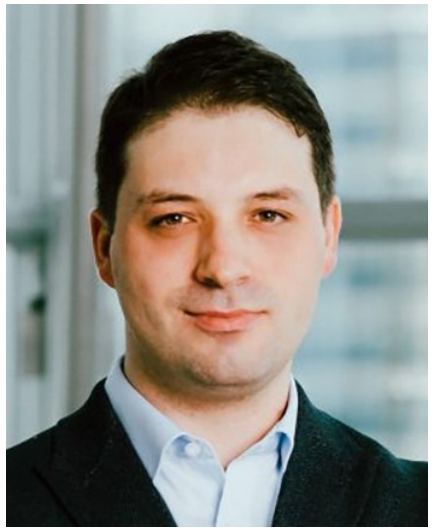
Exploration of Solid-State Electrolytes Based on Lithium (Thio) Boracites through Computer Simulation

Natalie Holzwarth, Dept. of Physics, Wake Forest University, Winston-Salem, NC

Collaborators:

D. Cory Lynch
Wake Forest U.

Dr. Yan Li
National U. of Singapore



Professor P. Canepa
U. of Houston

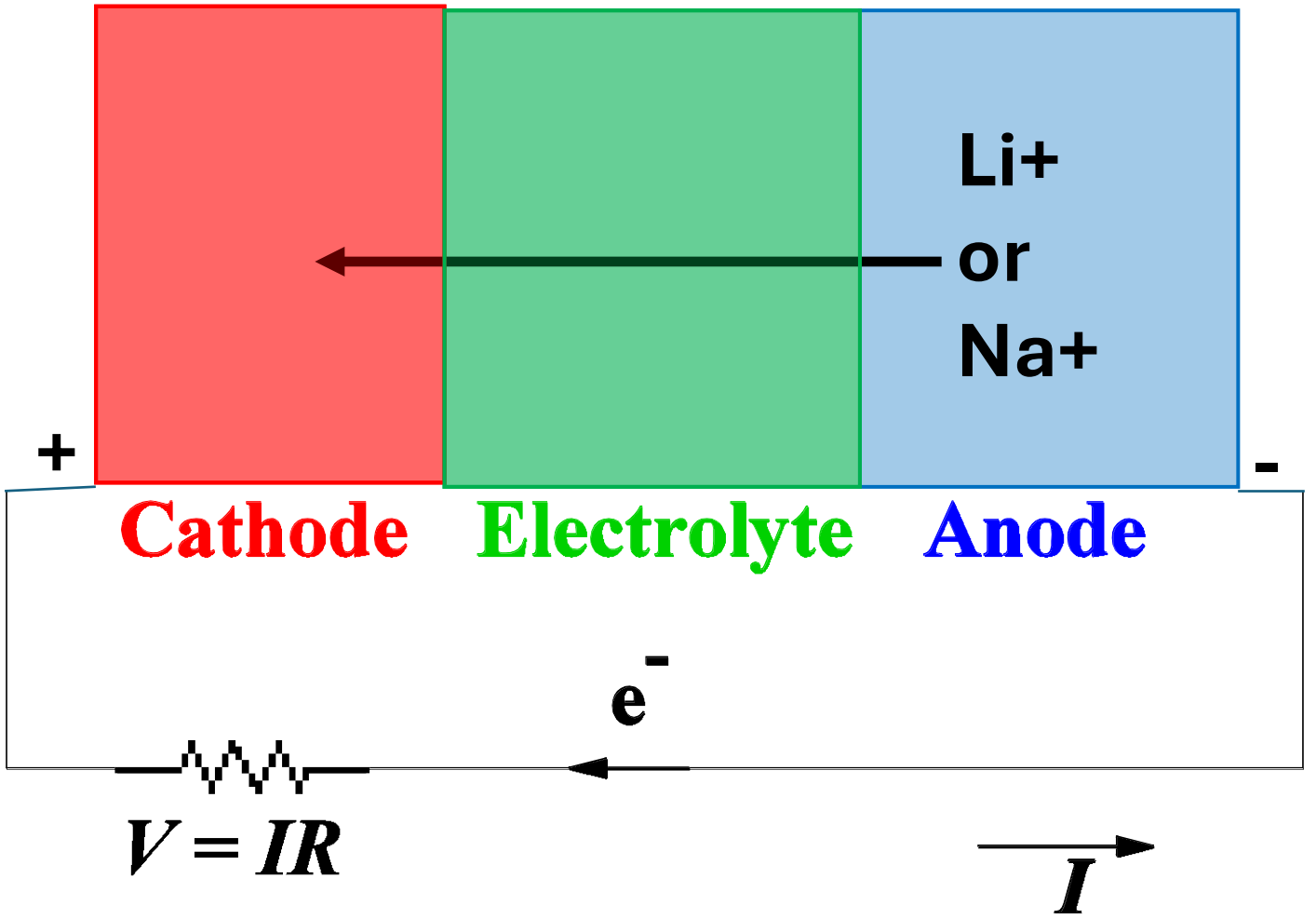
Outline

- Why all-solid-state batteries?
- Why boracites and related materials?
- Computational methods
- Static lattice internal energies to study/predict structures
- Phonons and dynamic stabilities
- Qualitative ionic conductivities
- Summary and conclusions

Idealized all-solid-state batteries

Materials components of a Li or Na ion battery

Role of the ideal solid electrolyte is to allow for the transport of Li+ or Na+ ions, excluding electrons from the battery and forcing them through the external circuit.



Illustrating the discharge mode

Historical development all-solid-state batteries

Research on LiPON electrolyte films at Oak Ridge National Laboratory

Solid State Ionics 53–56 (1992) 655–661
North-Holland

SOLID STATE IONICS

Sputtering of lithium compounds for preparation of electrolyte thin films

N.J. Dudney, J.B. Bates, R.A. Zuhr and C.F. Luck
Solid State Division, Oak Ridge National Laboratory, P O Box 2008, Oak Ridge, TN 37831-6030, USA

and

J.D. Robertson
Department of Chemistry, University of Kentucky, 800 Rose St . Lexington, KY 40506-0055, USA

$$\mathbf{LiPON} \equiv \mathbf{Li}_x\mathbf{PO}_y\mathbf{N}_z$$

with $x = 2y + 3z - 5$

A case for all-solid-state batteries

Advantages

- Compatible and stable with high voltage cathodes
- Compatible and stable with Li metal anodes
- Can be effective in thin formats

Disadvantages

- Relatively low ionic conductivity
- Lower total capacity compared with liquid electrolytes
- Possible physical and chemical interface issues

Materials Views
www.MaterialsViews.com
Adv. Energy Mater. **2015**, *5*, 1401408
DOI: 10.1002/aenm.201401408
ADVANCED ENERGY MATERIALS
www.advenergymat.de

Solid Electrolyte: the Key for High-Voltage Lithium Batteries

Juchuan Li, Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney** **ORNL**

Demonstrated for $LiNi_{0.5}Mn_{1.5}O_4$/LiPON/Li

- **10^{-6} m LiPON electrolyte layer achieved adequate conductivity**
- **10,000 cycles* with 90% capacity retention**

***1 cycle per day for 27 years**

More details on LiPON/Li interface

NANO LETTERS

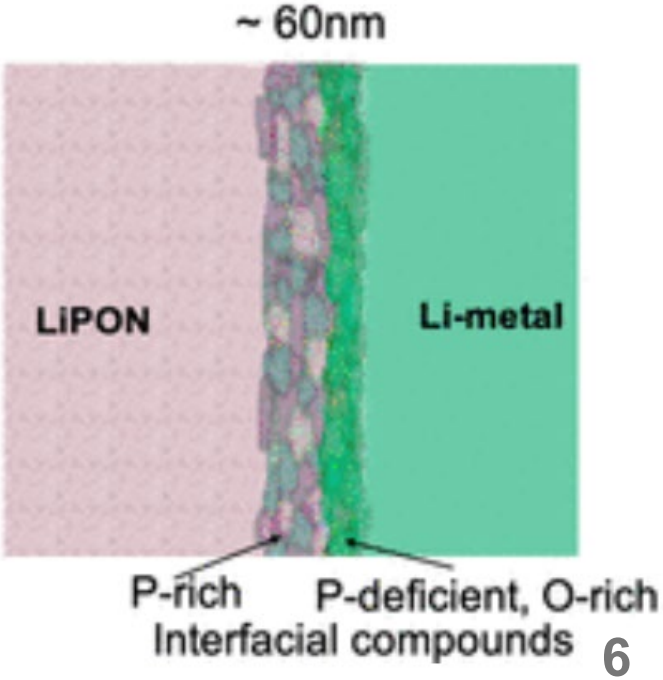
pubs.acs.org/NanoLett Letter

Elucidating Interfacial Stability between Lithium Metal Anode and Li Phosphorus Oxynitride via *In Situ* Electron Microscopy

Zachary D. Hood,[▽] Xi Chen,[▽] Robert L. Sacci,[▽] Xiaoming Liu, Gabriel M. Veith, Yifei Mo, Junjie Niu,* Nancy J. Dudney,* and Miaofang Chi*

Cite This: *Nano Lett.* 2021, 21, 151−157 Read Online

Schematic view of steady-state LiPON/Li interface based on microscopic analysis, showing thin, relatively stable interface layer



Search for highly conductive solid electrolytes

ADVANCED ENERGY MATERIALS

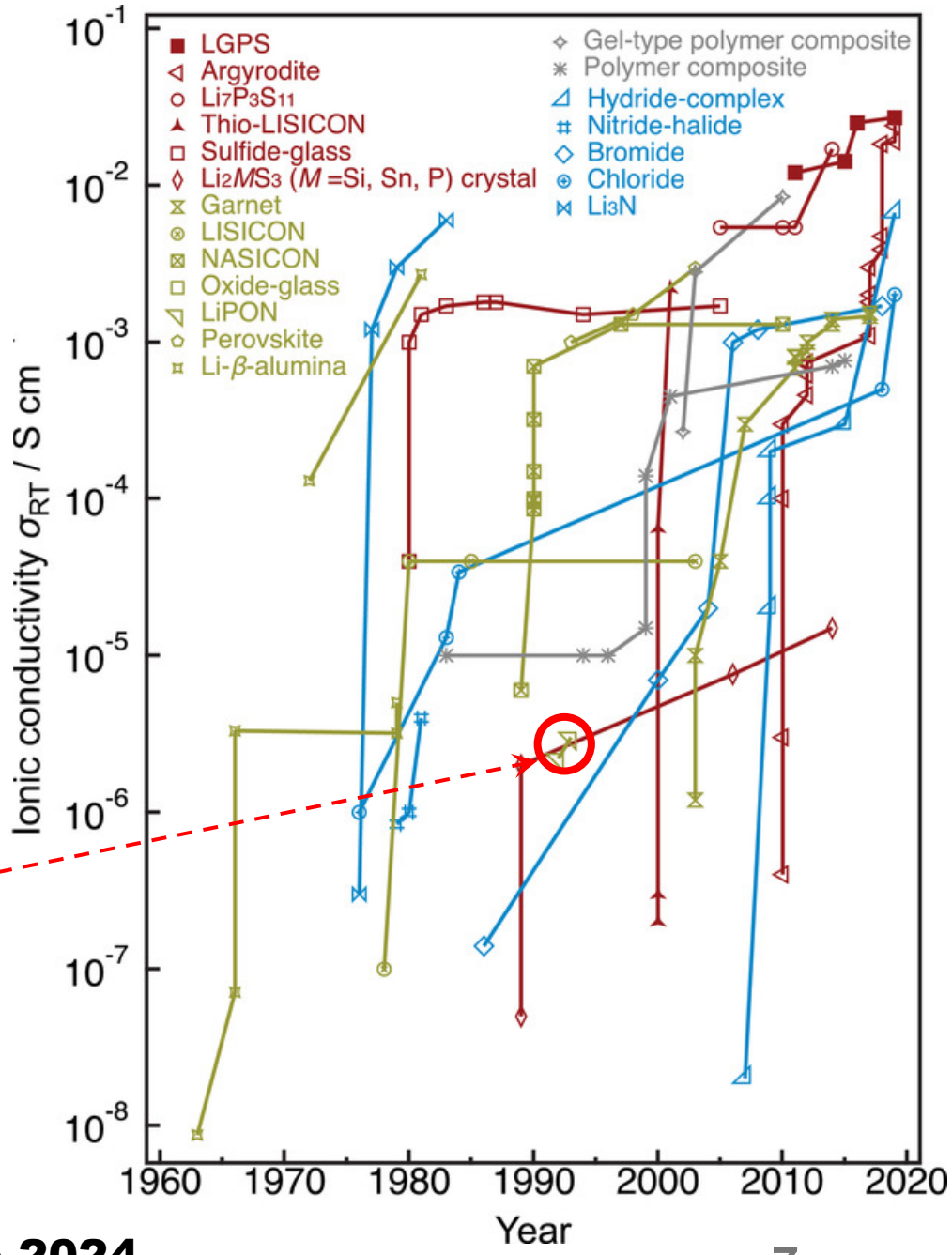
Review | Full Access

$Li_{10}GeP_2S_{12}$-Type Superionic Conductors: Synthesis, Structure, and Ionic Transportation

Yuki Kato, Satoshi Hori, Ryoji Kanno

First published: 27 September 2020 | https://doi.org/10.1002/aenm.202002153 |

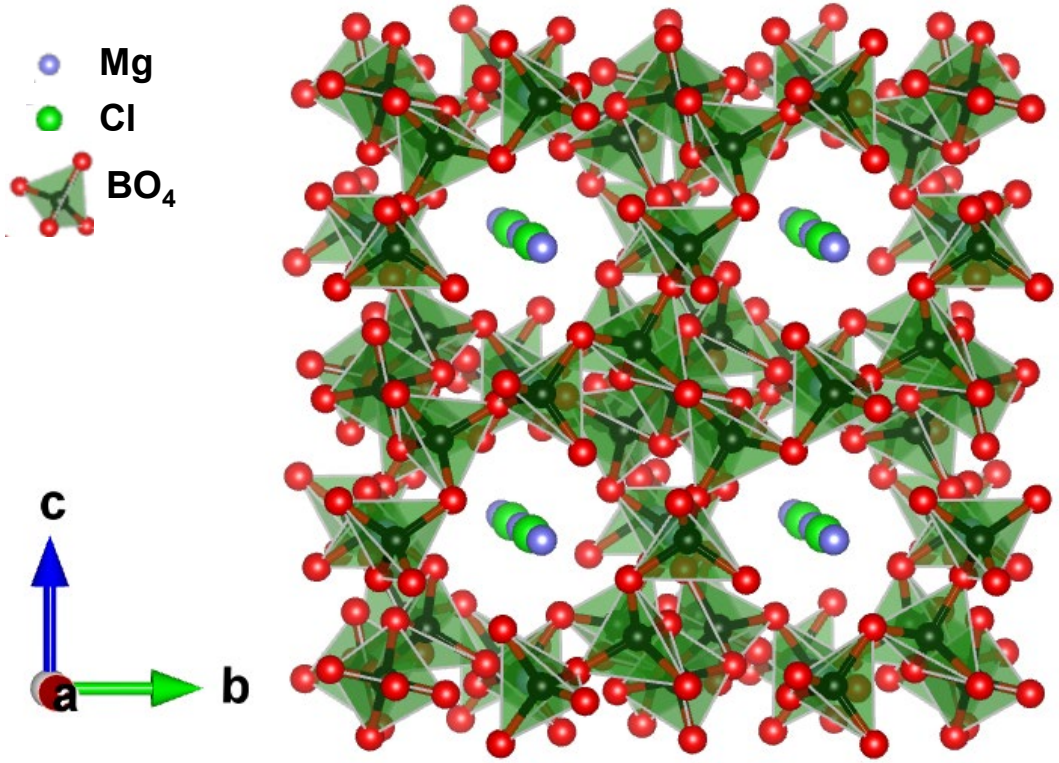
LiPON



Introducing boracite

More details available in recent publication:
Physical Review Materials **8** , 065401 (2024)
and in previous work:
Physical Review Materials **6** , 025401 (2022)

Boracite gem stones – face centered cubic structure

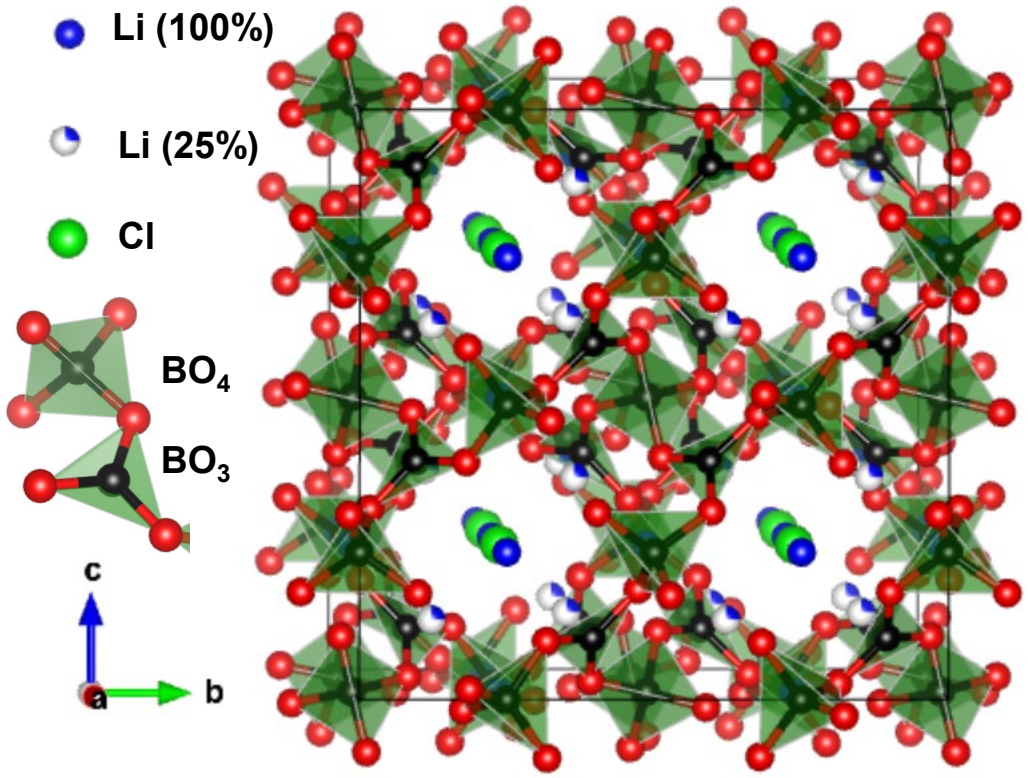


Pictured above: Gemmy, sharp green-blue boracite crystals from England deposit; Charlie Key Collection | Image credit: Rob Lavinsky, iRocks.com – CC-BY-SA-3.0

$Mg_3B_7O_{13}Cl$ (*F-43c*)

https://www.gemrockauctions.com/learn/a-z-of-gemstones/boracite

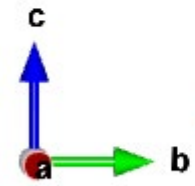
Li modified boracite

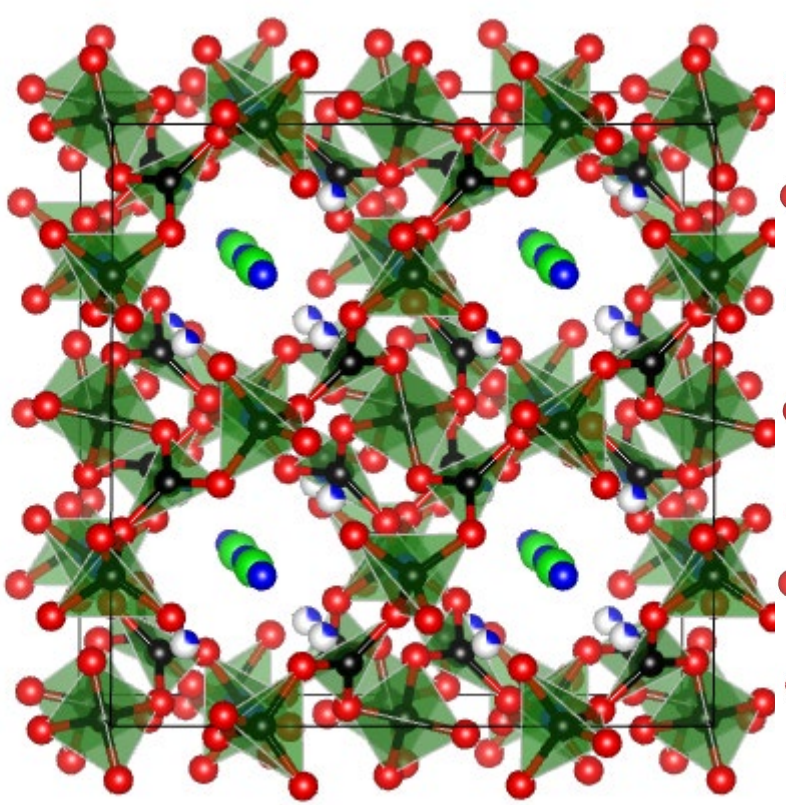


$Li_4B_7O_{12}Cl$ (*F-43c*)

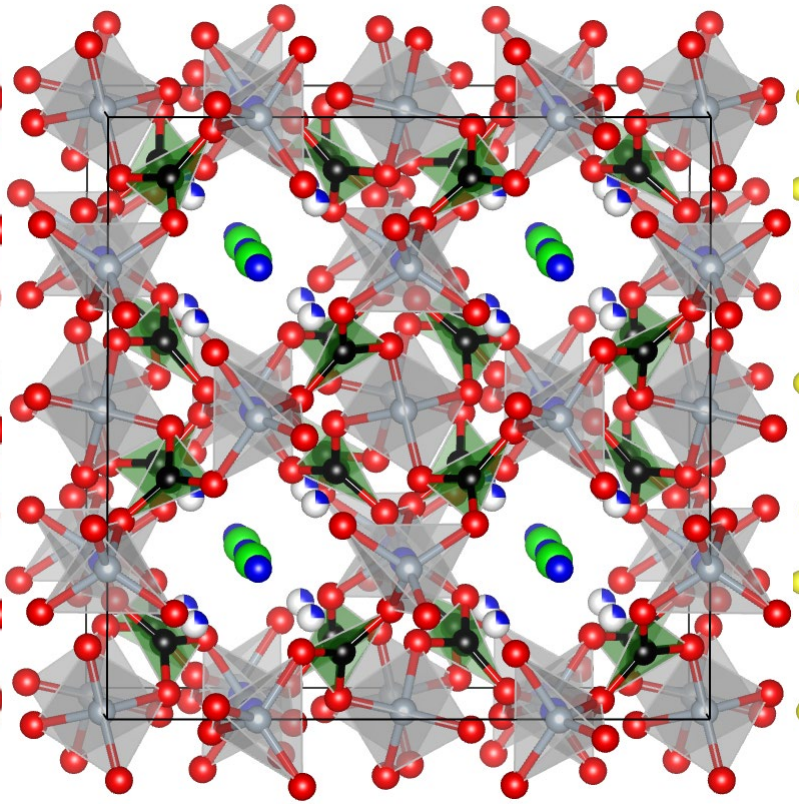
Experimental structure:W. Jeitschko, et al. Acta Crystallogr. Sect. B **33**, 2767 (1977),

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

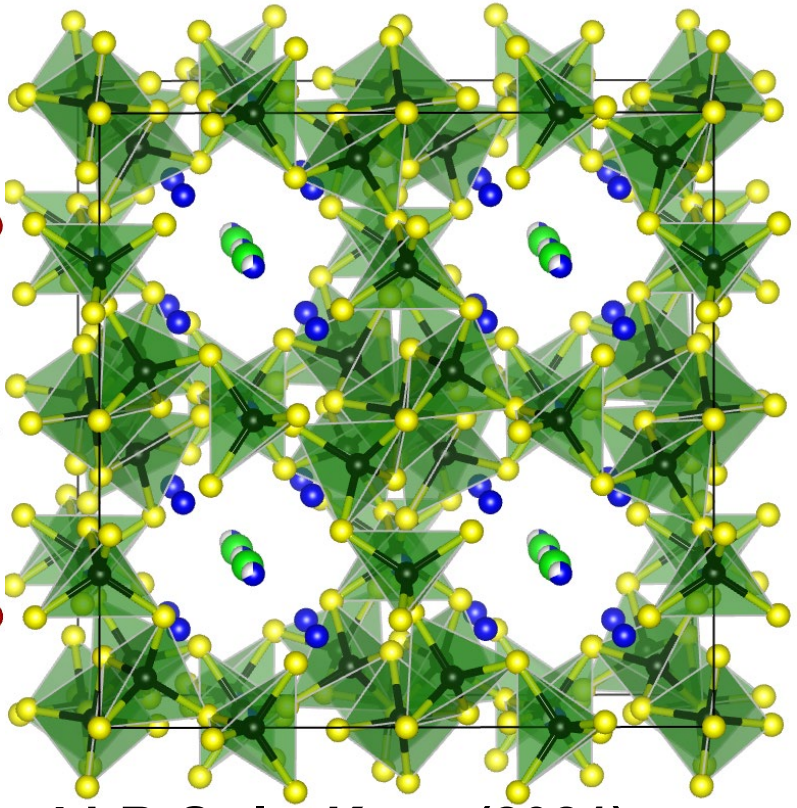




$Li_4B_7O_{12}Cl$ – Jeitschko (1977)
DOI: 10.1107/S0567740877009443



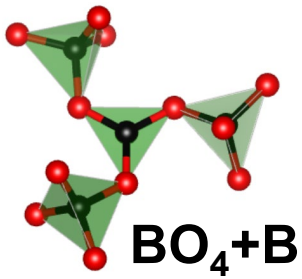
$Li_4Al_3B_4O_{12}Cl$ – Kajihara (2017)
DOI: 10.1246/bcsj.20170242



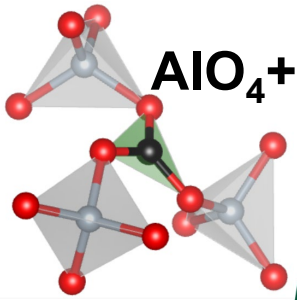
$Li_6B_7S_{13}I$ – Kaup (2021)
DOI: 10.1021/jacs.1c00941

$\sigma_{RT} = 5 \times 10^{-4}$ S/cm

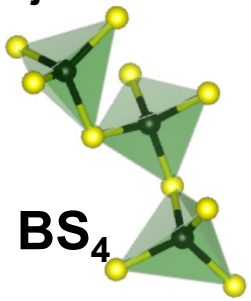
Framework components:



BO_4+BO_3



AlO_4+BO_3



BS_4

Ions:

Cl or I

Li

Computational methods

- Born-Oppenheimer approximation + 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/
- Phonons calculated with the help of Phonopy https://phonopy.github.io/phonopy/

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

Stability approximated in terms of the Helmholtz free energy as a function of temperature T :

$$F(T) = F_{SL}(T) + F_{vib}(T) \approx U_{SL} + F_{vib}(T)$$

Static lattice approx

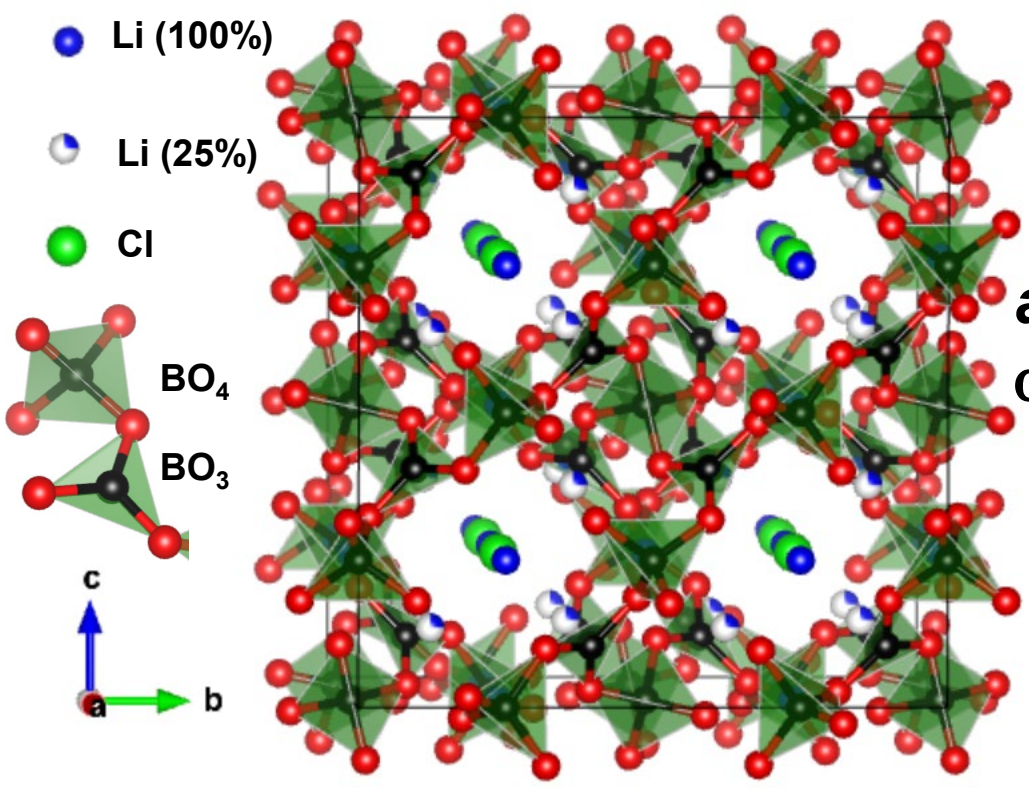
Harmonic phonon approx

Internal energy from DFT

$$F_{vib}(T) = k_B T \int_0^\infty d\omega \ \ln\left(2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right) g(\omega)$$

phonon DOS

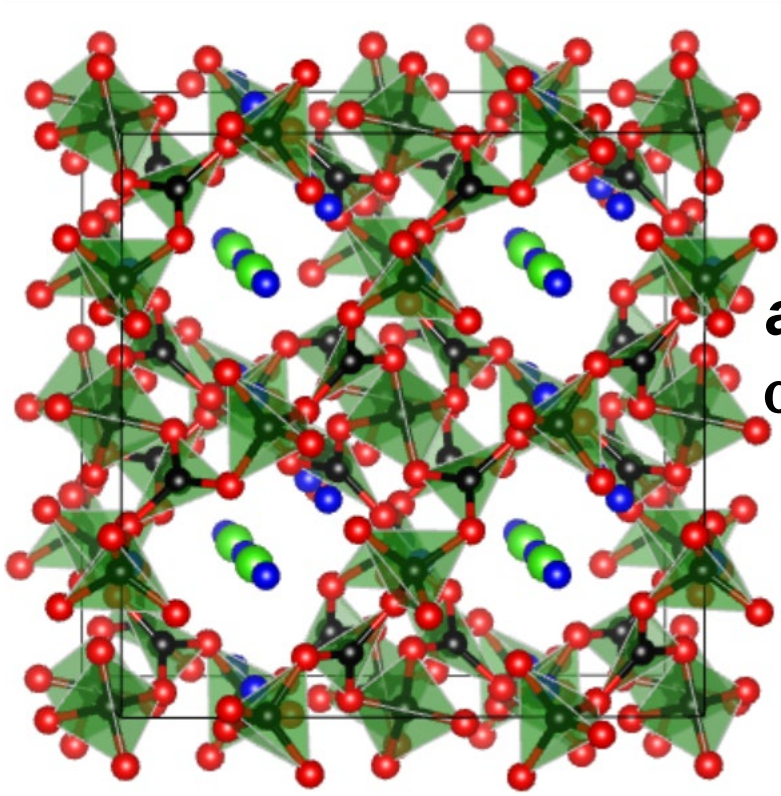
Li modified Boracite



Exp

a=12.141 Å

α=90.0 deg



Comp

a=12.1 Å

α=90.1 deg

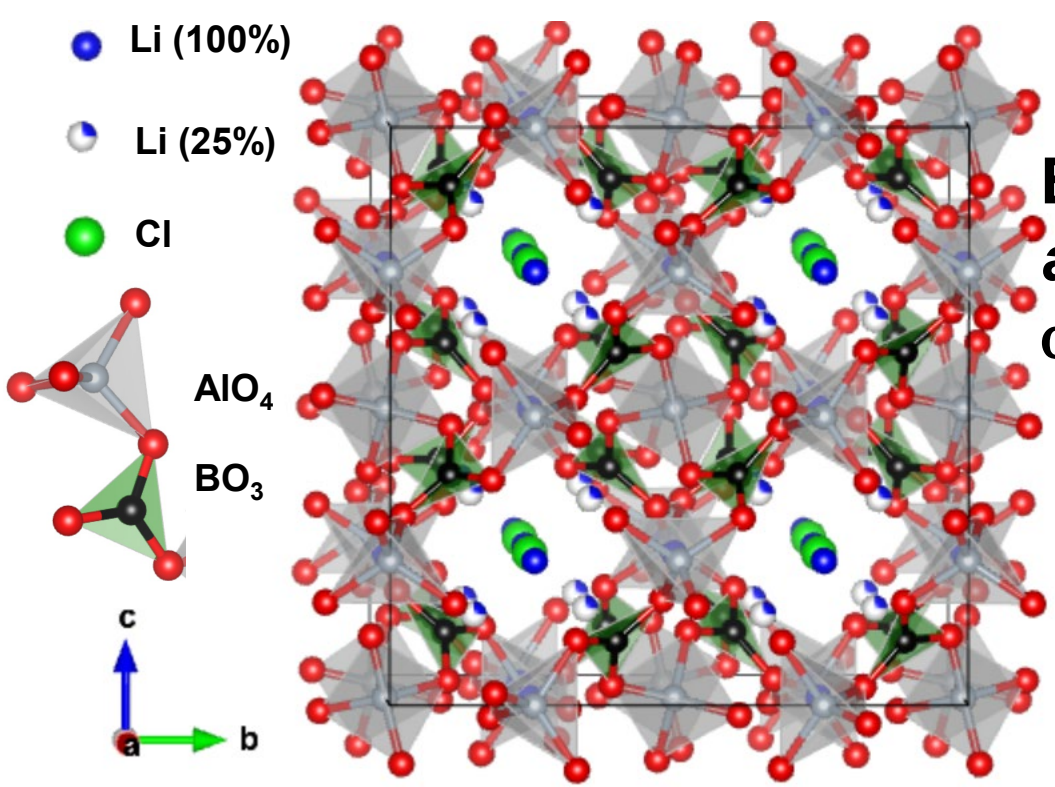
$Li_4B_7O_{12}Cl$ (disordered *F-43c*)

Experimental structure:W. Jeitschko, et al. Acta Crystallogr. Sect. B **33**, 2767 (1977)

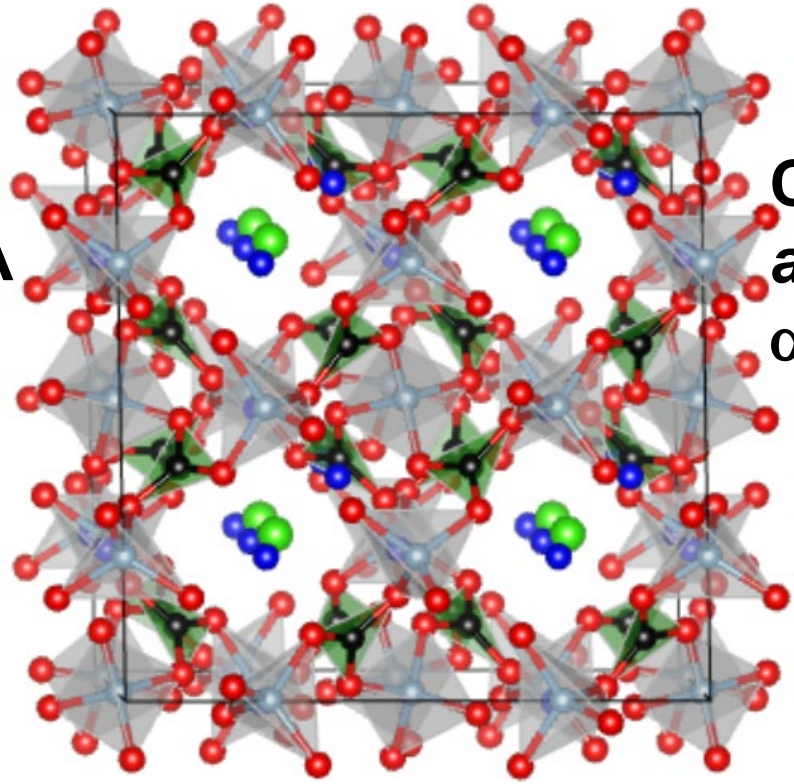
$Li_4B_7O_{12}Cl$ (ordered *R3c*)

Computationally optimized structure

Li modified Boracite with Al substitution



Exp
a=12.9687 Å
α=90.0 deg

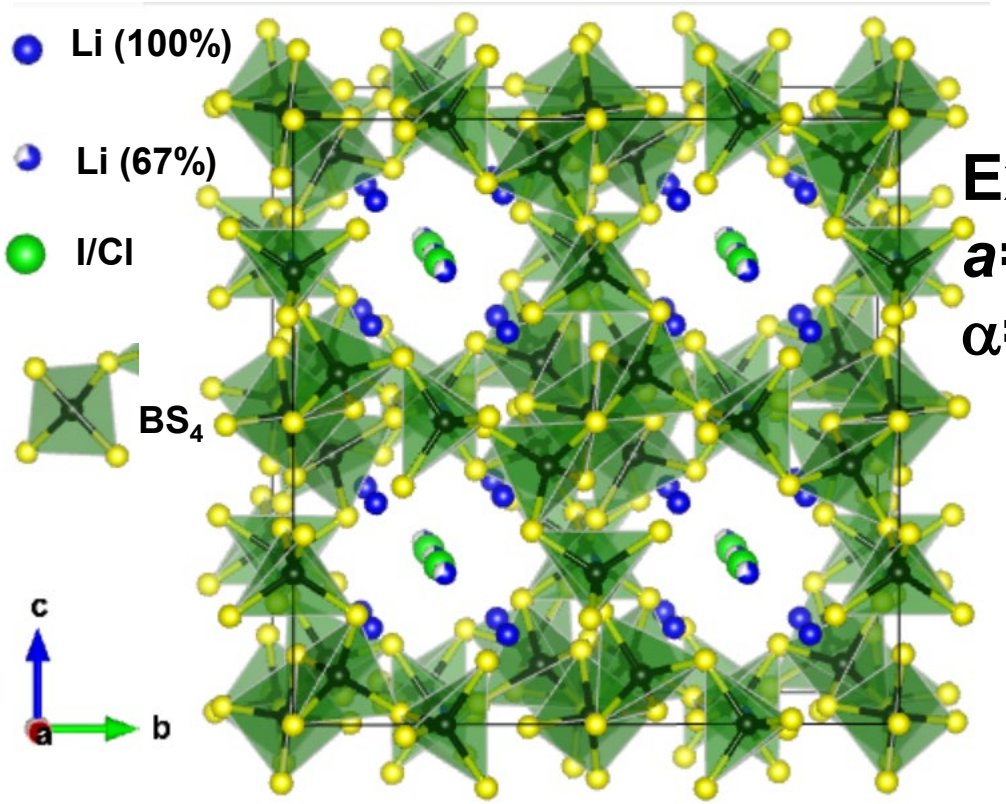


Comp
a=13.0 Å
α=91.1 deg

$Li_4Al_3B_4O_{12}Cl$ (disordered *F-43c*)
Experimental structure:K. Kajihara, et al. Bull. Chem. Soc. Jpn. **90**, 1279 (2017).

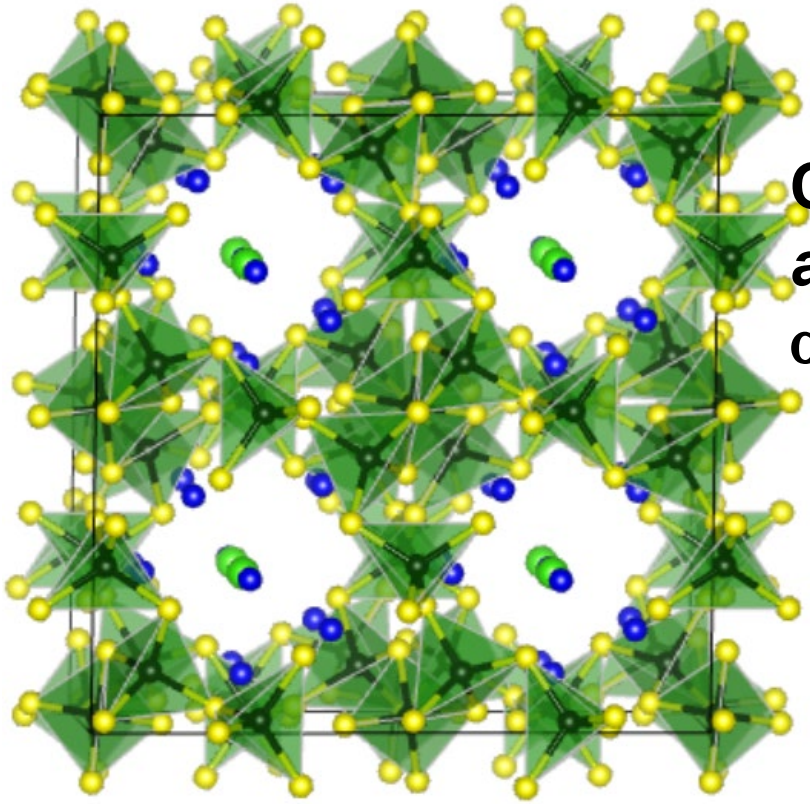
$Li_4Al_3B_4O_{12}Cl$ (ordered *R3c*)
Computationally optimized structure

“Stuffed” Li thioboracite



Exp
a=15.245 Å
α=90.0 deg

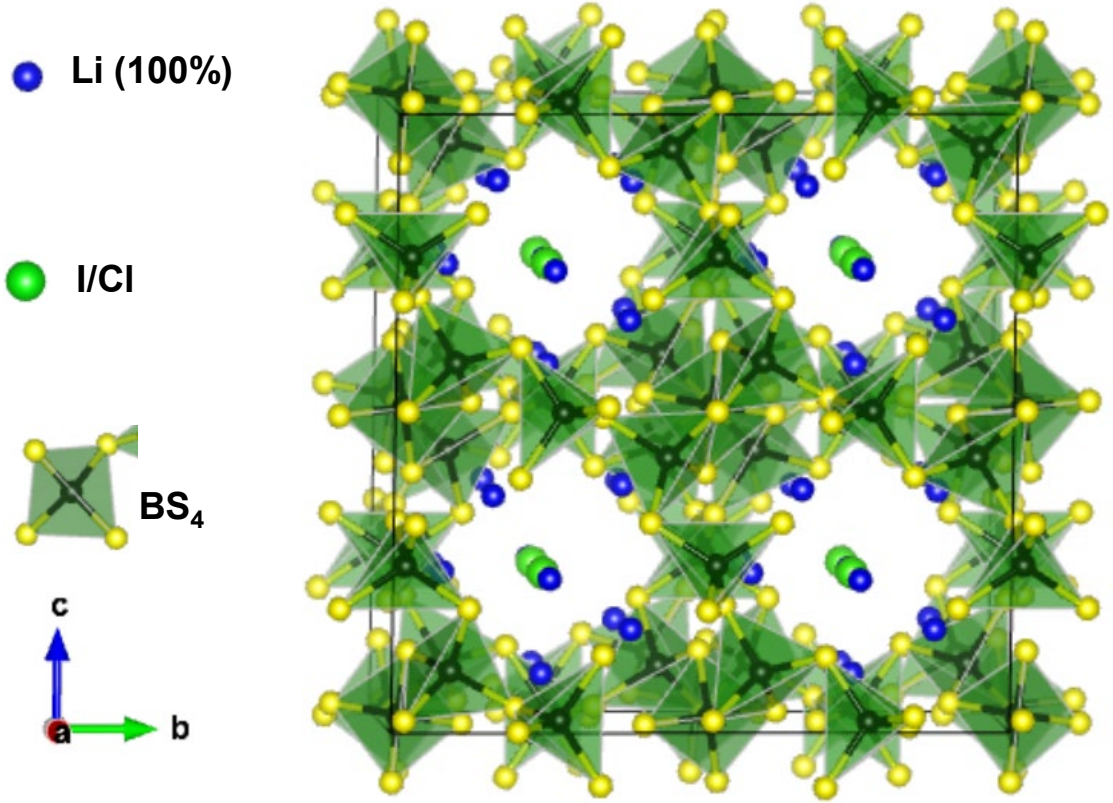
$Li_6B_7S_{13}I$ (disordered *F-43c*)
Experimental structure:K. Kaup, et al.
J. Am. Chem. Soc. **143**, 6952 (2021).

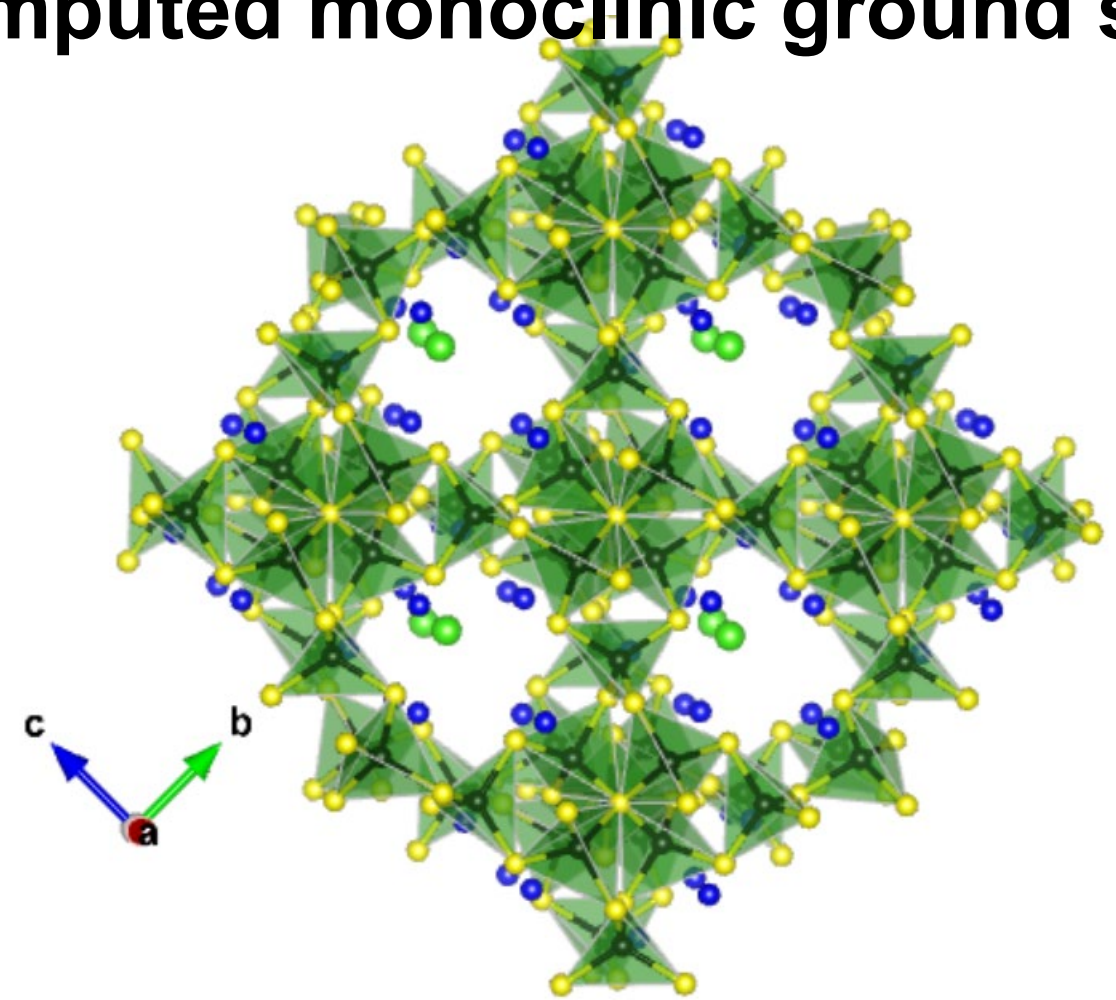


Comp
a=15.1 Å
α=89.2 deg

$Li_6B_7S_{13}Cl$ (ordered *R3c*)
Computationally optimized structure

“Stuffed” Li thioboracite – computed monoclinic ground state





$Li_6B_7S_{13}Cl$ (ordered *R3c*)
Computationally optimized structure;
conventional cell parameters:

***a*=15.1 Å α=89.2 deg**

$Li_6B_7S_{13}Cl$ (ordered *Cc*)
Computationally optimized structure; conventional cell parameters : ***a*=18.5 *b*=10.5 *c*=10.8 Å**
α= γ= 90.0 β=124.6 deg

Focus of this talk:

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 **(No. 161)**

F-43c **(No. 219)**

Cc **(No. 9)**

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.**

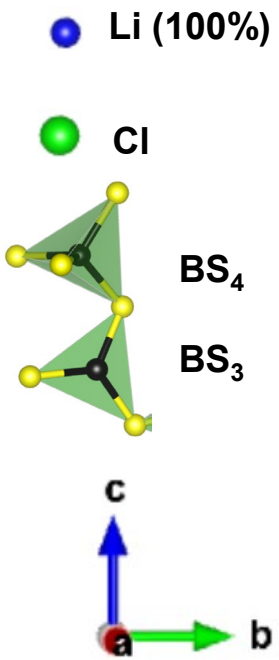
Summary of static lattice optimization results for ordered structures

	$Li_4B_7O_{12}Cl+Li_2O$	$Li_4Al_3B_4O_{12}Cl+Li_2O$	$Li_4B_7S_{12}Cl+Li_2S$	$Li_4Al_3B_4S_{12}Cl+Li_2S$
SG: R3c (ref.)	0.00 eV/FU	0.00 eV/FU	0.00 eV/FU	0.00 eV/FU
SG: F-43c	+0.21 eV/FU	+1.19 eV/FU	-0.05 eV/FU	+0.85 eV/FU

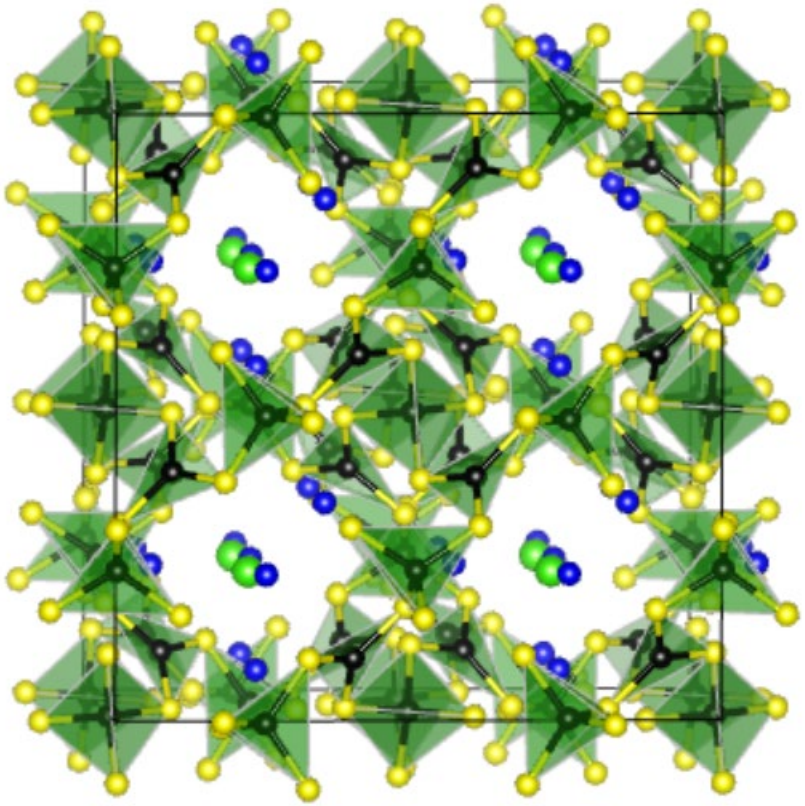
	$Li_6B_7O_{13}Cl$	$Li_6Al_3B_4O_{13}Cl$	$Li_6B_7S_{13}Cl$	$Li_6Al_3B_4S_{13}Cl$
SG: R3c	-1.58 eV/FU	-0.22 eV/FU	-0.96 eV/FU	-0.34 eV/FU
SG: Cc	-1.26 eV/FU	-0.40 eV/FU	-1.05 eV/FU	-0.65 eV/FU

➔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

Computed ordered structures of $Li_4B_7S_{12}Cl$

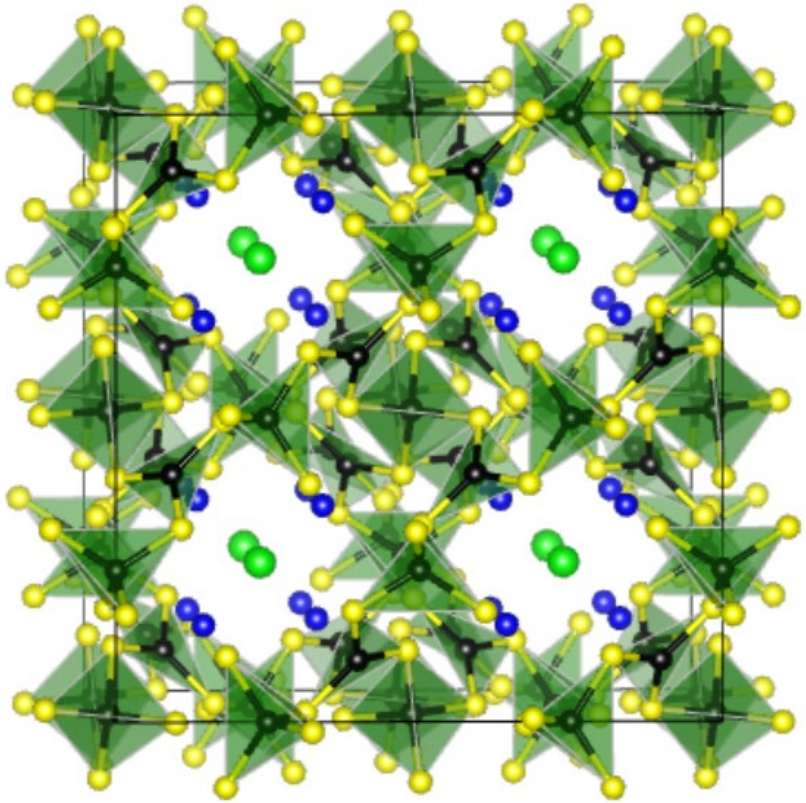


R3c



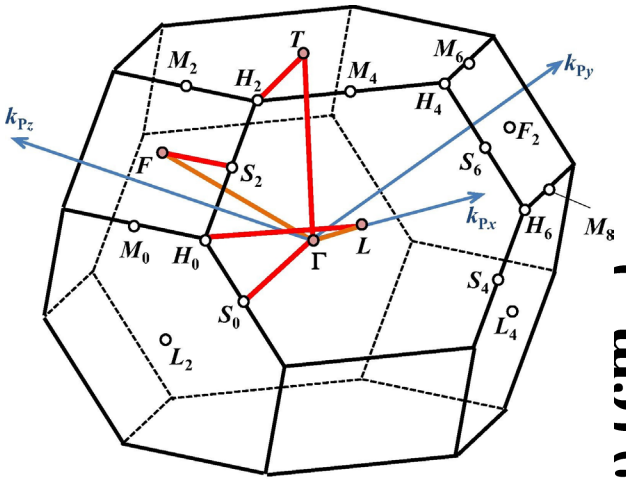
U_{SL}= 0.00 eV/FU (ref.)
a=14.9 Å α=89.9 deg

F-43c

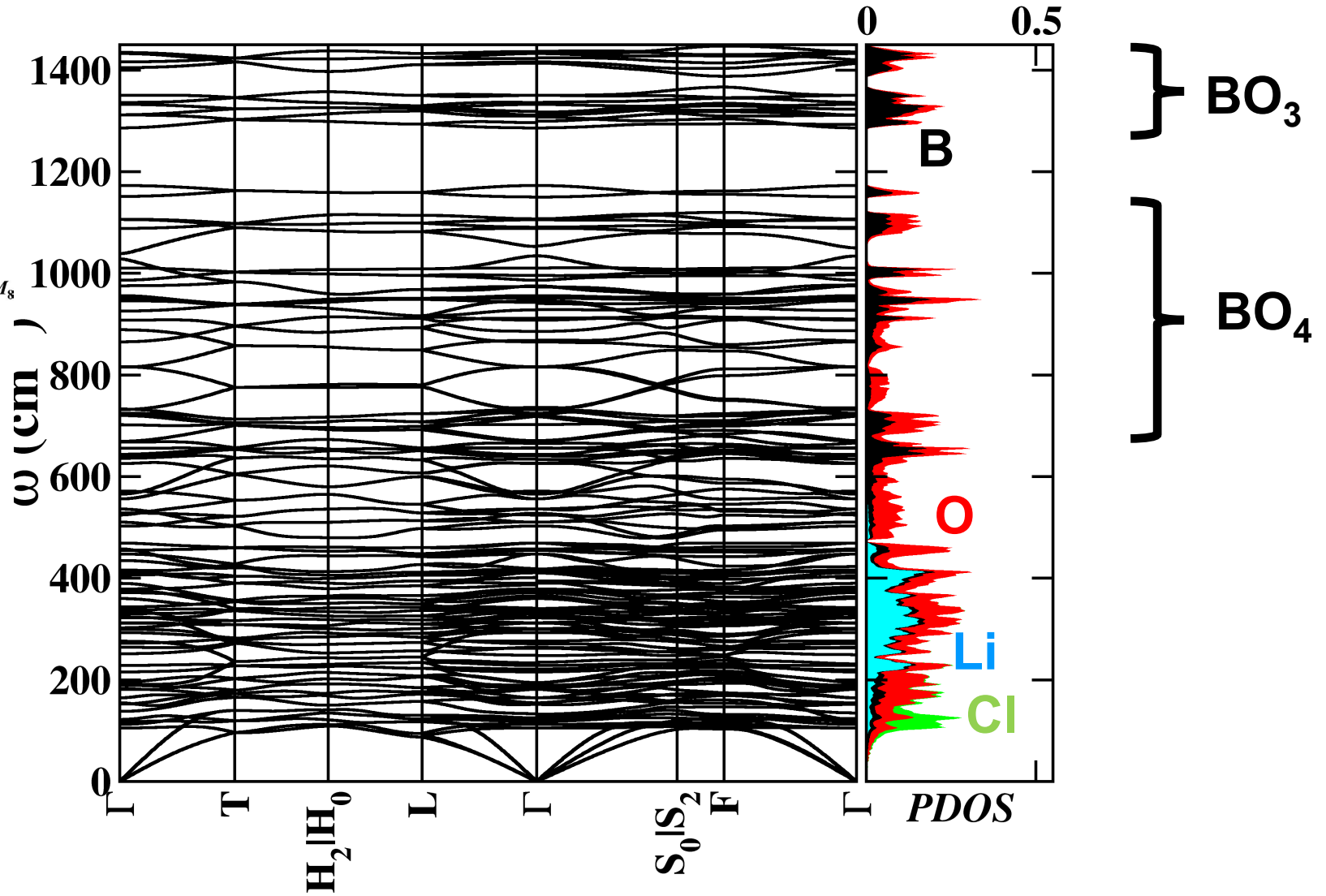


U_{SL}= -0.05 eV/FU
a=14.9 Å α=90.0 deg

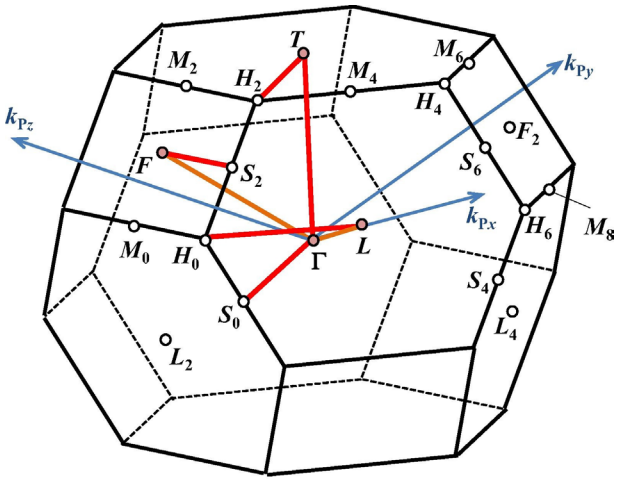
Some phonon band structures and densities of states $Li_4B_7O_{12}Cl$ *R3c*



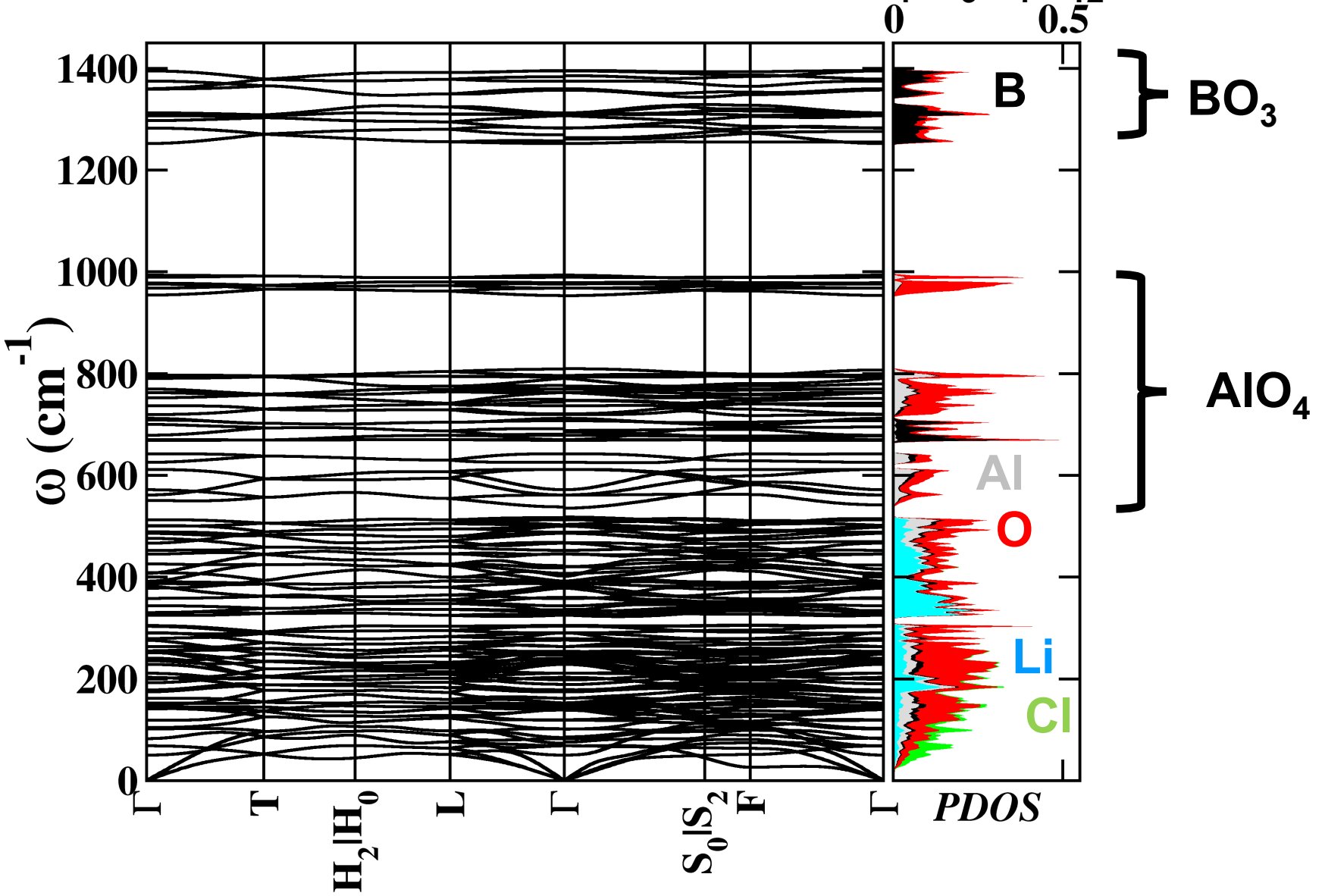
hR (√3 *a* < √2 *c*):
Γ–*T*–H_2 | H_0–*L*–Γ–S_0 | S_2–*F*–Γ



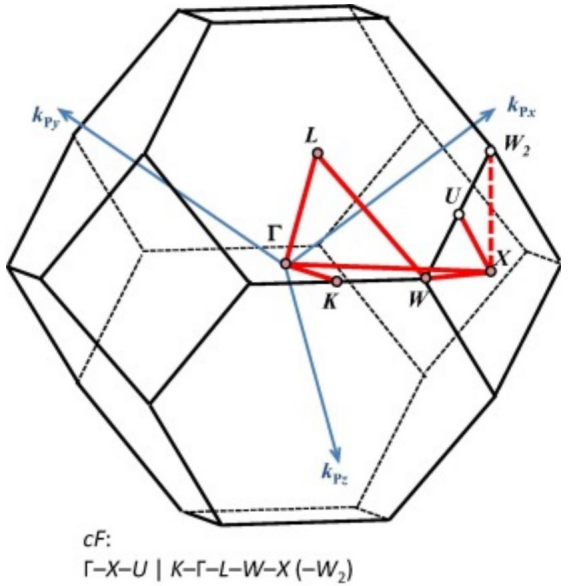
Some phonon band structures and densities of states $Li_4Al_3B_4O_{12}Cl$ *R3c*

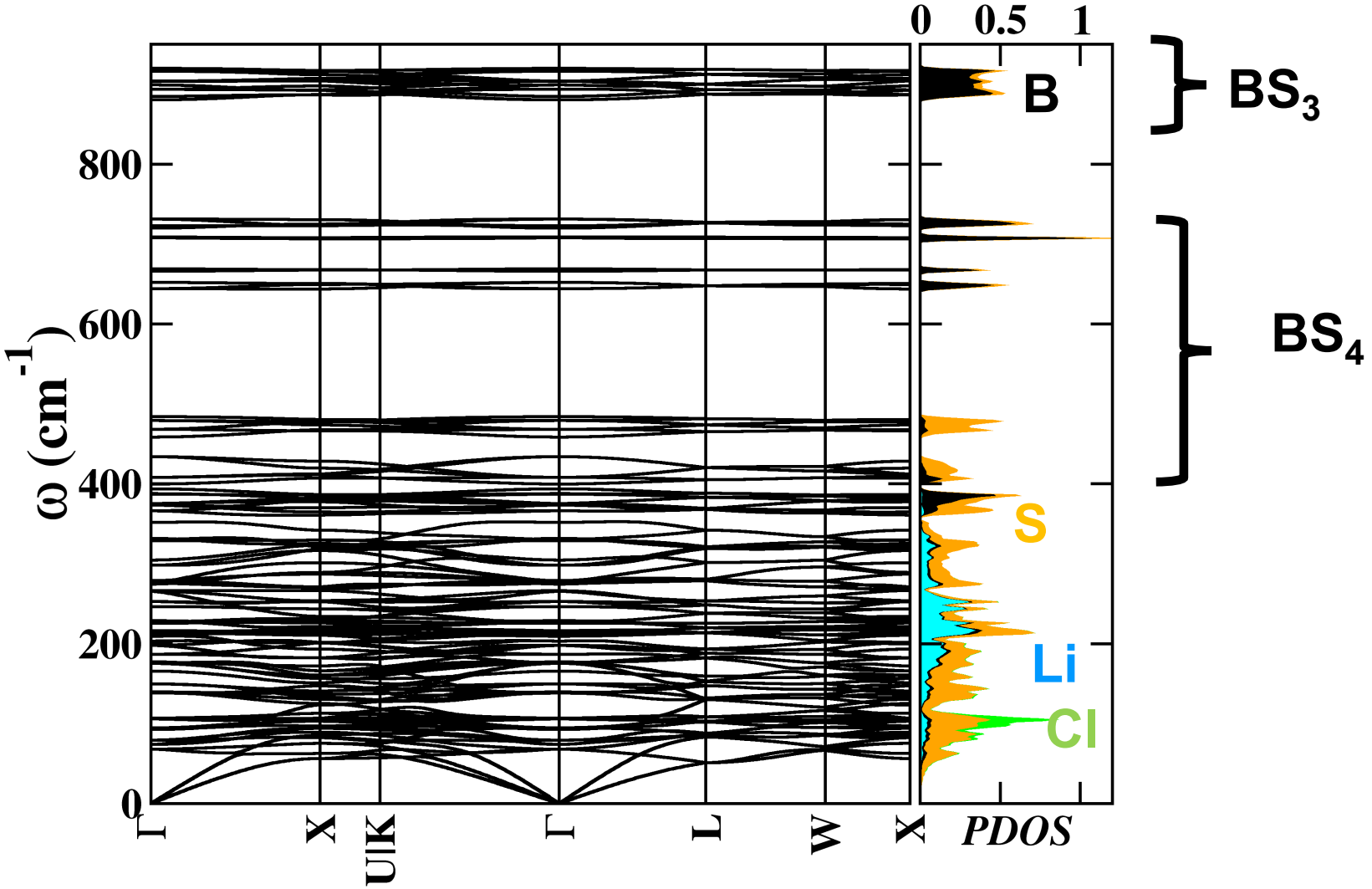


hR (√3 *a* < √2 *c*):
Γ–*T*–H_2 | H_0–*L*–Γ–S_0 | S_2–*F*–Γ

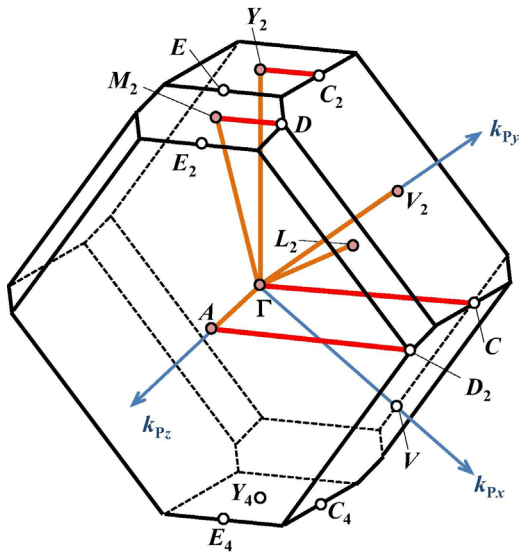


Some phonon band structures and densities of states $Li_4B_7S_{12}Cl$ *F-43c*

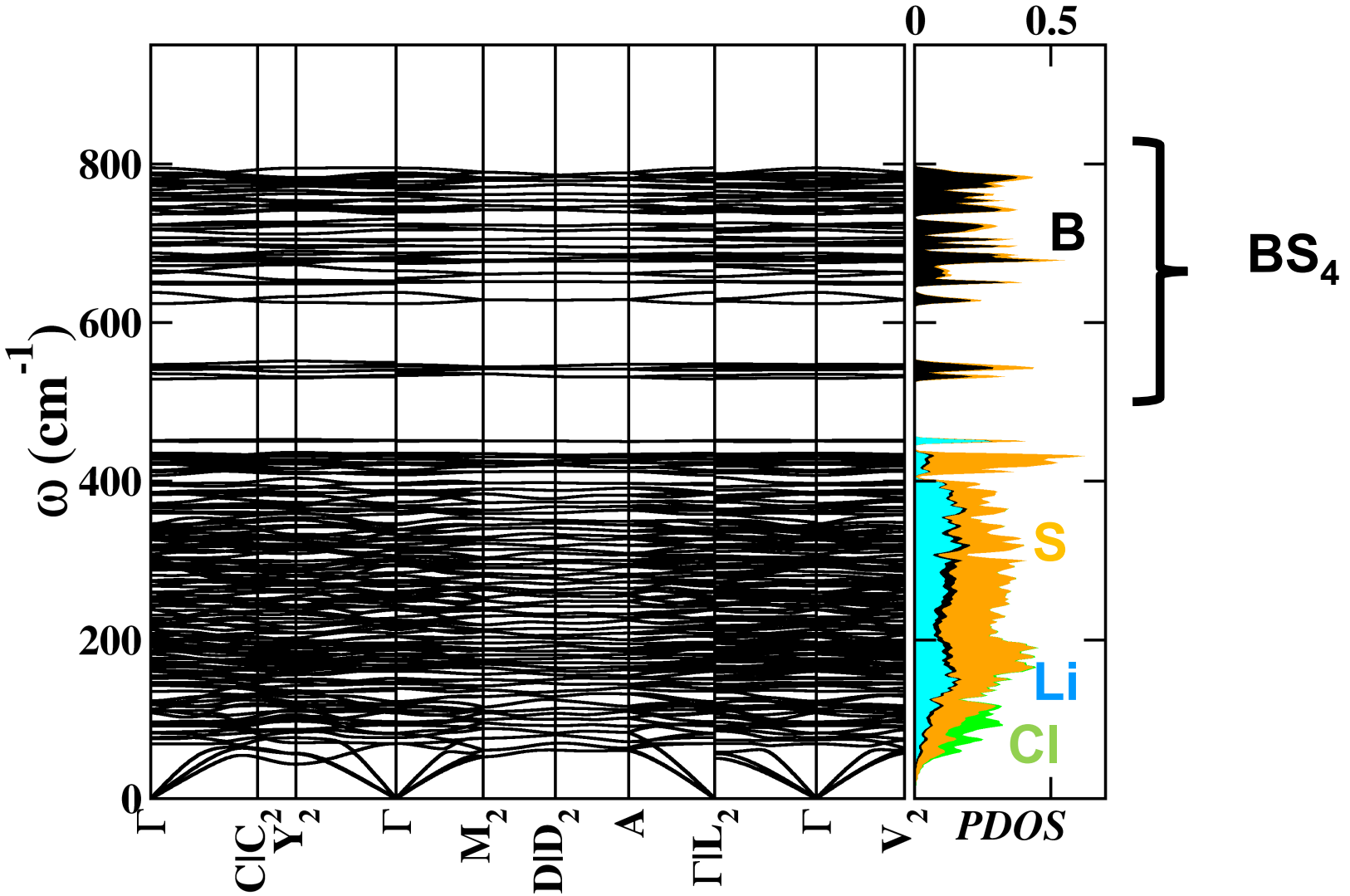




Some phonon band structures and densities of states $Li_6B_7S_{13}Cl$ *Cc*



mC (*b*<*a*sinβ):
Γ–*C* | C_2–Y_2–Γ–M_2–*D* | D_2–*A*–Γ | L_2–Γ–V_2



Helmholtz free energies with phonon contributions $F(T) \approx U_{SL} + F_{vib}(T)$

$$\Delta F(T) = F(T) - F_{ref}(T)$$

TABLE III. Summary of results for $\Delta F(T, V, \{N_i\})$ in units of eV/formula unit as estimated from Eqs. (25) and (26), referenced to the corresponding Li_4 boracite in its $R3c$ structure plus Li_2O or Li_2S, as appropriate, calculated at temperatures $T = 0$, 300, and 400 K.

Formula	SG	ΔF $T = 0$ K	ΔF $T = 300$ K	ΔF $T = 400$ K
$Li_4B_7O_{12}Cl$	$R3c$	0.00	0.00	0.00
$Li_6B_7O_{13}Cl$	$R3c$	−1.59	−1.53	−1.50
$Li_6B_7O_{13}Cl$	Cc	−1.27	−1.22	−1.20
$Li_4Al_3B_4O_{12}Cl$	$R3c$	0.00	0.00	0.00
$Li_6Al_3B_4O_{13}Cl$	$R3c$	−0.25	−0.20	−0.18
$Li_6Al_3B_4O_{13}Cl$	Cc	−0.42	−0.35	−0.32
$Li_4B_7S_{12}Cl$	$R3c$	0.00	0.00	0.00
$Li_4B_7S_{12}Cl$	$F\bar{4}3c$	−0.07	−0.09	−0.10
$Li_6B_7S_{13}Cl$	$R3c$	−0.96	−0.92	−0.89
$Li_6B_7S_{13}Cl$	Cc	−1.05	−0.99	−0.96
$Li_4Al_3B_4S_{12}Cl$	$R3c$	0.00	0.00	0.00
$Li_6Al_3B_4S_{13}Cl$	$R3c$	−0.33	−0.23	−0.19
$Li_6Al_3B_4S_{13}Cl$	Cc	−0.63	−0.52	−0.47

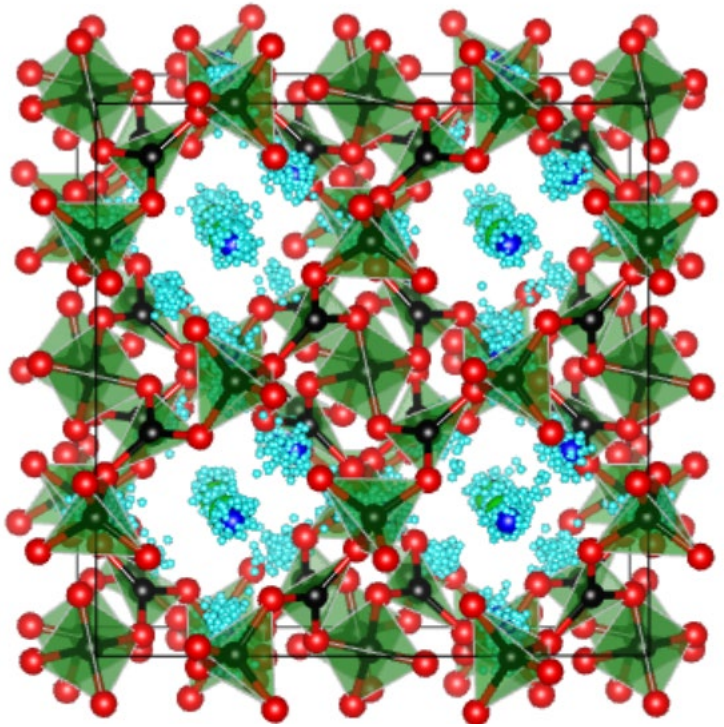
What about the ion conductivities of these materials

Preliminary results --

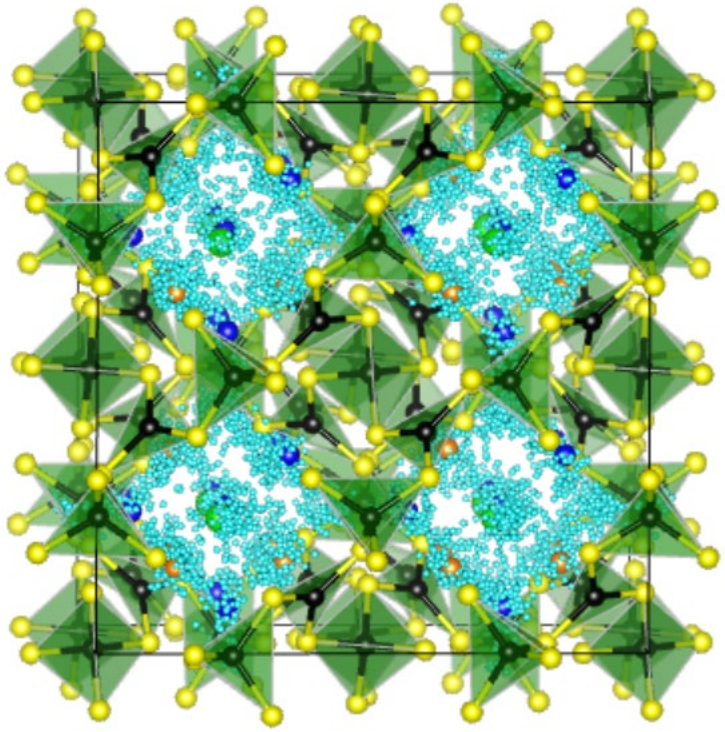
- **Qualitative indications of Li ion conductivity from molecular dynamics simulations – superposed images of Li positions at multiple time steps**

Qualitative indications of Li ion conductivity from molecular dynamics simulations

$Li_4B_7O_{12}Cl$ (*R3c*)



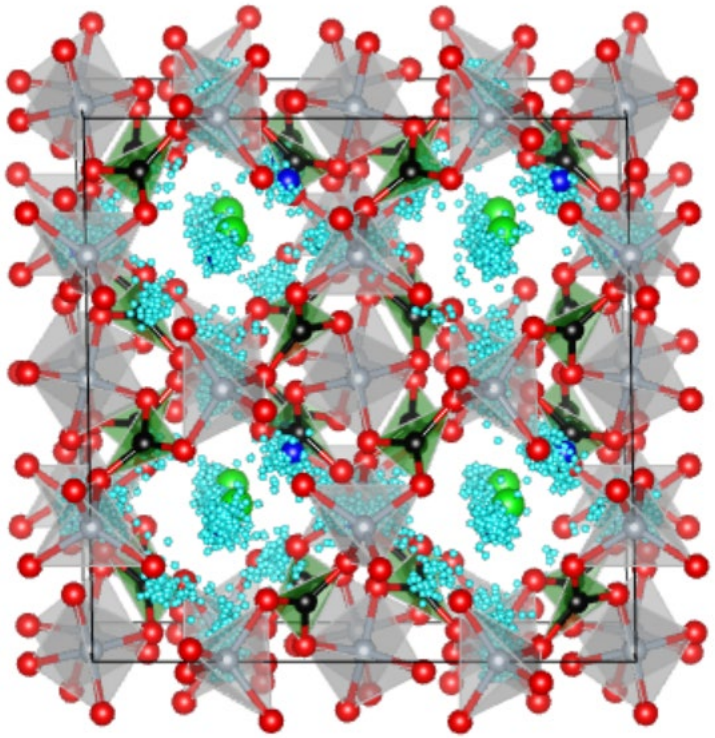
$Li_4B_7S_{12}Cl$ (*R3c*)



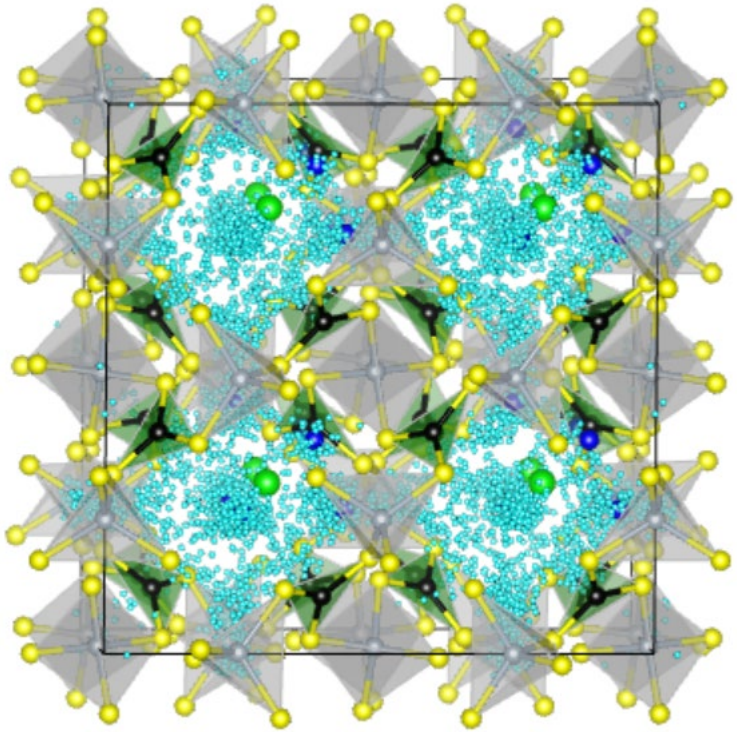
MD simulations at <*T*>=900K; approximately 200 images of Li ion positions within a 24 ps simulation, sampled each 0.12 ps.

Qualitative indications of Li ion conductivity from molecular dynamics simulations

$Li_4Al_3B_4O_{12}Cl$ (*R3c*)



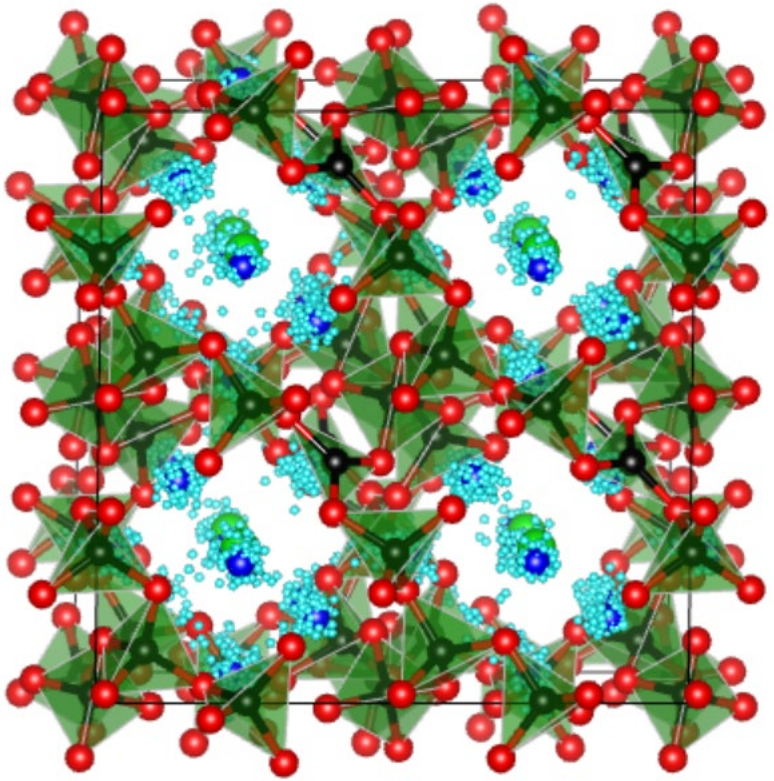
$Li_4Al_3B_4S_{12}Cl$ (*R3c*)



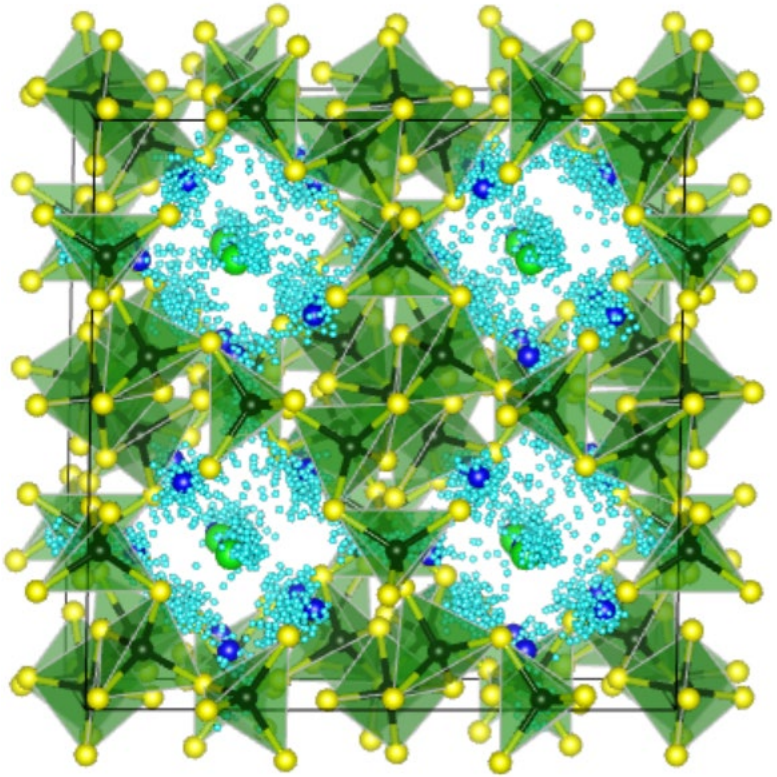
MD simulations at <*T*>=900K; approximately 200 images of Li ion positions within a 24 ps simulation, sampled each 0.12 ps.

Qualitative indications of Li ion conductivity from molecular dynamics simulations

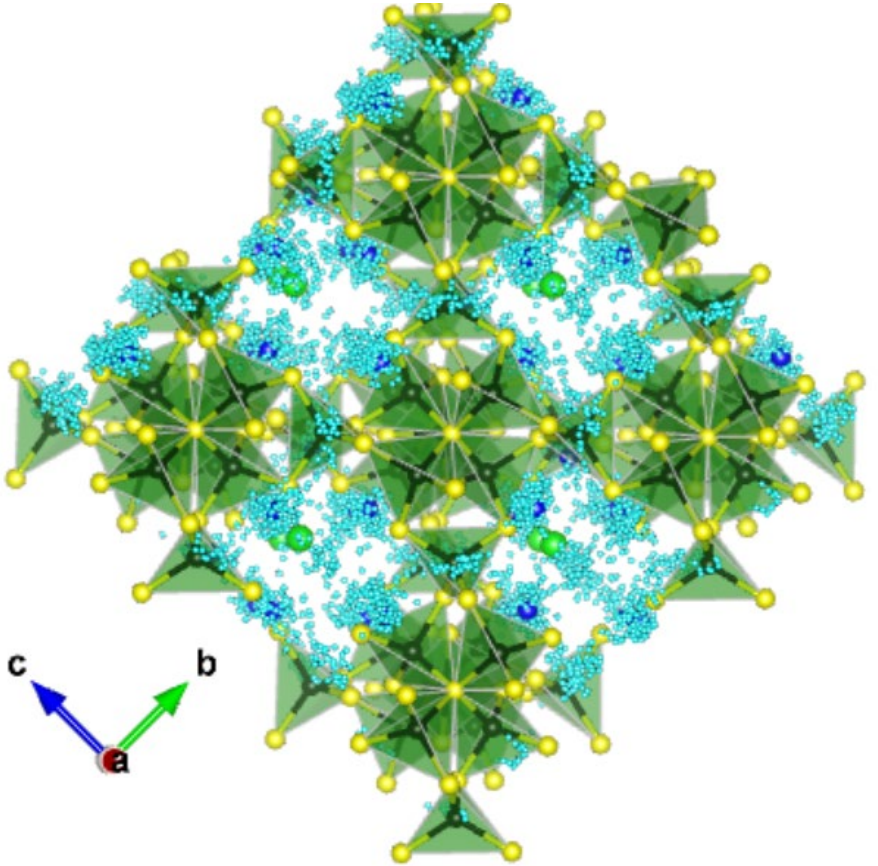
$Li_6B_7O_{13}Cl$ (*R3c*



$Li_6B_7S_{13}Cl$ (*R3c*)



$Li_6B_7S_{13}Cl$ (*Cc*)



MD simulations at <*T*>=900K; approximately 100 images of Li ion positions within a 5.4 ps simulation, sampled each 0.05 ps.

Ideas for consideration --

- There is a case for keeping all-solid-state batteries on the “table”
- Value in studying materials derived from natural minerals
- There is a lot to learn from studying the Li (thio)boracite family of materials
  - Framework + void structure; notion of “natural” interstitial sites
  - Some new materials have been predicted
- To do –
  - Realistic computation of Li ion conductivity
  - Model interfaces with Li metal anode
  - Opportunities for collaboration between theory and experiment

Acknowledge: NSF – DMR-1940324 and 2242959
-- WFU High Performance Computers

Thank you!