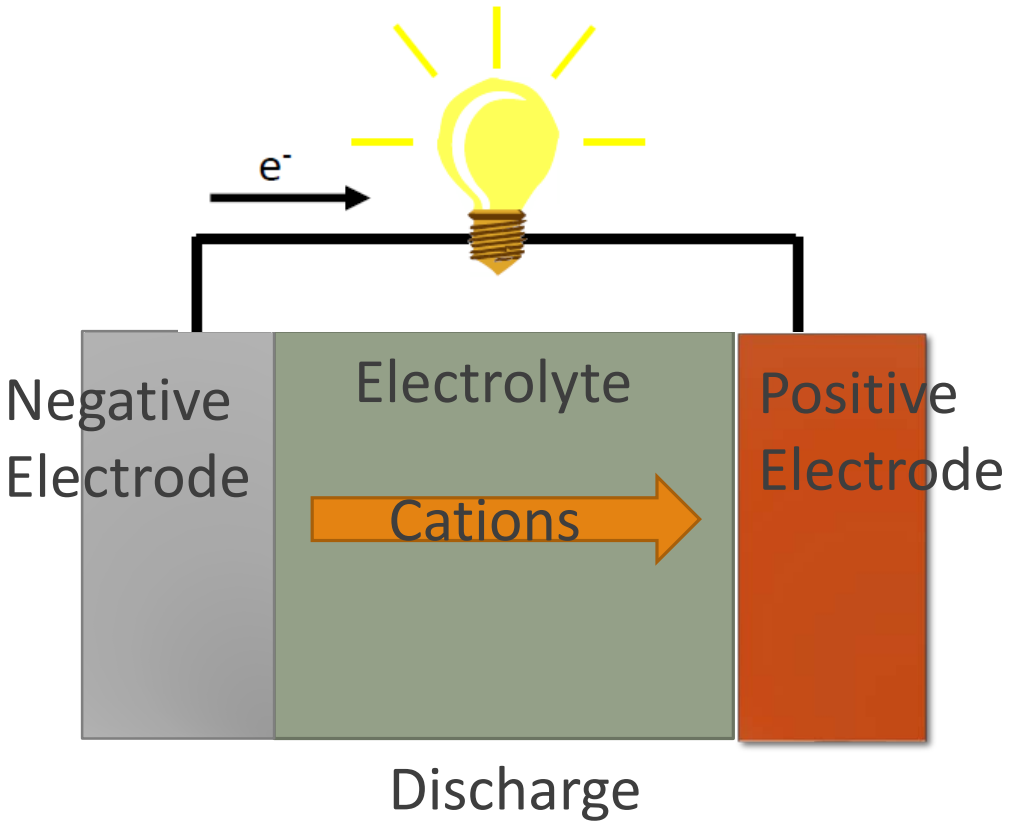
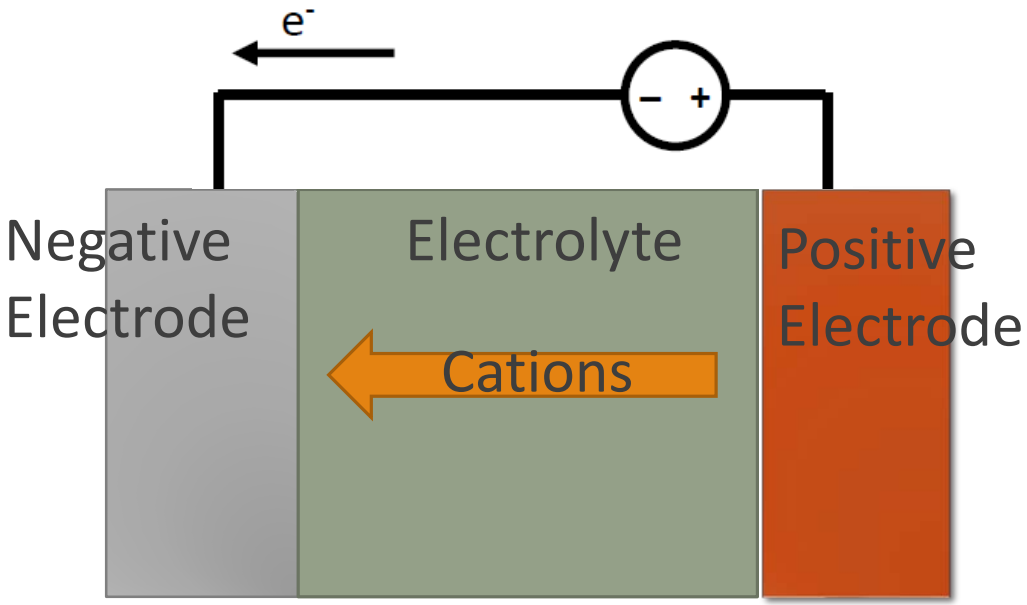
Introduction

Goal: To synthesize non-Li-conducting salts and test their conductivity to see if they would be suitable solid electrolytes for all-solid-state batteries

How batteries work



Discharge



Charge

Lithium-ion Batteries

- Liquid electrolyte leaks: corrosive, flammable, explosions
- Hazardous byproducts: possible HF release
- Low abundance of lithium(20-70 ppm)- relatively expensive

All-Solid State Batteries

- Solid Electrolyte: no leakage
- No HF release
- More compact

Samsung
Galaxy Note 7

Images: news.softpedia.com, today.com

Cations

- Sodium
  - Abundant: 23,000 ppm (sea water)
  - Less expensive
  - Similar properties with Lithium (alkali metals):
    - $^{+}1$ charge
    - Small
- Calcium
  - 36,000 ppm
  - Less expensive
  - Moderately similar properties (alkali earth metal):
    - $^{+}2$ charge: will take 2 electrons. Conduct faster?

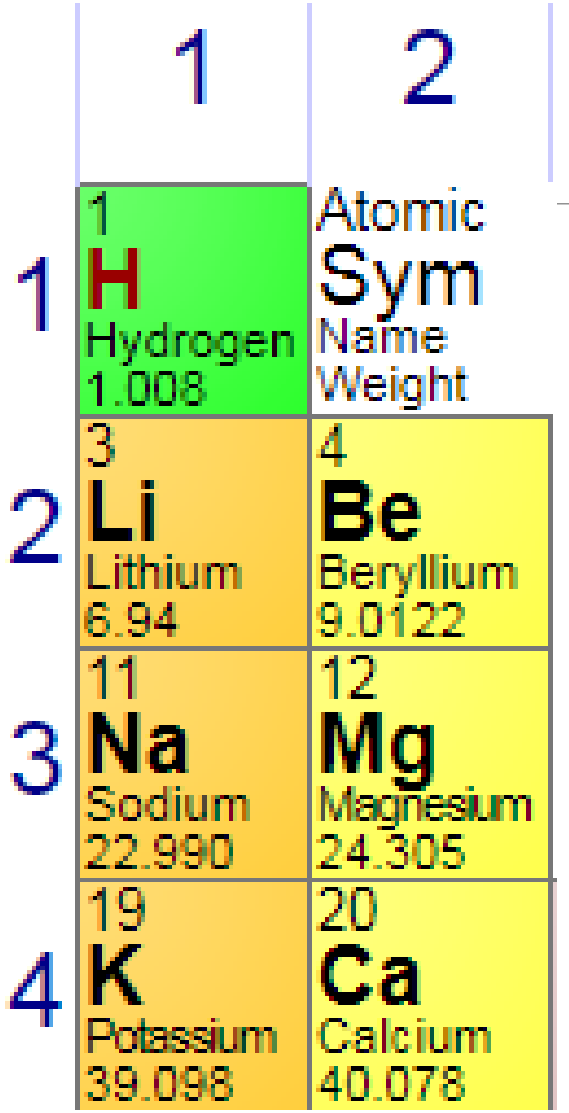
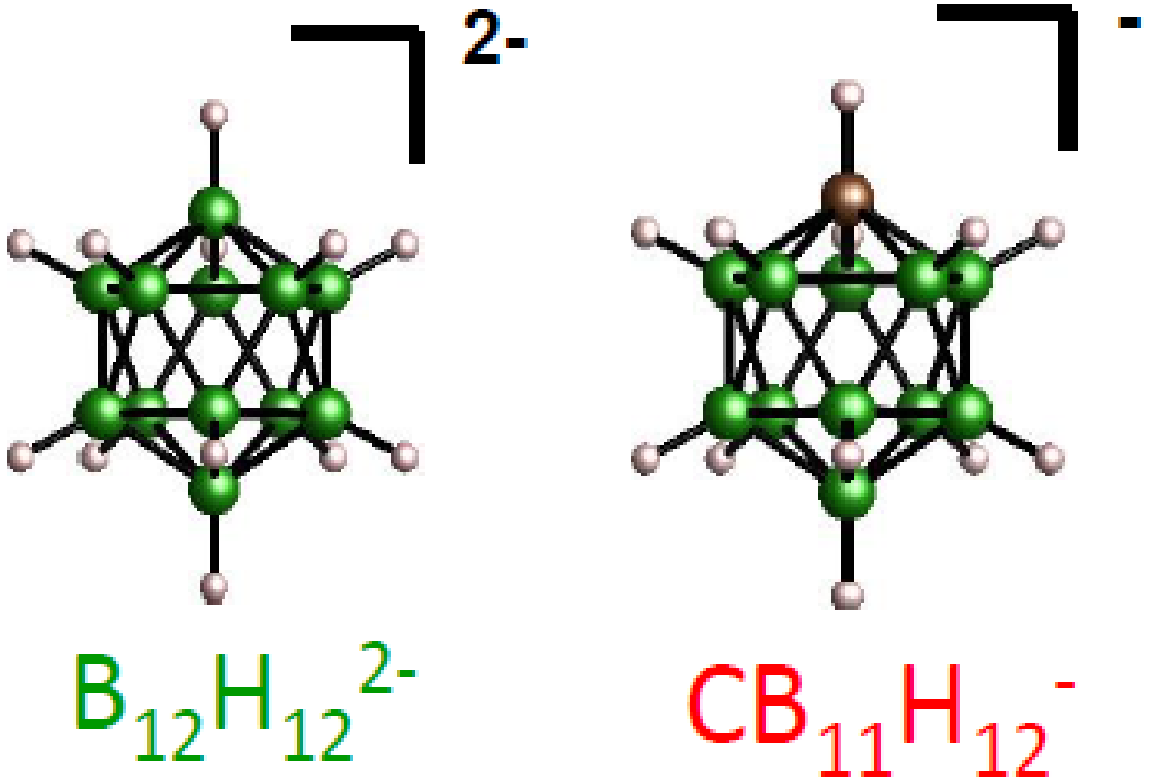


Image: ptable.com

Anions

- closo-polyborate (polycarborate)- based complex hydrides
- Replaced 1 B with a C
  - C is more electronegative
  - Changes charge distribution of anion cluster

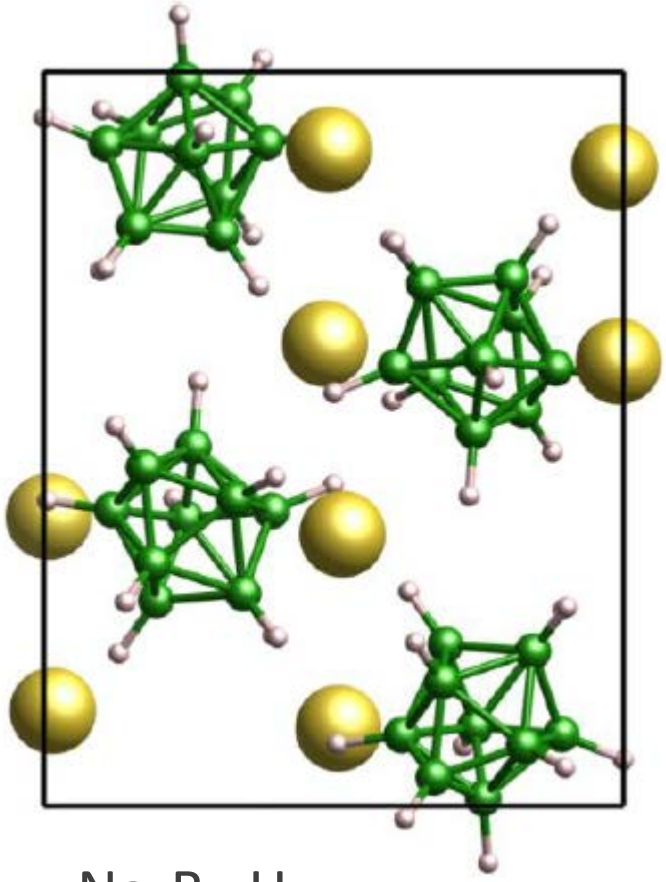


Boron-Hydrogen Based Solid Electrolytes

- Conductive solids
- Light weight
- Ordered to disordered phase change :

Entropy causes increase in conductivity

- Superionic conductivity in solids
  - Cations: hop through structure
  - Anions: high reorientation mobility

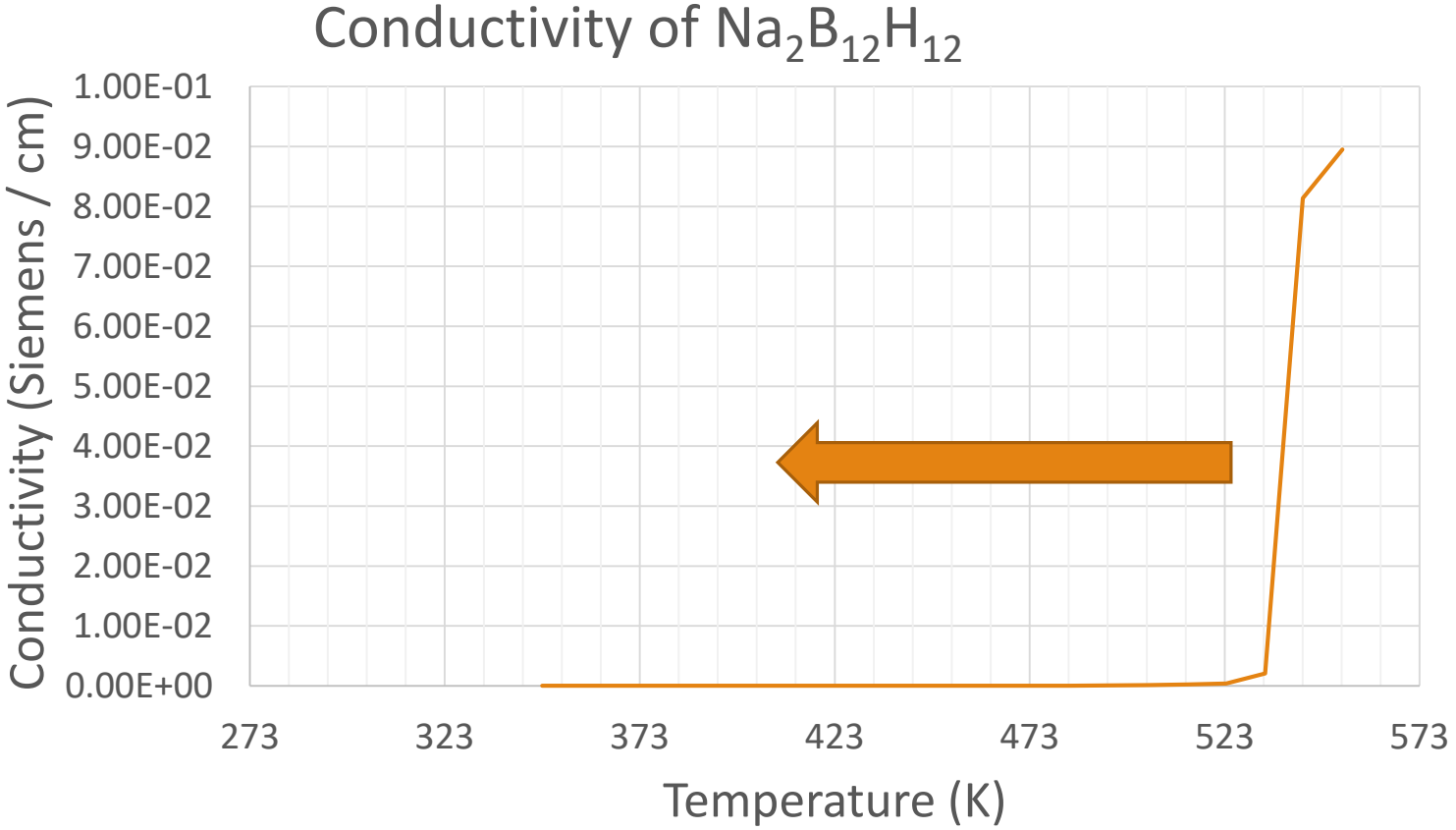


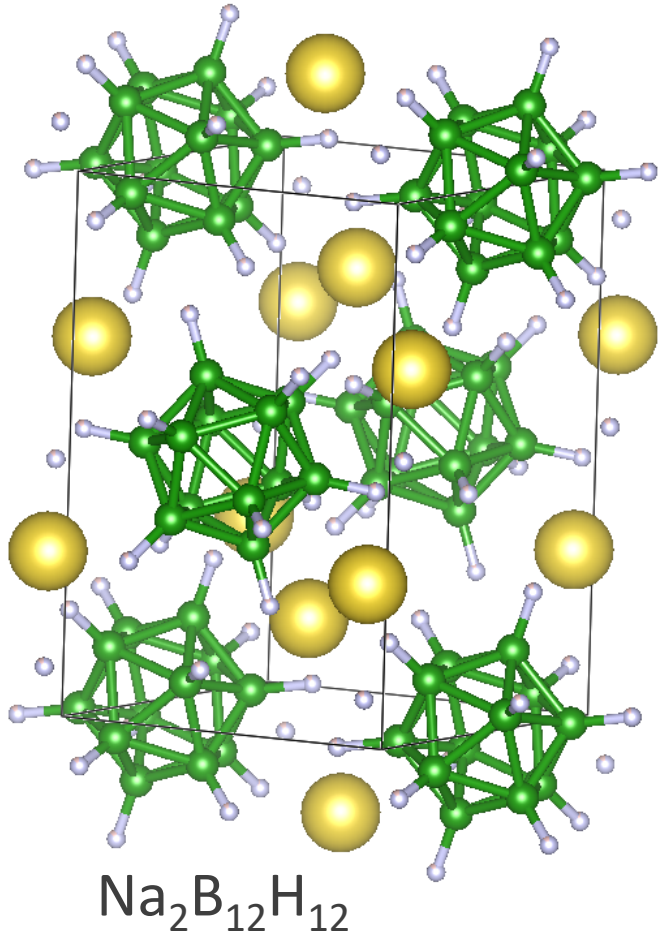
$Na_2B_{10}H_{10}$

T. J. Udovic, M. Matsuo, W. S. Tang, H. Wu, V. Stavila, A. V. Soloninin, R. V. Skoryunov, O. A. Babanova, A. V. Skripov, J.J. Rush, A. Unemoto, H. Takamura and S. Orimo, *Adv. Mat.* 26 (2014) 7622.

Image: Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* 2011, *44*, 1272-1276.

$Na_2B_{12}H_{12}$



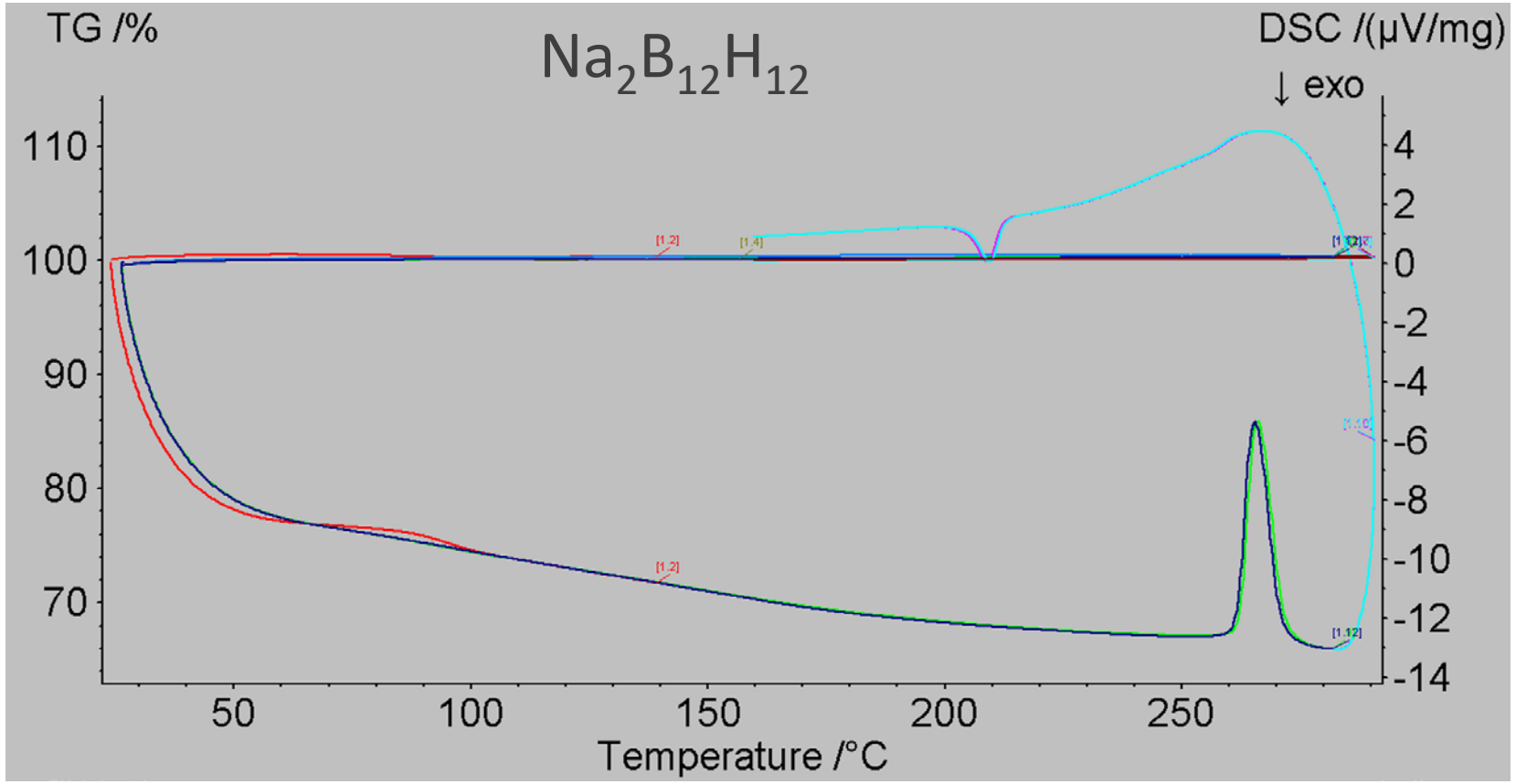


$Na_2B_{12}H_{12}$

Data: T. J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A. V. Skripov, J. J. Rush, H. Takamura and S. Orimo, *Chem. Commun.*, 2014, *50*, 3750.

Image: Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* 2011, *44*, 1272-1276.

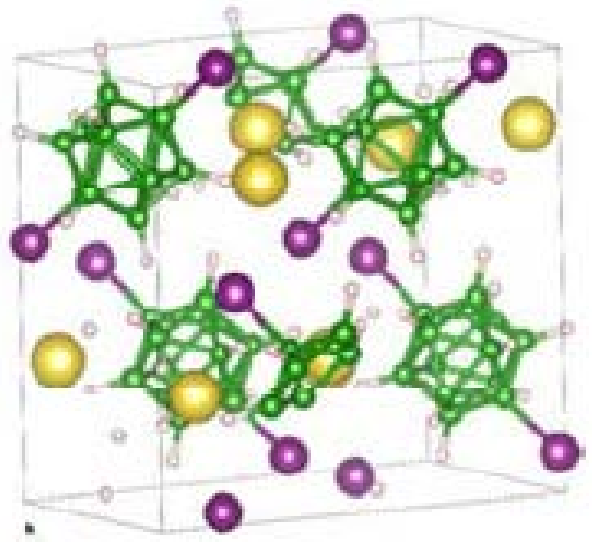
Differential Scanning Calorimetry (DSC)



DSC

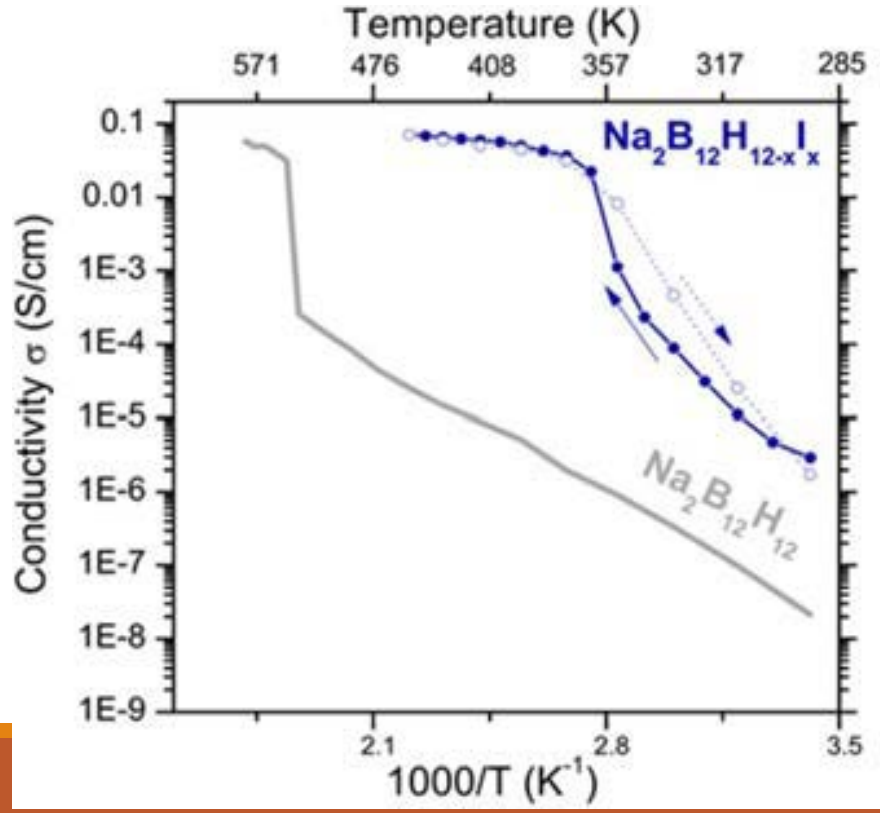
$Na_2B_{12}H_{12-x}I_x$

Adding Iodine to $Na_2B_{12}H_{12}$ increases the conductivity at lower temperatures.



$Na_2B_{12}H_{12-x}I_x$

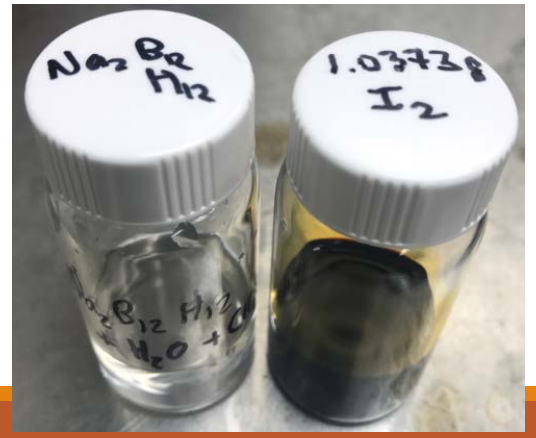
Conductivity of $Na_2B_{12}H_{12}$ and $Na_2B_{12}H_{12-x}I_x$



Y. Sadikin, P. Schouwink, M. Brighi, Z. Łodziana, and R. Černý, *Inorganic Chemistry*, **2017,** *56* (9), 5006-5016.

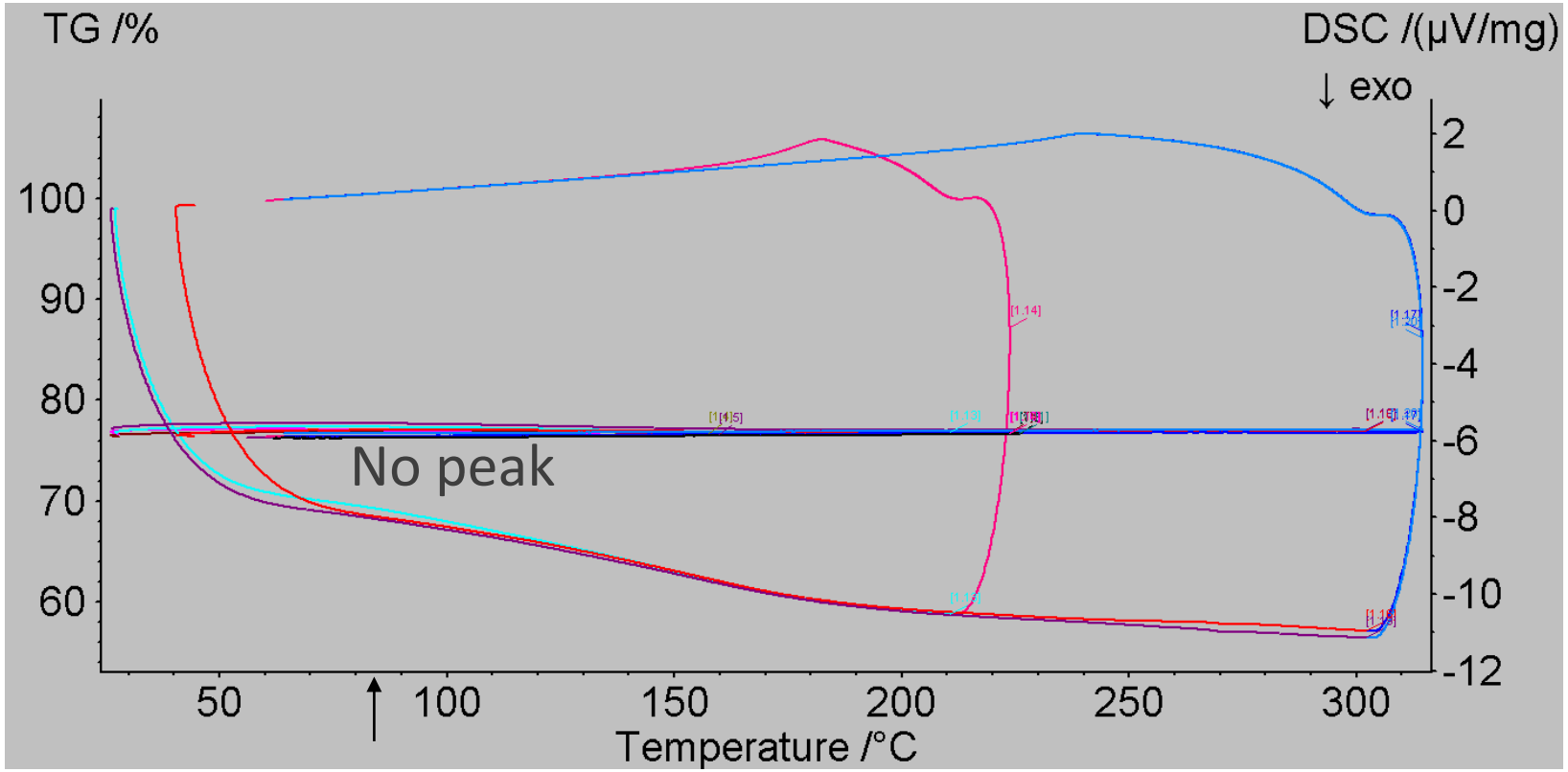
Adding Iodine to $Na_2B_{12}H_{12}$

- Iodine Solution: 4 mmol of I_2 in 8 mL of CH_3OH
- Sodium Salt Solution: 4 mmol of $Na_2B_{12}H_{12}$ in 2 mL of water and 6 mL of CH_3OH.
- 1 Iodine Solution(I_2 + CH_3OH) : 1 Sodium Salt Solution ($Na_2B_{12}H_{12}$ + CH_3OH + H_20)
- $Na_2B_{12}H_{12} + I_2 \longrightarrow Na_2B_{12}H_{12-x}I_x + HI$
- Add gradually, let evaporate/heat in oven to form solid and give off HI.



Stock Solutions

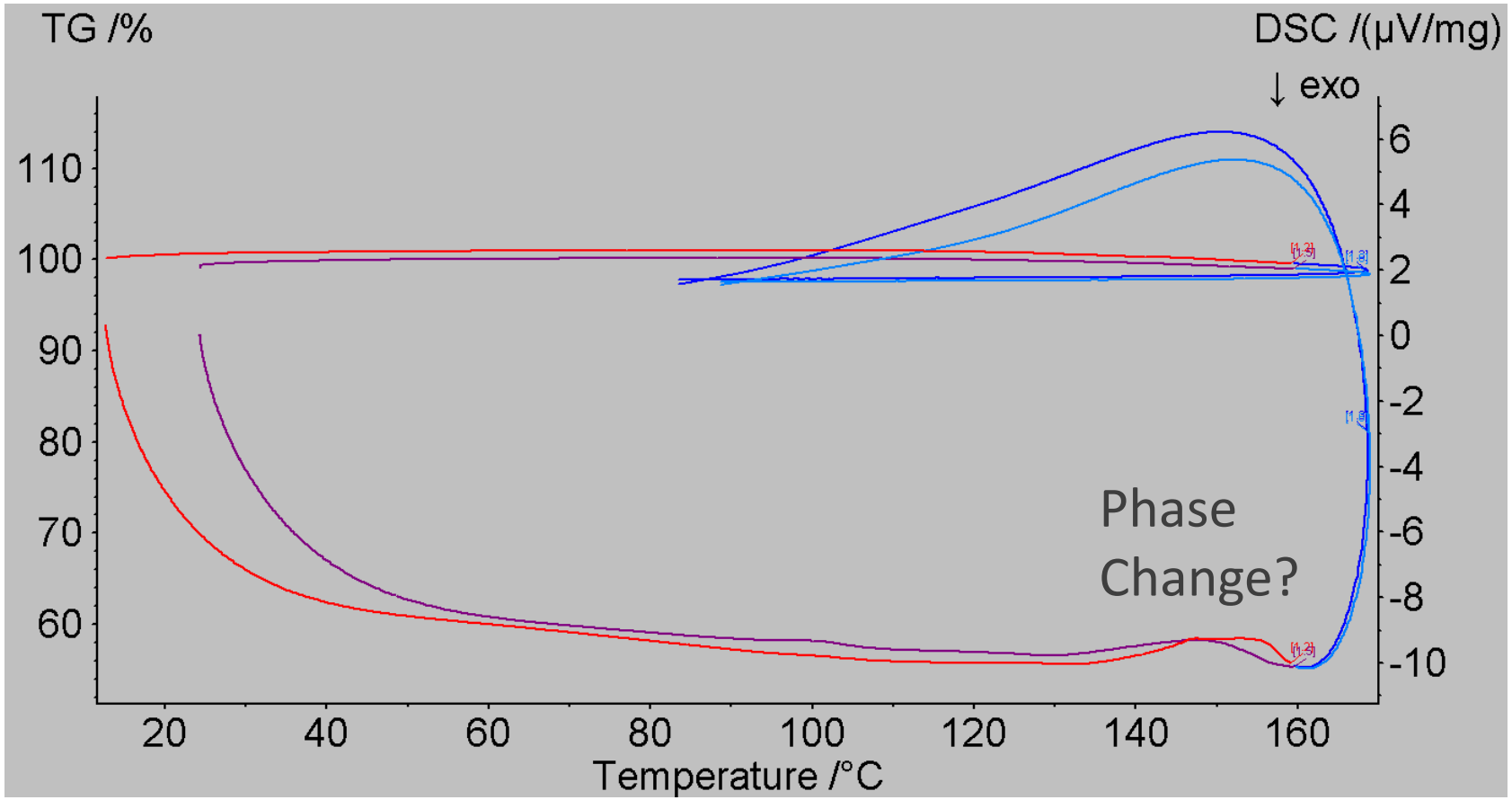
$Na_2B_{12}H_{12-x}I_x$



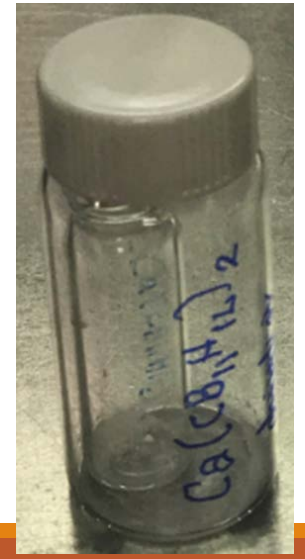
- -200 °C – 600 °C: no peak
- Need to check structure

Expected to see peak at 84 °C

$Ca(CB_{11}H_{12})_2$



- Phase Change at 150 °C is closer to the temperature we want
- Not the clearest peak

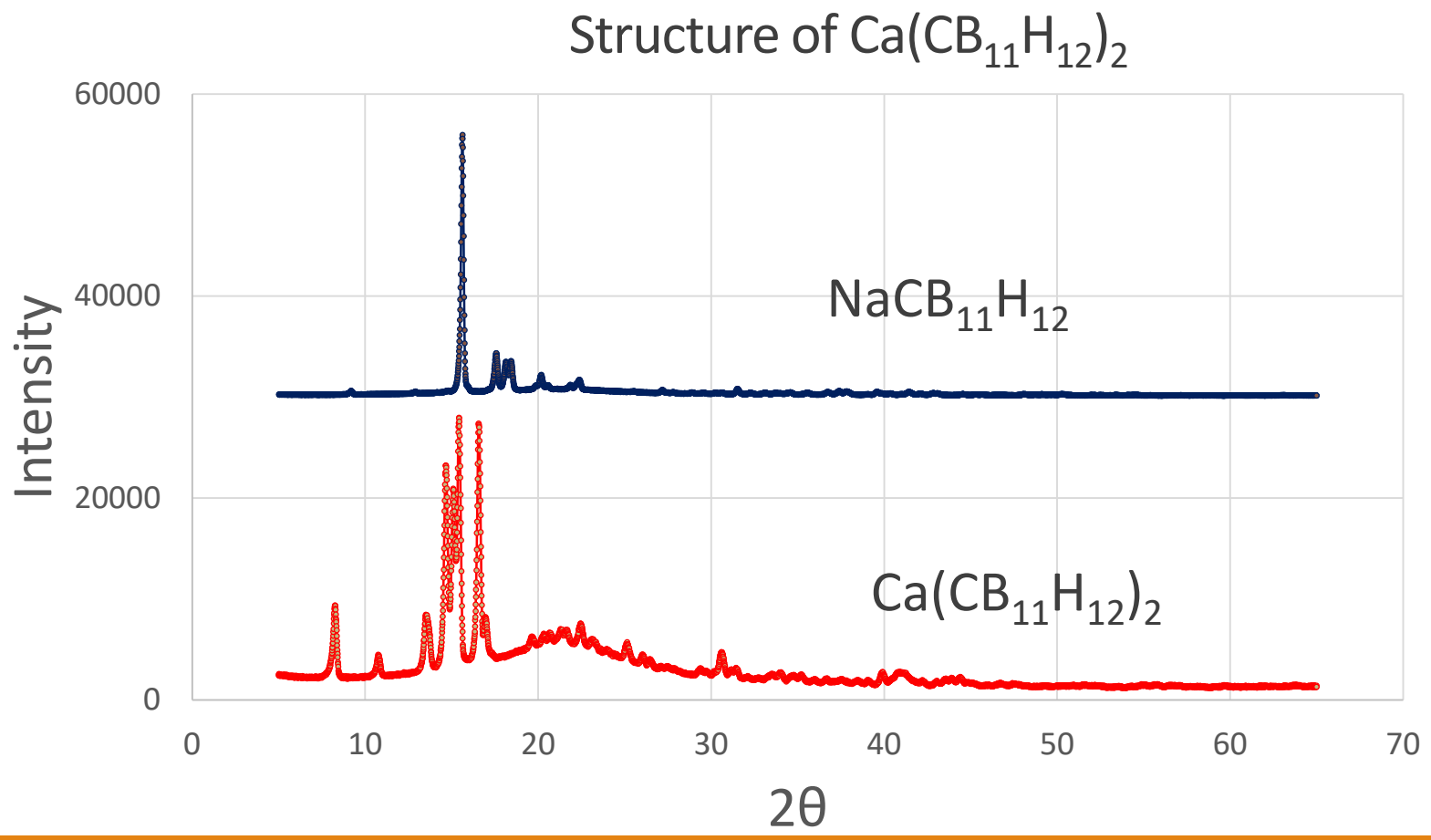


$Ca(CB_{11}H_{12})_2$ Sample

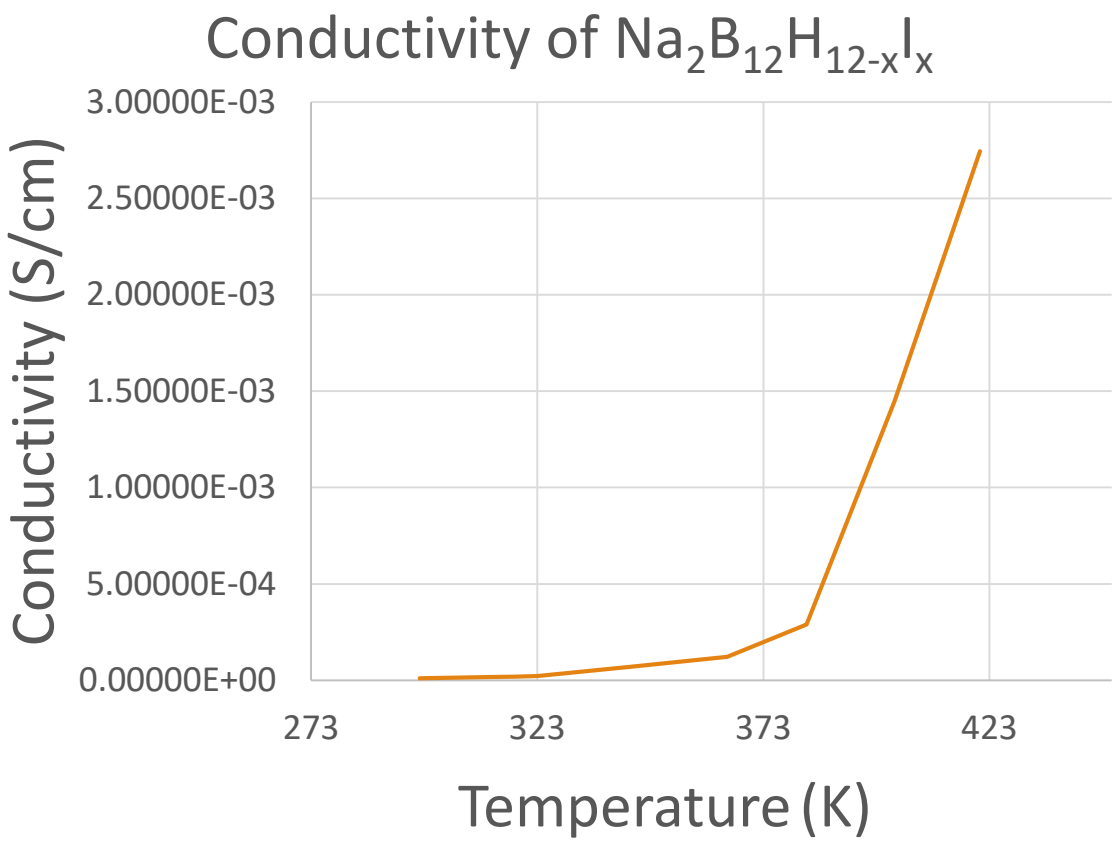
X-ray Powder Diffraction

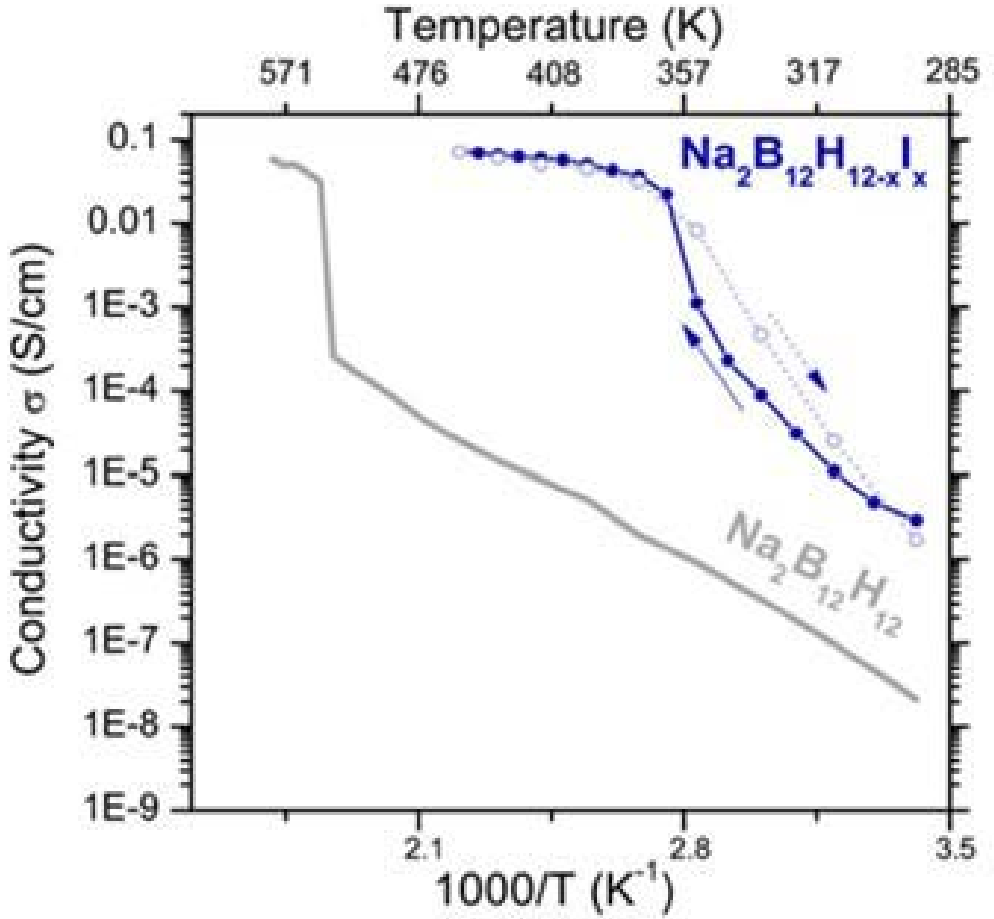
Structure of $Na_2B_{12}H_{12-x}I_x$

- Amorphous
- Supposed to have an Hexagonal Closed Pack Crystal Structure



Electrochemical Impedance Spectroscopy





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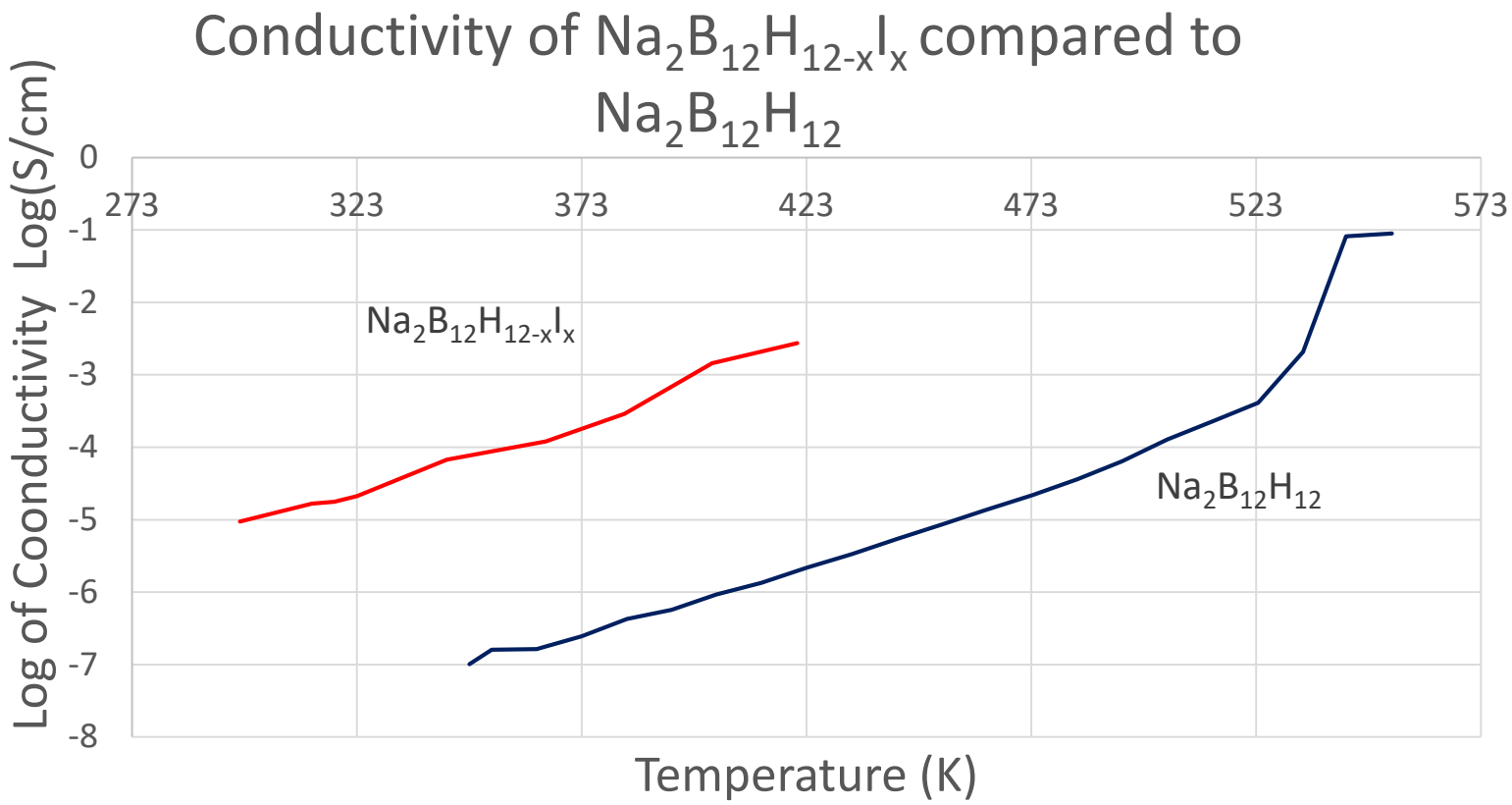
Inorganic Chemistry, **2017,** *56* (9), 5006-5016.

Conductivity Results



Conclusion

- Can optimize conductivity of $Na_2B_{12}H_{12-x}I_x$
- Look closer at our structure of $Na_2B_{12}H_{12-x}I_x$ using neutrons
- Test Conductivity of $Ca(CB_{11}H_{12})_2$
- Mix $Ca(CB_{11}H_{12})_2$ with another conducting salt or infiltrate it into nanopourous silica

Acknowledgements

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