Serendipitous

^ Design and synthesis of a crystalline LiPON electrolyte*

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**With help from: Nicholas Lepley (physics graduate student), Yaojun Du (previous physics postdoc) and colleagues from WFU chemistry department – Dr. Keerthi Senevirathne, Dr. Cynthia Day, Professor Michael Gross (visiting from Bucknell U.) and Professor Abdessadek Lachgar.

Outline

- Computational methods & validation
- Li_2PO_2N
  - Prediction
  - Synthesis -- *SD*-Li_2PO_2N
  - Characterization
- Interfaces of electrolyte with Li metal
  - *SD*-Li_2PO_2N and other Li phosphonitrides
  - Li thiophosphates
- Summary and conclusions

Computational methods

Summary of "first-principles" calculation methods

Exact problem :

Electronic coordinates

Atomic coordinates

$$\mathcal{H}(\{\mathbf{r}_i\},\{\mathbf{R}^a\})\Psi_\alpha(\{\mathbf{r}_i\},\{\mathbf{R}^a\}) = E_\alpha \Psi_\alpha(\{\mathbf{r}_i\},\{\mathbf{R}^a\})$$

Born-Oppenheimer approximation

Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)

Density functional theory

Hohenberg and Kohn, *Phys. Rev*. **136** B864 (1964)

Kohn and Sham, *Phys. Rev*. **140** A1133 (1965)

Approximately equivalent problem :

Electron density

Ground state energy (mean field approximation) : $E_0(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})$

$$H_{eff}(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \qquad H_{eff}(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\}) = \frac{\delta E_0(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\})}{\delta\rho(\mathbf{r})}$$

More computational details:

$$H_{eff}(\mathbf{r},\rho(\mathbf{r}),\{\mathbf{R}^a\}) = -\frac{\hbar^2\nabla^2}{2m} + \sum_a \underbrace{\frac{-Z^a e^2}{|\mathbf{r}-\mathbf{R}^a|}}_{\text{electron-nucleus}} + \underbrace{e^2\int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{electron-electron}} + \underbrace{V_{xc}\left(\rho(\mathbf{r})\right)}_{\text{exchange-correlation}}$$

Exchange-correlation functionals:

LDA: J. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)

GGA: J. Perdew, K. Burke, and M. Ernzerhof, PRL **77**, 3865 (1996)

HSE06: J. Heyd, G. E. Scuseria, and M. Ernzerhof, JCP **118**, 8207 (2003)

Numerical methods:

"Muffin-tin" construction: Augmented Plane Wave developed by Slater → "linearized" version by Andersen:

J. C. Slater, Phys. Rev. **51** 846 (1937)

O. K. Andersen, Phys. Rev. B **12** 3060 (1975) (LAPW)

Pseudopotential methods:

J. C. Phillips and L. Kleinman, Phys. Rev. **116** 287 (1959) -- original idea

P. Blöchl, Phys. Rev. B. 50 17953 (1994) – Projector Augmented Wave (PAW) method

Outputs of calculations:

Ground state energy :

$$E_0(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) \quad \Rightarrow \text{ Determine formation energies}$$

$$\min|_{\{\mathbf{R}^a\}} \left(E_0(\mathbf{r}, \rho(\mathbf{r}), \{\mathbf{R}^a\}) \right) \quad \Rightarrow \text{ Determine structural parameters}$$

$$\Rightarrow \text{ Stable and meta - stable structures}$$

$$\Rightarrow \text{ Normal modes of vibration}$$

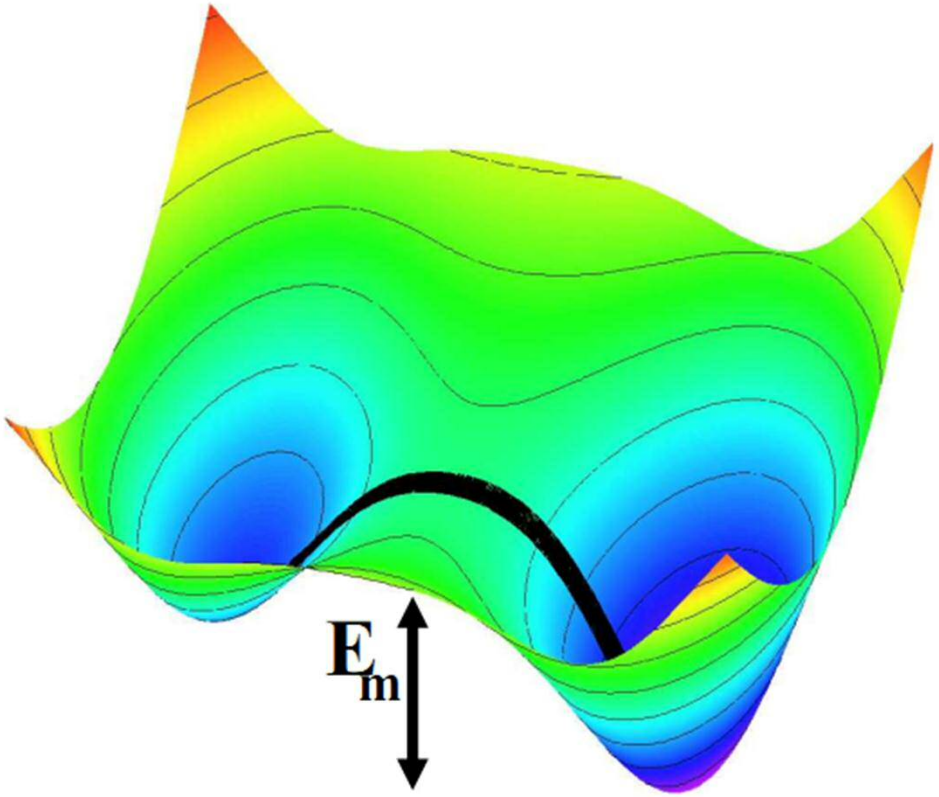
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \quad \Rightarrow \text{ Self - consistent electron density}$$

$$\{\varepsilon_n\} \quad \Rightarrow \text{ One - electron energies; densities of states}$$

Estimate of ionic conductivity assuming activated hopping

Schematic diagram of minimal energy path

Approximated using NEB algorithm[a]
– "Nudged Elastic Band"



[a] Henkelman and Jónsson, *JCP* **113**, 9978 (2000)

Arrhenius relation

$$\sigma \cdot T = K e^{-E_A/kT}$$

From: Ivanov-Shitz and co-workers, *Cryst. Reports* **46**, 864 (2001):

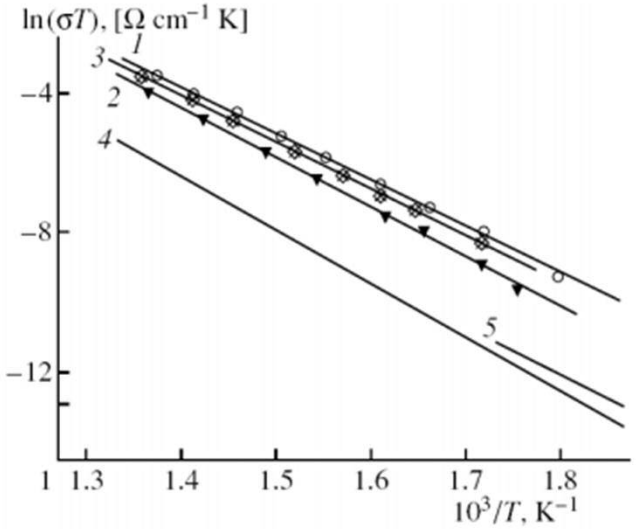


Fig. 2. Temperature dependences of conductivity in γ-Li_3PO_4: (*1*–*3*) for single crystals measured along the (*1*) *a*-axis, (*2*) *b*-axis, (*3*) *c*-axis and (*4*, *5*) for a polycrystal (*4*) according to [4, 5] and (*5*) according to [7].

E_A = 1.14, 1.23, 1.14, 1.31, 1.24 eV for 1,2,3,4,5, respectively.

Public domain codes available for electronic structure calculations

Method	Codes	Comments
LAPW	www.wien2k.at elk.sourceforge.net	Works well for smaller unit cells; variable unit cell optimization not implemented. Need to choose non-overlapping muffin tin radii and avoid "ghost" solutions.
PAW	www.abinit.org www.quantum-espresso.org	Works well for large unit cells (<200 atoms or so); includes variable unit cell optimization.
ATOMPAW	pwpaw.wfu.edu	Generates PAW datasets for *abinit* and *quantum-espresso* (and other codes)

Other efforts:

- Gerbrand Ceder's group at MIT – Materials Project; A Materials Genome Approach -- http://www.materialsproject.org/
- Stefano Curtarolo's group at Duke – Energy Materials Laboratory -- http://materials.duke.edu/

ATOMPAW Code for generating atomic datasets for PAW calculations

Holzwarth, Tackett, and Matthews, CPC 135 329 (2001) http://pwpaw.wfu.edu

ATOMPAW
INFO
DATASETS
NAWH Web
PHYSICS Web
WFU Web

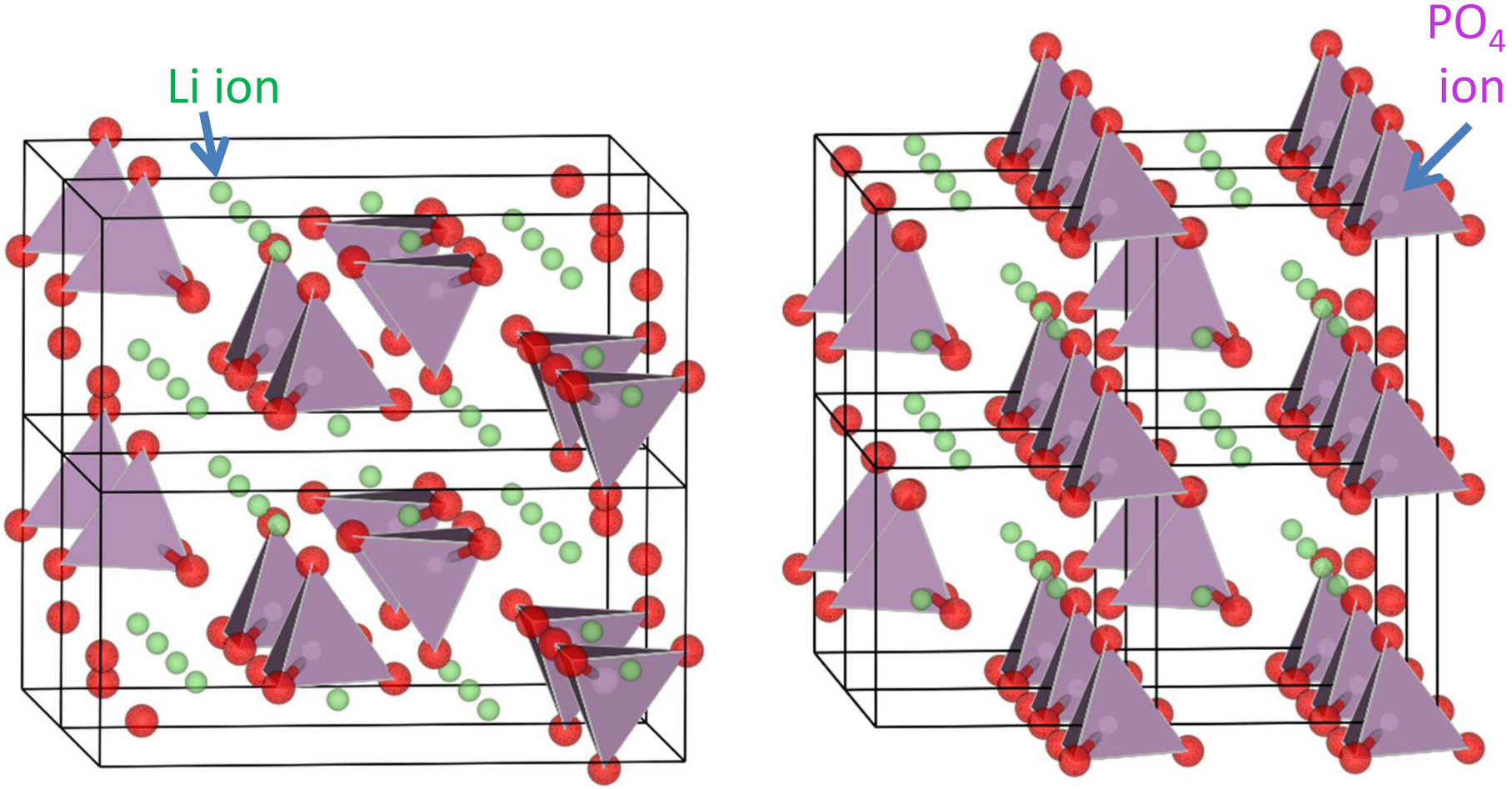
ATOMPAW (updates and testing in progress --)

Download source code and example files:

- atompaw-3.0.1.9.tar.gz (3.8mb) Updated version of *atompaw* code (09/20/2012 -- Yann Pouillon updated the autotools for constructing the tar file; 07/16/2012 -- Geoffrey Pourois corrected GIPAW portion of pwscfinterface.f90; 06/26/12 -- NAWH corrected bug in pwscfinterface.f90 on top of previous revisions on 06/13/12 and 04/14/12 by Marc Torrent), and previous changes 10/03/11 by Marc Torrent and Yann Pouillon updating interface for use with LibXc. This version is still compatible with pwscf including recent addition by D. Ceresoli for gipaw calculations. The 3.0+ versions have several features due largely to the magic of Marc Torrent (CEA, France) and Yann Pouillon (ETSF, Spain) including compatability for use with LibXC.
  - The code package now complies with linux installation standards.
  - Using new options in the input file, datasets for use with *abinit* (replacing the need to run the separate atompaw2abinit code) or *pwscf, quantum-espresso* can be generated. (For developing the UPF file for use with *pwscf*, help from Lorenzo Paulatto and Paolo Giannozzi is gratefully acknowledged.)
  - The use of atompaw with LibXC library of exchange-correlation functionals are now possible for generating datasets for *abinit*.
  - Details are given in the user's guide written by Marc Torrent.
  - Some details concerning choices of the shapes of compensation charge densities have been clarified as explained in a recent publication.
  - Simple gnuplot scripts are available to help analyze some of the outputs of the atompaw program.

Example validation of computation methods

Li_3PO_4 crystals

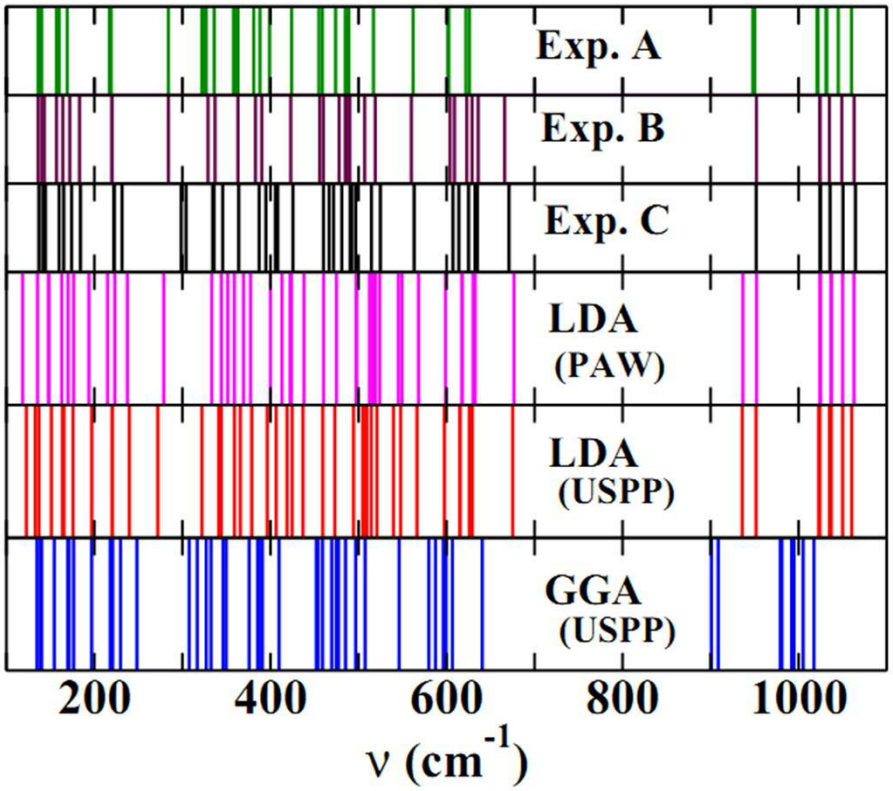


γ-Li_3PO_4 *(Pnma)*

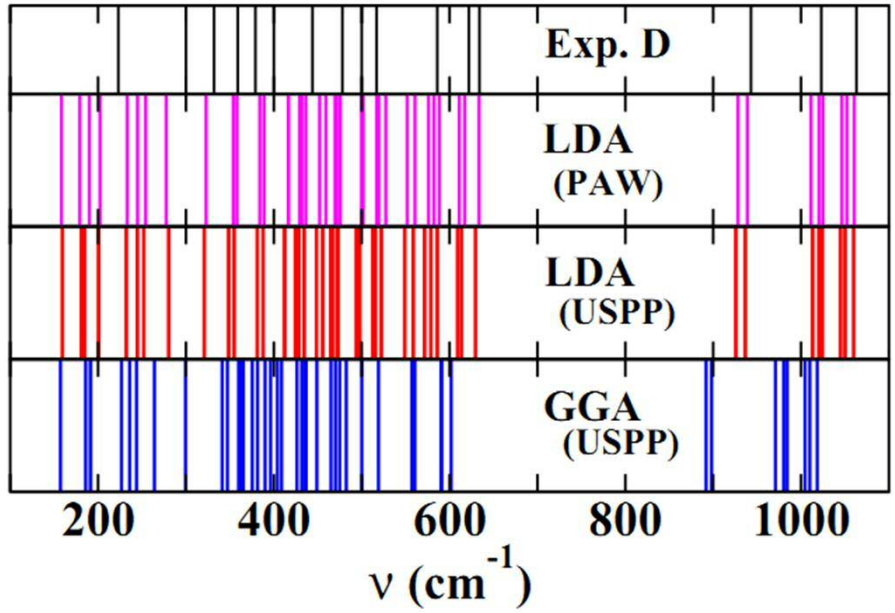
β-Li_3PO_4 *(Pnm2$_1$)*

Validation of calculations

Raman spectra – Experiment & Calculation



γ-Li_3PO_4

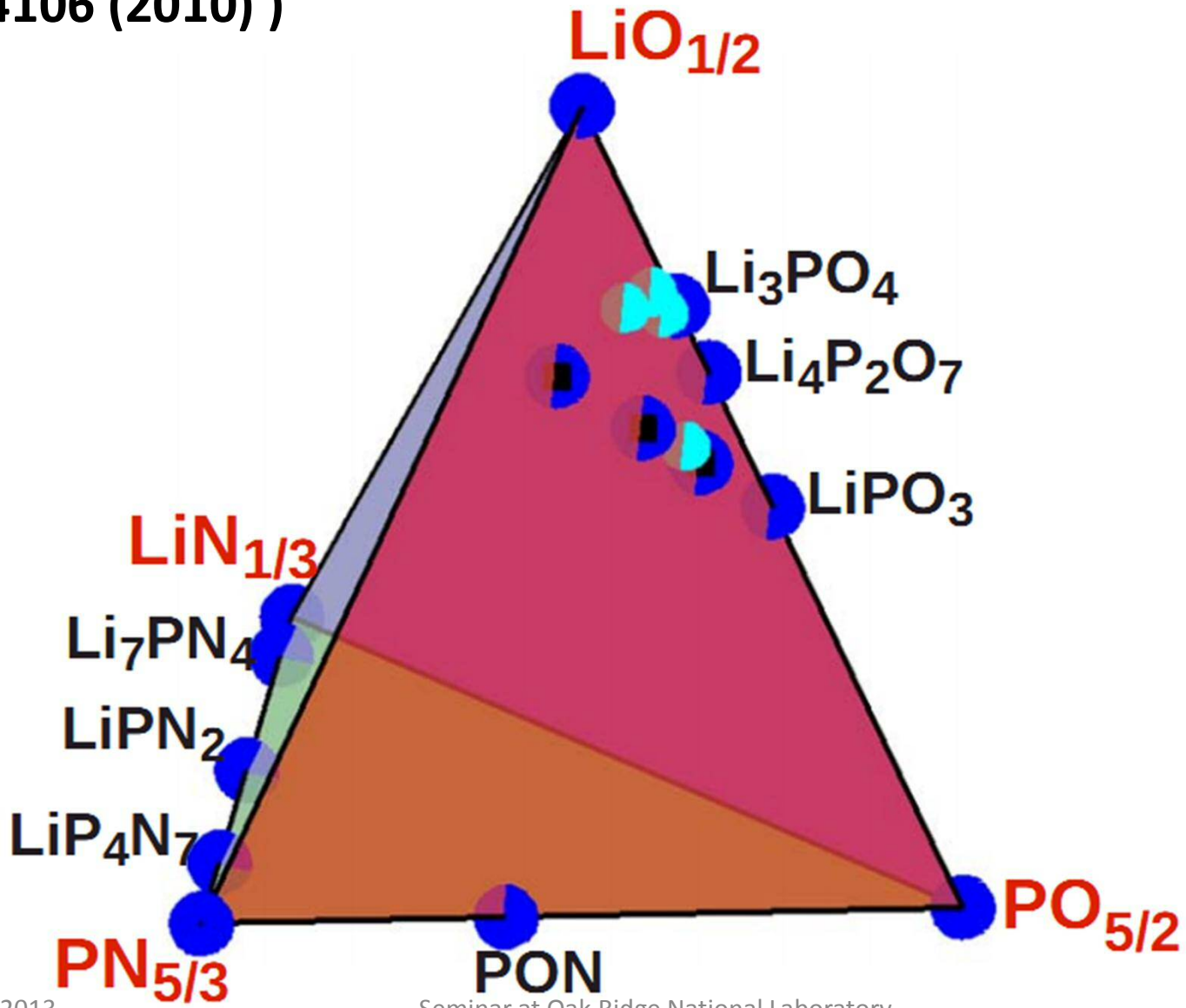


β-Li_3PO_4

A: B. N. Mavrin et al, J. Exp. Theor. Phys. **96**,53 (2003); B: F. Harbach and F. Fischer, Phys. Status Solidi B **66**, 237 (1974) – room temp. C: Ref. B at liquid nitrogen temp.; D: L. Popović et al, J. Raman Spectrosc. **34**,77 (2003).

The Li_2PO_2N story

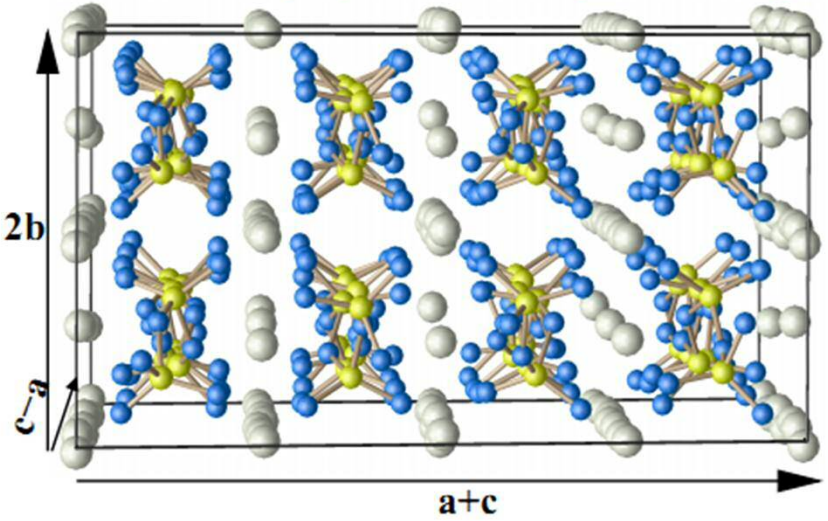
Systematic study of LiPON materials – $Li_xPO_yN_z$ – (Yaojun A. Du and N. A. W. Holzwarth, Phys. Rev. B 81, 184106 (2010))



Phosphate chain materials: $LiPO_3$ plus N

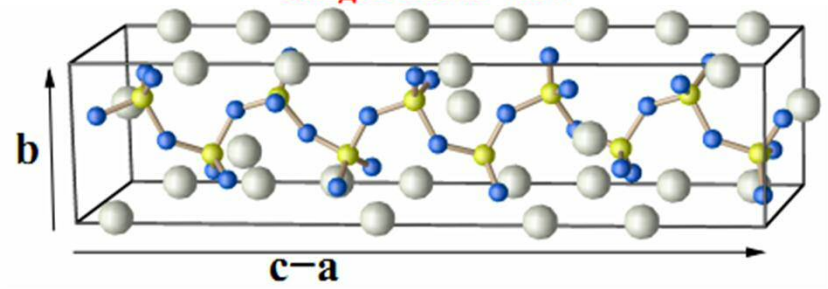
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



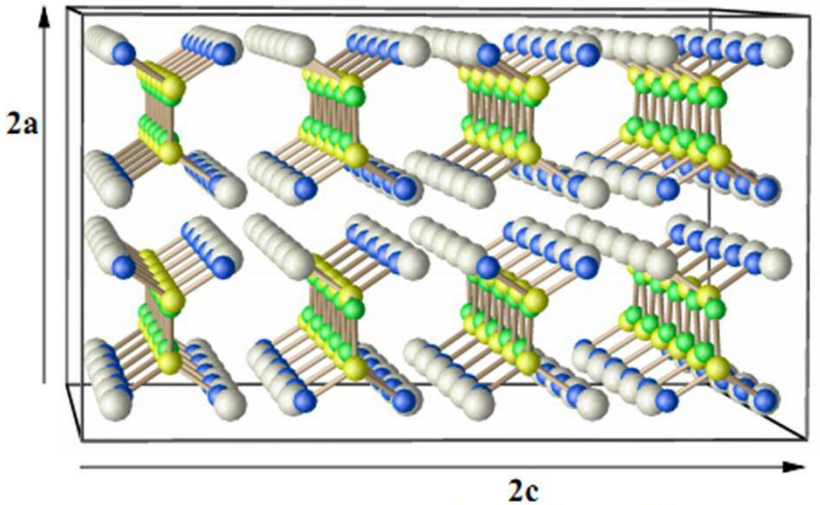
Ball colors: =Li, =P, =O.

Single chain view



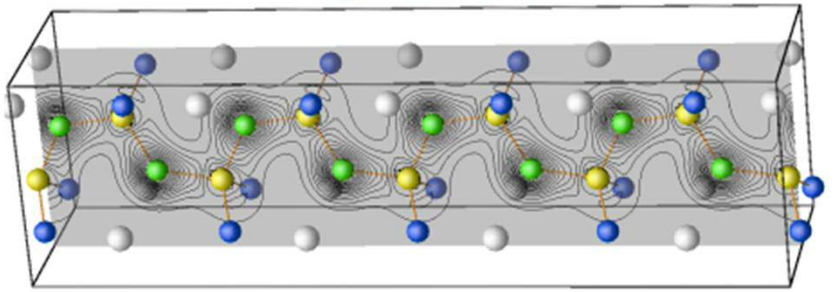
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram

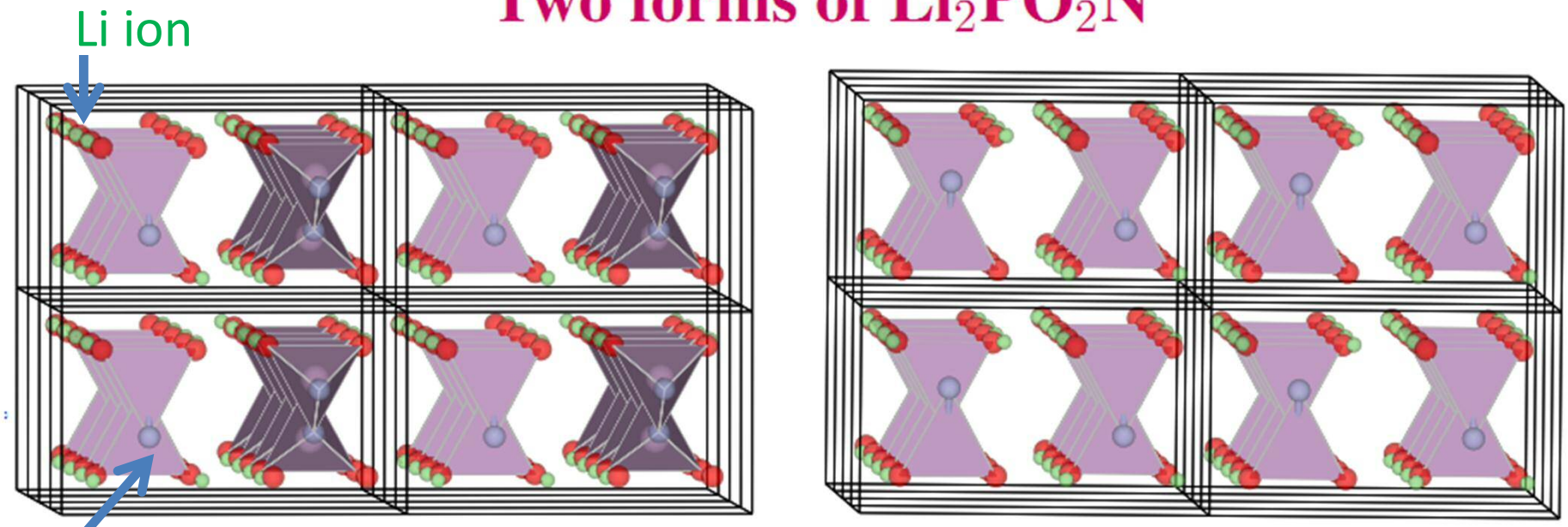


Ball colors: =Li, =P, =O, =N.

Single chain view



Two forms of Li_2PO_2N



s_1-Li_2PO_2N *(Pbcm)*

s_2-Li_2PO_2N *(Aem2)*

Possible exothermic reaction pathways:

$$\tfrac{1}{5}P_2O_5 + \tfrac{1}{5}P_3N_5 + Li_2O \rightarrow Li_2PO_2N + 2.5\,\text{eV}.$$

$$Li_2O_2 + \tfrac{1}{5}P_3N_5 + \tfrac{2}{5}P \rightarrow Li_2PO_2N + 5.3\,\text{eV}.$$

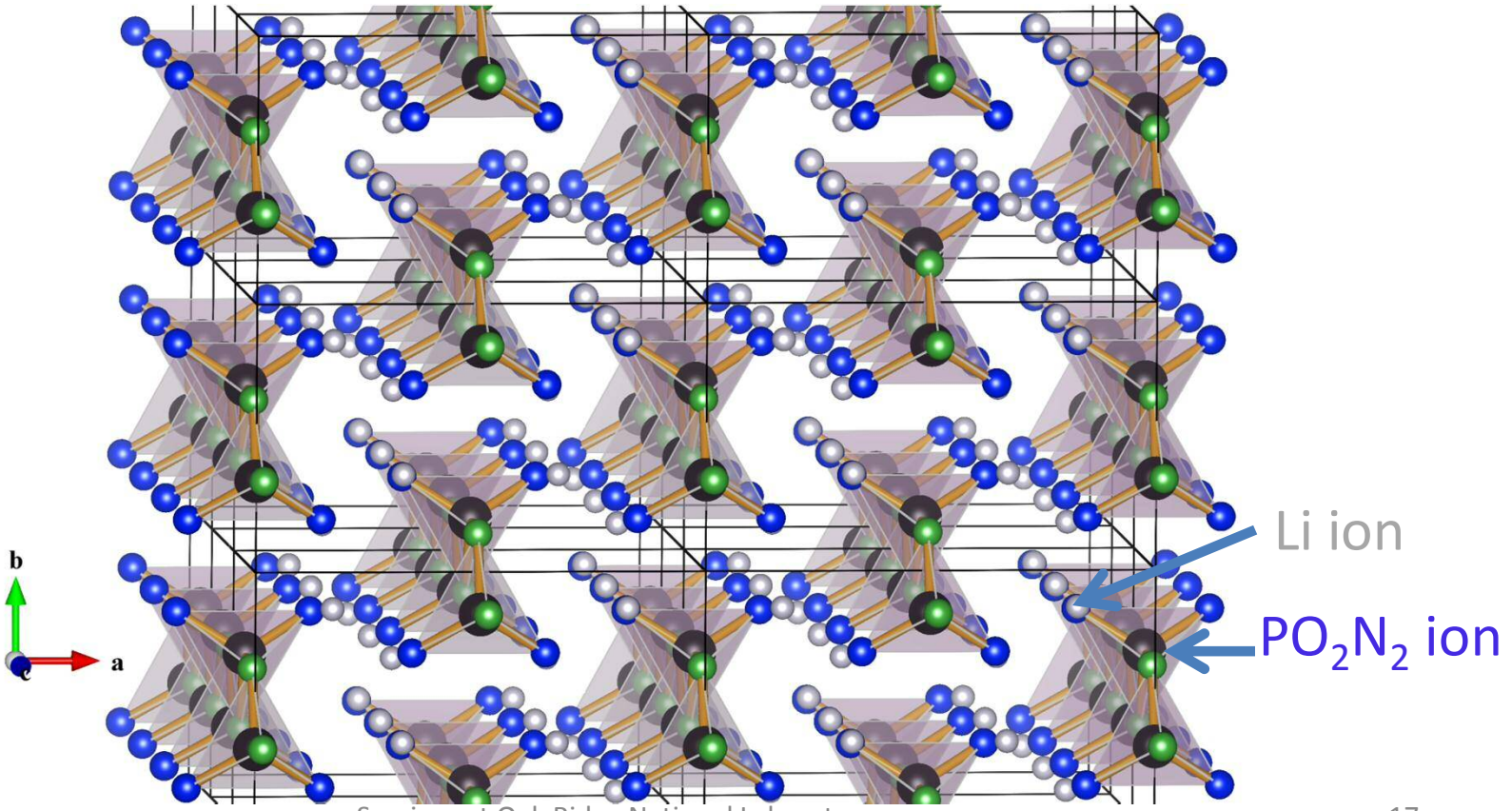
$$LiNO_3 + Li + P \rightarrow Li_2PO_2N + \tfrac{1}{2}O_2 + 7.0\,\text{eV}.$$

Synthesis of Li_2PO_2N by Keerthi Senevirathne, Cynthia Day, Michael Gross, and Abdessadek Lachgar

Method: High temperature solid state synthesis based on reaction

$$Li_2O + \tfrac{1}{5}P_2O_5 + \tfrac{1}{5}P_3N_5 \rightarrow Li_2PO_2N$$

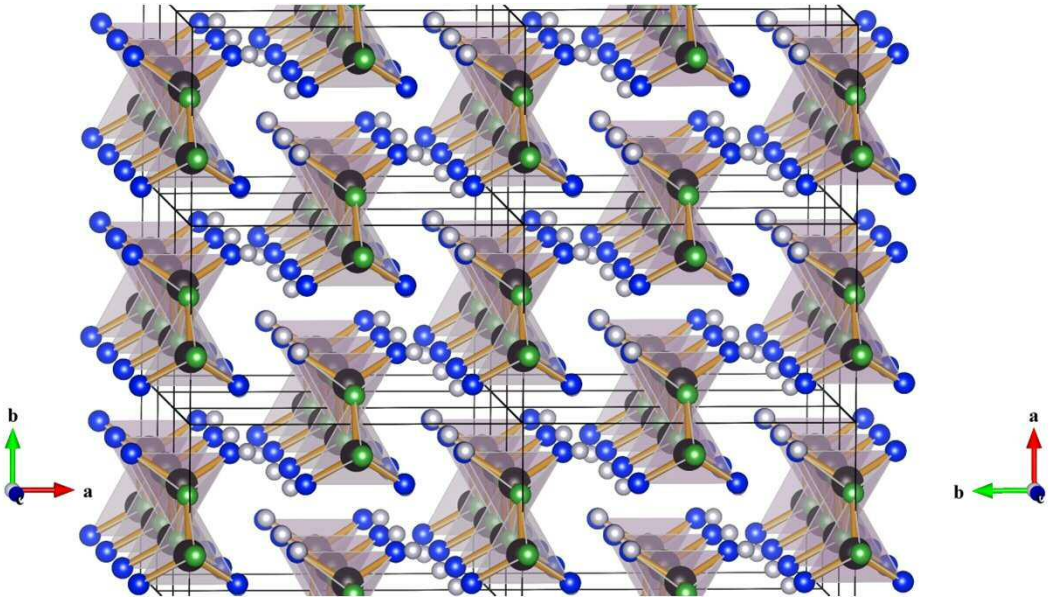
Structure from X-ray refinement: $Cmc2_1$

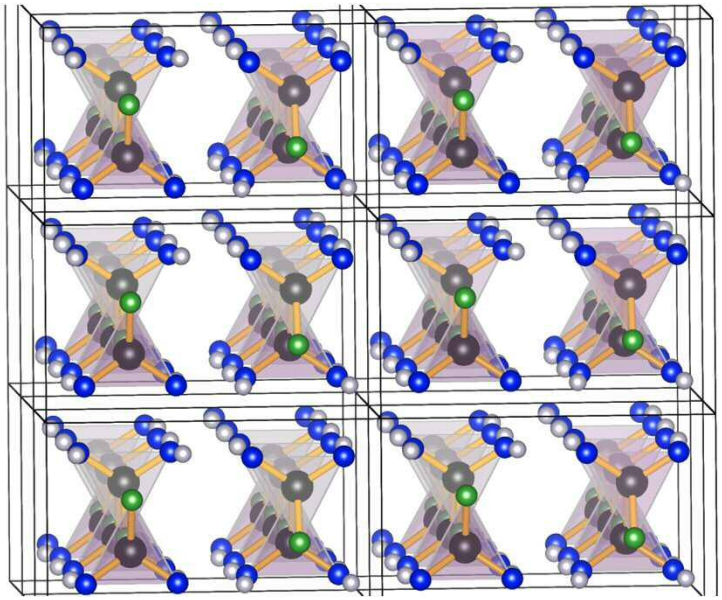


Comparison of synthesized and predicted structures of Li_2PO_2N:

Synthesized

Predicted





Li P O N

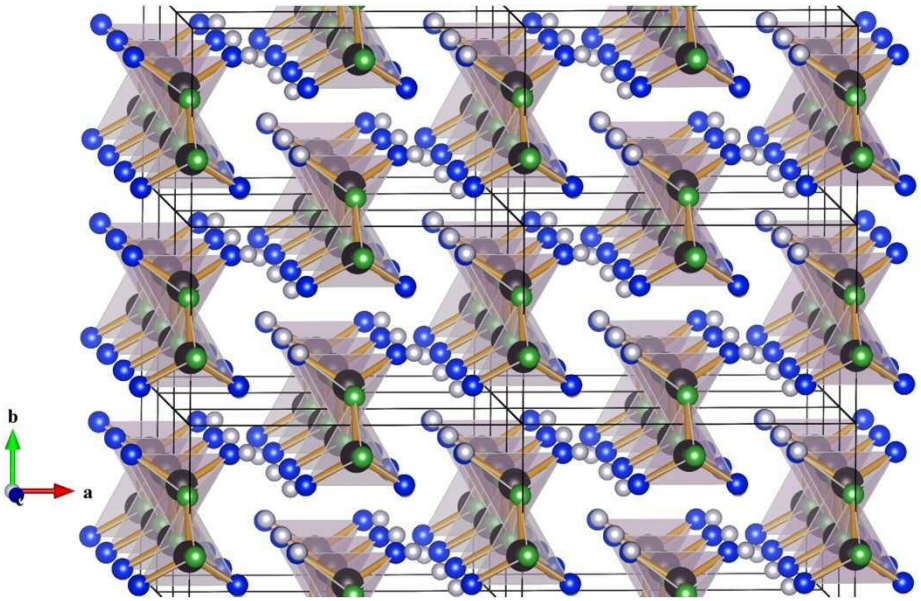
SD*-Li_2PO_2N *(Cmc2$_1$)

s$_2$*-Li_2PO_2N *(Aem2)

Calculations have now verified that the SD structure is more stable than the s_2 structure by 0.1 eV/FU.

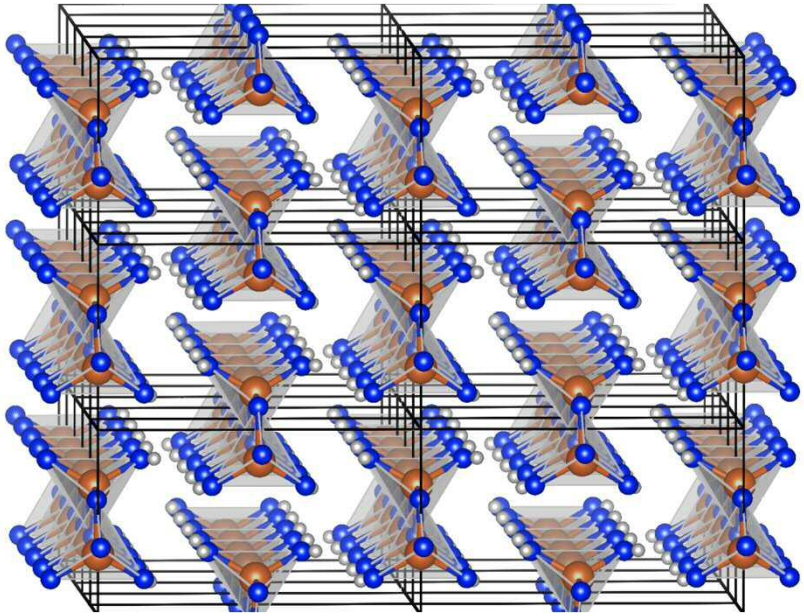
Comparison of synthesized Li_2PO_2N with Li_2SiO_3

SD-Li_2PO_2N (*Cmc2₁*)



a=9.07 Å, b=5.40 Å, c=4.60 Å

Li_2SiO_3 (*Cmc2₁*)

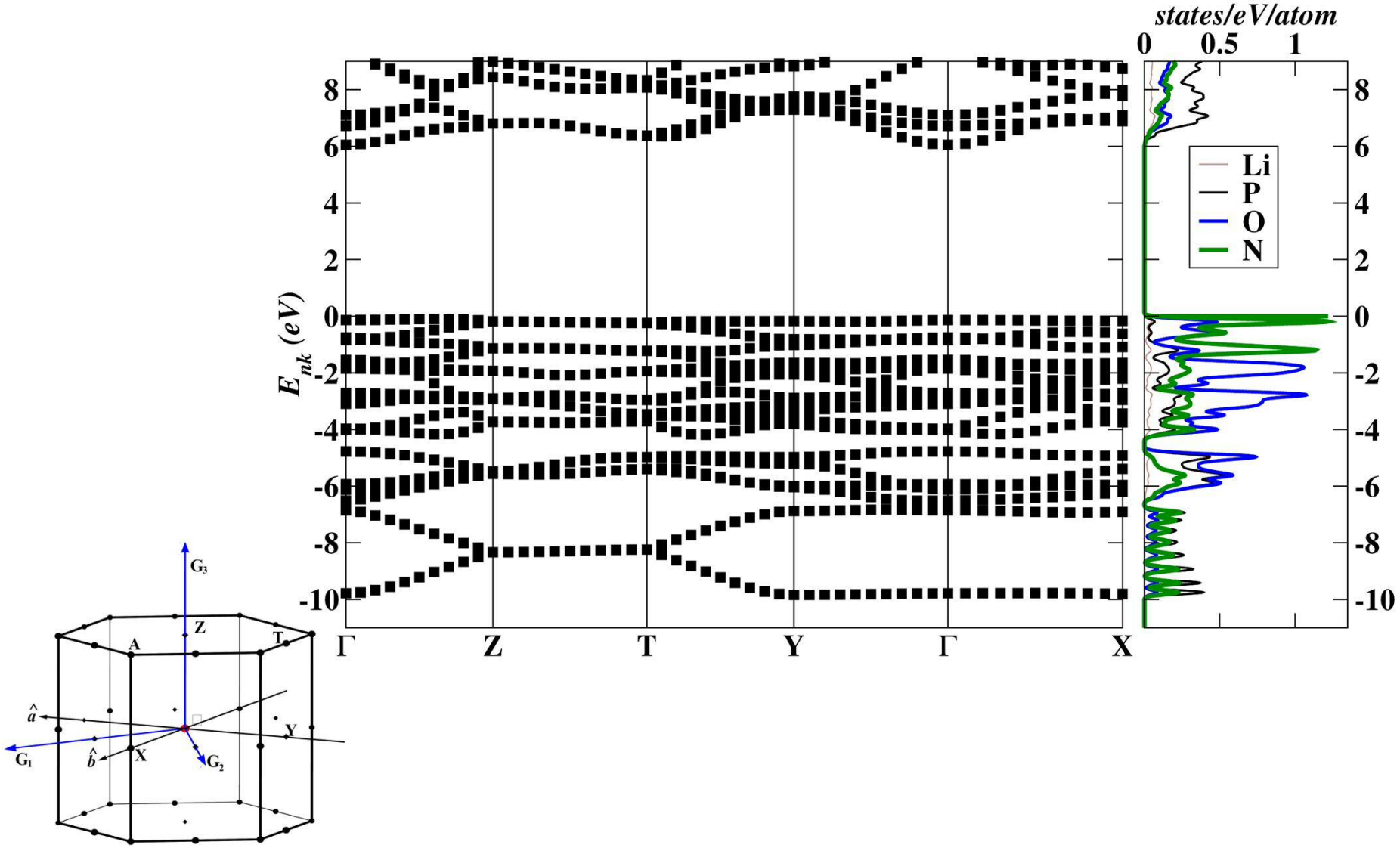


a=9.39 Å, b=5.40 Å, c=4.66 Å

K.-F. Hesse, Acta Cryst. B33, 901 (1977)

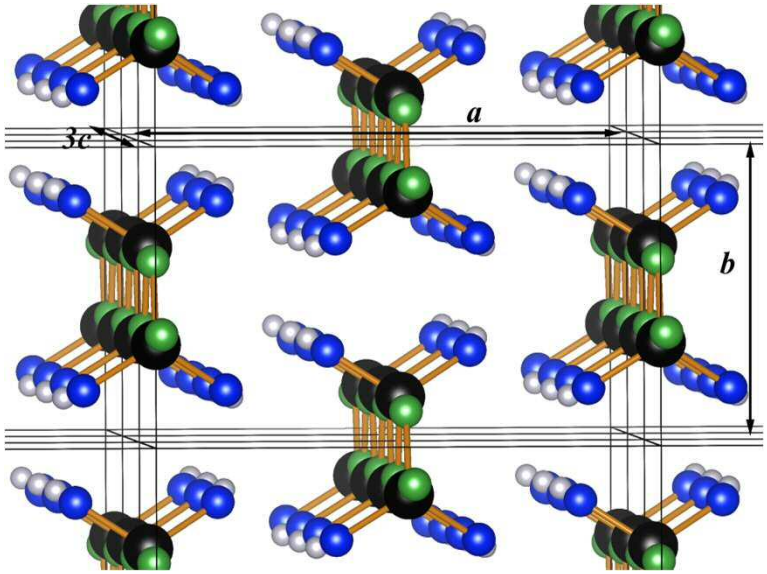
Li P O N Si

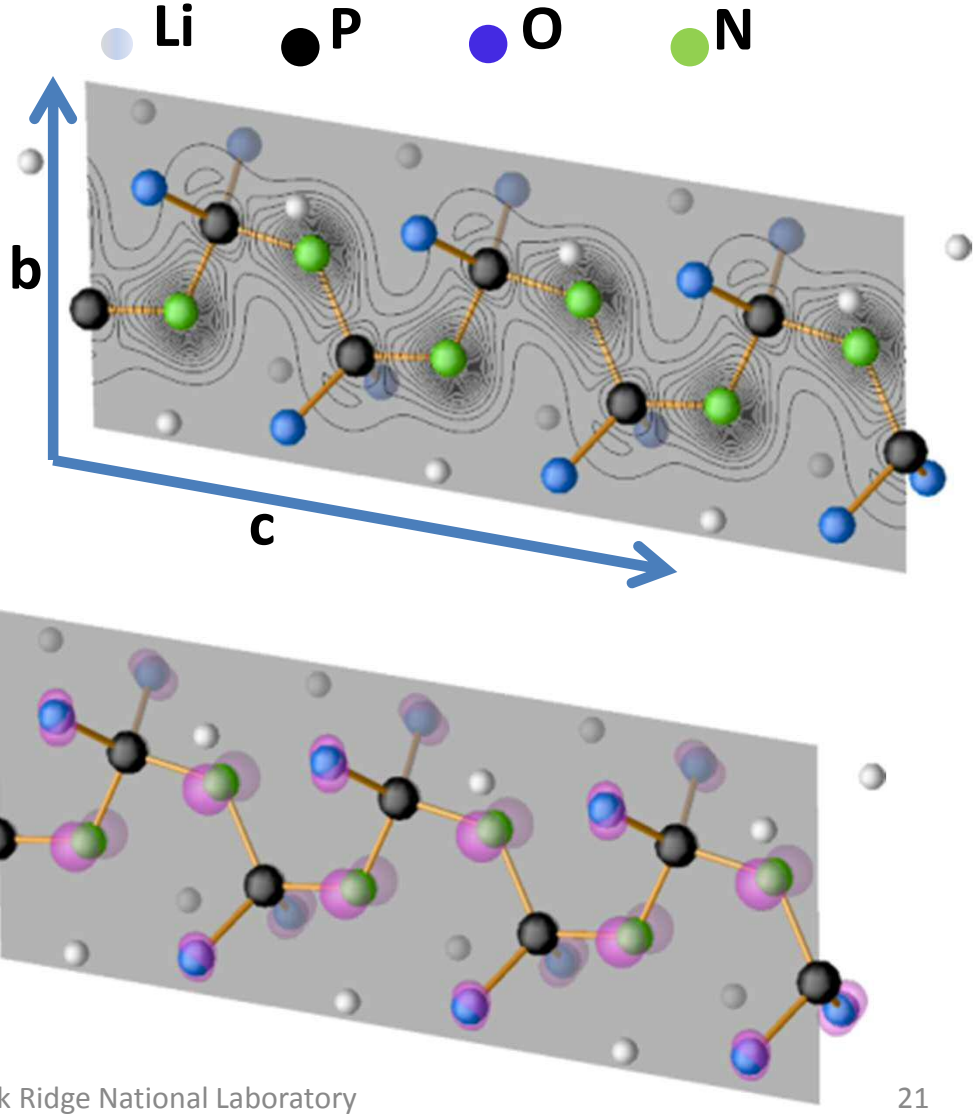
Electronic band structure of *SD*-Li_2PO_2N



More details of *SD*-Li_2PO_2N structure

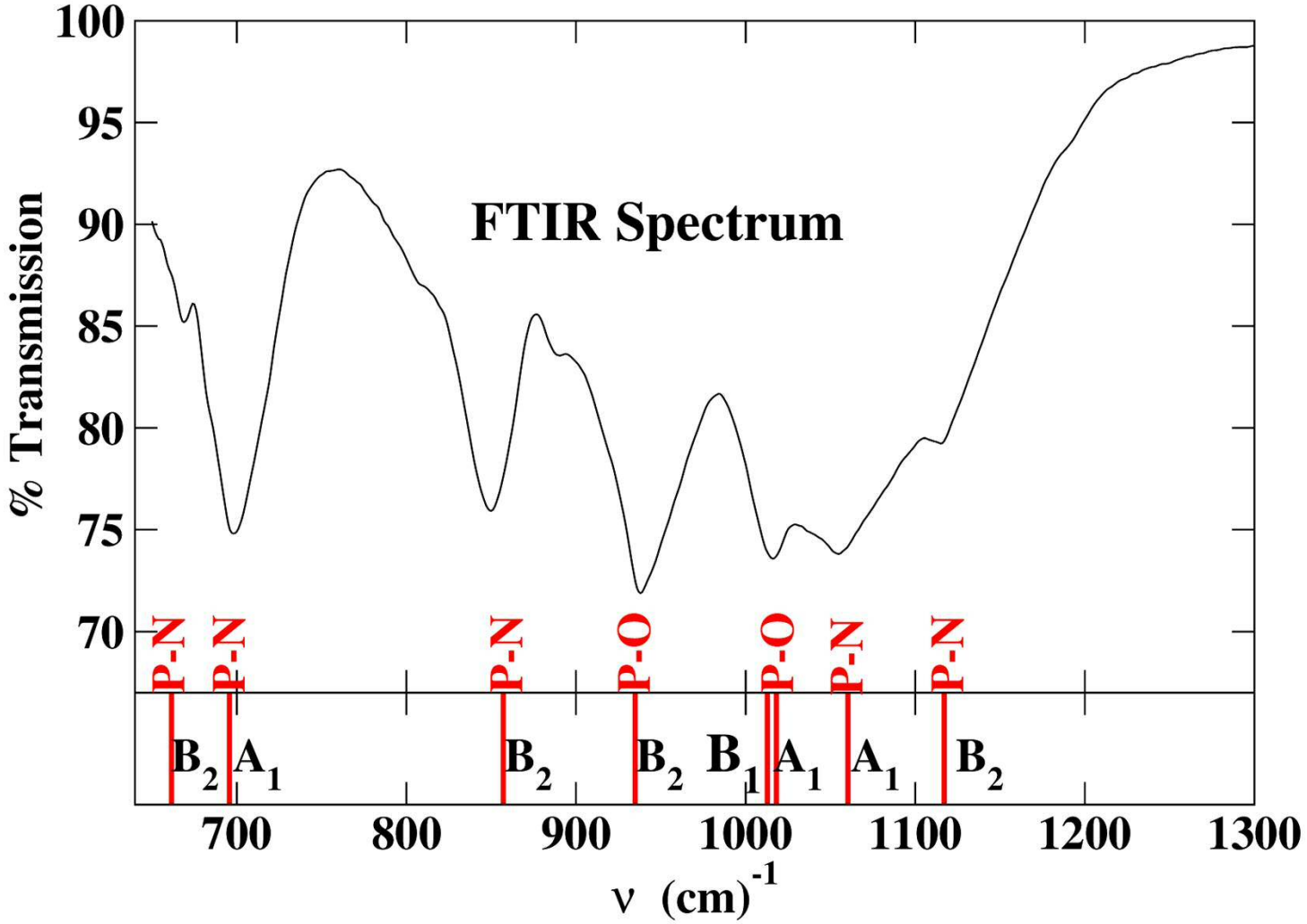
Ball and stick model



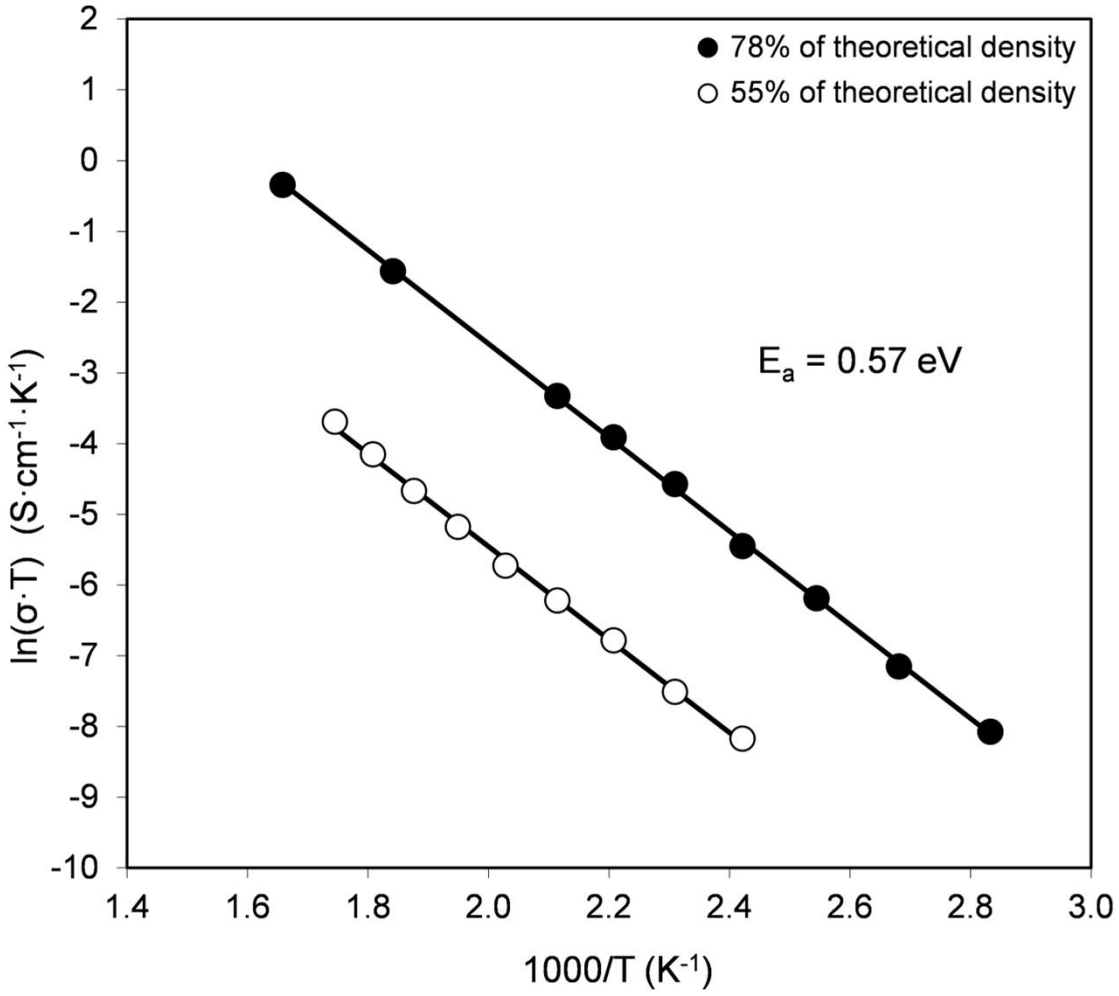


Isosurfaces (maroon) of charge density of states at top of valence band, primarily π states on N.

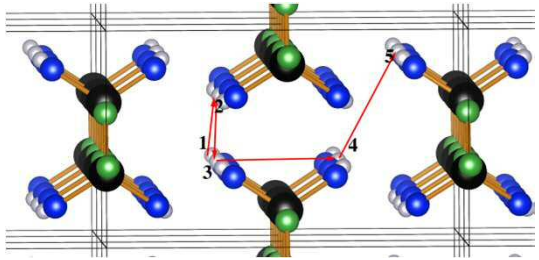
Vibrational spectrum of *SD*-Li_2PO_2N

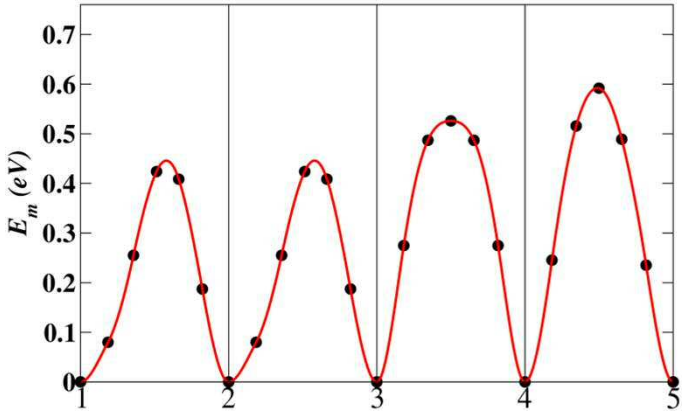


Ionic conductivity of *SD*-Li_2PO_2N



NEB analysis of E_m (vacancy mechanism)





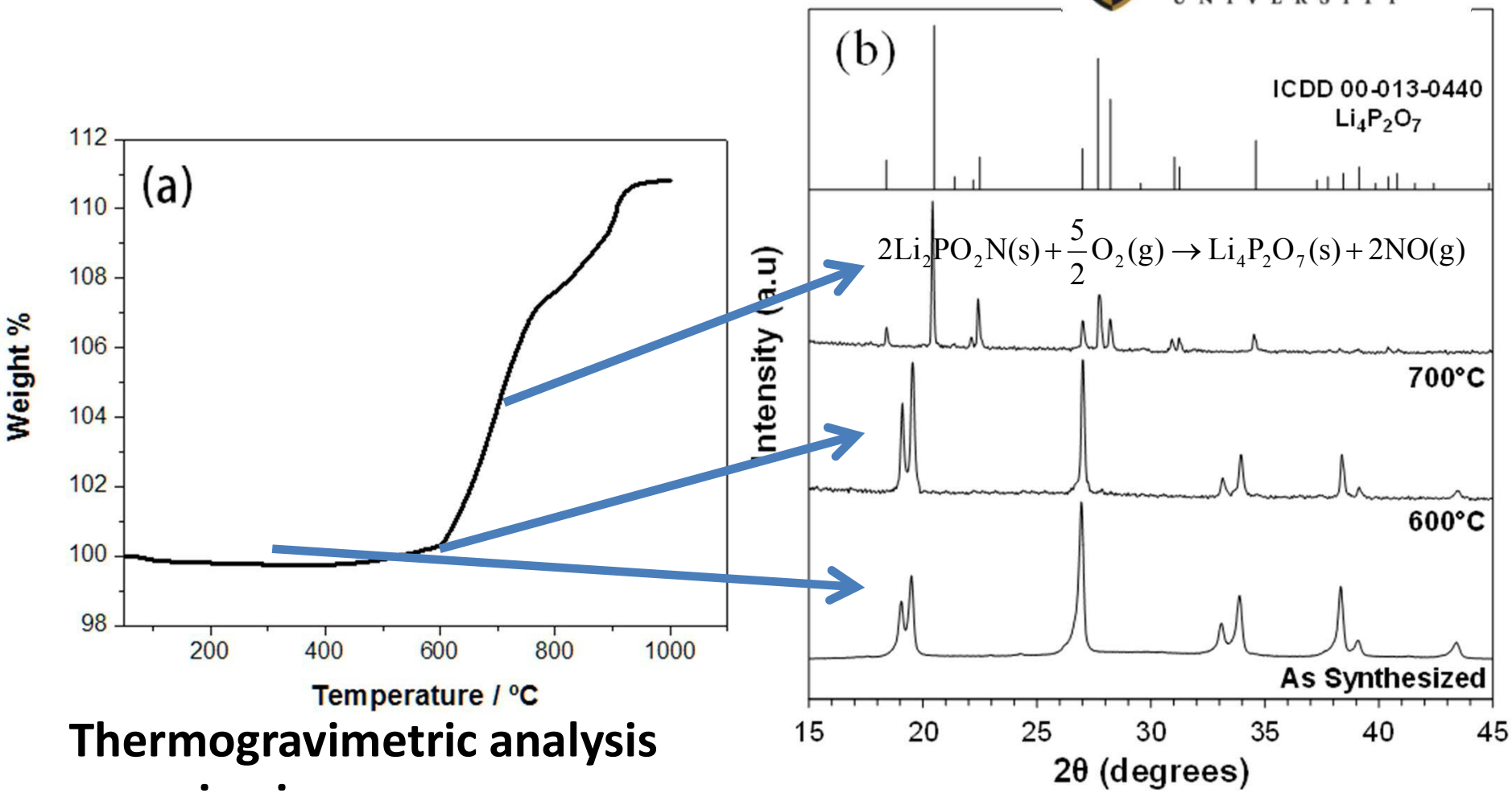
WAKE FOREST UNIVERSITY

Summary of measured and calculated conductivity parameters in $Li_xPO_yN_z$ materials

Measured activation energies E_A^{exp} compared with calculated migration energies for vacancy (E_m^{cal} (vac.)) and interstitial (E_m^{cal} (int.)) mechanisms and vacancy-interstitial formation energies (E_f^{cal}). All energies are given in eV.

Material	Form	E_A^{exp}	E_m^{cal} (vac.)	E_m^{cal} (int.)	E_f^{cal}	E_A^{cal}
γ-Li_3PO_4	single crystal[a]	1.23, 1.14	0.7, 0.7	0.4, 0.3	1.7	1.3, 1.1
$Li_{2.88}PO_{3.73}N_{0.14}$	poly cryst.	0.97				
$Li_{3.3}PO_{3.9}N_{0.17}$	amorphous	0.56				
$Li_{1.35}PO_{2.99}N_{0.13}$	amorphous	0.60				
$LiPO_3$	poly cryst.	1.4	0.6, 0.7	0.7	1.2	1.1-1.2
$LiPO_3$	amorphous	0.76-1.2				
s_1-Li_2PO_2N	single crystal		0.5, 0.6		1.7	1.3-1.5
$LiPN_2$	poly cryst.	0.6	0.4		2.5	1.7
Li_7PN_4	poly cryst.	0.5				

Stability of *SD*-Li_2PO_2N in air

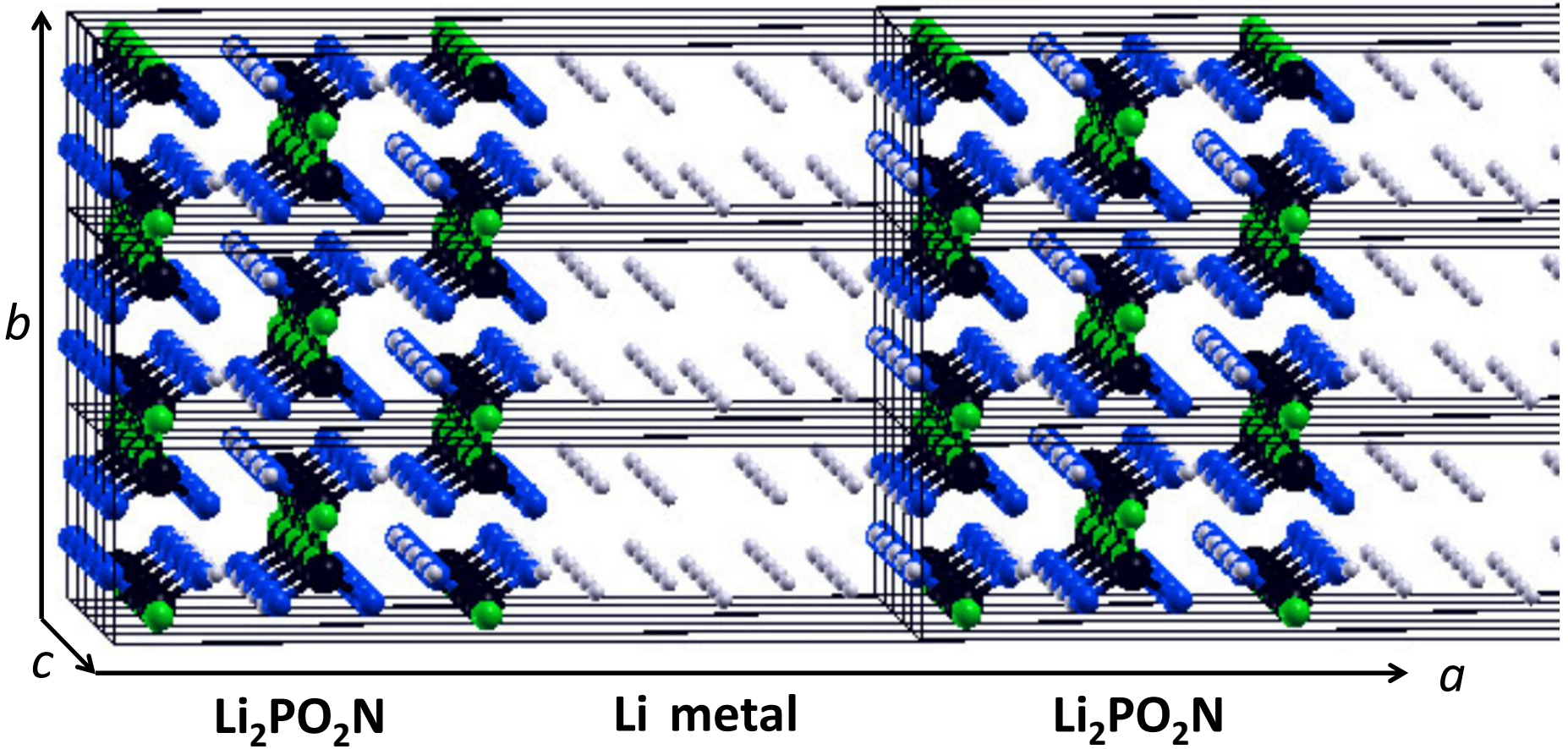


Thermogravimetric analysis curve in air

Note: no structural changes were observed while heating in vacuum up to 1050° C.

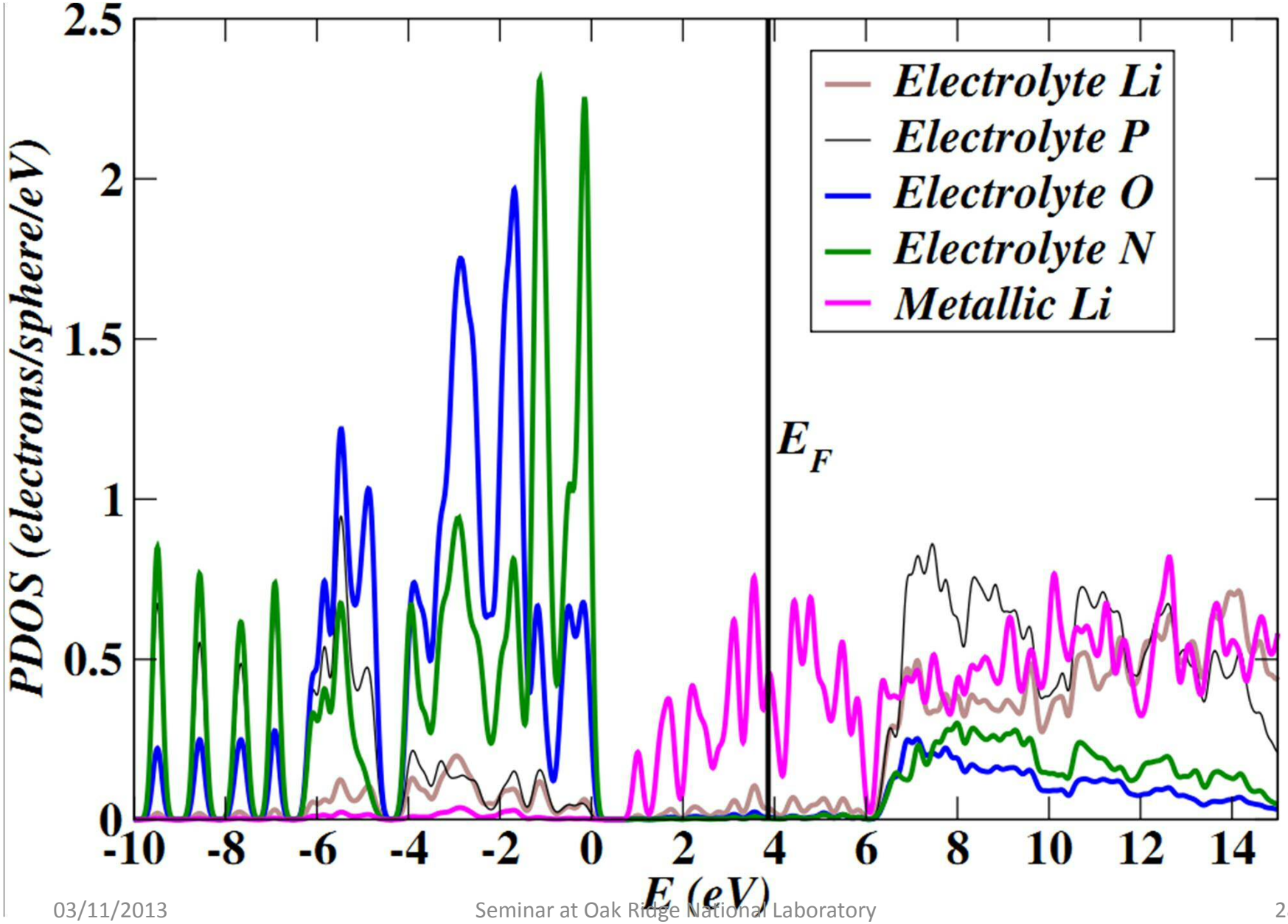
Models of electrolyte interfaces with Li metal

Model of stable $Li_2PO_2N/Li/Li_2PO_2N/$ … interface structure



(Supercell contains 6 Li_2PO_2N and 9 Li)

PDOS for model interface -- $Li_2PO_2N/Li/Li_2PO_2N/$ …



Thiophosphate electrolytes

Other electrolyte materials -- thiophosphate

LiPON and LiS_2-P_2S_5 conductivities

X. Yu, J. B. Bates, G. E. Jellison, Jr., and F. X. Hart, J. Electrochem. Soc. **144** 524-532 (1997):

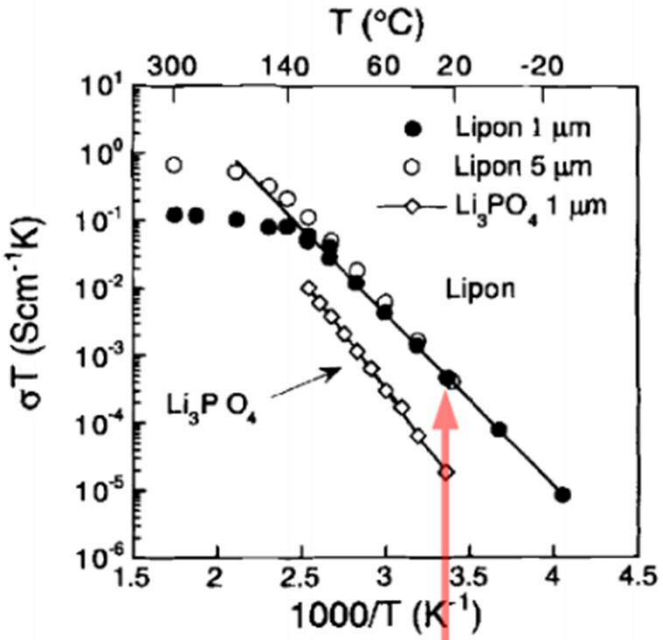


Fig. 3. Arrhenius plot of ionic conductivity of Lipon and Li_3PO_4 vs. temperature.

$\sigma = 2 \times 10^{-6}$ S/cm
$E_a = 0.5$ eV

M. Tatsumisago and A. Hayashi, J. Non-Cryst. Solids **354** 1411-1417 (2008):

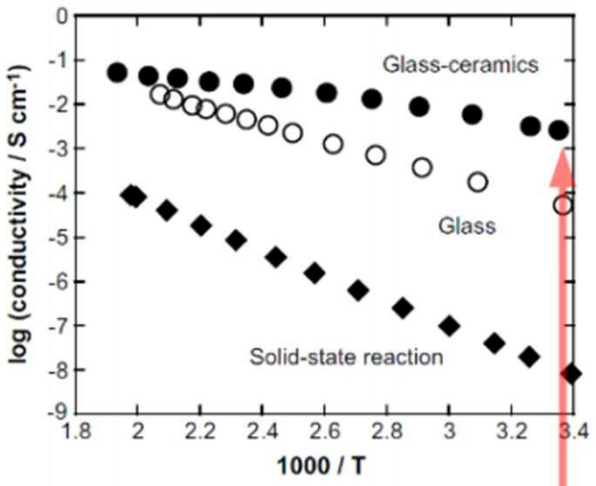
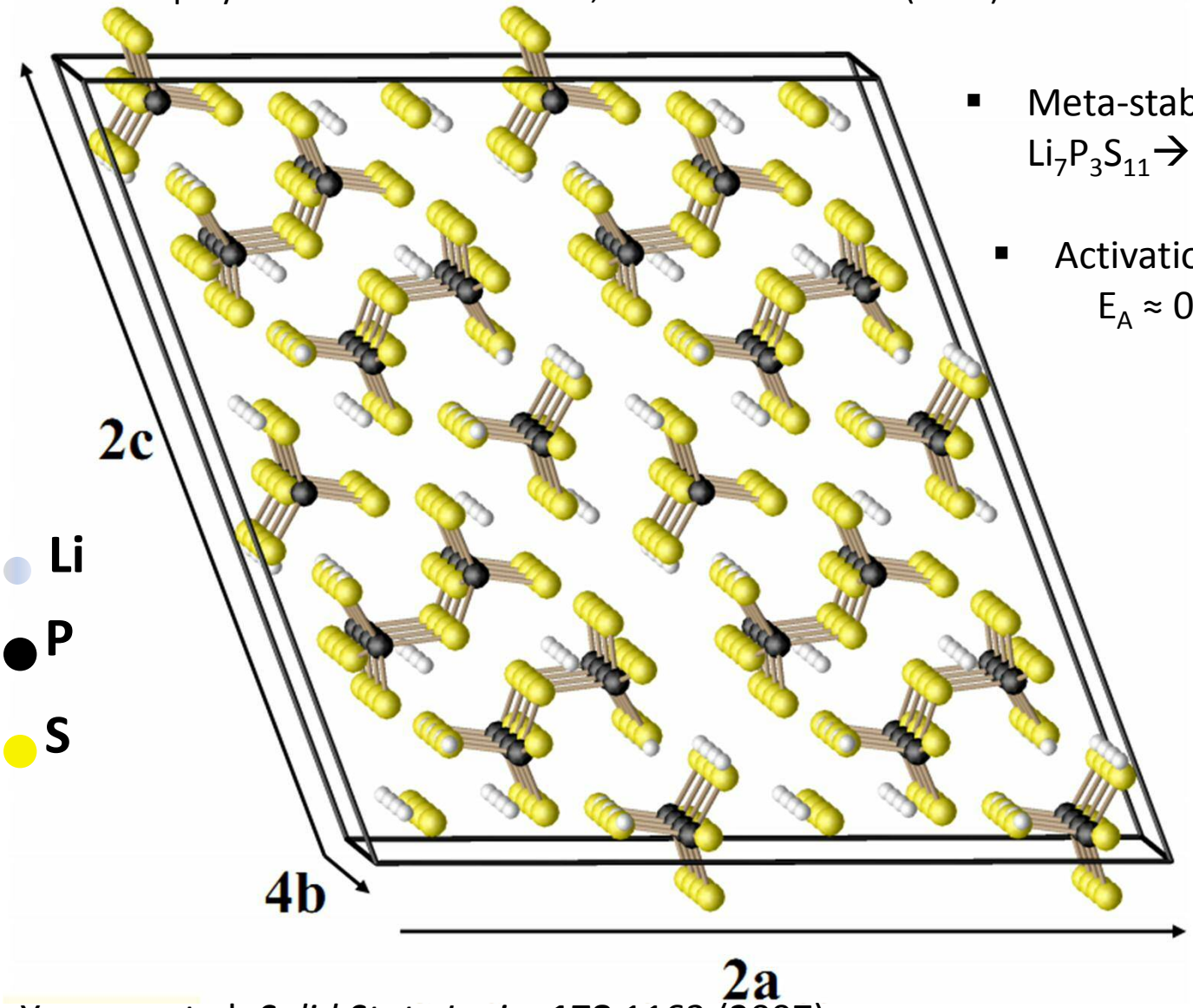


Fig. 5. Temperature dependences of the conductivities for the $70Li_2S \cdot 30P_2S_5$ glass and glass–ceramics. The conductivity data for the sample prepared by solid-state reaction are also shown.

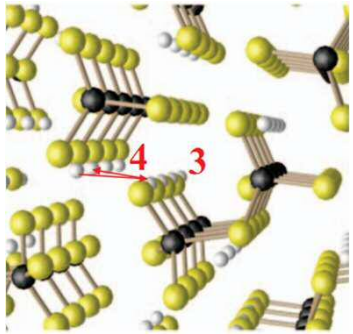
$\sigma = 3 \times 10^{-3}$ S/cm
$E_a = 0.1$ eV

"Superionic conductor" $Li_7P_3S_{11}$

N. D. Lepley and N. A. W. Holzwarth, JES **159** A538-A547 (2012)



- Meta-stable to decomposition: $Li_7P_3S_{11} \rightarrow Li_3PS_4 + Li_4P_2S_6 + S$
- Activation energy estimate: $E_A \approx 0.2$ eV (Exp. 0.1 eV)



- Interstitial-vacancy pair formation energy $E_f \approx 0$

Yamane et al, *Solid State Ionics* **178** 1163 (2007)

Other electrolyte materials -- thiophosphate

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Anomalous High Ionic Conductivity of Nanoporous β-Li_3PS_4

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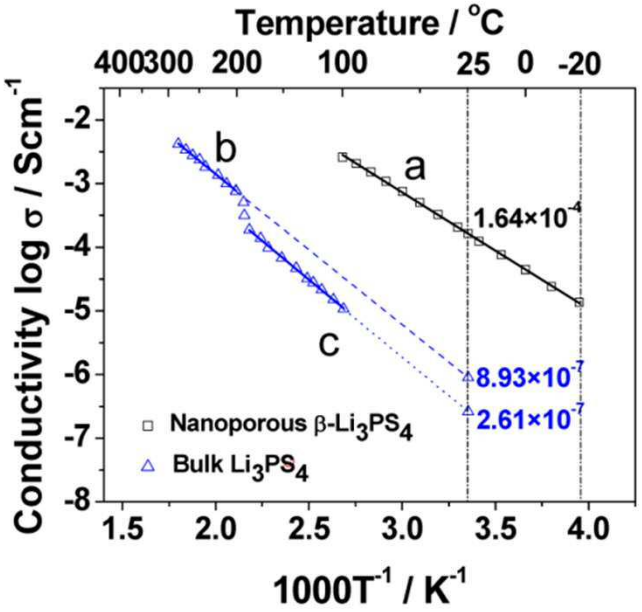
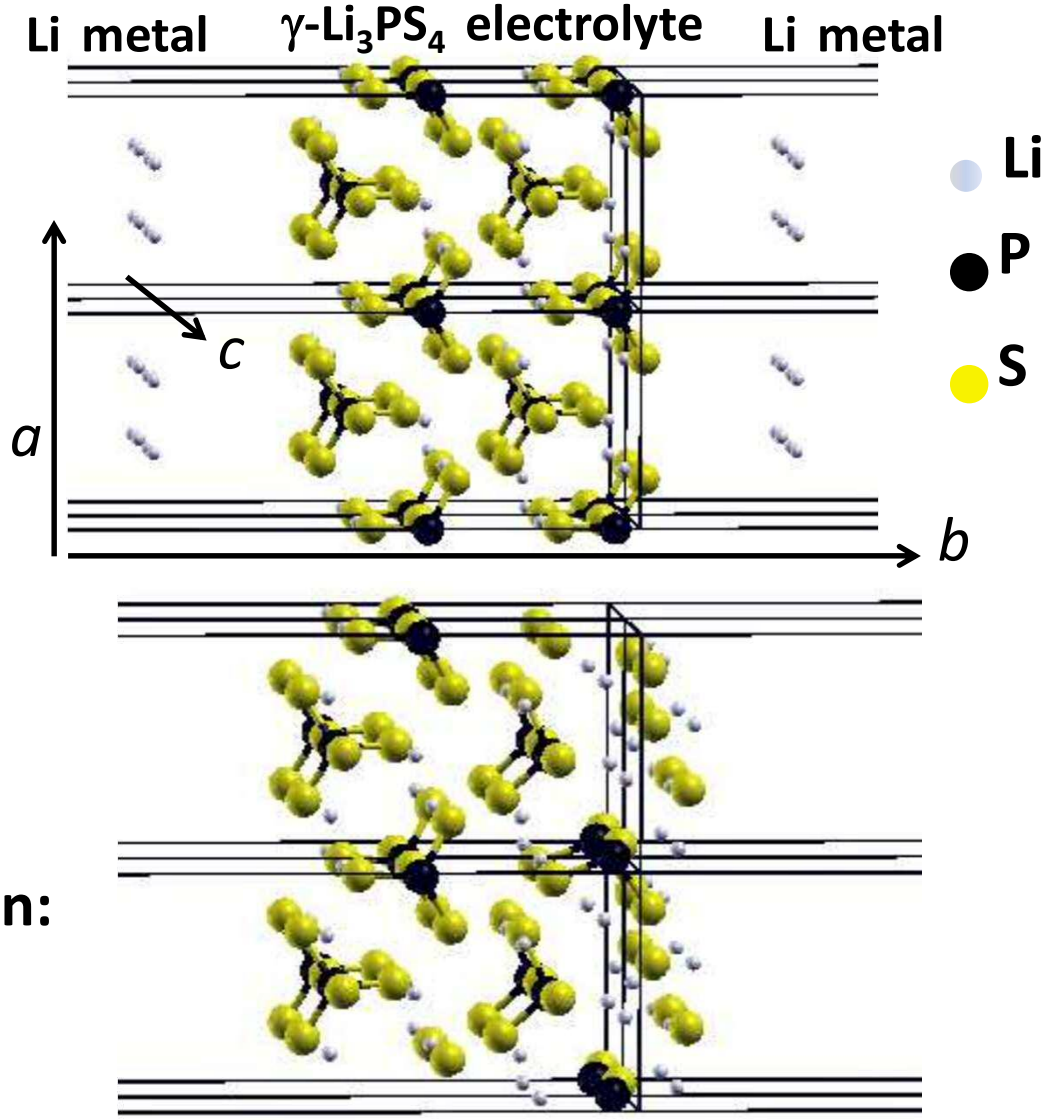


Figure 1. Arrhenius plots for nanoporous β-Li_3PS_4 (line a), bulk β-Li_3PS_4 (line b), and bulk γ-Li_3PS_4 (line c). The conductivity data for bulk Li_3PS_4 are reproduced from the work of Tachez.[10].

Simulation of model interface – Li/γ-Li_3PS_4/Li …

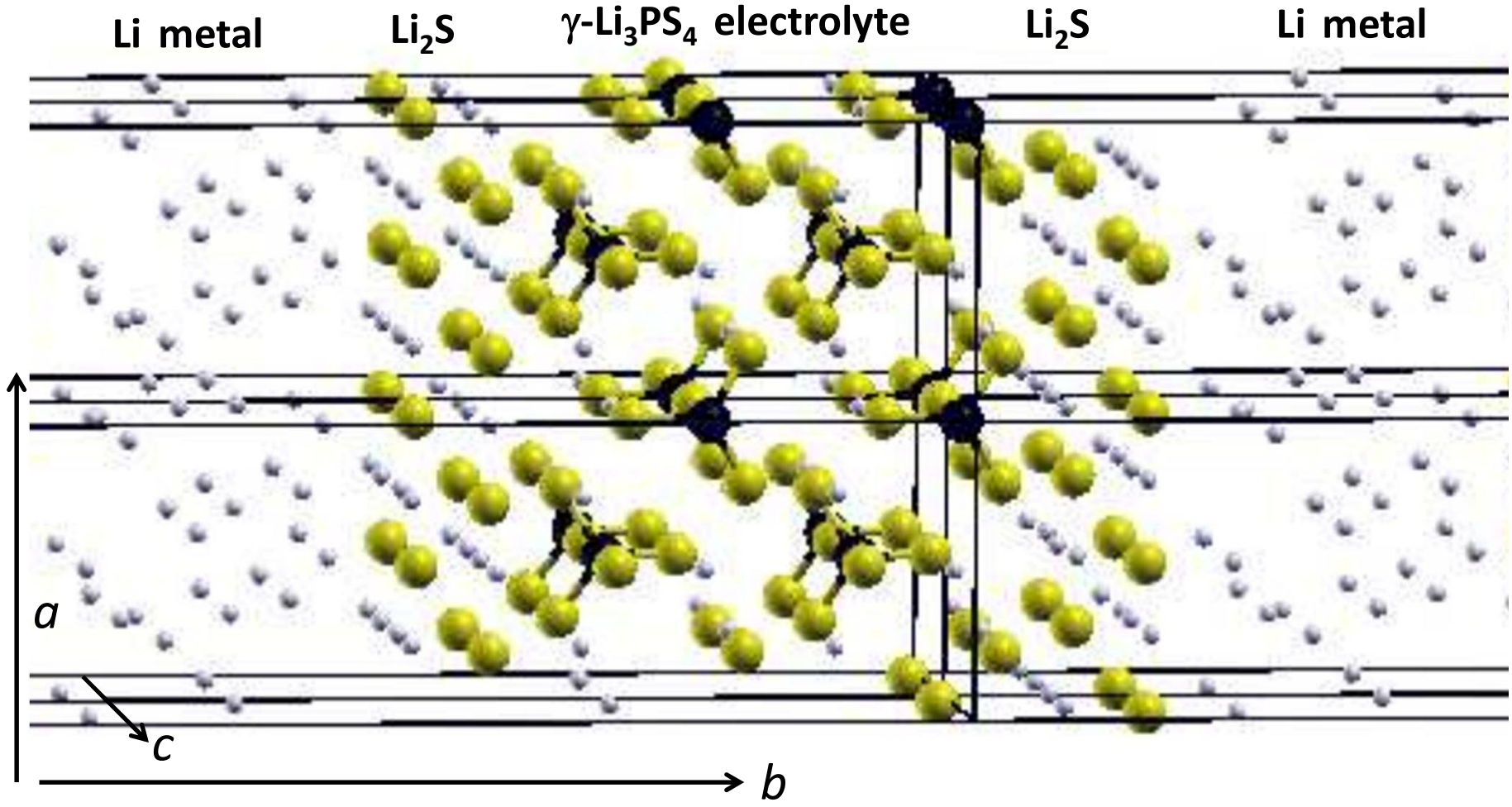
Initial interface:

(Supercell contains 4 Li_3PS_4 and 4 Li)



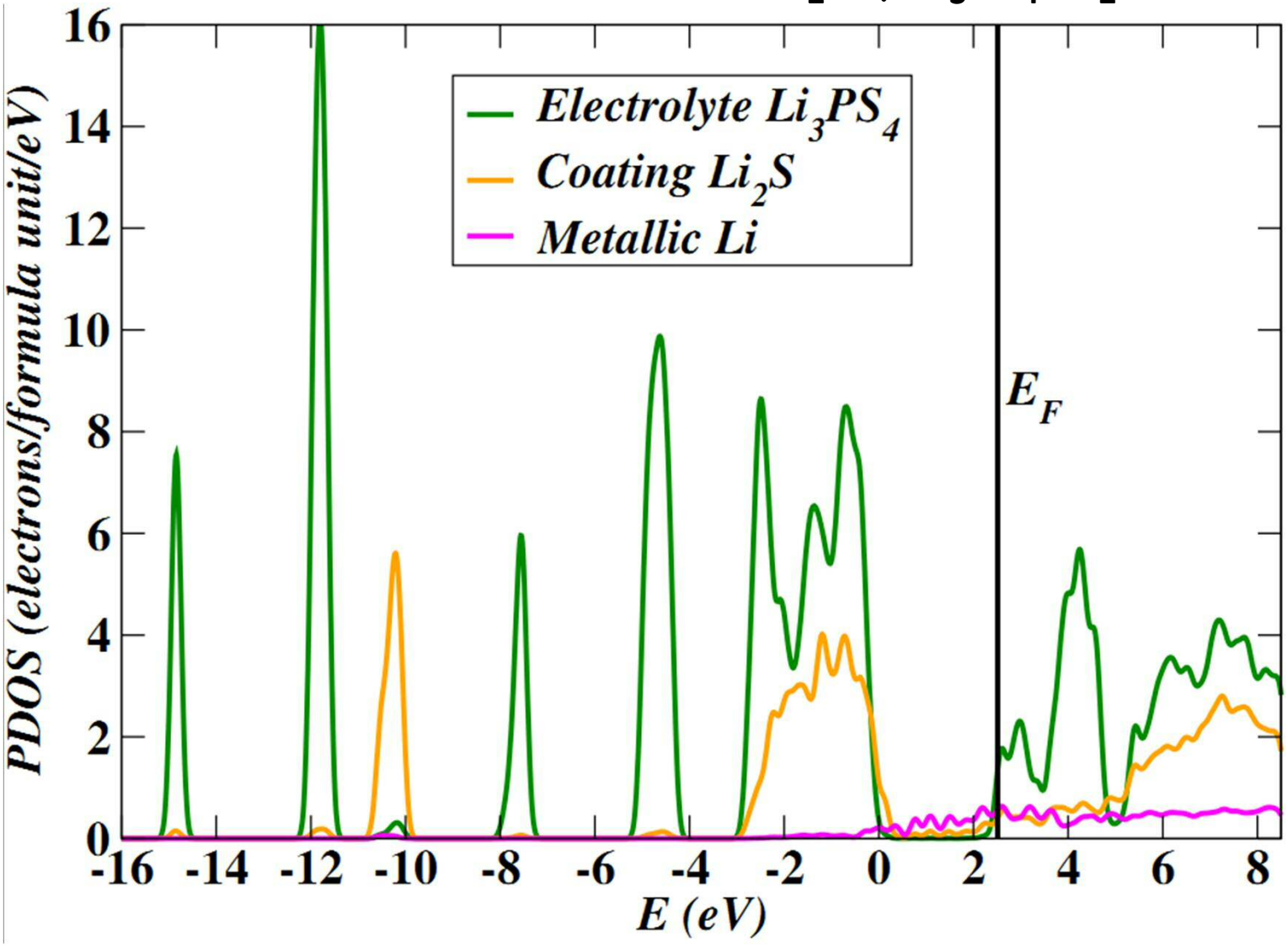
After several steps of structural relaxation:

Simulation of model interface – $Li/Li_2S/\gamma\text{-}Li_3PS_4/Li_2S/Li$ …

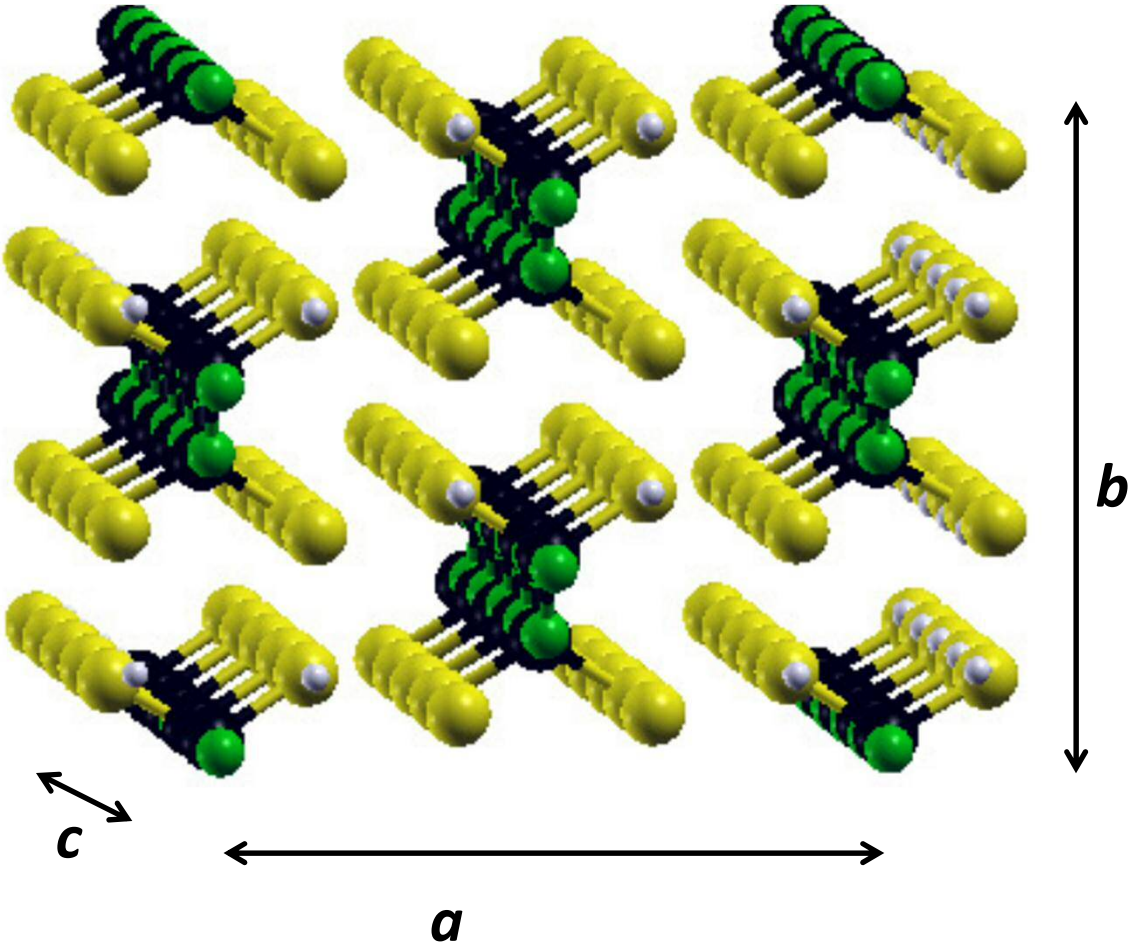


(Supercell contains 4 Li_3PS_4, 6 Li_2S, and 14 Li)

PDOS for model interface Li/Li_2S/γ-Li_3PS_4/Li_2S/Li …



Chengdu Liang's suggestion: Li_2PS_2N ??



Computed lattice: (Å)

Li_2PS_2N	Li_2PO_2N
a=11.5	8.7
b= 6.3	5.3
c= 4.9	4.6

Computed reaction

$$Li_2S + \tfrac{1}{5}P_2S_5 + \tfrac{1}{5}P_3N_5 \rightarrow Li_2PS_2N + 0.4\,eV$$

Summary and conclusions

- Ideal research effort in materials includes close collaboration of both simulations and experimental measurements.
- For battery technology, there remain many opportunities for new materials development.
- Case studies carried out by our group for solid electrolyte materials including Li phosphorus oxinitrides with new results on SD-Li_2PO_2N and som Li thiophosphates.

Acknowledgements

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