First principles simulations of Li ion migration in materials related to LiPON electrolytes [a]

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- Comments on solid electrolytes
- Overview of LiPON family
- Computational methods
- Simulations of $LiPO_3$
- Simulations of ***predicted*** $\mathbf{Li_2PO_2N}$
- Summary and conclusions

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[a] Supported by NSF grants DMR-0427055 and 0705239; Wake Forest University DEAC computer cluster.

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Solid *vs* liquid electrolytes in Li ion batteries

Solid electrolytes

Advantages

1. Excellent chemical and physical stability.
2. Performs 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

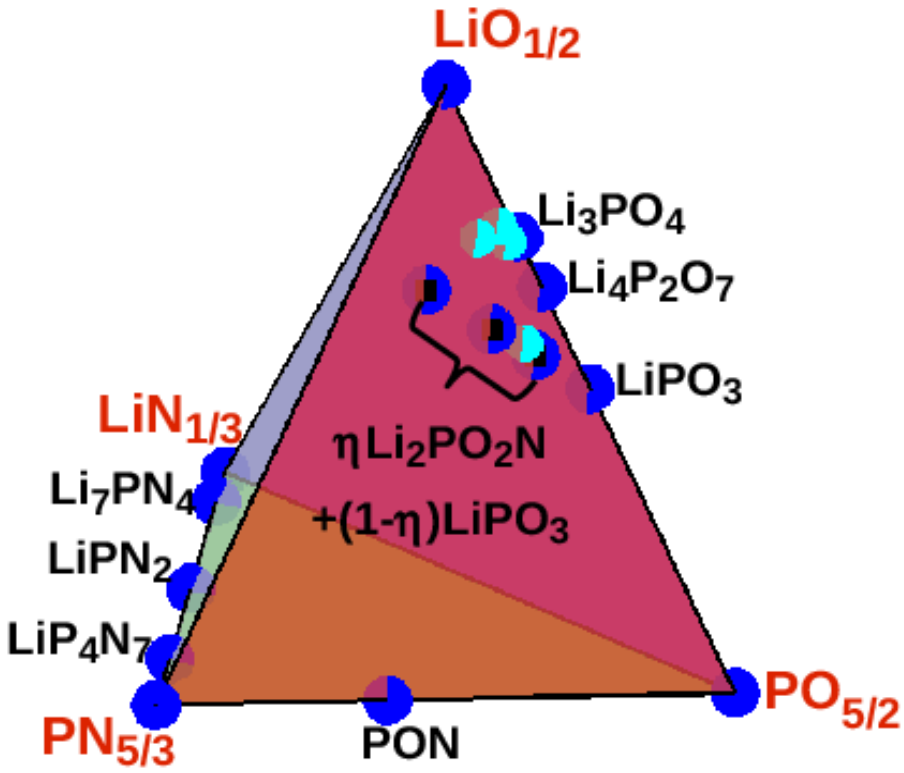
1. Excellent contact area with high capacity electrodes.
2. Can accomodate size changes of electrodes during charge and discharge cycles.
3. Relatively high conductivity per unit area.

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.

Overview of LiPON family of electrolytes

The thin film solid electrolyte LiPON developed at Oak Ridge National Laboratory[a] is the most widely used solid electrolyte for thin film batteries and a number of other related technologies. While commercial LiPON electrolytes are disordered, much can be learned from related crystalline materials in the $Li_xPO_yN_z$ family ($x = 2y + 3z - 5$). In order to systematize the current state of undertanding of the crystalline members of the family, it is helpful to visualize a quaternary phase diagram of known materials reported in the literature together with new stable and meta-stable predicted by computer simulation. The corners of the composition tetrahedron indicate the starting materials of $LiO_{1/2}$, $LiN_{1/3}$, $PO_{5/2}$, and $PN_{5/3}$.



Natural and synthetic crystalline materials (●), LiPON thin film materials (●), and computer simulated idealized phosphate chain structure materials (■).

[a] Bates, Dudney, *et al Solid State Ionics* **53-54**, 647 (1992); Dudney *Interface* **17**, 44 (2008)

Measured conductivity in $Li_xPO_yN_z$ materials

Arrhenius equation for ionic conduction (σ) as a function of temperature (T):

$$\sigma \cdot T = \underbrace{K}_{\text{Constant}} \; e^{-E_A/kT}.$$

For crystalline materials:

$$E_A = \underbrace{E_m}_{\text{Migration}} + \frac{1}{2} \underbrace{E_f}_{\text{Formation}} .$$

For disordered materials:

$$E_A = \underbrace{E_m}_{\text{Migration}} .$$

Measured activation energies E_A in some $Li_xPO_yN_z$ materials

Material	Form	E_A (eV)
γ-Li_3PO_4	single crystal[a]	1.23, 1.14
$Li_{2.88}PO_{3.73}N_{0.14}$	poly cryst.[b]	0.97
$Li_{3.3}PO_{3.9}N_{0.17}$	amorphous[b]	0.56
$Li_{1.35}PO_{2.99}N_{0.13}$	amorphous[c]	0.60
$LiPO_3$	poly cryst.[d]	1.4
$LiPO_3$	amorphous[d]	0.76-1.2
$LiPN_2$	poly cryst.[e]	0.6
Li_7PN_4	poly cryst.[e]	0.5

[a] Ivanov-Shitz *et al*, *Cryst. Rep.* **46** 864 (2001)
[b] Wang *et al*, *J. Solid State Chem.* **115** 313 (1995)
[c] Mũnoz *et al*, *Solid State Ionics* **179** 574 (2008)
[d] Money *et al*, *Appl. Phys. A* **88** 647 (2007)
[e] Schnick *et al*, *Solid State Ionics* **38** 271 (1990)

Open questions on LiPON materials

- What are the Li ion migration mechanisms?
- Which phosphonitride structures and stoichiometries are the most stable and which optimize Li ion conductivity?
- What is the relationship between the ordered and disordered structures?

Computational methods

- "First principles" simulations using density functional theory[a] to treat the electrons and the Born-Oppenheimer approximation to treat the nuclear positions $\{\mathbf{R}^a\}$, to determine the "total energy" $E(\{\mathbf{R}^a\})$ of the system.
- Variety of computer codes – PWscf[b], pwpaw[c], abinit[d]

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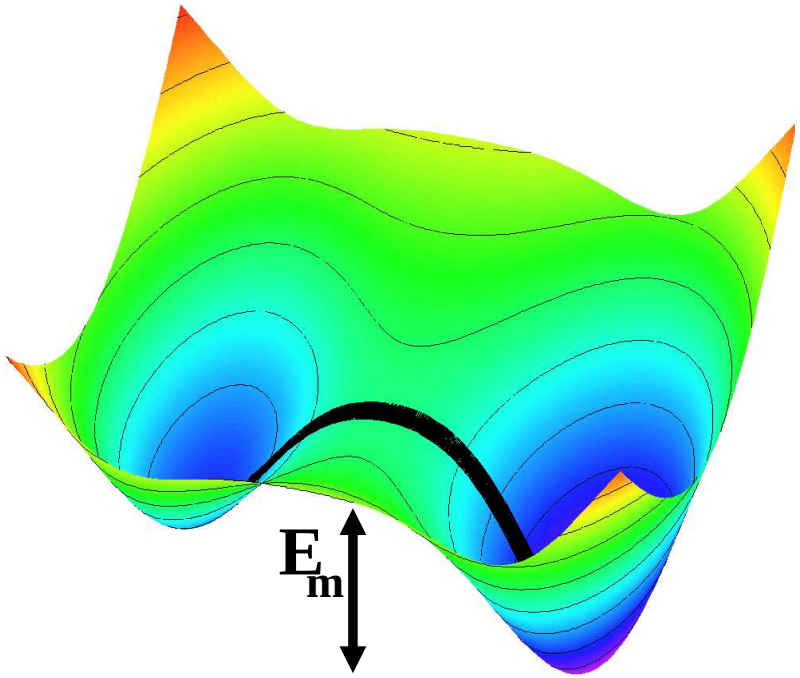
[a] Hohenberg and Kohn, *Phys. Rev.*, **136** B864 (1964); Kohn and Sham, *Phys. Rev.*, **140** A1133 (1965).
[b] Giannozzi *et al*, *J. Phys.: Condens. Matter* **21** 394402 (2009) `www.quantum-espresso.org`
[c] Tackett *et al*, *Comp. Phys. Comm.* **135** 348 (2001) `pwpaw.wfu.edu`
[d] Gonze *et al*, *Zeit. Kristallogr.* **220** 550 (2005) `www.abinit.org`.

Computational methods – more details

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)

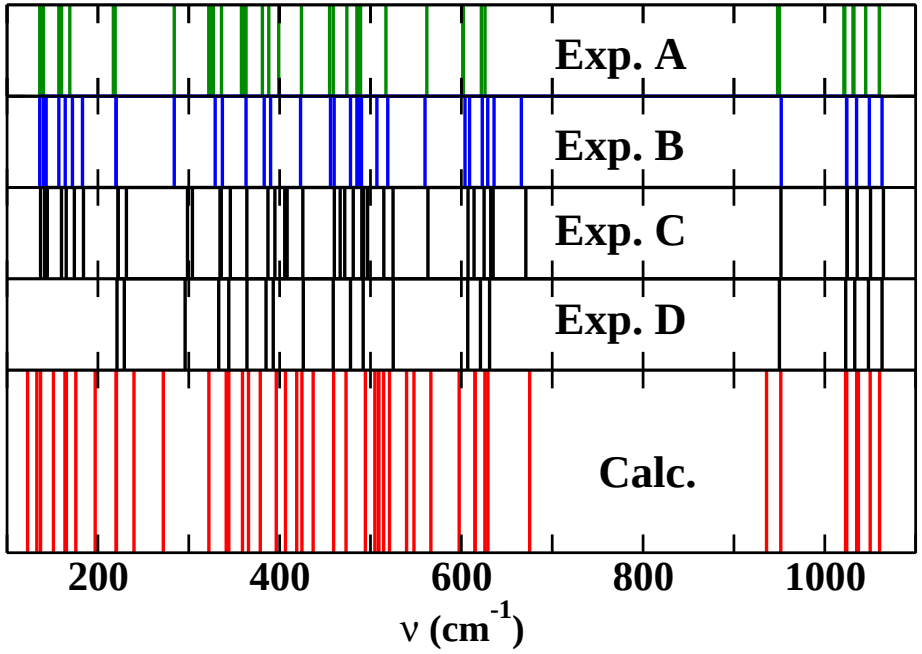
E_m from "Nudged elastic band"[a] estimate of minimal energy path:



[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).

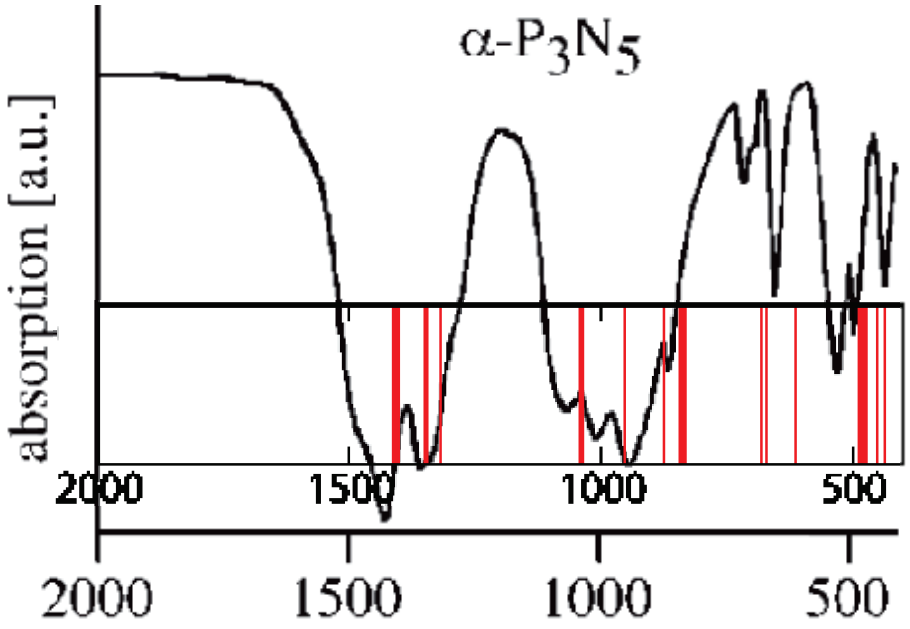
Computational methods – validation

Raman spectra for γ-Li_3PO_4



Calculated Raman spectra (red) compared with Exp. A – (RT) – Mavrin & co-workers, *JETP* **96**, 53 (2003); Exp. B – (RT) – Harbach & co-workers, *Phys. Stat. Sol. B* **66**, 237 (1974); Exp. C – (LNT) – Harbach; Exp. D – (LNT) Popović & co-workers, *J. Raman Spec.* **34** 77, (2003)

Infrared spectra for α-P_3N_5

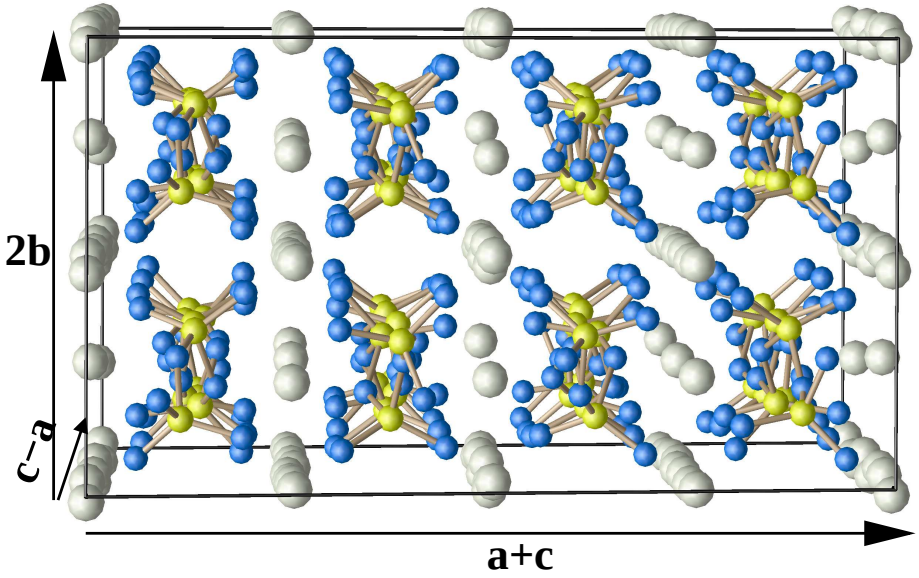


Calculated infrared spectra (red) compared with experiment of Kroll and Schnick, *Chem. Eur. J* **8** 3530 (2002).

Phosphate chain material: $LiPO_3$

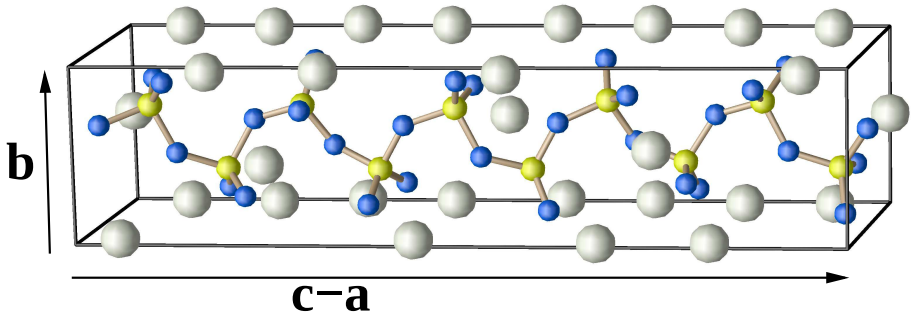
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



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

Single chain view



$P2/c$ $LiPO_3$ can be prepared from a Li_2O-P_2O_5 glass by heating to the crystallization temperature of 486^o C.[a]

Lattice parameters (in Å) for $LiPO_3$

	a	b	c	β
Cal.	13.00	5.30	16.31	98.8^o
Exp.[b]	13.074	5.4068	16.452	99.00^o

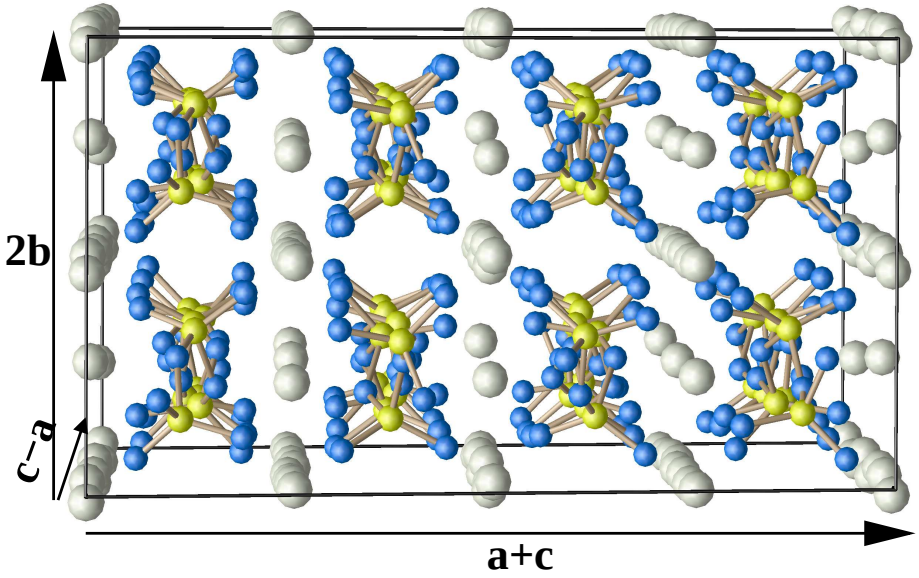
[a] Money and Hariharan, *Appl. Physics A* **88** 647 (2007)

[b] Murashova and Chudinova, *Crystall. Rep.* **46** 942 (2001)

Phosphate chain materials: $LiPO_3$ plus N

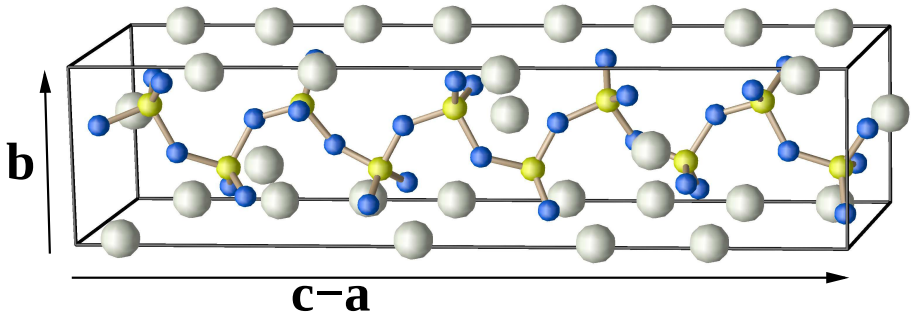
$LiPO_3$ in $P2/c$ structure; 100 atom unit cell

Chain direction perpendicular to plane of diagram



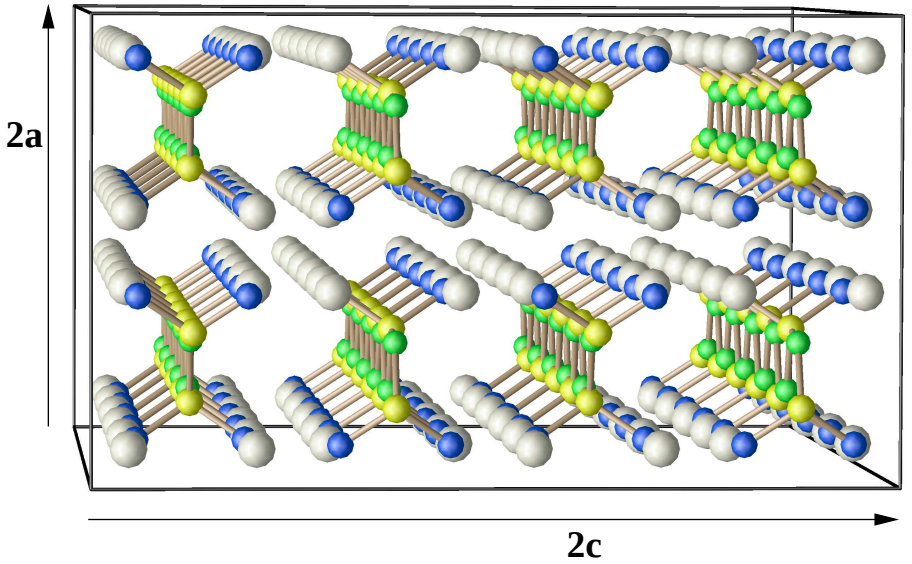
Ball colors: =Li, =P, =O.

Single chain view



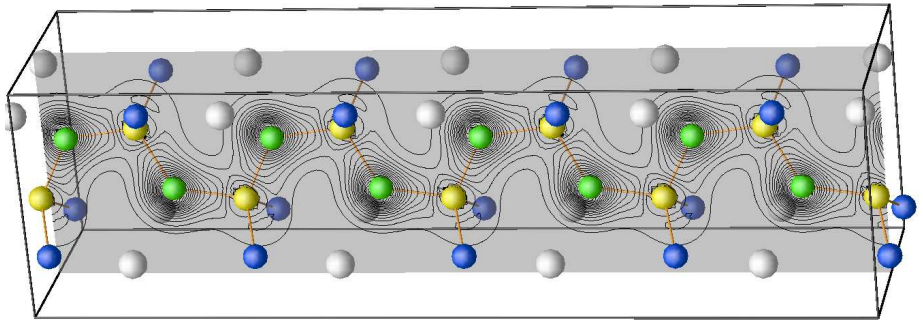
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram



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

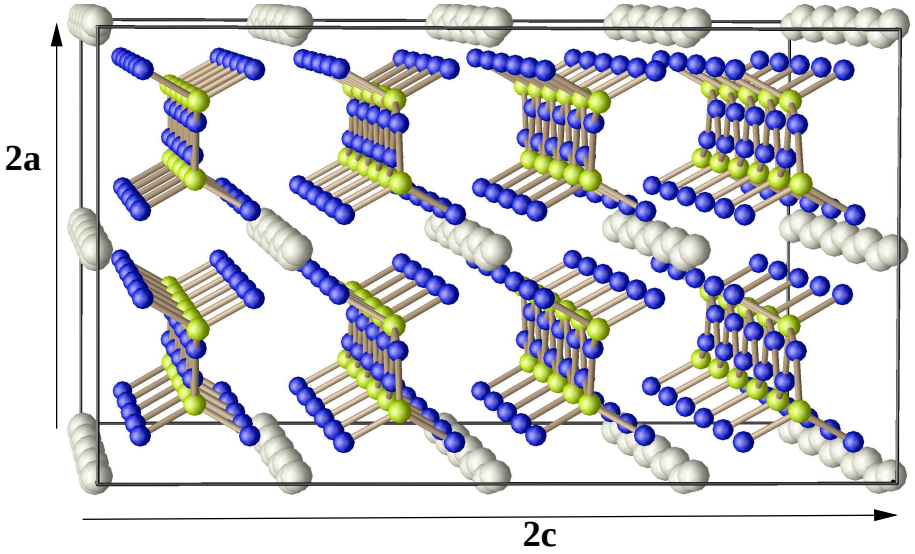
Single chain view



Phosphate chain materials: s_1-$LiPO_3$ and s_1-Li_2PO_2N

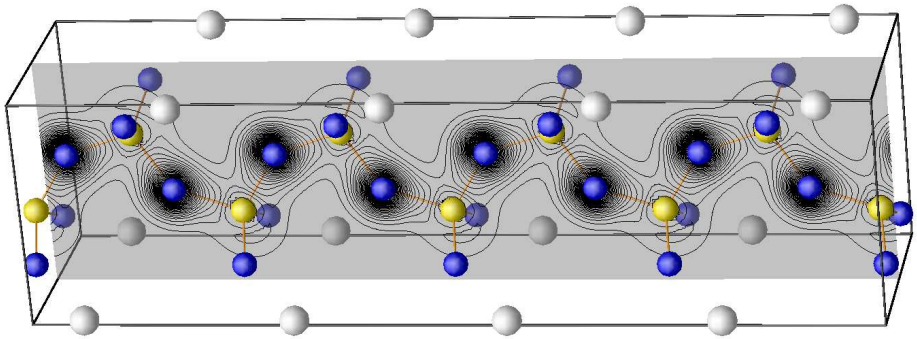
s_1-$LiPO_3$ in $Pbcm$ structure; 20 atom unit cell

Chain direction perpendicular to plane of diagram



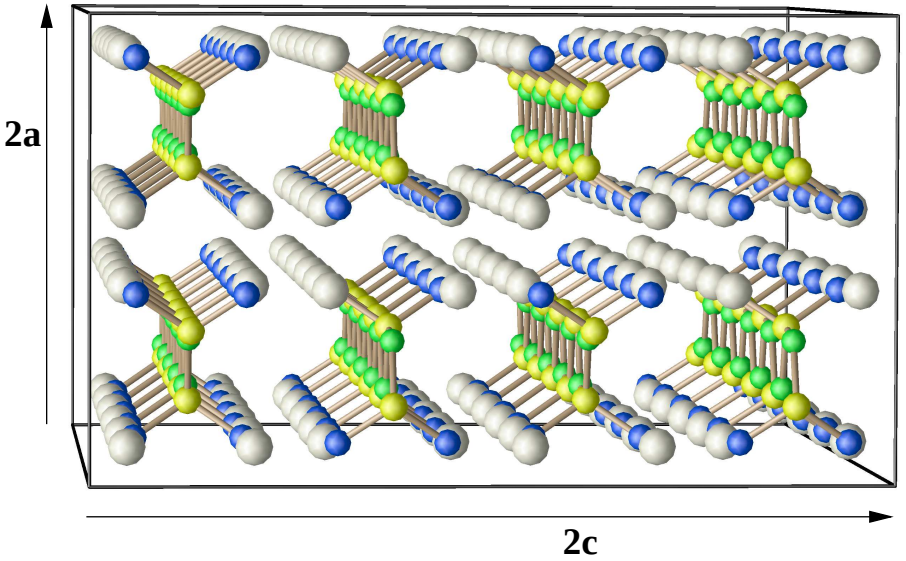
Ball colors: =Li, =P, =O.

Single chain view



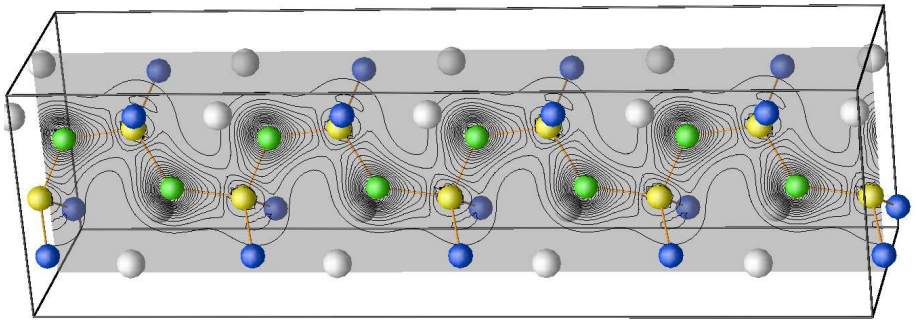
s_1-Li_2PO_2N in $Pbcm$ structure; 24 atom unit cell

Chain direction perpendicular to plane of diagram



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

Single chain view

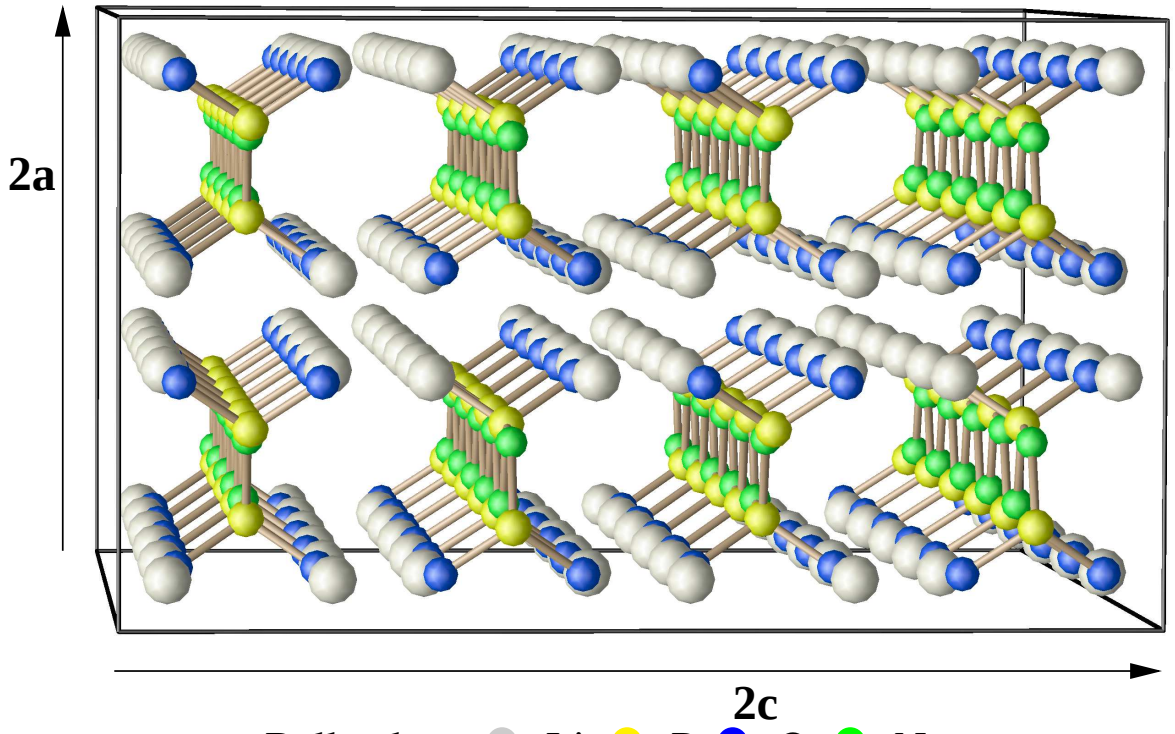


Phosphate chain materials: $LiPO_3$ and Li_2PO_2N

Comparison of different structural forms of $LiPO_3$ and Li_2PO_2N in terms of their heats of formation ($\Delta H_{\rm cal}$) and volumes $\mathcal{V}_{\rm cal}$ (per formula unit).

Material	Structure	$\Delta H_{\rm cal}$ (eV)	$\mathcal{V}_{\rm cal}$ ($\mathring{A}^3$)
$LiPO_3$	$P2/c$ [#13]	-12.80	56
s_1-$LiPO_3$	$Pbcm$ [#57]	-12.73	58
s_2-$LiPO_3$	$Aem2$ [#39]	-12.73	58
s_3-$LiPO_3$	$Pmc2_1$ [#26]	-12.70	67
s_1-Li_2PO_2N	$Pbcm$ [#57]	-12.42	57
s_2-Li_2PO_2N	$Aem2$ [#39]	-12.45	57
s_3-Li_2PO_2N	$Pmc2_1$ [#26]	-12.08	66

s_1-Li_2PO_2N: Can it be made?



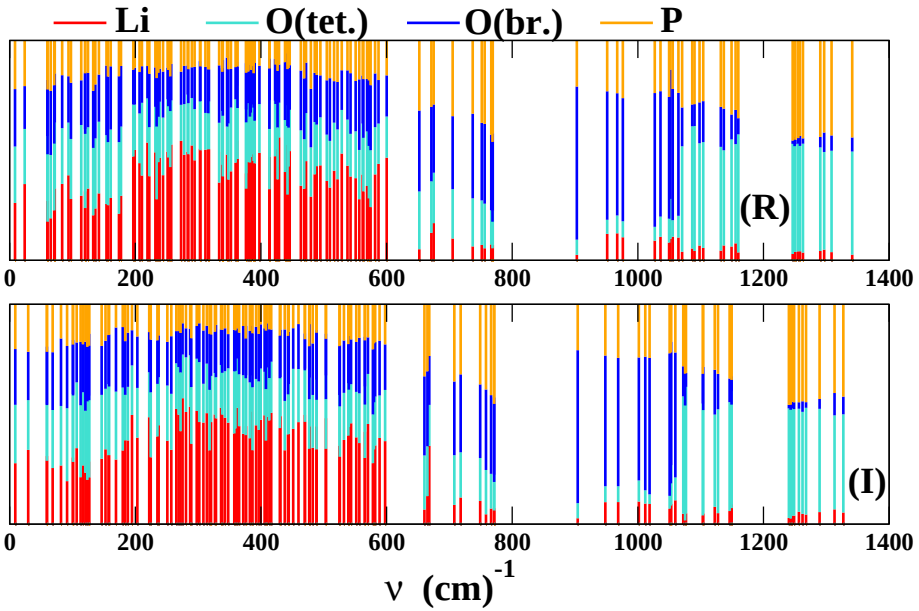
Possible exothermic reaction pathways:

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

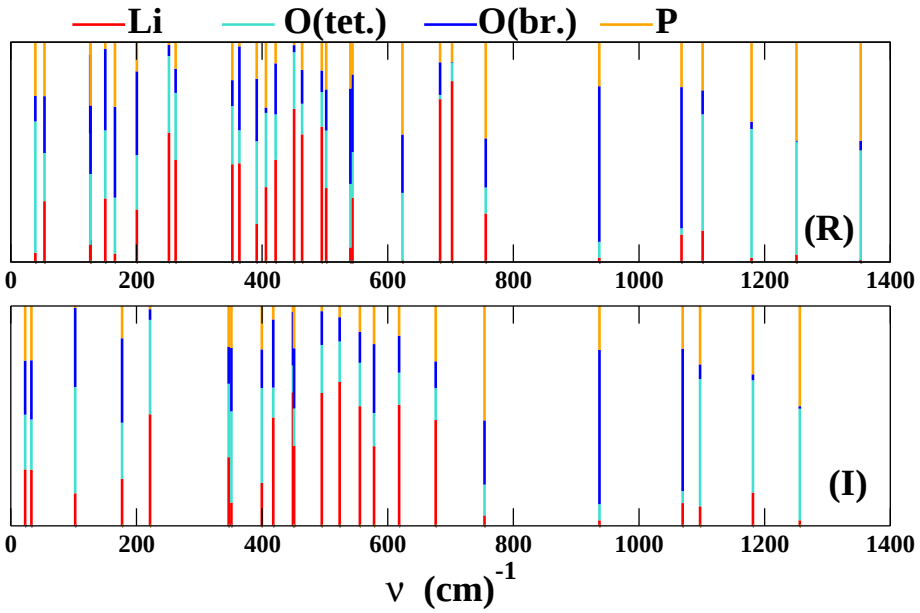
$$LiPO_3 + Li_3N \rightarrow Li_2PO_2N + Li_2O + 4.2\ \text{eV}.$$

Lattice vibration in phosphate chain materials

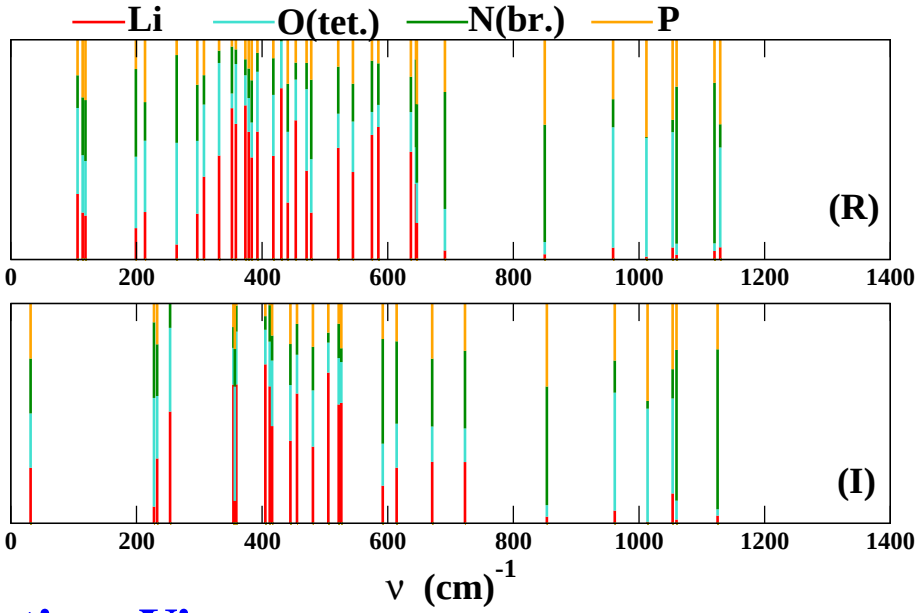
$P2/c$ **LiPO$_3$**



$Pbcm$ **LiPO$_3$**

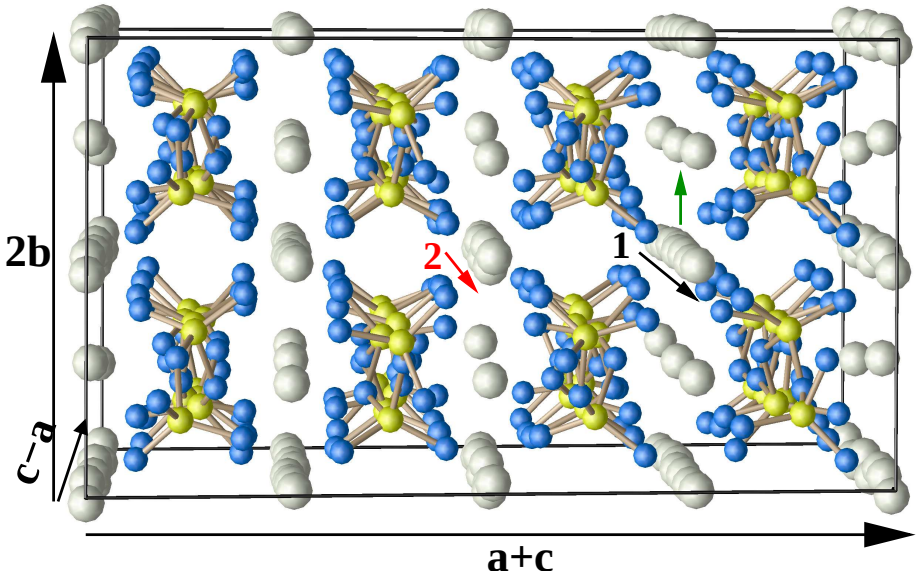


$Pbcm$ **Li$_2$PO$_2$N**

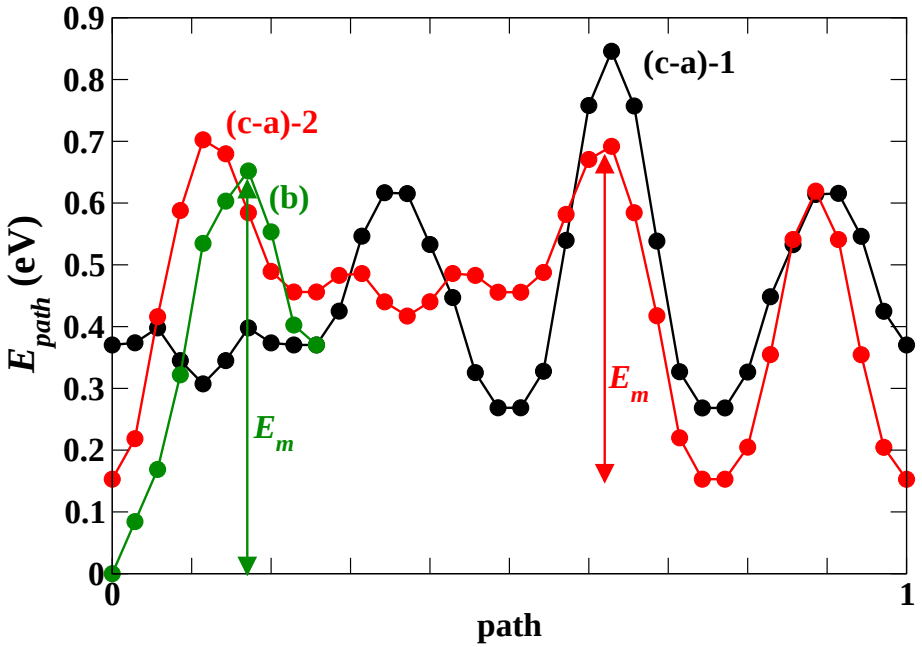


Li ion diffusion in $P2/c$ $LiPO_3$

Paths for vacancy diffusion



Vacancy diffusion path diagrams



Summary of migration energies (in eV)

	Vacancy			
	(c-a)-1	**(c-a)-2**	**(b)**	Interstitial
E_m	0.6	0.6	0.7	0.7

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 aire 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				

Summary of results so far

Open questions on LiPON materials and some results

- What are the Li ion migration mechanisms?

  For crystalline materials studied so far, Li ion migration via vacancy and interstitial mechanisms are found to to be $E_m = 0.3 - 0.7$ eV.

- Which phosphonitride structures and stoichiometries are the most stable and which optimize Li ion conductivity?

  We have identified several stable/meta-stable phosphonitride chain structures having the stoichiometry Li_2PO_2N, the most stable of which are characterized by a planar $-N-P-N-P-$ backbone.

  These highly symmetric structures have yet to be experimentally realized.

- What is the relationship between the ordered and disordered structures?

  Ongoing work on mixed crystals of stoichiometries η-Li_2PO_2N+ (1-η)$LiPO_3$ suggest a competition between increasing the number of mobile ions and trapping effects of inhomogeneous environments.