Structure and interface properties of the electrolyte material $Li_4P_2S_6$*

Zachary D. Hood,[a] Cameron M. Kates,[b,c] and N. A. W. Holzwarth[b]

[a]Center for Nanophase Materials Sciences,
Oak Ridge National Laboratory, Oak Ridge, TN 37831,
[b]Department of Physics, Wake Forest University, Winston-Salem, NC, USA, 27109,
[c]Currently attending the Pratt School of Engineering at Duke University

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$Li_4P_2S_6$

Why--

- Part of search for ideal solid electrolyte materials for all-solid state Li ion batteries
- Reported in by Mercier et. al. , J. Solid State Chemistry **43,** 151-164 (1982); hexagonal structure with disorder on the P sites
- Frequently identified as unintended constituent of solid electrolyte preparations; relatively stability in air

What-- Combined experimental and computation study including:

- Structural analysis
- Thermal stability
- Transport properties

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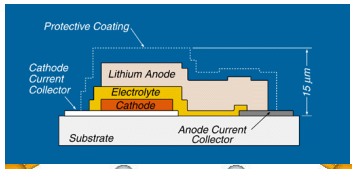
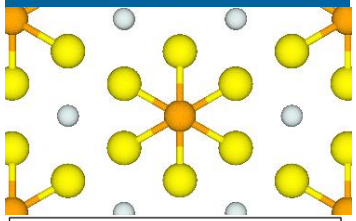
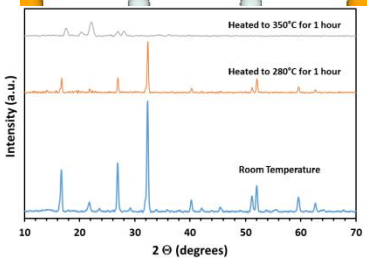
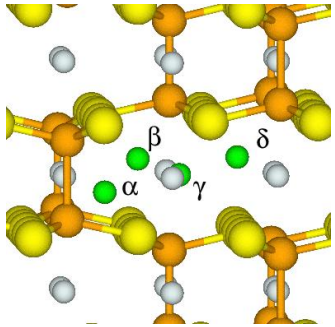
Outline

- Motivation
- Structural analysis
- Thermal stability
- Ionic conductivity
- Summary and conclusions









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Motivation for studying $Li_4P_2S_6$:

- Part of the search for the ideal solid electrolyte material for all-solid state Li ion batteries
- **$Li_4P_2S_6$** frequently identified as unintended stable component of solid electrolyte preparations
- Interesting structural properties, including disorder
- Transport and stability properties

Previous work:

JOURNAL OF SOLID STATE CHEMISTRY 43, 151–162 (1982)

Synthese, structure cristalline et analyse vibrationnelle de l'hexathiohypodiphosphate de lithium $Li_4P_2S_6$

R. MERCIER, J. P. MALUGANI, B. FAHYS, J. DOUGLADE,* ET G. ROBERT

*Laboratoire d'Electrochimie des Solides, ERA 810, et *Laboratoire de Chimie Physique, Université de Franche-Comté, 25030 Besancon Cedex, France*

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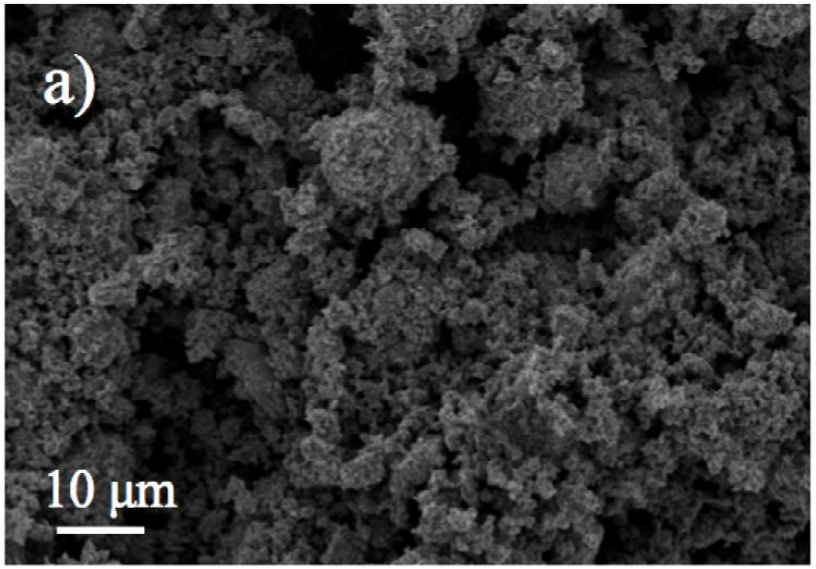
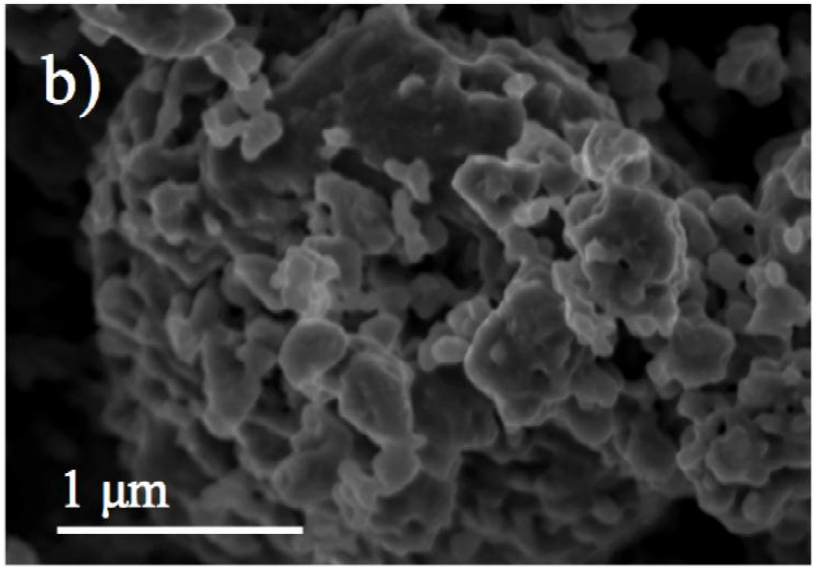
Synthesis:

$$2Li_2S + P_2S_5 \xrightarrow[900^o\,C]{} Li_4P_2S_6 + S$$

Sulfur removed by treatment with solvent; sample prepared for electrochemical applications using ball milling.

Scanning Electron Micrograph of prepared sample:





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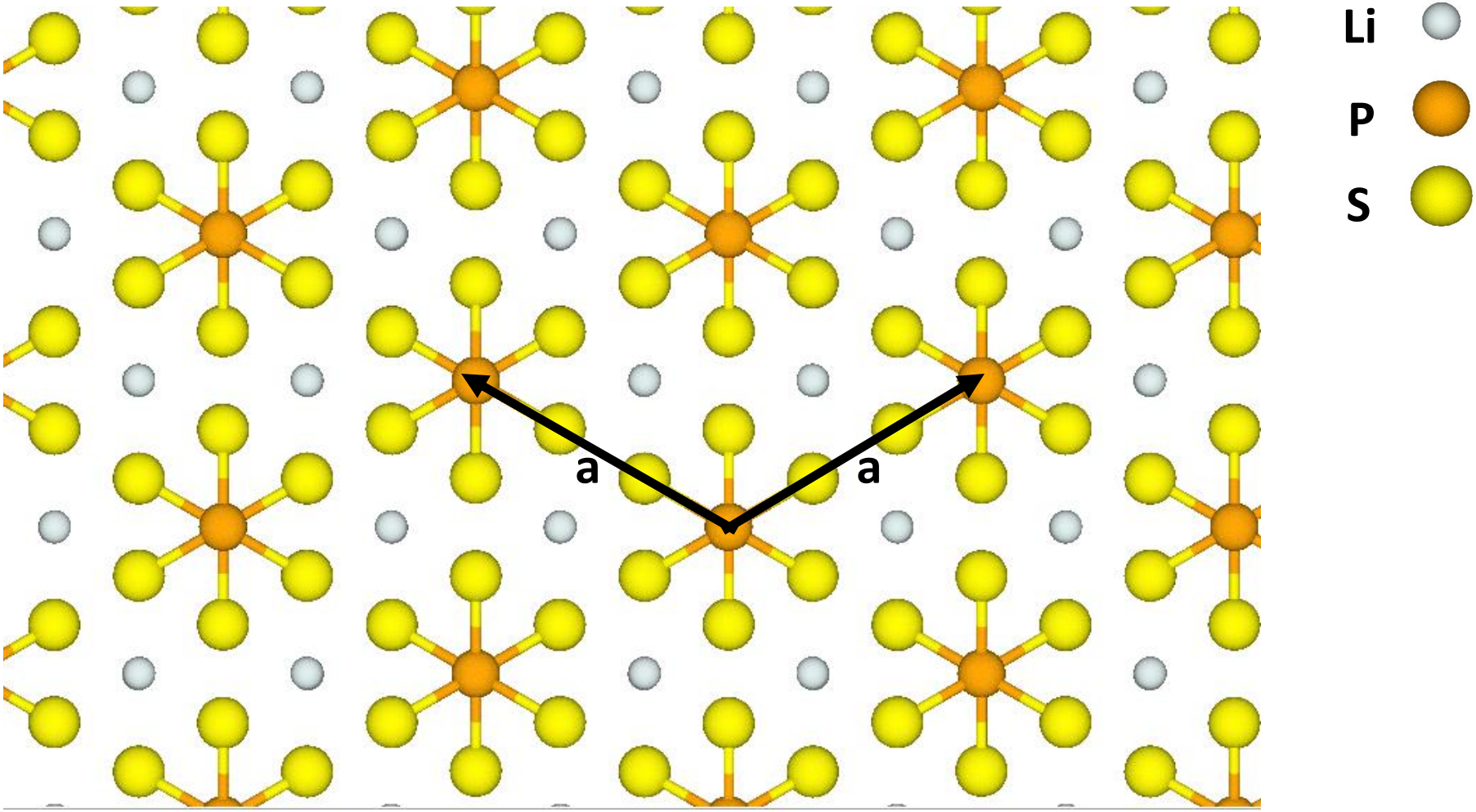
Computational methods

- Density functional theory with LDA
- PAW formalism using datasets generated with ***ATOMPAW*** code
- Electronic structure calculations performed using ***QUANTUM ESPRESSO*** and ***ABINIT*** codes
- Plane wave expansion for wave functions with $|\mathbf{k}+\mathbf{G}|^2 \leq 64 \text{ Ry}$
- Brillouin zone integration mesh of 0.003 bohr^{-3}
- Visualization software: ***Xcrysden*** and ***VESTA***; X-ray powder diffract simulated using ***Mercury***

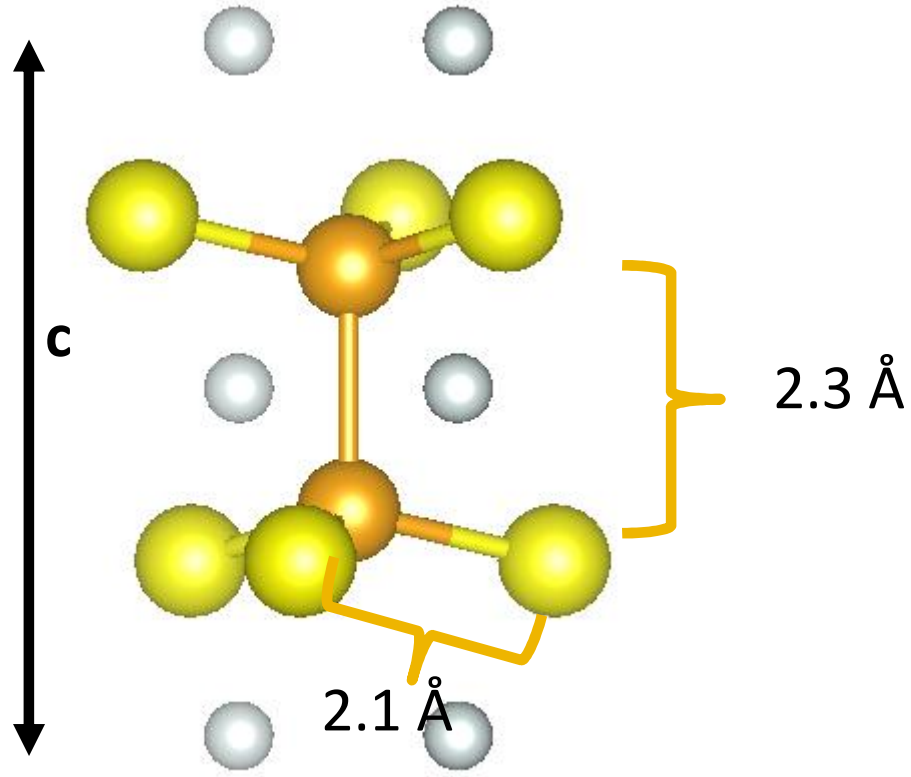
Crystal structure: Space Group $P6_3/mcm$ (#193)

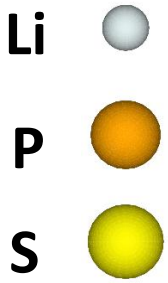
Projection on to hexagonal plane:



Crystal structure: Space Group *P6$_3$/mcm* (#193)

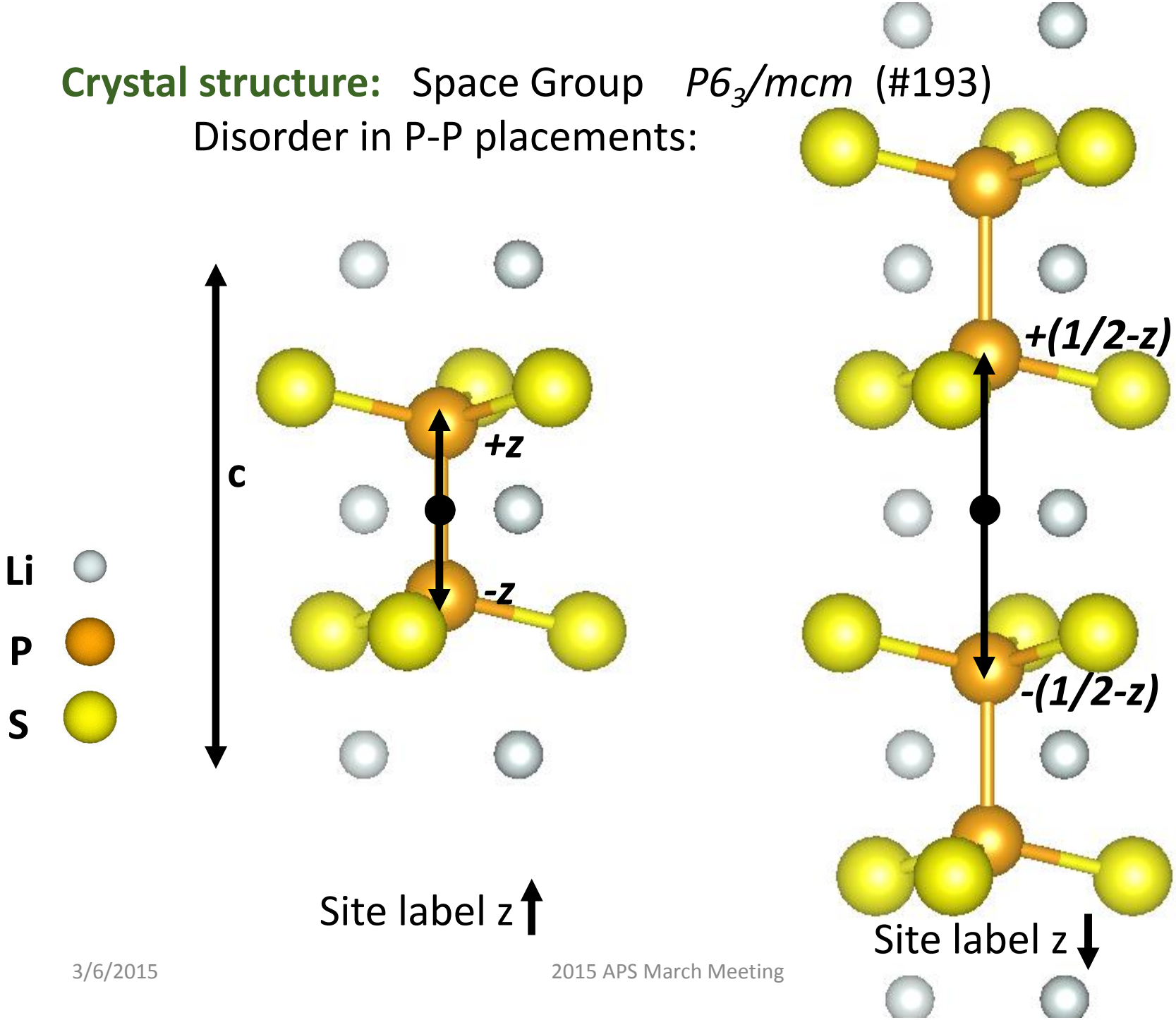
$Li_4P_2S_6$ units:



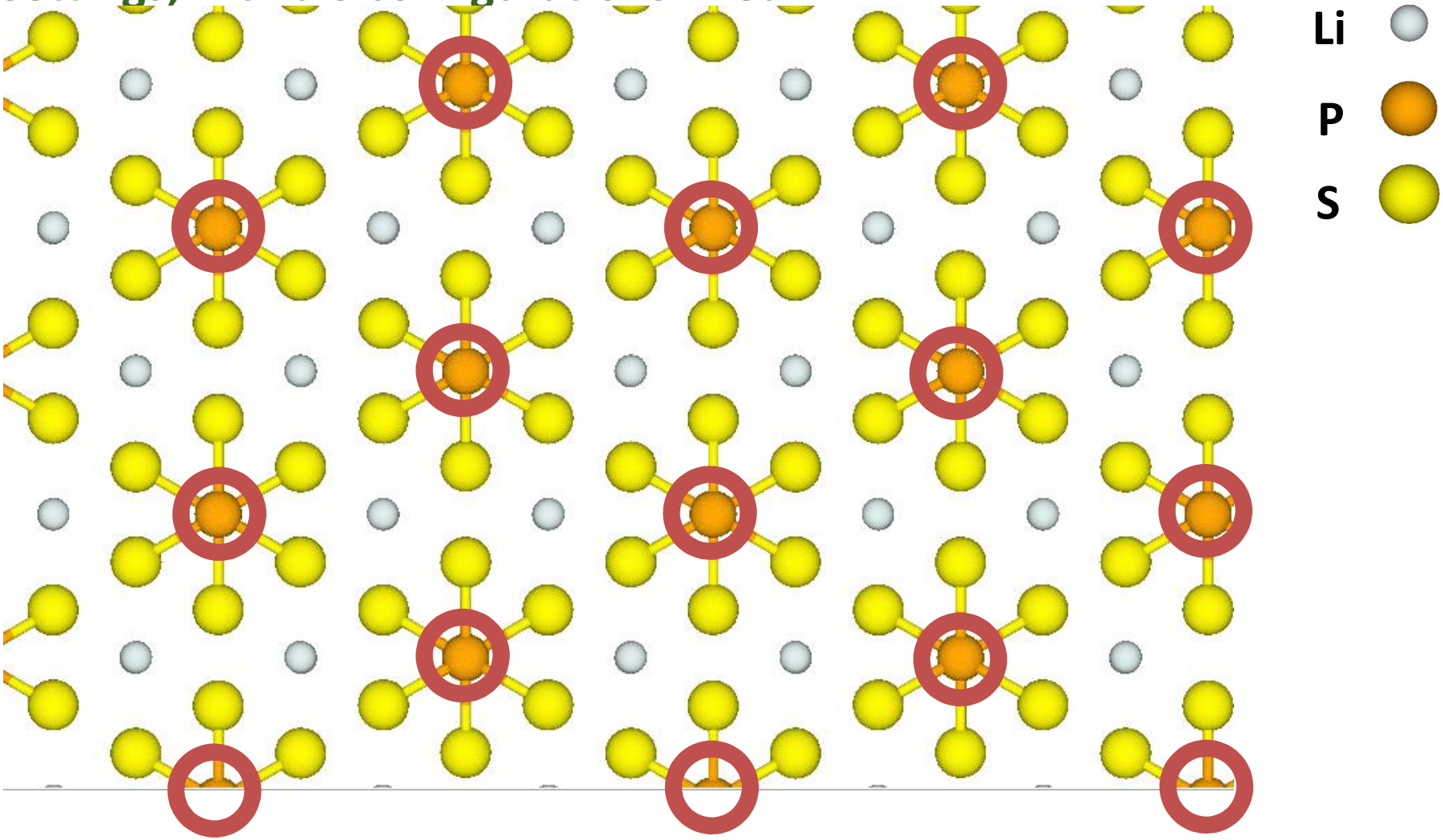


Crystal structure: Space Group $P6_3/mcm$ (#193)

Disorder in P-P placements:

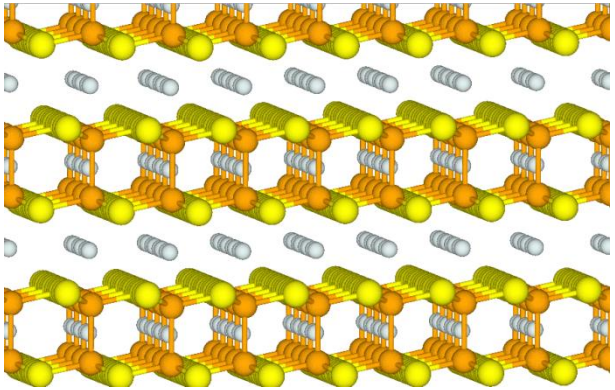


Structural variation can be mapped on to a two-dimensional hexagonal lattice with each P configuration taking z↑ or z↓ settings; Li and S configurations fixed



Examples:

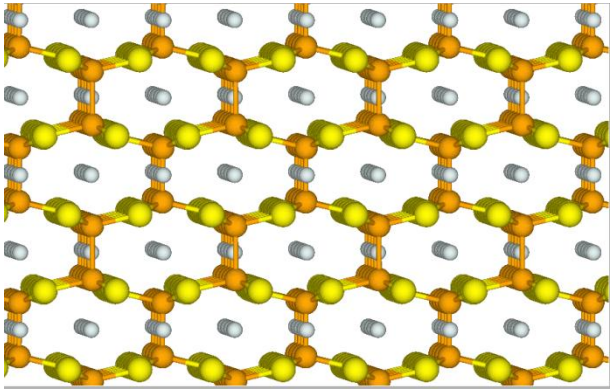
Structure “b”



$\Delta E = 0.03\ eV$

100% z↑

Structure “c”

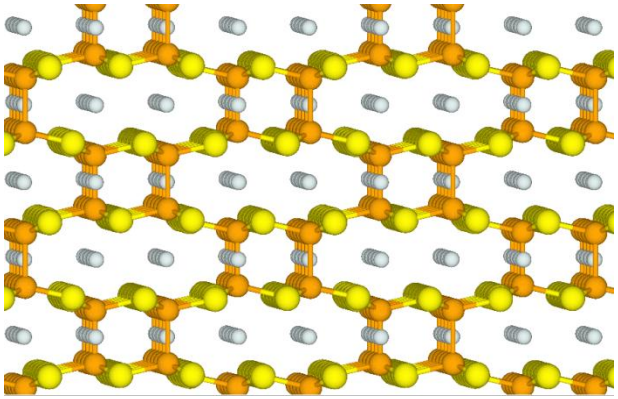


$\Delta E = 0$

50% z↑

50% z↓

Structure “d”



$\Delta E = 0$

50% z↑

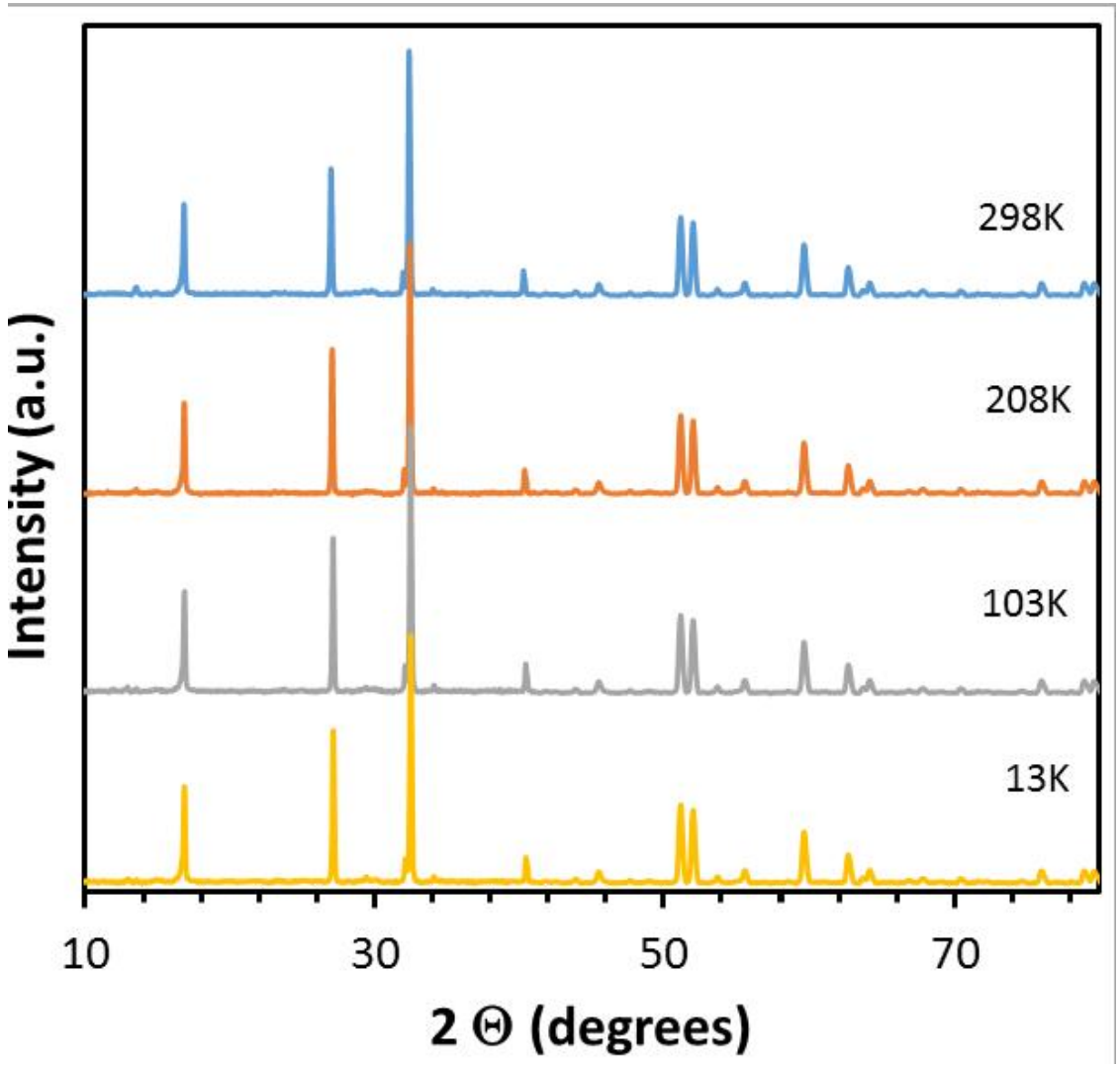
50% z↓

Li

P

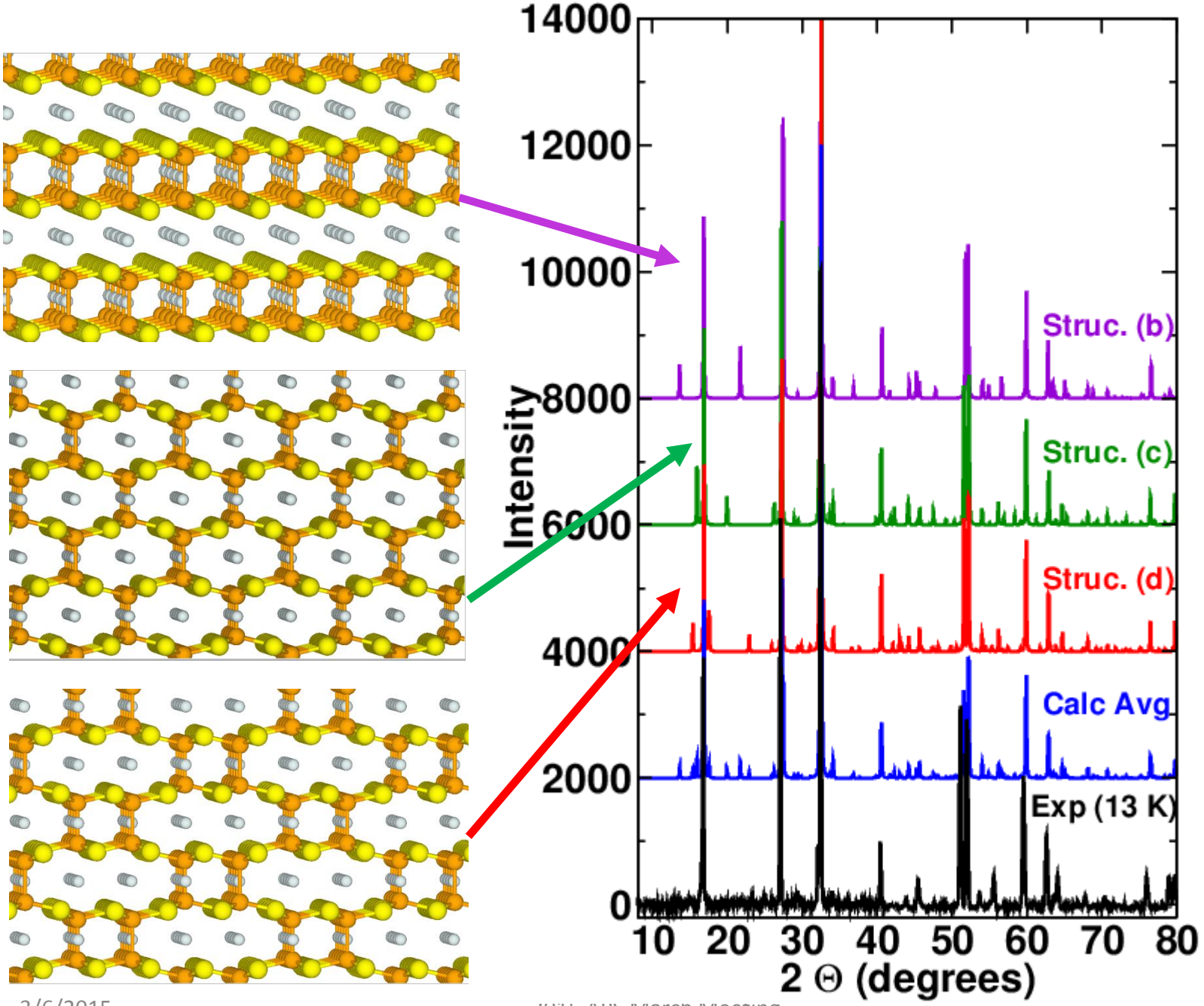
S

Temperature ^in dependence of X-ray powder diffraction



Diffraction analysis

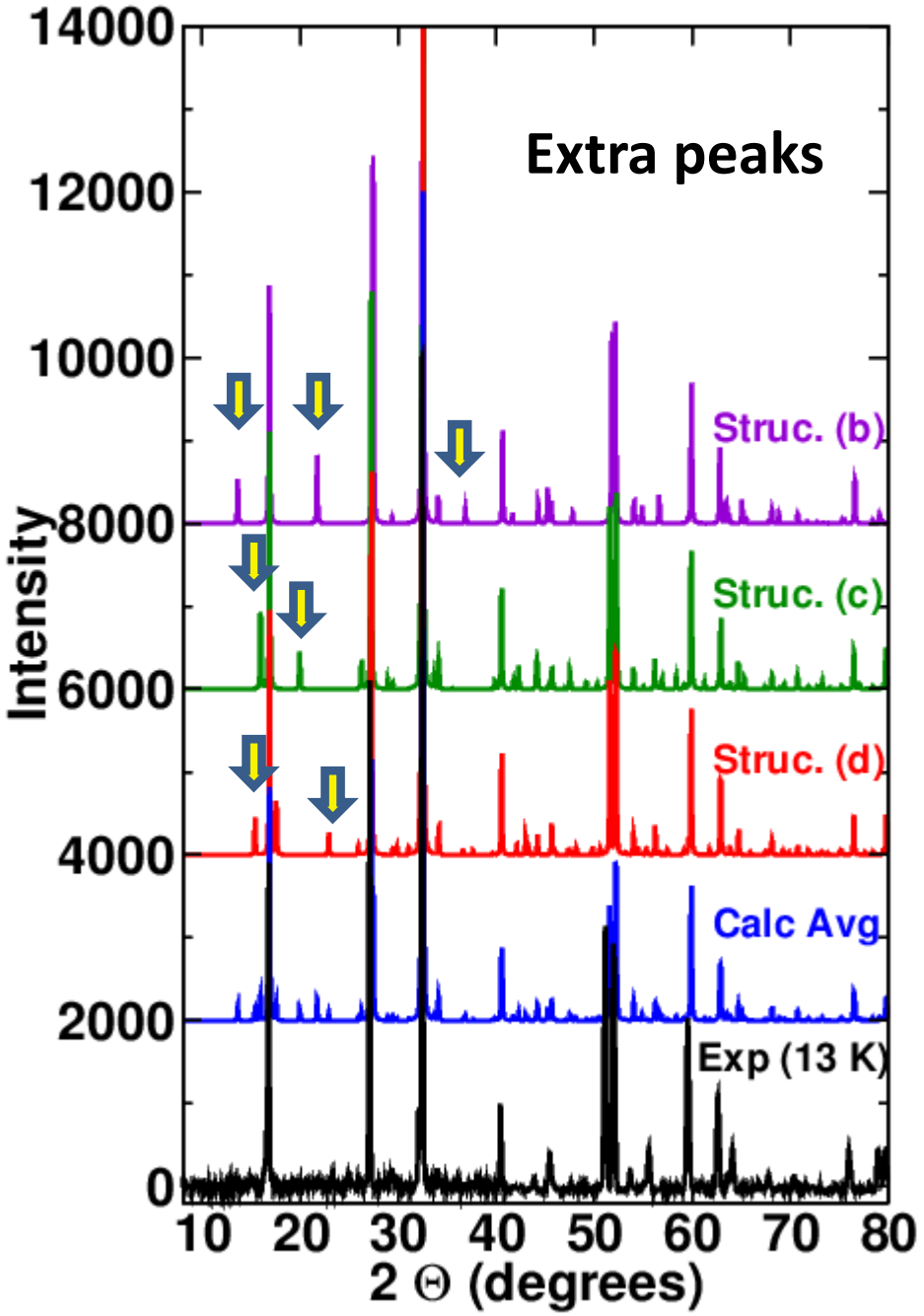
	a (Å)	*c* (Å)	z_P	z_S
Exp. 298K (X-ray)	6.0709	6.5903	0.1715	0.3237
Exp. 13K (X-ray)	6.0747	6.5966	0.1715	0.3237
Exp. 13K (neutron)	6.0761	6.5961	0.1698	0.3284


14000
12000
10000
8000
6000
4000
2000
0
Intensity
Struc. (b)
Struc. (c)
Struc. (d)
Calc Avg
Exp (13 K)
10
20
30
40
50
60
70
80
2 Θ (degrees)

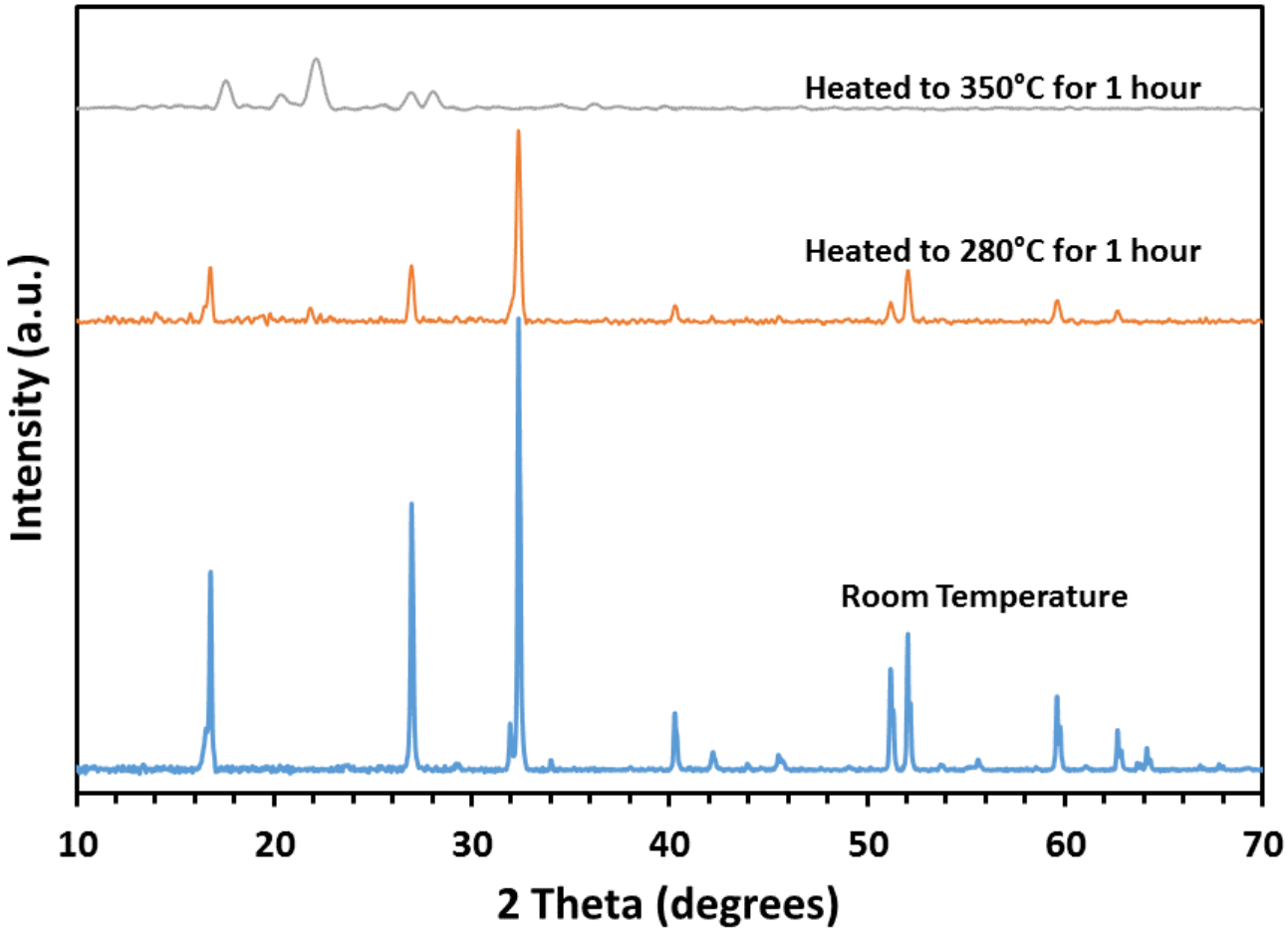
Comparison of 13 K X-ray data with simulation

Note: simulations scaled by 102% to compensate for systematic LDA error.

Simulations consistent with incoherent average over all P z↑ and z↓ configurations

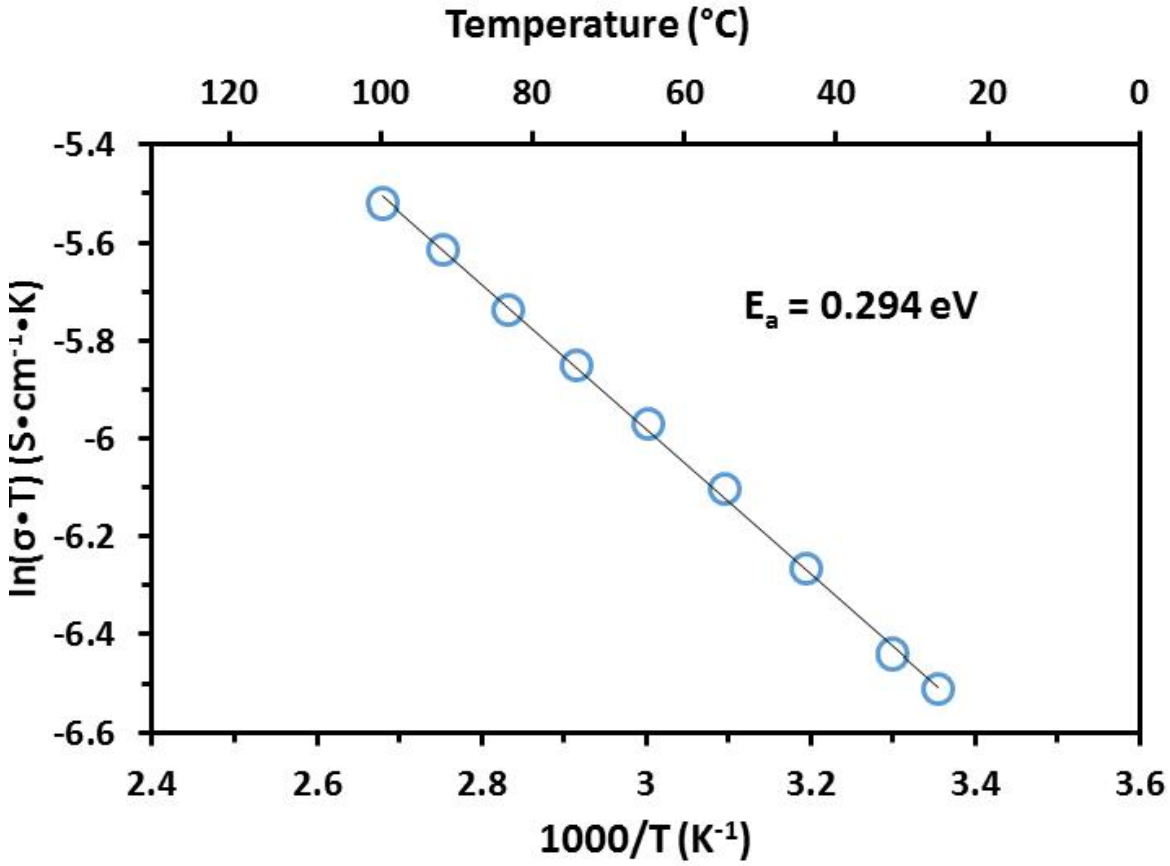


Stability: $Li_4P_2S_6$ is much less reactive than other lithium thio-phosphates, but it decomposes in air, especially at higher temperature



Decomposition products:
P_2O_5
$Li_4P_2O_7$
Li_2SO_4

Ionic conductivity and Activation Energy



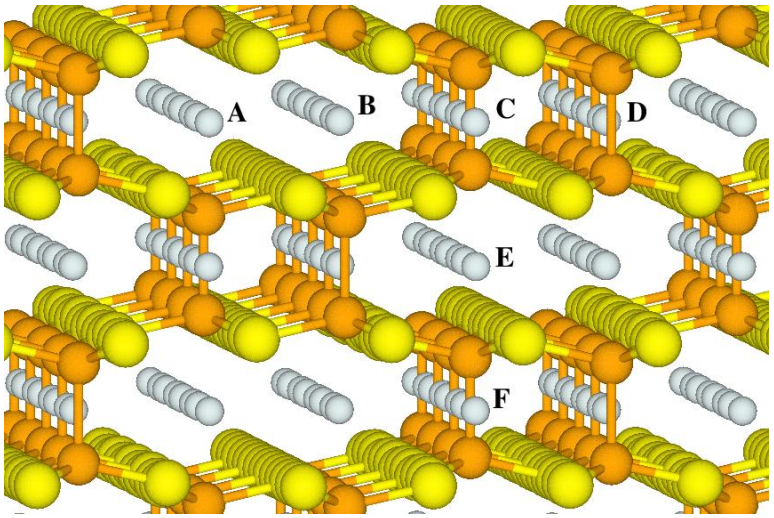
2.38 x 10^{-7} S/cm at 25˚C and 2.33 x 10^{-6} S/cm at 100˚C

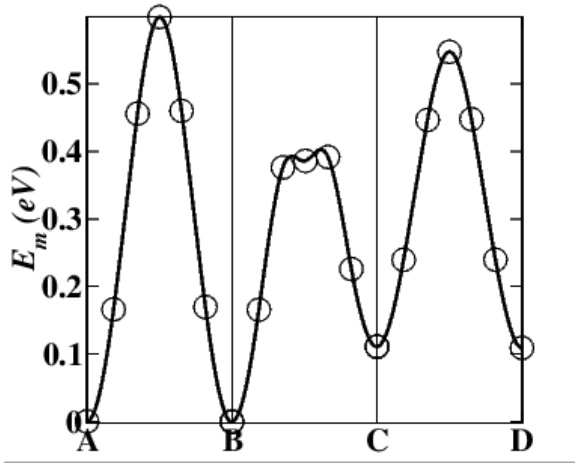
$Li_4P_2S_6$ pressed pellets with blocking (Al/C) electrodes

Simulations of ion mobility using Nudged Elastic Band Model

Vacancy mechanism:
ΔE>0.6 eV

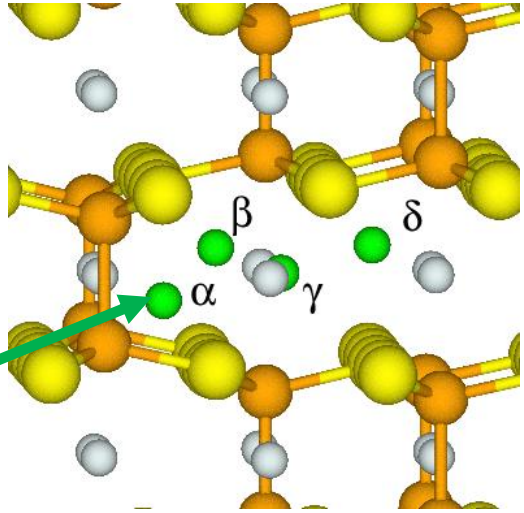
Li
P
S

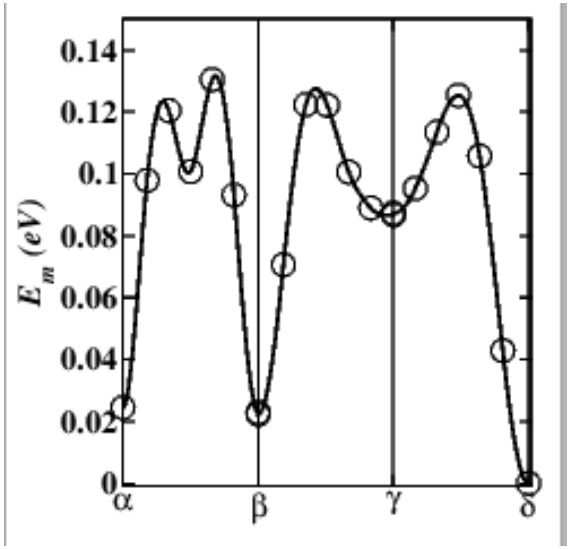




Interstitial mechanism:
ΔE>0.1 eV

Possible interstitial sites





Models of $Li_4P_2S_6$/Li interfaces -- Surface parallel to P-P bonds:

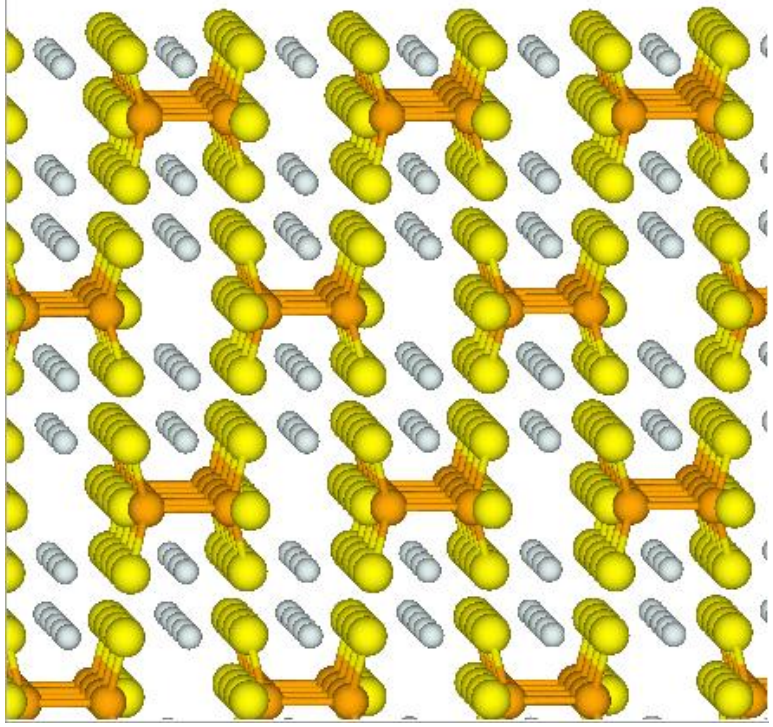
Surface with vacuum

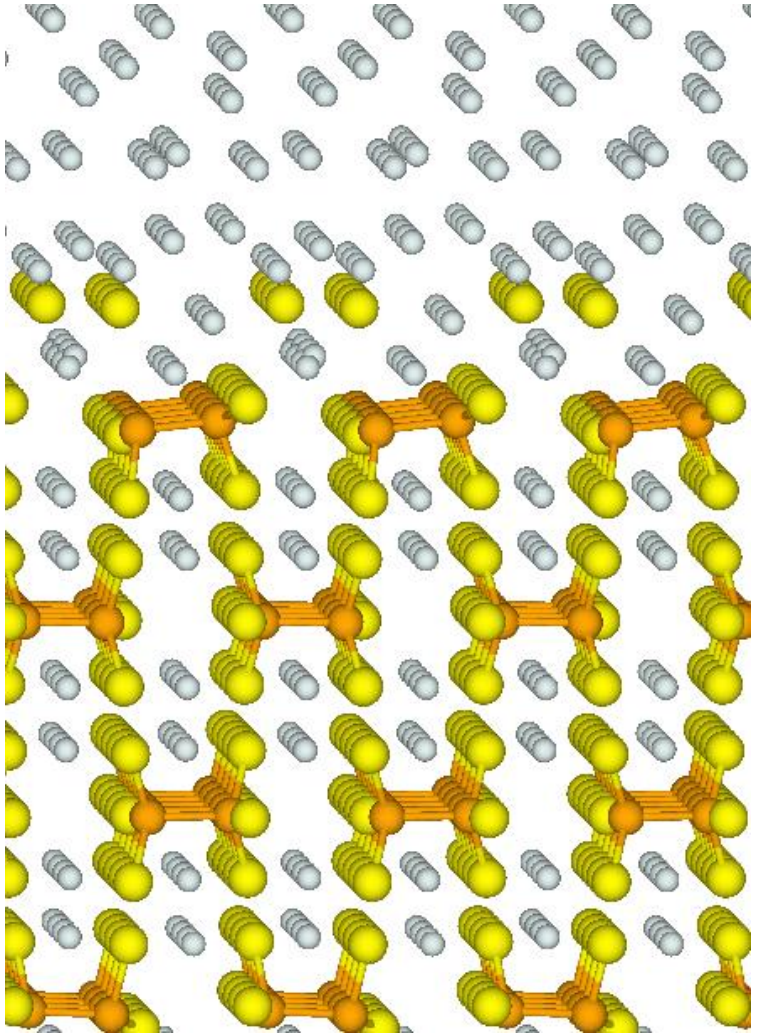
Surface with lithium

Li

P

S





Models of $Li_4P_2S_6$/Li interfaces -- Surface perpendicular to P-P bonds:

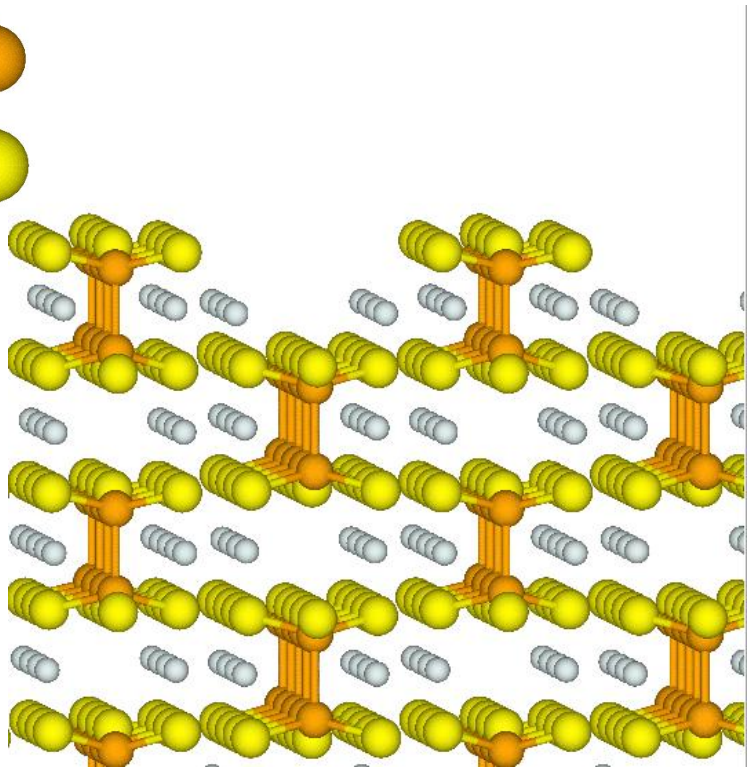
Surface with vacuum

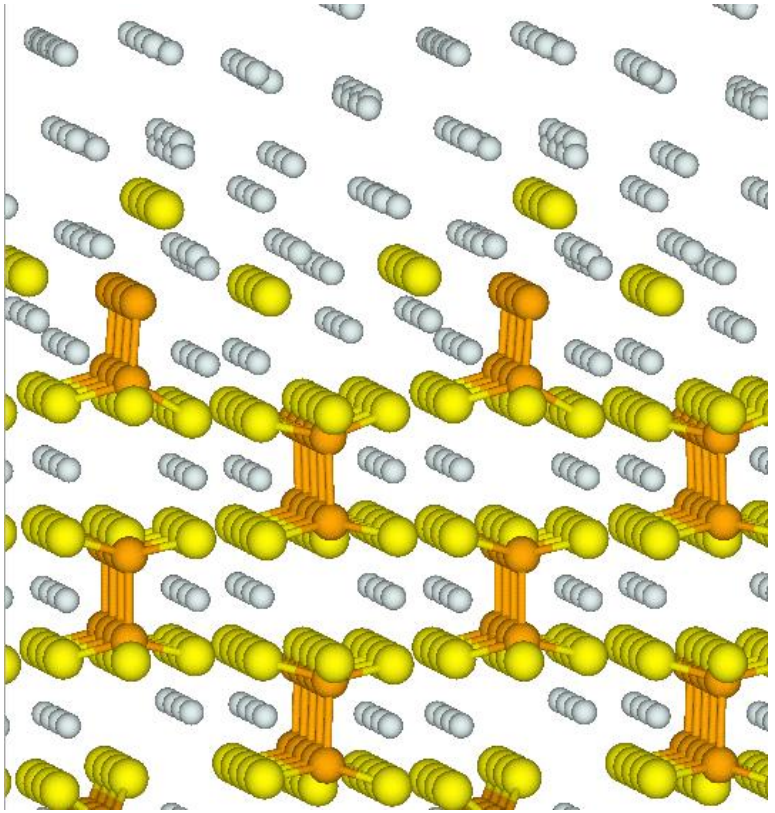
Surface with lithium

Li

P

S





Conclusions:

- Diffraction results are consistent with Mercier's 1982 analysis with disorder on P sites due to small energy differences of alignment of P_2S_6 fragments; remarkably temperature independent
- Small activation energy (E_a = 0.3 eV) for ion conductivity consistent with interstitial mechanism
- Thermal stability relative to other thio-phosphates
- Simulations of $Li_4P_2S_6$/Li interfaces suggest that meta-stable buffer layers may be formed
- Further processing of materials needed to improve conductivity and stabilize Li/$Li_4P_2S_6$/Li cells

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