Simulations and Analyses of Li_4 and Li_6 (Thio)Boracites As Promising Li Ion Conducting Electrolytes for All-Solid-State Batteries

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Acknowledgements:

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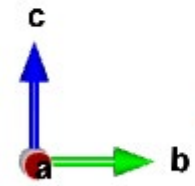
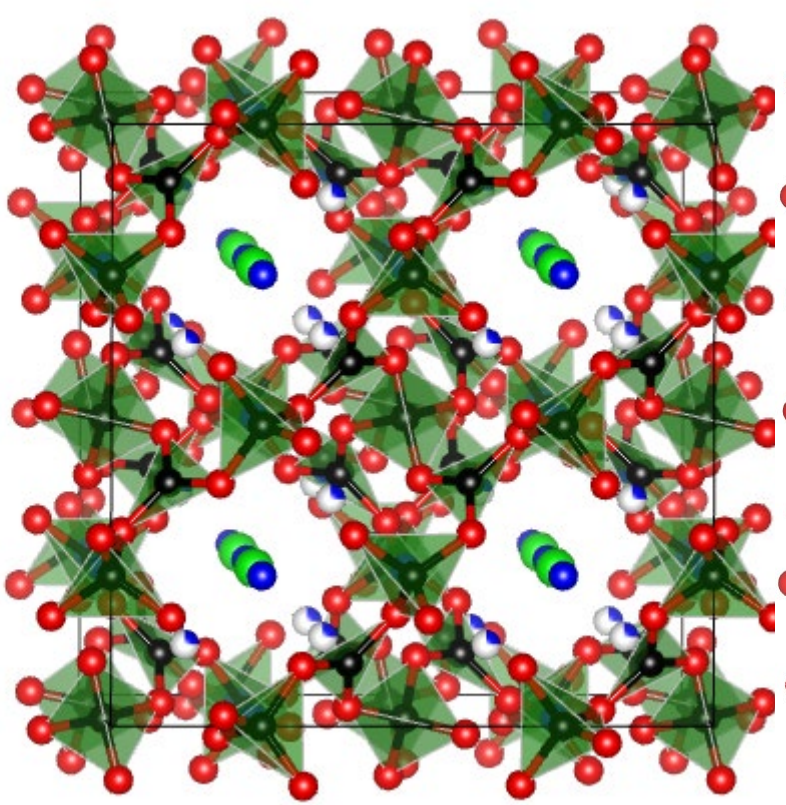
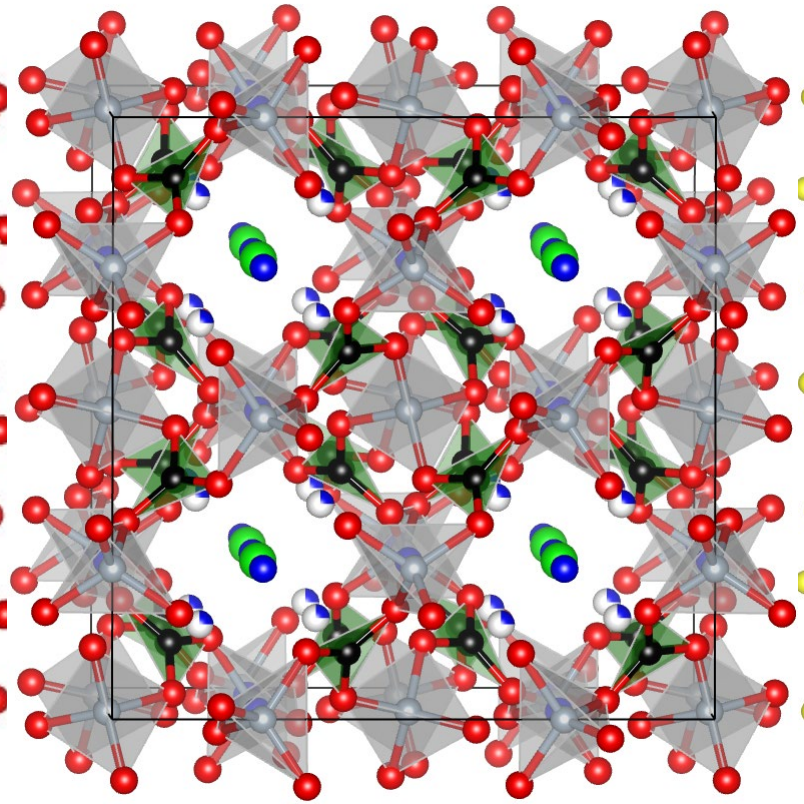
Discussions with Professor P. Canepa, Y. Li's postdoctoral mentor at NUS, are also gratefully acknowledged.

Introducing the (thio)boracite family known from experiment: SG F-43c (No. 219)

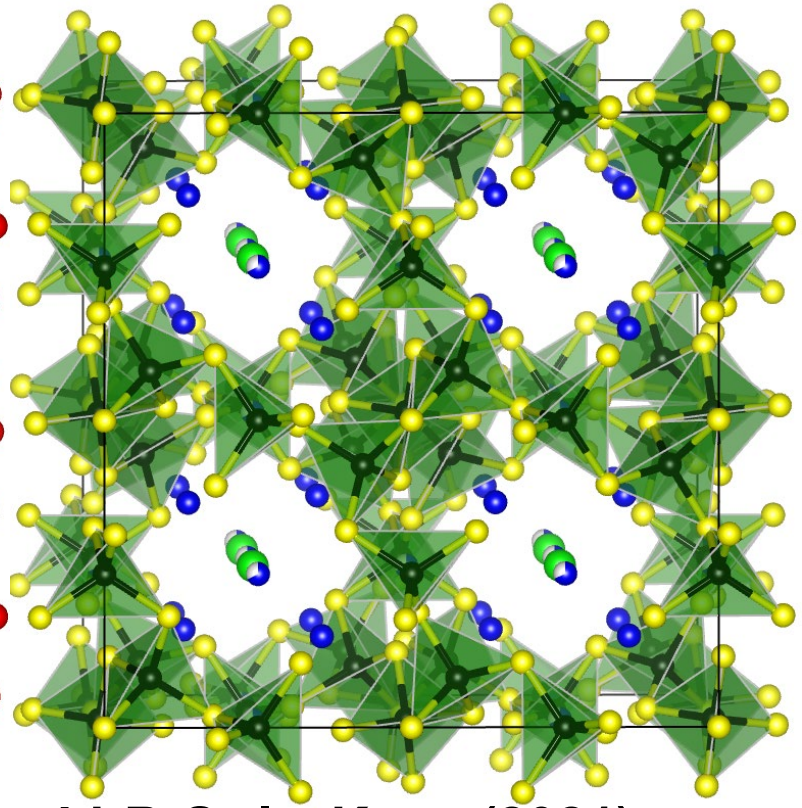




$Li_4B_7O_{12}Cl$ – Jeitschko (1977)
DOI: 10.1107/S0567740877009443

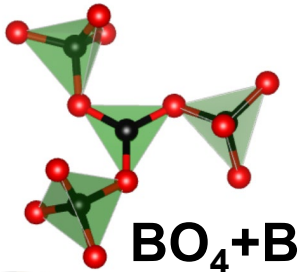


$Li_4Al_3B_4O_{12}Cl$ – Kajihara (2017)
DOI: 10.1246/bcsj.20170242

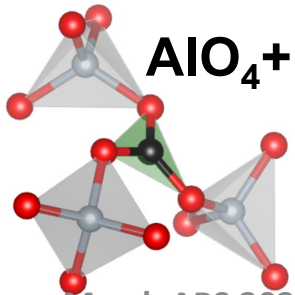


$Li_6B_7S_{13}I$ – Kaup (2021)
DOI: 10.1021/jacs.1c00941

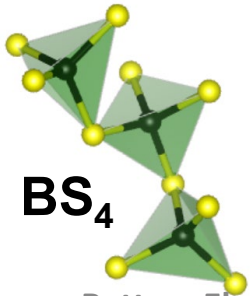
Framework components:



BO_4+BO_3



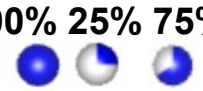
AlO_4+BO_3



BS_4

Ions:

Cl or I



Li

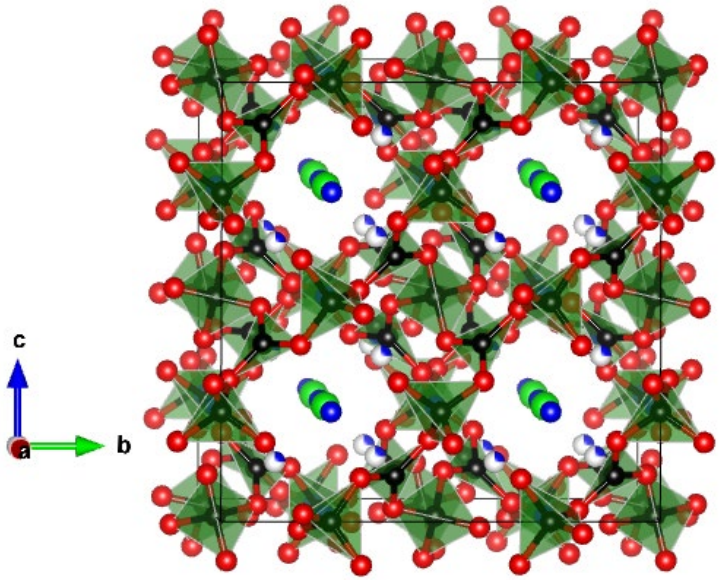
Experimental knowledge:

Experimentally analyzed (thio)boracites, characterized by F-43c symmetry with fractional occupancy on the Li sites, provide natural vacancy sites within void regions of the material, allowing for good Li ion mobility.

Previous computational results:

Y. Li (2022) DOI: 10.1103/PhysRevMaterials.6.025401

Using density functional optimization, an ordered phase of $Li_4B_7O_{12}Cl$ was found to have SG R3c (No. 161) symmetry (a subgroup of F-43c), with a very small rhombohedral distortion.

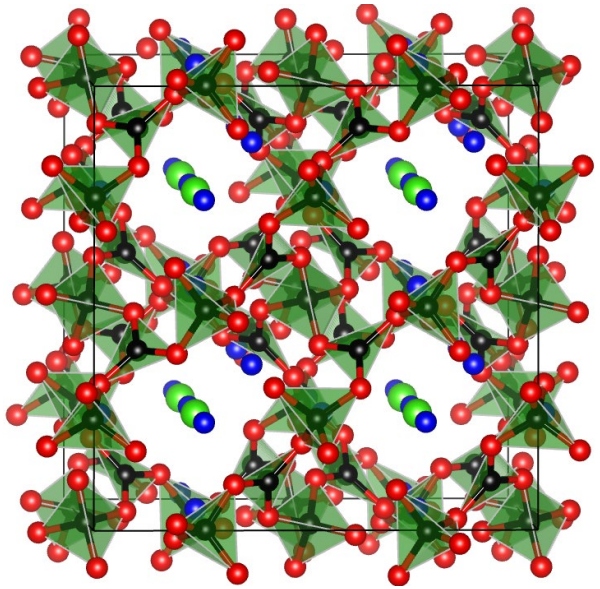


Exp

***a*=12.141 Å**

α=90.0 deg

$Li_4B_7O_{12}Cl$ – Jeitschko (1977)
Disordered F-43c structure



Comp

***a*=12.1 Å**

α=90.1 deg

$Li_4B_7O_{12}Cl$ – Y. Li (2022)
Ordered R3c structure

This work:

Computational investigation of the ordered structures and energetics of an extended family of Li (thio)boracites.

Compounds:

$Li_4B_7O_{12}Cl$	$Li_4B_7S_{12}Cl$
$Li_4Al_3B_4O_{12}Cl$	$Li_4Al_3B_4S_{12}Cl$
$Li_6B_7O_{13}Cl$	$Li_6B_7S_{13}Cl$
$Li_6Al_3B_4O_{13}Cl$	$Li_6Al_3B_4S_{13}Cl$

Ordered structures

R3c

F-43c

Cc

Questions concerning the Li (thio)boracite family of materials:

- What are the most stable ordered structures?
- What are their dynamical and chemical stabilities?
- Explorations of Li ion mobility properties.

Computational methods

- **Density functional theory using the PBESOL exchange-correlation functional Perdew (2008)** DOI: 10.1103/PhysRevLett.100.136406

https://www.quantum-espresso.org/

https://www.abinit.org/

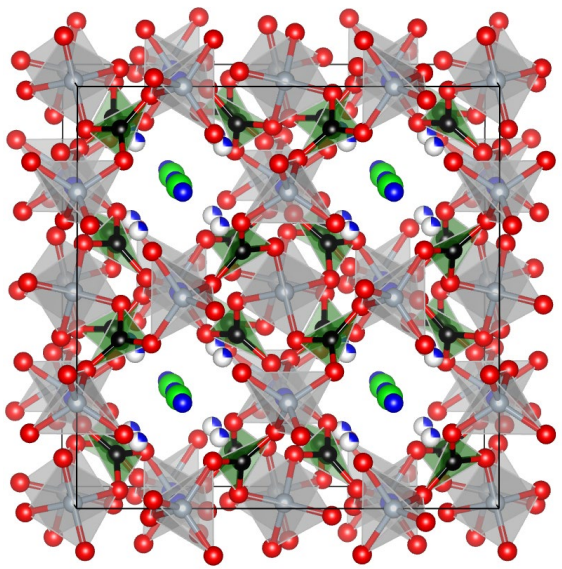
- **Projector Augmented Wave formalism Blöchl (1994)** DOI: 10.1103/PhysRevB.50.17953 **with datasets using the ATOMPAW code** http://pwpaw.wfu.edu

Many analysis tools –

- **Visualization: VESTA: http://jp-minerals.org/vesta/en/**
- **Symmetry: Findsym: https://stokes.byu.edu/iso/**
  SeeK-path: https://www.materialscloud.org/work/tools/seekpath

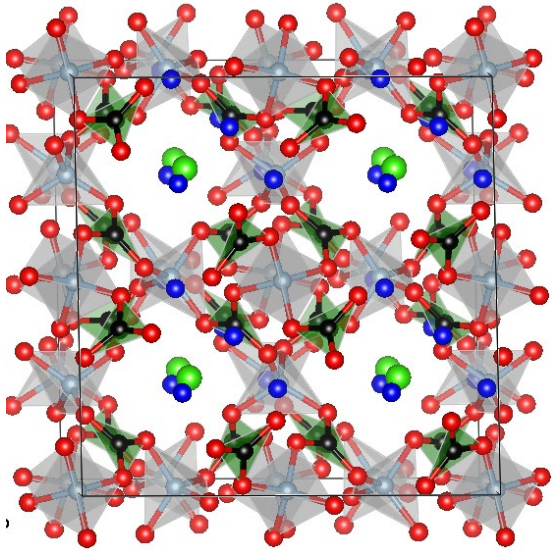
Comparison of experimental disordered F-43c and ordered R3c structures

$Li_4Al_3B_4O_{12}Cl$



Exp – F-43c
Kajihara (2017)

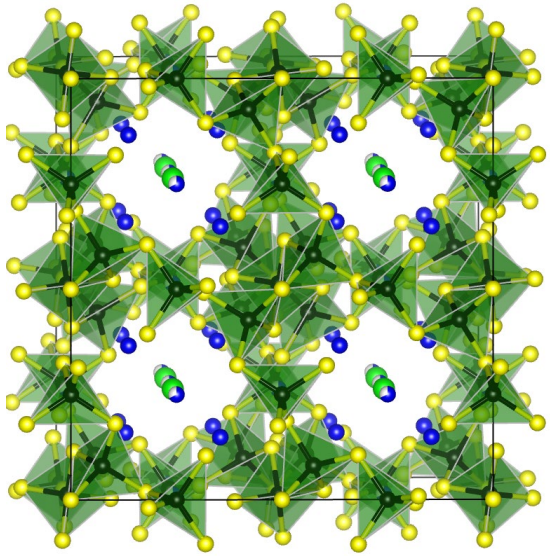
a=12.9687 Å
α=90.0 deg



Opt – R3c
(this work)

a=13.0 Å
α=91.1 deg

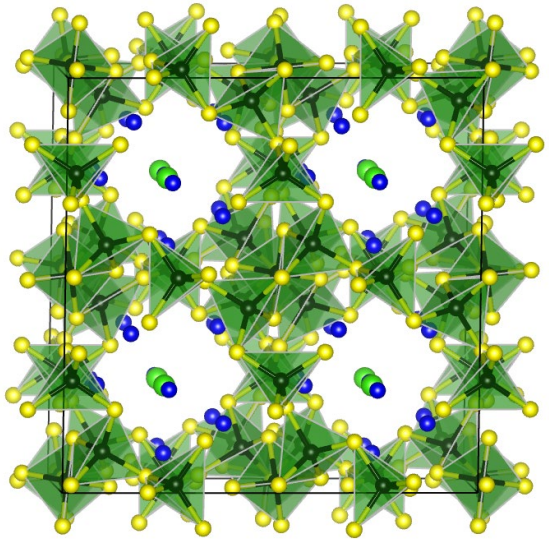
$Li_6B_7S_{13}I$



Exp – F-43c
Kaup (2021)

a=15.245 Å
α=90.0 deg

$Li_6B_7S_{13}Cl$

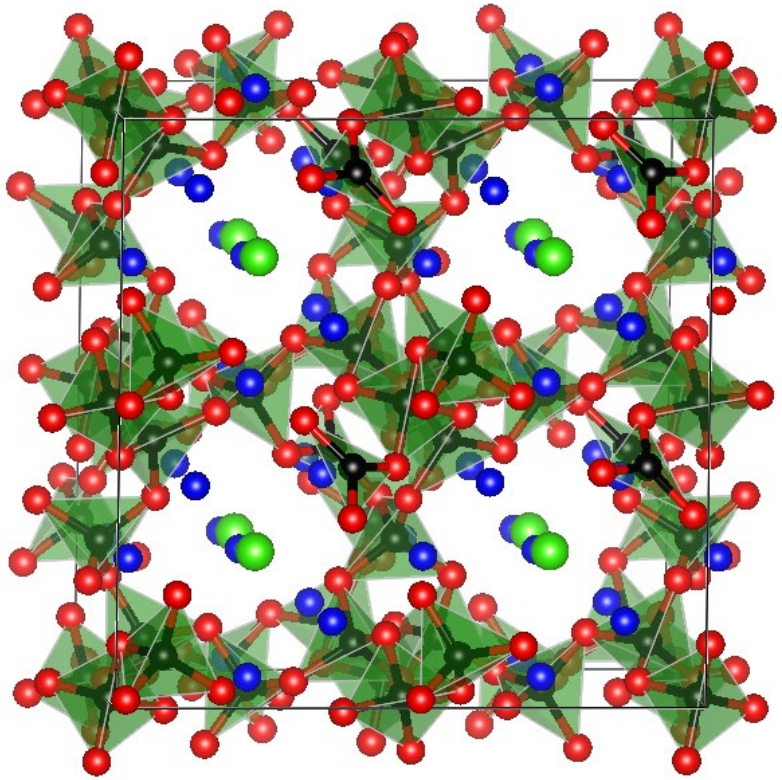


Opt – R3c
(this work)

a=15.1 Å
α=89.2 deg

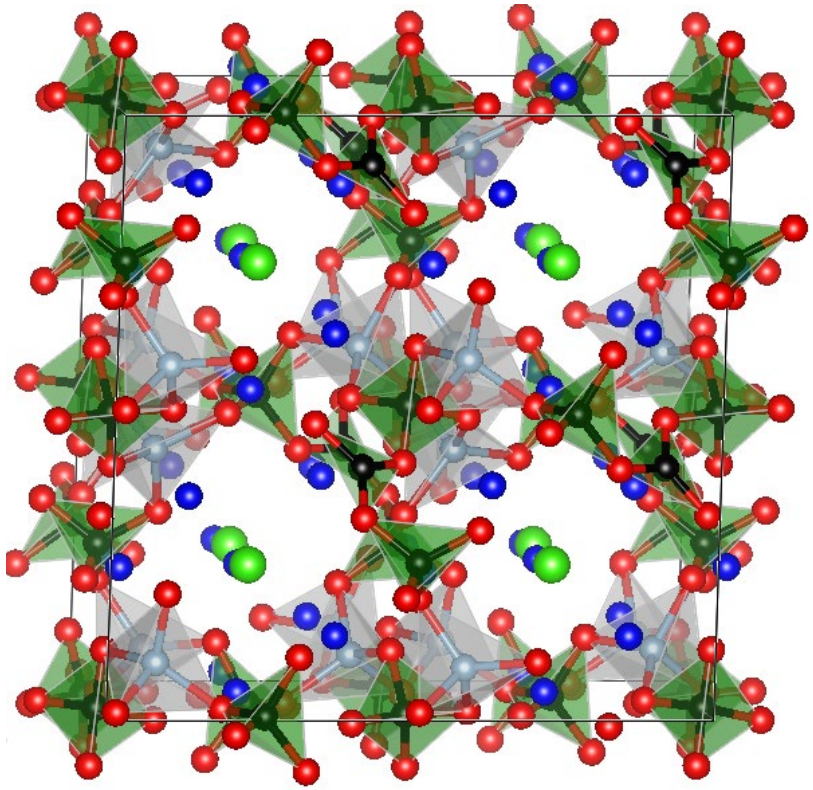
More predicted R3c boracites

$Li_6B_7O_{13}Cl$



a=12.2 Å
α=89.4 deg

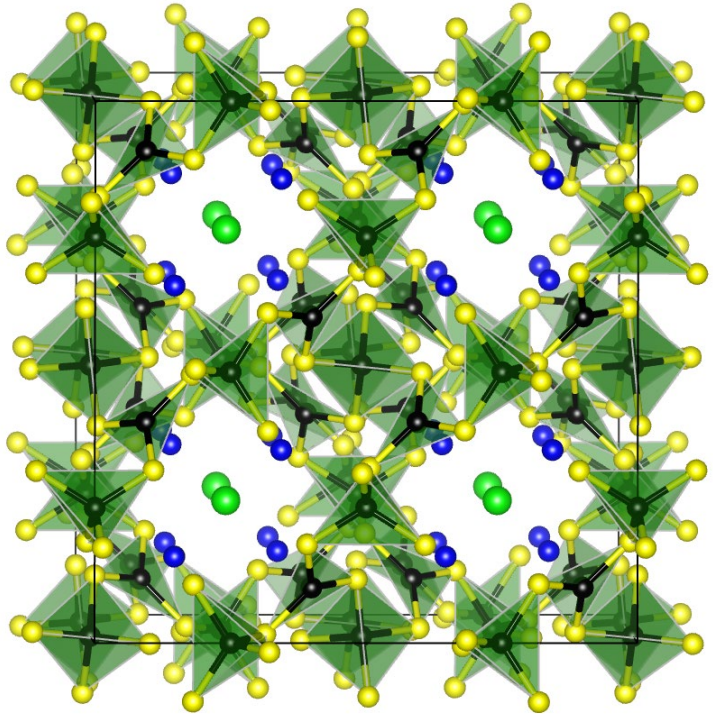
$Li_6Al_3B_4O_{13}Cl$



a=13.0 Å
α=88.3 deg

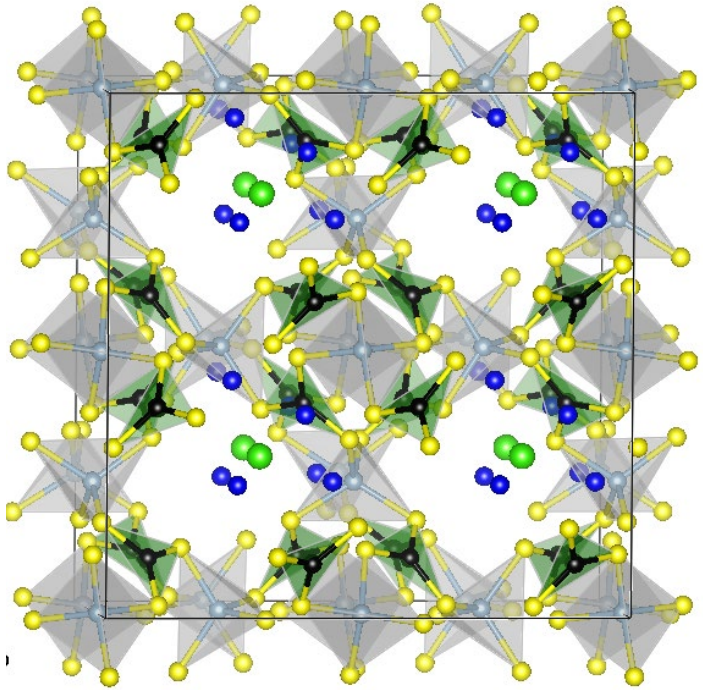
More predicted ordered thioboracites

$Li_4B_7S_{12}Cl$



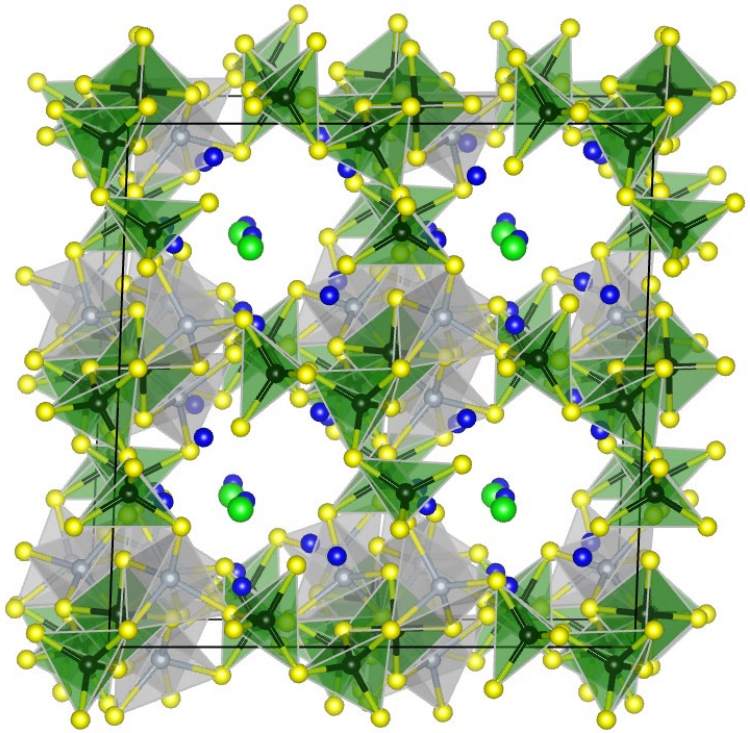
F-43c (ordered)
a=14.9 Å
α=90.0 deg

$Li_4Al_3B_4S_{12}Cl$



R3c
a=16.1 Å
α=89.6 deg

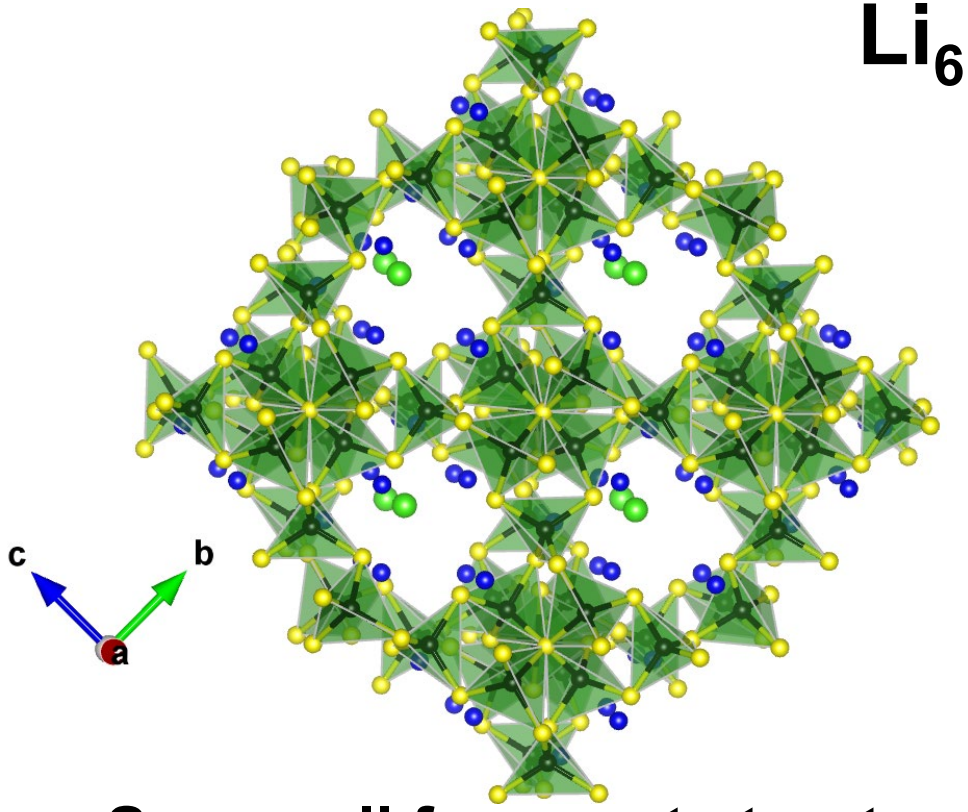
$Li_6Al_3B_4S_{13}Cl$

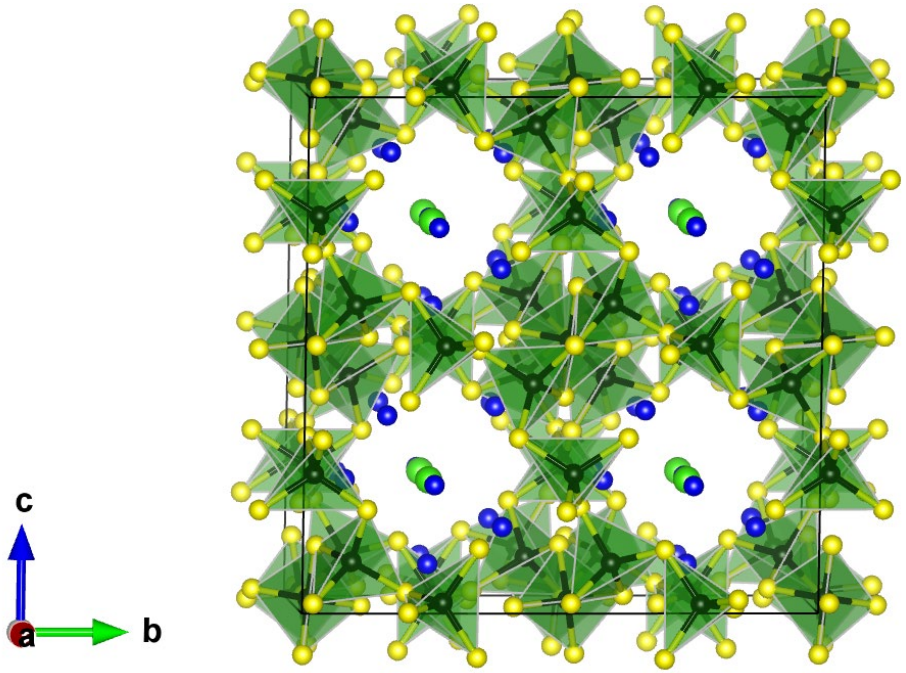


R3c
a=16.1 Å
α=87.8 deg

For some of the (thio)boracites, a monoclinic structure: SG Cc (No. 9) is predicted

$Li_6B_7S_{13}Cl$





Supercell fragment structure
(Cc) V=429.9 Å^3/FU
a=18.5 b=10.5 c=10.8 Å
α=90.0 β=124.6 γ=90.0 deg

Conventional cell structure
(R3c) V=431.3 Å^3/FU
a=14.9 Å
α=90.0 deg

Summary of static lattice optimization results for ordered structures

	$Li_4B_7O_{12}Cl+Li_2O$	$Li_4Al_3B_4O_{12}Cl+Li_2O$	$Li_4B_7S_{12}Cl+Li_2S$	$Li_4Al_3B_4S_{12}Cl+Li_2S$
SG: R3c	0.00 eV/FU	0.00 eV/FU	0.00 eV/FU	0.00 eV/FU ← Ref.
SG: F-43c	+0.21 eV/FU	+1.19 eV/FU	-0.05 eV/FU	+0.85 eV/FU
SG: Cc	+0.32 eV/FU	+1.91 eV/FU	+0.05 eV/FU	+0.98 eV/FU

	$Li_6B_7O_{13}Cl$	$Li_6Al_3B_4O_{13}Cl$	$Li_6B_7S_{13}Cl$	$Li_6Al_3B_4S_{13}Cl$
SG: R3c	-1.58 eV/FU	-0.22 eV/FU	-0.96 eV/FU	-0.34 eV/FU
SG: Cc	-1.26 eV/FU	-0.40 eV/FU	-1.05 eV/FU	-0.65 eV/FU

➔For all 4 families, the Li_6 (thio)boracite compound is stable with respect to decomposition into Li_6 (thio)boracite → Li_4 (thio)boracite + Li_2S/O

More comprehensive stability analysis of the (thio) boracite family using the convex hull approach (Ong (2008) DOI: 10.1021/cm702327g)

In order to perform the convex hull analysis, it is necessary to calculate the formation energies of all of the (thio) boracites and their possible decomposition products. Following the Materials project (https://materialsproject.org/) and using structures listed in the ICSD (https://icsd.fiz-karlsruhe.de/) database, the following solid state materials were used as the common elemental references for the formation energies E_f which were evaluated using Quantum Espresso with PBESOL exchange-correlation.

Element	Structure
Li	Im-3m (No. 229)
B	R-3m (No. 166)
O	C2/m (No. 12)
Al	Fm-3m (No. 225)
S	P2/c (No. 13)
Cl	Cmce (No. 64)

Formula for calculating formation energy for compound $A_aB_bC_c$:

$$E_f(A_aB_bC_c) \equiv \frac{E(A_aB_bC_c) - aE(A) - bE(B) - cE(C)}{a+b+c}$$

where $E(X)$ is the DFT static lattice energy of X in its optimized structure.

Convex hull analysis, continued –

From the formation energies E_f of the (thio)boracites and possible decomposition products, it is possible to estimate the E_{hull} energies using the pymatgen software (Ong (2013) DOI: 10.1016/j.commatsci.2012.10.028).

For example, if a compound F containing N^F atoms undergoes a reaction:

$F \rightarrow \sum_i X_i P_i$ where P_i denotes a product and X_i denotes the stiochiometric coefficient,

the formation energies can be used to calculate $\Delta E(F) \equiv N^F E_f(F) - \sum_i X_i N^{P_i} E_f(P_i)$

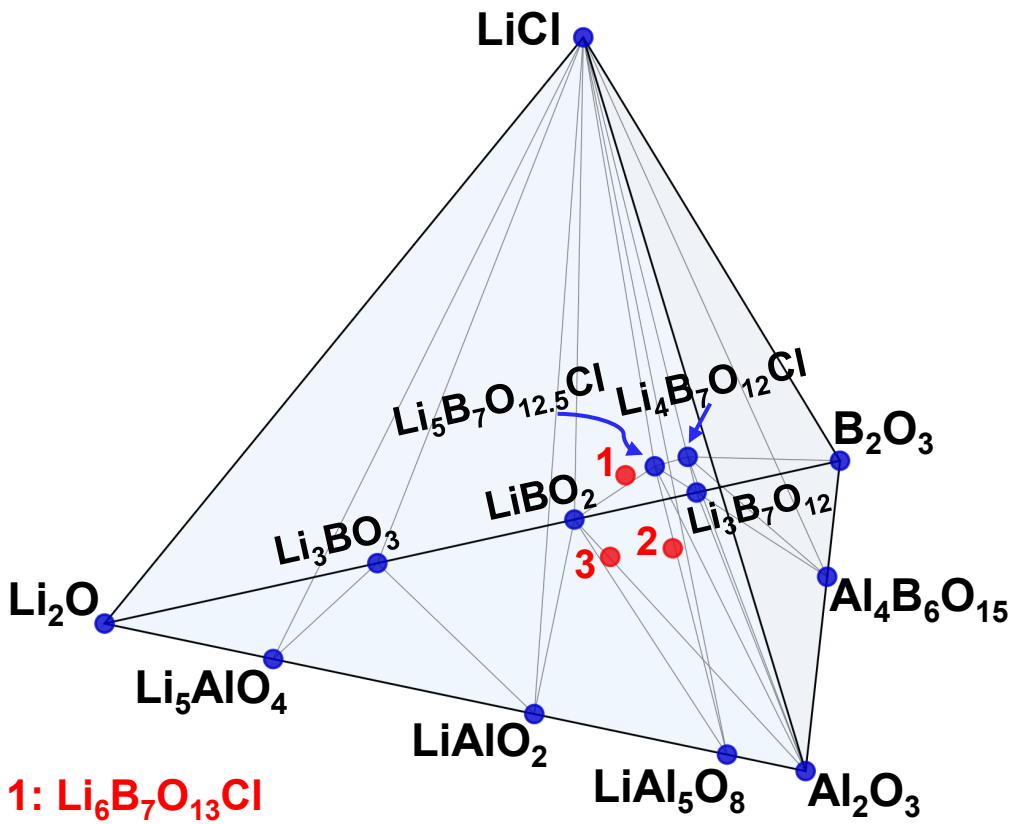
From these reaction energies, we can determine $E_{hull}(F)$ defined for each compound F as the energy on or above the convex hull according to:

$$E_{hull}(F) \equiv \begin{cases} 0 & \text{for } \Delta E(F) \leq 0 \\ \dfrac{\Delta E(F)}{N^F} & \text{for } \Delta E(F) > 0 \end{cases}$$

For all possible products, indicating *F* to be a stable phase

For the largest positive *ΔE(F)*, suggesting likely decomposition.

Convex hull analysis of Li-B-Al-O-Cl system



1: $Li_6B_7O_{13}Cl$

2: $Li_4Al_3B_4O_{12}Cl$; 3: $Li_6Al_3B_4O_{13}Cl$

- E_{hull}=0
- E_{hull}>0

Convex hull energies for boracites

$Li_4B_7O_{12}Cl$ (R3c)	E_{hull}=0.0000 eV/atom
$Li_6B_7O_{13}Cl$ (R3c)	0.0039
$Li_4Al_3B_4O_{12}Cl$ (R3c)	0.0532
$Li_6Al_3B_4O_{13}Cl$ (Cc)	0.0799

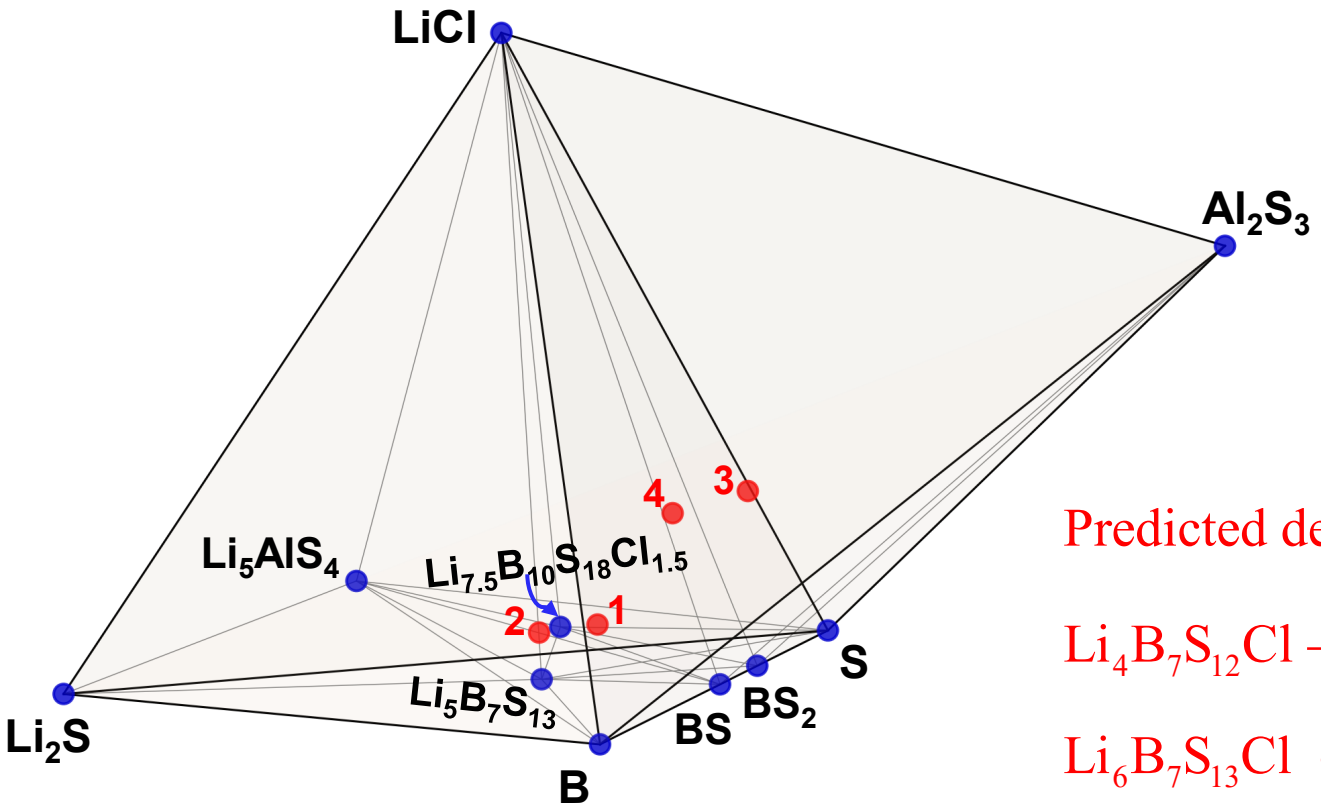
Predicted decomposition reactions:

$$Li_6B_7O_{13}Cl \rightarrow \frac{7}{3}LiBO_2 + \frac{2}{3}Li_5B_7O_{12.5}Cl + \frac{1}{3}LiCl$$

$$Li_4Al_3B_4O_{12}Cl \rightarrow \frac{4}{15}LiBO_2 + \frac{3}{5}LiAl_5O_8 + \frac{8}{15}Li_5B_7O_{12.5}Cl + \frac{7}{15}LiCl$$

$$Li_6Al_3B_4O_{13}Cl \rightarrow 4\,LiBO_2 + \frac{1}{2}LiAl_5O_8 + \frac{1}{2}LiAlO_2 + LiCl$$

Convex hull analysis of Li-B-Al-S-Cl system



1: $Li_4B_7S_{12}Cl$; 2: $Li_6B_7S_{13}Cl$
3: $Li_4Al_3B_4S_{12}Cl$; 4: $Li_6Al_3B_4S_{13}Cl$

- E_{hull}=0
- E_{hull}>0

Convex hull energies for thioboracites

$Li_4B_7S_{12}Cl$ (F-43c)	E_{hull}=0.0129 eV/atom
$Li_6B_7S_{13}Cl$ (Cc)	0.0079
$Li_4Al_3B_4S_{12}Cl$ (R3c)	0.0593
$Li_6Al_3B_4S_{13}Cl$ (Cc)	0.0337

Predicted decomposition reactions:

$$Li_4B_7S_{12}Cl \rightarrow \frac{1}{2}Li_{7.5}B_{10}S_{18}Cl_{1.5} + BS_2 + BS + \frac{1}{4}LiCl$$

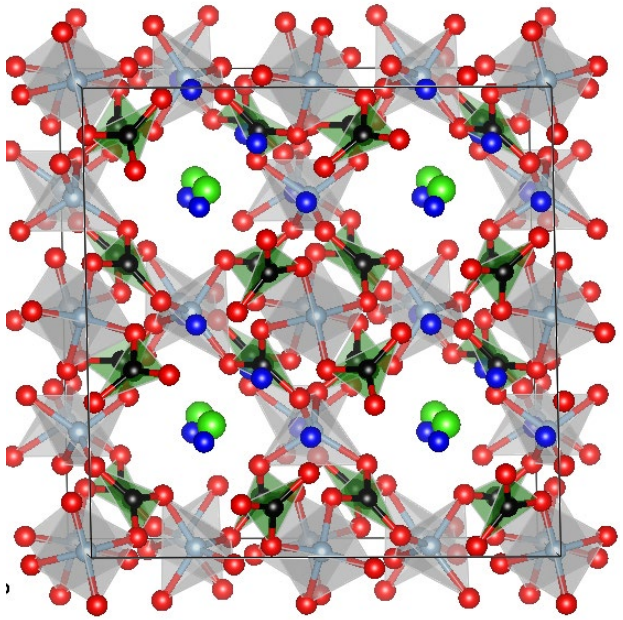
$$Li_6B_7S_{13}Cl \rightarrow Li_5B_7S_{13} + LiCl$$

$$Li_4Al_3B_4S_{12}Cl \rightarrow \frac{4}{7}Li_5B_7S_{13} + \frac{1}{35}Li_5AlS_4 + \frac{52}{35}Al_2S_3 + LiCl$$

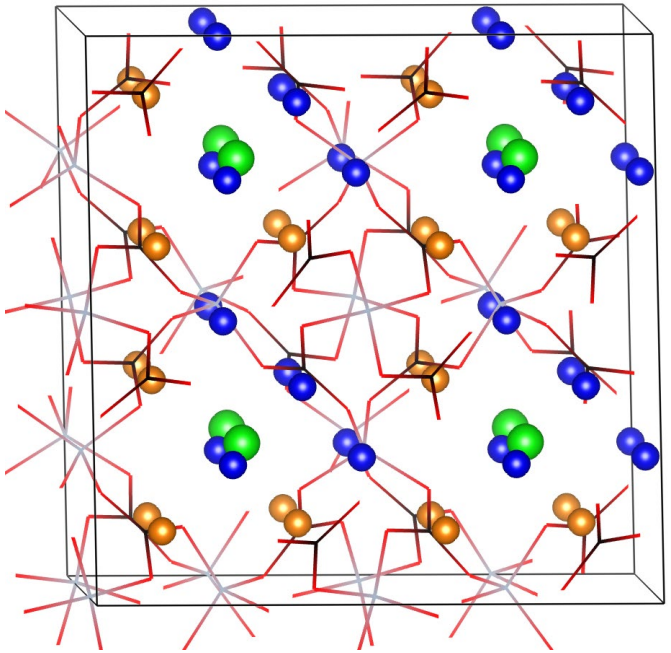
$$Li_6Al_3B_4S_{13}Cl \rightarrow \frac{4}{7}Li_5B_7S_{13} + \frac{3}{7}Li_5AlS_4 + \frac{9}{7}Al_2S_3 + LiCl$$

Evidence of Li ion migration from molecular dynamics simulations

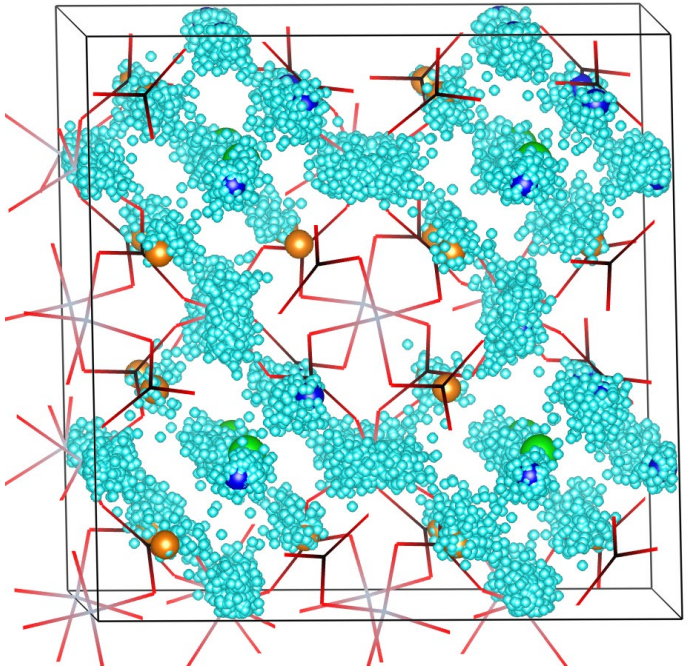
$Li_4Al_3B_4O_{12}Cl$ in R3c structure



Visualization of optimized structure using polyhedra to represent framework



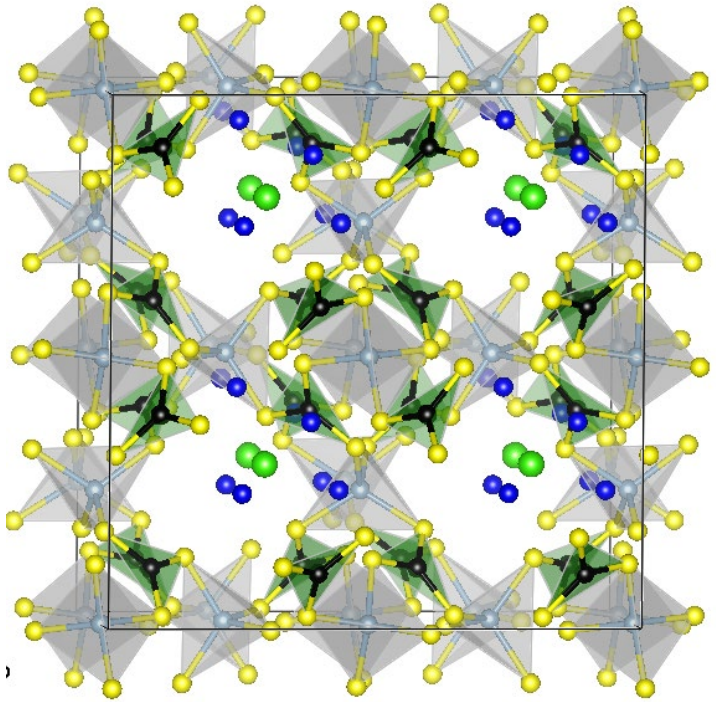
Same structure using stick representation for framework and orange balls for natural interstitial sites



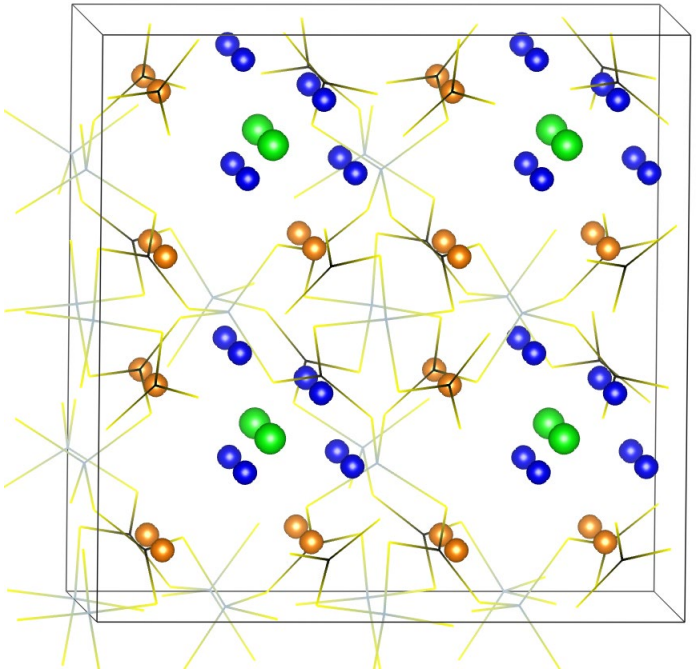
Small blue balls represent Li positions from MD simulation at T_{avg} = 900K for 67 ps, sampled every each 0.12 ps.

Evidence of Li ion migration from molecular dynamics simulations

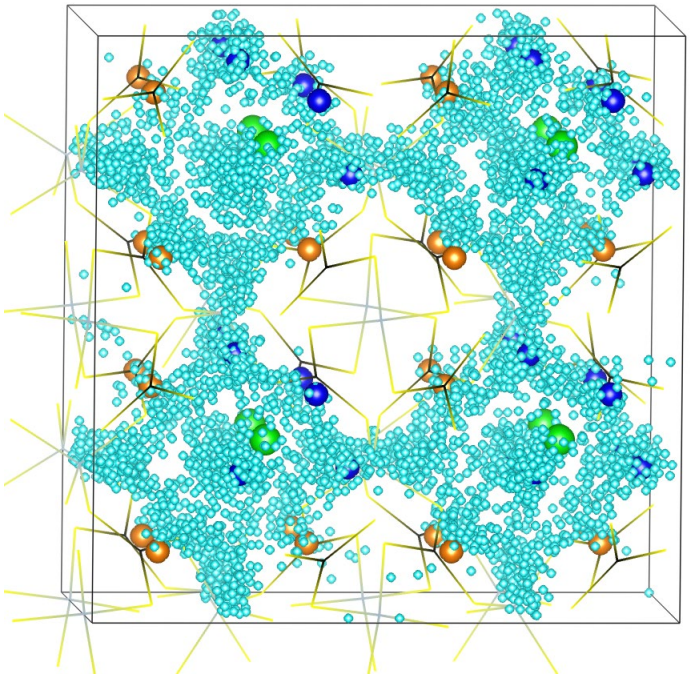
$Li_4Al_3B_4S_{12}Cl$ in R3c structure



Visualization of optimized structure using polyhedra to represent framework



Same structure using stick representation of framework and orange balls for natural interstitial sites



Small blue balls represent Li positions from MD simulation at T_{avg} = 900K for 24 ps, sampled every each 0.12 ps.

Summary and conclusions

- ❑ The 8 members of the Li (thio)boracite family are explored and found to have high symmetry, reasonably good stability, and promising Li ion conductivity.
- ❑ Ordered ground state structures for the three experimentally identified materials and five predicted materials with the R3c, F-43c, and Cc space groups. Preliminary results for phonon analysis indicate dynamic stability (but additional calculations need to be completed).
- ❑ Convex hull analysis shows that of the eight the Li (thio) boracite family members, only $Li_4B_7O_{12}Cl$ is on the hull, while the other seven members are slightly above the hull, including two that have been experimentally observed.
- ❑ Preliminary Li ion mobility analysis shows significant Li ion motion within the void regions of the crystals.
- ❑ While the Li (thio) boracite family is not (yet) one of the prime technological candidates for all-solid-state batteries, academic interest is strong and suggestive of possible technological viability.