Solid electrolytes for battery applications – a theoretical perspective [a]

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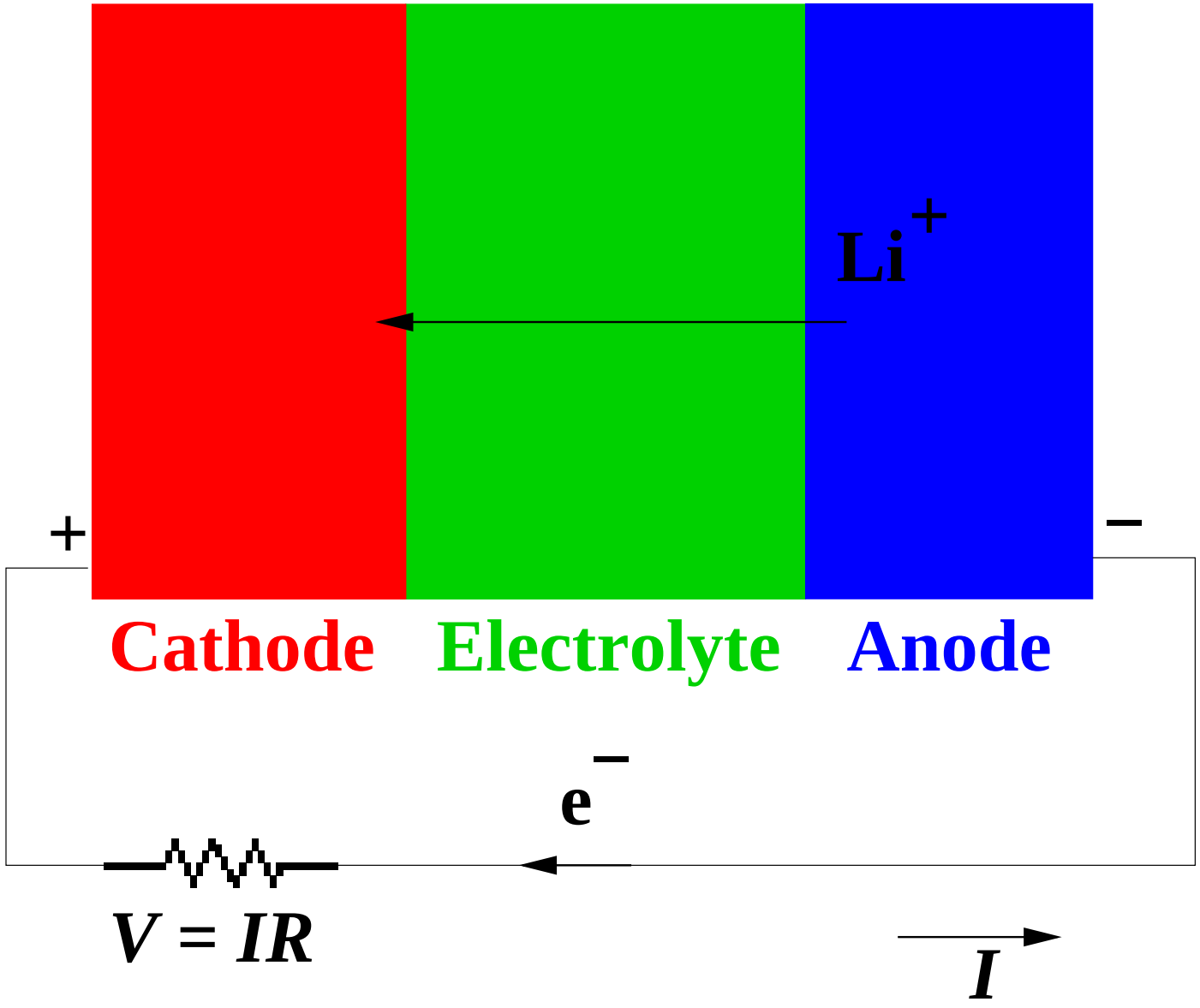
- Introduction and motivation for solid electrolytes
- What can computation do for this project?
- Specific examples – LiPON, thio phosphates, other solid electrolytes
- Suggestions for collaboration between theory and experiment

[a] Supported by NSF grants DMR-0427055, 0705239, and 1150501; WFU's DEAC computer cluster.

Materials components of a Li ion battery



Solid *vs* liquid electrolytes in Li ion batteries

Solid electrolytes

Advantages

1. Excellent chemical and physical stability.
2. Perform well as thin film ($\approx 1\mu$).
3. Li^+ conduction only (excludes electrons).

Disadvantages

1. Thin film geometry provides poor contact area for high capacity electrodes.
2. Subject to interface stress if electrodes change size during charge and discharge cycles.
3. Relatively low conductivity per unit area.

Liquid electrolytes

Advantages

1. Excellent contact area with high capacity electrodes.
2. Can accomodate size changes of electrodes during charge and discharge cycles.
3. Relatively high conductivity per unit area.

Disadvantages

1. Relatively poor physical and chemical stability.
2. Relies on the formation of "solid electrolyte interface" (SEI) layer.
3. May have both Li^+ and electron conduction.

Current solid state usage

Ref: Presentation by Prof. Kevin S. Jones, Department of Materials Science, and Engineering, University of Florida

- $< 1\%$ of the battery business is invested in all solid state batteries at the present time.
- Several companies are involved in all solids state battery development: Cymbet, Excellatron, Front Edge, Infinite Power, Sakti3, Seeo, Toyota/AIST, Planar Energy.
- Micro battery applications are in production; larger applications are perhaps possible??

Example: `http://www.frontedgetechnology.com/gen.htm`

"NanoEnergy® is a miniature power source designed for highly space limited micro devices such as smart card, portable sensors, and RFID tag. "

Key Features:	
Ultra thin	As thin as 0.05 mm (0.002 inch) including package.
Safe & environmentally friendly	All solid-state, using ceramic electrolyte LiPON developed by Oak Ridge National Laboratories. Contains no liquid or environmental hazardous material.
Long cycle life	More than 1, 000 cycles at 100% depth discharge.
High current charge	Can be charged to 70% of rated capacity in 2 minutes.
High current discharge	Can be discharged at rates of more than 10 C.
Flexible form factor	Can be made into different shapes and sizes.
Low self-discharge	Less than 5% per year.
Bendable	Can be bent and twisted without damage.

Another example: `http://www.planarenergy.com`

PORTFOLIO

PLANAR ENERGY

Planar Energy

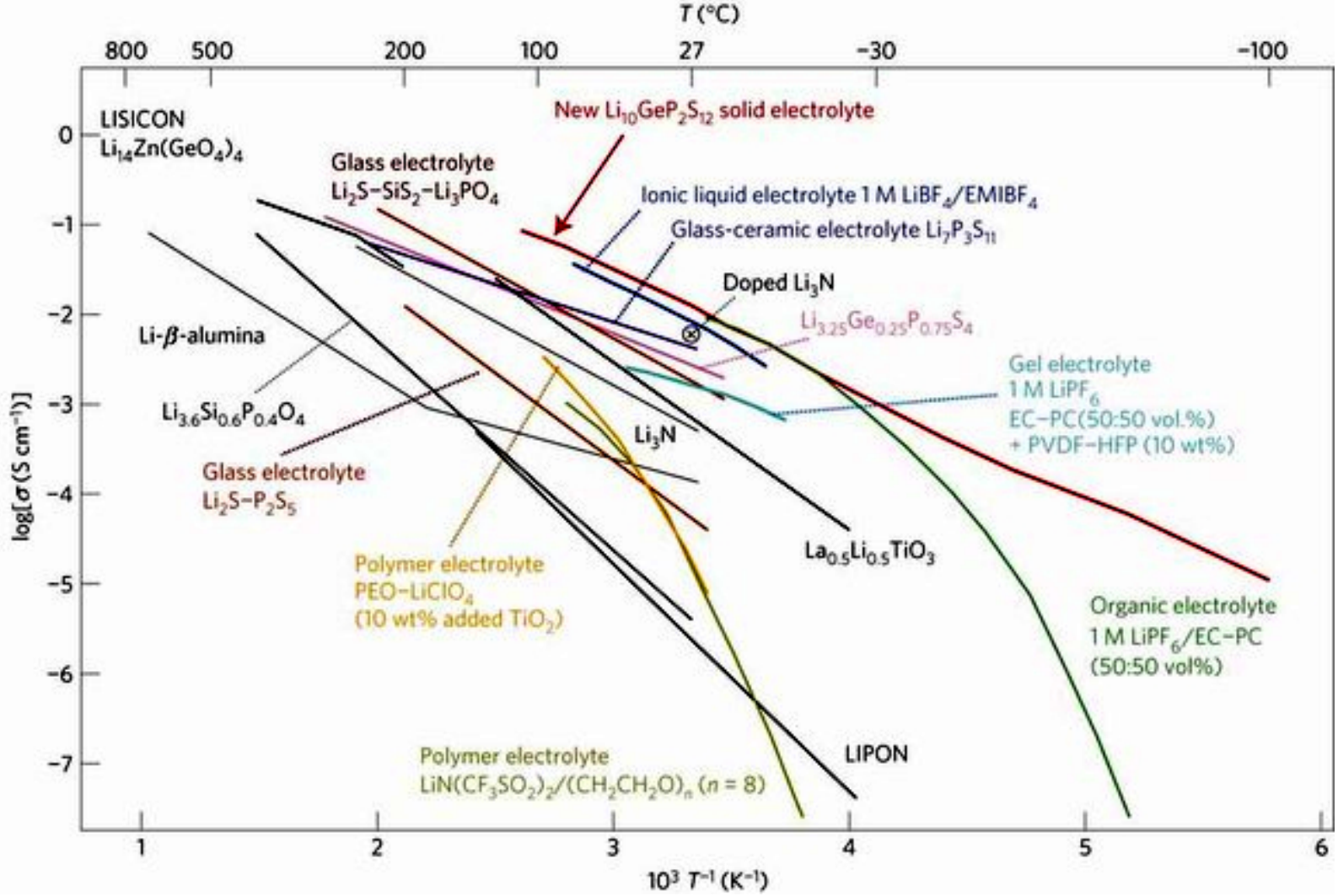
Planar Energy, a spinout of the U.S. Department of Energy's National Renewable Energy Laboratory, is the developer of large-format, solid state batteries at half the cost and triple the performance of lithium-ion batteries. The Orlando, Fla.-based company's new generation of solid state electrolyes have ionic conductivity metrics comparable to liquid electrolytes used in traditional chemical batteries, which is a fundamental materials breakthrough, confirmed by researchers at the University of Central Florida. The company also has identified a new deposition technology, Streaming Protocol for Electroless Electrochemical Deposition, or SPEED, a high-speed, roll-to-roll deposition process that is dramatically more flexible and scalable than existing methods, allowing Planar Energy to overcome production barriers to low-cost solid state batteries. General Partner Kef Kasdin sits on the Board of Directors. *(See announcement.)*

Company news and select media highlights

Company Web Site
www.planarenergy.com

Conductivity profiles of electrolytes

Ref: N. Kamaya *et al* ***Nature Materials*** **10** 682-686 (2011)



Comments on Nature Materials article

Ref: N. Kamaya *et al Nature Materials* 10 682-686 (2011)

- $Li_{10}GeP_2S_{12}$; crystal structure determined by X-ray and neutron diffraction
- Measured the highest lithium ion conductivity ever measured for a solid: $\sigma = 0.012$ S/m at room temperature and $\sigma = 0.001$ S/m at -20^o F. (Exceeding performance of organic liquid electrolytes.)
- Comment by Christian Masquelier: "The results of Kamaya *et al* demonstrate how continuous investment into energy storage systems – such as the 30-year-long effort that Japanese authorities and companies in particular have made in lithium-ion technology – can lead to significant breakthroughs arising from previously disregarded chemistries."

How can computer modeling help?

- Given a class of materials, can find optimal structures and estimate their heats of formation. $\Rightarrow$ **Can predict new materials**
- For each stable structure, can estimate phonon spectra.
- Using Nudged Elastic Band approximation (NEB), can estimate activation energy for ion mobility.

Combined experiment and computer modeling

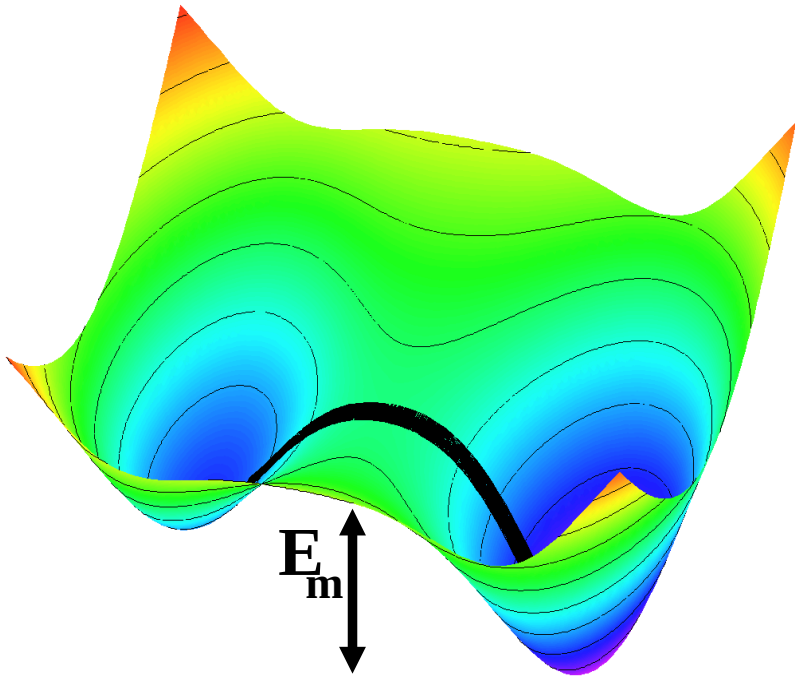
- Validation and refinement of materials prediction and analysis
- Provide a framework for understanding ion migration mechanisms

Computational methods – (brief summary)

Quantities derived from $\min_{\{\mathbf{R}^a\}} E(\{\mathbf{R}^a\})$:

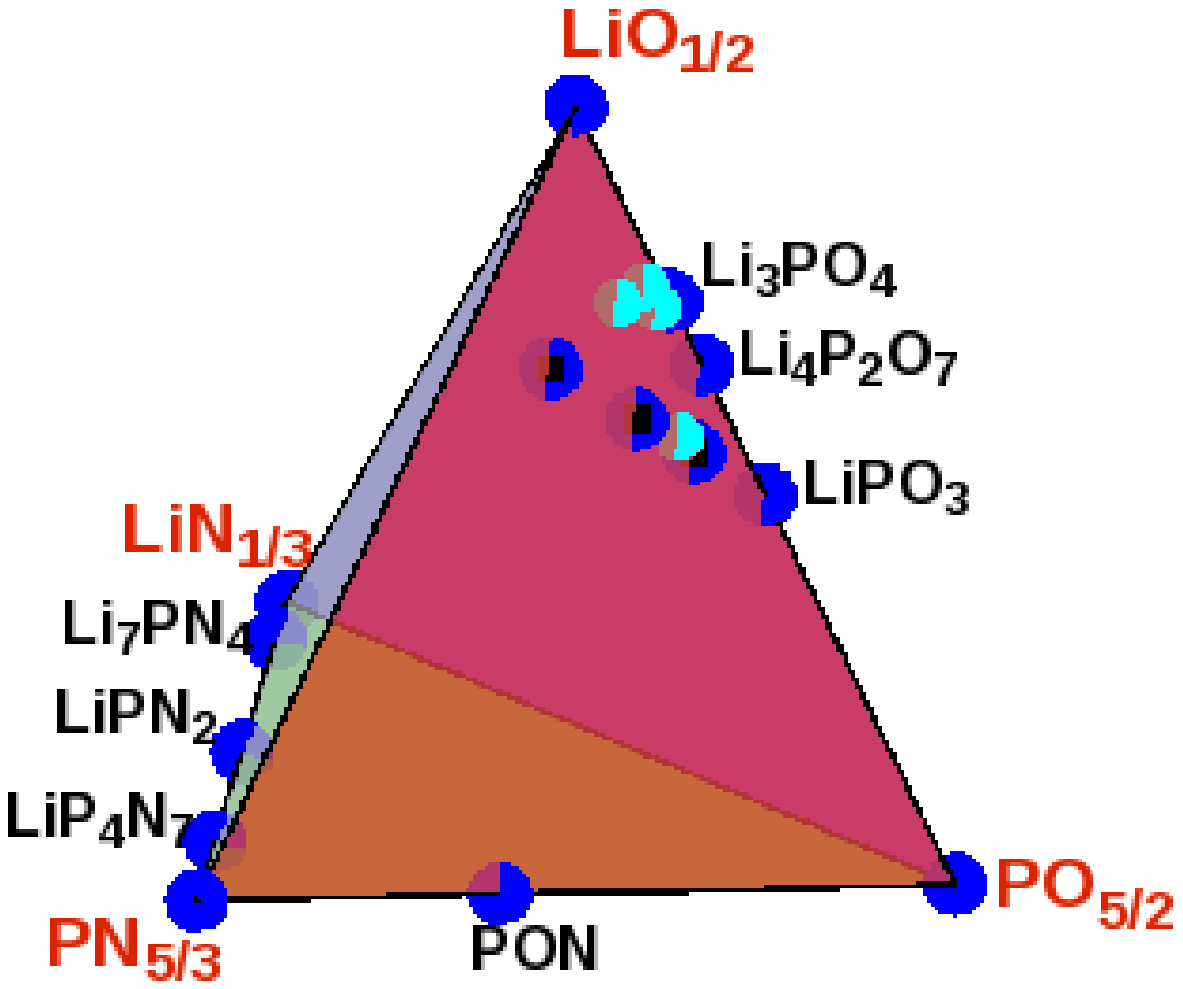
- Stable and meta-stable structures
- Lattice lattice vibration modes and frequencies (ν)
- Heats of formation (ΔH)
- Migration energies (E_m)
- Energies for interstitial-vacancy pair formation (E_f)

E_m from "Nudged elastic band"[a] estimate of minimal energy path:

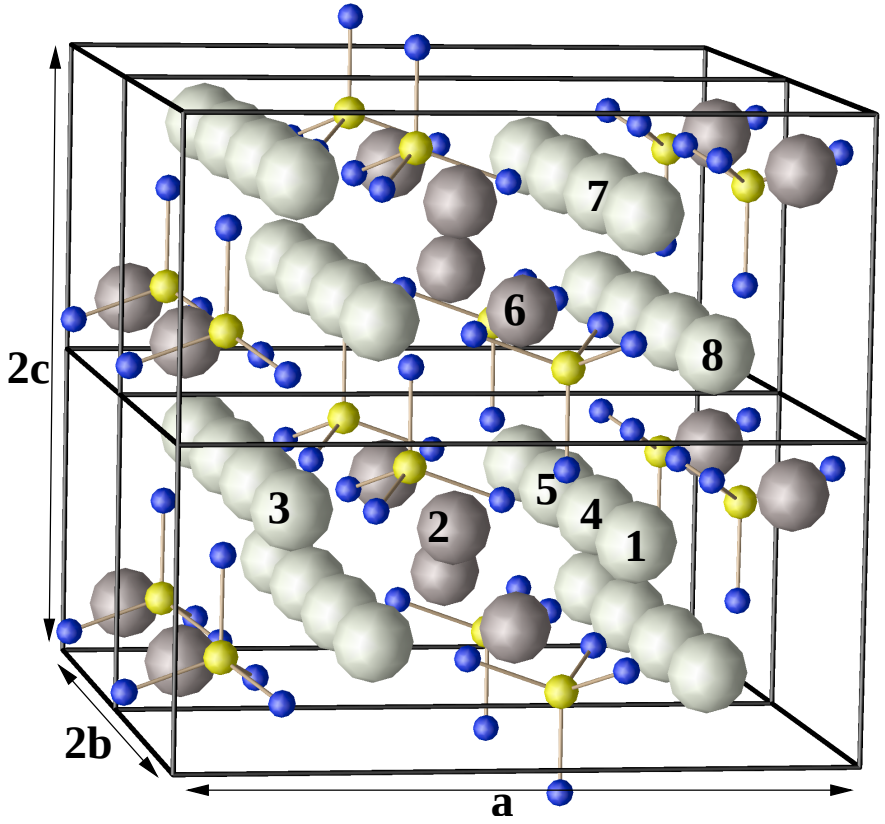


[a] Jónsson *et al* in **Classical and Quantum Dynamics in Condensed Phase Simulations**, edited by Berne et al (World Scientific, 1998), p. 385; Henkelman *et al*, *J. Chem. Phys.* **113** 9901, 9978 (2000).

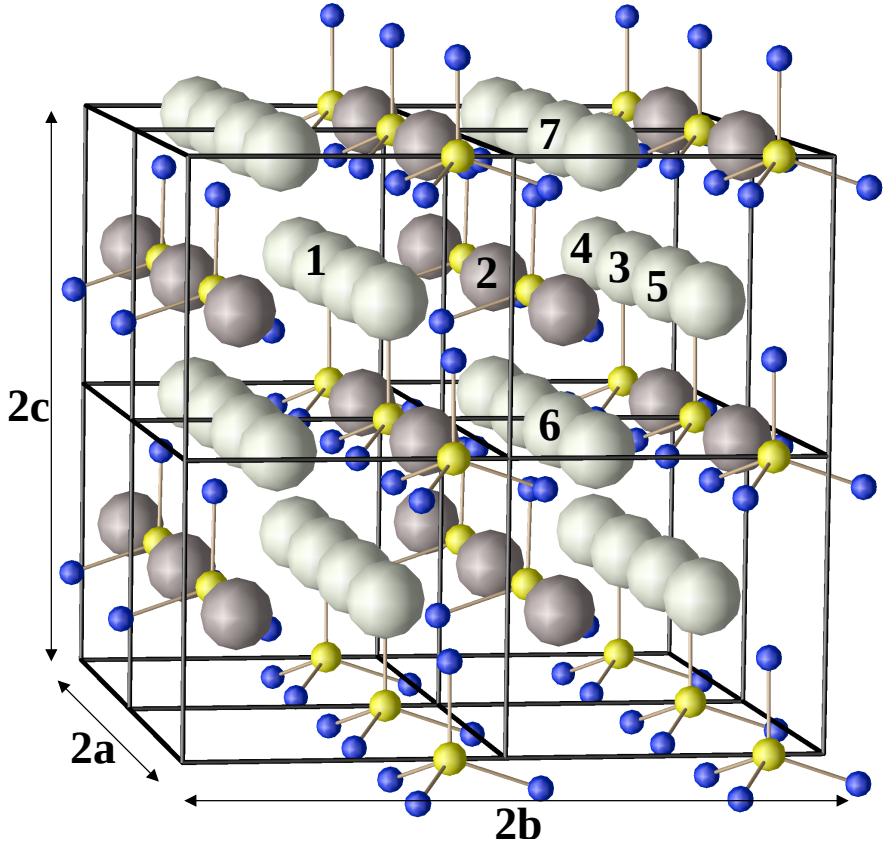
LiPON family of materials – $Li_xPO_yN_z$



Li_3PO_4

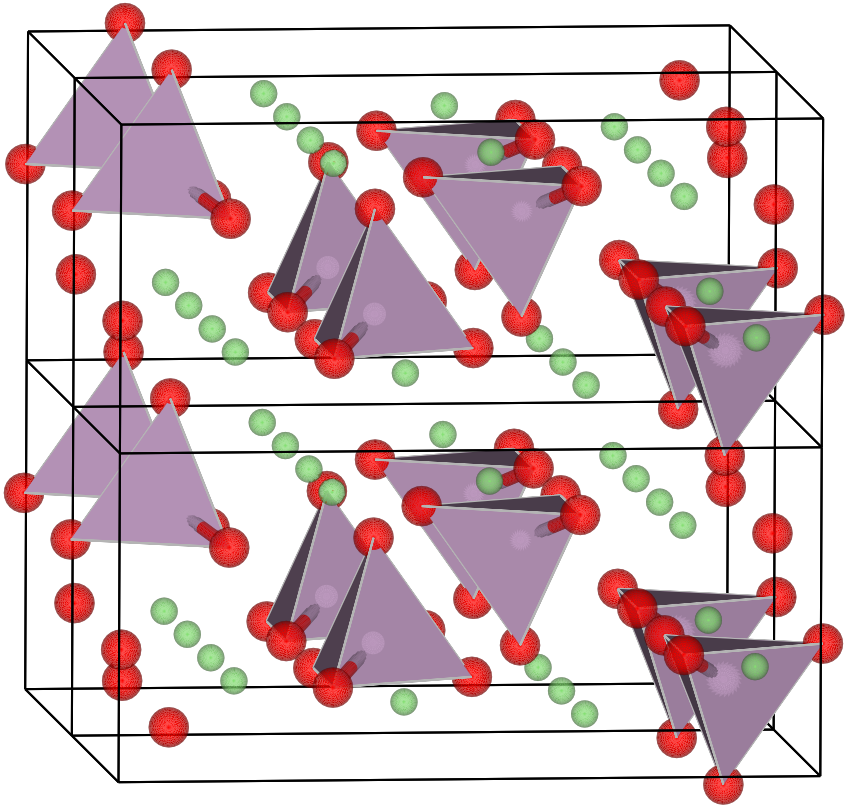


γ-Li_3PO_4

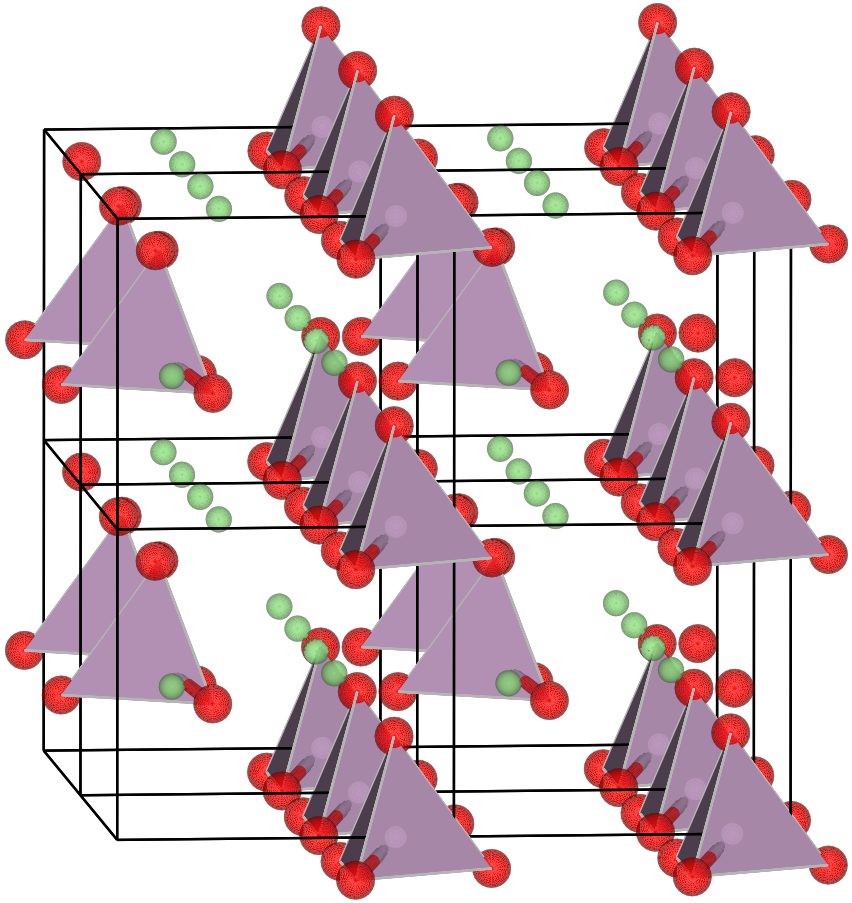


β-Li_3PO_4

Li_3PO_4(different view)

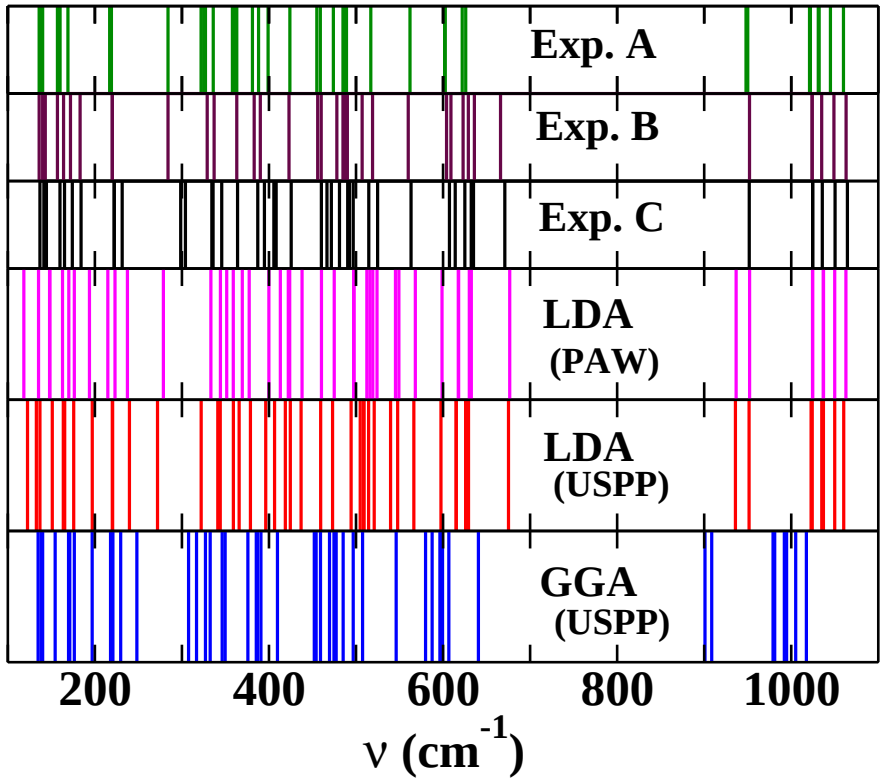


γ-Li_3PO_4

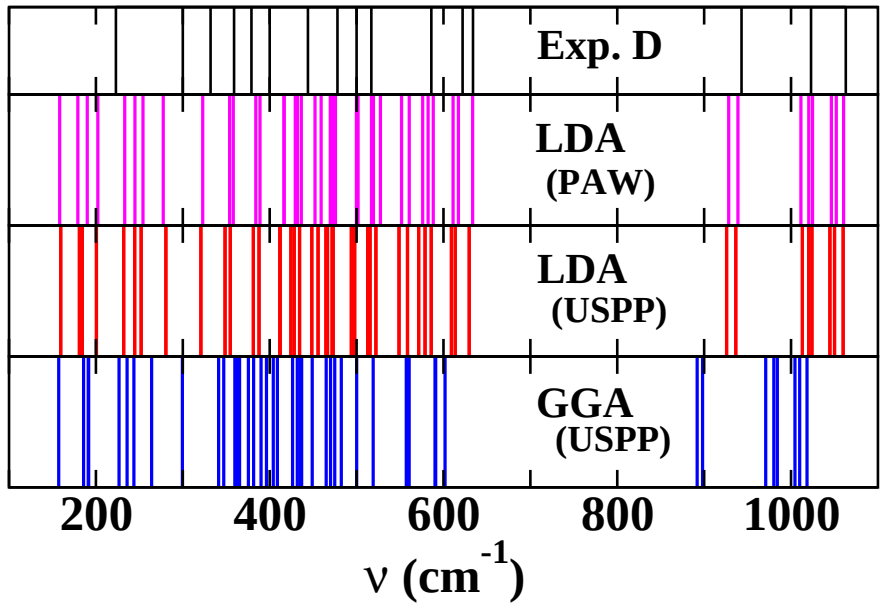


β-Li_3PO_4

Raman spectra – Experiment & Calculation



γ-Li_3PO_4



β-Li_3PO_4

Exp A: Room temp.: B. N. Mavrin *et al*, J. Exp. Theor. Phys. **96**, 53 (2003)

Exp B: Room temp. & Exp C: Liquid N_2 temp.: F. Harbach *et al*, Phys. Stat. Sol. (b), **66** 237 (1974)

Exp D: Liquid N_2 temp.: L. Popović *et al*, J. Raman Spec. **34** 77 (2003)

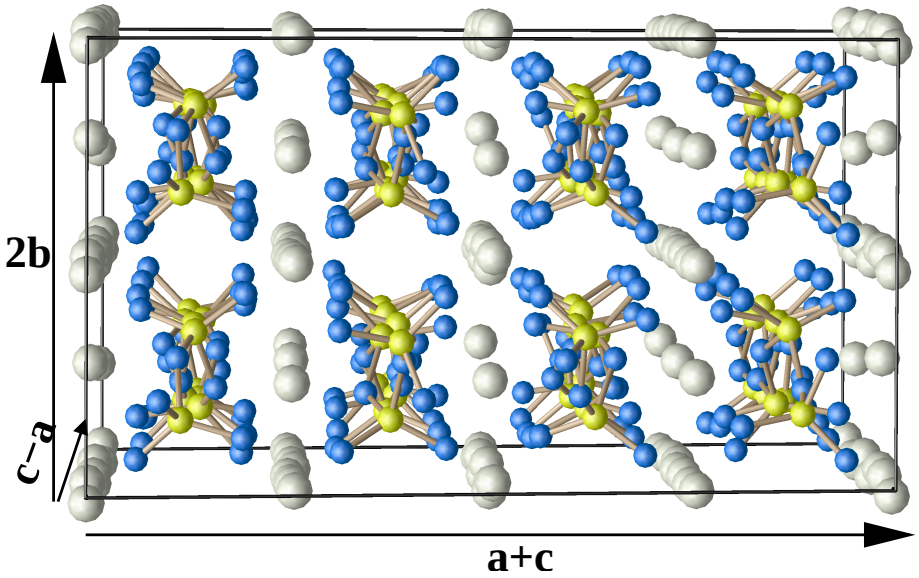
Some heats of formation

Material	Structure	ΔH (eV per formula unit) (USPP)	(EXP)
Li_2O	$Fm\bar{3}m$ (#225)	-6.18	-6.20
Li_2O_2	$P6_3/mmc$ (#194)	-6.54	-6.57
β-Li_3PO_4	$Pmn2_1$ (#31)	-21.41	
γ-Li_3PO_4	$Pnma$ (#62)	-21.38	-21.72
$LiPO_3$	$P2/c$ (#13)	-12.85	
$Li_4P_2O_6$	$P\bar{3}1m$ (#162)	-30.03	
$Li_4P_2O_7$	$P\bar{1}$ (#2)	-34.26	
$Li_7P_3O_{11}$	$P\bar{1}$ (#2)	-55.32	
α-Li_3N	$P6/mmm$ (#191)	-1.64	-1.71
γ-Li_3N	$Fm\bar{3}m$ (#225)	-1.19	
s_1-Li_2PO_2N	$Pbcm$ (#57)	-12.48	
s_2-Li_2PO_2N	$Aem2$ (#39)	-12.51	
$Li_5P_2O_6N$	$P\bar{1}$ (#2)	-33.49	
$Li_8P_3O_{10}N$	$P\bar{1}$ (#2)	-54.85	
$LiNO_3$	$R\bar{3}c$ (# 167)	-5.49	-5.01
h-P_2O_5	$R3c$ (#161)	-15.54	-15.53
α-P_3N_5	$C2/c$ (#15)	-3.24	-3.32

Phosphate chain materials: $LiPO_3$ plus N

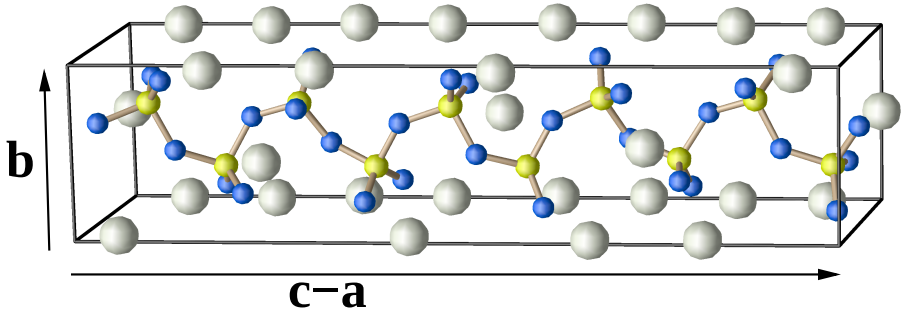
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



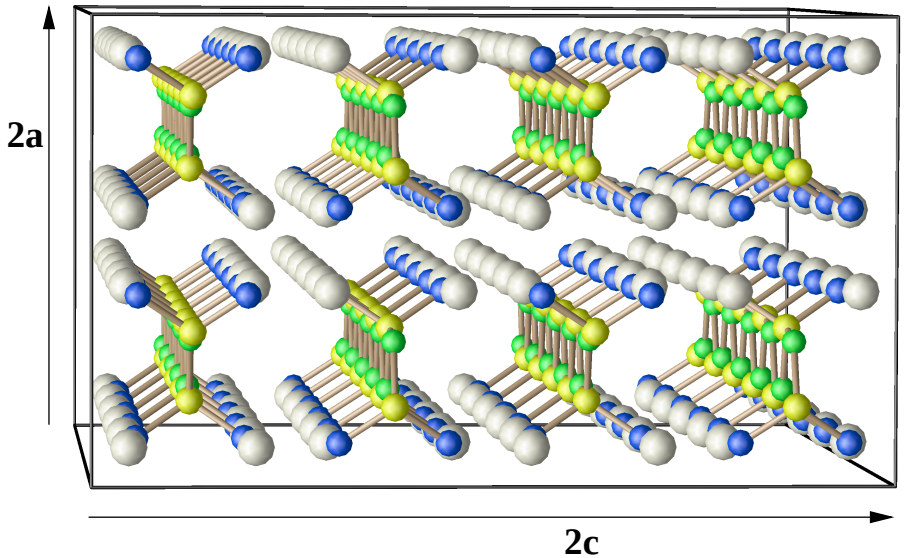
Ball colors: =Li, =P, =O.

Single chain view



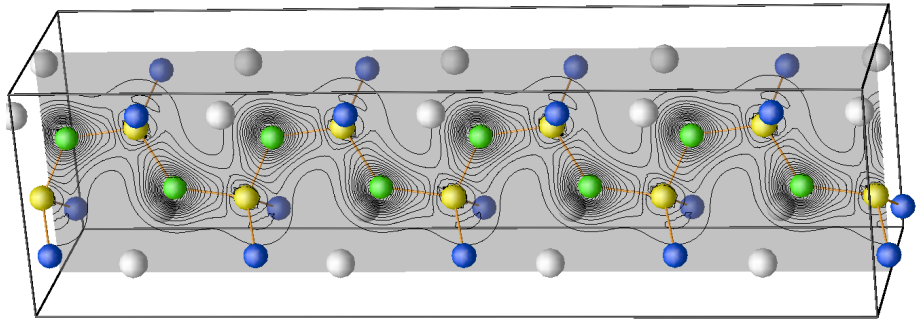
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram

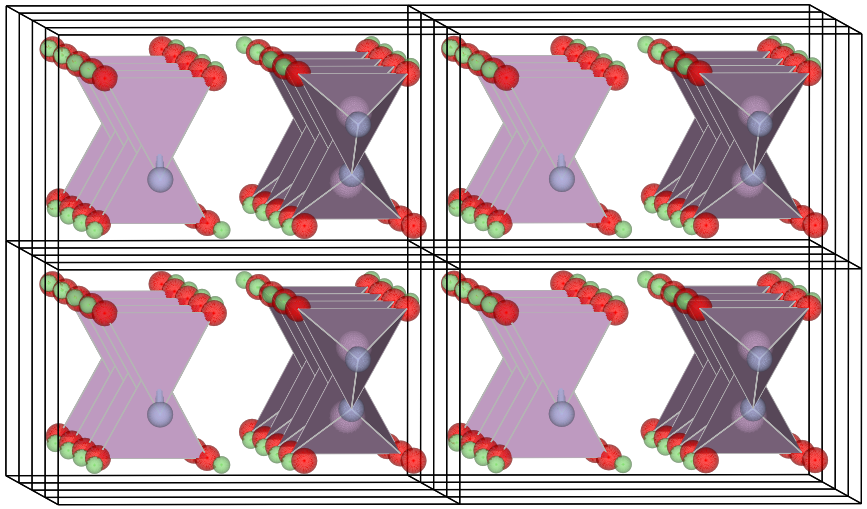


Ball colors: =Li, =P, =O, =N.

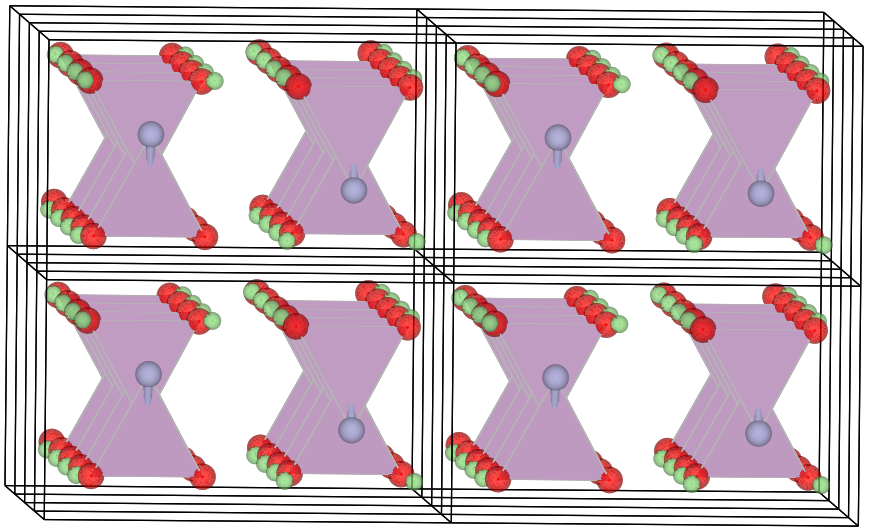
Single chain view



Two forms of Li_2PO_2N



s_1-Li_2PO_2N



s_2-Li_2PO_2N

Possible exothermic reaction pathways:

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

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

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

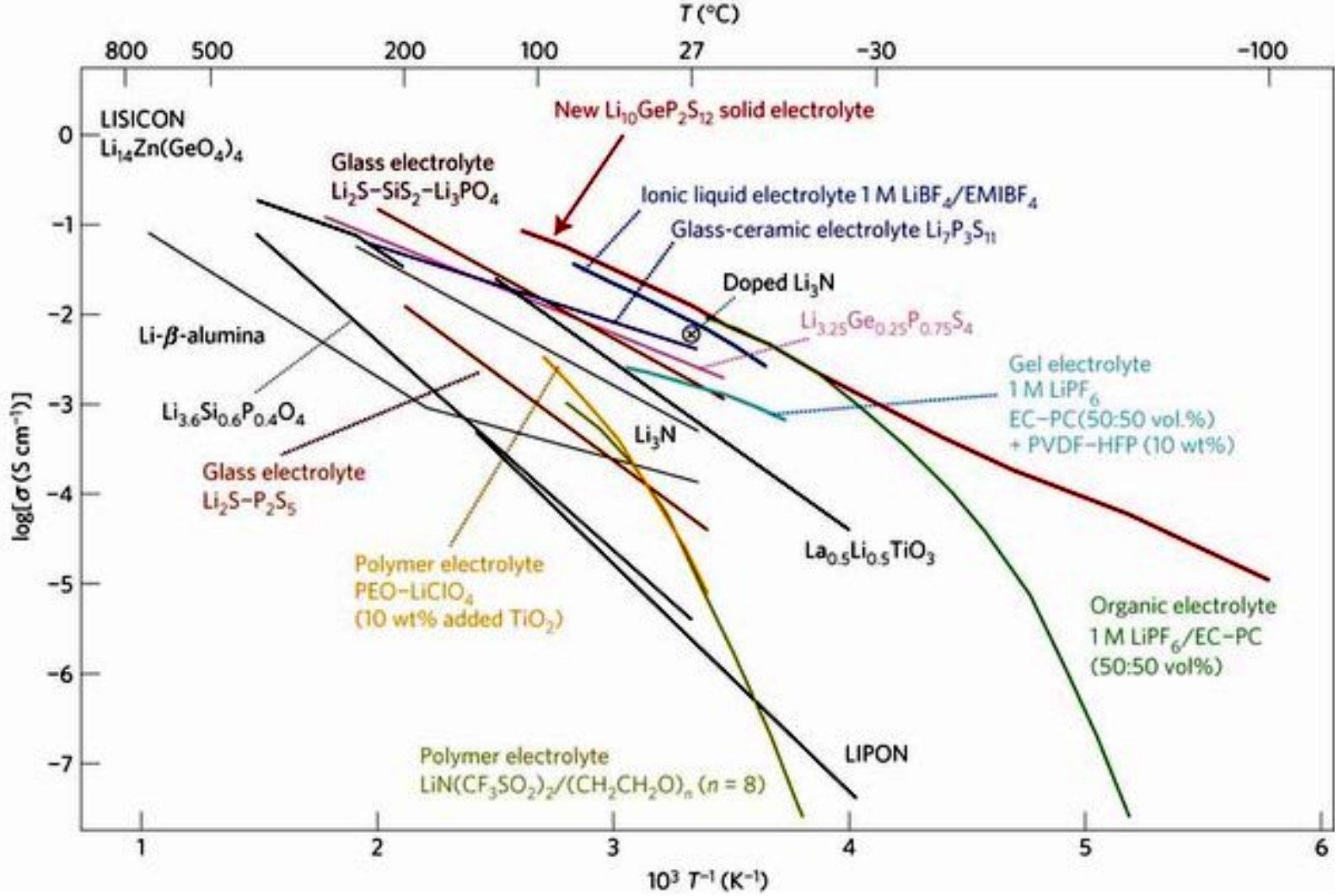
Summary of measured and calculated conductivity parameters in $Li_xPO_yN_z$ materials

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				

Conductivity profiles of electrolytes

Ref: N. Kamaya *et al* ***Nature Materials*** **10** 682-686 (2011)



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):

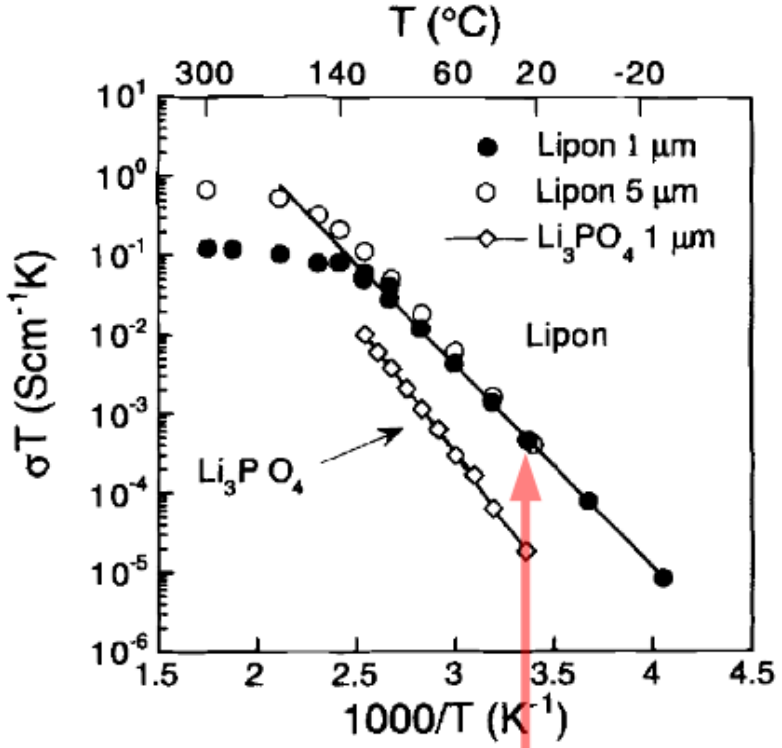


Fig. 3. Arrhenius plot of ionic conductivity of Lipon and Li_3PO_4 vs. temperature.

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

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

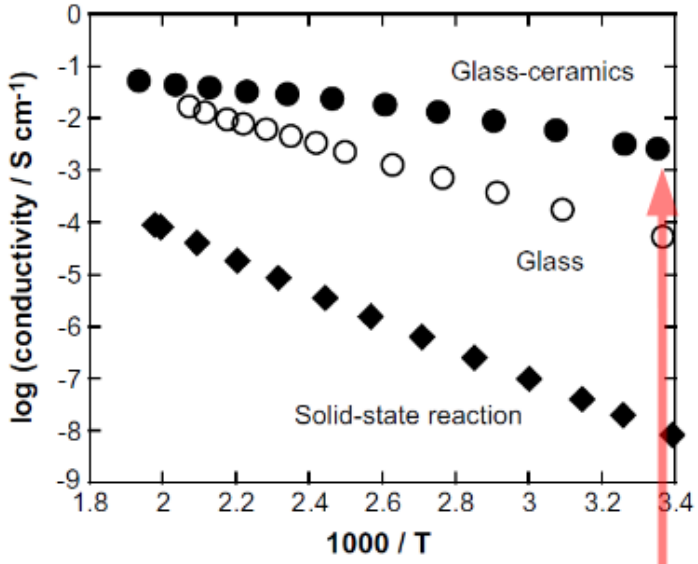
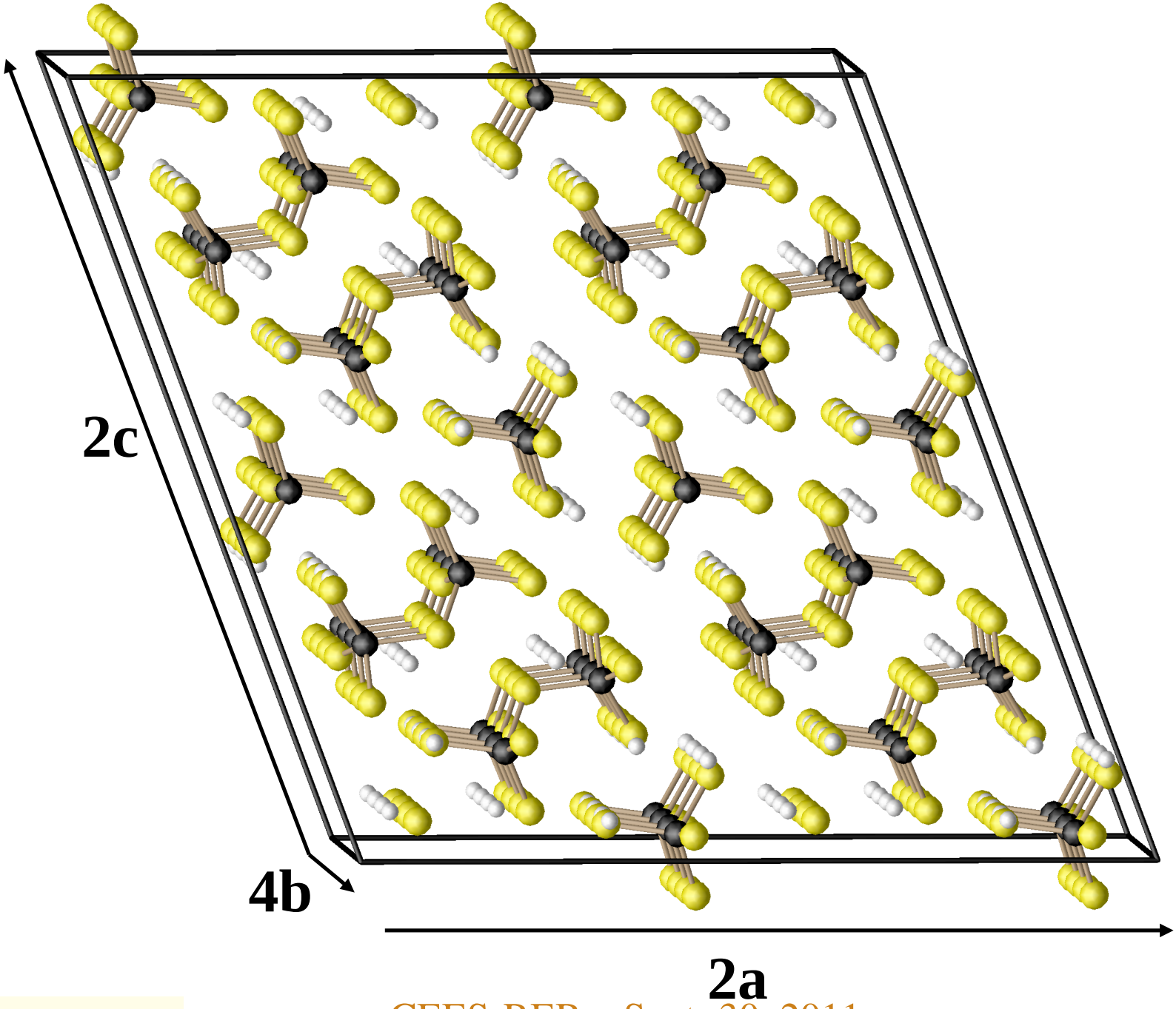


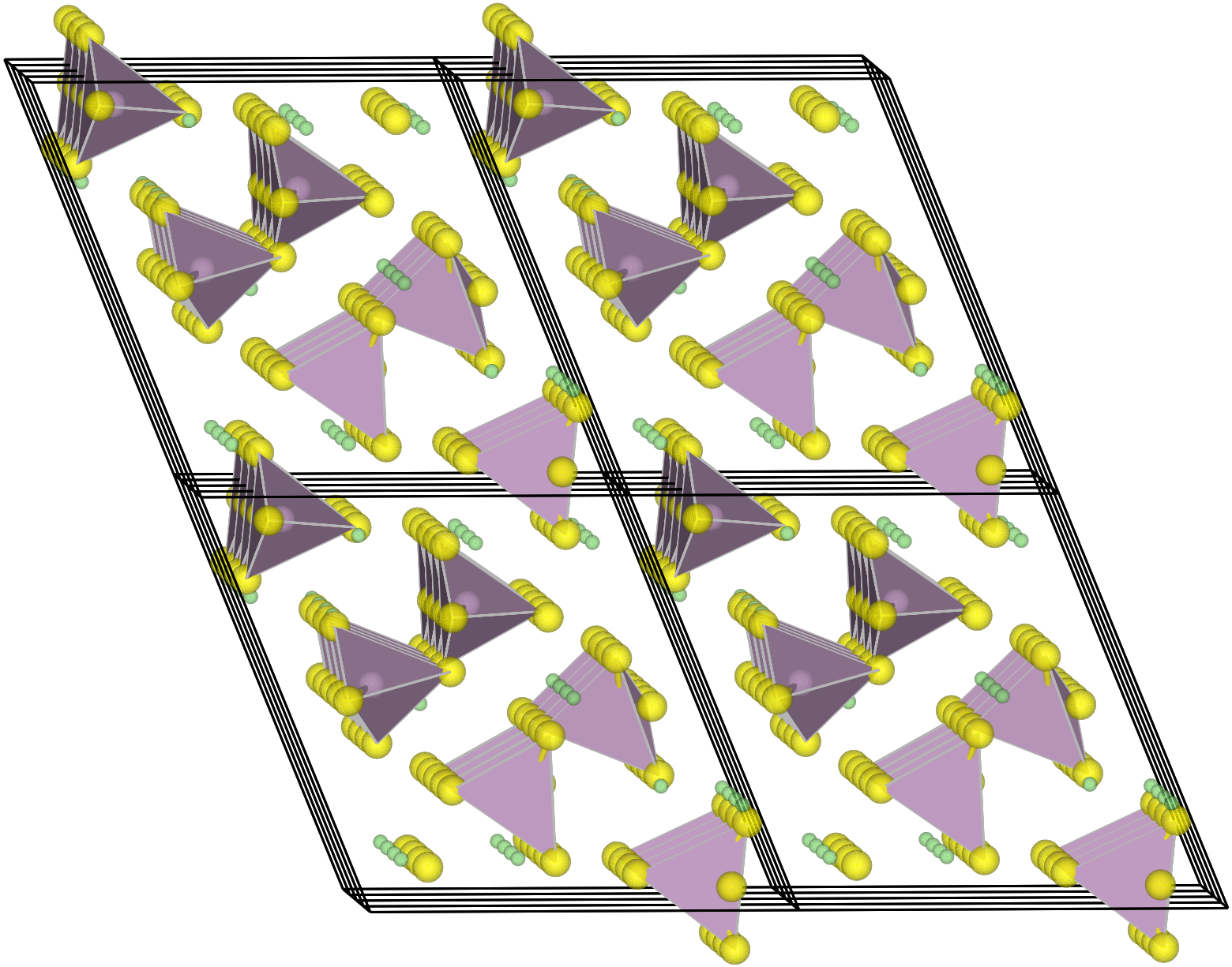
Fig. 5. Temperature dependences of the conductivities for the $70Li_2S \cdot 30P_2S_5$ glass and glass–ceramics. The conductivity data for the sample prepared by solid-state reaction are also shown.

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

Structure of $Li_7P_3S_{11}$



Structure of $Li_7P_3S_{11}$ – another view



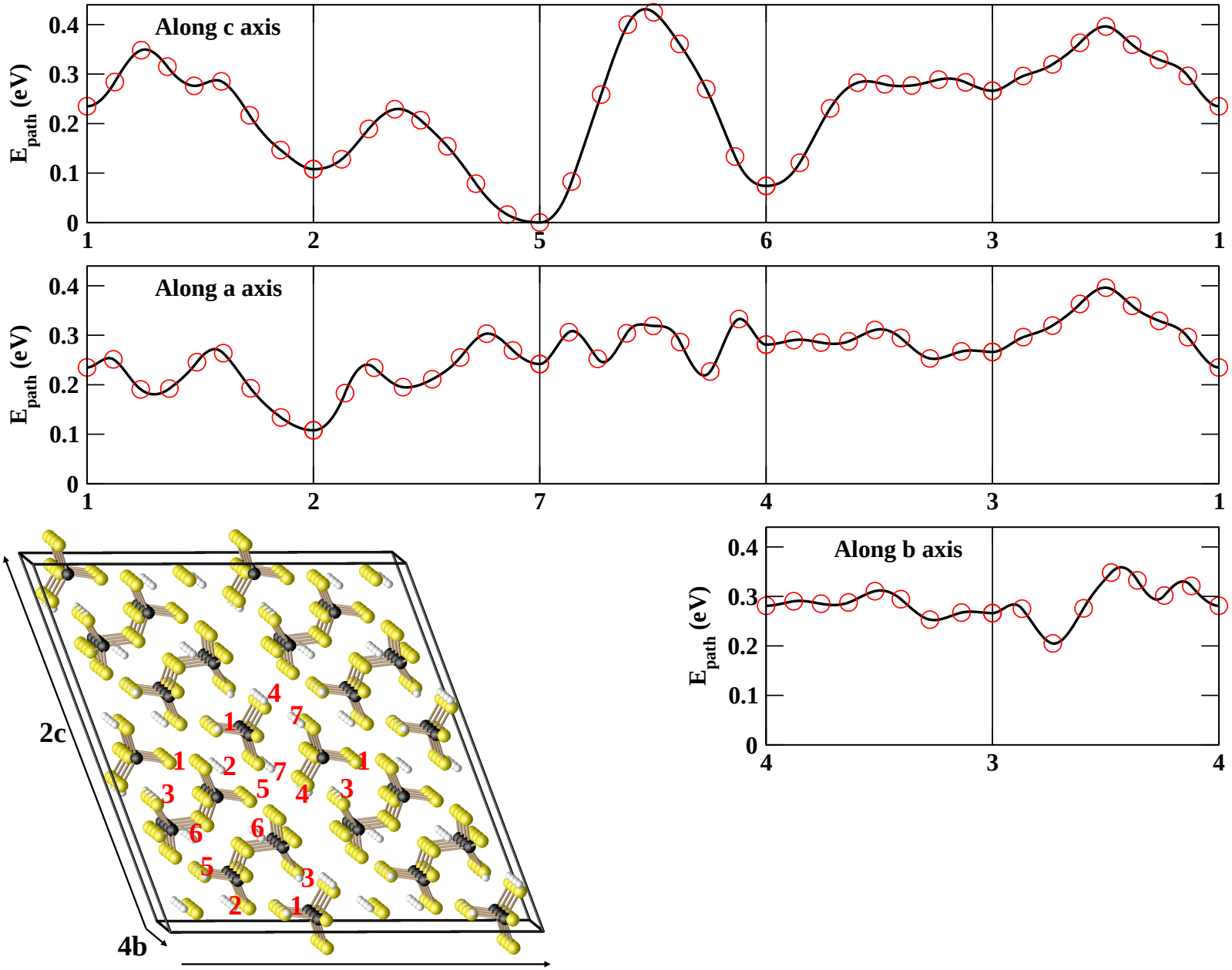
Some heats of formation

Material	Structure	ΔH (eV per formula unit) (USPP)	(EXP)
Li_2S	$Fm\bar{3}m$ (#225)	-4.29	-4.57
Li_2S_2	$P6_3/mmc$ (#194)	-4.09	
β-Li_3PS_4	$Pmn2_1$ (#31)	-8.36	
γ-Li_3PS_4	$Pnma$ (#62)	-8.17	
$Li_4P_2S_6$	$P\bar{3}1m$ (#162)	-12.41	
$Li_4P_2S_7$	$P\bar{1}$ (#2)	-11.58	
$Li_7P_3S_{11}$	$P\bar{1}$ (#2)	-20.00	
$Li_7P_3S^*_{11}$	$P\bar{1}$ (#2)	-19.93	
SO_3	$Pna2_1$ (#33)	-4.83	-4.71
Li_2SO_4	$P2_1/a$ (#14)	-14.74	-14.89

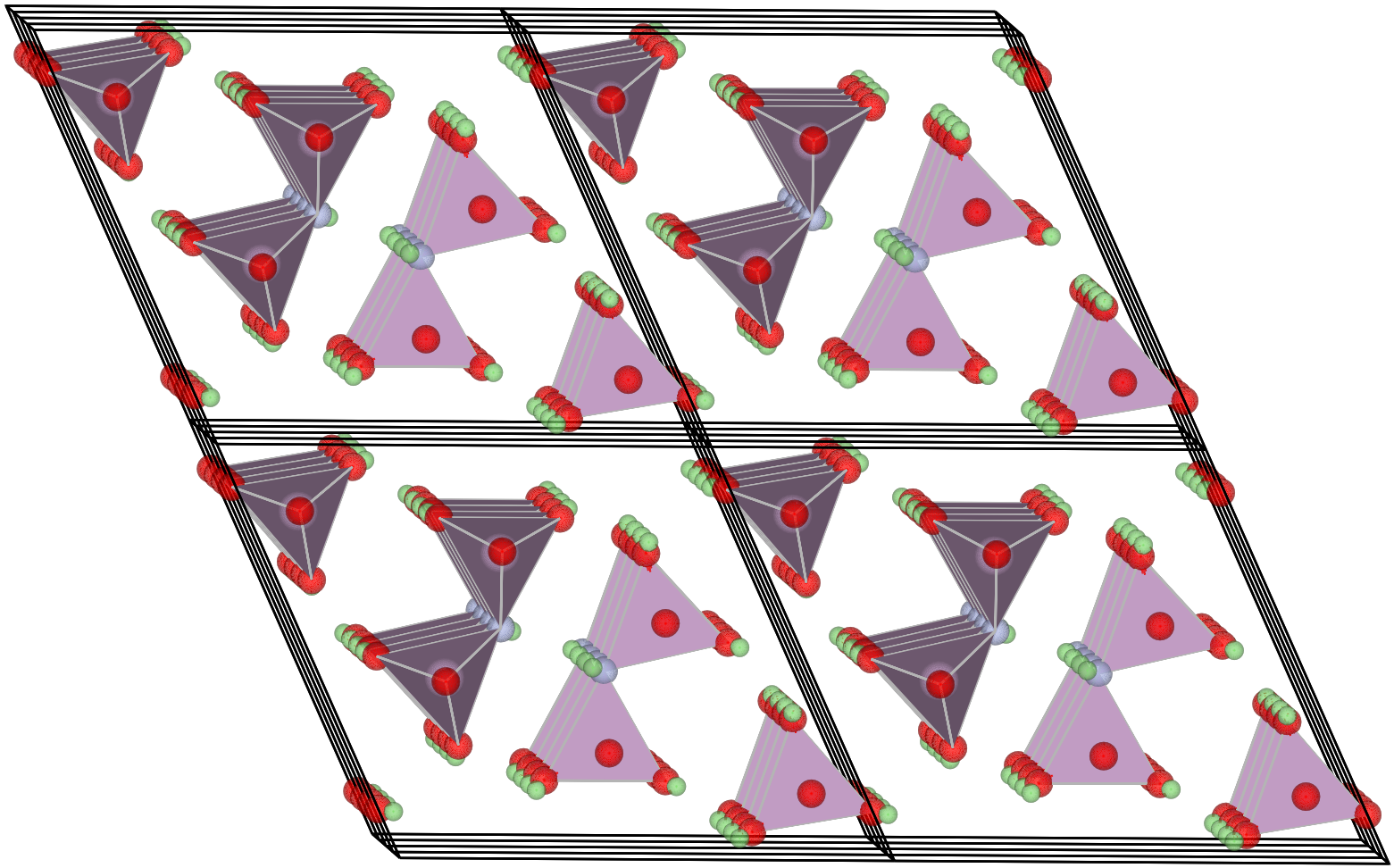
Some decomposition reactions

Reaction	ΔH (eV)
$Li_7P_3S_{11} \rightarrow Li_3PS_4 + Li_4P_2S_7$	0.06
$Li_7P_3S_{11} \rightarrow Li_3PS_4 + Li_4P_2S_6 + S$	-0.69
$Li_7P_3S^*_{11} \rightarrow Li_3PS_4 + Li_4P_2S_7$	-0.01
$Li_7P_3O_{11} \rightarrow Li_3PO_4 + Li_4P_2O_7$	-0.35
$Li_8P_3O_{10}N \rightarrow Li_3PO_4 + Li_5P_2O_6N$	-0.06

Some energy path diagrams for Li vacancy migration



Possible structure of $Li_8P_3O_{10}N$



Possibilities for collaboration

- Experimental verification (or otherwise) of the predicted Li_2PO_2N structure
- Iterative refinement of other LiPON and LiPS materials
- Investigation of new materials such as the supersuper ionic conductor $Li_{10}GeP_2S_{12}$.

General comments

- From "theory" perspective – there is a need to know the range of predictive power of "first-principles" calculations
- From the renewal energy perspective – there is an incentive to make progress on solid state electrolytes
- From the prospective of possible projects – there seem to be many possibilities