Computational Investigation of Li Boracite $Li_4B_7O_{12}Cl$ and Related Materials as Solid Electrolytes

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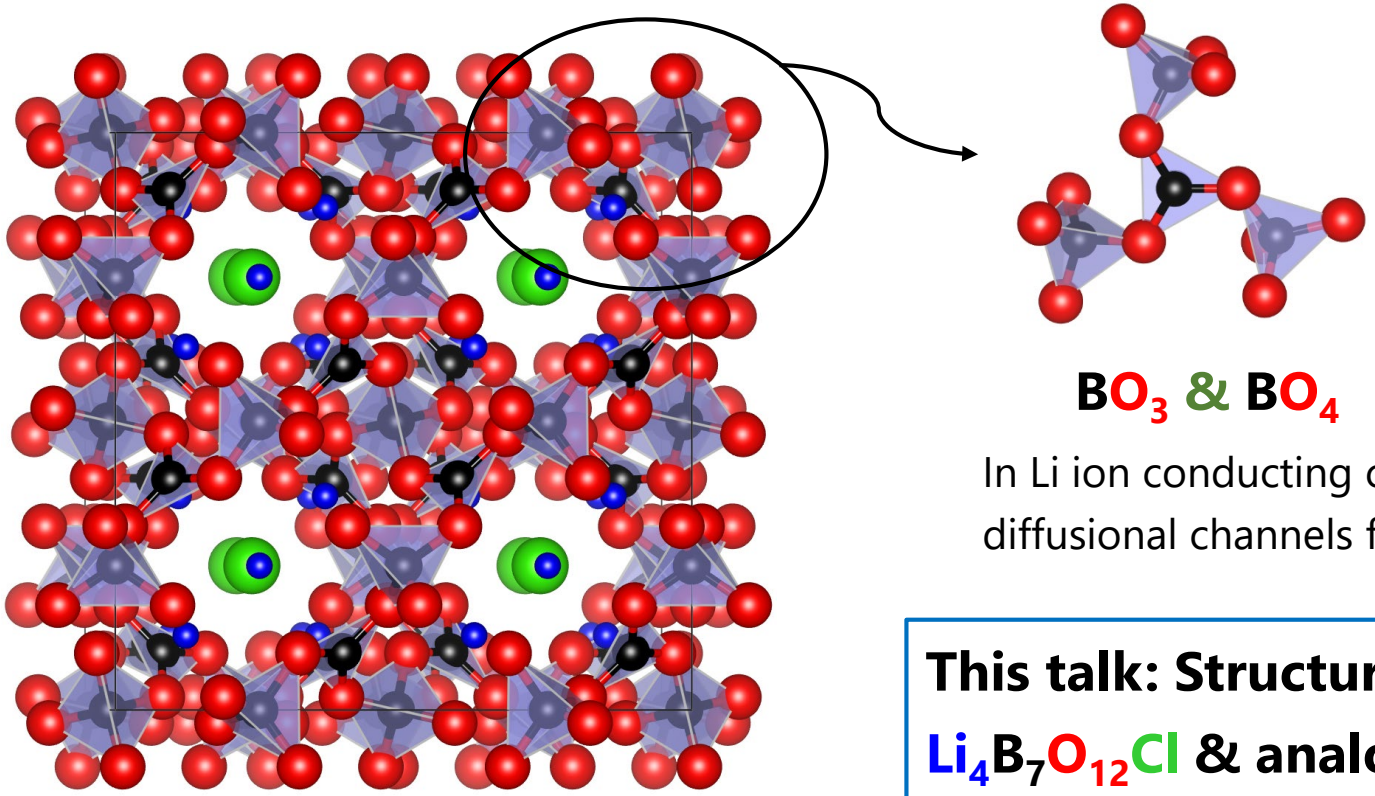
Li Boracites

Mineral boracites $\mathbf{M_3B_7O_{13}X}$, where M = Mg, Cr, Mn, Fe, Co, Ni, Zn or Cd, and X = Cl, Br or I

Li-containing boracites $\mathbf{Li_{4+x}B_7O_{12+x/2}X}$, where $0 \leq x \leq 1$, and X = Cl, Br or I



BO_3 & BO_4

In Li ion conducting compounds, the **Li** ions are arranged in diffusional channels formed by the $\mathbf{B_7O_{12}}$ framework.

This talk: Structural and electrolyte properties of $Li_4B_7O_{12}Cl$ & analogs obtained by ionic substitution

Summary of computation methods

- Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) with the modified Perdew-Burke-Ernzerhof generalized gradient approximation **(PBEsol GGA)**

  Perdew *et al.*, *PRL* **100**, 136406 (2008)

- The projector augmented wave (PAW) formalism with atomic datasets generated by **ATOMPAW** code available at http://pwpaw.wfu.edu

- First principles electronic-structure calculations and materials modeling

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

  https://www.abinit.org/

- Structural visualization, symmetry identification, X-ray patterns

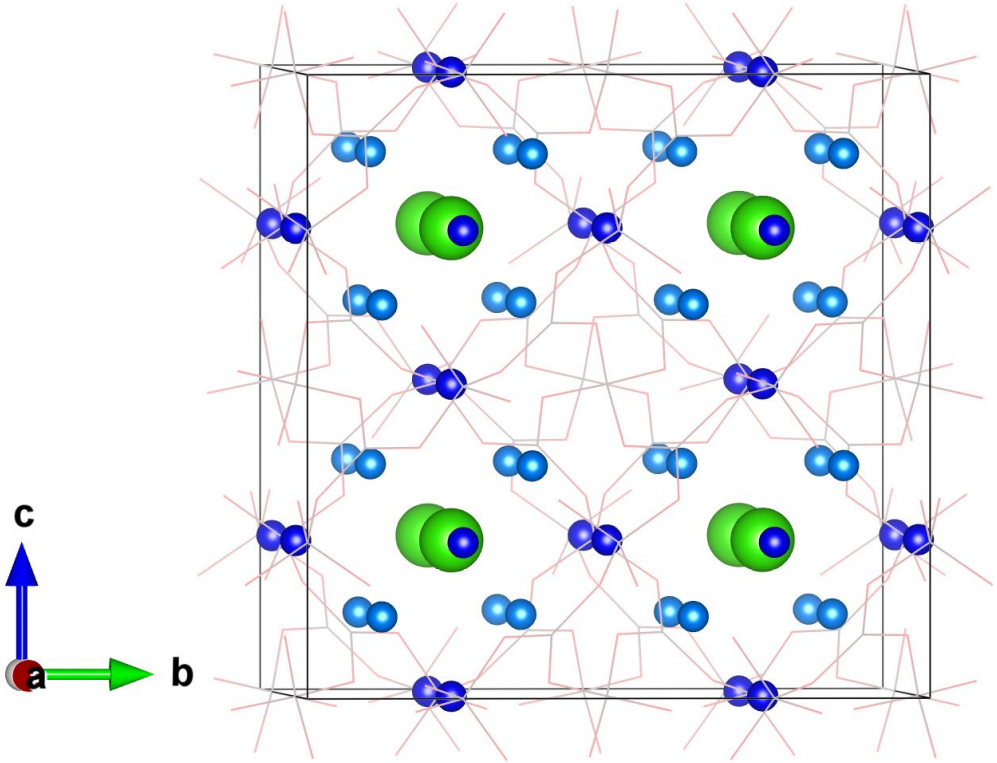
  https://jp-minerals.org/vesta/

  http://www.xcrysden.org/

  https://stokes.byu.edu/iso/findsym.php

  https://www.ccdc.cam.ac.uk/solutions/csd-core/components/mercury/

Reported structures of $Li_4B_7O_{12}Cl$ from 1977*



Ideal cubic model

8 formula units/cell

Three disordered phases

*Jeitschko *et al.*, *Acta Cryst.* B33, 2767-2775 (1977)

Above 348 K — **γ phase ($F\bar{4}3c$, No. 219)**
Li(24c): 93.7% occupied
Li(32e): 31.6% occupied

310 – 348 K — **β phase ($P\bar{4}3c$, No. 218)**
Ideal $F\bar{4}3c$ model
Li(24c): 96.7% occupied
Li(32e): 27.8% occupied

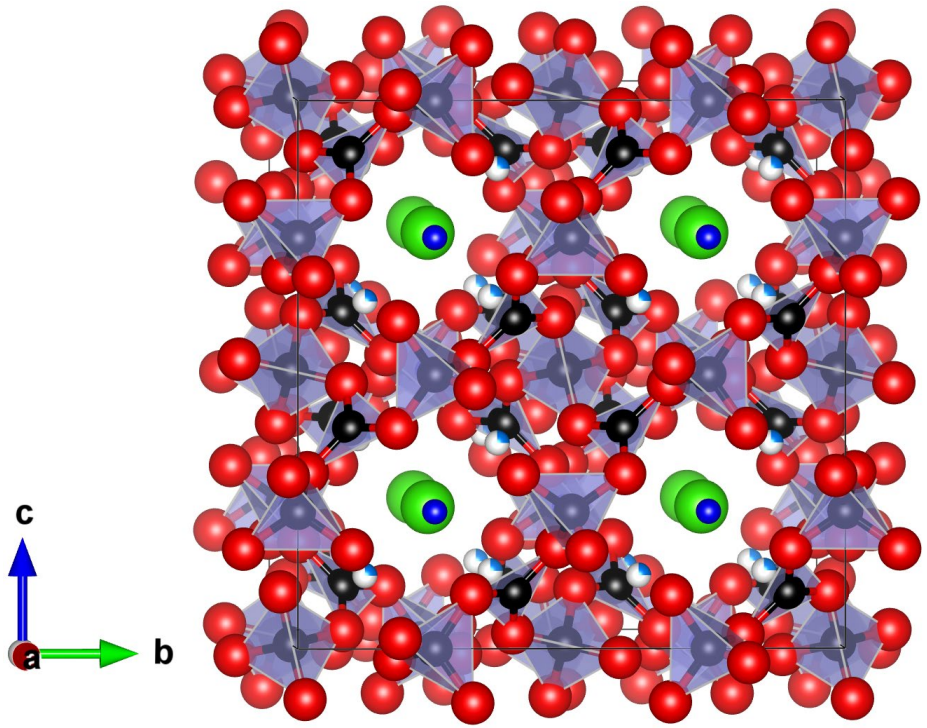
Room T — **α phase (Exp. R3, No. 146)**
Ideal $F\bar{4}3c$ model
Li(24c): 100% occupied
Li(32e): 25% occupied

* The real space groups of the α and β phases are subgroups of $F\bar{4}3c$.

** The atomic positions for both α and β phases are not known in experiment

Find the ground state structure for α-$Li_4B_7O_{12}Cl$

Li(24c) Li(32e) B O Cl

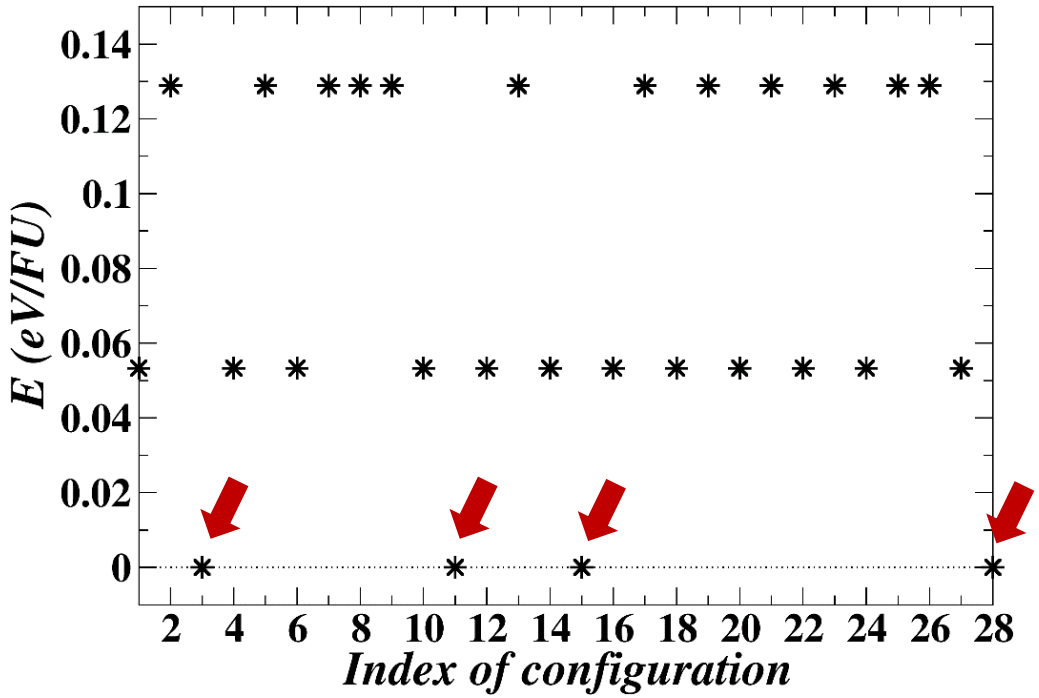


Cubic F$\bar{4}$3c model of the α phase

Li(24c): 100% occupied

Li(32e): 25% occupied

Perform geometry optimizations for 28 unique configurations in the primitive cell setting



The calculation finds four identical lowest-energy configurations with the **rhombohedral R3c (No. 161)** symmetry

α-$Li_4B_7O_{12}Cl$ in rhombohedral R3c structure

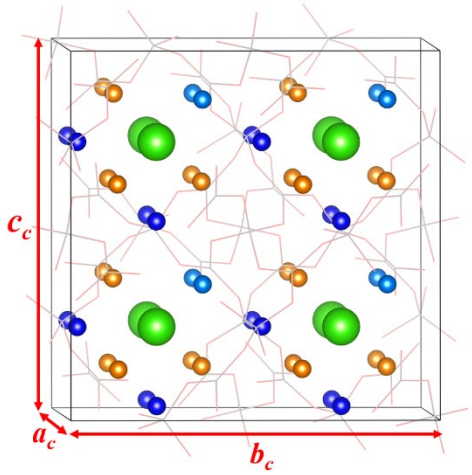
Host Li sites

B-O Wireframe

Native Li vacancies

Cl

Conventional cell
8 formula units



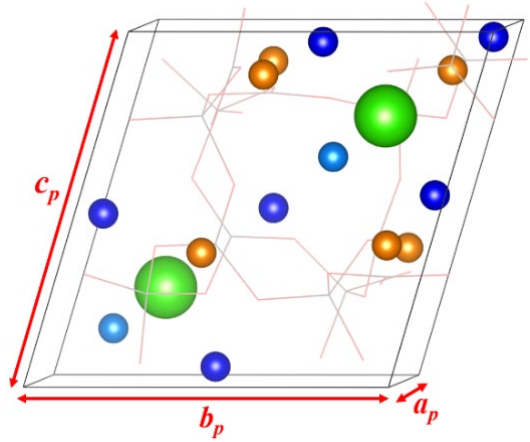
$a_c = b_c = c_c$ and $\alpha = \beta = \gamma = \theta_c \approx 90°$

$$\mathbf{a_c} = a_c(\hat{\mathbf{x}}(\lambda_c + 2\mu_c) + \hat{\mathbf{y}}(\lambda_c - \mu_c) + \hat{\mathbf{z}}(\lambda_c - \mu_c))$$
$$\mathbf{b}_c = a_c(\hat{\mathbf{x}}(\lambda_c - \mu_c) + \hat{\mathbf{y}}(\lambda_c + 2\mu_c) + \hat{\mathbf{z}}(\lambda_c - \mu_c))$$
$$\mathbf{c_c} = a_c(\hat{\mathbf{x}}(\lambda_c - \mu_c) + \hat{\mathbf{y}}(\lambda_c - \mu_c) + \hat{\mathbf{z}}(\lambda_c + 2\mu_c))$$

$$\lambda_c \equiv \frac{\sqrt{1 + 2\cos\theta_c}}{3} \text{ and } \mu_c \equiv \frac{\sqrt{1 - \cos\theta_c}}{3}$$

$$\cos(\theta_c) = \frac{2\cos(\theta_p) - 1}{3 - 2\cos(\theta_p)}$$

Face-centered primitive cell
2 formula units



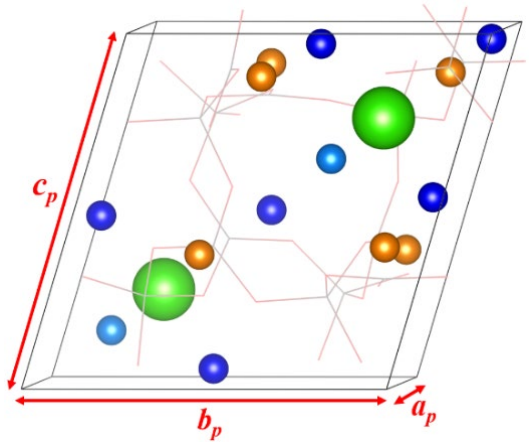
$a_p = b_p = c_p$ and $\alpha = \beta = \gamma = \theta_p \approx 60°$

$$\mathbf{a_p} = (\mathbf{a_c} + \mathbf{b_c})/2 = a_p(\hat{\mathbf{x}}(\lambda_p + \mu_p) + \hat{\mathbf{y}}(\lambda_p + \mu_p) + \hat{\mathbf{z}}(\lambda_p - 2\mu_p))$$
$$\mathbf{b_p} = (\mathbf{b_c} + \mathbf{c_c})/2 = a_p(\hat{\mathbf{x}}(\lambda_p - 2\mu_p) + \hat{\mathbf{y}}(\lambda_p + \mu_p) + \hat{\mathbf{z}}(\lambda_p + \mu_p))$$
$$\mathbf{c_p} = (\mathbf{a_c} + \mathbf{c_c})/2 = a_p(\hat{\mathbf{x}}(\lambda_p + \mu_p) + \hat{\mathbf{y}}(\lambda_p - 2\mu_p) + \hat{\mathbf{z}}(\lambda_p + \mu_p))$$

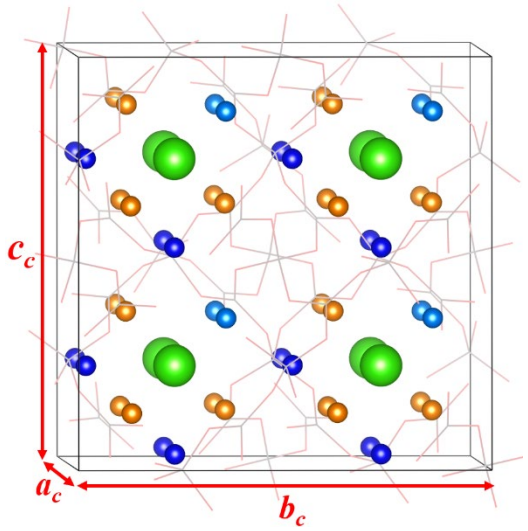
$$\lambda_p \equiv \frac{\sqrt{1 + 2\cos\theta_p}}{3} \text{ and } \mu_p \equiv \frac{\sqrt{1 - \cos\theta_p}}{3} \text{ and } a_p = \frac{a_c}{\sqrt{3 - 2\cos(\theta_p)}}$$

$$\cos(\theta_p) = \frac{1 + 3\cos(\theta_c)}{2(1 + \cos(\theta_c))}$$

α-$Li_4B_7O_{12}Cl$ in rhombohedral R3c structure



Primitive cell model



Conventional cell model

Lattice parameters and Li ion fractional coordinates for the R3c structure of α-$Li_4B_7O_{12}Cl$, comparing calculated results with the experimental measurements.

$Li_4B_7O_{12}Cl$	a = b = c (Å)	α= β = γ (deg)
Cal. R3c	12.137	90.108
Exp.* R3	12.141	90.084
Exp.* F$\bar{4}$3c model	12.141	90.000

Cal. R3c				Exp. F$\bar{4}$3c model			
Atom	**Wyck**	**f(x, y, z) (conv.)**	**Occ.**	**Atom**	**Wyck**	**f(x, y, z)**	**Occ.**
Li(1)	4x6 b	(0.030, 0.245, 0.245)	1.00	Li(1)	24 c	(0.000, 0.250, 0.250)	1.00
Li(2)	4x2 a	(0.865, 0.865, 0.865)	1.00	Li(2)	32 e	(0.871, 0.871, 0.871)	0.25
Vac. Li	4x6 b	(0.633, 0.635, 0.873)	0.00				

Host Li sites

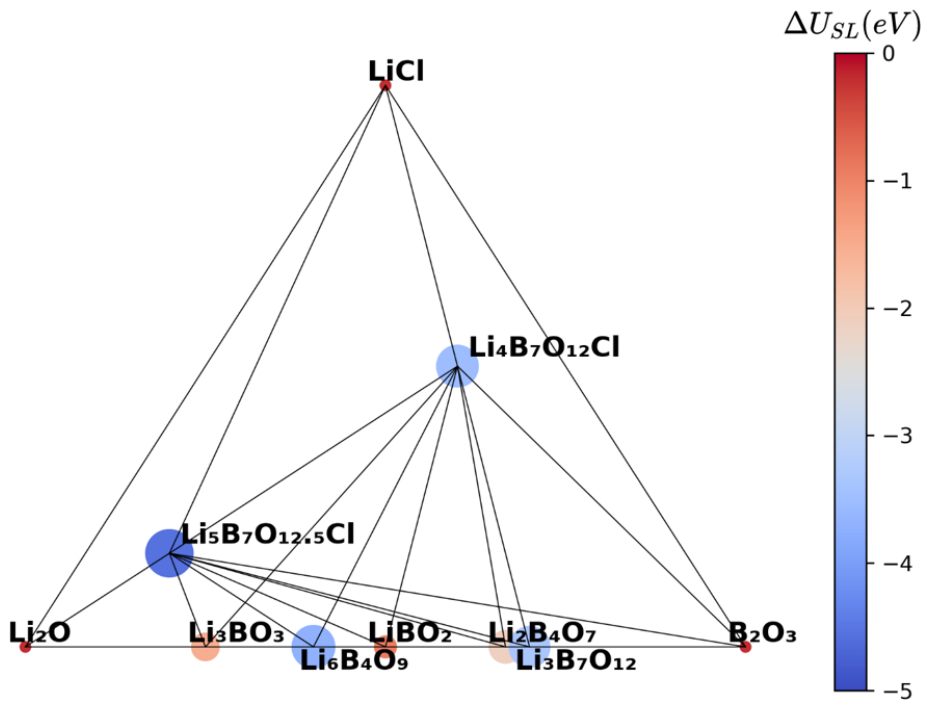
Native Li vacancies

B-O Wireframe

Cl

*Experimental data taken from Jeitschko *et al.*, *Acta Cryst.* B. **33**, 2767-2775 (1977)

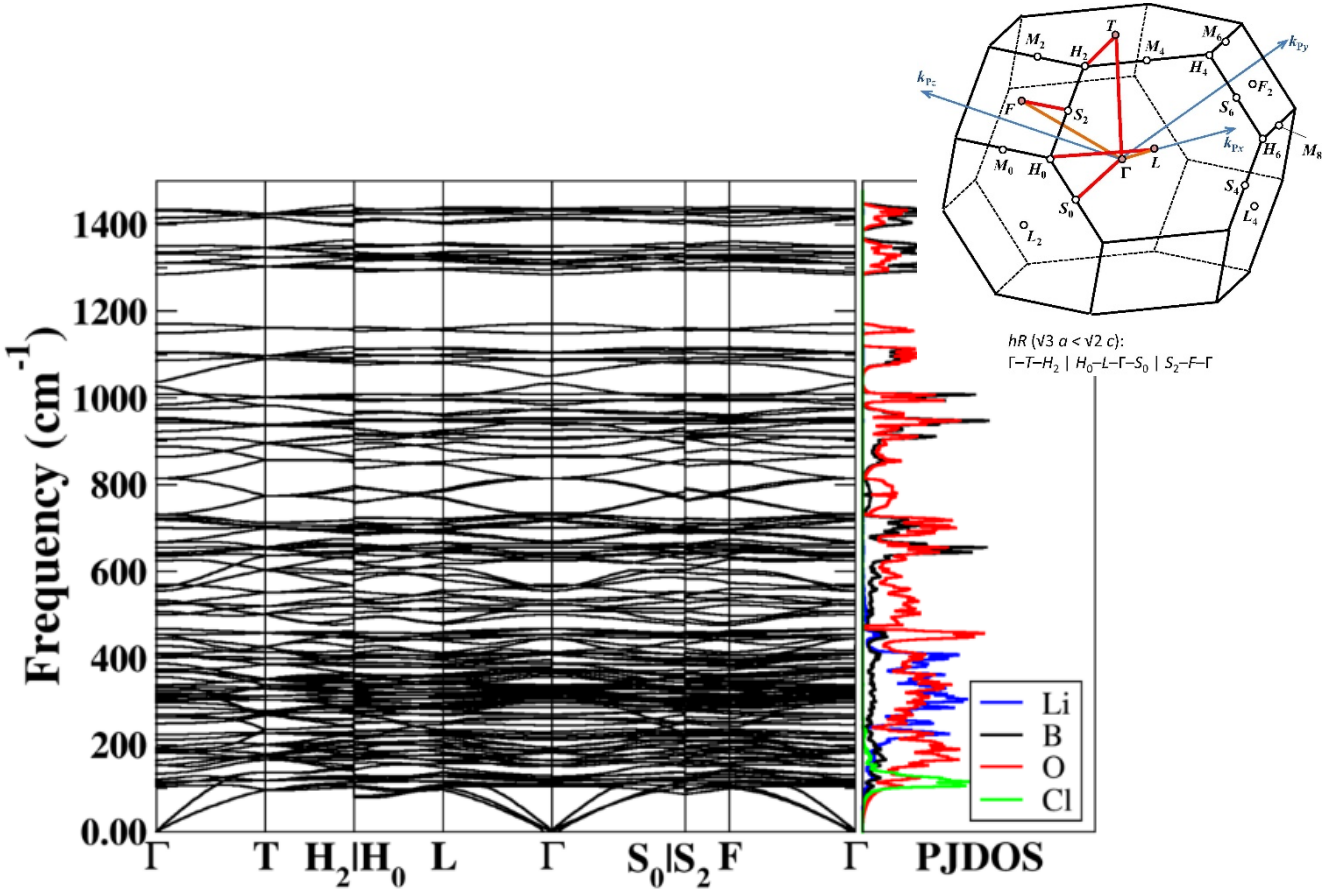
Phase stability of α-$Li_4B_7O_{12}Cl$



Li_2O-B_2O_3-LiCl phase diagram at 0 K and 0 atm

Reaction energy: $\Delta U_{SL} = U_{SL} - \sum x_i U_{SL}^i$

Where U_{SL} is the total static energy per formula unit of a specific compound. x_i with i = Li_2O, B_2O_3, and LiCl represents the compositional ratio of each reference phase for which the total static energy per formula unit is denoted by U_{SL}^i.

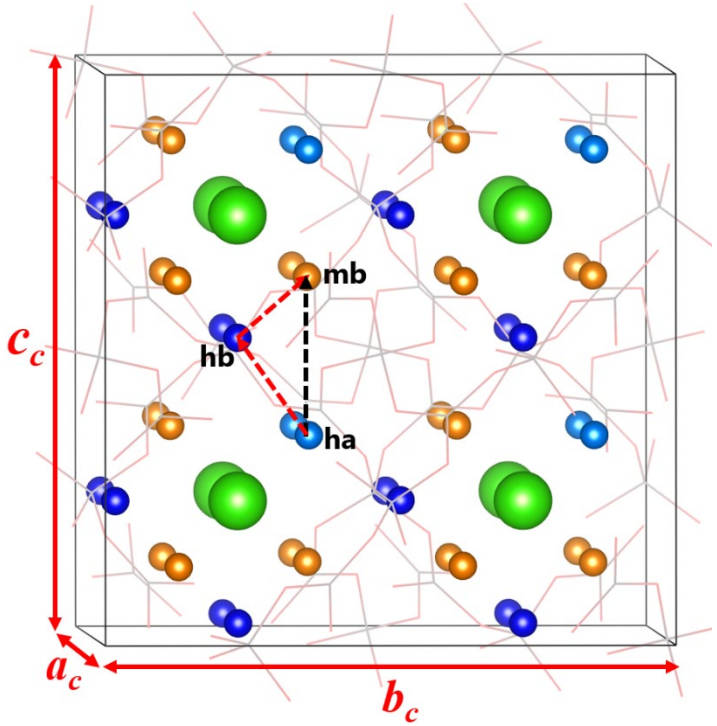


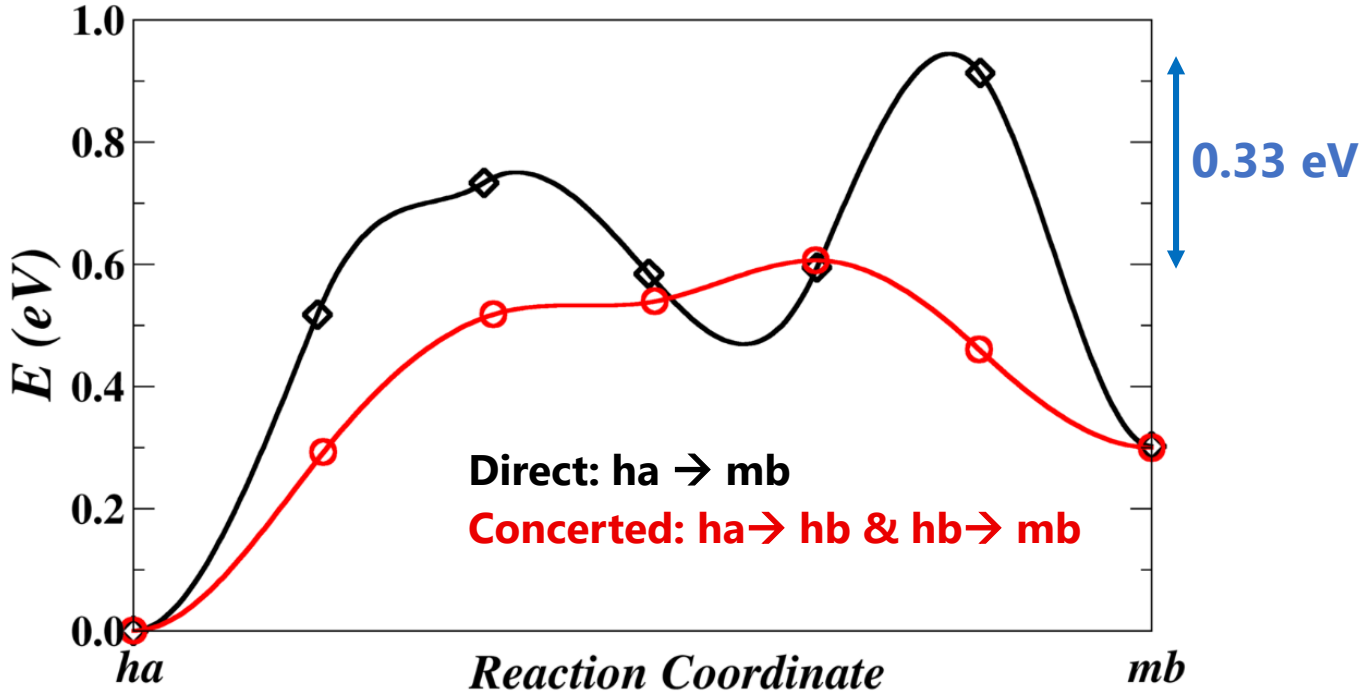
Phonon dispersion curves and projected density states of $Li_4B_7O_{12}Cl$ with frequencies ranging from 0 ~ 1440 cm^{-1}.

Brillouin zone diagram: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017). Note that the rhombohedral lattice is described by an equivalent hexagonal system.

Nudged Elastic Band (NEB) analysis for α-$Li_4B_7O_{12}Cl$

$E_{hb} < E_{ha} < E_{mb}$





hb: host b-type site; **ha:** host a-type site

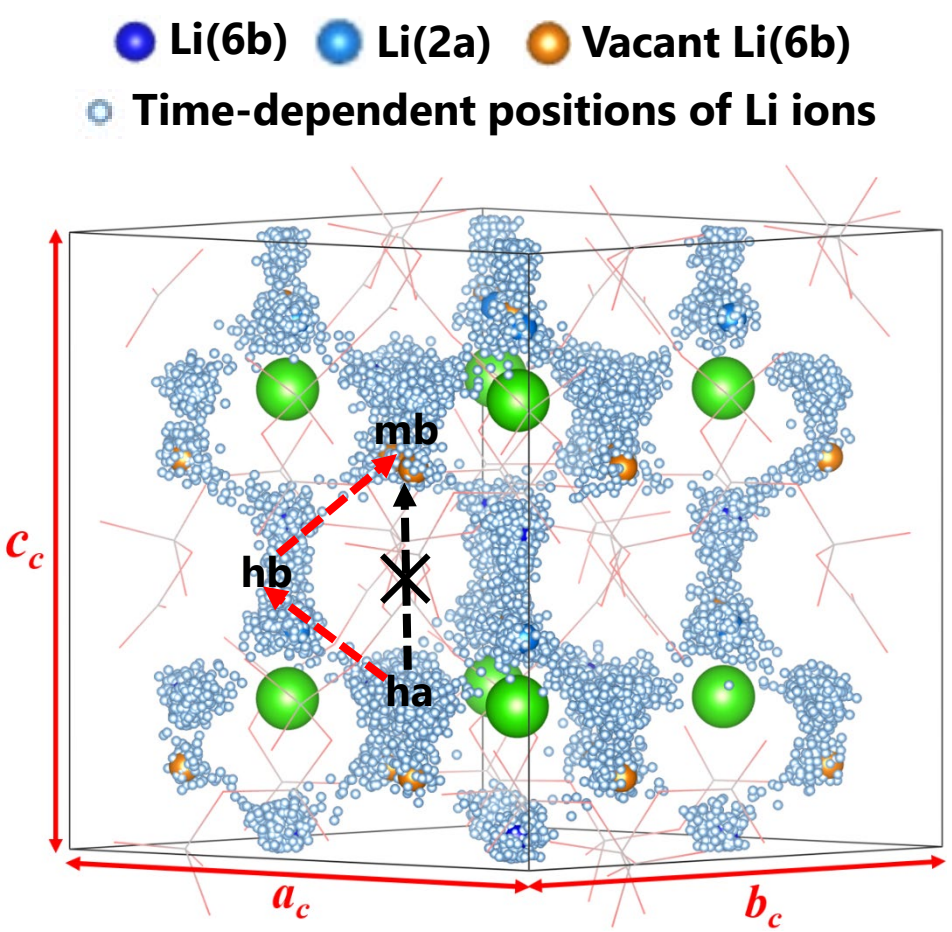
mb: metastable b-type site (native vacancy)

→ The concerted migration mechanism reduces the energy barrier for Li ion conduction in α-$Li_4B_7O_{12}Cl$.

NEB: [1]Jónsson et al., *in Classical and Quantum Dynamics in Condensed Phase Simulations*, World Scientific, Singapore (1998)

[2]Henkelman et al., *J. Chem. Phys.* **113**, 9901-9904 (2000)

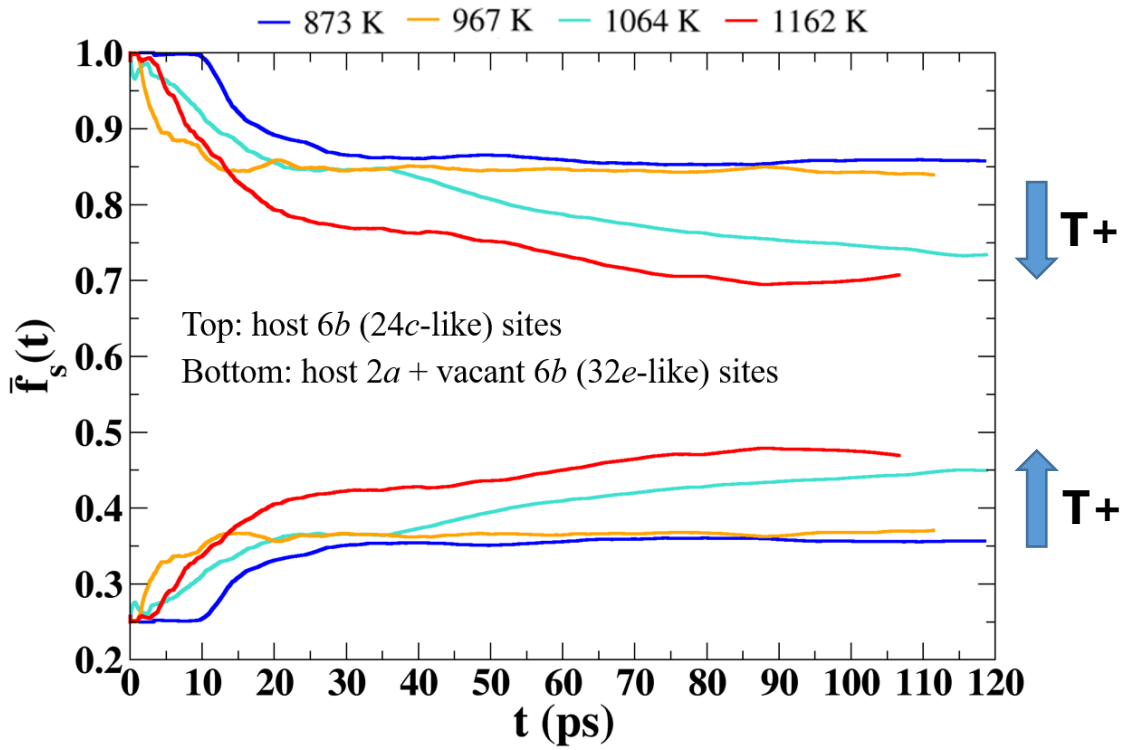
Results of molecular dynamic simulations



Model of $Li_4B_7O_{12}Cl$ crystal cell with superposed Li positions of molecular dynamics simulation at <T> = 1162 K.

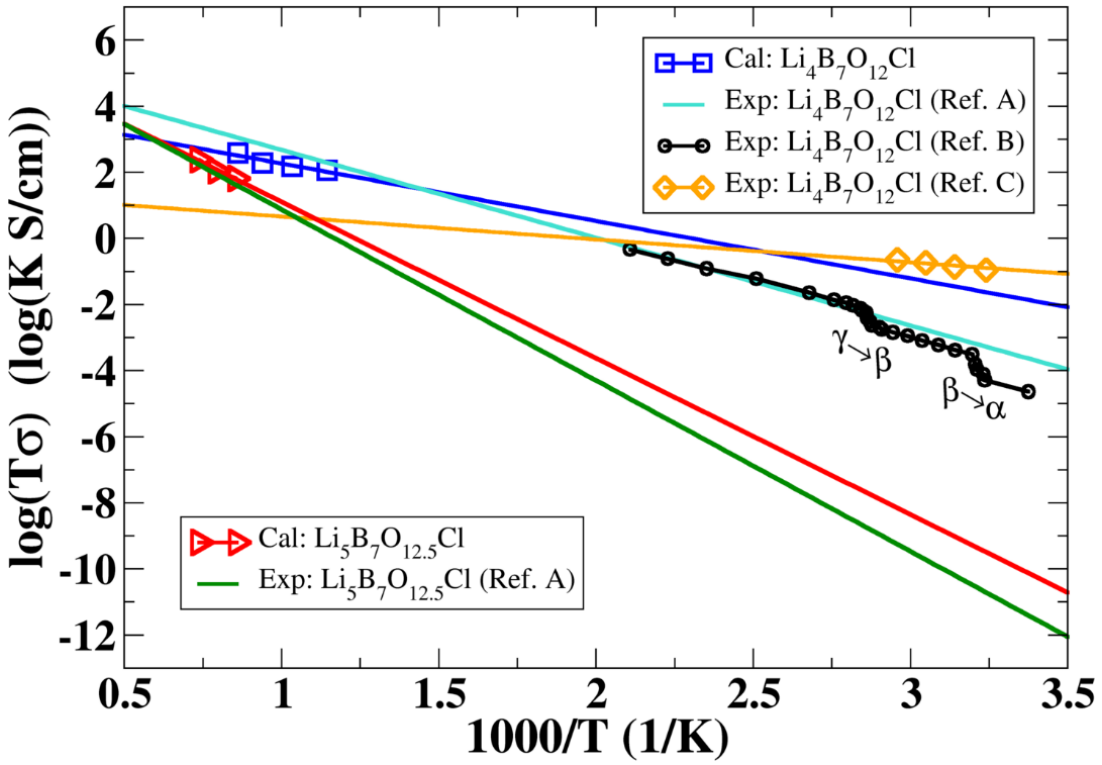
Site occupancy factor: $f_s(\mathrm{t}) = \frac{1}{N_s^{Li}} \sum_{i=1}^{N^{\mathrm{Li}}} n_s^i(t), i = 1, 2, \ldots, N^{\mathrm{Li}}$

Time-averaged: $\bar{f}_s(\mathrm{t}) = \frac{1}{t} \int_0^t f_s(t')dt'$



*Recall: the three reported forms **α (T< 310 K), β (310 K <T < 348 K), γ (T > 348 K)** mainly differ in lattice site occupancy.

Results of molecular dynamic simulations



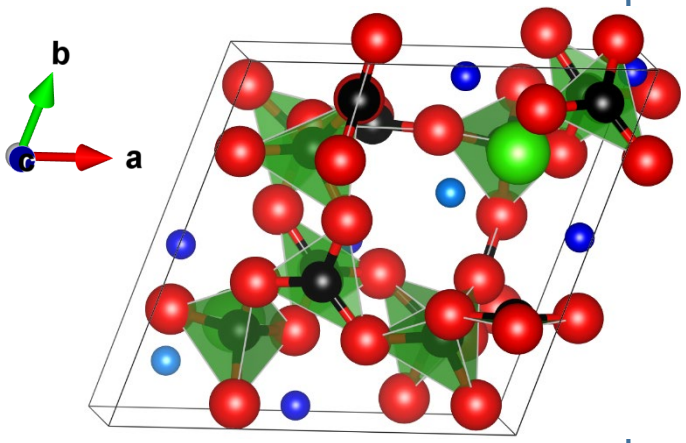
Materials	Analysis	Samples	E_a (eV)	σ (T = 300 K, S/cm)
$Li_4B_7O_{12}Cl$	Cal.	Ideal	0.34	3.83×10^{-4}
	Exp: Ref (A)	Polycrystalline	0.53	1.00×10^{-7}
	Exp: Ref (B)	Single crystal	0.49	0.98×10^{-7}
	Exp: Ref (C)	Polycrystalline	0.14	3.68×10^{-4}
$Li_5B_7O_{12.5}Cl$*	Cal.	Ideal	0.84	6.58×10^{-12}
	Exp: Ref (A)	Polycrystalline	1.03	2.14×10^{-14}

$$\sigma(T) = \rho q^2 \frac{D_{tr}(T)}{k_B T H_r} \quad \text{with} \quad H_r = 1,\ D_{tr}(T) = D_0 e^{-E_a^{\mathrm{MD}}/k_B T}$$

*$Li_5B_7O_{12.5}Cl$ has a similar B-O framework with $Li_4B_7O_{12}Cl$ but a different ordering of Li ions.

Ref. A: Cales *et al., Solid State Commun.* **24**, 323 (1977)
Ref. B: Jeitschko *et al., Acta Cryst.* B. **33**, 2767-2775 (1977)
Ref. C: Tan *et al., ACS Appl. Energy Mater.* **2**, 5140 (2019).

Ionic substitutions in α-$Li_4B_7O_{12}Cl$



$Li_4B_7O_{12}Cl$

Original material

Rhombohedral R3c

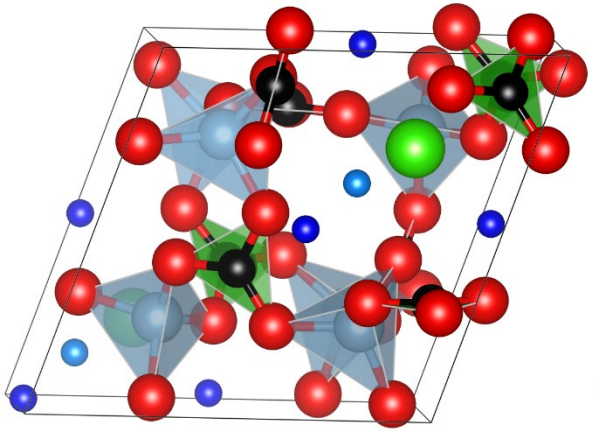
$a_p = b_p = c_p = 8.574$ Å

$\alpha_p = \beta_p = \gamma_p = 60.124°$

$a_c = b_c = c_c = 12.137$ Å

$\alpha_c = \beta_c = \gamma_c = 90.108°$

B(1) → Al



$Li_4Al_3B_4O_{12}Cl$

Realized in experiment*

Rhombohedral R3c

$a_p = b_p = c_p = 9.133$ Å

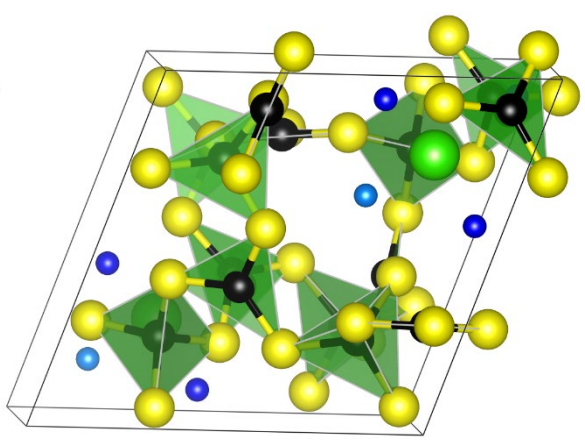
$\alpha_p = \beta_p = \gamma_p = 61.194°$

$a_c = b_c = c_c = 13.033$ Å

$\alpha_c = \beta_c = \gamma_c = 91.022°$

*Kajihara *et al.*, *Bull. Chem. Soc. Jpn.* **90**, 1279–1286 (2017)

O → S



$Li_4B_7S_{12}Cl$

Predicted in this work

Rhombohedral R3c

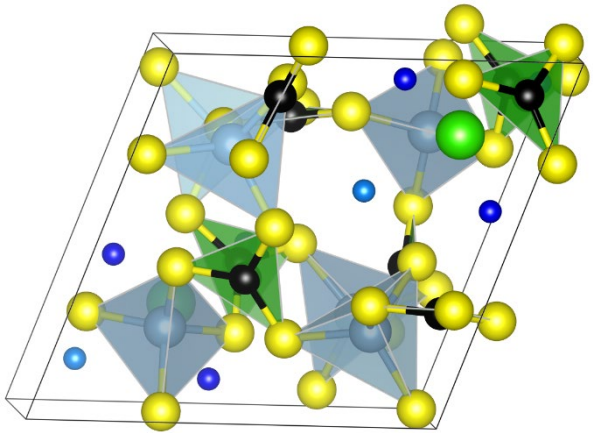
$a_p = b_p = c_p = 10.584$ Å

$\alpha_p = \beta_p = \gamma_p = 59.704°$

$a_c = b_c = c_c = 14.934$ Å

$\alpha_c = \beta_c = \gamma_c = 89.743°$

B(1) → Al & O → S



$Li_4Al_3B_4S_{12}Cl$

Predicted in this work

Rhombohedral R3c

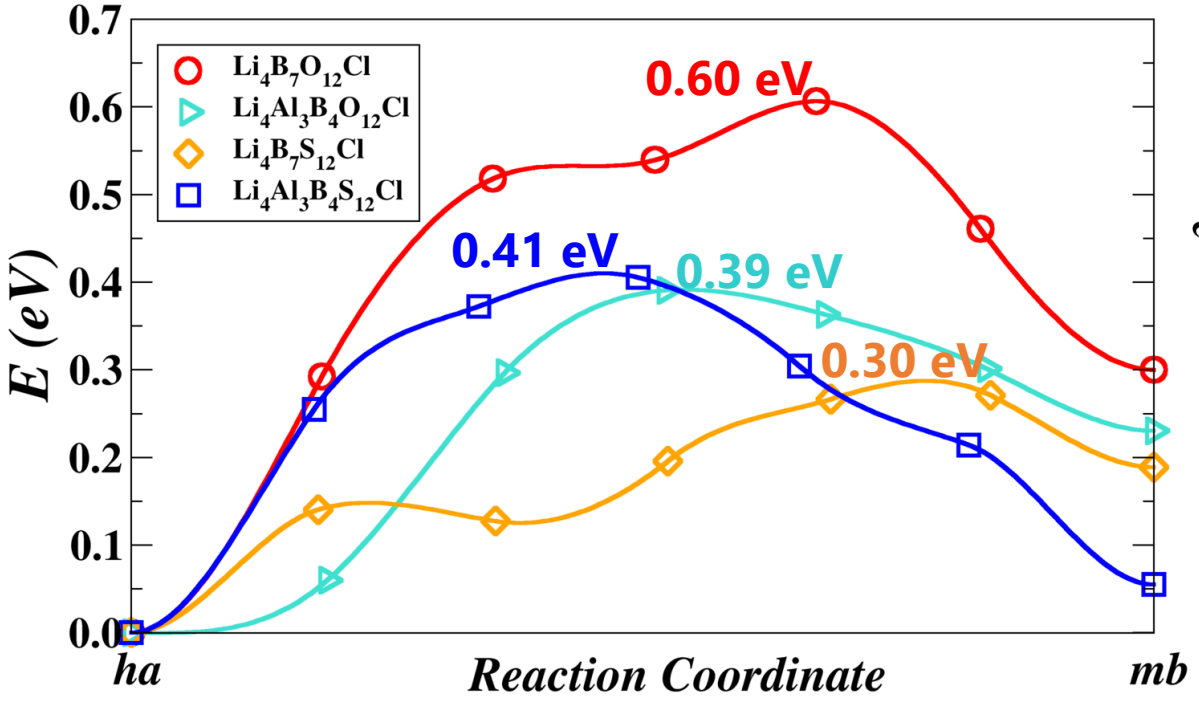
$a_p = b_p = c_p = 11.386$ Å

$\alpha_p = \beta_p = \gamma_p = 68.601°$

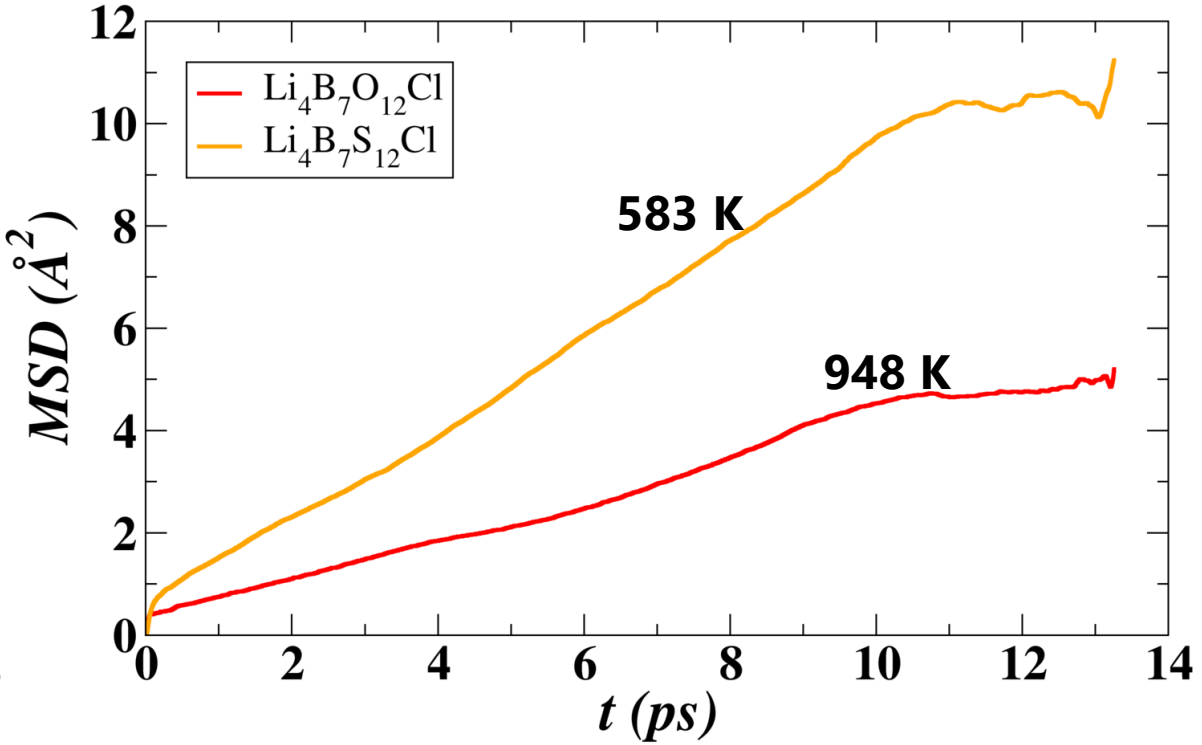
$a_c = b_c = c_c = 15.933$ Å

$\alpha_c = \beta_c = \gamma_c = 88.771°$

Comparison of diffusional properties



NEB energy diagram of concerted migrations



Mean squared displacement (MSD) vs. time interval

Are the analog compounds stable?

$Li_4Al_3B_4O_{12}Cl$

Kajihara *et al.*, *Bull. Chem. Soc. Jpn.* **90**, 1279–1286 (2017)

$$Li_4Al_3B_4O_{12}Cl \rightarrow 1/2\ Li_4B_7O_{12}Cl + 1/2\ LiB + 1/2\ LiClO_4 + LiAlO_2 + 2\ AlO - 14.29\ eV$$

$$Li_4Al_3B_4O_{12}Cl \rightarrow 1/2\ Li_4B_7O_{12}Cl + 1/2\ Al_5BO_9 + 1/2\ AlClO + Li_2O - 0.8\ eV$$

$Li_4B_7S_{12}Cl$ (proposed)

$$Li_4B_7S_{12}Cl \rightarrow 3\ Li + 7\ B + 12\ S + LiCl - 14.38\ eV$$

$$Li_4B_7S_{12}Cl \rightarrow Li_3BS_3 + 3\ B_2S_3 + LiCl + 0.46\ eV$$

$Li_4Al_3B_4S_{12}Cl$ (proposed)

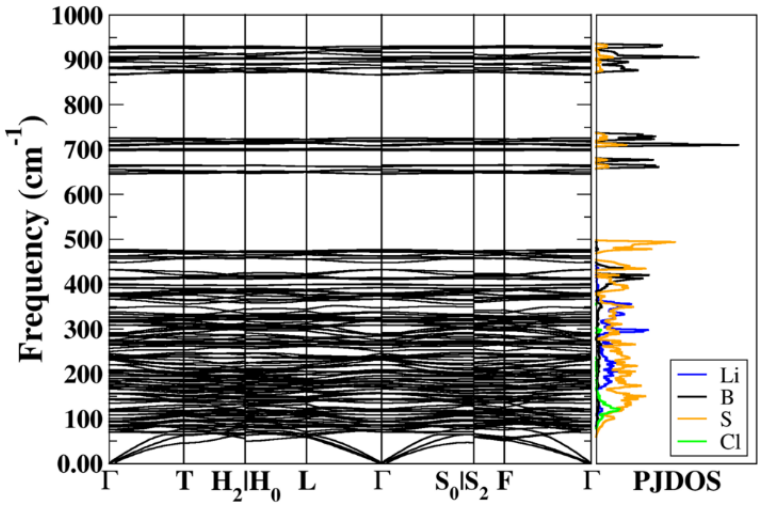
$$Li_4Al_3B_4S_{12}Cl \rightarrow 3\ Li + 3\ Al + 4\ B + 12\ S + LiCl - 18.35\ eV$$

$$Li_4Al_3B_4S_{12}Cl \rightarrow 3/2\ Li_2S + 3/2\ Al_2S_3 + 2\ B_2S_3 + LiCl + 0.87\ eV$$

Phonon calculations

Predicated

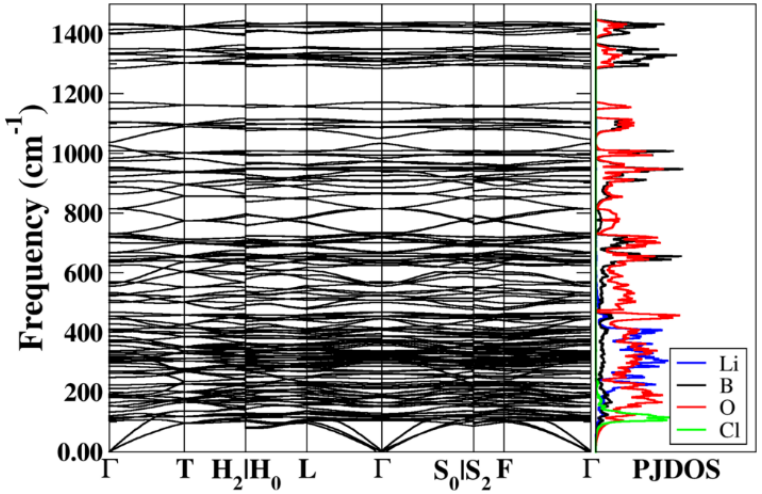
$Li_4B_7S_{12}Cl$



0 cm^{-1} ≤ ω(q) ≤ 931 cm^{-1}

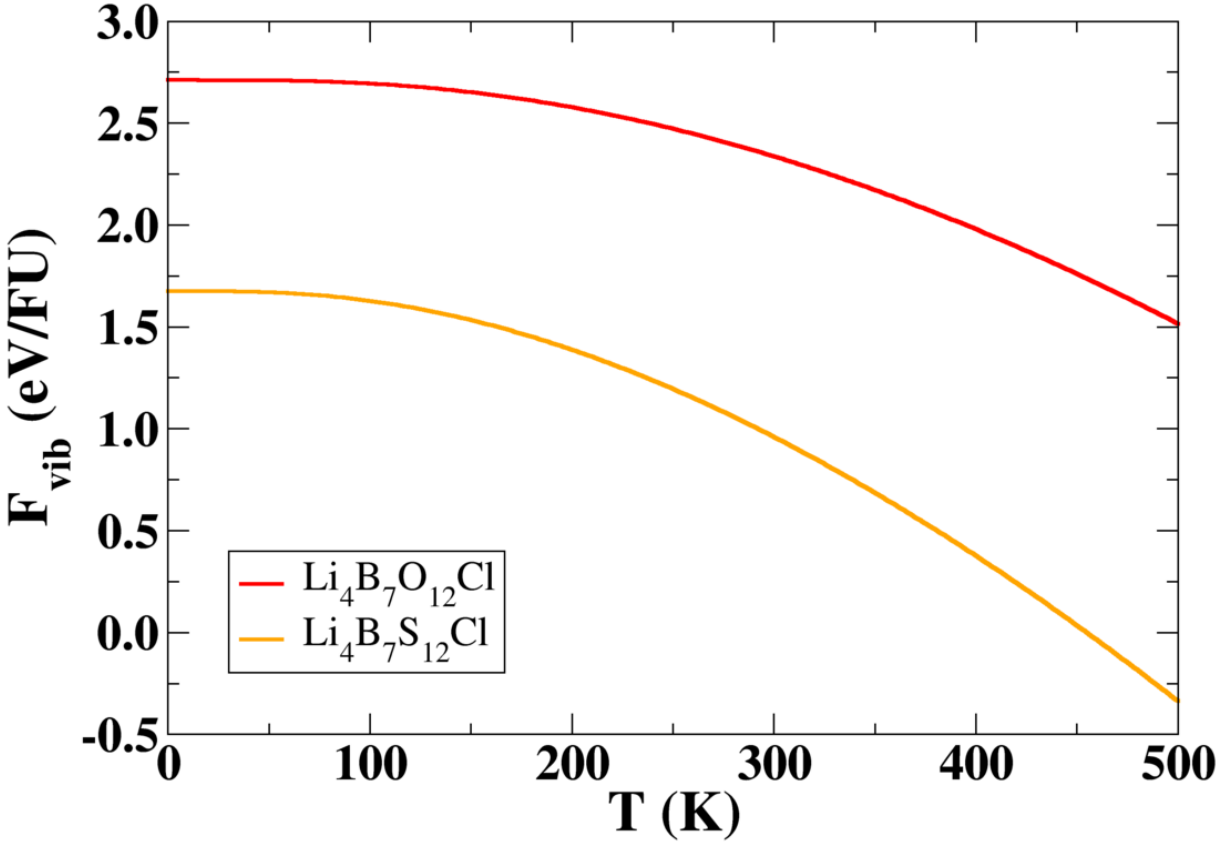
Known

$Li_4B_7O_{12}Cl$



0 cm^{-1} ≤ ω(q) ≤ 1440 cm^{-1}

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



ΔF_{vib} (T = 300 K) = 1.38 eV/FU

Summary

- The ground state structure of the room-temperature form of $Li_4B_7O_{12}Cl$ is identified to have rhombohedral R3c symmetry. The phase is estimated to be stable from the analysis of the convex hull approach and of the phonon spectrum.
- The NEB calculations indicate that Li ion migration in $Li_4B_7O_{12}Cl$ most likely proceeds via concerted migration mechanisms involving two host sites and one natural vacancy.
- The room-temperature ionic conductivity of $Li_4B_7O_{12}Cl$, calculated from the MD simulation results, is on the order of 10^{-4} S/cm, which is in good agreement with the recent experiment measurement for pure polycrystalline samples.
- Consistent with the recent experimental results, our preliminary calculations also find reduced Li ion migration barriers in the partially B-replaced compound $Li_4Al_3B_4O_{12}Cl$. The studies on predicted compounds $Li_4B_7S_{12}Cl$ and $Li_4Al_3B_4S_{12}Cl$ also suggest improved Li ion conducting performance compared with $Li_4B_7O_{12}Cl$.
- The chemical stabilities of the $Li_4B_7S_{12}Cl$ and $Li_4Al_3B_4S_{12}Cl$ need further investigation.