

# Computational (re)investigation of the structural and electrolyte properties of $\text{Li}_4\text{P}_2\text{S}_6$ , $\text{Na}_4\text{P}_2\text{S}_6$ , and $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$

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# Outline

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- ❑ Motivations
- ❑ Computational methods
- ❑ Structures and stabilities of  $\text{Na}_4\text{P}_2\text{S}_6$  and  $\text{Li}_4\text{P}_2\text{S}_6$
- ❑ Structures and stabilities of predicted  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$
- ❑ Comparison of electrolyte properties
- ❑ Summary and conclusions

# Motivations

- Kuhn et al.<sup>1</sup> observed that  $\text{Na}_4\text{P}_2\text{S}_6$  crystallizes to form monoclinic space group **C2/m (#12)**
- Computational results of Rush et al.<sup>2</sup>: **Kuhn structure is meta-stable**
- Recent experimental results of Hood et al.<sup>3</sup> also find the **C2/m** structure



**Reexamine previous calculations to understand the stability of the Kuhn structure**

- Using combined approach of NMR and X-ray, the new experimental analysis<sup>4</sup> on  $\text{Li}_4\text{P}_2\text{S}_6$  concludes the structure to be ordered with space group **P321 (#150)**
- Theoretically,  $\text{Na}_4\text{P}_2\text{S}_6$  and  $\text{Li}_4\text{P}_2\text{S}_6$  are chemically and structurally related



**Property similarities (discrepancies) between  $\text{Na}_4\text{P}_2\text{S}_6$  and  $\text{Li}_4\text{P}_2\text{S}_6$**

- Structure and stability of the mixed ion material  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$



**Material prediction**

- Performance of  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$  in comparison with  $\text{Na}_4\text{P}_2\text{S}_6$  as solid electrolytes



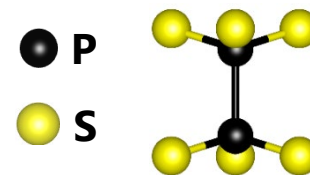
**Conductivity studies**

<sup>1</sup>Kuhn et al., *Z. Anorg. Allg. Chem.* **640**, 689-692 (2014)

<sup>2</sup>Rush et al., *Solid State Phys.* **286**, 45-50 (2016)

<sup>3</sup>Hood et al., Manuscript in preparation.

<sup>4</sup>Neuberger et al., *Dalton Trans.* **47**, 11691-11695 (2018)



$(\text{P}_2\text{S}_6)^{4-}$  with  $D_{3d}$  symmetry

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# Summary of Computational methods

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- ❑ Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) with the modified Perdew-Burke-Ernzerhof generalized gradient approximation<sup>1</sup> (**PBEsol GGA**)

*\*Previously reported results<sup>2</sup> obtained using Local-density approximation (LDA)*

- ❑ The projector augmented wave (PAW) formalism using ABINIT (<https://www.abinit.org>) & QUANTUM ESPRESSO (<http://www.quantum-espresso.org>)
- ❑ Datasets generated by ATOMPAW code available at <http://pwpaw.wfu.edu>
- ❑ Visualization software: XCrySDen, VESTA
- ❑ Space-group analysis: FINDSYM
- ❑ X-ray powder diffraction: Mercury

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<sup>1</sup>Perdew et al., *Phys. Rev. L.* **100**, 136406 (2008)

<sup>2</sup>Rush et al., *Solid State Phys.* **286**, 45-50 (2016)

# Outputs of DFT and DFPT

## Born-Oppenheimer approximation

### DFT

At equilibrium:  $\mathbf{F}_I = -\frac{\partial U(\{\mathbf{R}_I\})}{\partial \mathbf{R}_I} = 0$

- Optimized structural parameters
- Static lattice energy:  $U_{SL} = \min U(\{\mathbf{R}_I\})$
- Kohn-Sham orbitals and energies
- Migration related energies

### DFPT

Near equilibrium:  $M_s(\omega^\nu)^2 u_{s\alpha}^\nu(\mathbf{q}) = \sum_{t\beta} \tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) u_{t\beta}^\nu(\mathbf{q})$  and  $\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) \rightleftharpoons C_{st}^{\alpha\beta}(\mathbf{R})$

- Phonon frequencies and eigenvectors at any wavevector
- Phonon dispersions:  $\omega^\nu \sim \mathbf{q}$
- Phonon density of states (PDOS):  $g(\omega) = \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} \delta(\omega - \omega^\nu(\mathbf{q}))$
- Thermodynamic properties such as the vibrational energy:  $F_{vib}(T) = k_B T \int_0^\infty d\omega \ln \left( 2 \sinh \left( \frac{\hbar\omega}{2k_B T} \right) \right) g(\omega)$



The Helmholtz free energy:

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



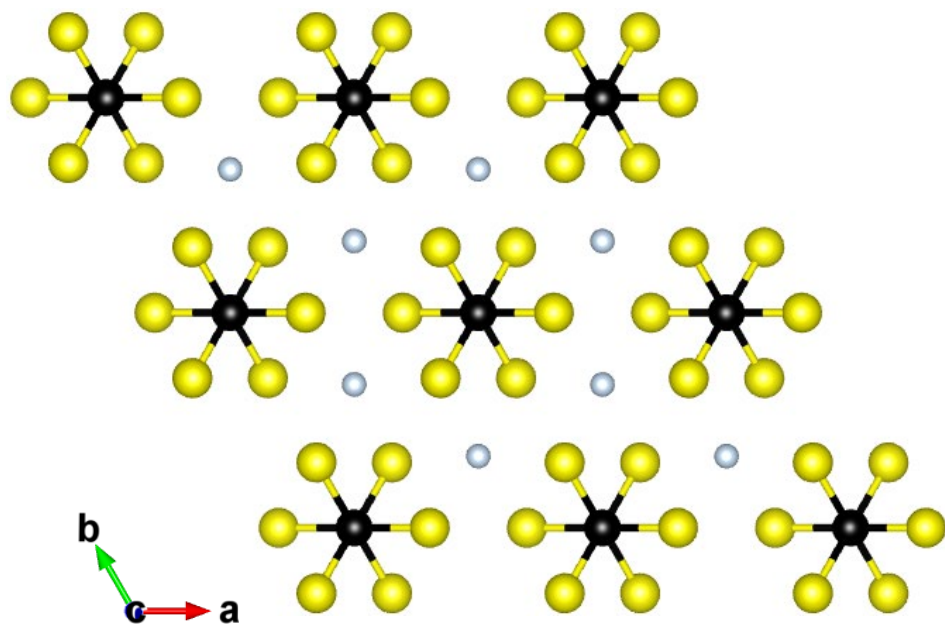
**Stable and metastable structures**

# Outline

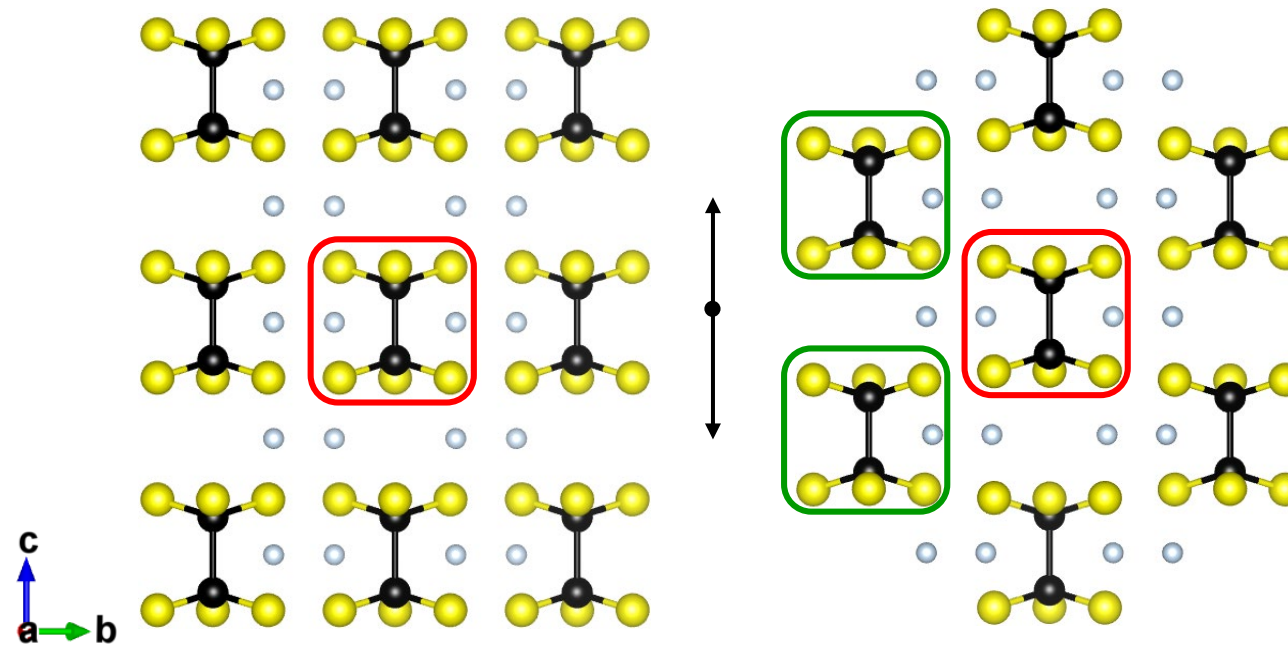
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# Structure analysis



Projection of the basic structure



$$\mathbf{P}_{\uparrow} = \pm Z_P \vec{C}$$

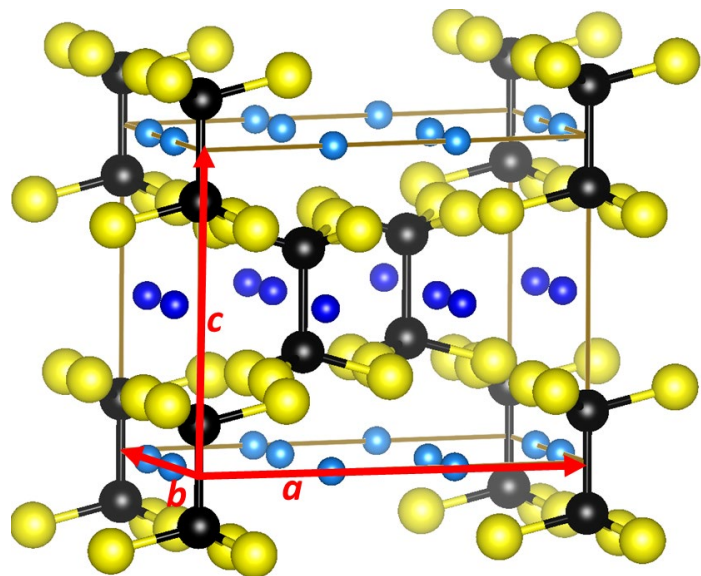
$$\mathbf{P}_{\downarrow} = \pm \left( \frac{1}{2} - Z_P \right) \vec{C}$$

Hood et al., *J. Solid State Ionics* **284**, 61 (2016).



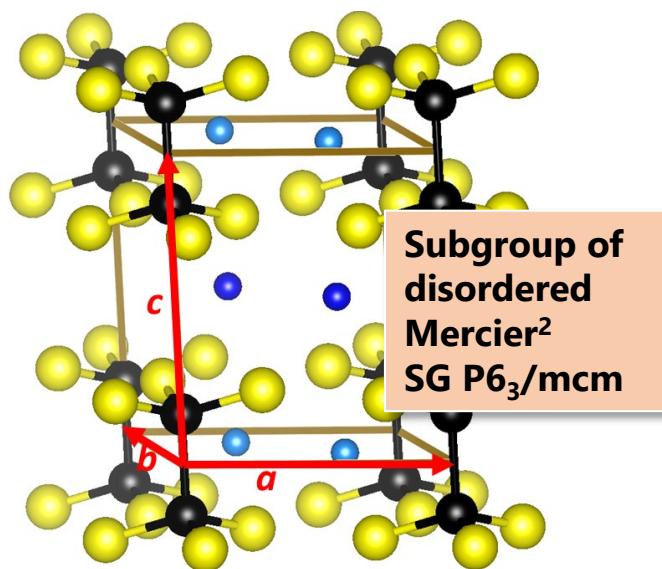
# Model structures considered

●● Inequiv. Na(Li) ● P ● S



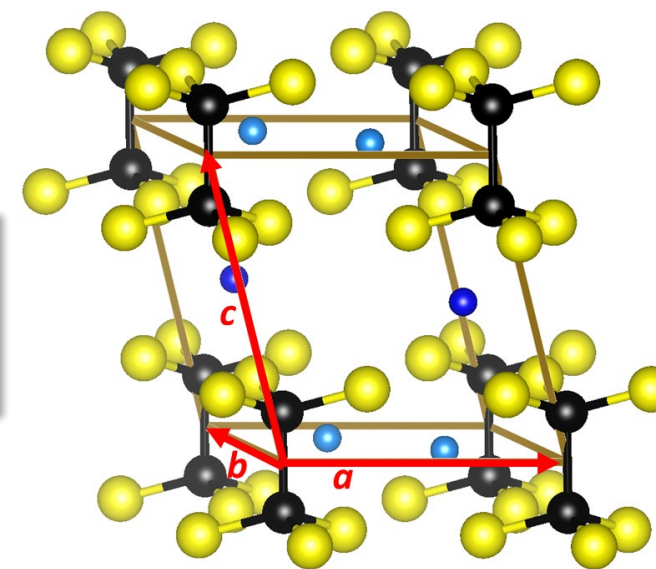
Hexagonal **P321** (#150)<sup>1</sup>  
3 formula units / unit cell

$$\frac{1}{3} \mathbf{P}_{\uparrow} \quad \frac{2}{3} \mathbf{P}_{\downarrow}$$



Hexagonal **P $\bar{3}$ 1m** (#162)<sup>3</sup>  
1 formula unit / primitive unit cell

$$100\% \mathbf{P}_{\uparrow}$$



Monoclinic **C2/m** (#12)<sup>4</sup>  
1 formula unit / primitive unit cell

$$100\% \mathbf{P}_{\uparrow}$$

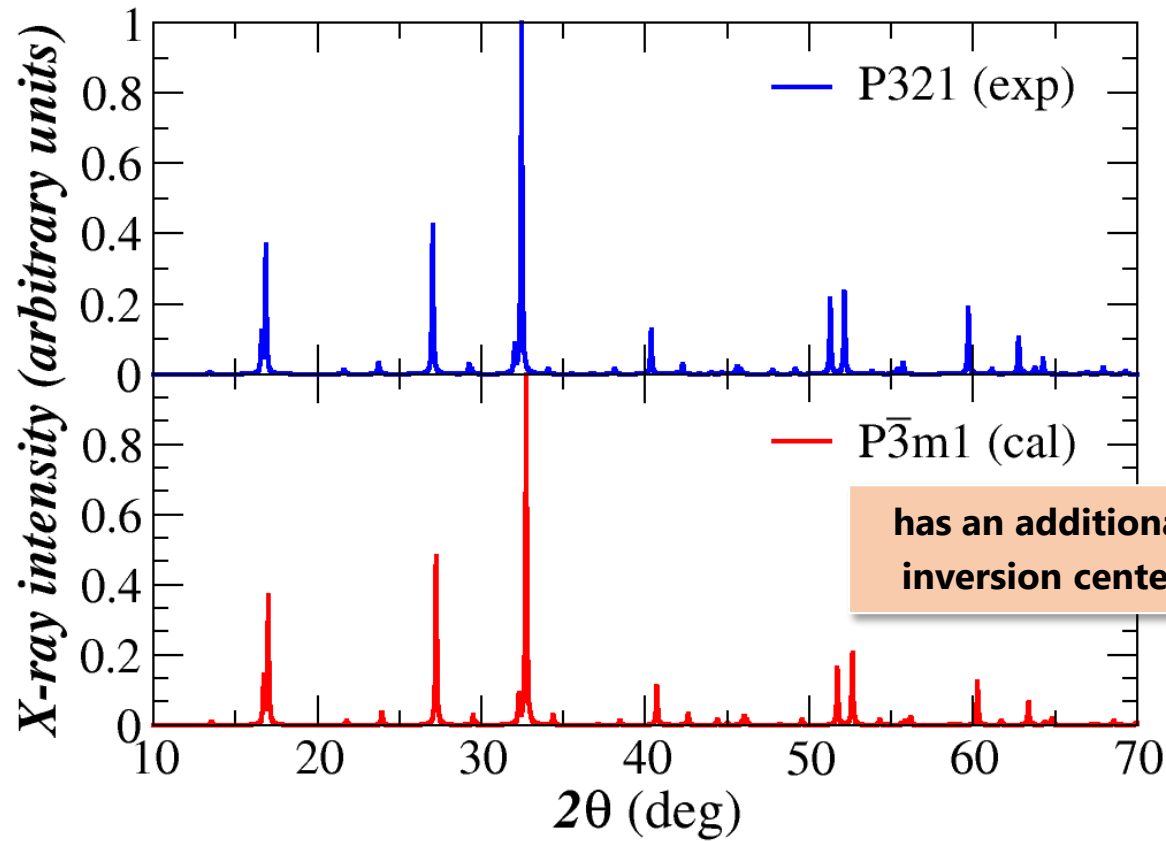
<sup>1</sup>Neuberger et al., *Dalton Trans.* **47**, 11691-11695 (2018)

<sup>2</sup>Mercier et al., *J. Solid State Chem.* **43**, 151-162 (1982)

<sup>3</sup>Hood et al., *J. Solid State Ionics*, **284**, 61 (2016)

<sup>4</sup>Kuhn et al., *Z. Anorg. Allg. Chem.* **640**, 689-692 (2014)

# More about the P321 structure



Comparing X-ray diffraction patterns at  $\lambda = 1.54056 \text{ \AA}$

Comparison of the fractional coordinates of  $\text{Li}_4\text{P}_2\text{S}_6$  and  $\text{Na}_4\text{P}_2\text{S}_6$  based on the Neuberger structure<sup>1</sup>.

$\text{Li}_4\text{P}_2\text{S}_6$		Calculated			Experiment			
Atom	Wyck	$x$	$y$	$z$	Wyck	$x$	$y$	$z$
Li	6 $g$	0.666	0.000	0.000	3 $e$	0.625/0.683	0.000	0.0000
Li	6 $h$	0.667	0.000	$\frac{1}{2}$	3 $f$	0.631/0.671	0.000	$\frac{1}{2}$
P	2 $c$	0.000	0.000	0.171	2 $c$	0.000	0.000	0.170
P	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.663	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.668
P	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.324	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.335
S	6 $i$	0.110	0.220	0.242	6 $g$	0.108	0.217	0.241
S	6 $i$	0.114	0.557	0.254	6 $g$	0.122	0.561	0.250
S	6 $i$	0.447	0.224	0.259	6 $g$	0.452	0.226	0.255

$\text{Na}_4\text{P}_2\text{S}_6$		Calculated		
Atom	Wyck	$x$	$y$	$z$
Na	6 $g$	0.659	0.000	0.000
Na	6 $h$	0.676	0.000	$\frac{1}{2}$
P	2 $c$	0.000	0.000	0.157
P	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.660
P	2 $d$	$\frac{1}{3}$	$\frac{2}{3}$	0.342
S	6 $i$	0.102	0.205	0.229
S	6 $i$	0.129	0.564	0.271
S	6 $i$	0.463	0.231	0.264

<sup>1</sup>Neuberger et al. *Dalton Trans.* **47**, 11691-11695 (2018)

# Static lattice results

**TABLE: Summary of static lattice results calculated with PBEsol GGA formalism. Lattice constants for the primitive unit cells are listed in units of Å and angles in degrees. The static lattice energy differences  $\Delta U_{SL}$  are listed as eV/(formula unit) referenced to the energy of the  $P\bar{3}m1$  structure.**

$Li_4P_2S_6$	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$\Delta U_{SL}$
$P\bar{3}1m$ (#162)	6.03	6.03	6.48	90.0	90.0	120.0	0.04
$C2/m$ (#12)	6.08	6.08	6.89	97.9	97.9	119.1	0.31
$P\bar{3}m1$ (#164) <sup>a</sup>	10.42	10.42	6.54	90.0	90.0	120.0	0.00
$Na_4P_2S_6$	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$\Delta U_{SL}$
$P\bar{3}1m$ (#162)	6.45	6.45	7.13	90.0	90.0	120.0	0.09
$C2/m$ (#12) <sup>b</sup>	6.51	6.51	7.52	98.5	98.5	117.6	0.00
$P\bar{3}m1$ (#164)	11.10	11.10	7.25	90.0	90.0	120.0	0.00

LDA results suggest that  $C2/m$  structure is meta-stable

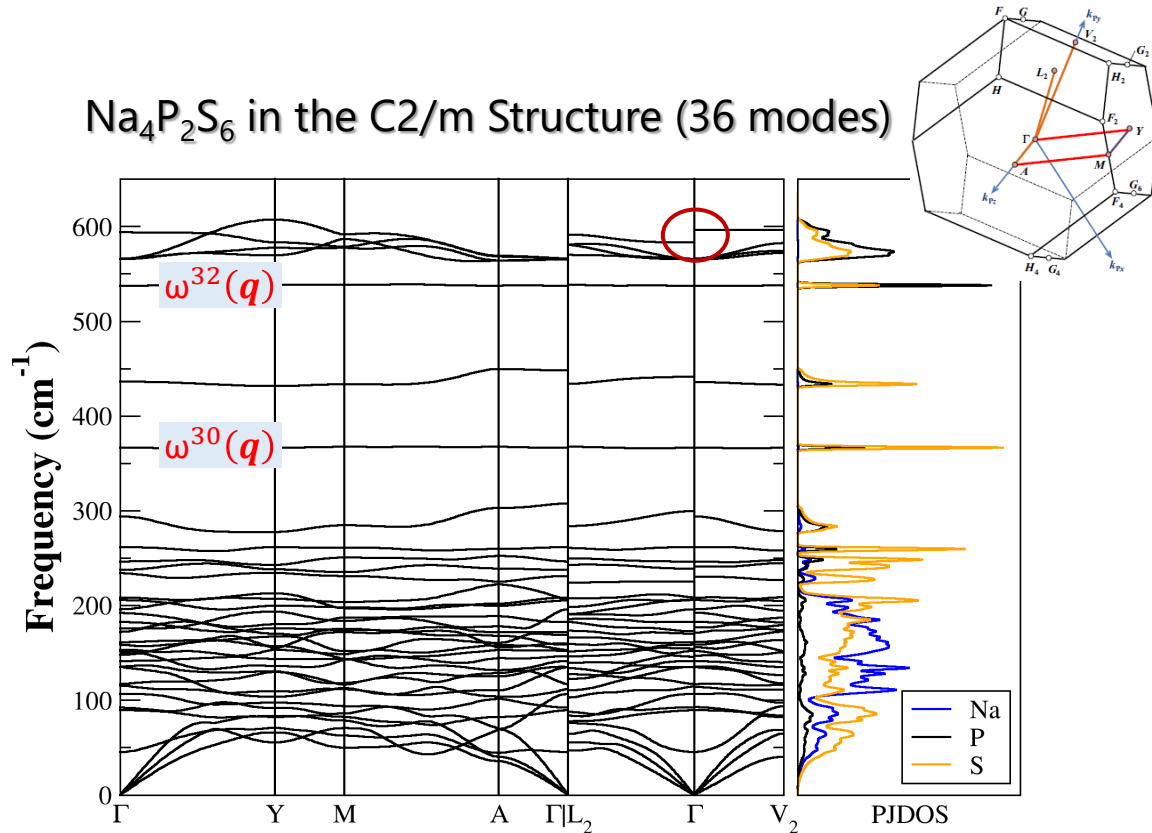
↑  
**static and vibrational** →

<sup>a</sup> Corresponding experimental values quoted from Neuberger et al., *Dalton Trans.* 47, 11691-11695 (2018) are  $a = b = 10.51$  Å,  $c = 6.59$  Å

<sup>b</sup> Corresponding experimental values deduced from Kuhn et al., *Z. Anorg. Allg. Chem.* 640, 689-692 (2014) are  $a = b = 6.54$  Å,  $c = 7.54$  Å,  $\alpha = \beta = 98.7$  deg,  $\gamma = 118.1$  deg.

# Phonon spectrum

$\text{Na}_4\text{P}_2\text{S}_6$  in the  $C2/m$  Structure (36 modes)

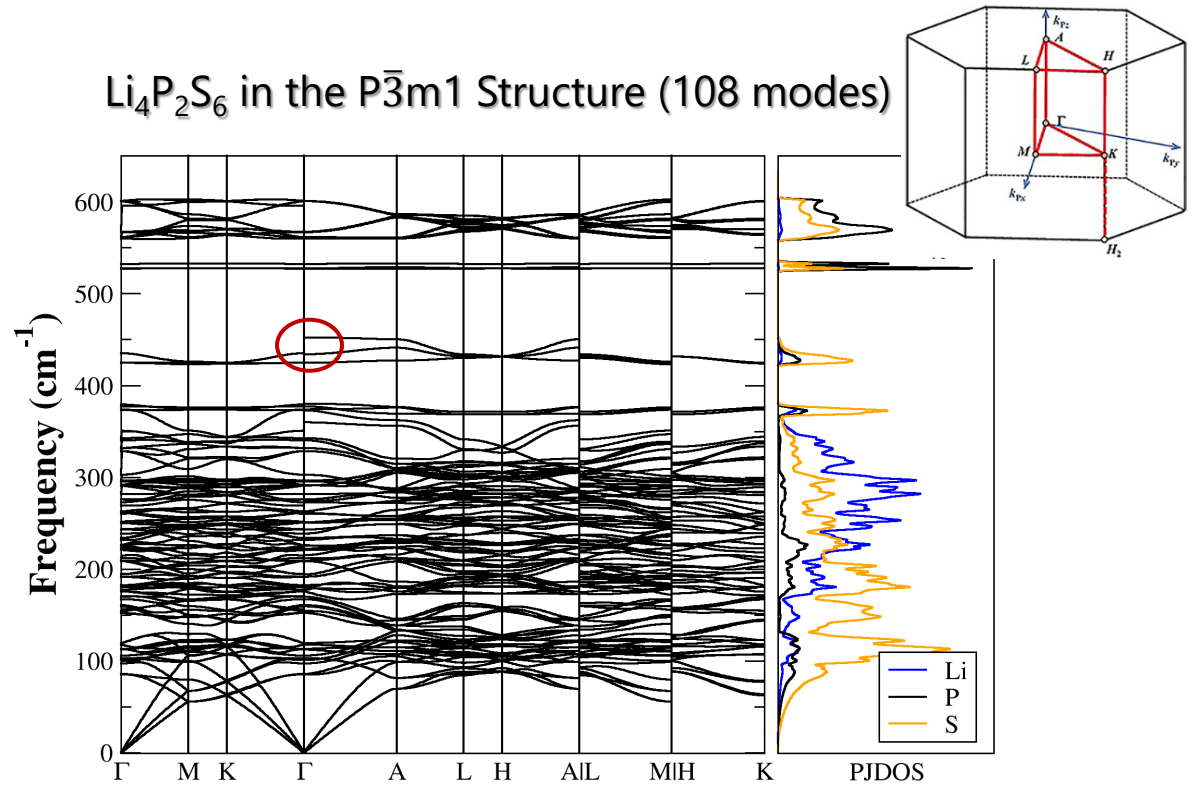


$\text{Na}^+$  0~300  $\text{cm}^{-1}$   
 $(\text{P}_2\text{S}_6)^{4-}$  300~600  $\text{cm}^{-1}$

<sup>1</sup>Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)

<sup>2</sup>Li et al., *J. Phys. Condens. Matter*, accepted

$\text{Li}_4\text{P}_2\text{S}_6$  in the  $P\bar{3}m1$  Structure (108 modes)



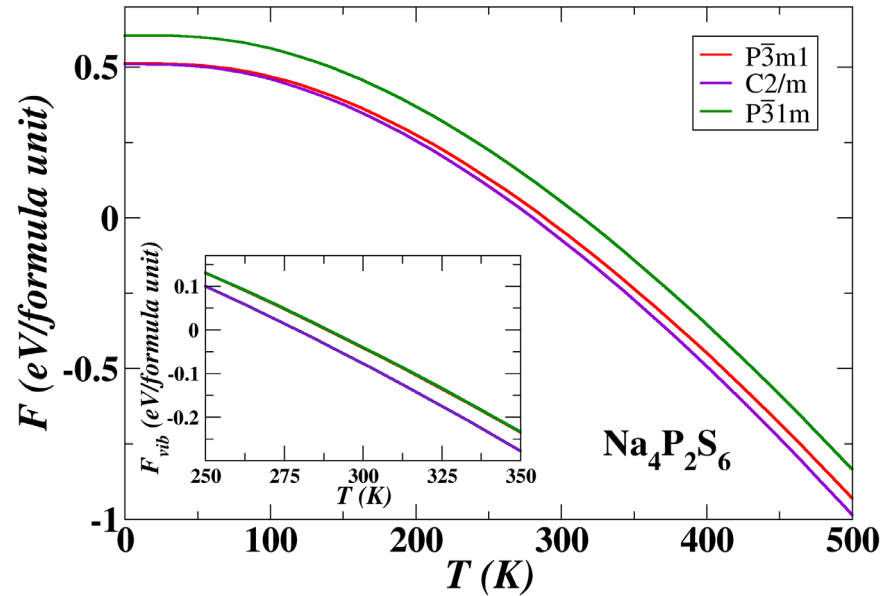
$\text{Li}^+$  0~370  $\text{cm}^{-1}$   
 $(\text{P}_2\text{S}_6)^{4-}$  370~600  $\text{cm}^{-1}$

PJDOS: 
$$g^a(\omega) \equiv \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} (\delta(\omega - \omega_\nu(\mathbf{q})) W_a^\nu(\mathbf{q}))$$

Discontinuous branches at  $\Gamma$ : coupling between photon and photon<sup>2</sup>

# Stability analysis

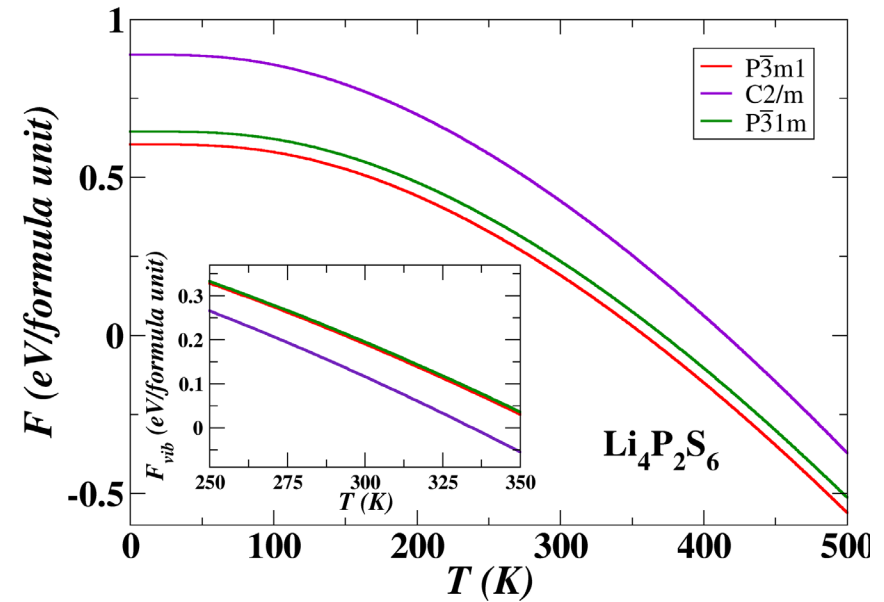
Helmholtz free energy:  $F = U_{\text{SL}} + F_{\text{vib}}$



$U_{\text{SL}}$ :  $\text{P}\bar{3}\text{m}1 = \text{C}2/\text{m} < \text{P}\bar{3}1\text{m}$

$F_{\text{vib}}$ :  $\text{C}2/\text{m} < \text{P}\bar{3}\text{m}1 = \text{P}\bar{3}1\text{m}$

➔  $F_{\text{lowest}}$ : **C2/m (expt.<sup>1,2</sup>)**



$U_{\text{SL}}$ :  $\text{P}\bar{3}\text{m}1 < \text{P}\bar{3}1\text{m} < \text{C}2/\text{m}$

$F_{\text{vib}}$ :  $\text{C}2/\text{m} < \text{P}\bar{3}\text{m}1 = \text{P}\bar{3}1\text{m}$

➔  $F_{\text{lowest}}$ : **P3m1 (expt.<sup>3</sup>)**

<sup>1</sup>Kuhn et al., *Z. Anorg. Allg. Chem.* **640**, 689-692 (2014)

<sup>2</sup>Hood et al., *J. Solid State Ionics* **284**, 61 (2016)

<sup>3</sup>Neuberger et al., *Dalton Trans.* **47**, 11691-11695 (2018)

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# Structures of the predicted material: $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$

Replace the (a) *g*-type or (b) *h*-type Na ions in the monoclinic  $\text{Na}_4\text{P}_2\text{S}_6$  with Li ions

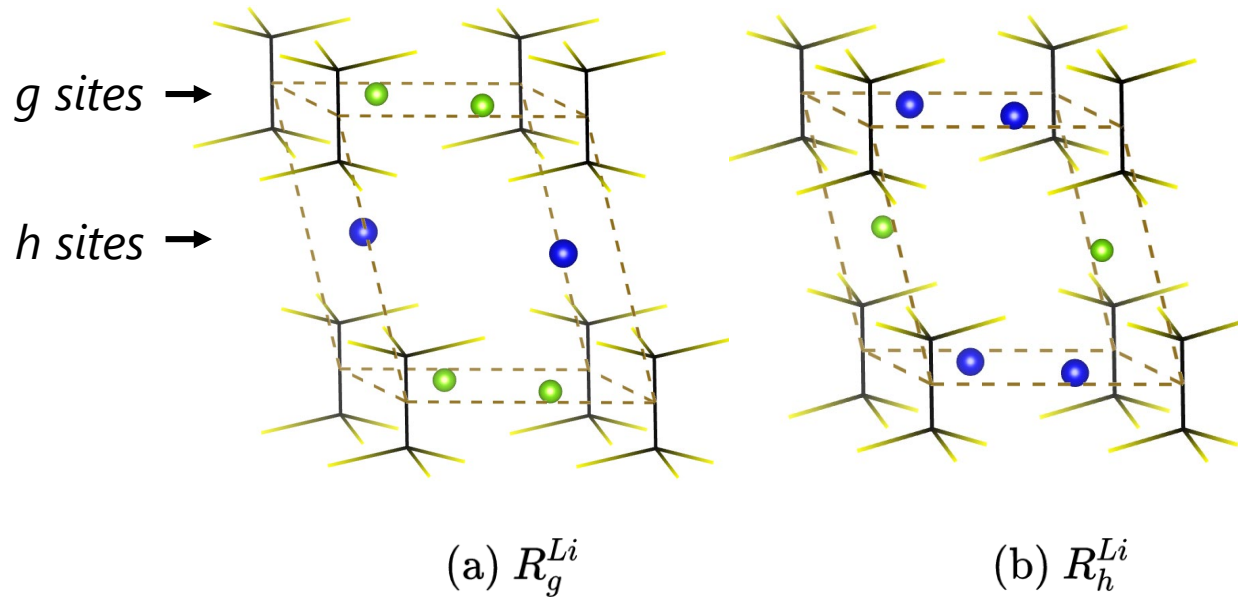


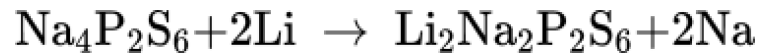
TABLE: Comparison of the optimized lattice parameters for  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$  in the  $R_g^{Li}$  and  $R_h^{Li}$  structures. Also listed is the static lattice energy differences  $U_{SL}$  referenced to the energy of the  $R_h^{Li}$  structure in units of eV/formula unit.

	$R_g^{Li}$	$R_h^{Li}$
Primitive cell:		
$a = b$ (Å)	6.18	6.46
$c$ (Å)	7.50	7.01
$\alpha = \beta$ (deg)	97.77	97.88
$\gamma$ (deg)	119.21	118.43
Conventional cell:		
$a_c$ (Å)	6.26	6.61
$b_c$ (Å)	10.67	11.10
$c_c$ (Å)	7.50	7.01
$\beta_c$ (deg)	105.50	105.54
$\Delta U_{SL}$ (eV/FU)	-0.16	0.00



# Stability of the predicted material: $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$

The possible reaction pathway:



$$\Delta F(T) = \Delta U_{SL} + \Delta F_{vib}(T) + \Delta F_{elec}^{metal}(T)$$

$$\Delta = \Delta_{Products} - \Delta_{Reactants}$$

*trivial contribution*  
( $10^{-3}$  eV)

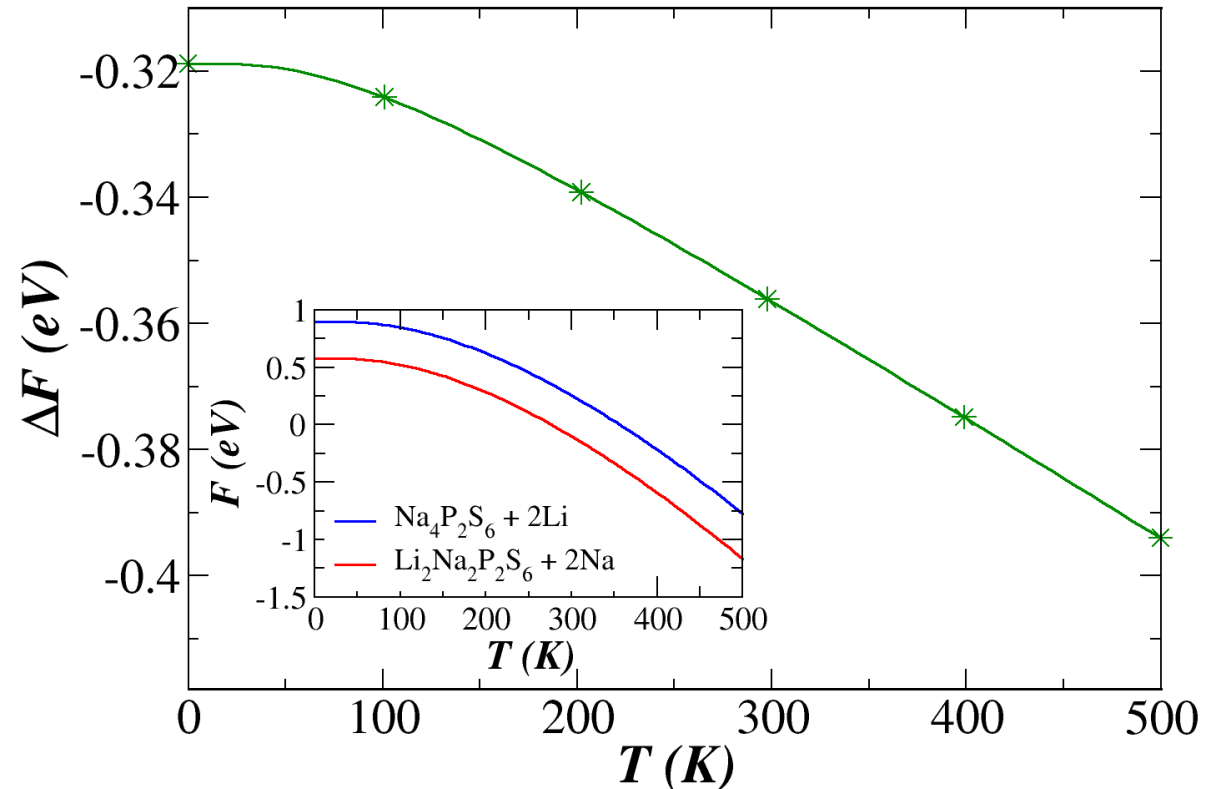
Energy changes at  $T = 300$  K in eV:

$$\Delta U_{SL} = -0.29$$



$$\Delta F = -0.35$$

$$\Delta F_{vib} = -0.06$$



Negative energies (net released energies) imply that the structure of  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$  is stable with respect to the possible exothermic process.

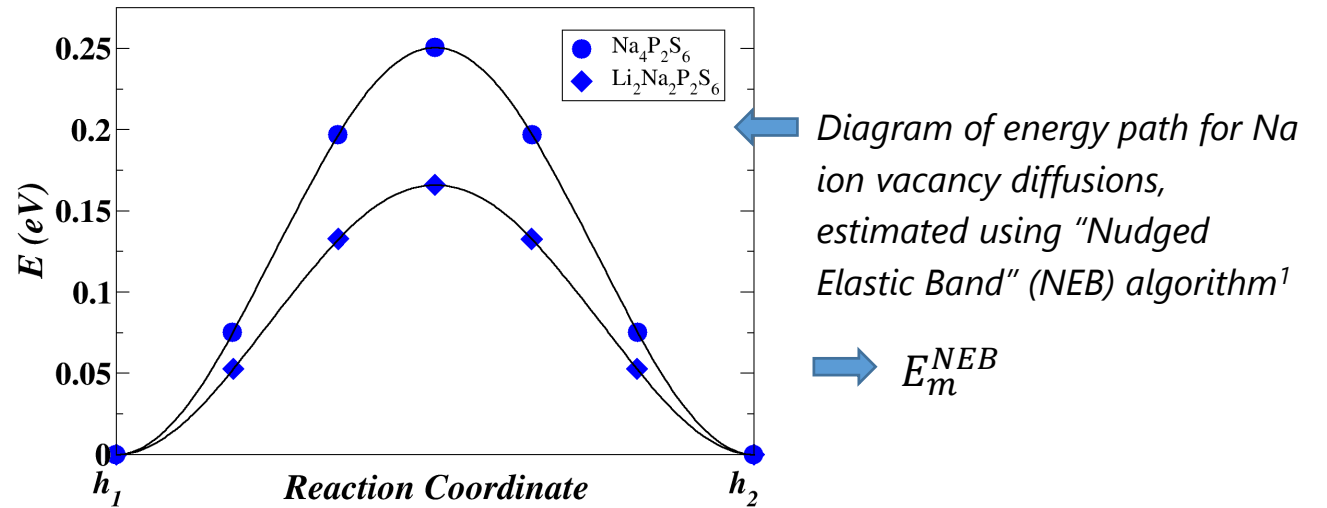
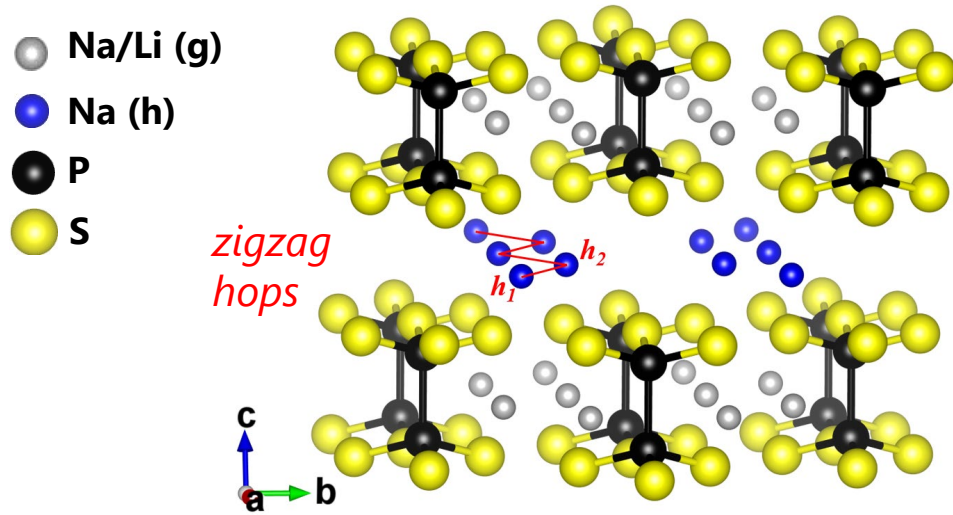


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# Ion migration of vacancy mechanisms



Activation energy:

$$E_a^{cal} = E_m^{NEB} + \frac{1}{2} E_f$$

Conductivity:

$$\sigma \cdot T = K e^{-E_a^{exp}/k_B T}$$

## Summary of vacancy diffusion results

Material	Functional	Step	Distance	$E_m^{cal}$	$E_f^{cal}$	$E_a^{cal}$	$E_a^{exp}$
$\text{Na}_4\text{P}_2\text{S}_6$	PBEsol GGA	$h_1 \rightarrow h_2$	3.67	0.25	0.18	0.34	0.39 <sup>3</sup>
	LDA	$h_1 \rightarrow h_2$	3.59	0.30	0.24	0.42 <sup>2</sup>	
$\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$	PBEsol GGA	$h_1 \rightarrow h_2$	3.44	0.16	0.13	0.23	--

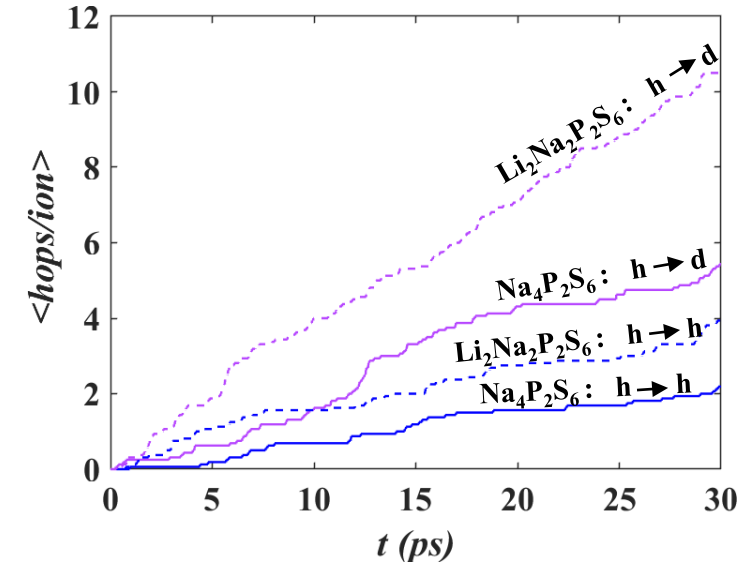
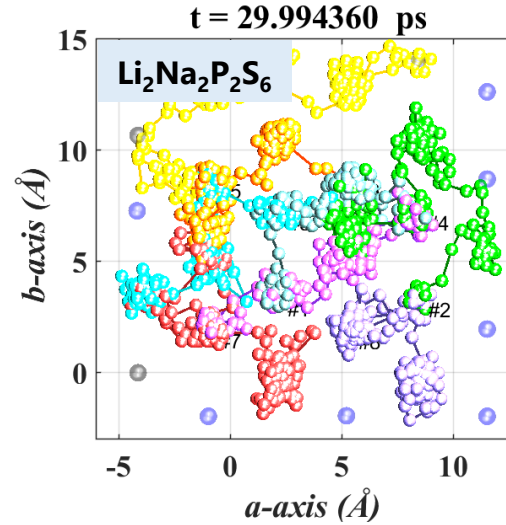
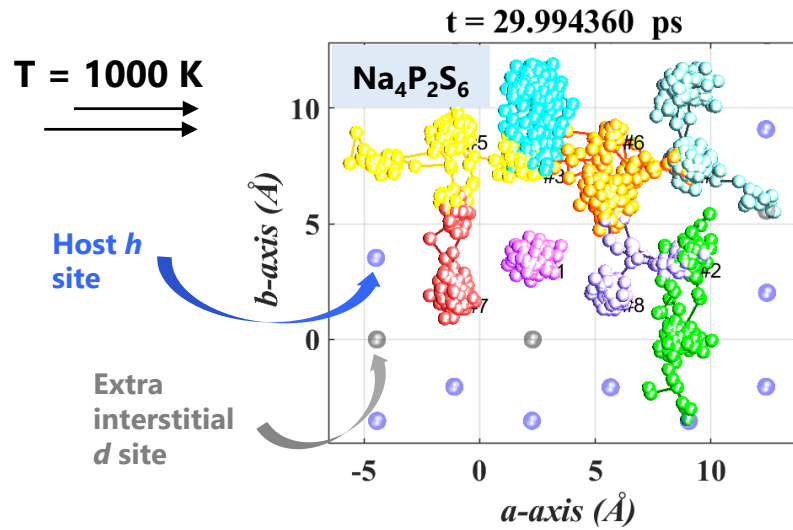
The distance in units of Å, and all energies are given in eV units

<sup>1</sup>Henkelman et al., *J. Chem. Phys.* **113**, 9901-9904 (2000)

<sup>2</sup>Rush et al., *Solid State Phys.* **286**, 45-50 (2016)

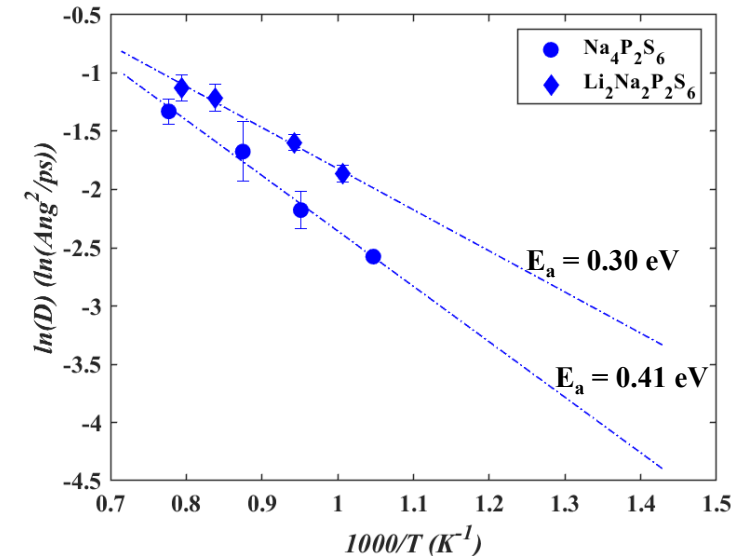
<sup>3</sup>Hood et al., Manuscript in preparation.

# Migration study using molecular dynamics simulations



- No  $g \rightarrow h$  and  $g \rightarrow g$  hopping
- All migrations occur within layer of  $h$  sites
- Direct  $h \rightarrow h$  vacancy migration is consistent with NEB analysis
- Indirect  $h \rightarrow d \rightarrow h$  vacancy migration is prevalent
- No interstitial  $d \rightarrow d$  migration
- Calculate  $E_a$  from  $D(T) = D_0 e^{-E_a/k_B T}$

$$\text{where } D = \frac{1}{6} \lim_{t \rightarrow \infty} \left( \frac{1}{t} \text{MSD}(t) \right)$$



\*AIMD simulations were carried out using supercells composed of  $2 \times 1 \times 2$  conventional units (96 atoms)

\*\*  $E_a$  was obtained from runs of 50-70 ps

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## Summary and conclusions

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- According to PBEsol GGA results,  $\text{Na}_4\text{P}_2\text{S}_6$  is to be stabilized in the C2/m structure and  $\text{Li}_4\text{P}_2\text{S}_6$  is to be stabilized in the  $\text{P}\bar{3}\text{m}1$  structure
- PBEsol GGA and LDA results of activation energy for Na ion migration reasonably agree with the experimental measurements which suggest a viable solid electrolyte
- The predicted crystal  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$  has a stable structure. Compared to  $\text{Na}_4\text{P}_2\text{S}_6$ , the mixed alkali electrolyte can substantially enhance Na ion conductivity
- Both NEB and MD simulations reveal that the Na ion diffusions in both  $\text{Na}_4\text{P}_2\text{S}_6$  and  $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$  are via vacancy mechanisms, and MD simulations provide more information on understanding the conductivity mechanisms