Simulations and Analyses of Li4 and Li6 Boracites and Thioboracites as Promising Li Ion Conducting Electrolytes

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WAKE FOREST UNIVERSITY

NSF

WFU DEAC HPC Cluster

Research Motivation: Active Field Interest

Number of Solid-State Battery Publications 2000-2020

Solid-State Battery Publications by Research Area
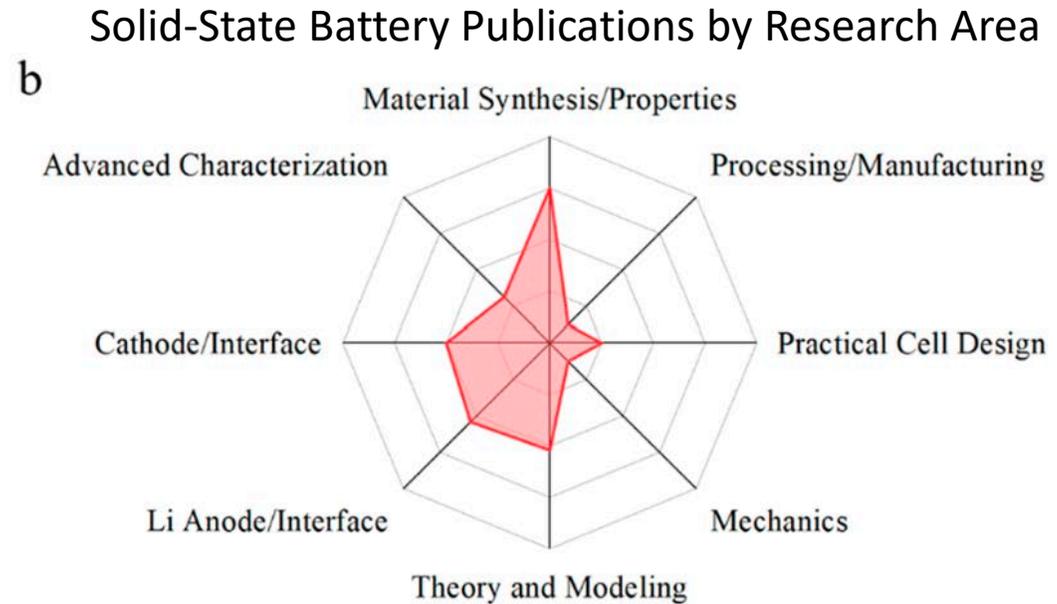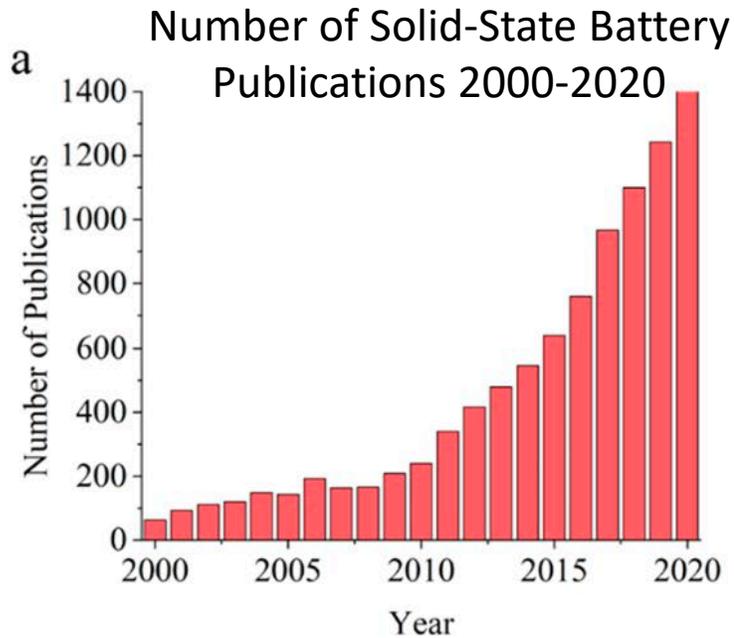
a.) Number of peer-reviewed scientific publications relating to solid-state lithium battery research from 2000-2020
b.) Solid-state lithium battery research breakdown by type
(Image credit: ACS Energy Letters, 2021   DOI: 10.1021/acsenergylett.1c00445)

- Publications in solid-state battery research increased by a factor of ~7 from 2010-2020
- Significant research interest is focused on Material Synthesis/Properties
- This leaves Theory and Modelling as an area in need of more research

Research Motivation: Why Solid-State Batteries?

Li-ion Battery (Liquid Electrolyte)

Solid-State Li-ion Battery Stack (Solid Electrolyte)

a.)

b.)
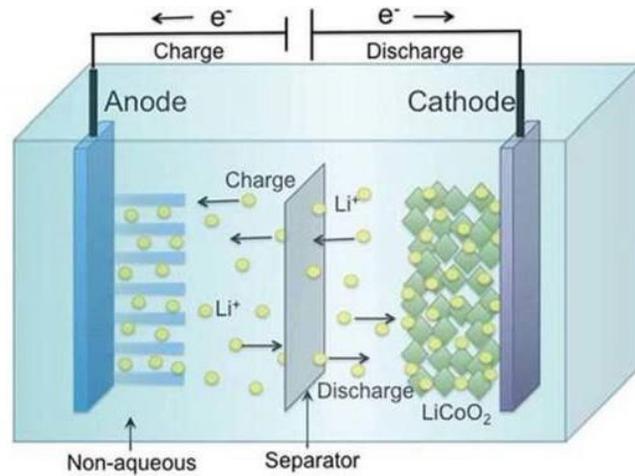
a.) Schematic illustration of the internal components of a typical Li-ion battery.   (Image credit: Journal of The Electrochemical Society, 2017.   DOI: 10.1149/2.1451709jes)
b.) Schematic illustration of an ideal high-energy Solid-State battery stack.   (Image credit: ACS Energy Letters, 2021.   DOI: 10.1021/acsenergylett.1c00445)

- Pure lithium anode can greatly improve performance
- Solid electrolytes have the following potential benefits:
    - Expected to be stable in contact with pure lithium
    - Competitive ionic conductivity with liquid electrolytes and negligible electronic conductivity
    - Improved safety by addressing leakage of toxic liquid electrolytes
    - Improved safety by addressing fire/explosion risk from flammable liquid electrolytes
    - Improved longevity by replacing liquid electrolytes that decompose and reduce functionality

Research Motivation: Previous Boracite Results

$Li_4B_7O_{12}Cl$ Cubic α Phase

$Li_4B_7O_{12}Cl$ Arrhenius Conductivity Plot

a.)

b.)

- Li
- B
- O
- Cl
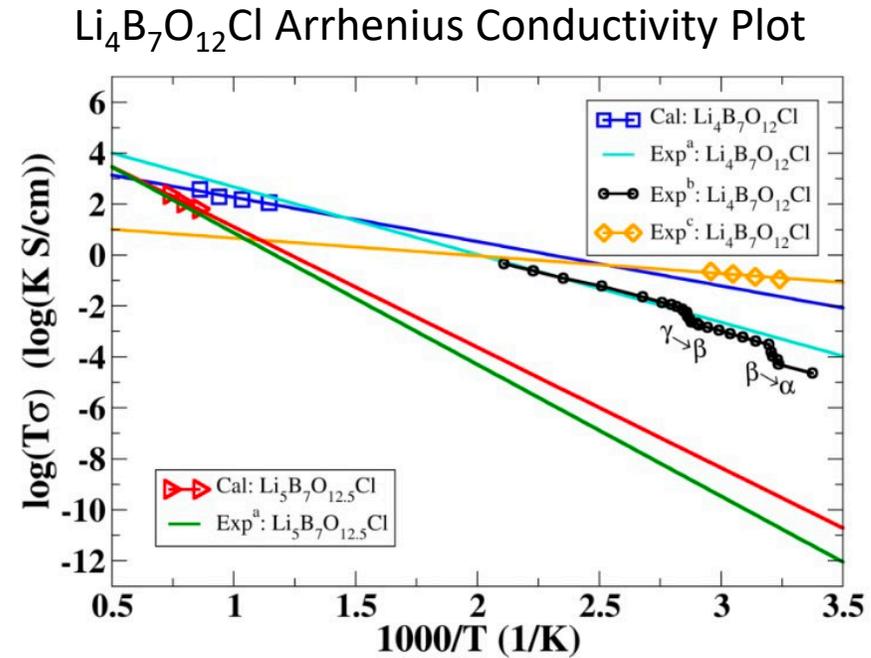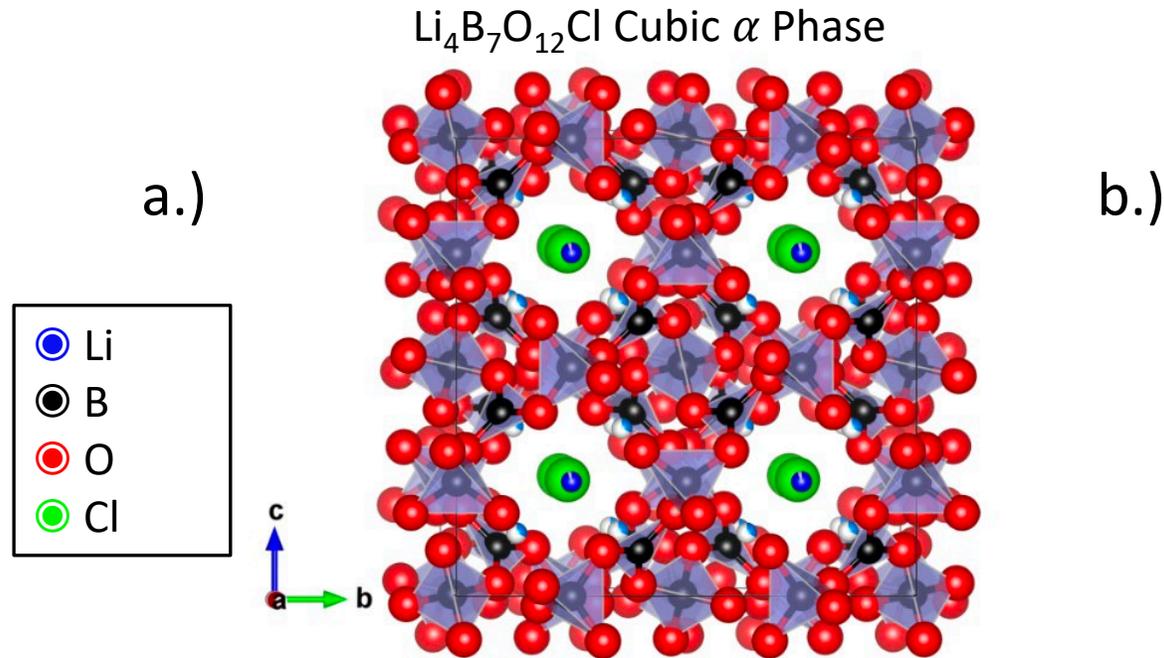
a.) $Li_4B_7O_{12}Cl$ experimental structure and b.) Arrhenius plot of the conductivity vs. temperature
Image credit: Li and Holzwarth, 2022.   DOI: 10.1103/PhysRevMaterials.6.025401

- Face Centered Cubic ($F\bar{4}3c$) α-phase reported at room temperature
- Disordered Lithium sites: 25% fractional occupancy
- Conductivity reported to be on the order of $3 \times 10^{-4}\ S/cm$ at room temperature by Tan et. al. (DOI: 10.1021/acsaem.9b00812)
- Work by Dr. Li and Dr. Holzwarth agree with experimental performance results with new discoveries:
  - G.S. is Face Centered Rhombohedral ($R3c$) distortion of the cubic phase
  - 25% fractional Li sites in $F\bar{4}3c$ map to fully occupied Li sites in R3c, remaining 75% map to interstitial sites
  - Ion migration mechanisms involving concerted ion motion and interstitial sites

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Research Motivation: Partial Al Substitution

$Li_4Al_3B_4O_{12}Cl$ Cubic Phase

$Li_4Al_3B_4O_{12}Cl$ Arrhenius Conductivity Plot

a.)

b.)

Legend:
- Li
- Al
- B
- O
- Cl
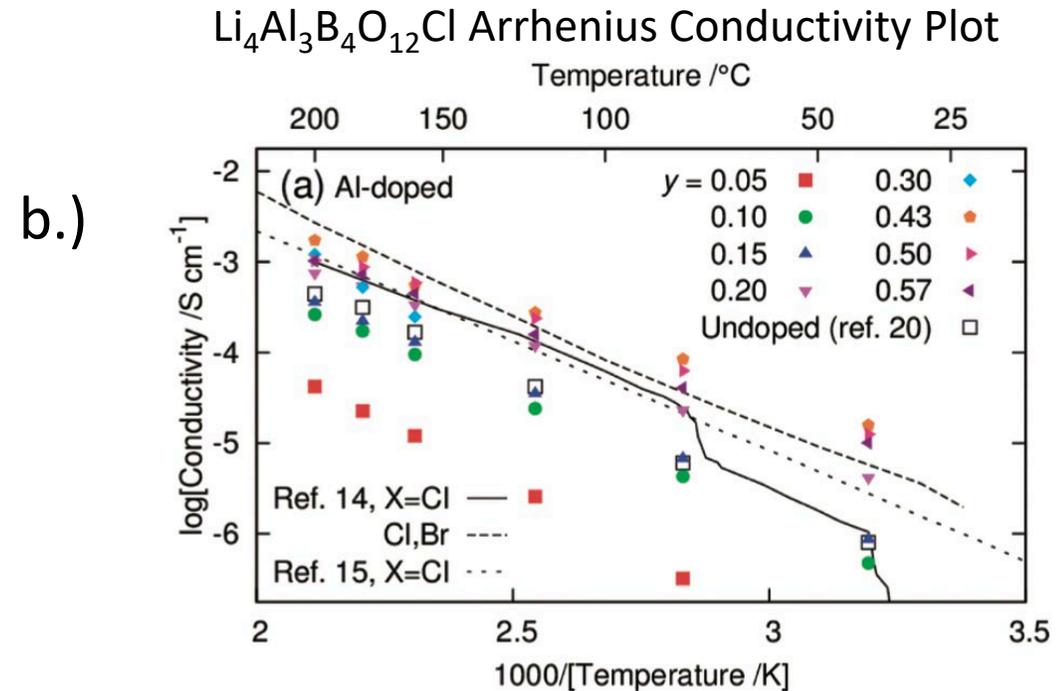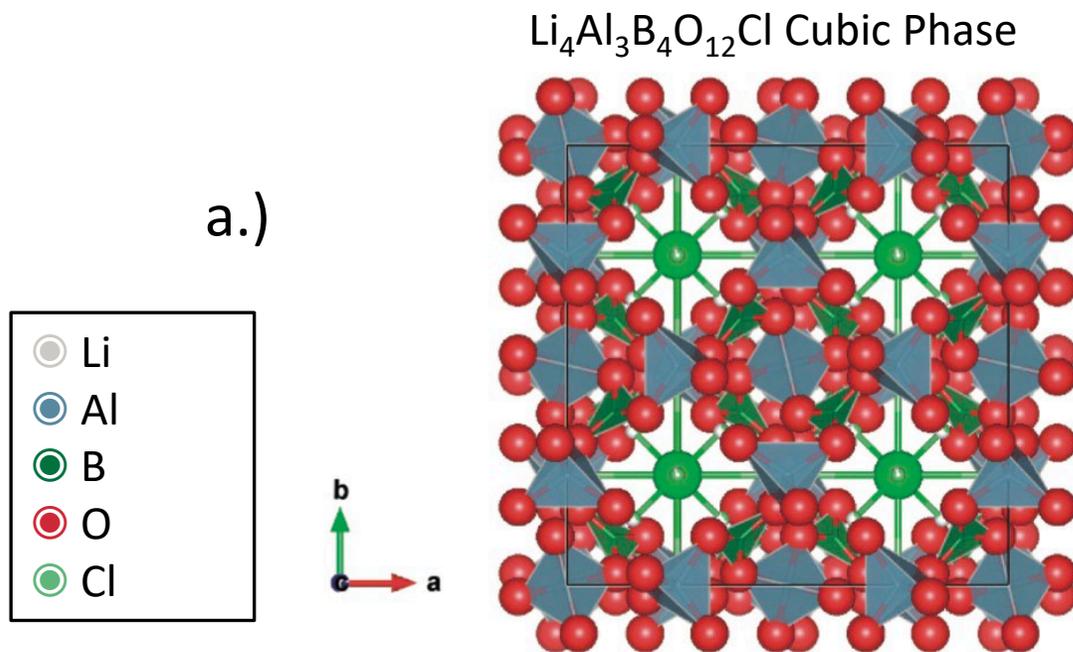
$Li_4Al_3B_4O_{12}Cl$ experimental structure (a) and Arrhenius plot of the conductivity vs. temperature (b)
Image credit: Kajihara et. al., 2017.   DOI: 10.1246/bcsj.20170242

- Experimental investigation of substituting boron sites in Li4B7O12Cl with aluminum
- Found optimal y value of 0.43 : the ratio of Al2O3 to B2O3 in the starting synthesis mixture
- Synthesized Li4Al3B4O12Cl and determined some of its properties:
  - Room temperature structure is similar to the original material: Face Centered Cubic ($F\bar{4}3c$)
  - Has similar performance - conductivity reported to be on the order of $1 \times 10^{-5}\ S/cm$
  - Reported to be stable in contact with pure lithium metal

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Research Motivation: S Substitution & Increased Li

Li$_6$B$_7$S$_{13}$I Cubic Phase

Li$_6$B$_7$S$_{13}$I Arrhenius Conductivity Plot

a.)

b.)

- ◉ Li
- ◉ BS4
- ◉ I
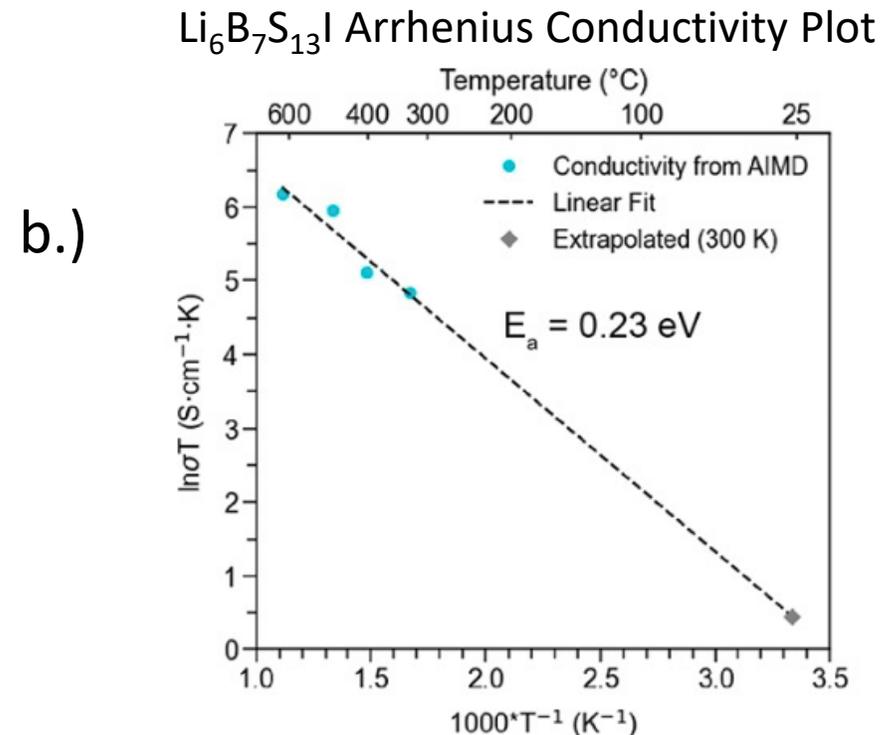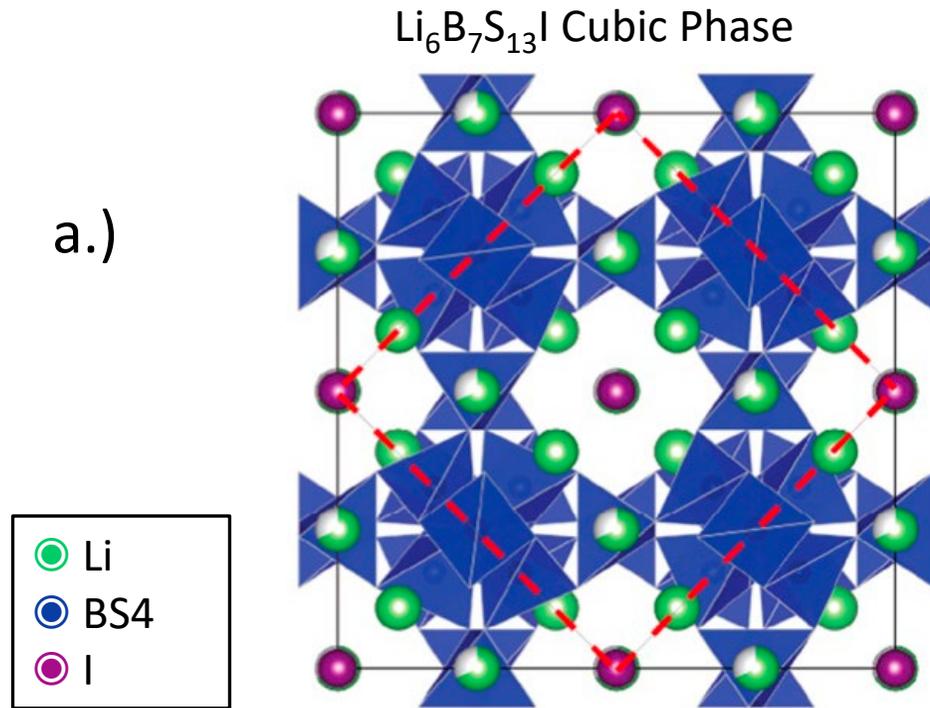
Li$_6$B$_7$S$_{13}$I experimental structure (a) and Arrhenius plot of the conductivity vs. temperature (b)
Image credit: Kaup et. al., 2021.   DOI: 10.1021/jacs.1c00941

- Experimental investigation of similar material with sulfur and higher lithium stoichiometry
- Compound has iodine instead of chlorine as the halogen in the structure
- Similar room temperature Face Centered Cubic ($F\bar{4}3c$) phase found, as well as new tetragonal ($I4_1/a$) phase
- Face Centered Cubic ($F\bar{4}3c$) phase found to be stable, tetragonal ($I4_1/a$) phase reported to be metastable
- Material found to have high conductivity and stability
- Experimental conductivity calculated for cubic phase; found to be on the order of $5 \times 10^{-4}\ S/cm$

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In This Work

- Starting from known boracites and thioboracites:
  - Li4B7O12Cl
  - Li4Al3B4O12Cl
  - Li6B7S13I
- Investigating predicted boracites and thioboracites:
  - Sulfur substitutions of known Li4-O materials:
    - Li4B7S12Cl
    - Li4Al3B4S12Cl
  - Chlorine substitution of known Li6-S material and similar derivatives (O, Al):
    - Li6B7S13Cl
    - Li6B7O13Cl
    - Li6Al3B4S13Cl
    - Li6Al3B4O13Cl

Computational Methods

- Ground State Structural Calculations
  - Density Functional Theory
- Phonon Density of States Calculations
  - Density Functional Perturbation Theory
- Ionic Diffusion and Conductivity
  - Ab Initio Molecular Dynamics
  - Born-Oppenheimer Approximation

QUANTUMESPRESSO

Known Structures: $Li_4B_7O_{12}Cl$ and $Li_4Al_3B_4O_{12}Cl$

$Li_4B_7O_{12}Cl$ Ground State (R3C)

$Li_4Al_3B_4O_{12}Cl$ Ground State (R3C)

a.)

b.)

🔵	Li
⚪	Al
⚫	B
🔴	O
🟢	Cl
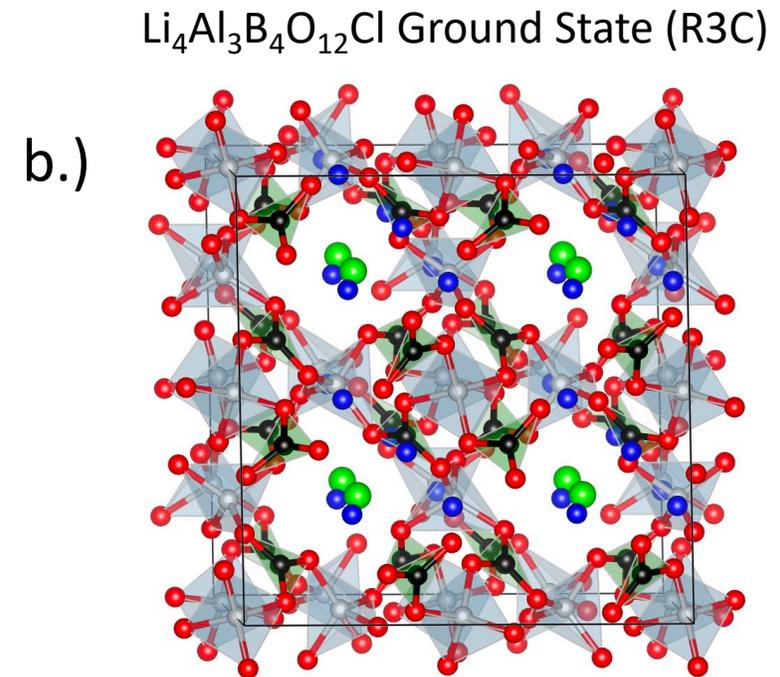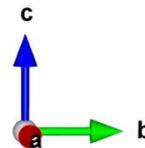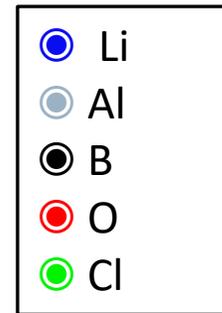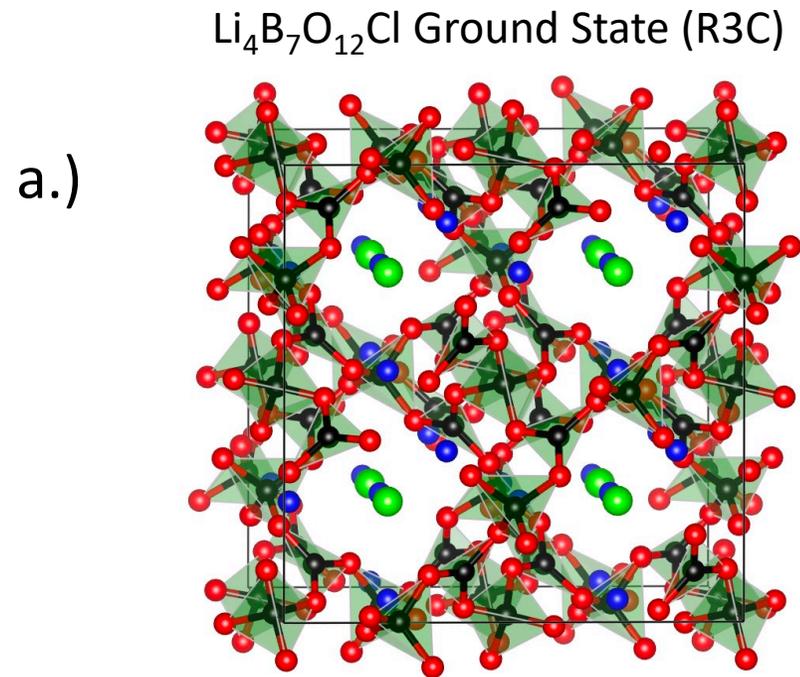
$Li_4B_7O_{12}Cl$ (a) and $Li_4Al_3B_4O_{12}Cl$ (b) rhombohedral R3c ground state structures

$Li_4B_7O_{12}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 12.1 angstroms
- Lattice Angle = 90.1 degrees

$Li_4Al_3B_4O_{12}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 13.0 angstroms
- Lattice Angle = 91.1 degrees

Predicted Structures: $Li_4B_7S_{12}Cl$ and $Li_4Al_3B_4S_{12}Cl$

$Li_4B_7S_{12}Cl$ Ground State (R3C)

$Li_4Al_3B_4S_{12}Cl$ Ground State (R3C)

a.)

b.)

Li
Al
B
S
Cl
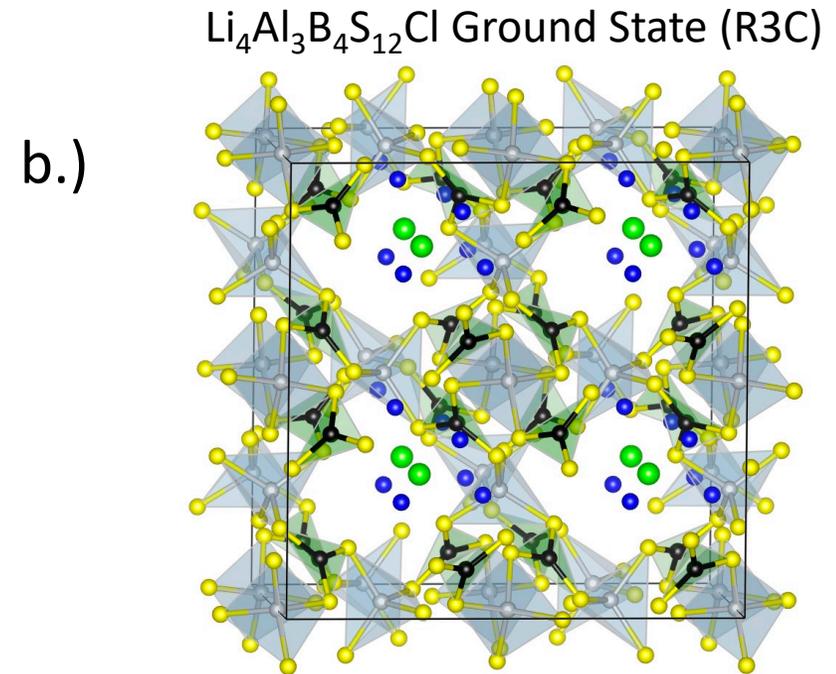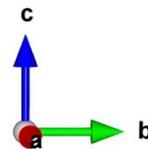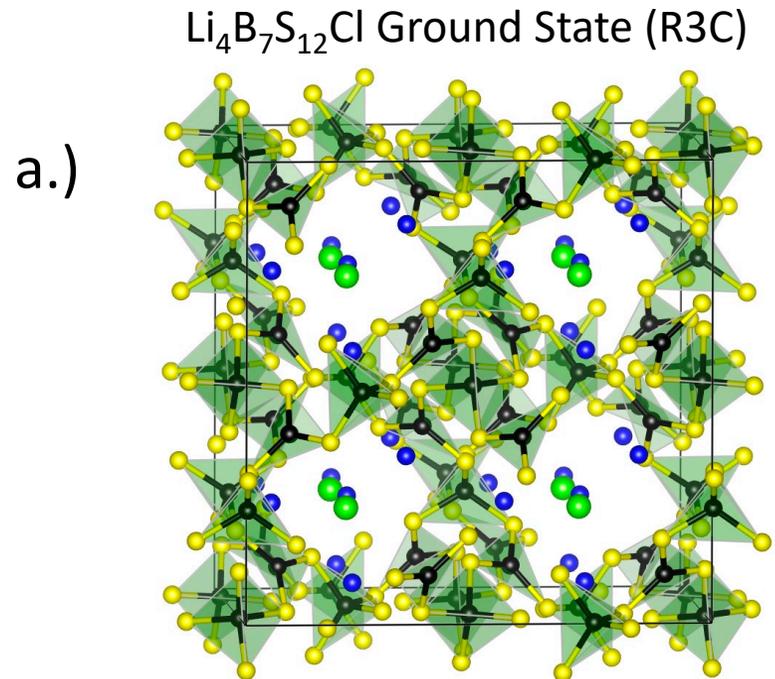
$Li_4B_4S_{12}Cl$ (a) and $Li_4Al_3B_4S_{12}Cl$ (b) rhombohedral R3c ground state structures

$Li_4B_7S_{12}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 14.9 angstroms
- Lattice Angle = 89.8 degrees

$Li_4Al_3B_4S_{12}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 16.1 angstroms
- Lattice Angle = 89.6 degrees

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Predicted Structures: $Li_6B_7O_{13}Cl$ and $Li_6Al_3B_4O_{13}Cl$

$Li_6B_7O_{13}Cl$ Ground State (R3C)

a.)
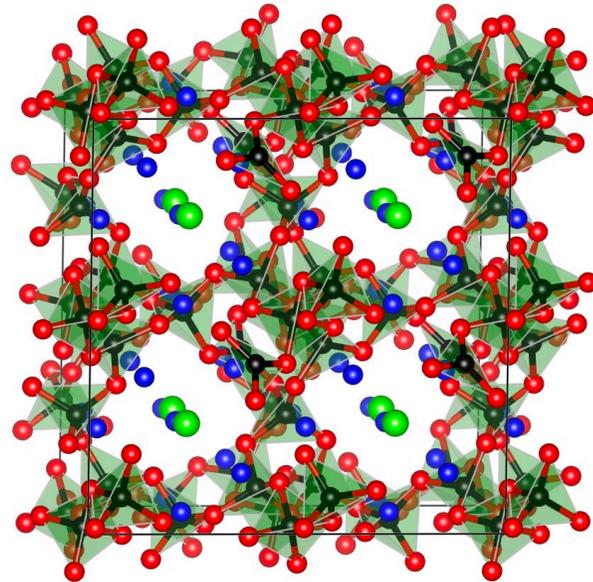
$Li_6Al_3B_4O_{13}Cl$ Ground State (R3C)

b.)

Legend:
- Li (blue)
- Al (grey)
- B (black)
- O (red)
- Cl (green)
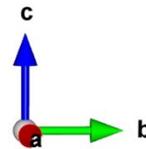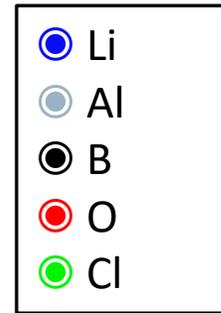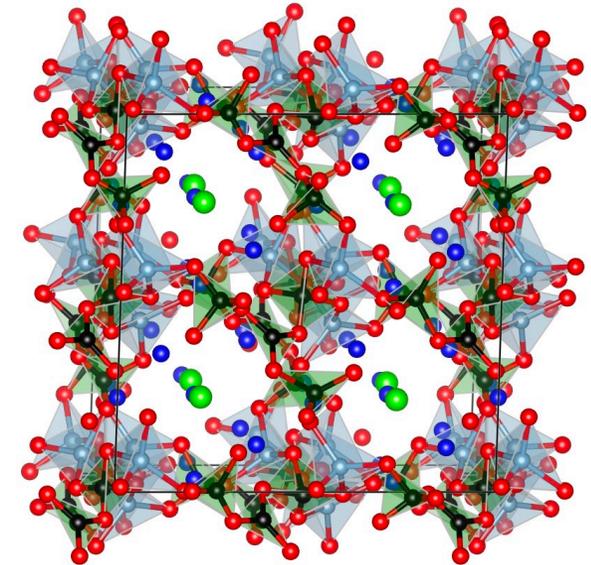
$Li_6B_7O_{13}Cl$ (a) and $Li_6Al_3B_4O_{13}Cl$ (b) rhombohedral R3c ground state structures

$Li_6B_7O_{13}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 12.2 angstroms
- Lattice Angle = 89.4 degrees

$Li_6Al_3B_4O_{13}Cl$ Conventional Cell

- R3c symmetry
- Lattice Constant = 13.0 angstroms
- Lattice Angle = 91.5 degrees

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Predicted Structures: $Li_6B_7S_{13}Cl$ [R3c and Cc]

Li$_6$B$_7$S$_{13}$Cl Rhombohedral Phase
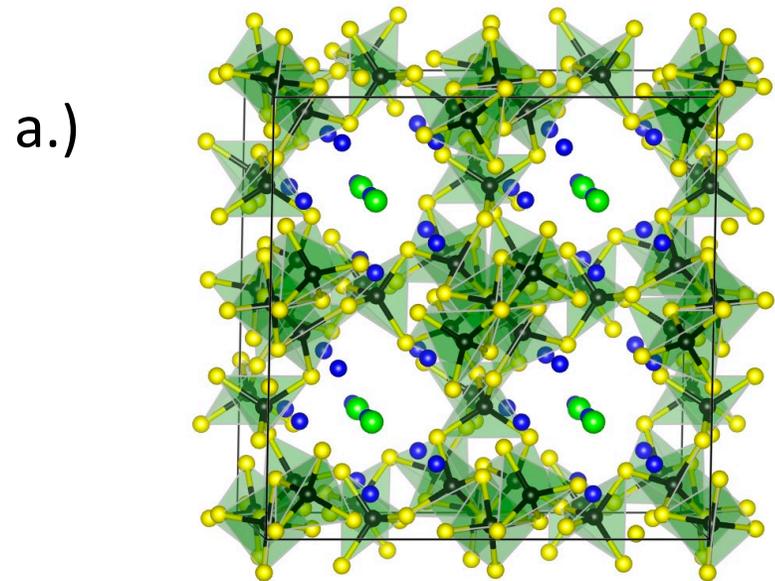
Li$_6$B$_7$S$_{13}$Cl Monoclinic Supercell

a.)

b.)

- Li
- B
- S
- Cl
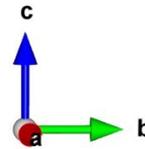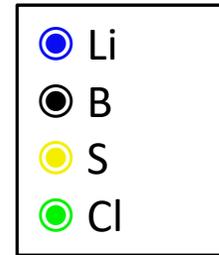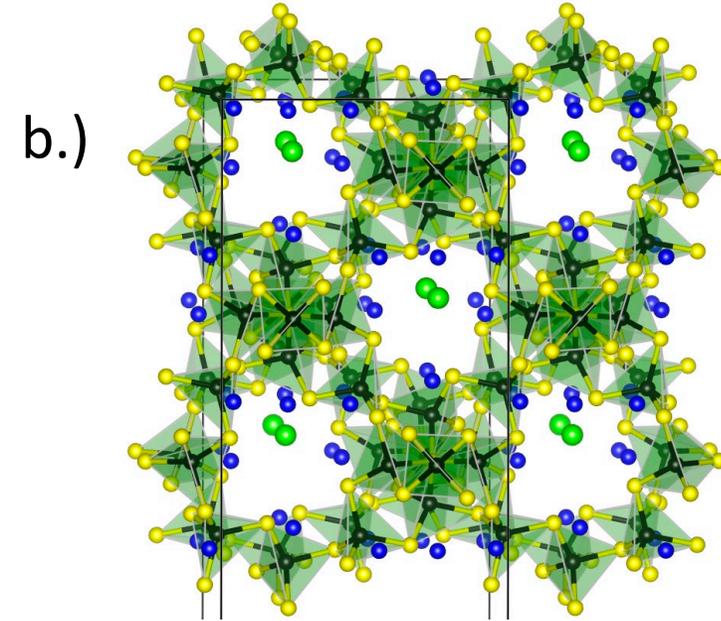
Li$_6$B$_7$S$_{13}$Cl rhombohedral R3c (a) and monoclinic Cc (b) structures

Li$_6$B$_7$S$_{13}$Cl Conventional Cell

Li$_6$B$_7$S$_{13}$Cl Conventional Cell

- R3c symmetry
- Lattice Constant = 15.1 angstroms
- Lattice Angle = 89.2 degrees

- Cc symmetry
- Lattice Constants = (18.5, 10.5, 10.8) angstroms
- Lattice Angles = (90.0, 124.6, 90.0) degrees

Finding the Ground State of the Li6 Materials

Li6O and Li6S Monoclinic (Cc) Structural Energies
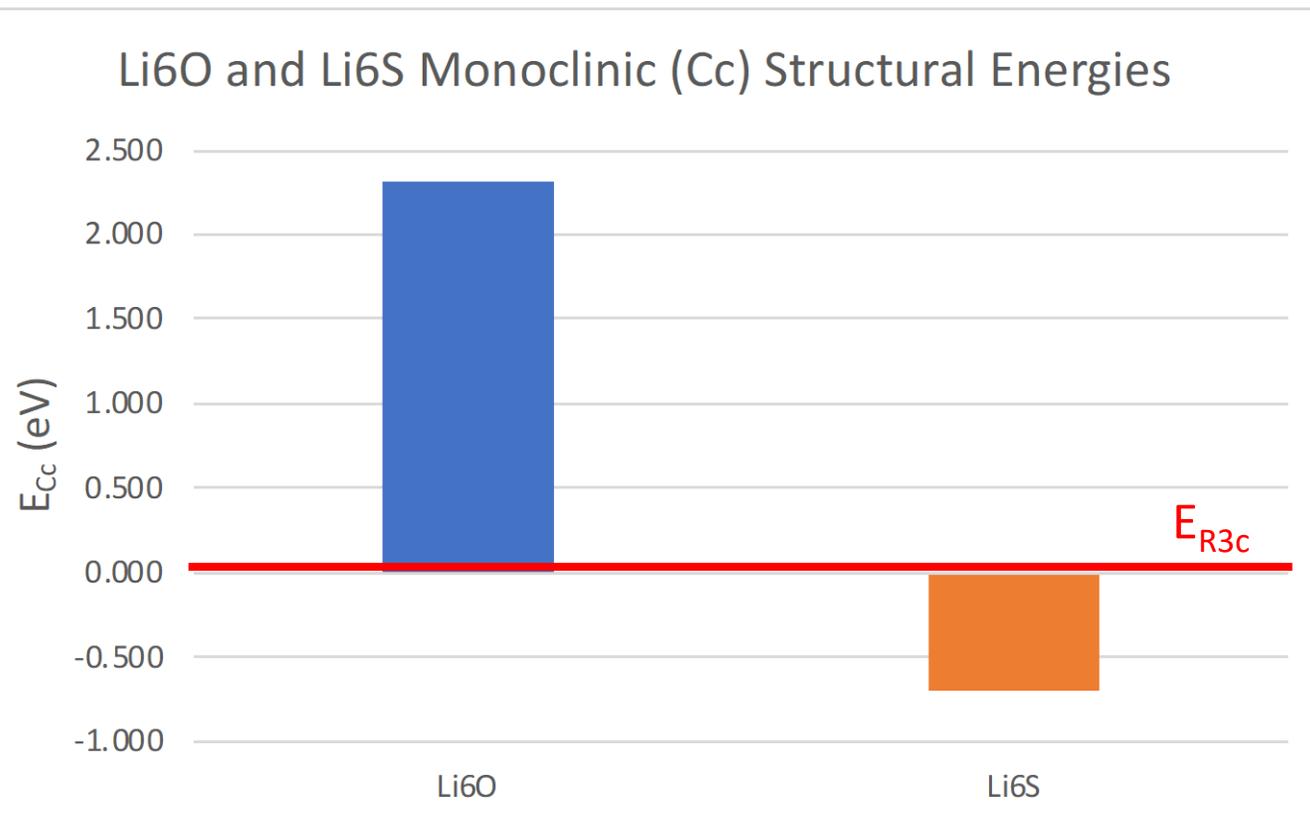
- Zero energy is set to the respective rhombohedral (R3c) structural energy

- For **Li6O**, we see the monoclinic structure is <u>higher</u> in energy by 2.31 eV
- This confirms the ground state structure is R3c as expected

- For **Li6S**, we see that the monoclinic structure is <u>lower</u> in energy by 0.70 eV
- This suggests the R3c structure is NOT the ground state structure

- The monoclinic structure is the current ground state candidate for Li6S

Chemical Stability: Li4 vs Li6

ΔE$_{rxn}$ for Li6 Materials

E/FU (eV) axis from 0.00 to -1.80
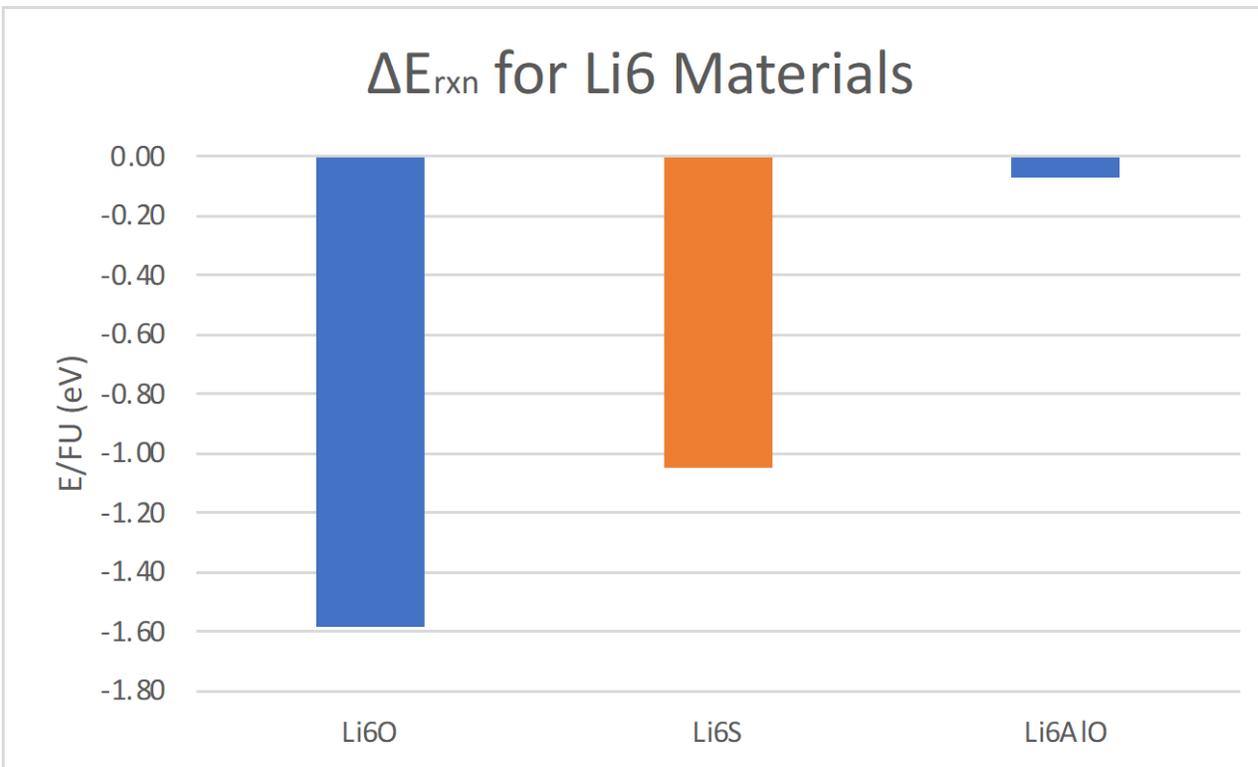
- ΔE$_{rxn}$ Li6O: -1.58 eV / FU
- ΔE$_{rxn}$ Li6S: -1.05 eV / FU
- ΔE$_{rxn}$ Li6AlO: -0.07 eV / FU

- How stable are the Li6 materials compared to the Li4 materials?
- Look at reaction energy difference, ΔE_{rxn}, of decomposition reaction:
- $Li_6B_7X_{13}Cl \rightarrow Li_4B_7X_{12}Cl + Li_2X$
- X = O or S
- If $\Delta E_{rxn} = E_{left} - E_{right} < 0$, then the material is more stable than the decomposition products
- All **Li6 materials** are <u>more energetically favorable</u> than Li4

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Chemical Stability: Al vs Pure Boron

ΔE$_{rxn}$ for Al Substituted Materials
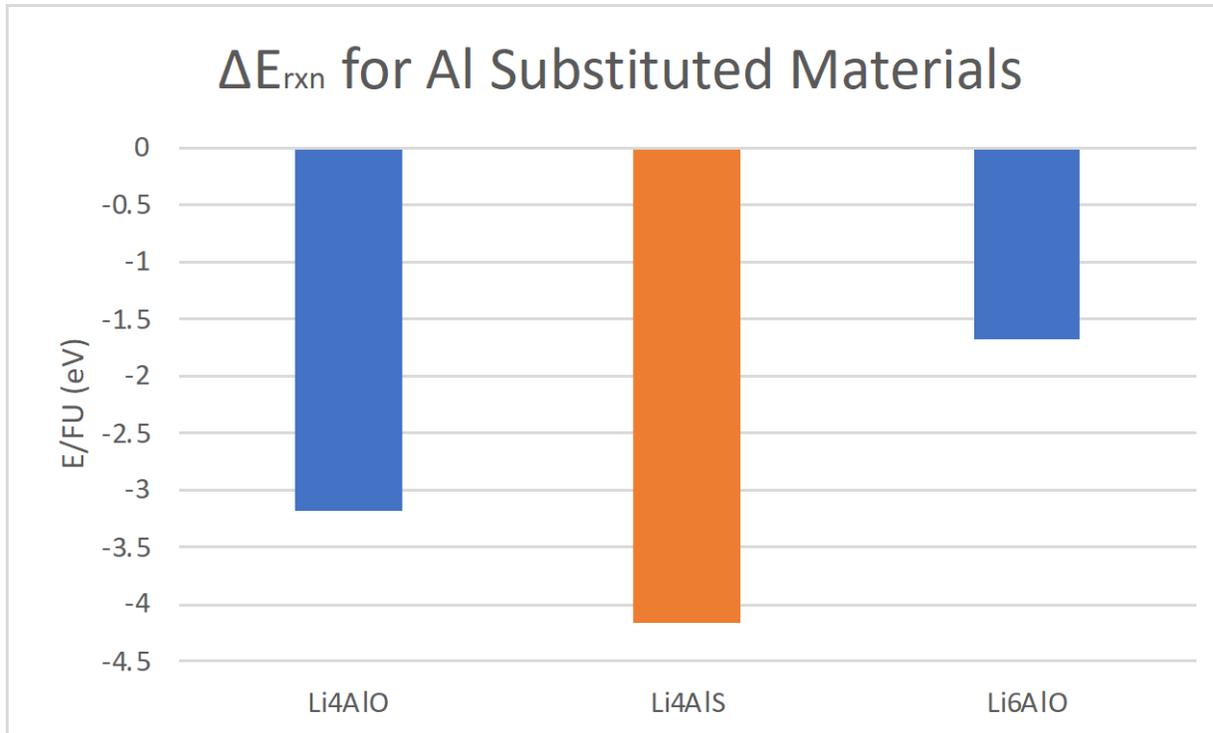
- ΔE$_{rxn}$ Li4AlO: -3.18 eV / FU
- ΔE$_{rxn}$ Li4AlS: -4.17 eV / FU
- ΔE$_{rxn}$ Li6AlO: -1.67 eV / FU

- How stable are Al substituted materials compared to pure boron materials?
- Look at reaction energy difference, ΔE_{rxn}, of decomposition reaction:
- $Li_n Al_3 B_4 X_m Cl + 3B \rightarrow$
  $\qquad\qquad Li_n B_7 X_m Cl + 3Al$
- X = O or S, n = 4 or 6, m = 12 or 13
- If $\Delta E_{rxn} = E_{left} - E_{right} < 0$, then the material is more stable than the decomposition products
- All **Al materials** are <u>more energetically favorable</u> than their pure boracites

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Dynamic Stability: Phonon Density of States

Phonon D.o.S. for Oxygen Materials
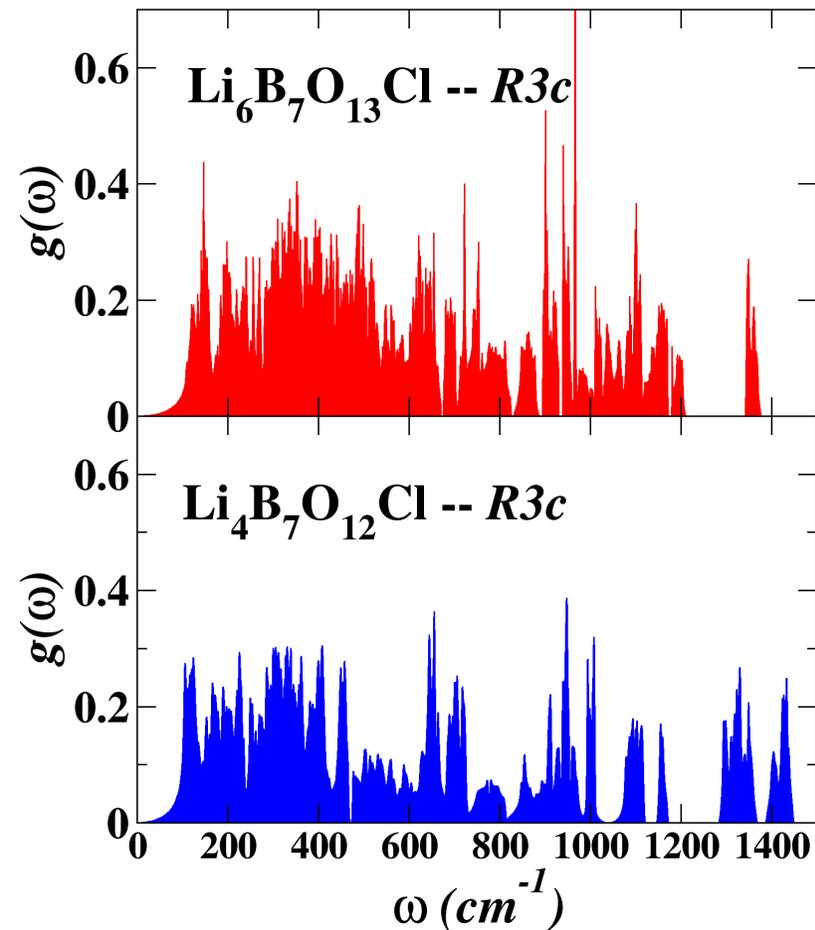
Phonon D.o.S. for Sulfur Materials

$Li_6B_7O_{13}Cl$ -- $R3c$

$Li_4B_7O_{12}Cl$ -- $R3c$

$Li_6B_7S_{13}Cl$ -- Cc

$Li_4B_7S_{12}Cl$ -- $R3c$

$\omega\ (cm^{-1})$
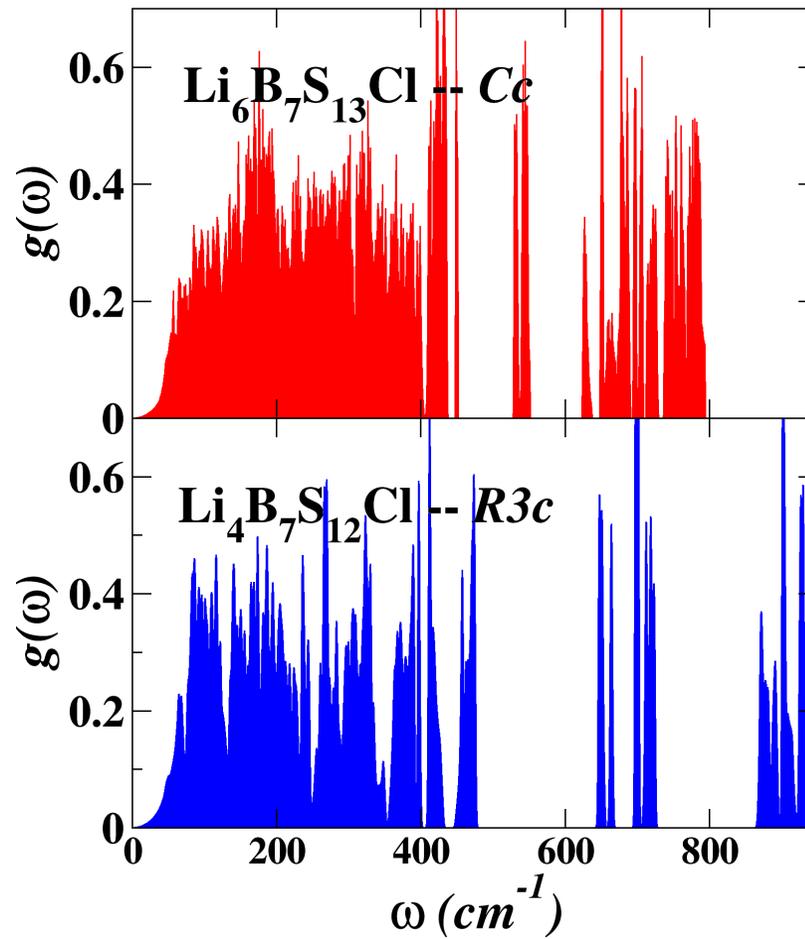
- Li6S R3c (not shown) has imaginary modes $\Rightarrow$ R3c not dynamically stable

- Li6S Cc is dynamically stable

- Li4O, Li4S, and Li6O R3c are dynamically stable

- Low frequencies < 400 cm^{-1} involve Li vibration

- Higher frequencies involve the boracite framework

- Highest frequencies are the triangular BO$_3$ modes

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Dynamic Stability: Framework Geometry

Li$_4$B$_7$S$_{12}$Cl Primitive Cell (R3c)

⊙ BS3 triangles
◉ BS4 tetrahedra
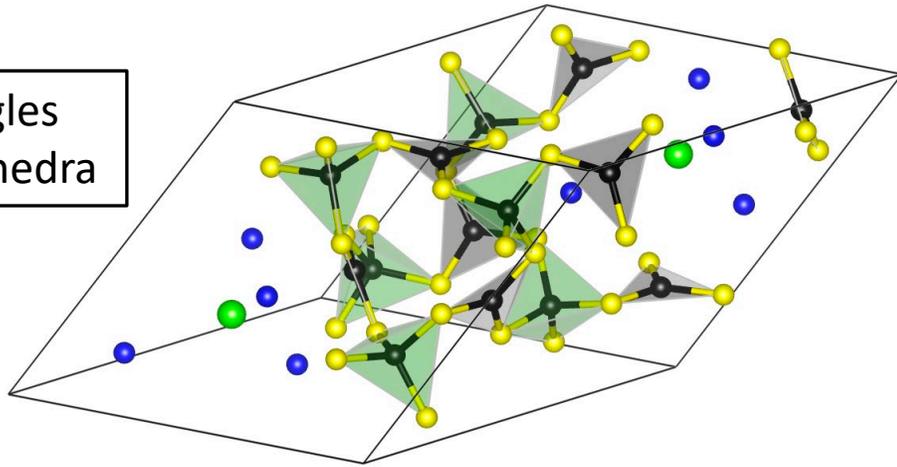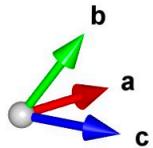
Li$_6$B$_7$S$_{13}$Cl Primitive Cell (Cc)
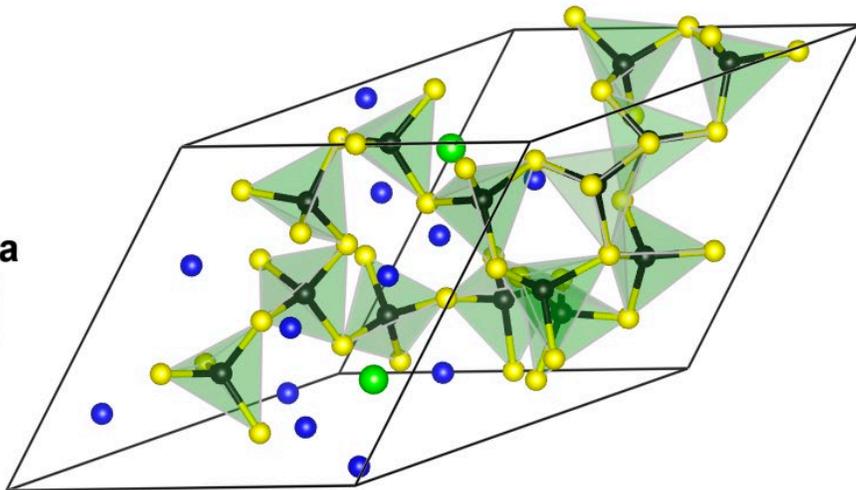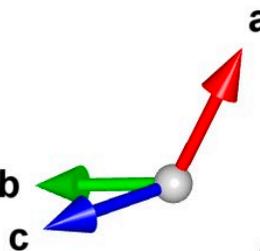
- Framework consists of BO3/BS3 planar triangles and BO4/BS4 tetrahedra

- Primitive Cell Analysis:

  All Li4 Structures:
  - 8 triangles (All B) and 6 tetrahedra (B or Al)

  All Li6O Structures:
  - 2 triangles (All B) and 12 tetrahedra (B or Al)

  Li6S Structures:
  - 14 tetrahedra, no triangles

- Structures with fewer BO3/BS3 triangles in the framework are more stable

Qualitative Performance: Sulfur vs. Oxygen

$Li_4Al_3B_4O_{12}Cl$ Li-ion Superposition
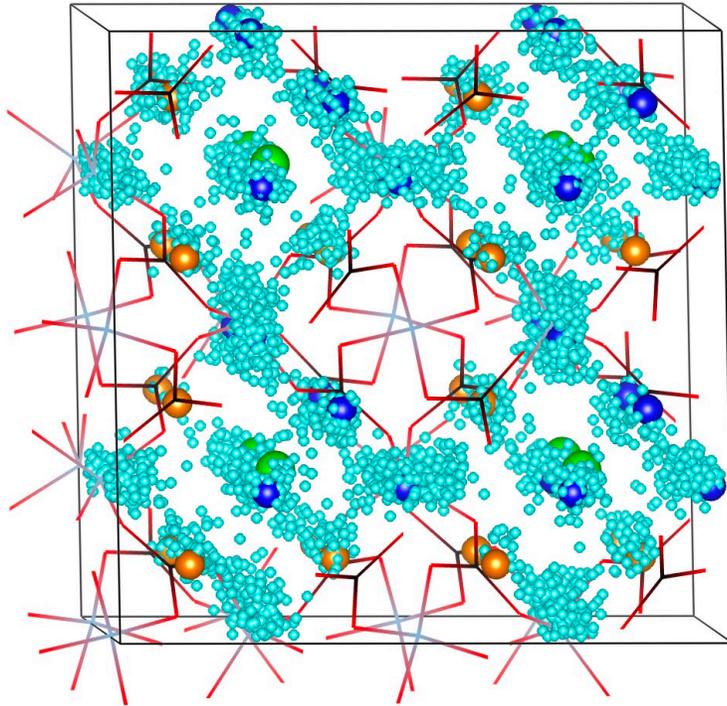
$Li_4Al_3B_4S_{12}Cl$ Li-ion Superposition
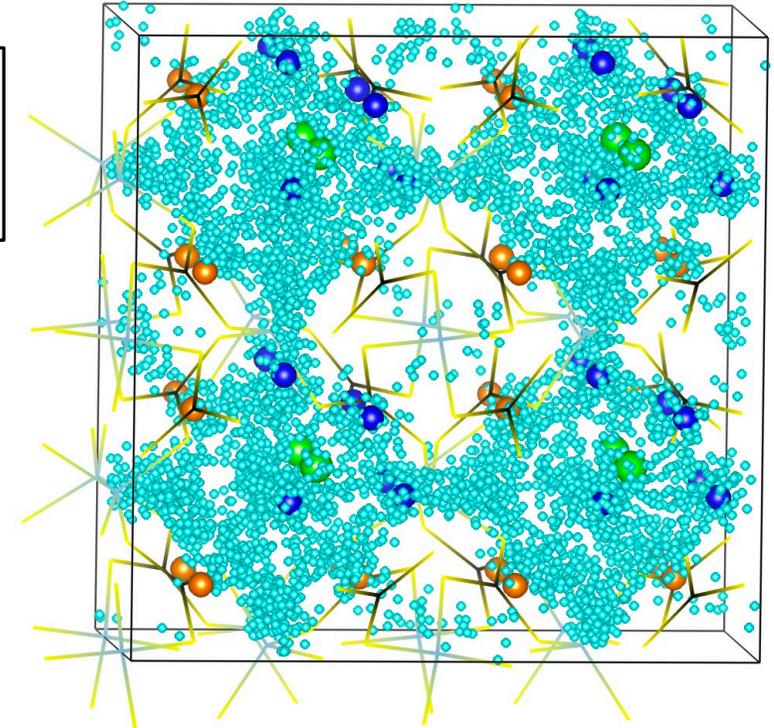
- ⦿ Occupied Li Site
- ⦿ Empty Li Interstitial Site
- ⦿ Superimposed Li Positions
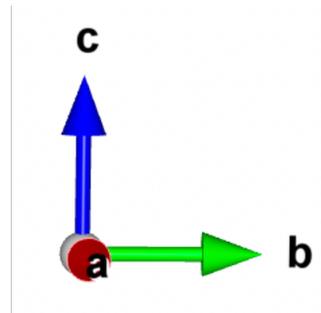
- $Li_4Al_3B_4O_{12}Cl$ (left) vs. $Li_4Al_3B_4S_{12}Cl$ (right) ion superposition diagrams
- Li positions superimposed over ~23 ps of simulation time
- Sampled every 50 timesteps at 1100K simulation temperature
- Much greater diffusion suggests sulfur significantly improves performance compared to oxygen

Qualitative Performance: Al Substitution vs. Pure B

$Li_4B_7S_{12}Cl$ Li-ion Superposition
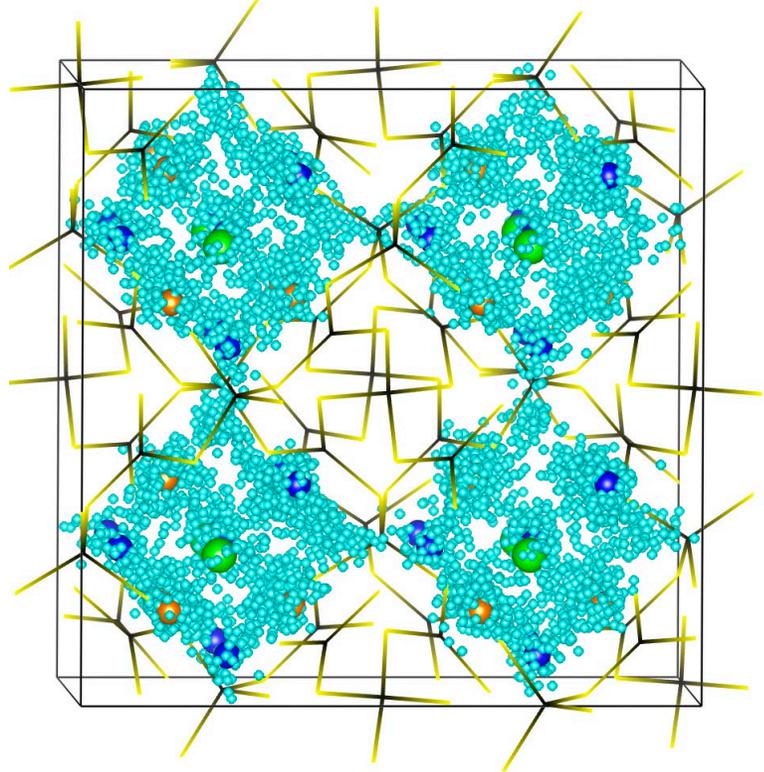
$Li_4Al_3B_4S_{12}Cl$ Li-ion Superposition
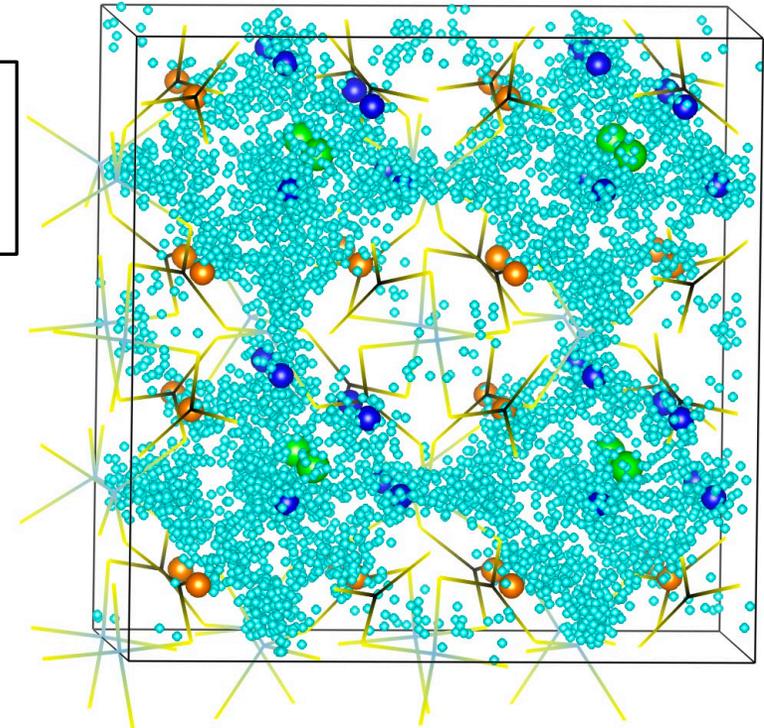
- ◉ Occupied Li Site
- ◉ Empty Li Interstitial Site
- ◉ Superimposed Li Positions
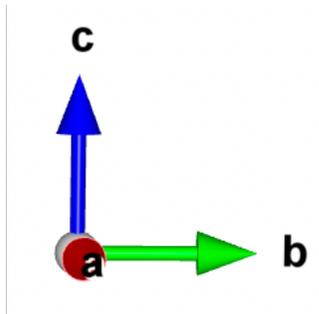
- $Li_4B_7S_{12}Cl$ (left) vs. $Li_4Al_3B_4S_{12}Cl$ (right) ion superposition diagrams
- Li positions superimposed over ~23 ps of simulation time
- Sampled every 50 timesteps at 1100K simulation temperature
- Greater diffusion may suggest Aluminum substitution improves performance compared to pure boron as well

Preliminary Summary

- Determined the ground state structures for predicted materials
  - All Li4 materials, Li6B7O13Cl, and Li6Al3B4O13Cl have rhombohedral (R3c) ground states
  - Li6B7S13Cl has a newly discovered monoclinic (Cc) ground state structure
- Determined relative chemical stability between substitutions
  - Li6 is energetically favorable compared to Li4
  - Partial aluminum substitution is energetically favorable compared to pure boron
- Determined dynamic stability of predicted materials
  - All pure boron Li4 and Li6 materials are dynamically stable
  - R3c phase of Li6B7S13Cl is not dynamically stable; ground state Cc is dynamically stable
- Determined qualitative measure of performance
  - Sulfur substitutions greatly improve diffusion and by extension, performance
  - Aluminum partial substitutions may also offer performance improvements

Future Investigation

- Find $Li_6Al_3B_4S_{13}Cl$ ground state
- Finish stability analysis on predicted materials
- Determine conductivities quantitatively with AIMD
- Investigate ion diffusion and ion migration mechanisms
- Investigate interface with Li metal