First principles computer simulations of $Li_{10}GeP_2S_{12}$ and related lithium superionic conductors*

N. A. W. Holzwarth

Wake Forest University, Winston-Salem, NC, USA, 27109

- Motivation and background information
- Structural optimization and energetic results
- Preliminary results on Li^+ migration mechanisms

*Supported by NSF Grants DMR-0705239 and DMR-1105485.

First principles computer simulations of $Li_{10}GeP_2S_{12}$ and related lithium superionic conductors* *preliminary results*

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Motivation: Paper by N. Kayama, *et. al* in ***Nature Materials*** **10**, 682-686 (2011)

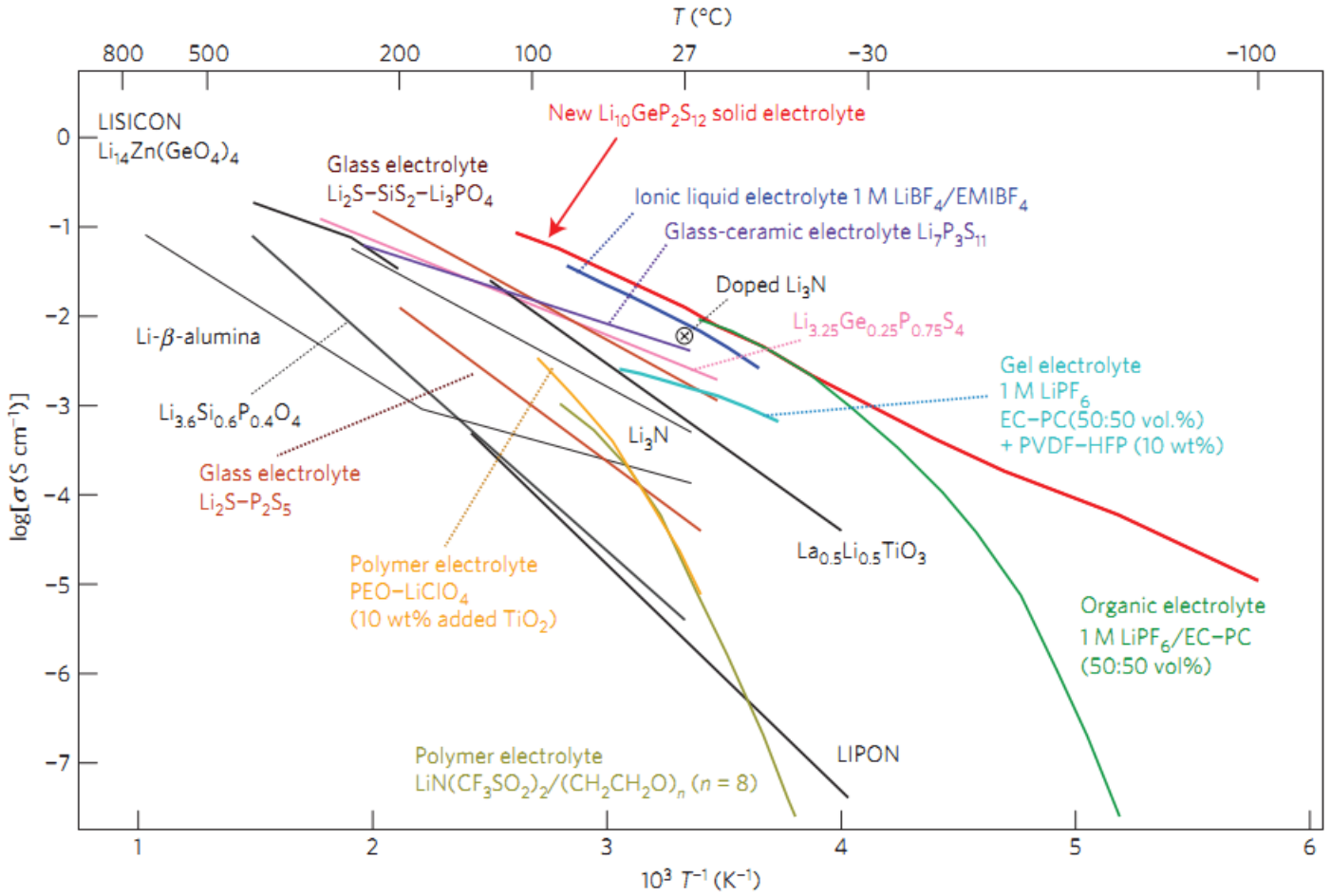

Figure 3 | Thermal evolution of ionic conductivity of the new $Li_{10}GeP_2S_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes[3-8,13-16,20,22]**.** The new $Li_{10}GeP_2S_{12}$ exhibits the highest lithium ionic conductivity (12 m S cm^{-1} at 27 °C) of the solid lithium conducting membranes of inorganic, polymer or composite systems. Because organic electrolytes usually have transport numbers below 0.5, inorganic lithium electrolytes have extremely high conductivities.

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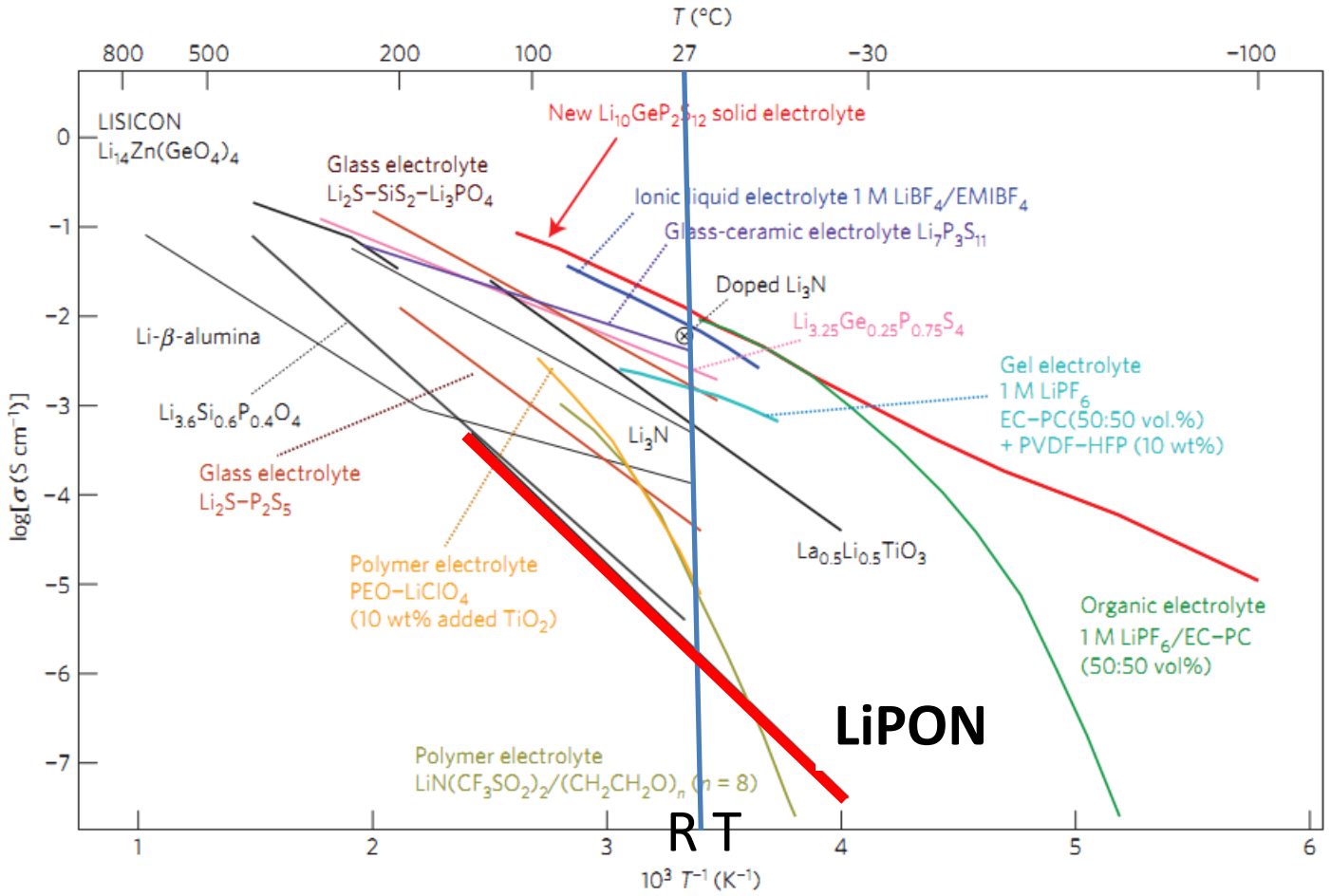

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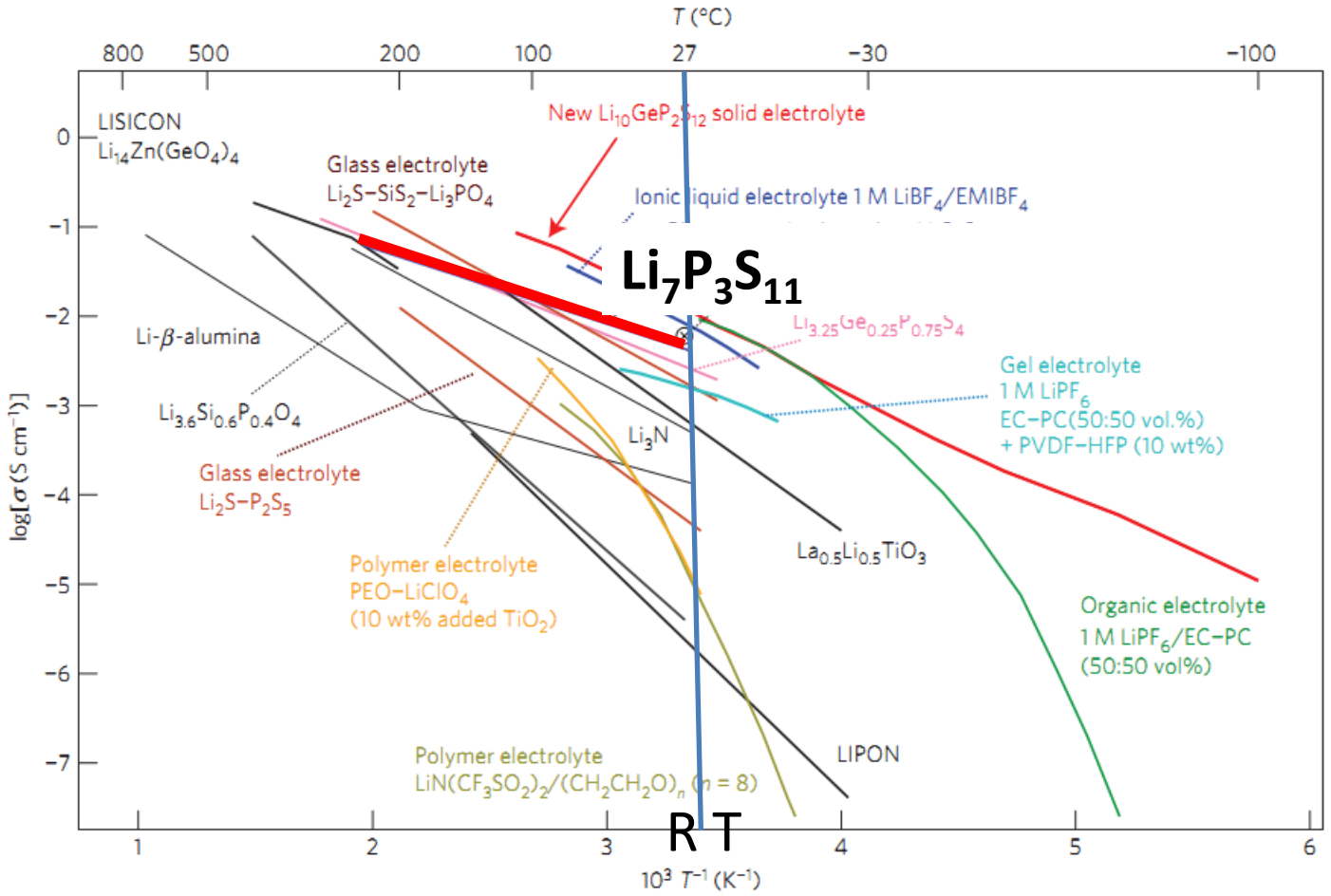

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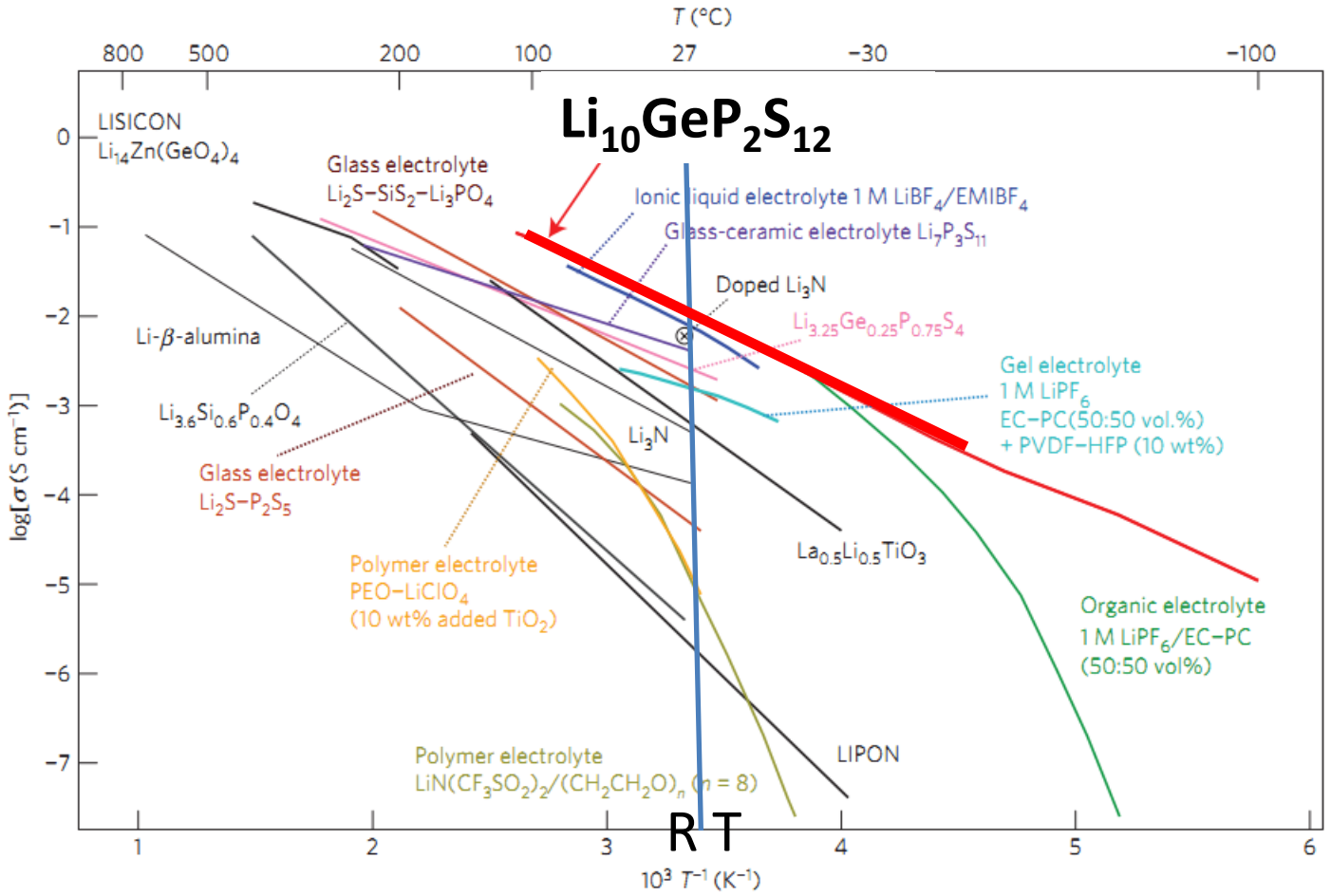

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Other simulation studies on this material:

Work by MIT group published in Dec. 2011

CHEMISTRY OF MATERIALS

Communication

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First Principles Study of the $Li_{10}GeP_2S_{12}$ Lithium Super Ionic Conductor Material

Yifei Mo, Shyue Ping Ong, and Gerbrand Ceder*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

KEYWORDS: *lithium ionic conductor, solid electrolyte, $Li_{10}GeP_2S_{12}$, ab initio, molecular dynamics, phase diagrams*

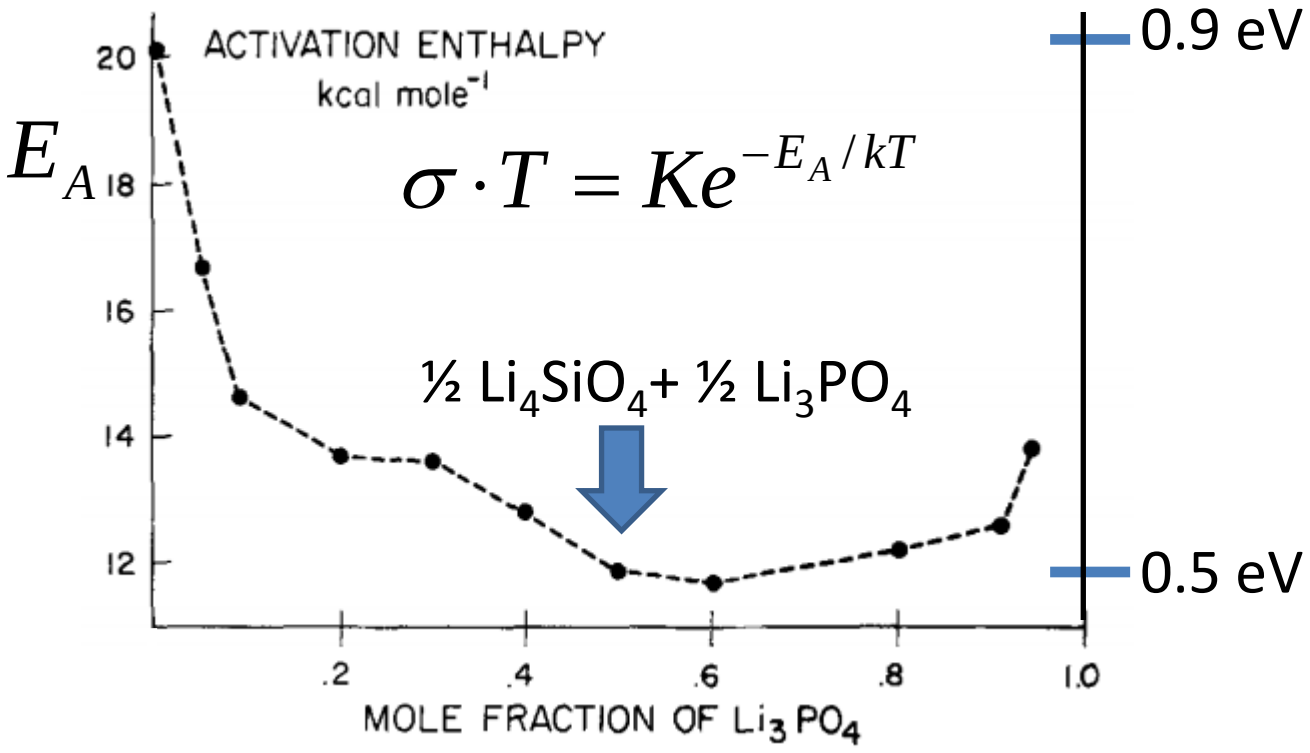
dx.doi.org/10.1021/cm203303y | Chem. Mater. 2012, 24, 15−17

J. Electrochem. Soc. **124**, 1240-1242 (1977)

Ionic Conductivity of Lithium Orthosilicate—Lithium Phosphate Solid Solutions

Y-W. Hu, I. D. Raistrick, and R. A. Huggins*

Center for Materials Research, Stanford University, Stanford, California 94305



42 Journal of The Electrochemical Society, 148 (7) A742-A746 (2001)
0013-4651/2001/148(7)/A742/5/$7.00 © The Electrochemical Society, Inc.

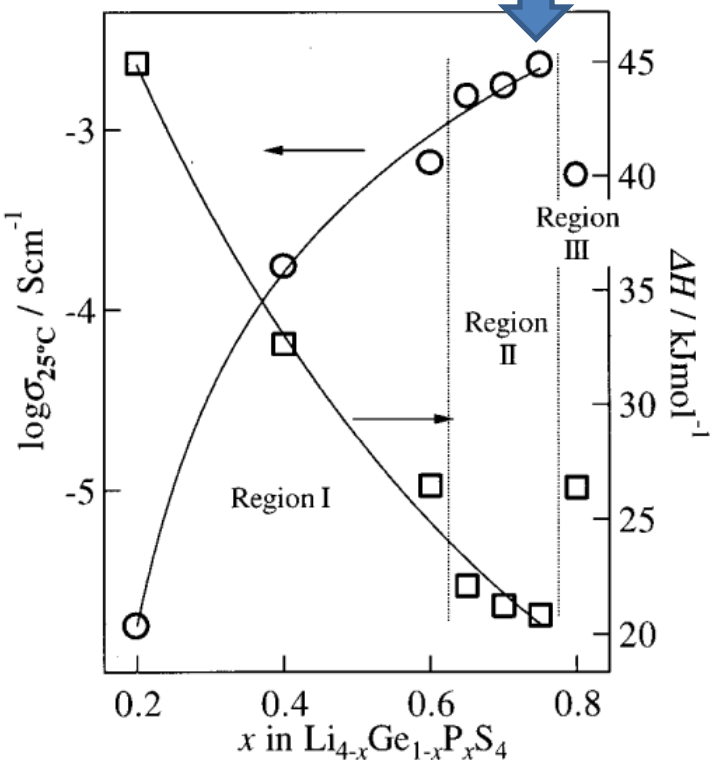
Lithium Ionic Conductor Thio-LISICON

The Li_2S-GeS_2-P_2S_5 System

Ryoji Kanno*,a,z and Masahiro Murayama

Department of Chemistry, Faculty of Science, Kobe University, Hyogo 657-8501, Japan

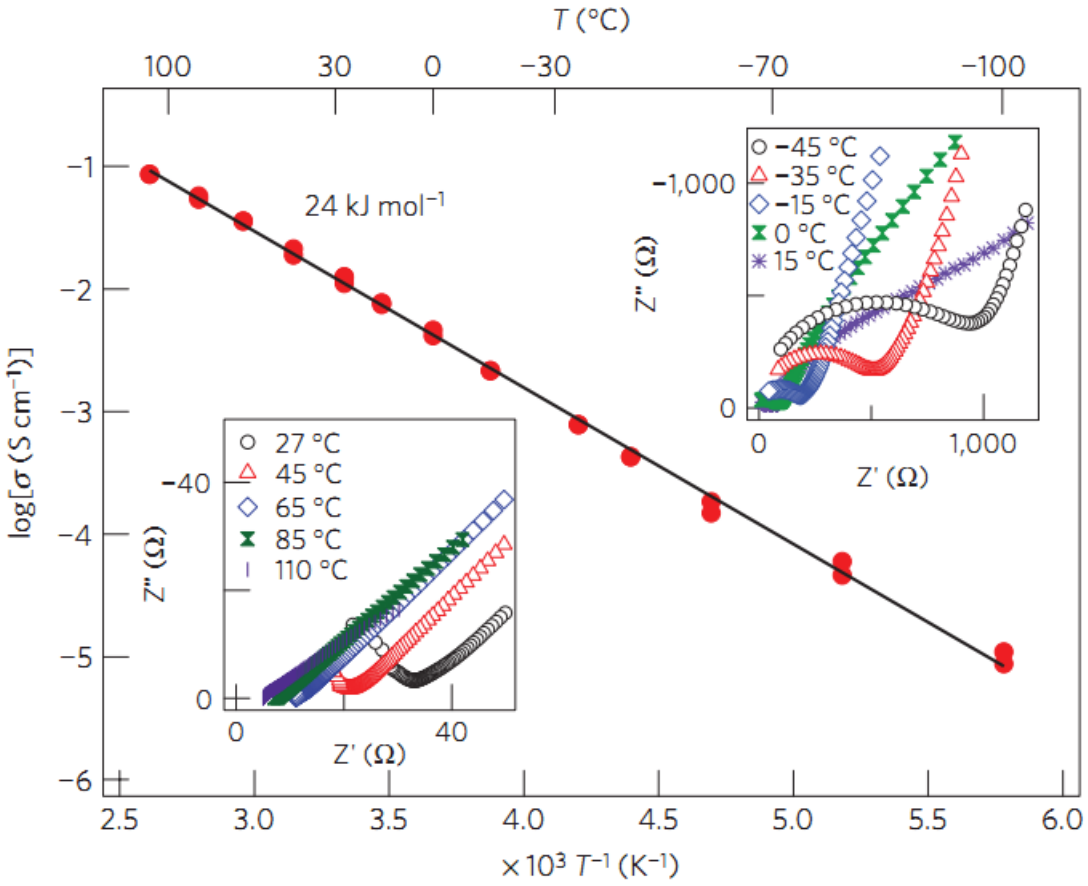
$\frac{1}{4}Li_4GeS_4 + \frac{3}{4}Li_3PS_4$



***Nature Materials* 10**, 682-686 (2011)

A lithium superionic conductor

Noriaki Kamaya[1], Kenji Homma[1], Yuichiro Yamakawa[1], Masaaki Hirayama[1], Ryoji Kanno[1]*, Masao Yonemura[2], Takashi Kamiyama[2], Yuki Kato[3], Shigenori Hama[3], Koji Kawamoto[3] and Akio Mitsui[4]



$$Li_{10}GeP_2S_{12} \Leftrightarrow \tfrac{1}{3}Li_4GeS_4 + \tfrac{2}{3}Li_3PS_4$$

$Li_{10}GeP_2S_{12}$ is a new material; not a solid solution of its constituents.

Goals of computer simulations

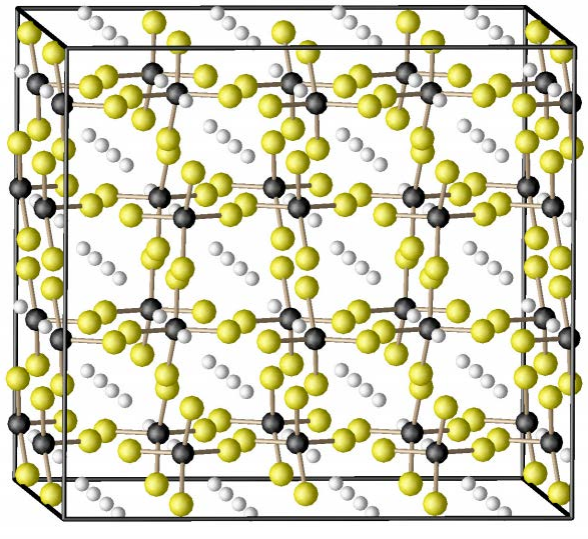
- Study structural and chemical stability
- Compare $Li_{10}GeP_2S_{12}$ and $Li_{10}SiP_2S_{12}$
- Investigate Li ion migration mechanisms

Calculational methods used in this study:

Calculations based on density functional theory with the local density approximation (LDA) using the *Quantum Espresso* and *Abinit* codes. USPP and PAW calculations compared

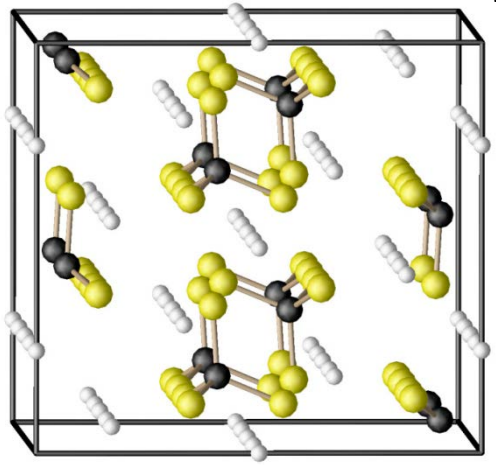
Li ion migration energies estimated using the Nudged Elastic Band (NEB) method (Hinkleman et al *J. Chem. Phys*. **113** 9901 & 9978 (2000) using 2x2x1 supercell

Constituents of $Li_{10}GeP_2S_{12}$:



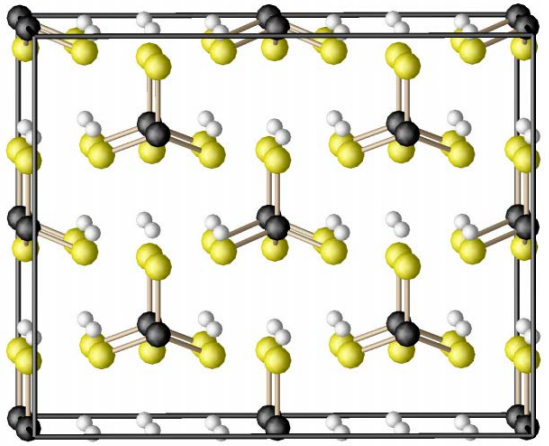
α^{*}- Li_3PS_4 $Pbcn$

$\Delta H = -8.12\,\text{eV}$



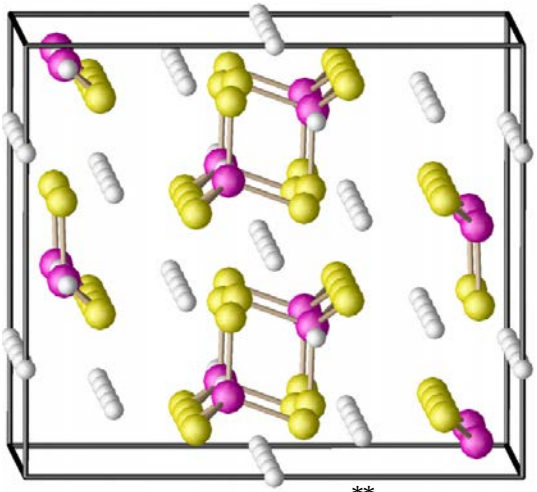
$\beta^{*} - Li_3PS_4$ $Pnma$

$\Delta H = -8.28\,\text{eV}$



$\gamma^{*} - Li_3PS_4$ $Pmn2_1$

$\Delta H = -8.36\,\text{eV}$



Li_4GeS_4 $Pnma^{**}$

$\Delta H = -10.19\,\text{eV}$

S
Li
P
Ge

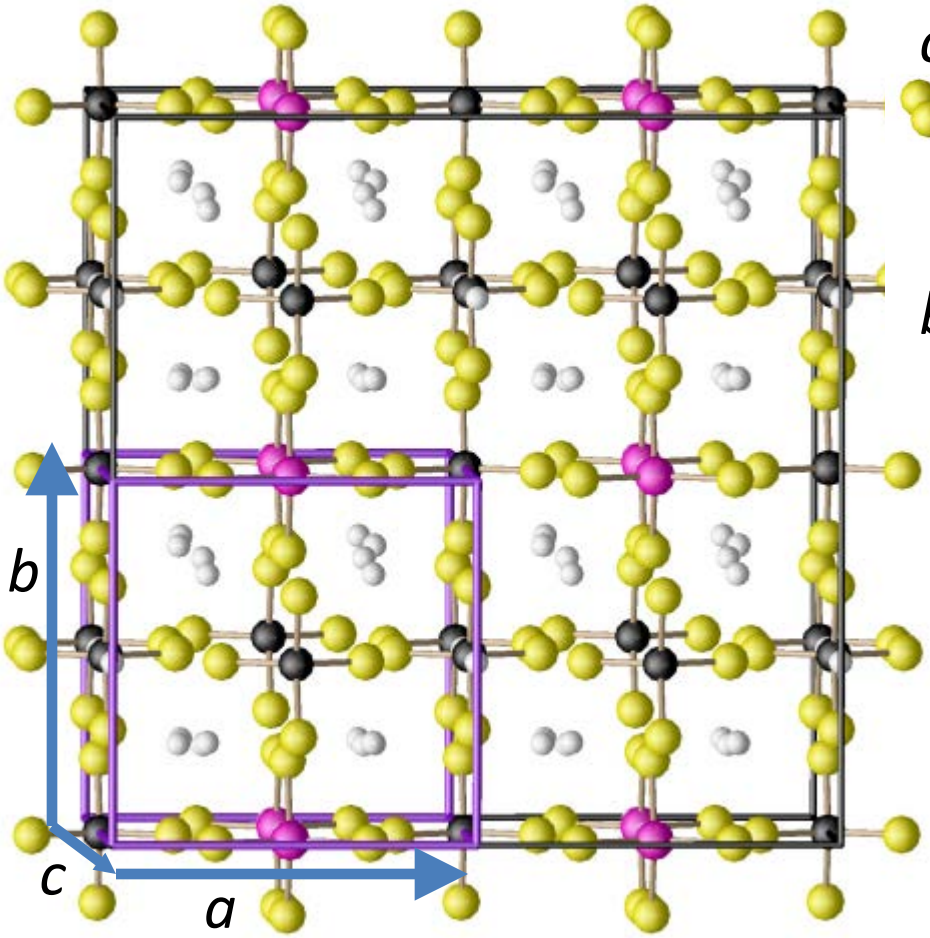
*K. Homma et al, *Solid State Ionics* **182**, 53-58 (2011)

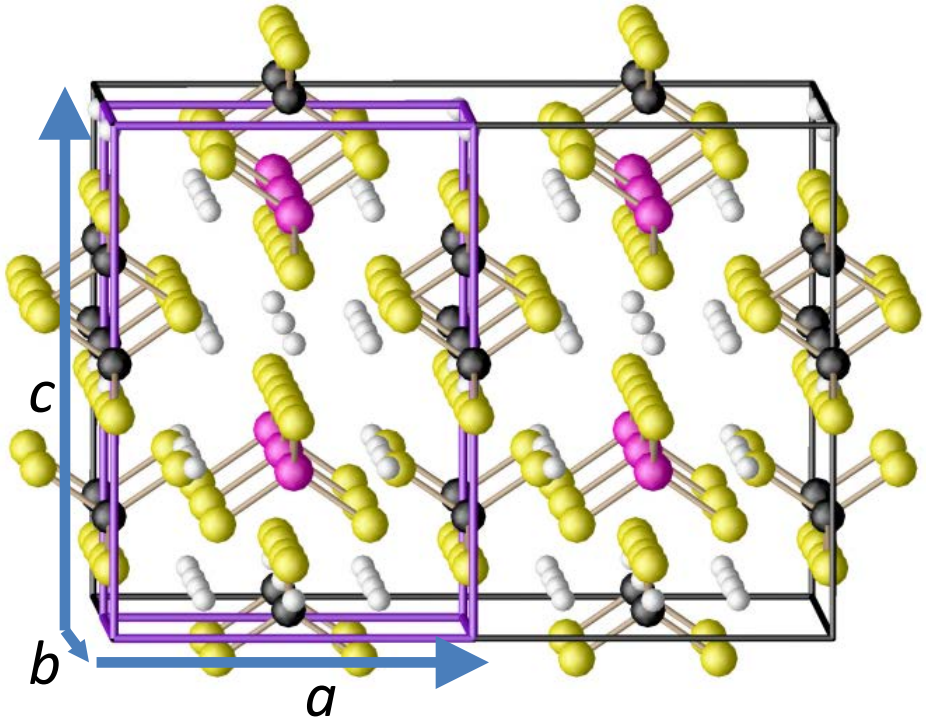
M. Murayama et al, *Solid State Ionics* **154-155, 789-794 (2002)

$Li_{10}GeP_2S_{12}$

Space group $P4_2/nmc$ (#137)

(from experiment)





S
Li
P
Ge

Lattice parameters

	a (Å)	*c* (Å)
$Li_{10}GeP_2S_{12}$ (exp*)	8.72	12.63
$Li_{10}GeP_2S_{12}$ (Calc)	8.56	12.23
$Li_{10}SiP_2S_{12}$ (Calc)	8.55	12.16

*Kamaya et al, *Nature Materials* **10**, 682-686 (2011)

Experimentally determined symmetry (fractional occupancy):
Space group $P4_2/nmc$ (#137)

Optimized structure with full occupancy:*
Space group $P4_2mc$ (#105)

$$(x, y, z) \rightarrow (y, x, -z)$$

*Determined using FINDSYM written by Stokes, Campbell, and Hatch at Brigham Young U. – http://stokes.byu.edu/iso/

Experiment structure:
Space group $P4_2/nmc$ (#137)

Atom	g	x	y	z
Li(1) 16h	0.69	0.26	0.27	0.18
Li(2) 4d	1.00	0.00	0.50	0.94
Li(3) 8f	0.64	0.25	0.25	0.00
Ge(1) 4d	0.52	0.00	0.50	0.69
P(1) 4d	0.49	0.00	0.50	0.69
Ge(2) 2b	0.00	0.00	0.00	0.50
P(2) 2b	1.00	0.00	0.00	0.50
S(1) 8g	1.00	0.00	0.18	0.41
S(2) 8g	1.00	0.00	0.30	0.10
S(3) 8g	1.00	0.00	0.70	0.79

Calculated structure:
Space group $P4_2mc$ (#105)*

Atom	g	x	y	z
Li(1) 8f	1.00	0.23	0.23	0.29
Li(2) 2a/2b	1.00	0.00	0.50	0.94
Li(3) 8f	1.00	0.26	0.22	0.03
Ge(1) 2b	1.00	0.50	0.00	0.79
P(1) 2a	1.00	0.00	0.50	0.68
P(2) 2c	1.00	0.00	0.00	0.50
S(1) 4d/4e	1.00	0.00	0.20	0.41
S(2) 4d/4e	1.00	0.00	0.30	0.09
S(3) 4d/4e	1.00	0.00	0.70	0.78

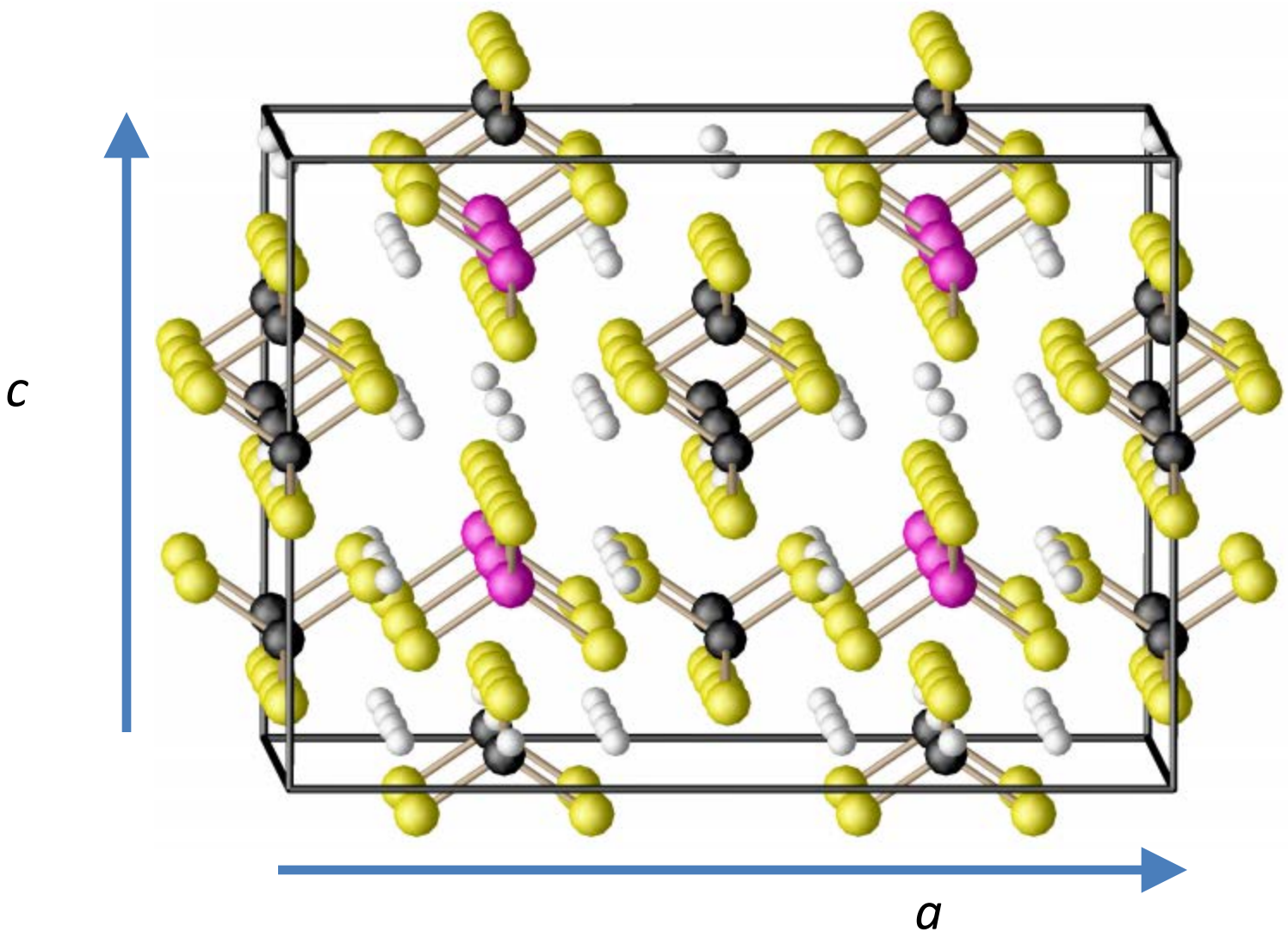
*Wyckoff symbols for #105, coordinates in #137 convention.

Decomposition reactions predicted on the basis of calculated enthalpies of formation (at zero temperature)

	ΔH (eV)
$Li_{10}GeP_2S_{12} \rightarrow 2Li_3PS_4 + Li_4GeS_4$	0.77
$Li_{10}SiP_2S_{12} \rightarrow 2Li_3PS_4 + Li_4SiS_4$	0.74
$Li_{13}GeP_3S_{16} \rightarrow 3Li_3PS_4 + Li_4GeS_4$	0.55
$Li_{13}SiP_3S_{16} \rightarrow 3Li_3PS_4 + Li_4SiS_4$	0.62

➔Preliminary results for formation enthalpies from zero-temperature simulations predict all of the compounds to be unstable with respect to their constituents.

Possible Li ion vacancy migrations in $Li_{10}GeP_2S_{12}$



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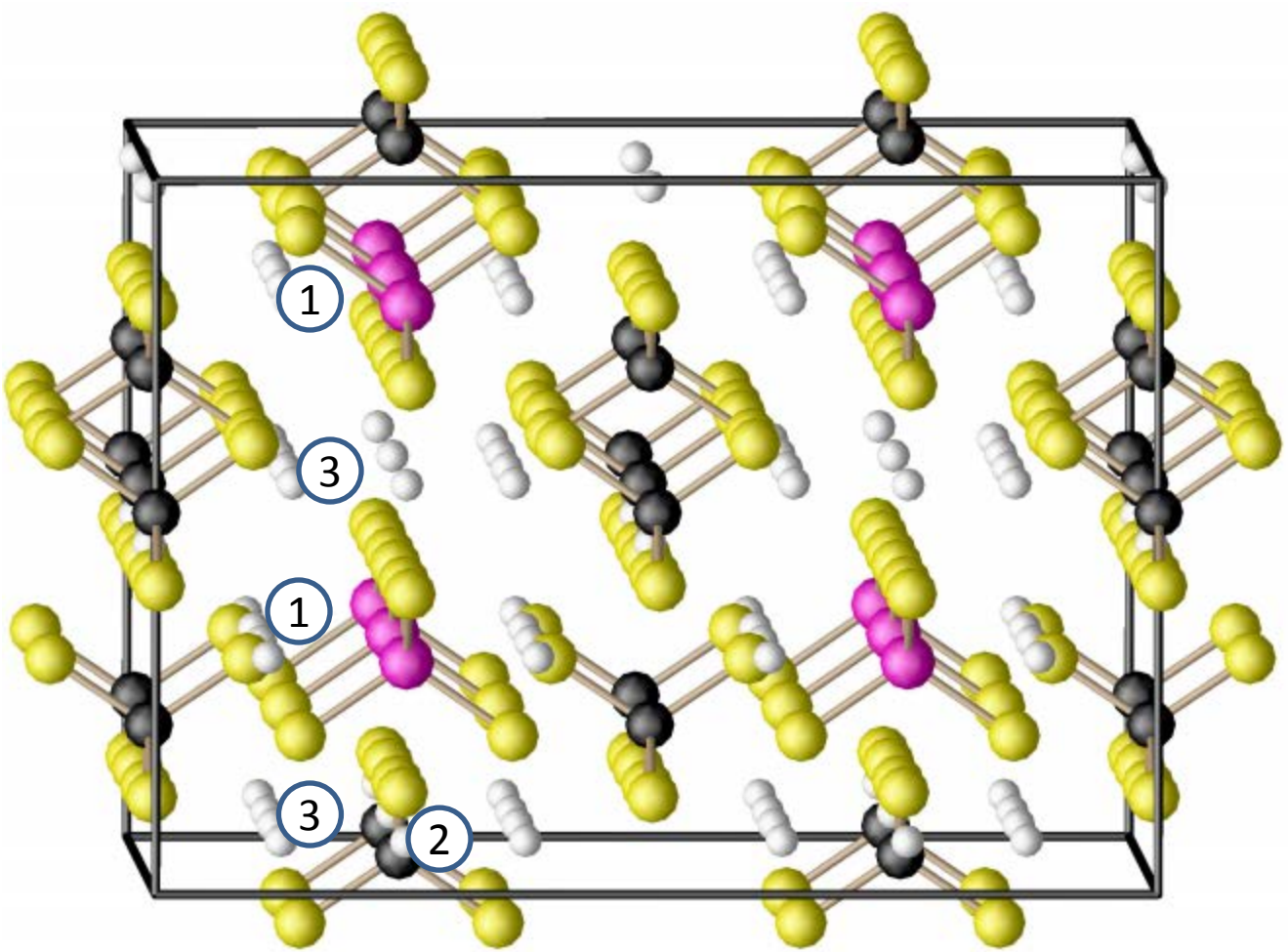

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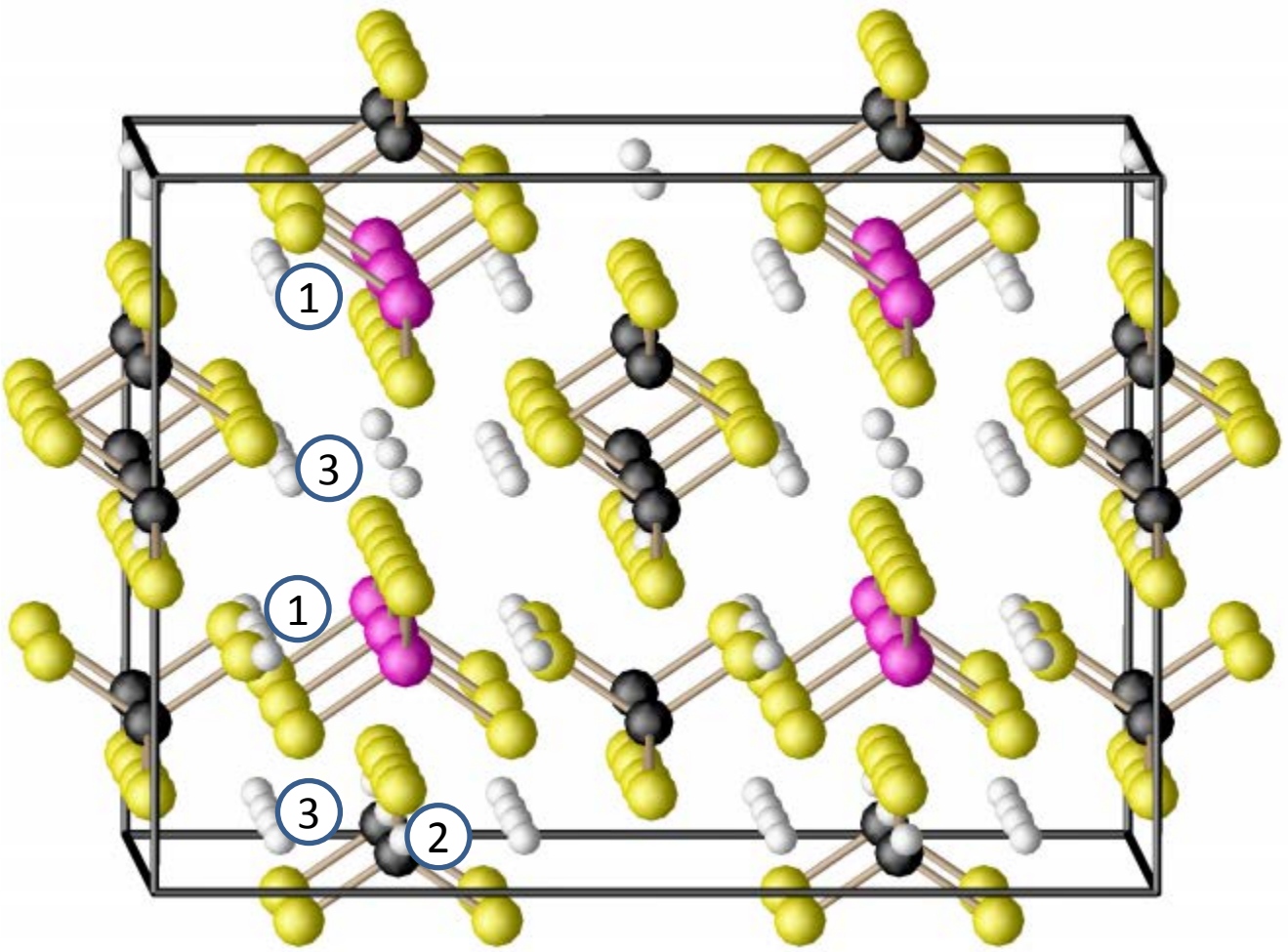
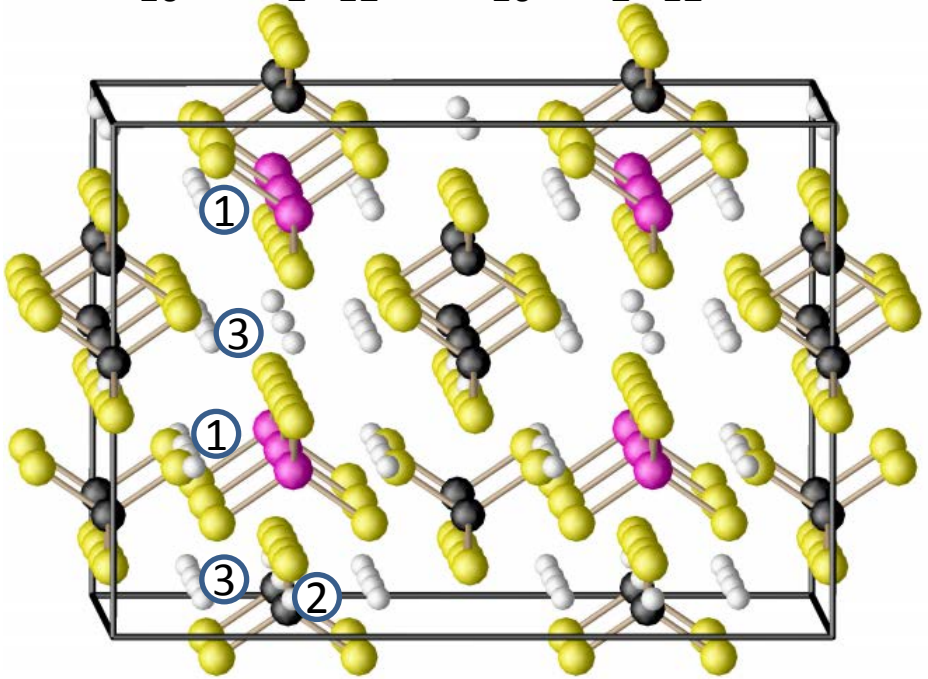


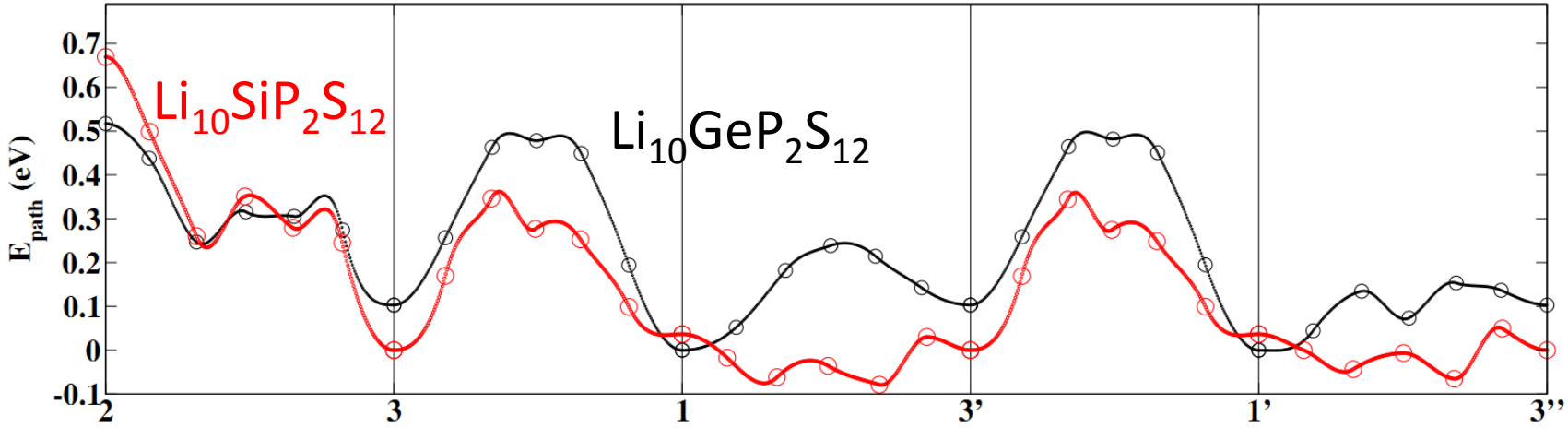
Vacancy site energies (eV)

1	0.0
2	0.5
3	0.1

Possible Li ion vacancy migrations in $Li_{10}GeP_2S_{12}$ & $Li_{10}SiP_2S_{12}$



Preliminary NEB results for Li ion migration



Summary of preliminary results and conclusions

- Found (meta) stable structures for both $Li_{10}GeP_2S_{12}$ and $Li_{10}SiP_2S_{12}$; ordered structure has space group $P4_2mc$ instead of experimental structure with partial occupancies $P4_2/nmc$
- Both $Li_{10}GeP_2S_{12}$ and $Li_{10}SiP_2S_{12}$ are calculated to be unstable with respect to decomposition into constituents; implying that either there is a kinetic barrier favoring the new materials or there are other stabilizing mechanisms.
- Preliminary NEB results suggest E_m = 0.5 eV for both materials vacancy migrations along the c-axis. Migration along the a-axis is ~0.2 eV higher for $Li_{10}SiP_2S_{12}$.
- Further work need to verify these preliminary results and to consider interstitial sites.