Serendipitous ^ Design and synthesis of a crystalline LiPON electrolyte*

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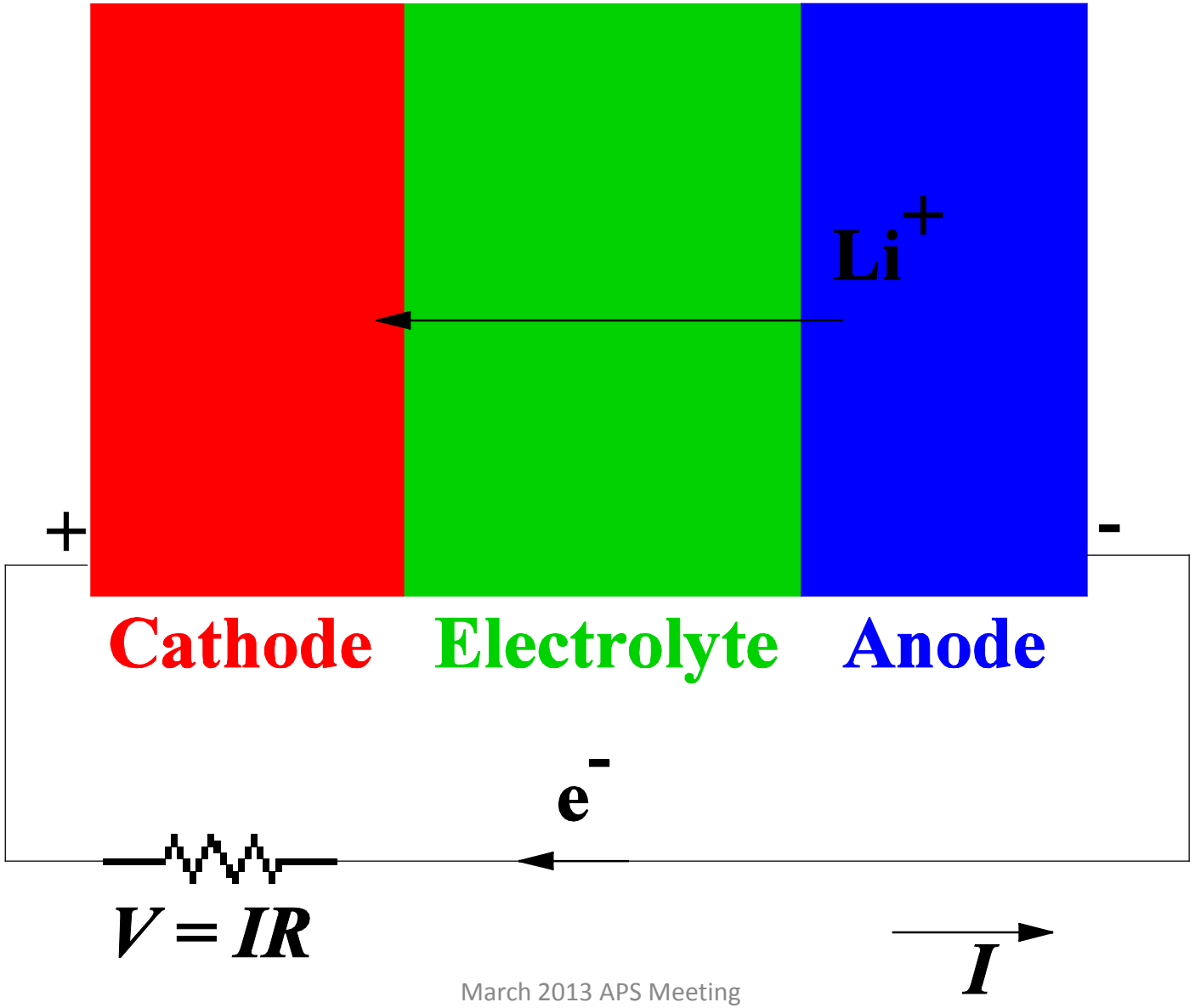
Materials components of a Li ion battery



Attributes on an ideal electrolyte

- Physically and chemically stable
- Electrically insulating for electrons, conducting for Li^+ ions
- Forms stable interfaces with cathodes and anodes

➔Growing development of solid electrolytes (as opposed to liquid or polymer electrolytes)

Example: Thin-film battery developed by Nancy Dudney and collaborators at Oak Ridge National Laboratory – **LiPON** (lithium phosphorus oxinitride)

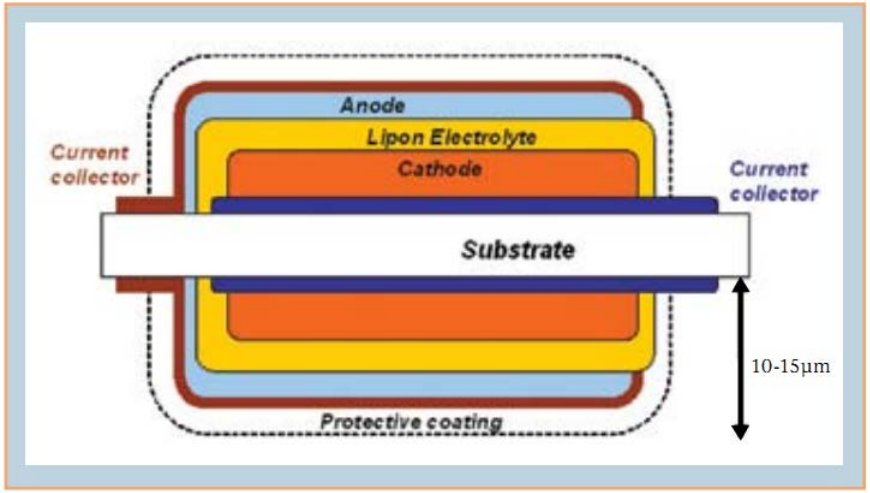


FIG. 1. *Schematic cross section of a thin film battery fabricated by vapor deposition onto both sides of a substrate support.*

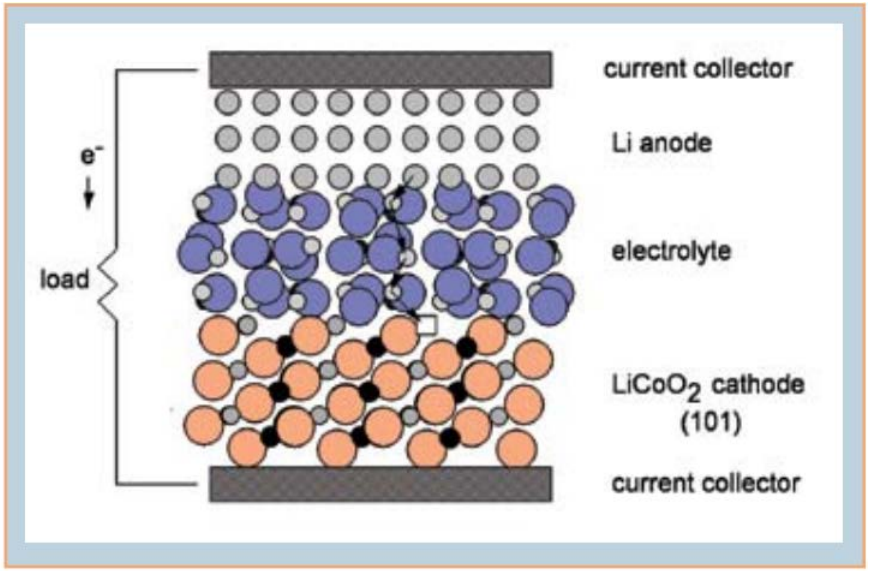


FIG. 2. *Schematic illustration of a thin film battery. The arrows indicate the discharge reaction where a Li ion diffuses from the lithium metal anode to fill a vacancy in an intercalation compound that serves as the cathode. The compensating electron is conducted through the device.*

From: N. J. Dudney, ***Interface* 77**(3) 44 (2008)

Summary of calculational methods

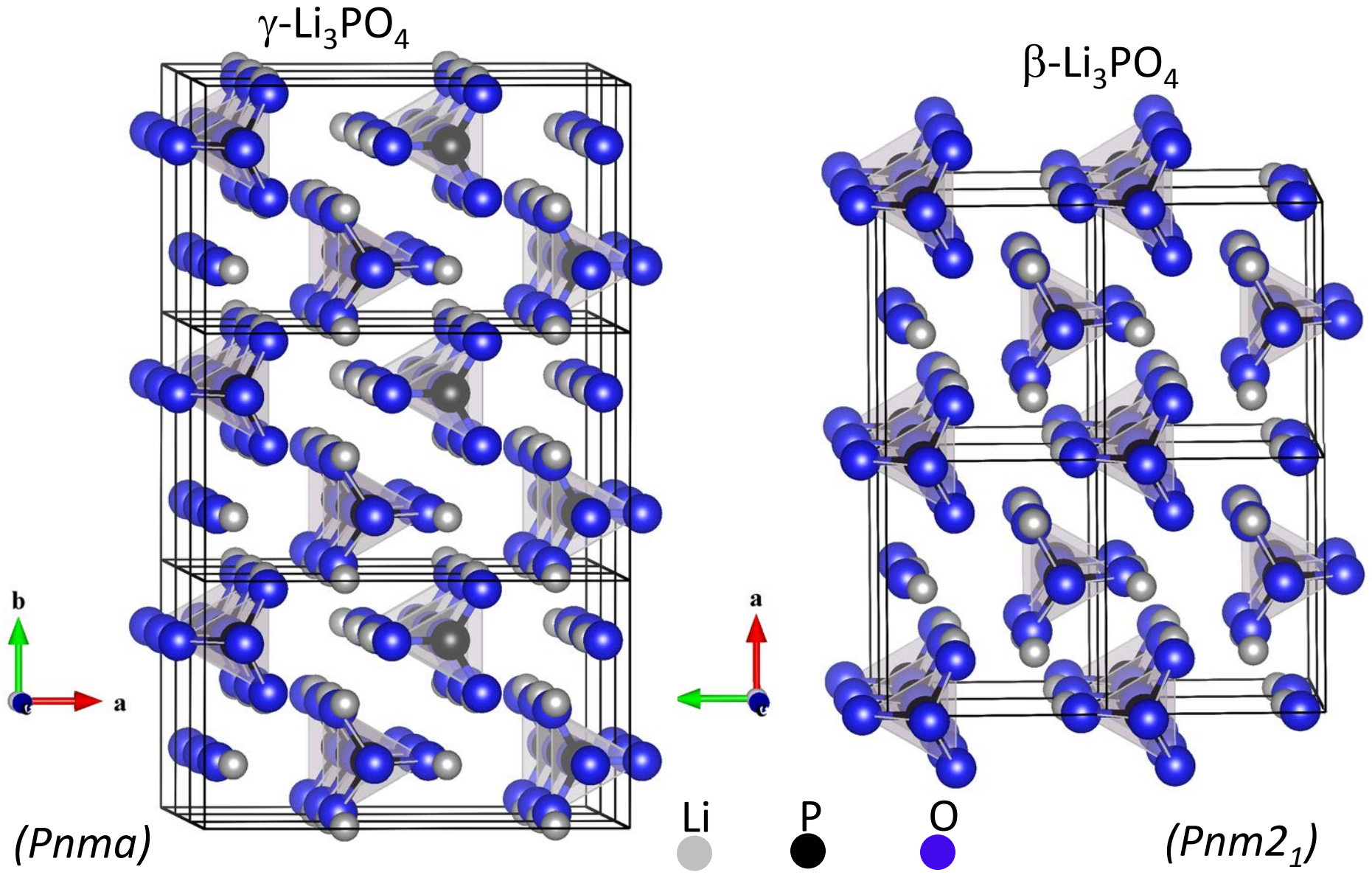
- Born-Oppenheimer approximation
  - Born & Huang, **Dynamical Theory of Crystal Lattices**, Oxford (1954)
- Density functional theory
  - Hohenberg and Kohn, *Phys. Rev*. **136** B864 (1964)
  - Kohn and Sham, *Phys. Rev.* **140** A1133 (1965)
- Exchange-correlation functionals
  - LDA: J. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)
- Numerical method
  - PAW: P. Blöchl, Phys. Rev. B. **50** 17953 (1994) – Projector Augmented Wave (PAW) method

Public domain computer codes

- Generation of PAW datasets: ATOMPAW (pwpaw.wfu.edu)
- DFT codes: quantum-espresso (www.quantum-espresso.org) and abinit (www.abinit.org)
- Visualization codes: OpenDX (www.opendx.org), Xcrysden (www.xcrysden.org/), VESTA (jp-minerals.org/en/)

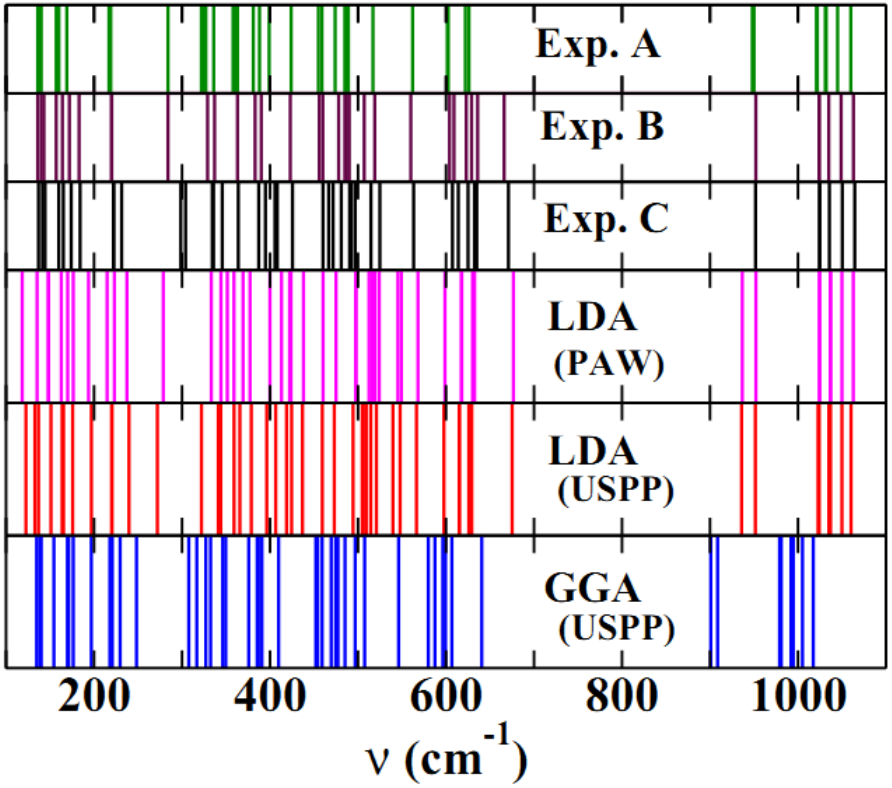
Example validation of computation methods

Li_3PO_4 crystals

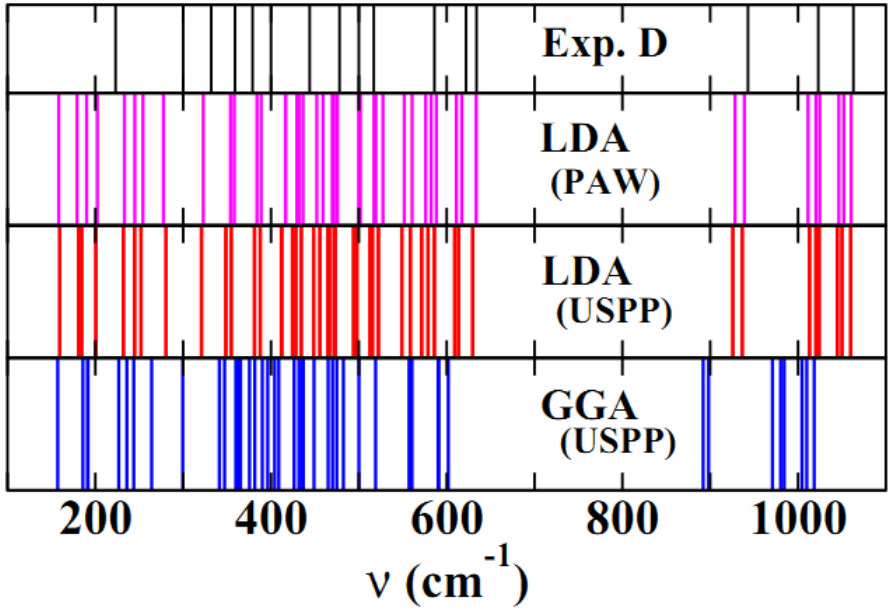


Validation of calculations

Raman spectra – Experiment & Calculation



γ-Li_3PO_4

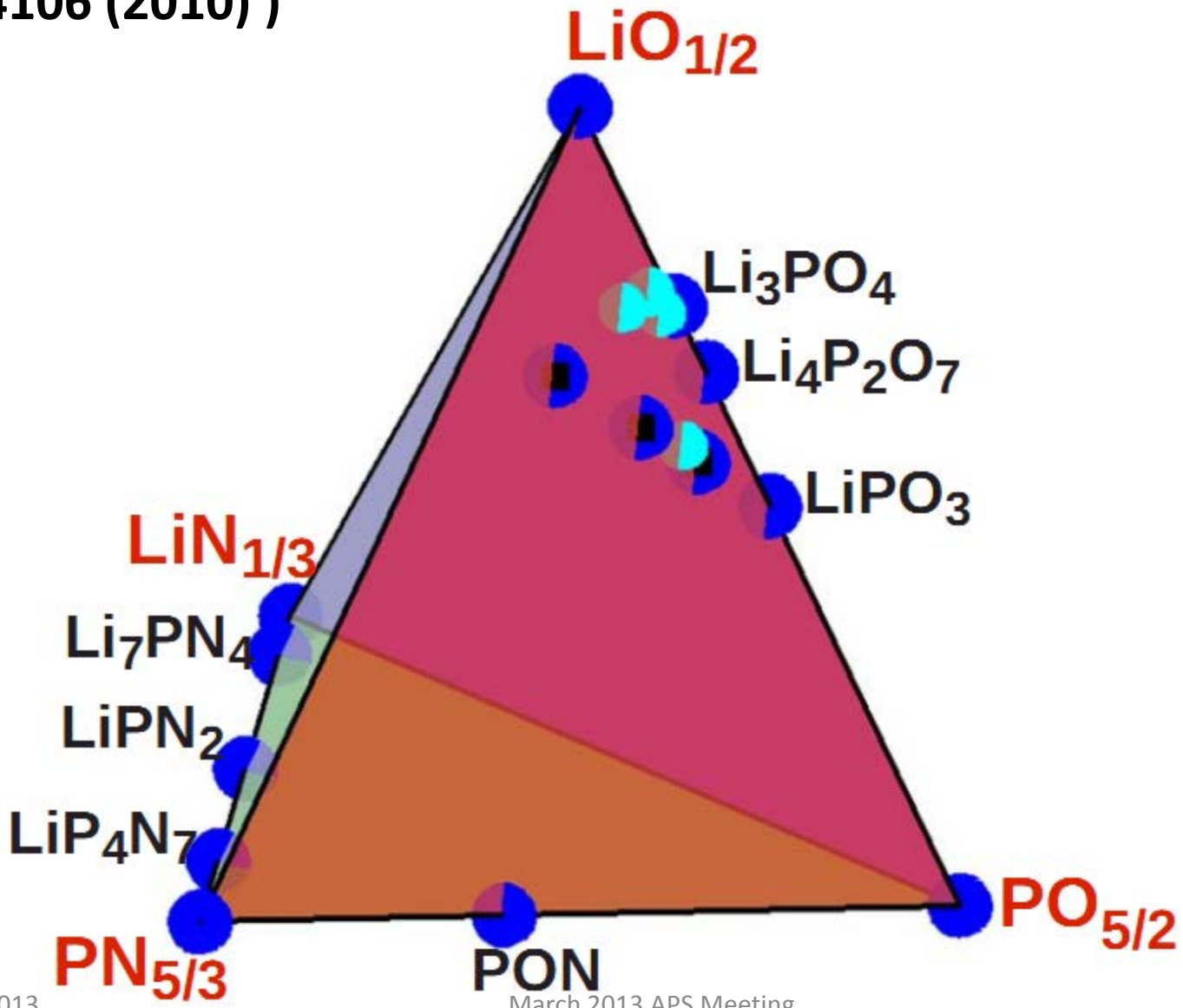


β-Li_3PO_4

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

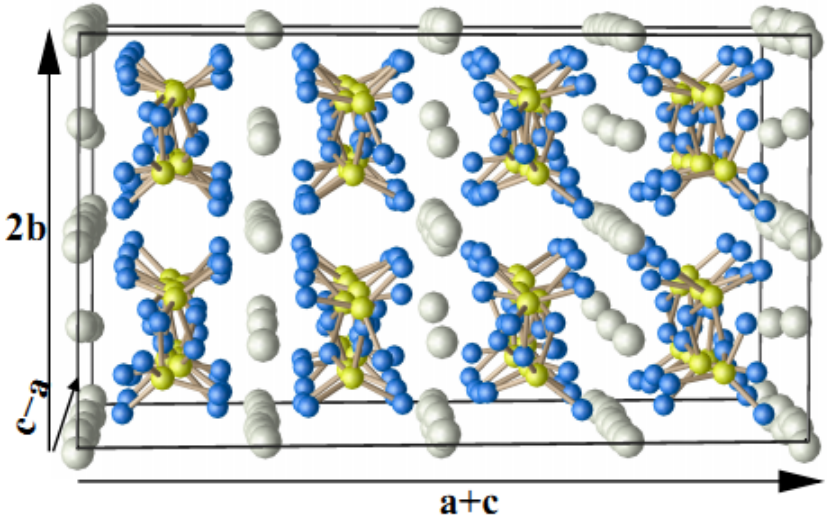
Systematic study of LiPON materials – $Li_xPO_yN_z$ – (Yaojun A. Du and N. A. W. Holzwarth, Phys. Rev. B 81, 184106 (2010))



Phosphate chain materials: $LiPO_3$ plus N

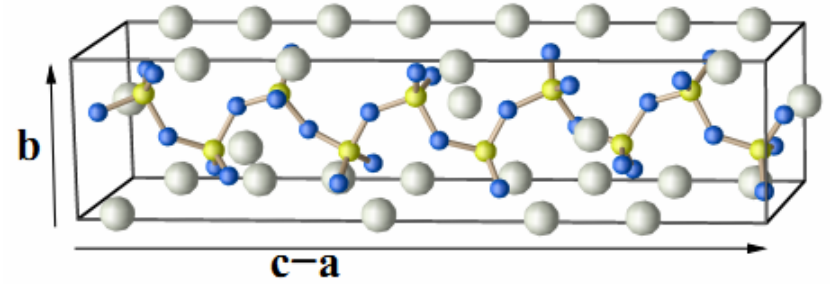
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



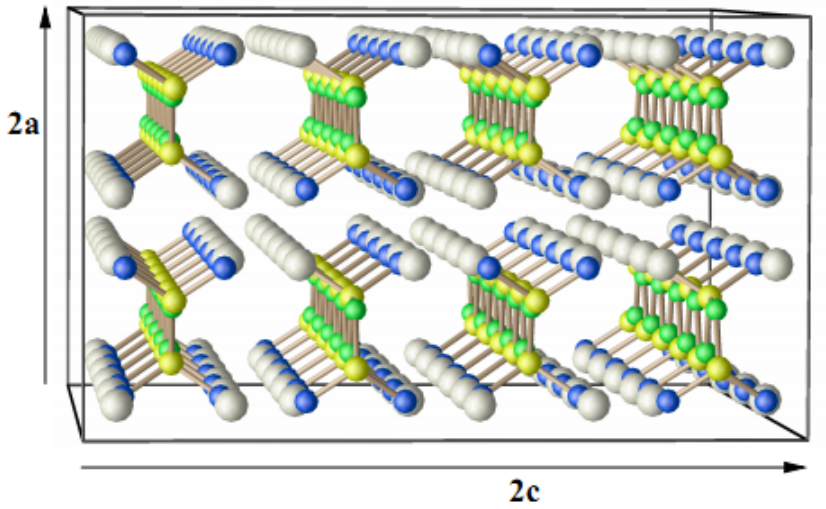
Ball colors: =Li, =P, =O.

Single chain view



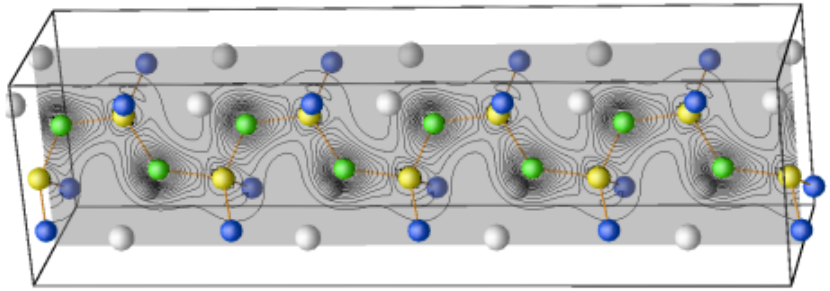
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram

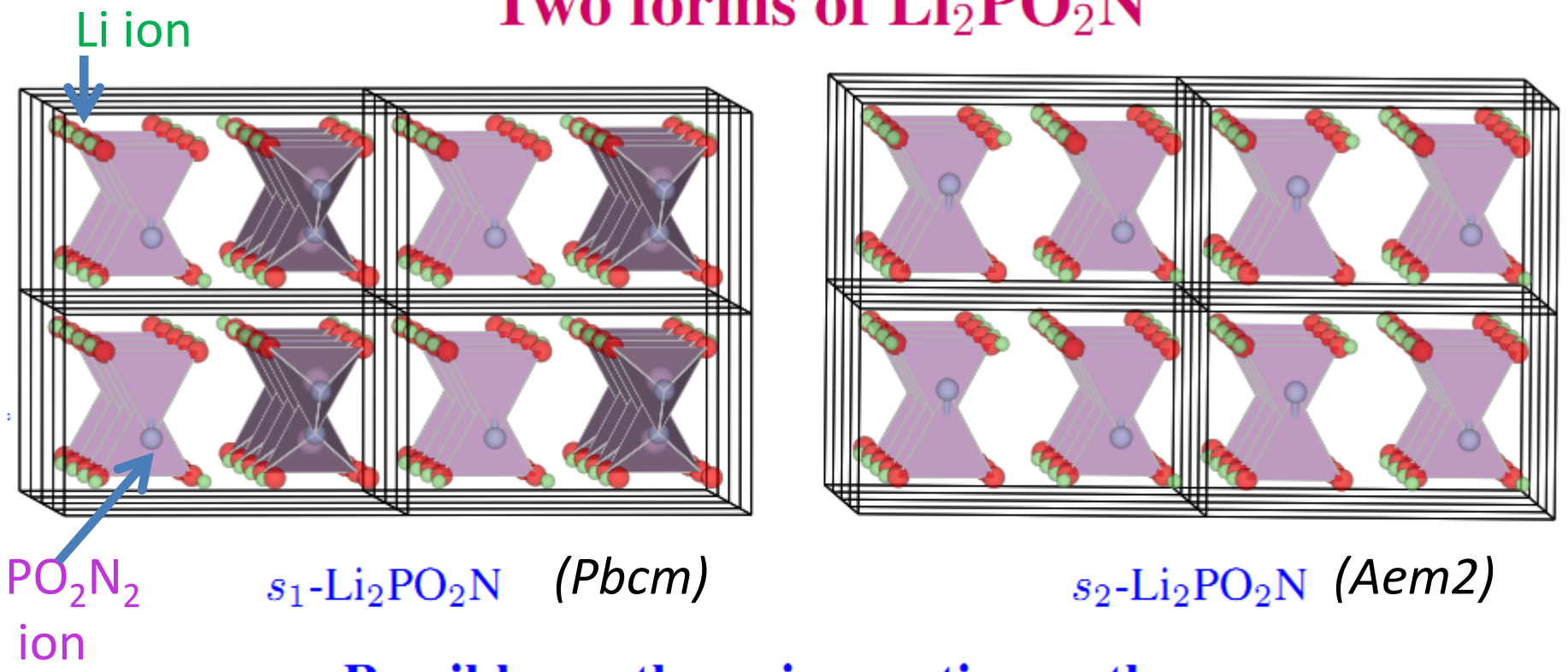


Ball colors: =Li, =P, =O, =N.

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:

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

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

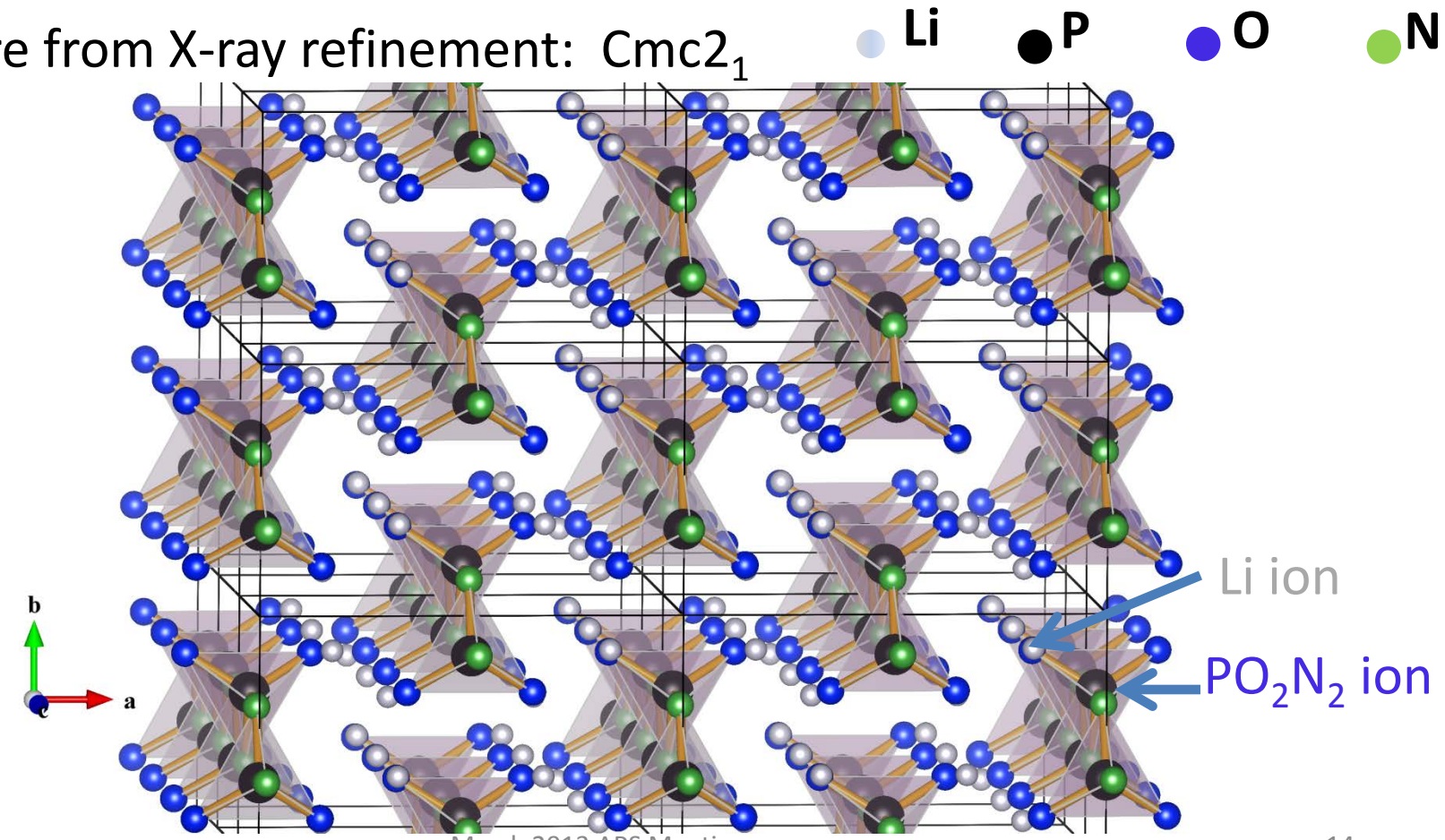
$$LiNO_3 + Li + P \rightarrow Li_2PO_2N + \tfrac{1}{2}O_2 + 7.0\ \text{eV}.$$

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

Published paper: Solid State Ionics, **233** (2013) 95-101

Method: High temperature solid state synthesis based on reaction $\mathrm{Li_2O + \frac{1}{5}P_2O_5 + \frac{1}{5}P_3N_5 \rightarrow Li_2PO_2N}$

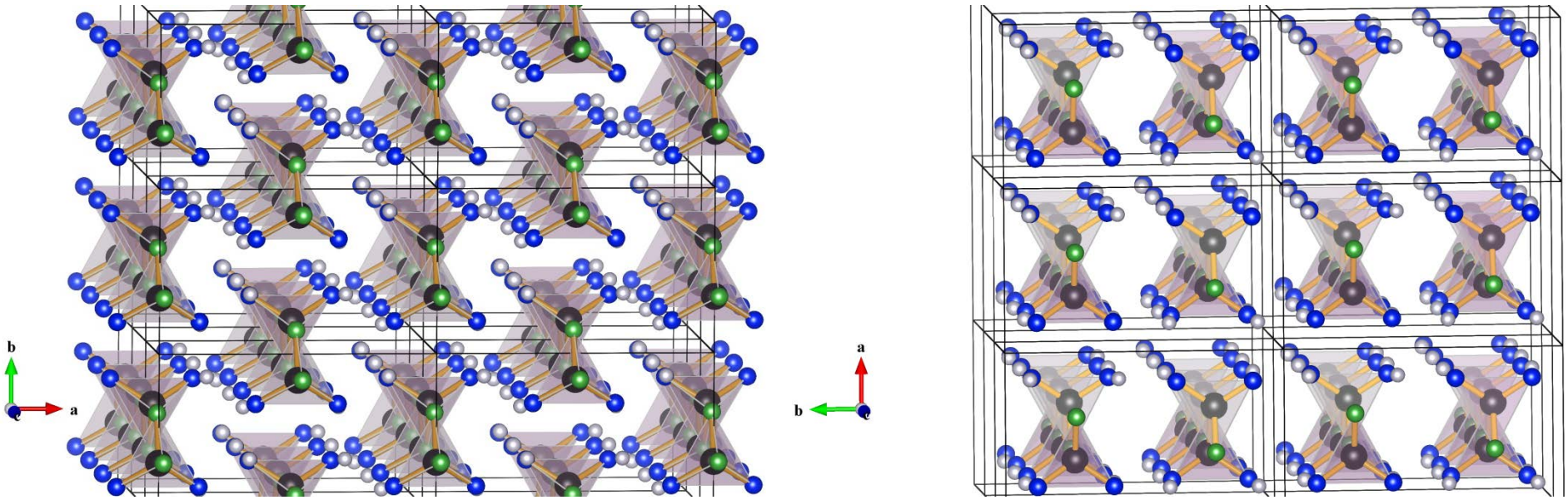
Structure from X-ray refinement: $Cmc2_1$



Comparison of synthesized and predicted structures of Li_2PO_2N:

Synthesized

Predicted



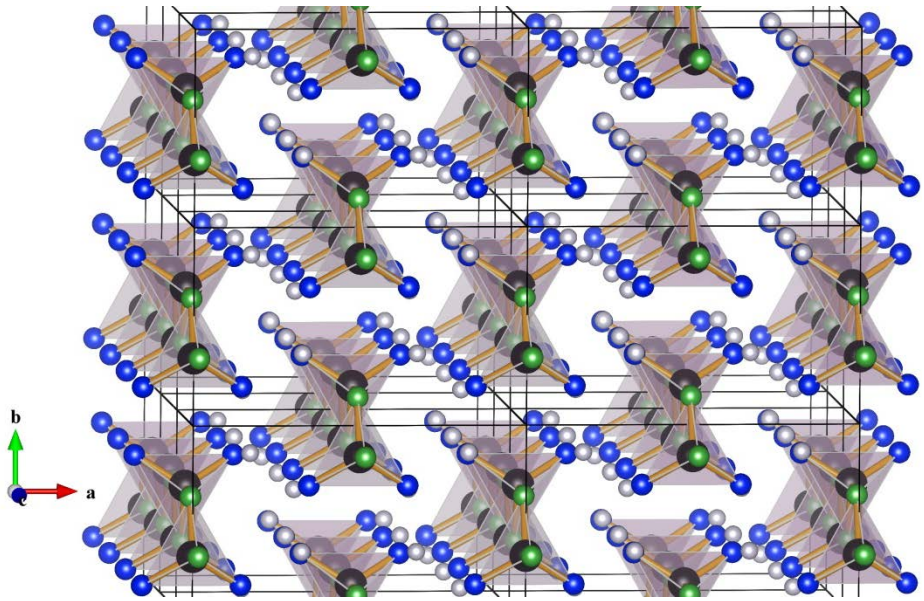
***SD*-Li_2PO_2N (*$Cmc2_1$*)**

***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.

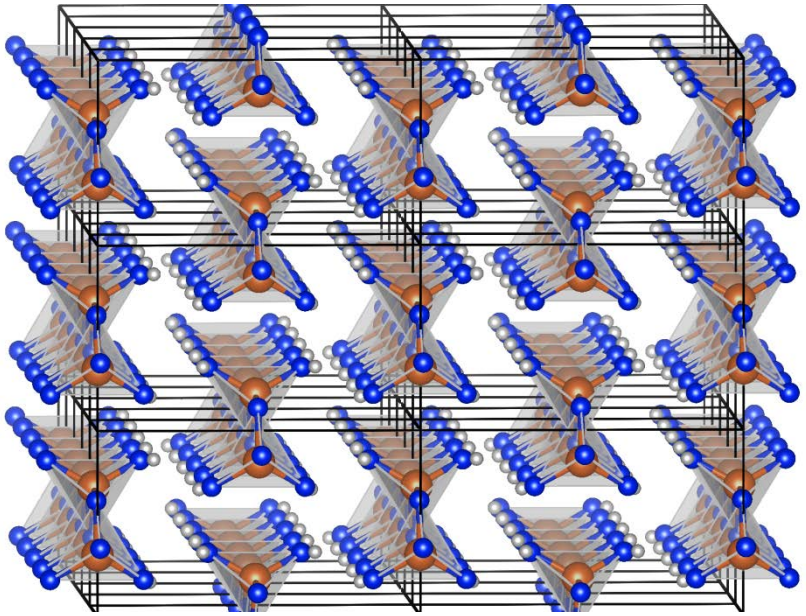
Comparison of synthesized Li_2PO_2N with Li_2SiO_3

SD-Li_2PO_2N (*Cmc2₁*)



a=9.07 Å, b=5.40 Å, c=4.60 Å

Li_2SiO_3 (*Cmc2₁*)

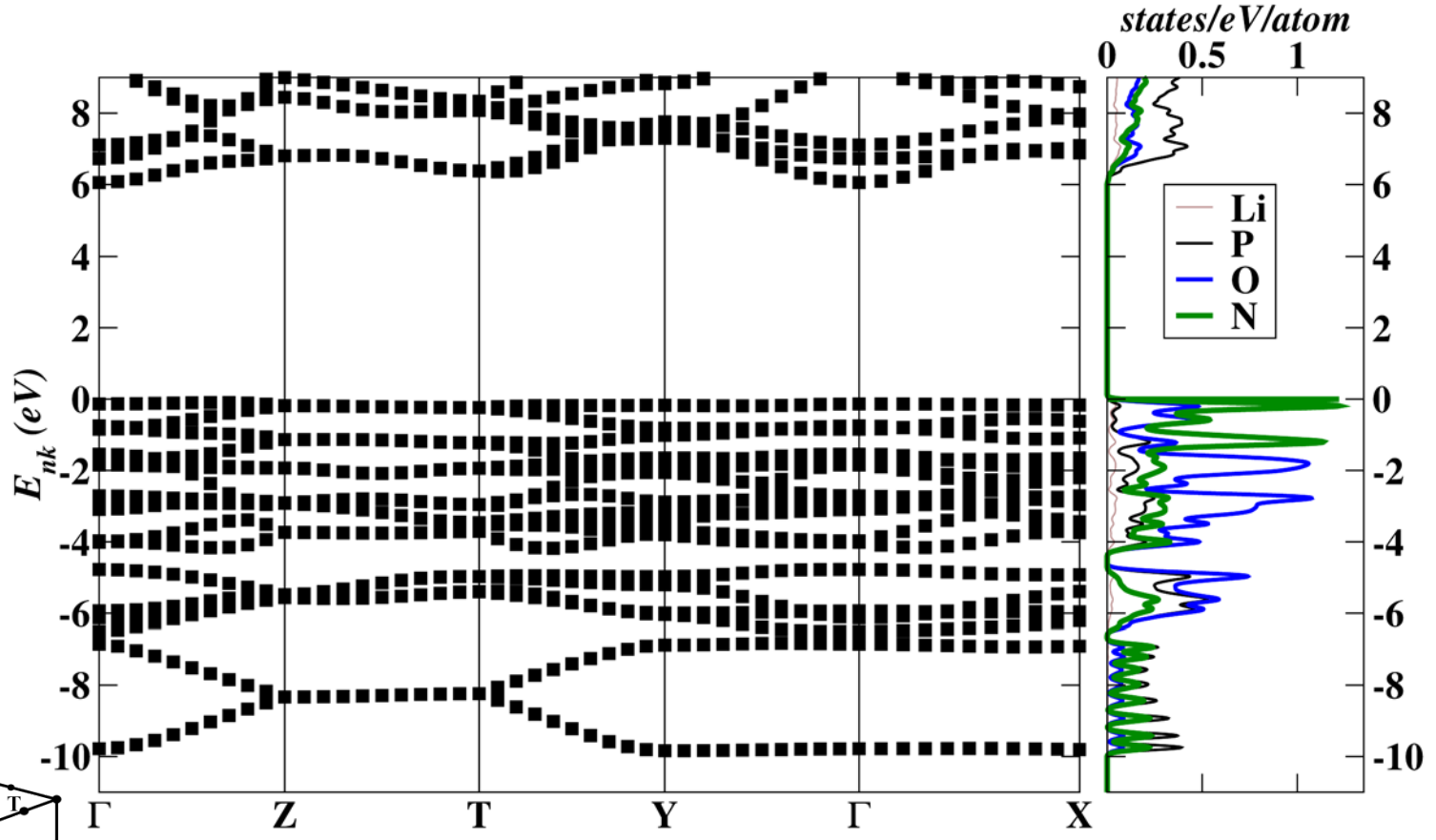


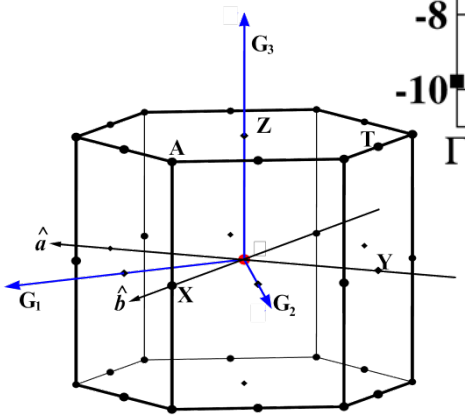
a=9.39 Å, b=5.40 Å, c=4.66 Å

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

Li P O N Si

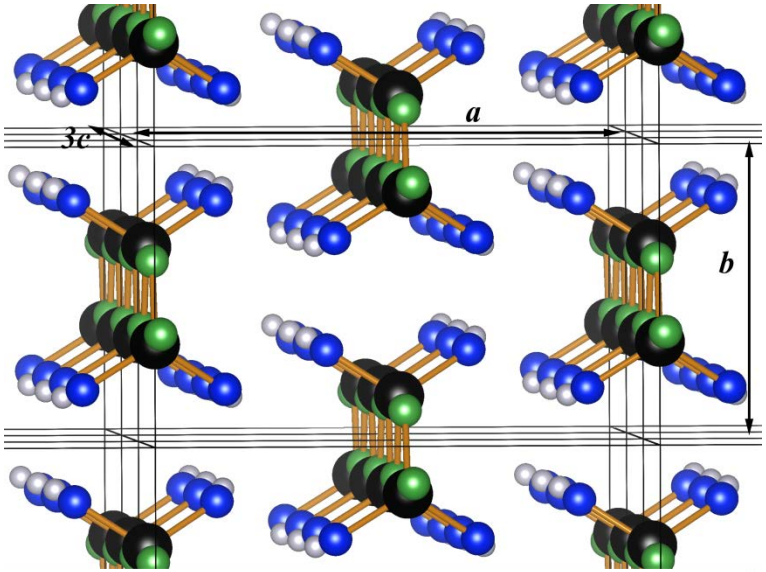
Electronic band structure of *SD*-Li_2PO_2N

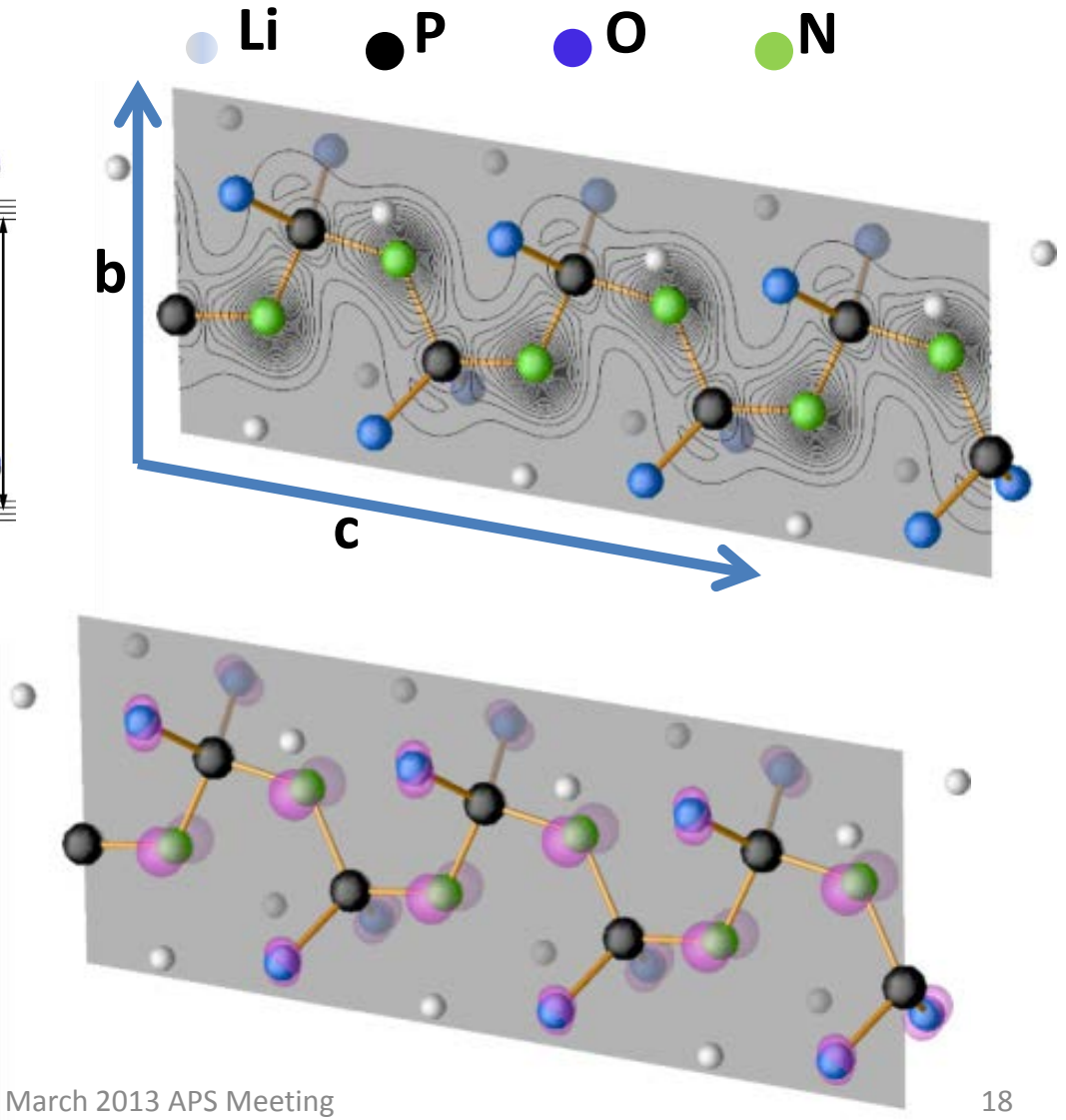




More details of *SD*-Li_2PO_2N structure

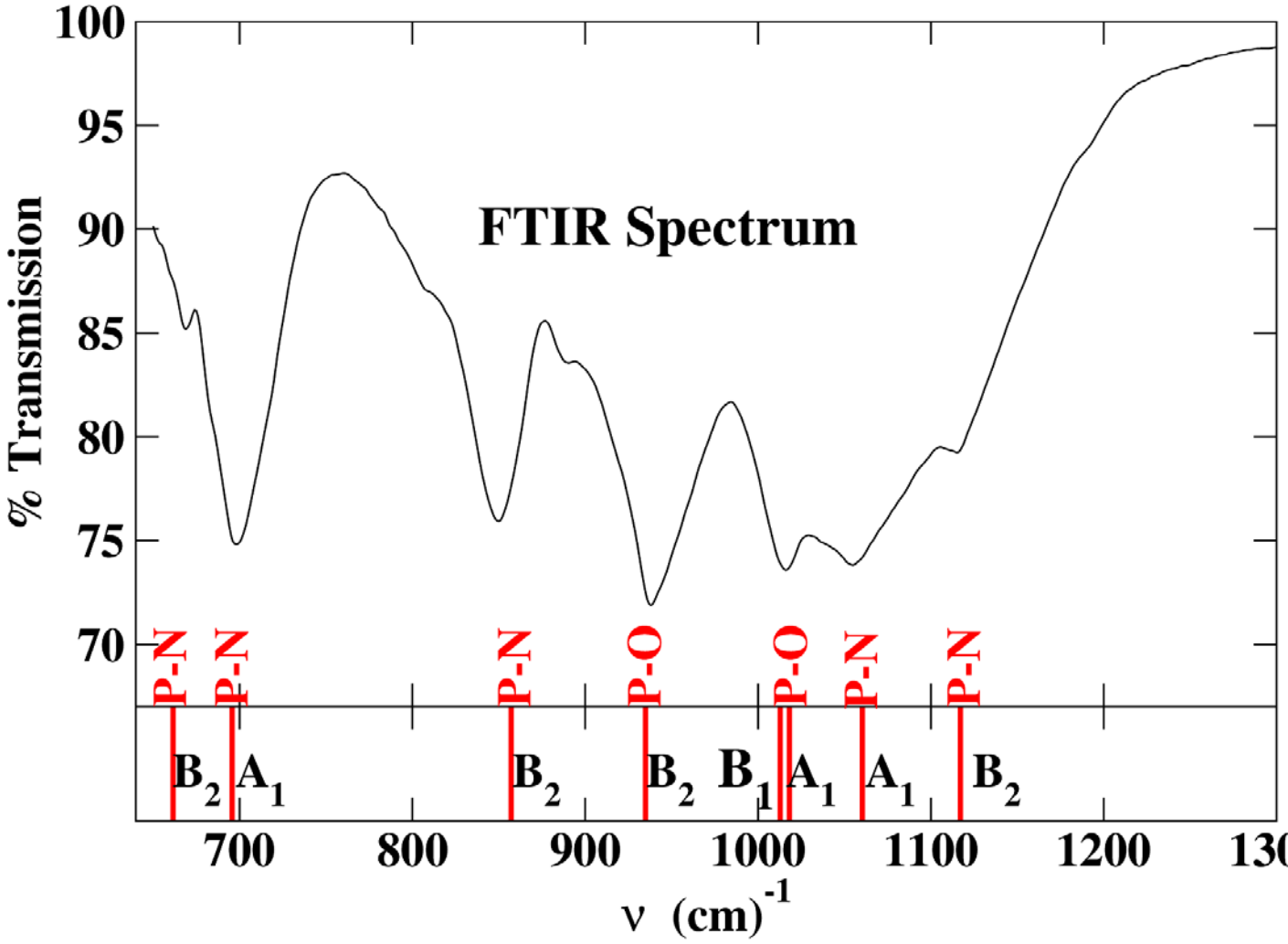
Ball and stick model





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

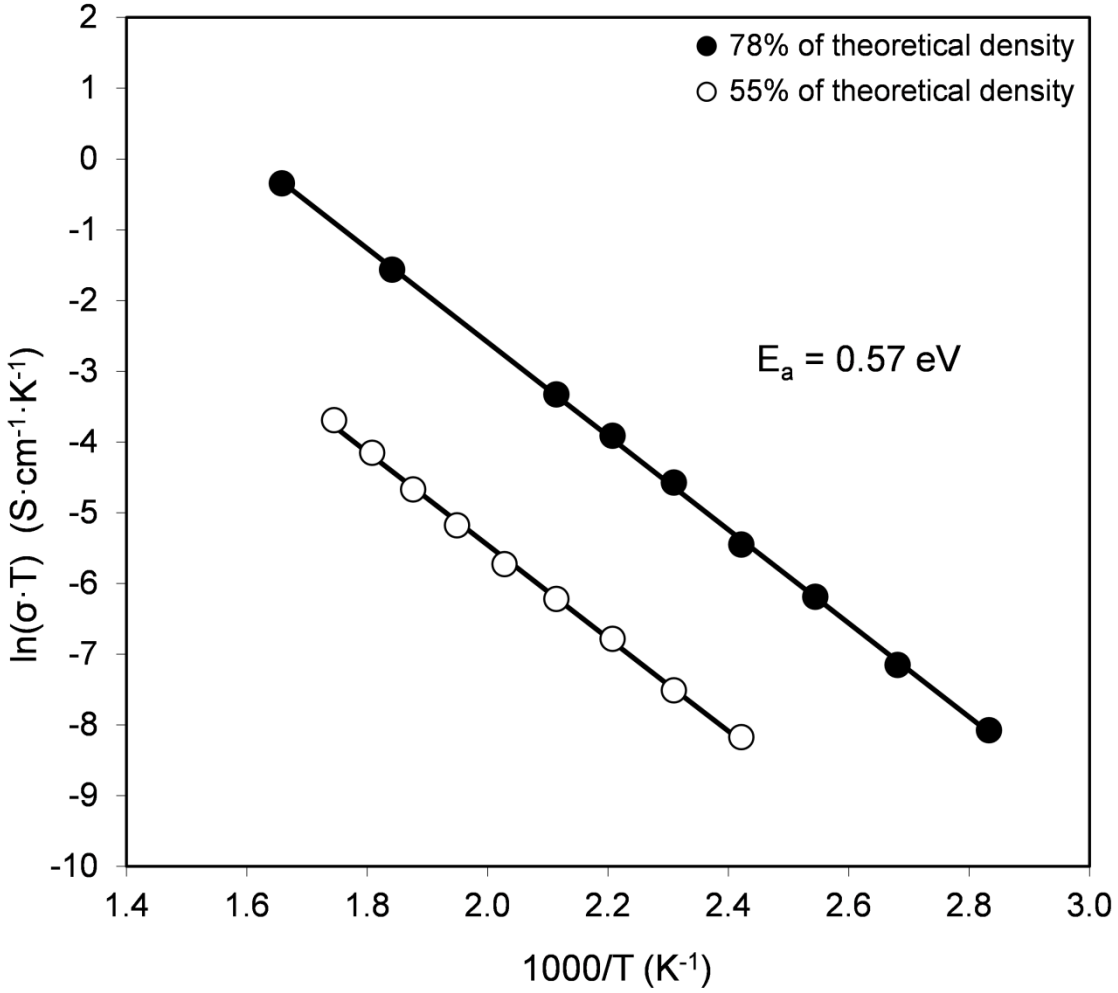
Vibrational spectrum of *SD*-Li_2PO_2N



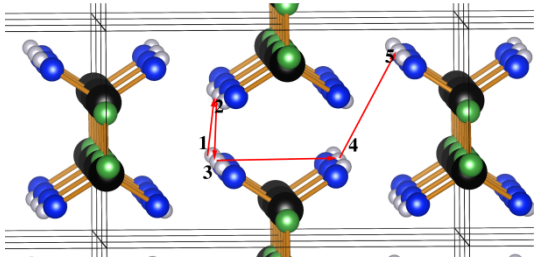
Experimental IR spectrum

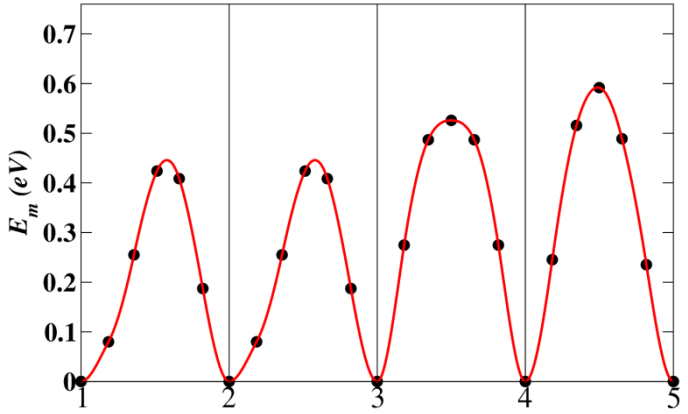
Calculated IR spectrum

Ionic conductivity of *SD*-Li_2PO_2N

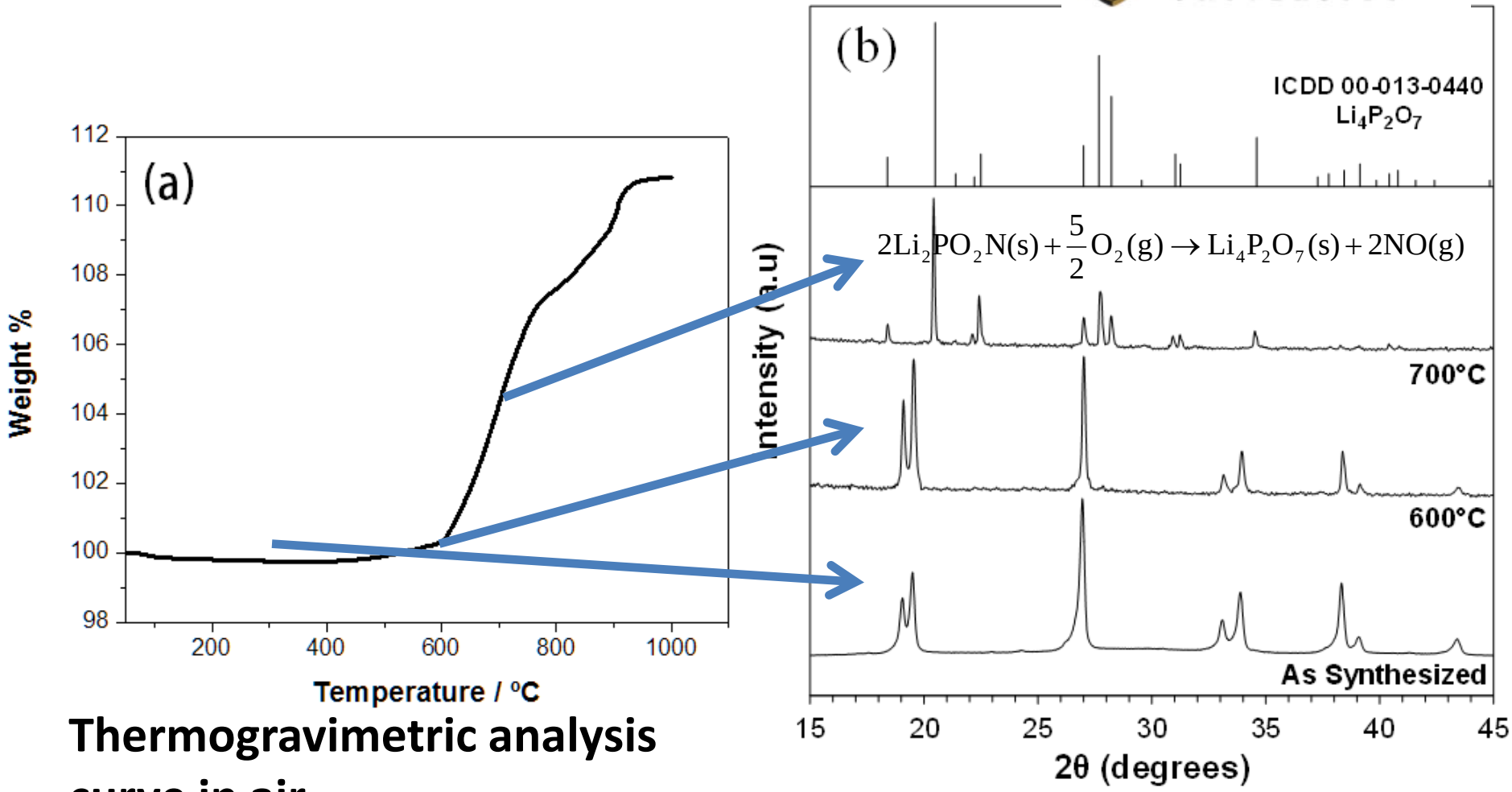


NEB analysis of E_m (vacancy mechanism)





Stability of *SD*-Li_2PO_2N in air

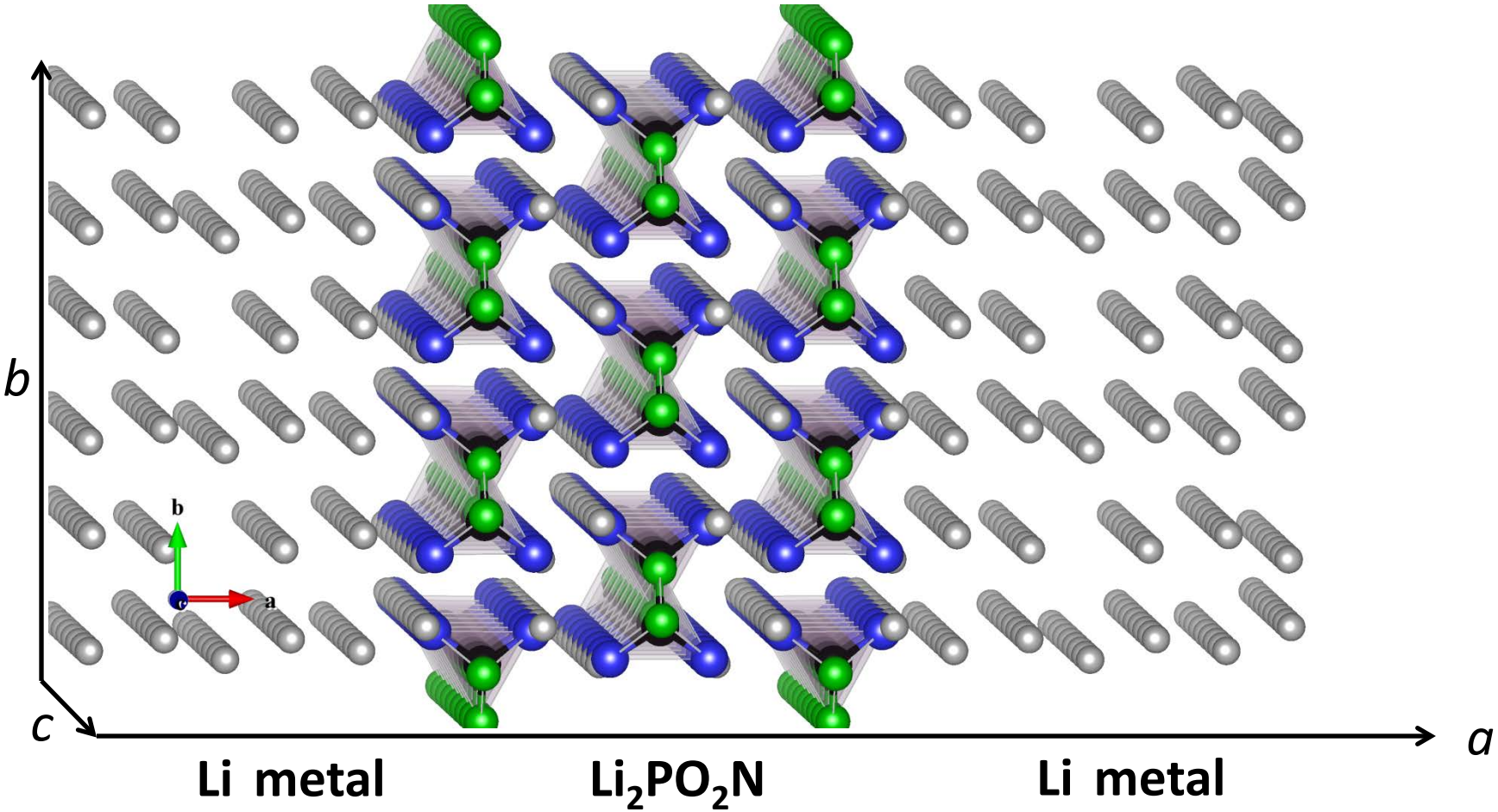


Thermogravimetric analysis curve in air

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

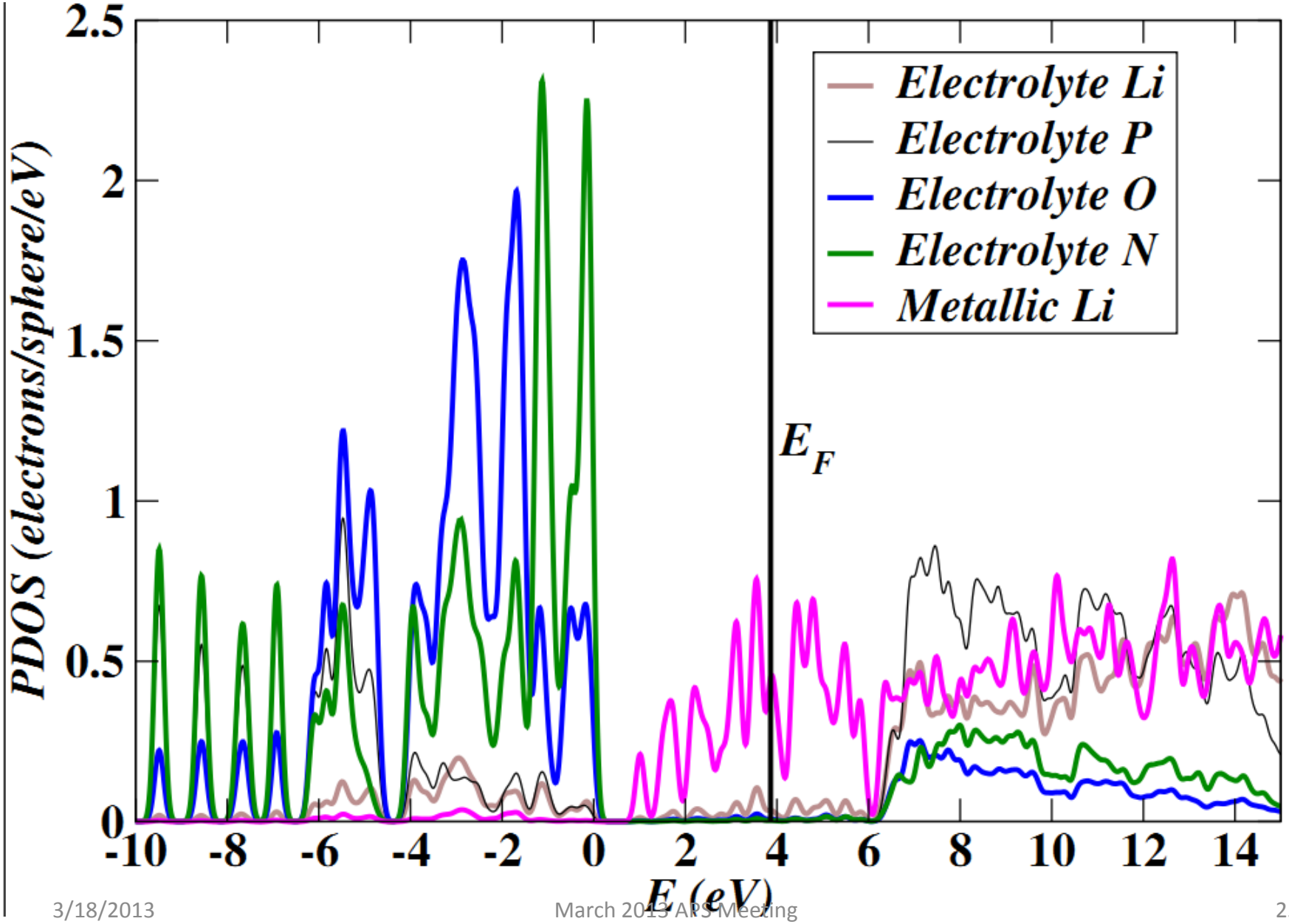
Models of electrolyte interfaces with Li metal

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



(Supercell contains 6 Li_2PO_2N and 9 Li)

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



Summary and conclusions

Published paper: Solid State Ionics**, 233** (2013) 95-101

- On the basis of first principles simulations of a variation of crystalline $LiPO_3$, stable crystalline forms of Li_2PO_2N were predicted, having parallel arrangements of anionic chains formed with planar P—N—P—N—P backbones, corner sharing PO_2N_2 tetrahedra, and mobile Li^+ anions.
- *SD*-Li_2PO_2N was synthesized from a stoichiometric mixture of Li_2O, P_2O_5, and P_3N_5 using high temperature methods. Analysis of X-ray data finds it to have a structure similar but not identical to the predicted structure.
- Theory and experiment now agree that the most stable form of Li_2PO_2N has the $Cmc2_1$ space group. There is also good agreement on the high frequency vibrational spectra and on the migration energy for thermally activated conductivity.
- *SD*-Li_2PO_2N is stable in air up to 600^o C and is modeled to be stable at a metallic Li interface.