

# Surface structure and stability in Li<sub>3</sub>PS<sub>4</sub> and Li<sub>3</sub>PO<sub>4</sub> electrolytes from first principles

N. Lepley

Wake Forest University

APS March Meeting 2013

## ① Motivation

Solid Electrolytes  
Li<sub>3</sub>PS<sub>4</sub> and Li<sub>3</sub>PO<sub>4</sub>

## ② Materials

Structure  
Energetics

## ③ Interfaces

Vacuum  
Li Metal

## Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

## Materials

Structure

Energetics

## Interfaces

Vacuum

Li Metal

# Motivation

# Solid Electrolytes: The Basics

Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

Materials

Structure

Energetics

Interfaces

Vacuum

Li Metal

Solid electrolytes show considerable promise for advancing battery technology

- Improved safety characteristics
- Allow novel electrodes (e.g. LiS)
- Li (thio)phosphate materials most interesting

Primary electrolyte properties are:

- Stability
- Interface stability
- Ionic Conductivity



Tesla Model S

# Solid Electrolytes: Li<sub>3</sub>PX<sub>4</sub>

- Relatively stable stoichiometry
- Traditionally low conductivity
- Nanoporous highly-conducting phase of Li<sub>3</sub>PS<sub>4</sub> recently produced<sup>1</sup>
- Details of this phase's properties and the mechanism of phase transition and stabilization need further investigation
- Extend previous modelling work on Li<sub>3</sub>PO<sub>4</sub>

---

<sup>1</sup>Liu et al. JACS 135(3) pg. 975 2013

Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

Materials

Structure

Energetics

Interfaces

Vacuum

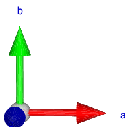
Li Metal

# Materials

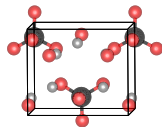
## Relevant Phases

2 Phases of interest for both materials

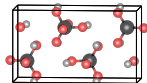
- Pmn2<sub>1</sub> symmetry
- Pmna symmetry



Pmn2<sub>1</sub>:



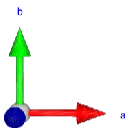
Pmna:



## Relevant Phases

2 Phases of interest for both materials

- Pmn2<sub>1</sub> symmetry
- Pmna symmetry
  - ◇ Li<sub>3</sub>PS<sub>4</sub> exhibits fractional occupancy



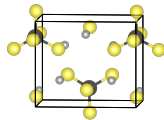
● Li

● P

● S

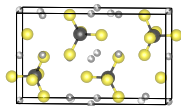
Pmn2<sub>1</sub>:

---



Pmna:

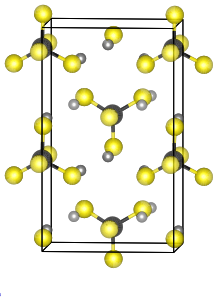
---



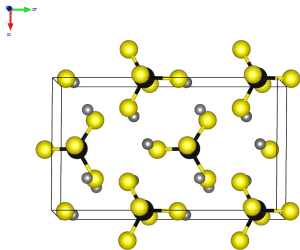


## Phase relationship

Pmn2<sub>1</sub>:



Pmn2<sub>1</sub>:



- Double b lattice vector
- Interchange a and b

## Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

## Materials

Structure

Energetics

## Interfaces

Vacuum

Li Metal

- Multiple phases of interest
- Pmn2<sub>1</sub> expected to be most stable at 0K
- Energy difference on the order of  $k_B T$  ( $\sim 0.025$  eV @ RT)

Material	$\Delta H$
Li <sub>3</sub> PO <sub>4</sub> -Pmn2 <sub>1</sub>	-21.41
Li <sub>3</sub> PO <sub>4</sub> -Pmna	-21.38
Li <sub>3</sub> PS <sub>4</sub> -Pmn2 <sub>1</sub>	-8.36
Li <sub>3</sub> PS <sub>4</sub> -Pmna(b)	-8.28
Li <sub>3</sub> PS <sub>4</sub> -Pmna(c)	-8.24

Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

Materials

Structure

Energetics

Interfaces

Vacuum

Li Metal

# Interfaces

Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

Materials

Structure

Energetics

Interfaces

Vacuum

Li Metal

# Motivation

- Highly conducting nanoporous phase is Pmna symmetry
- Surface energy effects may contribute to the stability.
- Good interfaces are crucial to electrolyte performance

# Surface Energy

In the presence of a surface the total energy is defined as

## Surface Energy

$$E_{total} = N \cdot E_{Form. Unit} + \gamma \cdot A$$

For the bulk,  $A=0$  and this reduces to:

$$E_{total} = N \cdot E_{Form. Unit}$$

Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

Materials

Structure

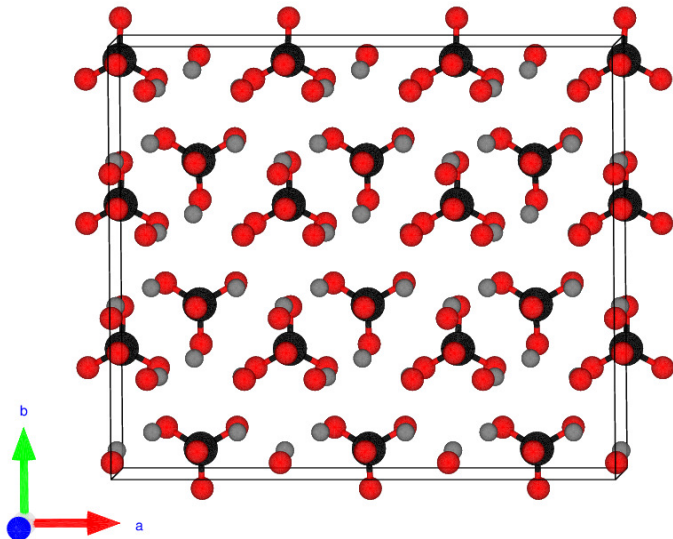
Energetics

Interfaces

Vacuum

Li Metal

# Cleavage Planes

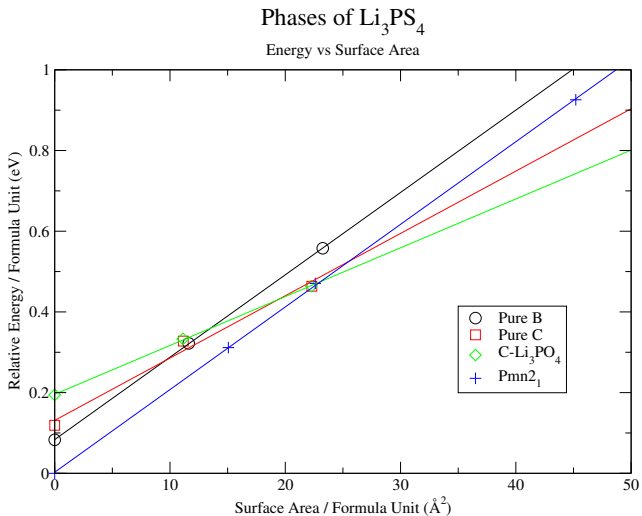


## Surface Energies

## Surface Energies

Material	Phase	Plane	Sigma(eV/Å <sup>2</sup> )
Li <sub>3</sub> PS <sub>4</sub>	Pmn21	[010]	0.021
	Pmna(b)	[100]	0.020
	Pmna(c)	[100]	0.015
	Pmna(c)-Li <sub>3</sub> PO <sub>4</sub>	[100]	0.012
Li <sub>3</sub> PO <sub>4</sub>	Pmn21	[010]	0.039
	Pmna	[100]	0.040
	Pmna	[010]	0.073
	Pmna	[100]*	0.078

Surface energies in eV per square angstrom for select faces. [100]\* denotes a [100] surface that is not flat, but has an additional Li<sub>3</sub>PO<sub>4</sub> group protruding from the [100] face.

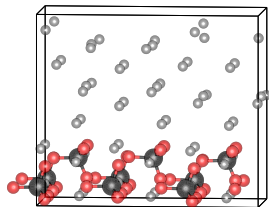
Li<sub>3</sub>PS<sub>4</sub> phases in nanofilms

Total energy as a function of surface area for select phases of Li<sub>3</sub>PS<sub>4</sub>.



## Interface with Li: Li<sub>3</sub>PO<sub>4</sub>

- Stability relative to Li electrode modelled directly
- Li<sub>3</sub>PO<sub>4</sub> predicted stable relative to Li metal



Relaxed Li<sub>3</sub>PO<sub>4</sub>-Li interface

## Interface with Li: Li<sub>3</sub>PS<sub>4</sub>

### Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

### Materials

Structure

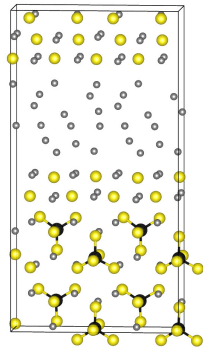
Energetics

### Interfaces

Vacuum

Li Metal

- Li<sub>3</sub>PS<sub>4</sub> predicted not inherently stable relative to Li metal
- Experimental work agrees, formation of SEI likely
- SEI layer believed to be composed primarily Li<sub>2</sub>S, some Li<sub>3</sub>P
- Li<sub>2</sub>S appears to be capable of stabilizing interface



Li<sub>3</sub>PS<sub>4</sub>+Li<sub>2</sub>S  
Li interface

## Motivation

Overview

Li<sub>3</sub>PX<sub>4</sub>

## Materials

Structure

Energetics

## Interfaces

Vacuum

Li Metal

- Agrees with formation enthalpy expectation

Material	$\Delta H$
Li <sub>3</sub> PO <sub>4</sub> -Pmn2 <sub>1</sub>	-21.41
Li <sub>3</sub> PO <sub>4</sub> -Pmna	-21.38
Li <sub>3</sub> PS <sub>4</sub> -Pmn2 <sub>1</sub>	-8.36
Li <sub>3</sub> PS <sub>4</sub> -Pmna(b)	-8.28
Li <sub>3</sub> PS <sub>4</sub> -Pmna(c)	-8.24
Li <sub>2</sub> O	-6.18
Li <sub>2</sub> S	-4.29

## Conclusions

- Vacuum surface effects are not the dominant mechanism of Pmna phase stabilization
- Li<sub>3</sub>PO<sub>4</sub> stable to Li
- Li<sub>3</sub>PS<sub>4</sub> + Li<sub>2</sub>S stable to Li
- Further work is needed to understand the influence of interfaces on phase stability