Computer modeling of crystalline electrolytes: Lithium thiophosphates and phosphates

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Solid Electrolytes
(compared to liquid electrolytes)

Advantages

- Physically and chemically stable
- Low electronic conductivity (prevents self-discharge)
- Performs well in thin film batteries

Disadvantages

- Poor contact area for high capacity electrodes
- Interface stress for electrode with volume changes
- Lower conductivity per area.

Thiophosphates vs. Phosphates

LiPON
(Oak Ridge National Lab)

$\sigma \sim 10^{-6}$ S/cm

$E_A \sim 0.3\text{-}0.7$ eV

Ref:
-N. J. Dudney, Interface 17 (3), 44 (2008).

-J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans, Solid State Ion. 135, 33 (2000).

$Li_2S\text{-}P_2S_5$
(Osaka University)

$\sigma \sim 10^{-3}$ S/cm

$E_A \sim 0.1\text{-}0.3$ eV

Ref:
-A. Hayashi, K. Minami, F. Mizuno and M. Tatsumisago, J. Mater. Sci. 43 (2008), pp. 1885–1889.

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

$Li_7P_3S_{11}$

Comparison of various $Li_2S-P_2S_5$ derivatives.

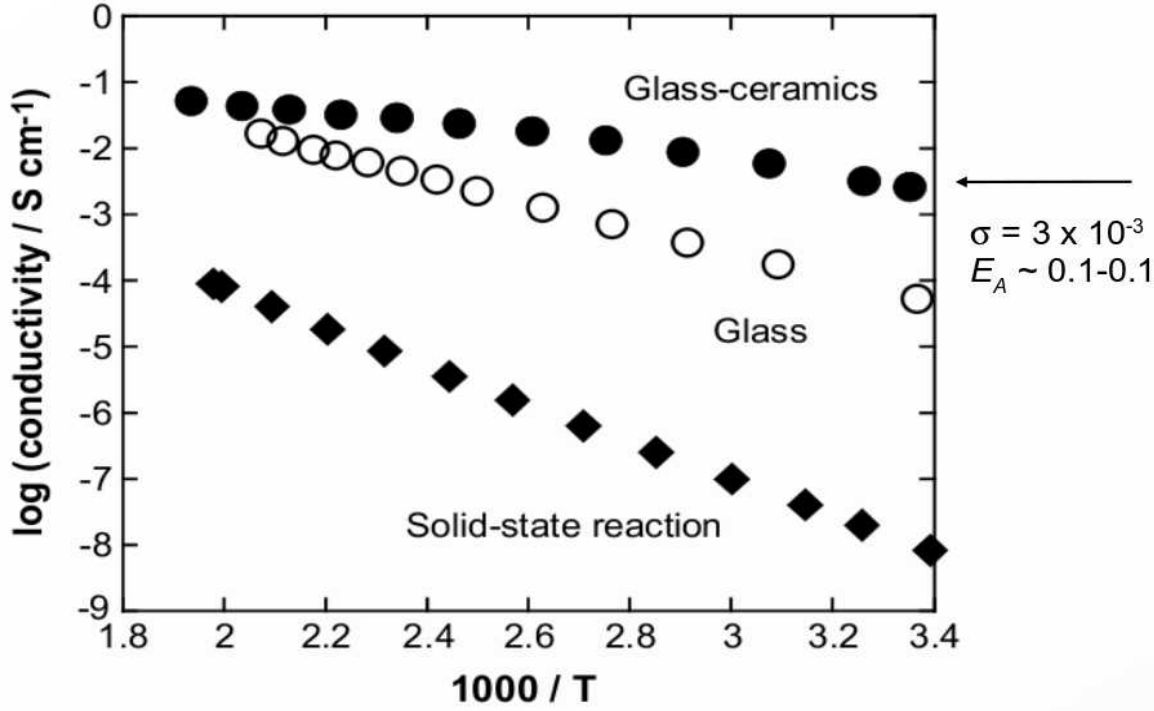


Fig. 5. Temperature dependences of the conductivities for the $70Li_2S \cdot 30P_2S_5$ glass and glass–ceramics. The conductivity data for the sample prepared by solid-state reaction are also shown.

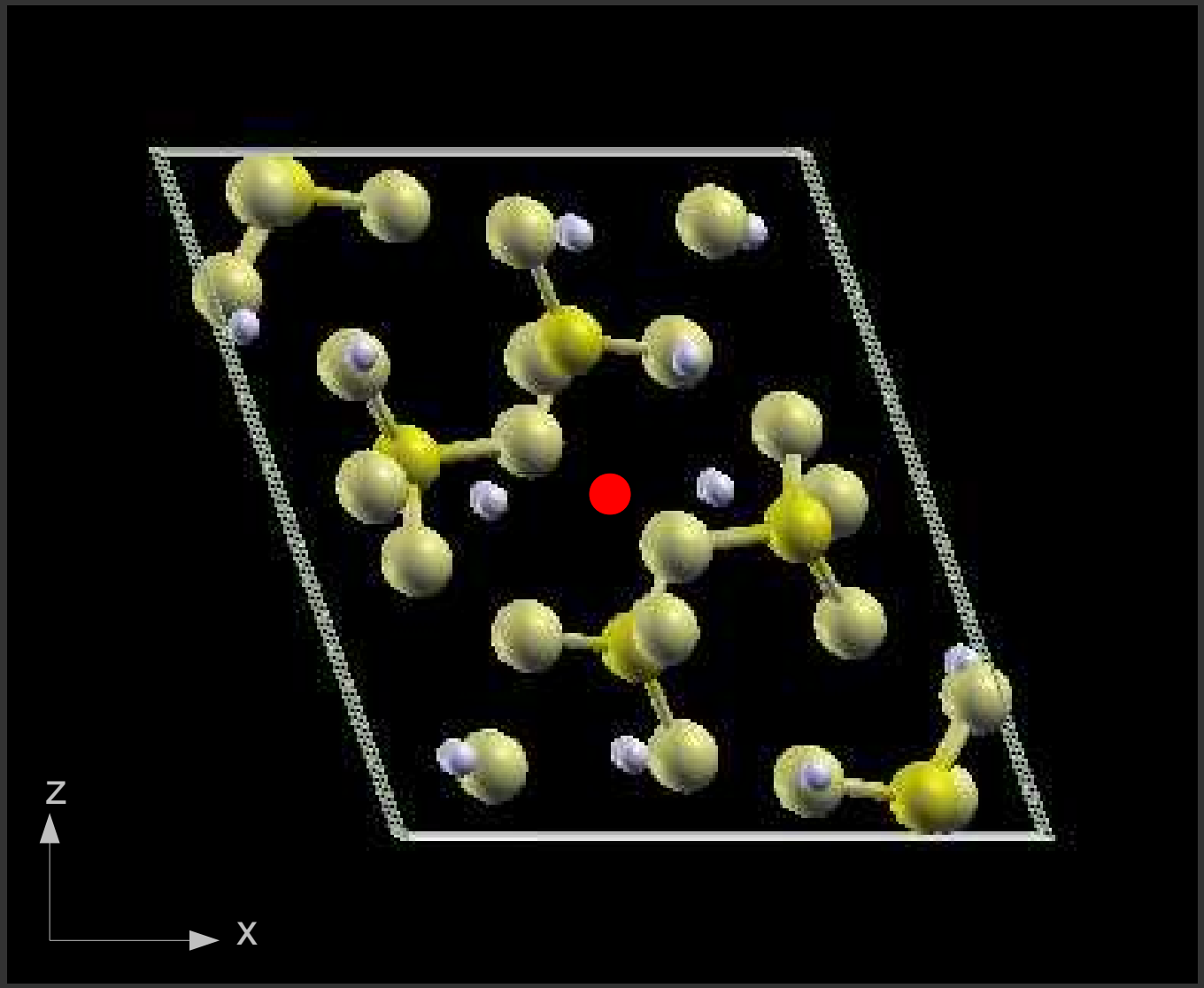
"Thus the superionic Li7P3S11 was precipitated as a metastable phase in the case of crystallization of glass. The superionic metastable phase is responsible for the high conductivity and low activation energy for conduction of the 70Li2 S•30P2 S5 glass-ceramic."

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

$Li_7P_3S_{11}$

Optimized Crystal Information
Unit cell:

- 42 atoms(2 formula units)
- Has inversion symmetry about the red dot
- Contains dimers and tetrahedral sites
- Lattice information
  - Triclinic Cell
    - Sgroup P1
  - X=22.69415500
  - Y=11.64725720
  - Z=23.14655326 (units in bohr)
  - α=102.462972
  - β=113.776362
  - γ=72.1333972



Yamane, Solid State Ionics 178 (2007) 1163-1167

Calculational Methods

- These calculations were carried out using Pwscf. *(www.pwscf.org).*
- Migration paths were calculated using the Nudged Elastic Band (NEB method) as implemented in Pwscf. *(G. Henkelman, B.P. Uberuaga, H. Jónsson, J. Chem. Phys. 113 (2000) 9901–9904.)*
- Calculations were carried out in a 1x2x1 supercell.
- Calculations were tested with both PAW based and Ultra-soft pseudopotentials.

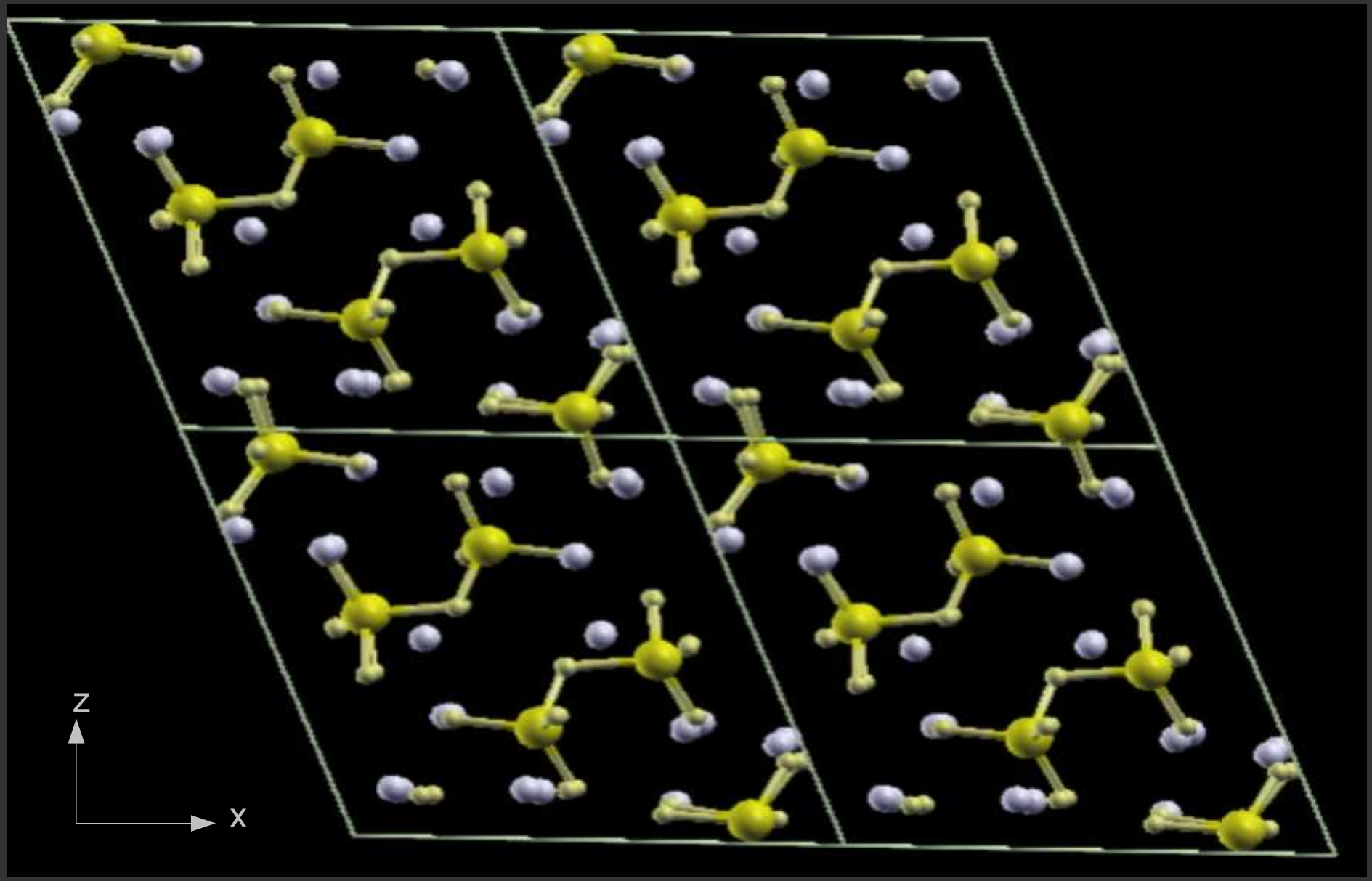
Superionic Conductors

- $Li_7P_3S_{11}$ is a superionic conductor
- Mechanism of ion conduction
  - Vacancy/interstitial pair formation
  - Diffusion through crystallographic voids, both inherent and created.
  - Energy costs
    - Forming pair
    - Moving Li-ions through the lattice.

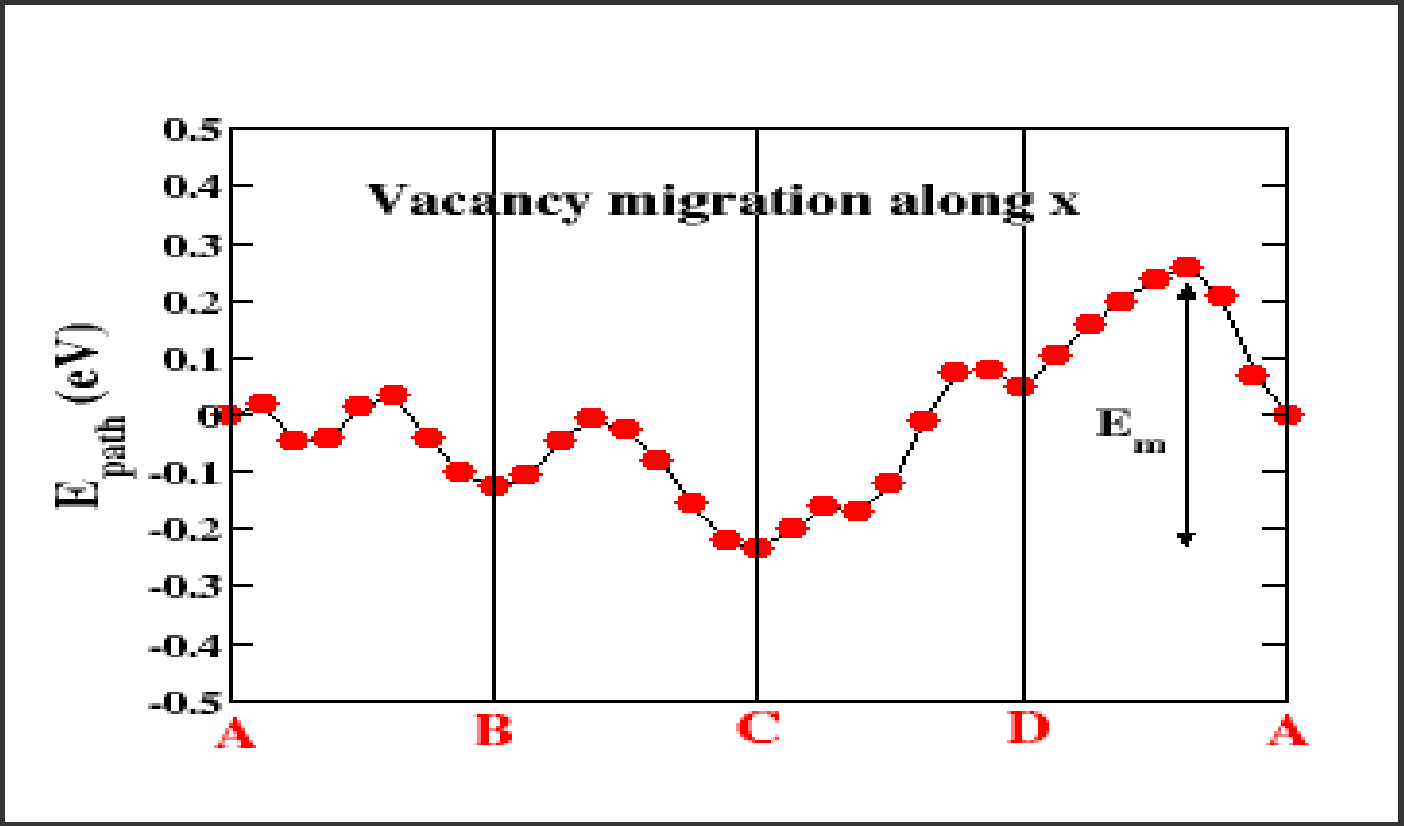
Vacancies

- The crystal contains 7 unique Li positions, and thus 7 unique vacancy sites/energies.
- Using the NEB method, we calculated barriers to migration and migration paths between vacancy sites along all three crystallographic directions.
- The X and Y paths were substantially more energetically favored.

X Path



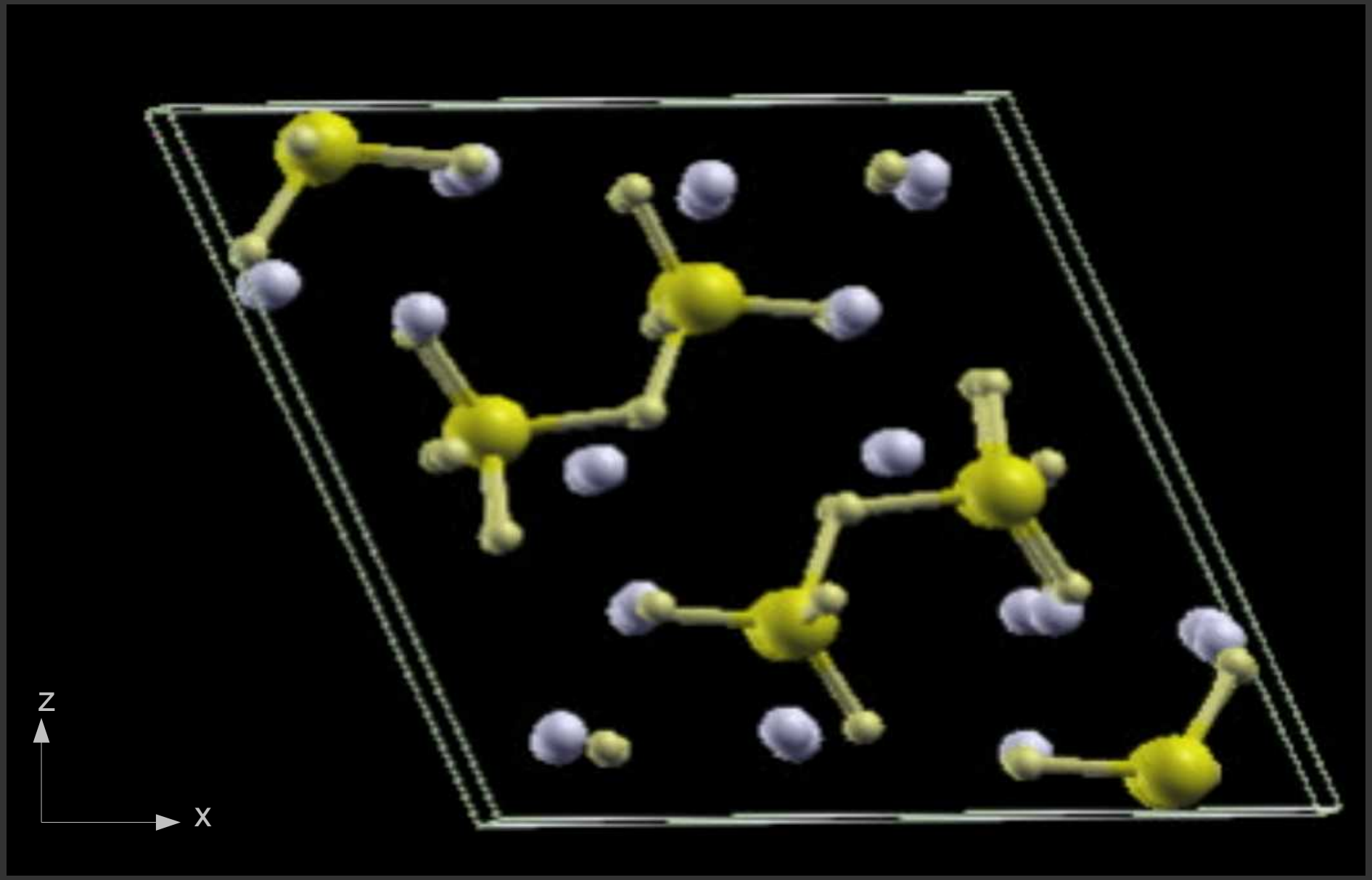
X-direction migration Path



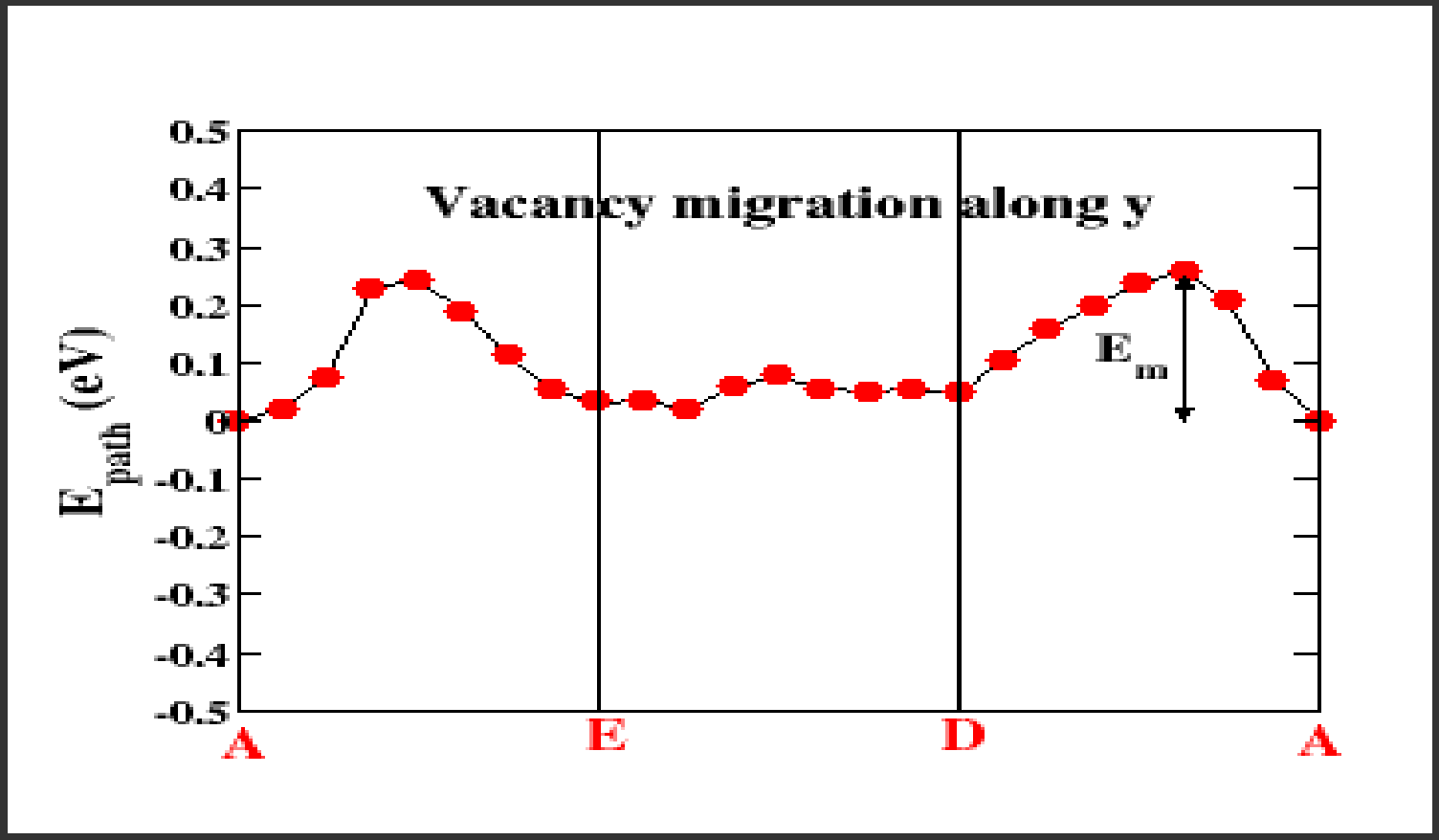
Energies	
A	0
B	-0.13
C	-0.23
D	0.05
E	0.03
F	0.16
G	0.01

- Migration Barrier is E_m~.5 eV as can be seen above
- Distance travelled in x-direction: 22.7 bohr

Y Path



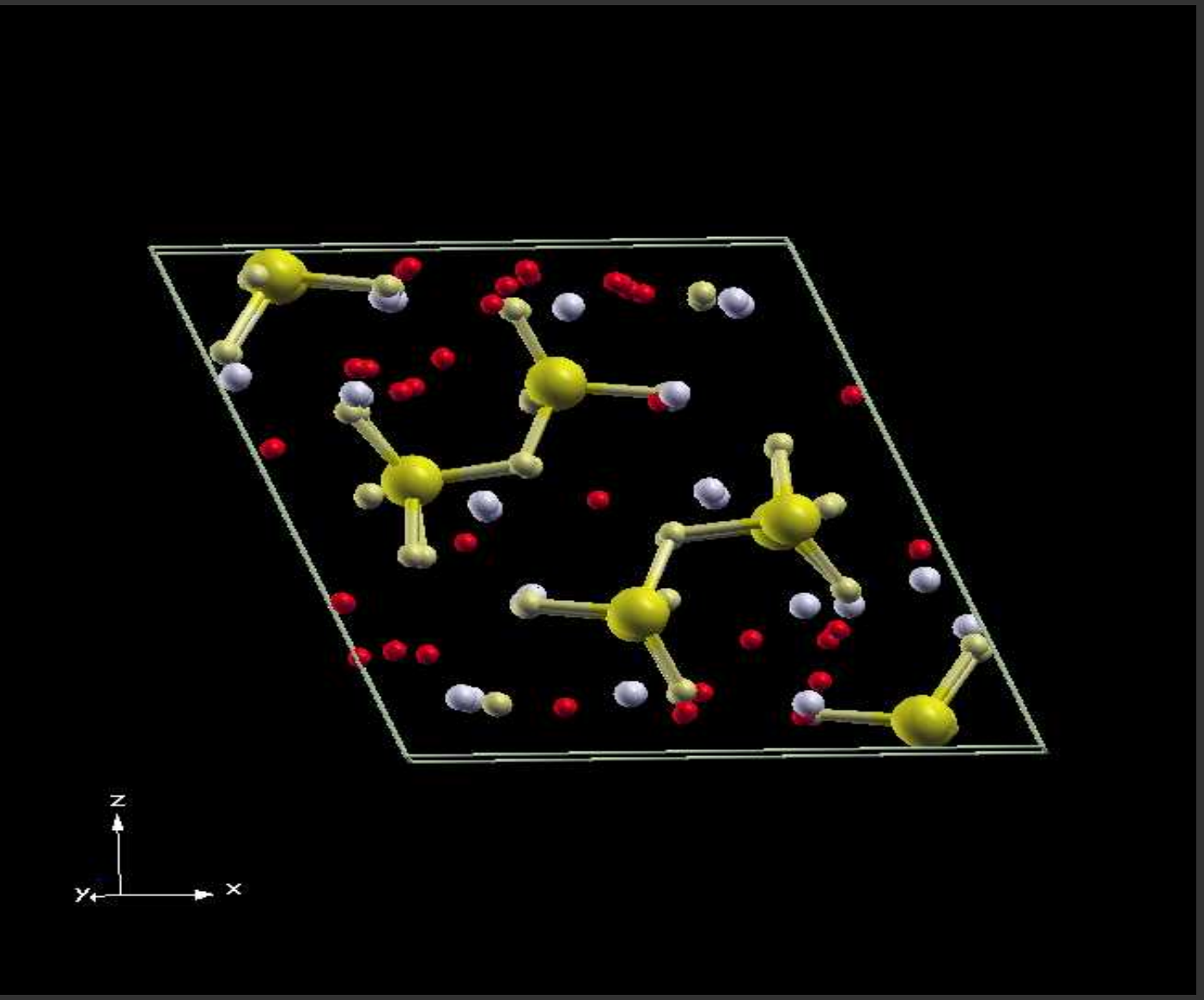
Y-direction migration Path



Energies	
A	0
B	-0.13
C	-0.23
D	0.05
E	0.03
F	0.16
G	0.01

- Migration Barrier is E_m~.25 eV as can be seen above
- Distance travelled in y-direction: 11.65 bohr

Interstitial Sites



A sampling of metastable interstitial sites is shown here in red

Vacancy/Interstitial Formation

- Vacancy/interstitial pairs are created by displacing a Li from a site in the crystal to a metastable interstitial site
- Vacancy interstitial pair formation requires a minimum of ~.2 eV for the sites we have investigated, though our simulations have yet to explore the complete configuration space.

$$\sigma = C \exp\left(-E_m / kT\right)$$

$$E_A = E_m + E_f / 2$$

Conclusions

- We have investigated several Li (thio)phosphates, finding several corresponding stable and metastable structures.
- For the superionic conductor $Li_7P_3S_{11}$ we find vacancy-mechanism driven migration along the y-axis with migration energy ~.25 eV
- More work needed.

References

- Supported by: NSF Grant DMR-0705239
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- N. A. W. Holzwarth, N. D. Lepley, Y. A. Du, J. Power Sources (2010) [in press: doi:10.1016/j.jpowsour.2010.08.042].
- P. Giannozzi, S. Baroni, et al., J. Phys.: Condens. Matter. 21, 394402 (2009); available from the website: http://www.pwscf.org/.
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- M. Tatsumisago and A. Hayashi, J. Non-Cryst. Solids 354 1411-1417 (2008)