Li ion diffusion mechanisms in Li_3PO_4 electrolytes

Yaojun Du and N. A. W. Holzwarth

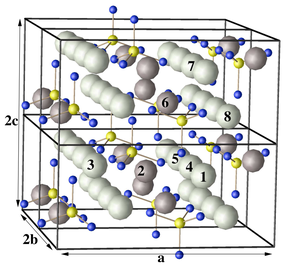
Department of Physics, Wake Forest University, Winston-Salem, NC, USA

Supported by NSF grants DMR-0405456 and 0427055.

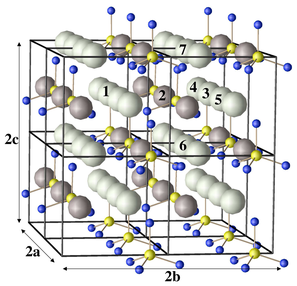
Introduction

- Solid-state lithium ion electrolytes such as Li_3PO_4-based materials[1] are becoming increasingly important in batteries and related technologies.
- Li ion diffusion in crystalline γ-Li_3PO_4 has been measured to be slightly anisotropic with activation energies of 1.1–1.3 eV.[2] The activation energies can be reduced to 0.97 eV by N doping[1] and to 0.5 eV by admixture with Li_4SiO_4.[3]
- In this work, first-principles calculations[4] have been performed to model the migration energies for both vacancy and interstitial mechanisms of Li ions in γ-Li_3PO_4 and β-Li_3PO_4. For extrinsic defects, activation energy E_A is the same as the migration energy of the defects, E_m. However, for intrinsic defects, using quasi-equilibrium statistical mechanics arguments,[5] it follows that $E_A = E_m + E_f/2$, where E_f is the formation energy of the vacancy-interstitial pair.

Crystal structures



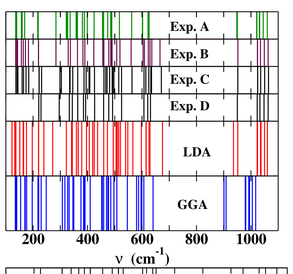
γ-Li_3PO_4 Space group: Pnma
Metastable at room temperature; experimentally measured. The Li ions are located on two crystallographically different sites indicated with different shadings (gray and dark balls) in the figure. Using the Wyckoff labels, the d site accounts for 8 equivalent atomic sites and the c site accounts for 4 equivalent atomic sites per unit cell. The P and O ions are indicated by small balls and sticks (colored yellow and blue respectively).



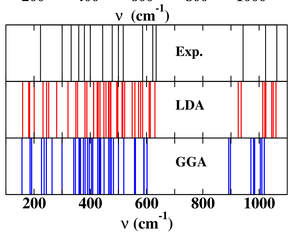
β-Li_3PO_4 Space group: $Pmn2_1$
Low-temperature phase and energetically more stable than γ-phase. Two crystallographically distinct Li sites are also indicated with different shadings in the figure. Using the Wyckoff labels, the b site accounts for 4 equivalent atomic sites and the a site accounts for 2 equivalent atomic sites per unit cell. Our calculations verify that the β form is energetically more stable: $E_\gamma - E_\beta = 0.03(0.01)$ eV/Li_3PO_4 for LDA (GGA) calculations.

Raman spectra

LDA calculations show better agreement with experimental spectra than GGA; simulation results in this poster are presented for the LDA functional unless otherwise specified.



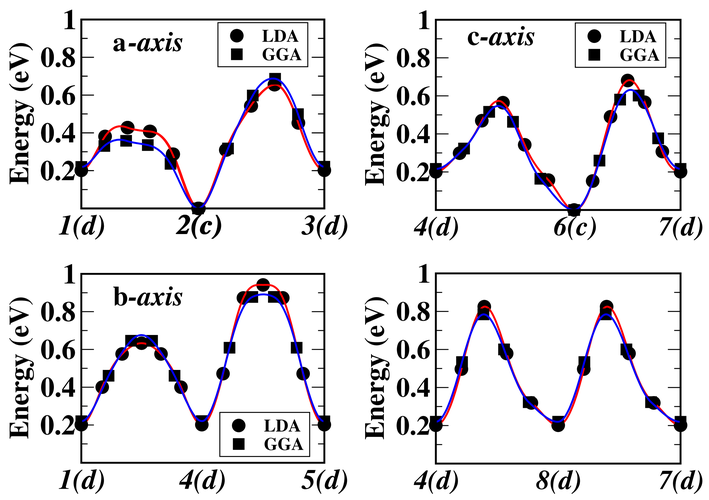
Raman active modes of γ-Li_3PO_4, comparing experimental results with LDA and GGA calculations. Experiment A (from Ref. 6) was measured at room temperature (RT). Experiment B and C (from Ref. 7) were measured at RT and liquid nitrogen temperature (LNT), respectively. Experiment D (from Ref. 8) was measured at LNT.



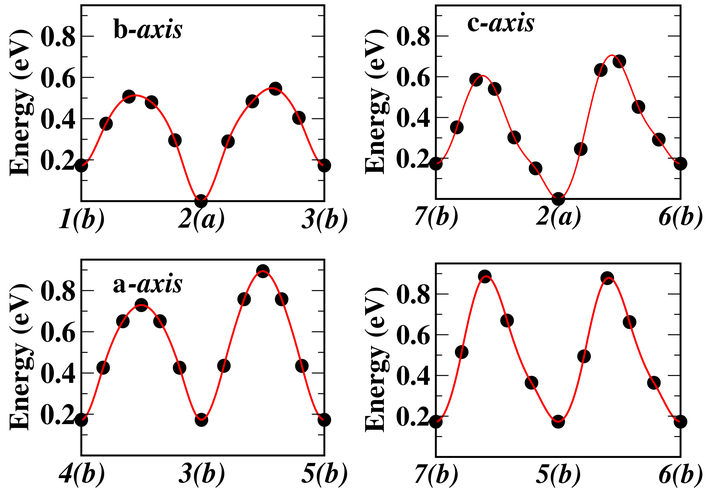
Raman active modes of β-Li_3PO_4, comparing experimental results with LDA and GGA calculations. Experimental data (from Ref. 8) were measured at LNT.

Vacancy mechanism

γ-Li_3PO_4



β-Li_3PO_4



Energy path diagrams for various vacancy migration paths in crystalline Li_3PO_4, showing minimal barriers of 0.62 eV along the **c**-axis path for the γ form and 0.55 eV along the **b**-axis path for the β form. These barriers are 0.3 eV lower than the measured activation energy for vacancy-rich $Li_{2.88}PO_{3.73}N_{0.14}$,[1] where oxygen-vacancies may affect the migration barrier.

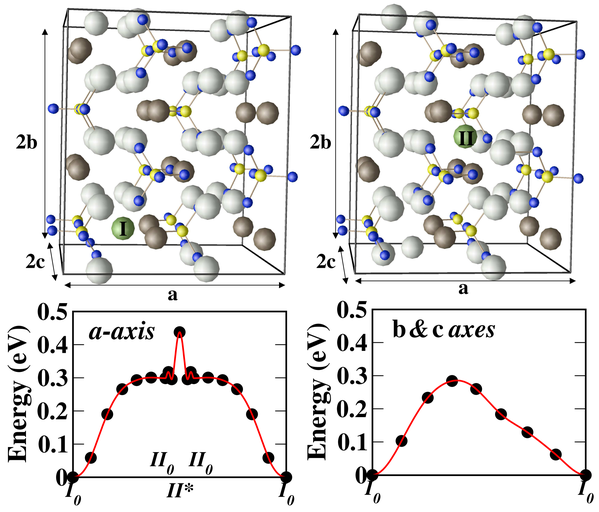
Intrinsic defects

The formation energies of interstitial-vacancy pairs are found to be $E_f(\gamma) = 1.7$ eV and $E_f(\beta) = 2.1$ eV. Estimating the intrinsic activation energy as $E_A = E_m(\text{interstitial}) + E_f/2$, we obtain good agreement with experiment.[2]

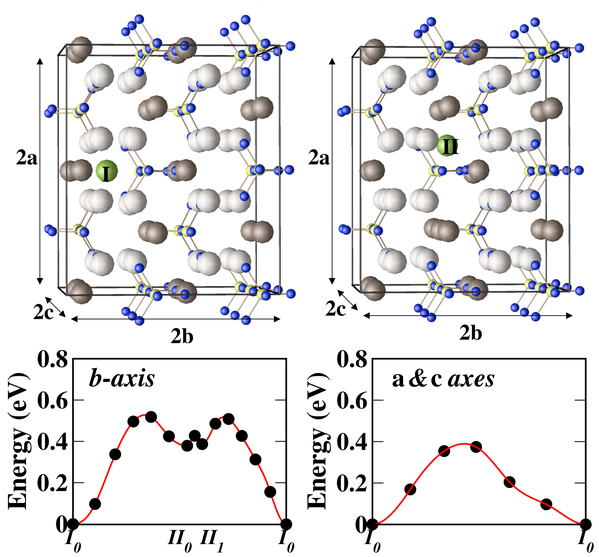
Crystal	Net direction	Experiment (eV)	This work (eV)
γ-Li_3PO_4	a	1.23	1.1
	b	1.14	1.1
	c	1.14	1.1
β-Li_3PO_4	b		1.6
	a		1.4
	c		1.4

Interstitial mechanism

γ-Li_3PO_4



β-Li_3PO_4



Interstitial migration paths show the most efficient ion transport mechanism for both γ- and β-Li_3PO_4, with computed migration barriers of 0.3–0.5 eV, in good agreement with the measured 0.5 eV activation energy of extrinsic interstitials for Li_4SiO_4-Li_3PO_4 solid solutions.[3] Structural diagrams show meta-stable interstitial sites I and II located in the two distinct void channels for both crystals.

Reference

[1] B. Wang *et al.*, *Journal of Solid State Chemistry* **115**, 313 (1995)
[2] A. K. Ivanov-Shitz *et al.*, *Crystallography Reports* **46**, 864 (2001).
[3] Y.-W.Hu *et al.*, *Journal of the Electrochemical society* **124**, 1240 (1977).
[4] *PWscf* – http://www.pwscf.org.
[5] A. R. West, *Basic Solid State Chemistry, Second Edition* (John Wiley & Sons, Inc. 2000)
[6] B. N. Mavrin *et al.*, *Journal of Experimental and Theoretical Physics* **96**, 53 (2003).
[7] F. Harbach and F. Fischer, *Physica Status Solidi B* **66**, 237 (1974).
[8] L. Popović *et al.*, *Journal of Raman Spectroscopy* **34**, 77 (2003).