Computational study of Li ion electrolytes composed of Li_3AsS_4 alloyed with Li_4GeS_4*

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Computations were performed on WFU's DEAC cluster.

Motivation :

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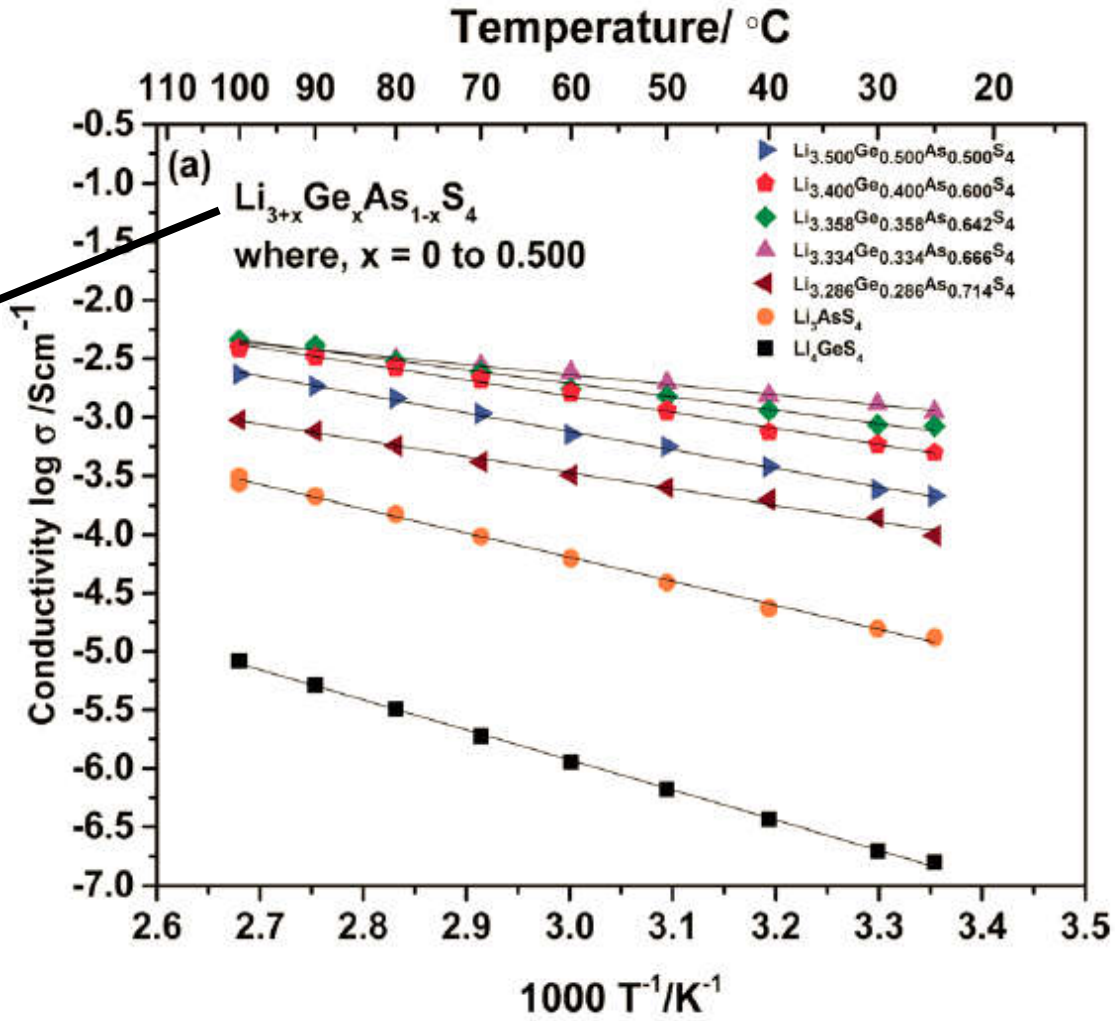
➢ Recent experimental studies by Sahu and co-workers (**J. Mater. Chem. A, 2014,2, 10396**) .

$Li_{3+x}Ge_xAs_{1-x}S_4$

X=0 to x=0.5



J. Mater. Chem. A, 2014,2, 10396

Structure of the pure Li_3AsS_4 ??

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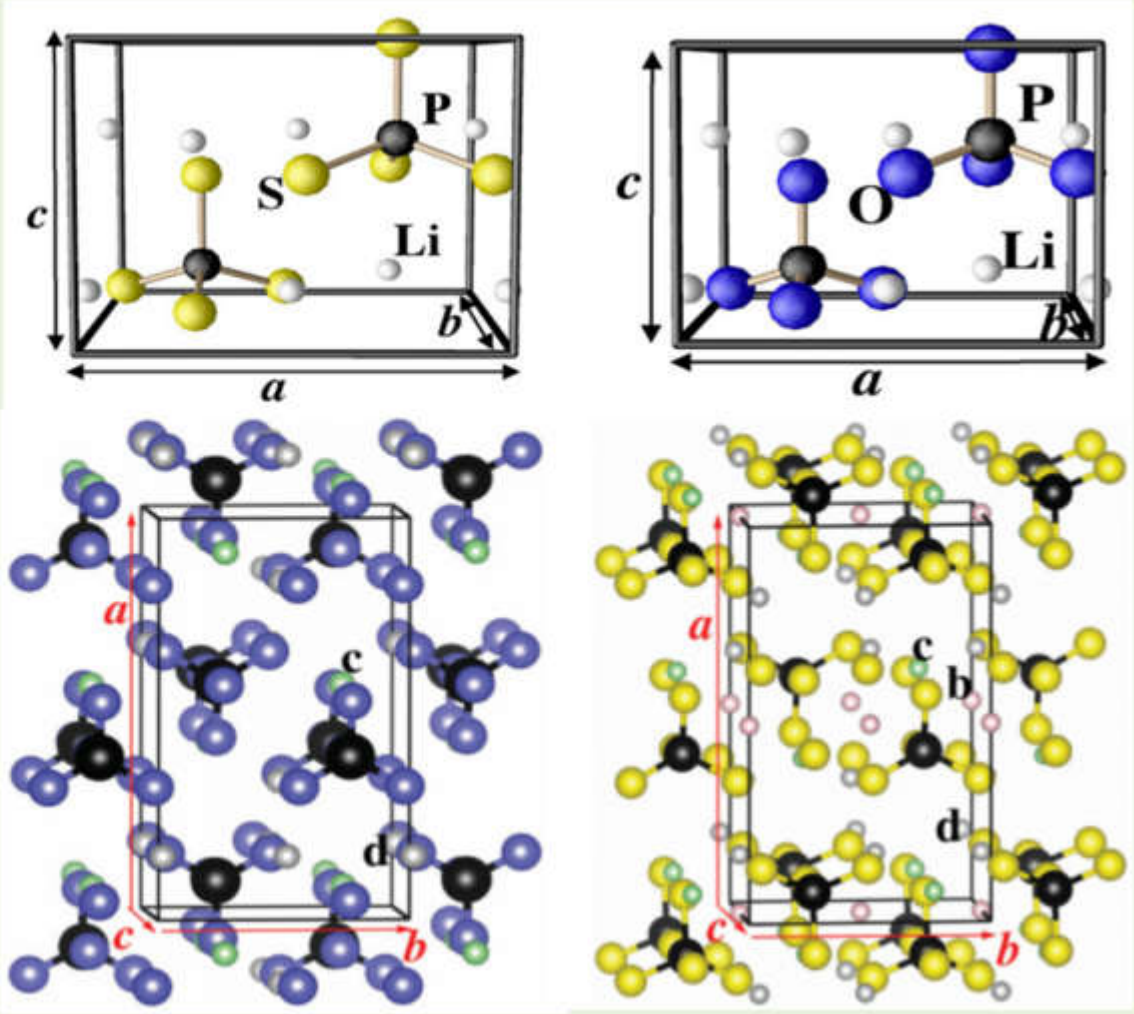
$Pmn2_1$ structure

- Low temperature

Pnma structure

- High temperature



PhysRevB.88.104103 (2013)

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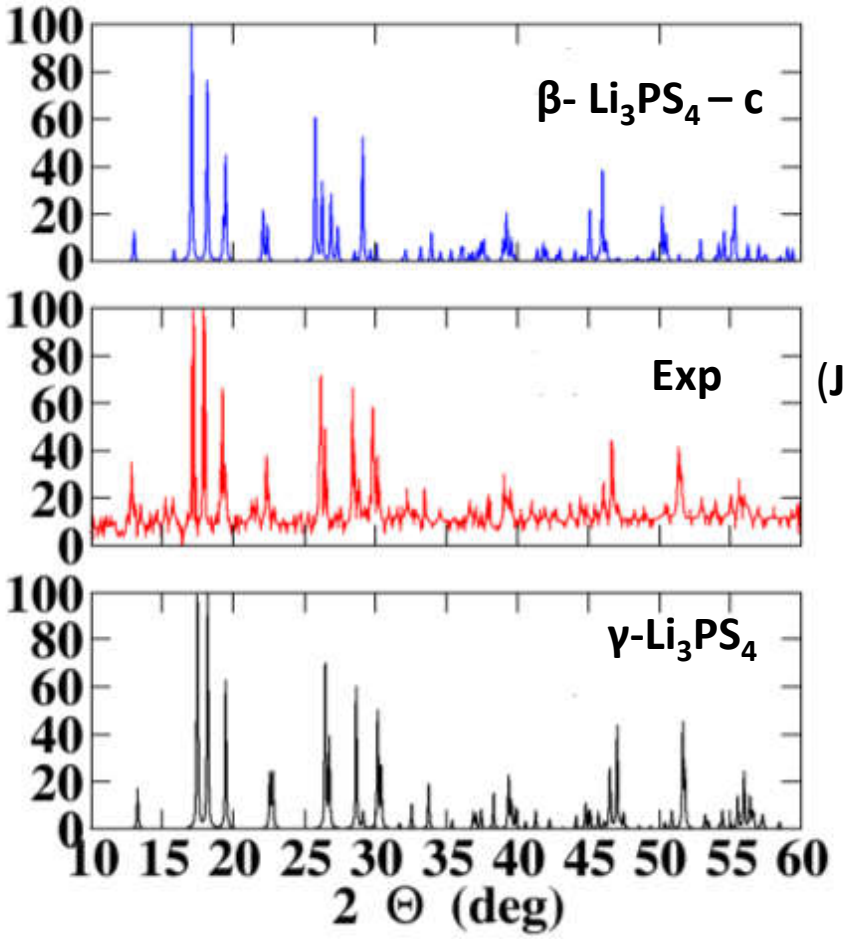
Structure of the pure Li_3AsS_4 ??

Structure	Li_3AsS_4 Δ H (eV)	Li_3PS_4 Δ H (eV)
γ-Li_3PS_4 (Pmn2_1)	-7.17	-8.37
γ-Li_3PO_4 (Pnma)	-6.95	-8.18
β- Li_3PS_4 – b (Pnma)	-7.00	-8.28
β- Li_3PS_4 – c (Pnma)	-7.03	-8.25

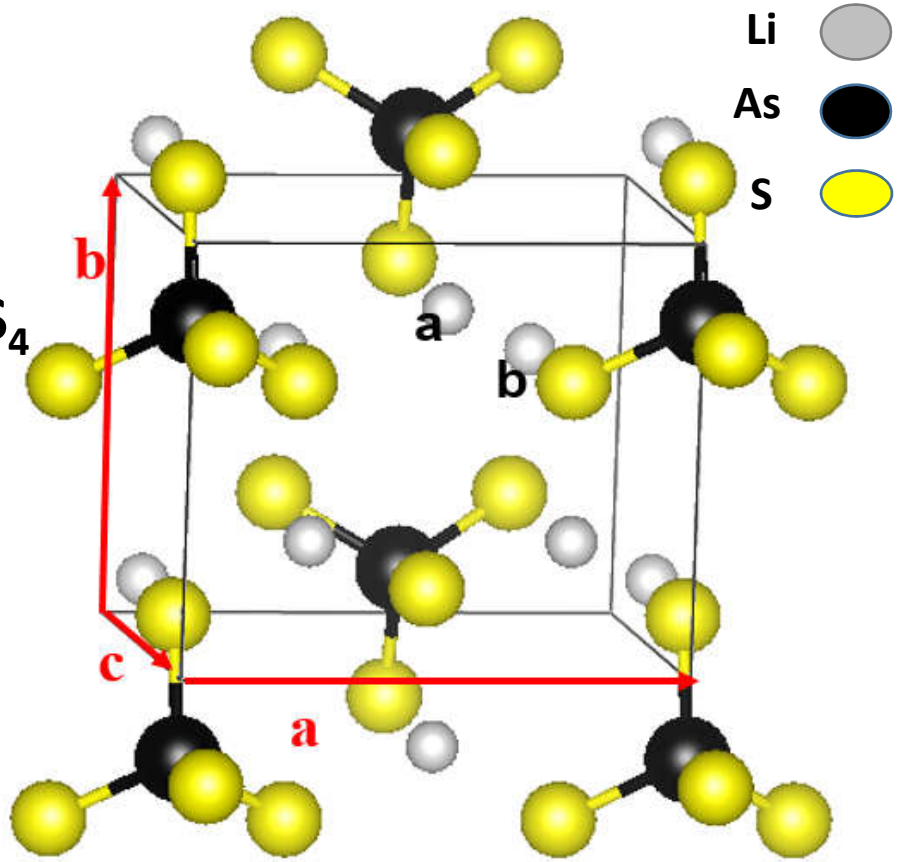
Structure of the pure Li_3AsS_4



(J. Mater. Chem. A, 2014,2, 10396)

Structure of the pure Li_3AsS_4

- $Pmn2_1$ group symmetry
- Symmetry group similar to γ-Li_3PS_4
- 2 unique Li sites
- Lattice constants and fractional Coordinates of atoms are very Similar to γ-Li_3PS_4



Structure of the pure Li_4GeS_4

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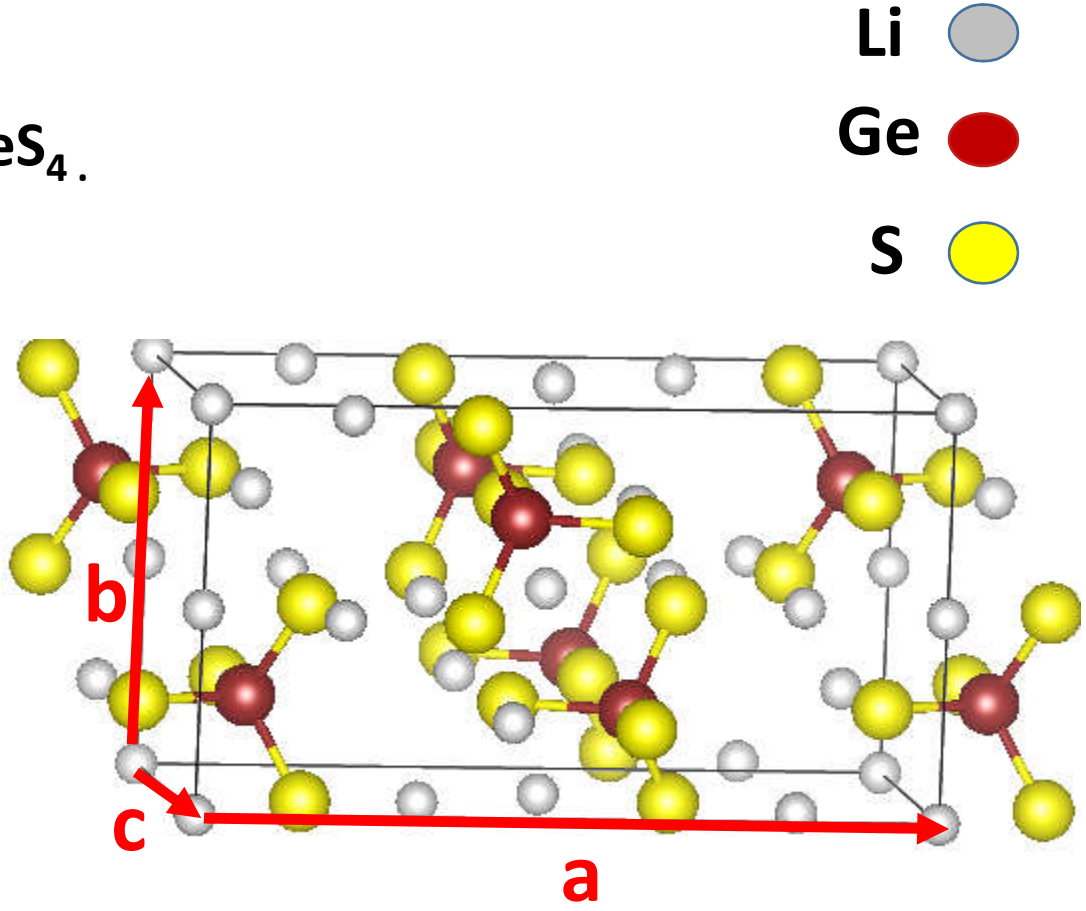
- The crystal structure of **Li_4GeS_4**.
- **Pnma** space group
- **The GeS_4 tetrahedra are very similar to those AsS_4 consistent with the formation of substitutional alloys .**

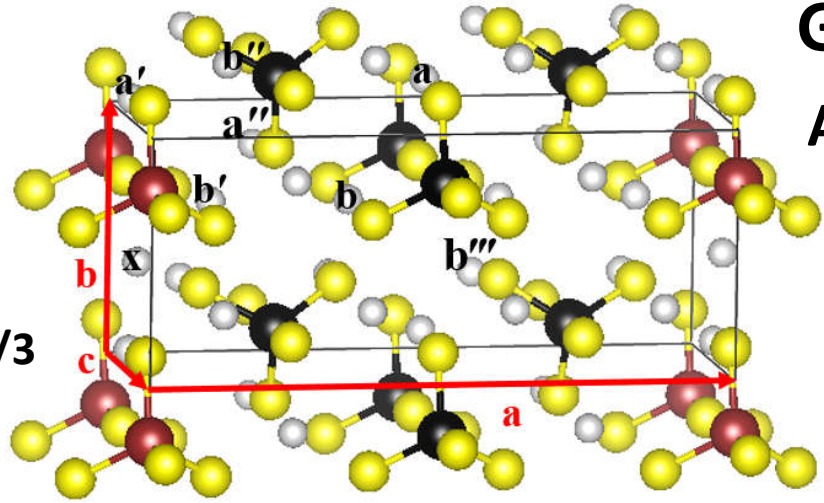


Structures of the Alloys

x=1/4

¾ Li_3AsS_4+ ¼ $LiGeS_4$ ⟶ $Li_{13/4}As_{3/4}Ge_{1/4}S_4$

- Pm group symmetry
- 8 unique Li sites

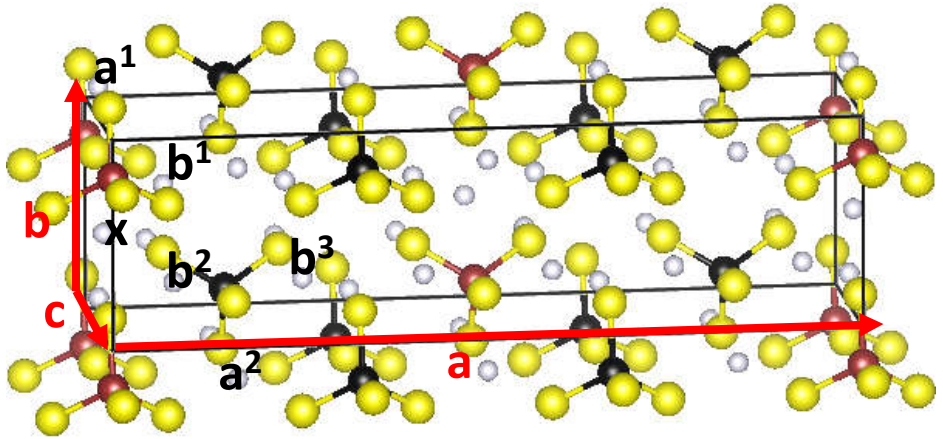


Li
Ge
As
S

x=1/3

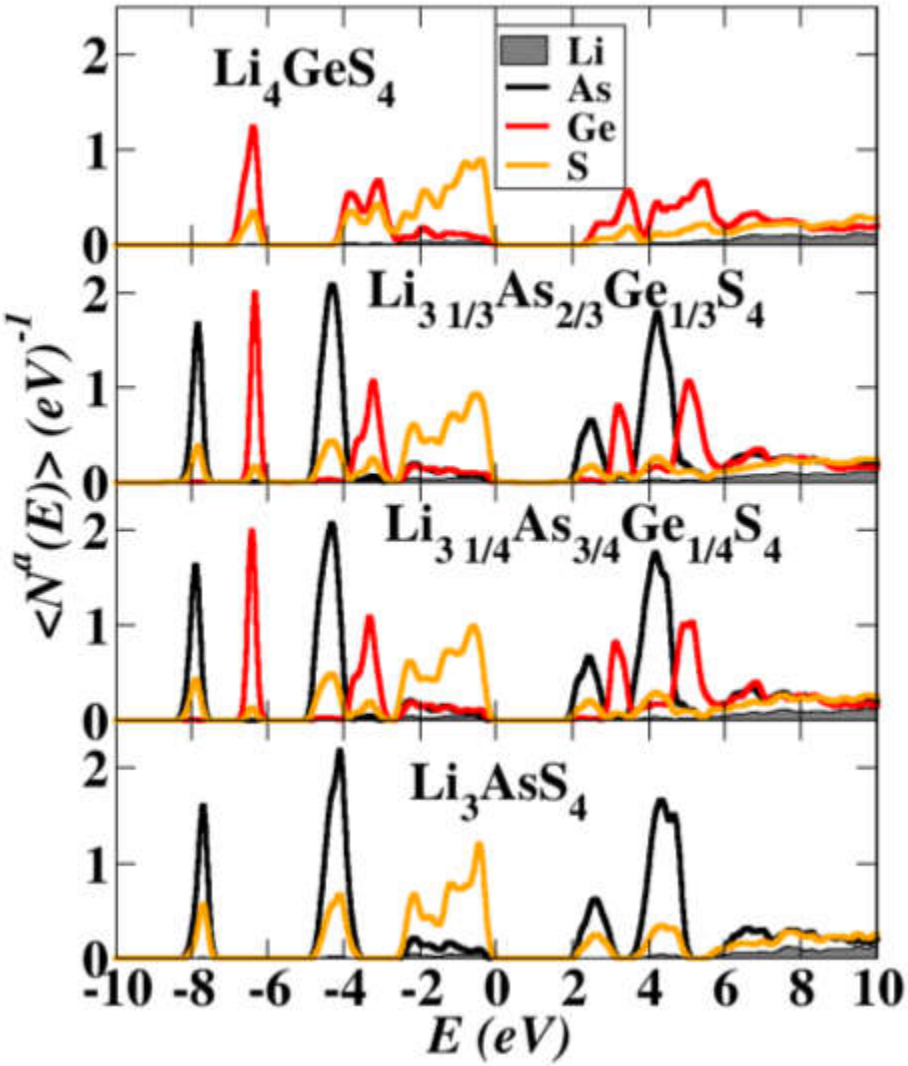
2/3 Li_3AsS_4+ 1/3 $LiGeS_4$ ⟶ $Li_{10/3}As_{2/3}Ge_{1/3}S_4$

- $Pmn2_1$ group symmetry
- 6 unique Li sites



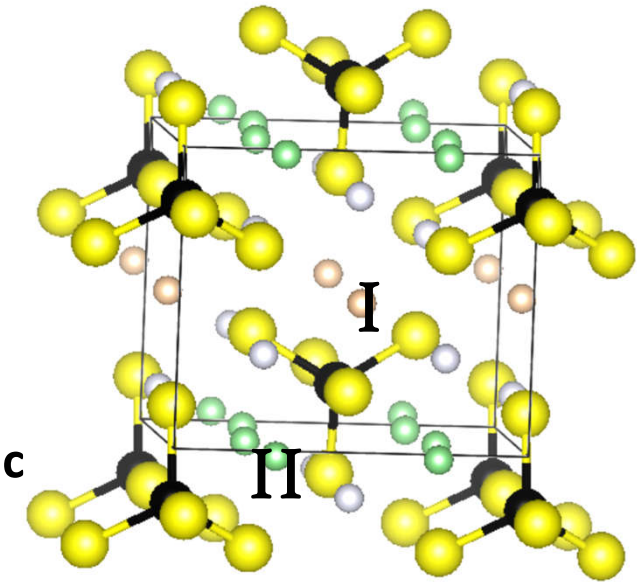
PDOS and HOF

	ΔH_f (eV)	ΔH_D(eV)
Li_3AsS_4	-7.17	
Li_4GeS_4	-10.18	
$Li_{13/4}Ge_{1/4}As_{3/4}S_4$	-7.86	0.06
$Li_{10/4}Ge_{1/3}As_{2/3}S_4$	-8.09	0.06



Ion migration in Li_3AsS_4

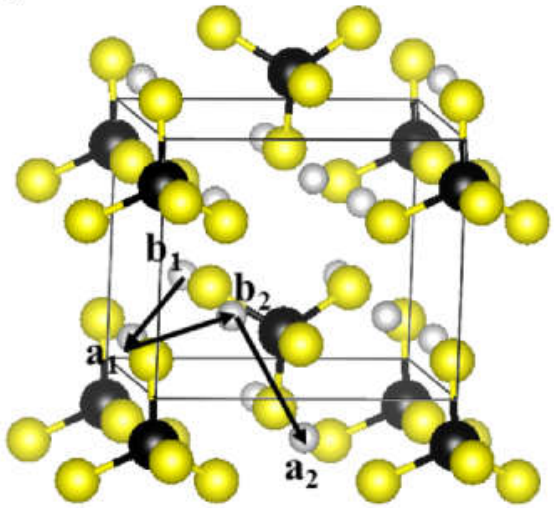
		Li_3AsS_4		γ-Li_3PS_4	
Type	Label	Position	ΔE	Position	ΔE
Vac	a	(0.00, 0.85, 0.99)	0.07	(0.00, 0.82, 1.00)	0.05
Vac	b	(0.24, 0.32, 0.00)	0	(0.24, 0.32, 0.00)	0
Inter	I	(0.00, 0.49, 0.65)	0	(0.00, 0.48, 0.64)	0
Inter	II	(0.23, 0.00, 0.68)	0.09	(0.24, 0.00, 0.66)	0.00

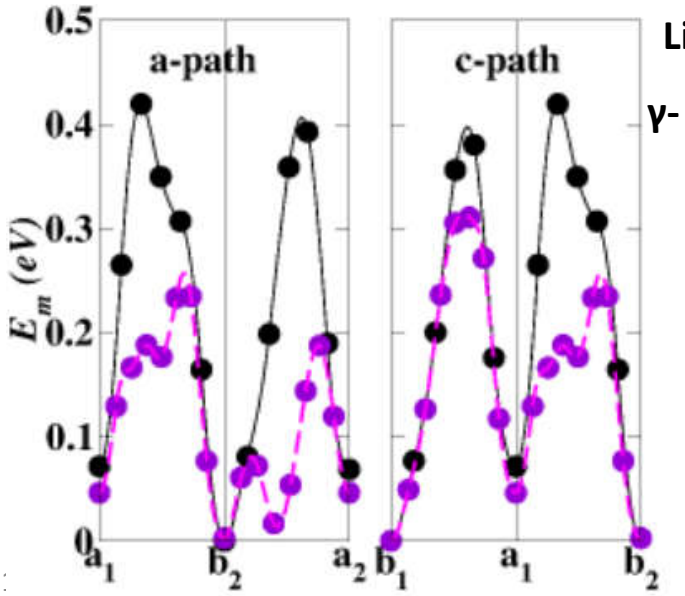


Li
As
S

- E_f = 0.85 eV by forming I inter and b vac

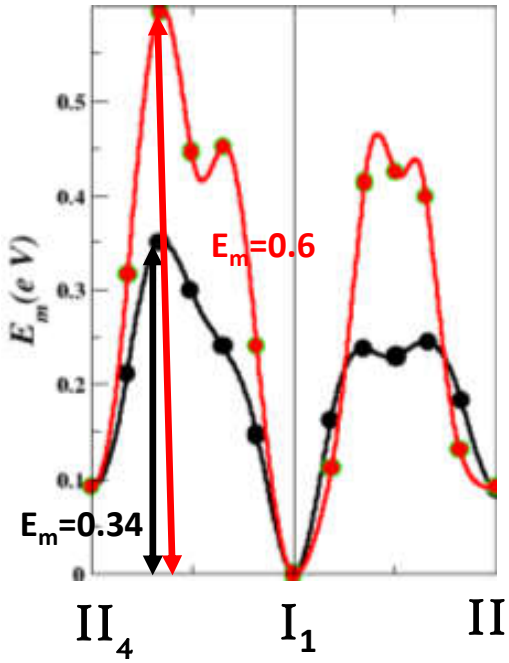
Vacancy migration

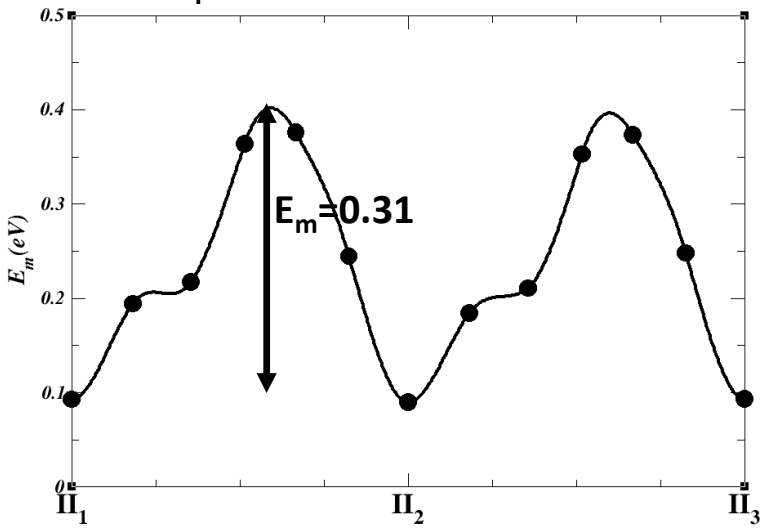


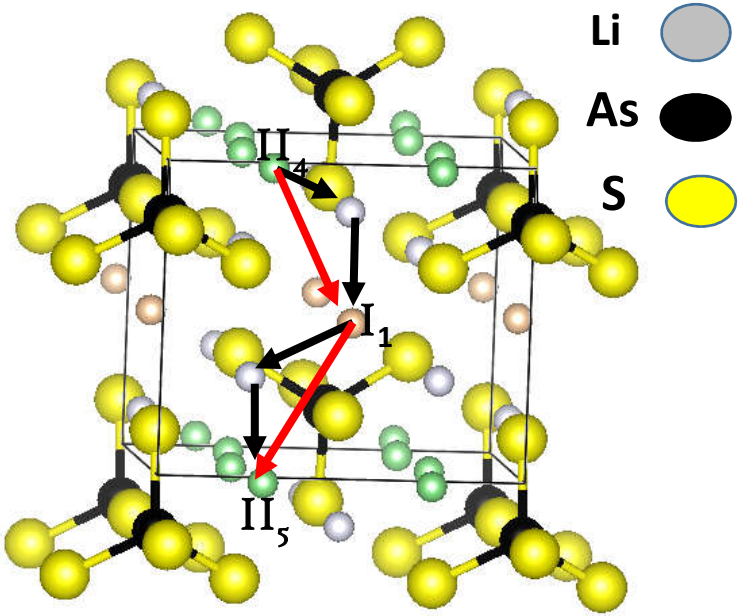


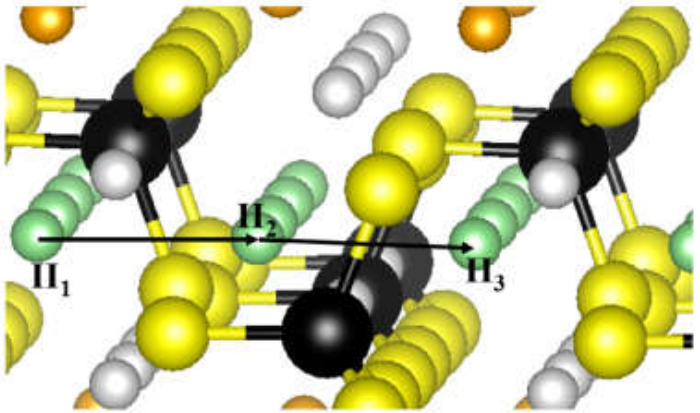
Li_3AsS_4
γ- Li_3PS_4

Interstitial migration in Li_3AsS_4



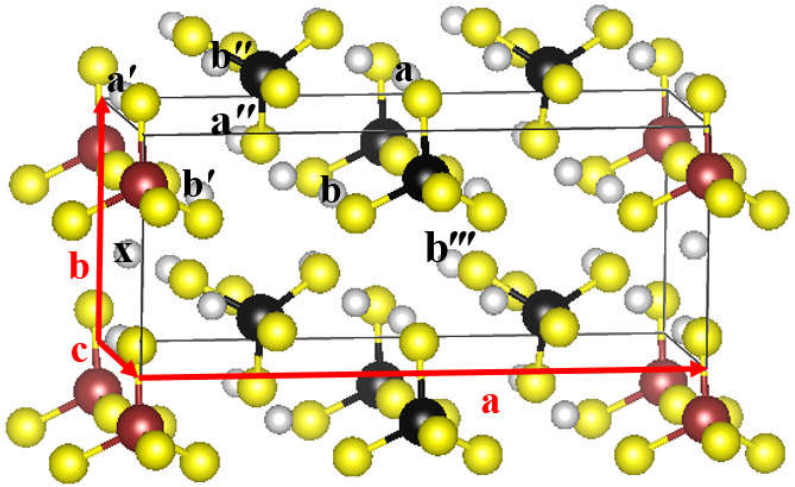


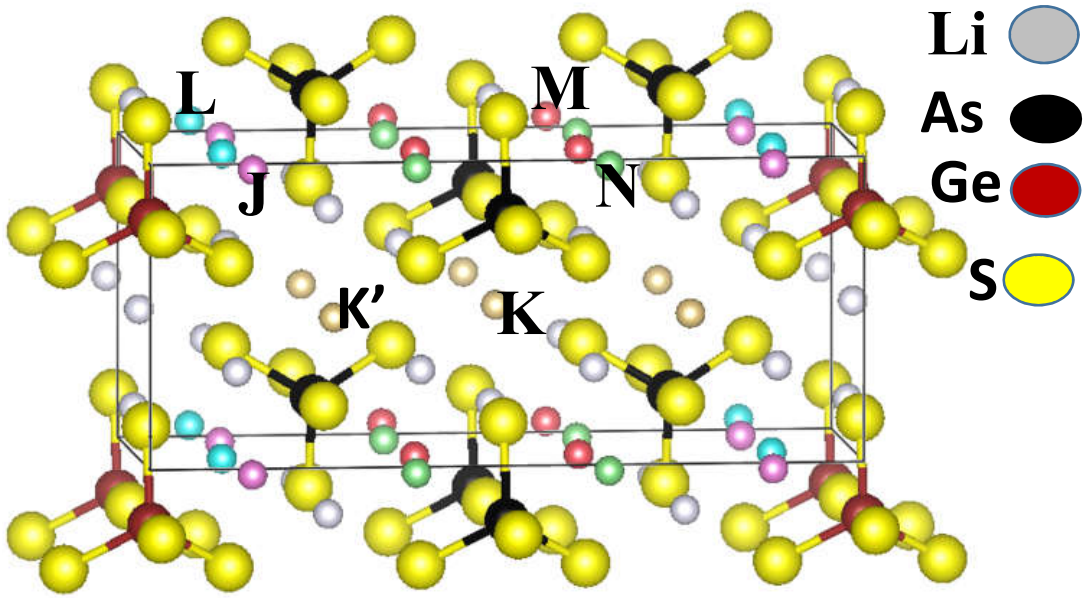




c

Ion migration in $Li_{13/4}Ge_{1/4}As_{3/4}S_4$

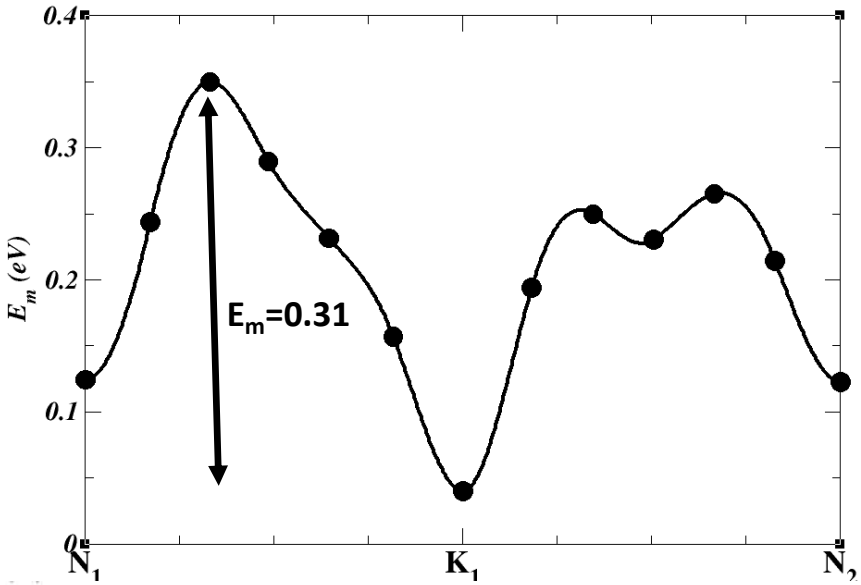


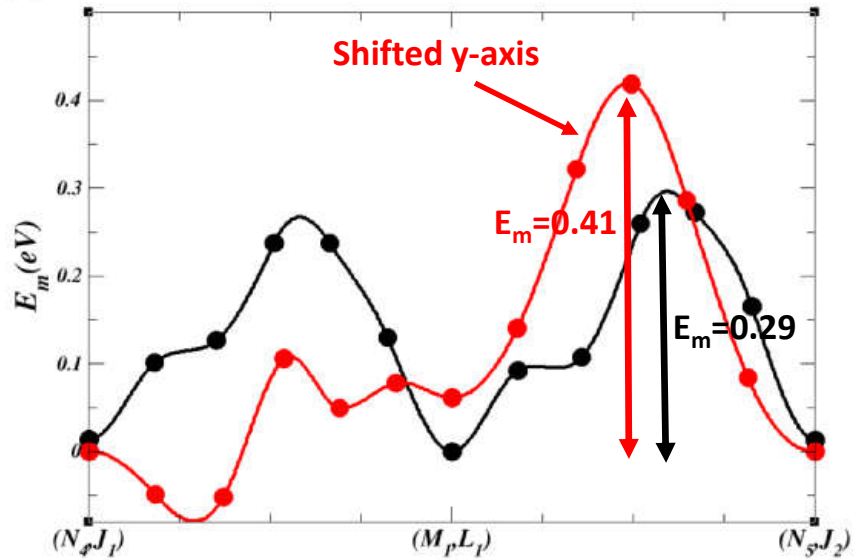


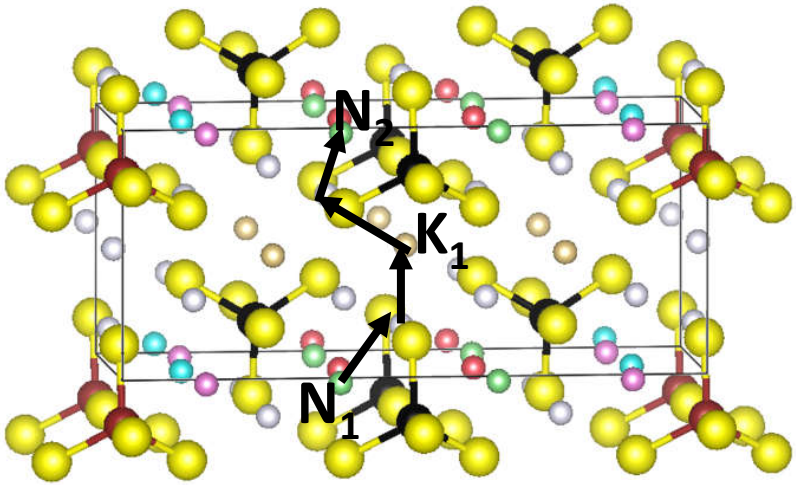
Type	Label	Ref	proximity (A^o)	ΔE
vac	a	a	8.51	0.61
vac	*a′	a	3.58	0.00
vac	a″	a	7.07	0.67
vac	b	b	6.52	0.56
vac	*b′	b	3.75	0.01
vac	*b″	b	3.77	0.01
vac	b‴	b	6.60	0.59
vac	x		3.01	0.01
Inter	J	II	4.52	0.0
Inter	L	II	2.62	0.07
Inter	N	II	7.20	0.13
Inter	M	II	5.94	0.12
Inter	K	I	8.81	0.06
Inter	K′	I	4.27	0.06

- **E_f=0.21 eV**
- **Involve the formation the J interstitial and x vacancy .**
- ***One interesting result of the calculations is that vacancies close to the Ge atom (a’, b’, b’’) are unstable; they relax to an x site vacancy .**

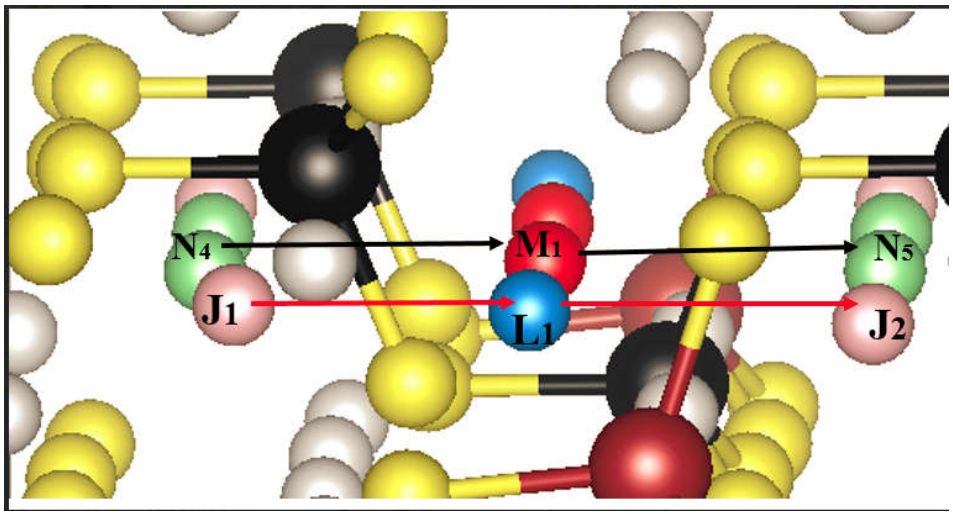
Ion migration in $Li_{13/4}Ge_{1/4}As_{3/4}S_4$





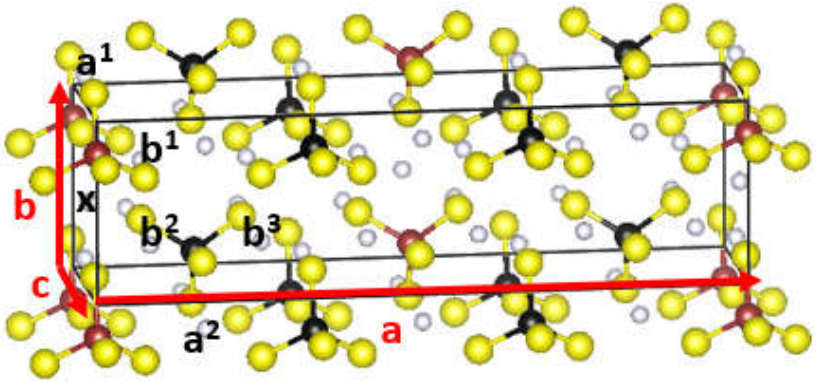


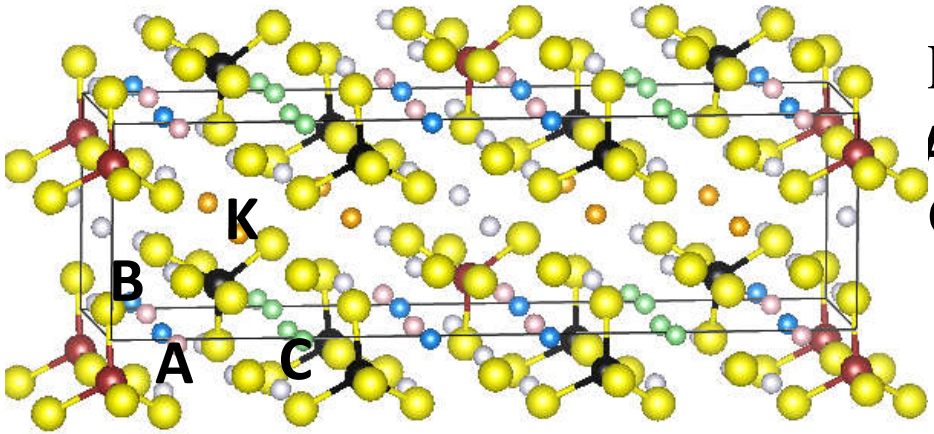
Li
As
Ge
S



c

Ion migration in $Li_{10/3}Ge_{1/3}As_{2/3}S_4$





Li
As
Ge
S

Type	Label	Ref	proximity (A°)	ΔE
vac	*a^1	a	3.57	0.02
vac	a^2	a	3.85	0.61
vac	*b^1	b	3.75	0.00
vac	*b^2	b	3.78	0.01
vac	b^3	b	6.54	0.51
vac	x		3.00	0.01
Inter	A	II	2.62	0.05
Inter	B	II	2.95	0.0
Inter	C	II	5.92	0.15
Inter	K	I	4.32	0.10

- **E_f=0.11 eV**
- **Which involves the formation of B interstitial and x vacancy.**
- ***One interesting result of the calculations is that vacancies close to the Ge atom (a^1, b^1, b^2) are unstable; they relax to an x site vacancy .**

Ion migration in $Li_{10/3}Ge_{1/3}As_{2/3}S_4$

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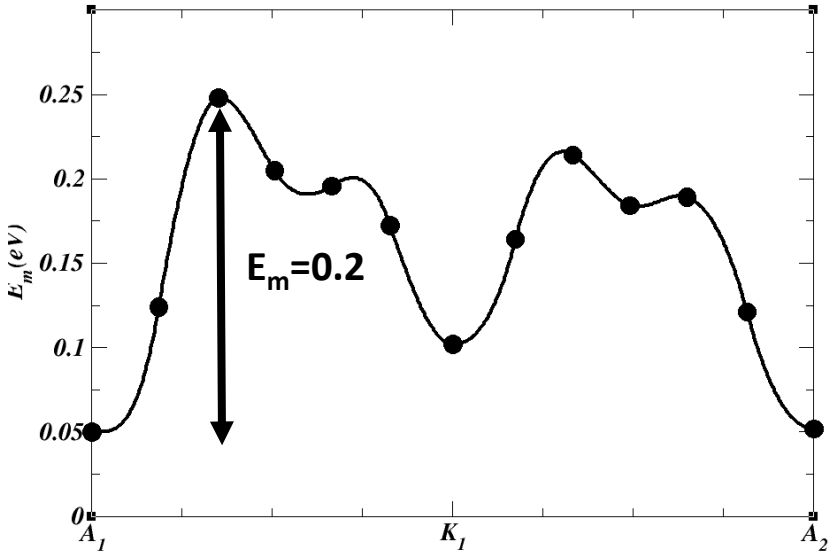

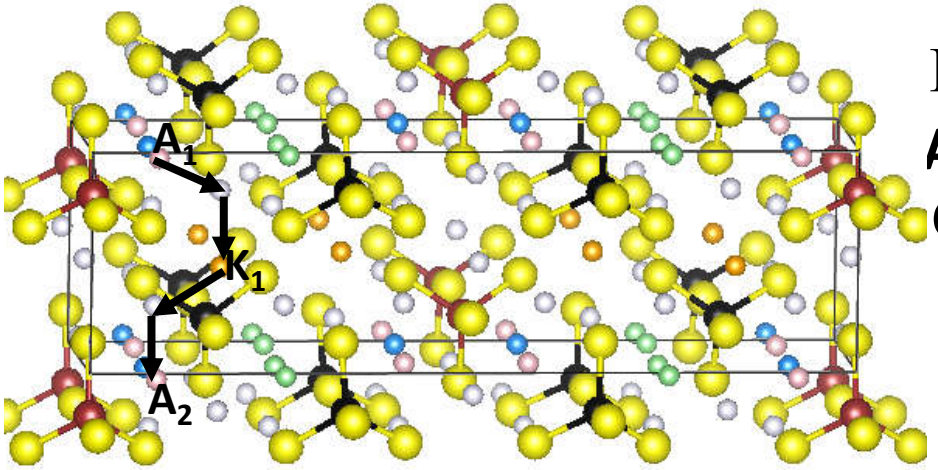

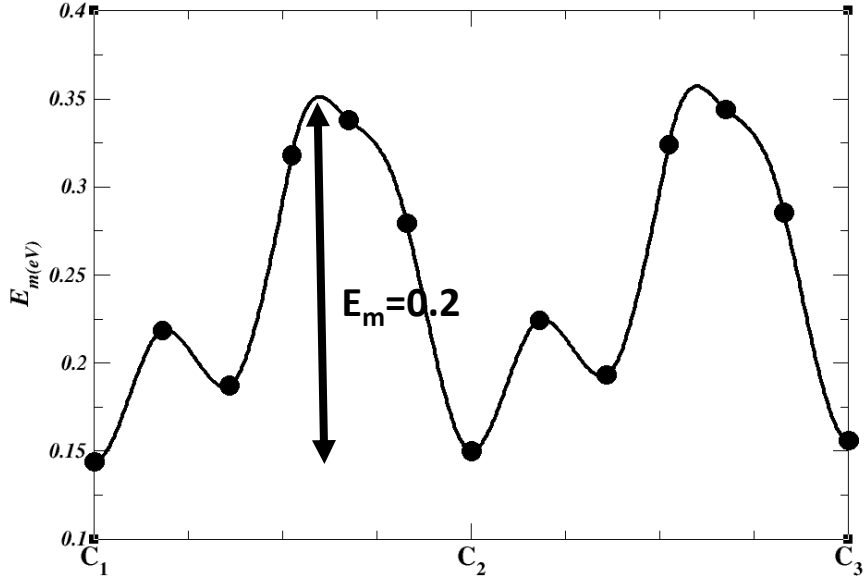

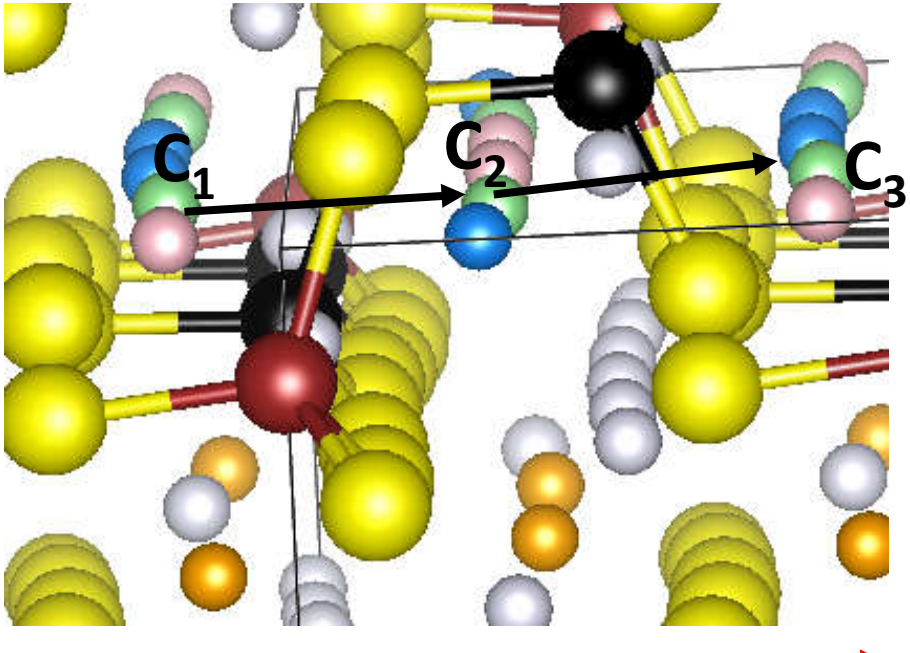

Ion migration in pure Li_3AsS_4 and its subtitutional alloys:

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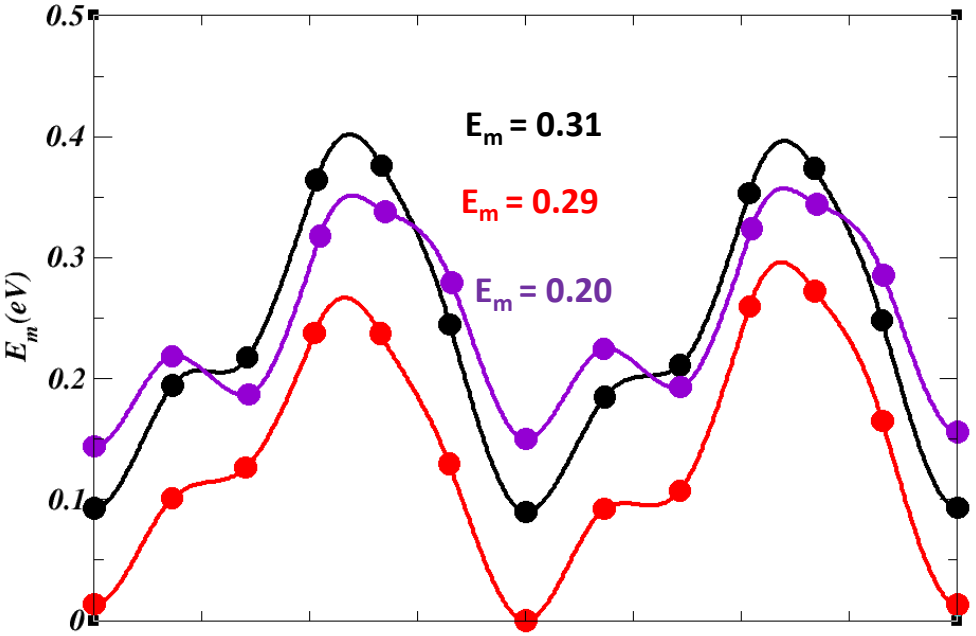
Li_3AsS_4

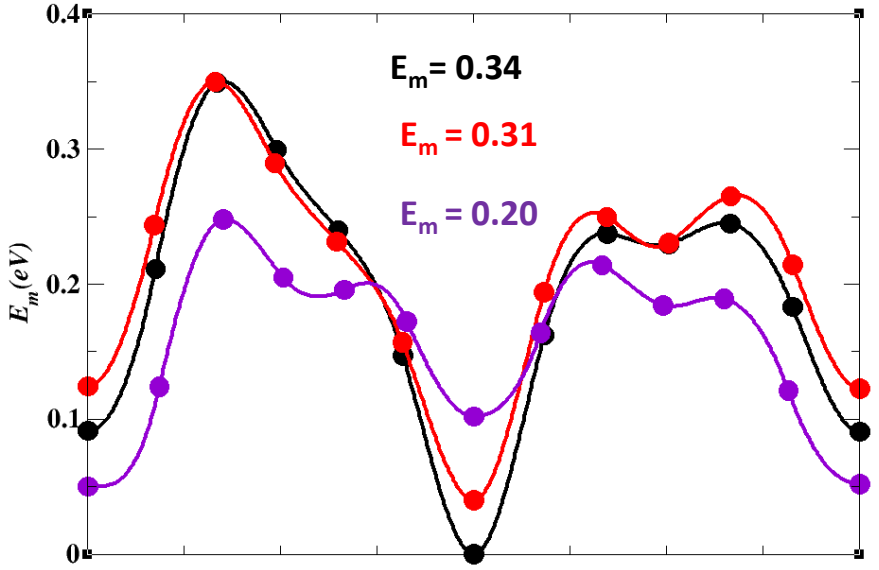
$Li_{13/4}Ge_{1/4}As_{3/4}S_4$

$Li_{10/3}Ge_{1/3}As_{2/3}S_4$

Interstitial migration along c



Kick-out along b



Ion migration in pure Li_3AsS_4 and its subtitutional alloys:

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calculated

Experimental

	E_m (eV)	E_f (eV)	E_A (eV)	E_A (eV)
Li_3AsS_4	0.3	0.9	0.3-0.7	0.4
$Li_{13/4}Ge_{1/4}As_{3/4}S_4$	0.3	0.2	0.3-0.4	0.27
$Li_{10/3}Ge_{1/3}As_{2/3}S_4$	0.2	0.1	0.2-0.3	0.17

Summary and conclusions:

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- In this study we report a likely structure for Li_3AsS_4 to be characterized by the *Pmn2*$_1$ space group, consistent with the X-ray measurements of Sahu and co-workers (J. Mater. Chem. A, 2014,2, 10396) .
- Plausible ordered structures for substitutional alloys of Li_3AsS_4 with Li_4GeS_4 -- (*1-x*)Li_3AsS_4+*x*Li_4GeS_4 are found for *x*=1/4 and *x*=1/3.
- The partial densities of states for the x=1/4 and x=1/3 alloys are very similar to each other and the band gaps are similar to that of Li_3AsS_4 .
- Li ion migration in Li_3AsS_4 is found to involve interstitial sites, with likely diffusion paths involving pure interstitial or kick-out mechanisms.
- Li ion migration pathways in the *x*=1/4 and *x*=1/3 alloys are found to be similar to those of Li_3AsS_4 but with lower barriers.
- The estimated activation energies for Li ion migration are consistent with the experimental trend.

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Computational methods

- Density functional theory with LDA
- PAW formalism using datasets generated with ***ATOMPAW*** code (Holzwarth et al. *CPC* **135**, 329 (2001)) http://pwpaw.wfu.edu
- Electronic structure calculations performed using ***QUANTUM ESPRESSO*** and ***ABINIT*** codes. (Giannozzi et al. *JPCM* **21,** 394402 (2009); http://www.quantum-espresso.org, Gonze et al., *CPC* **180**, 2582 (2009))
- Plane wave expansion for wave functions with $|\mathbf{k}+\mathbf{G}|^2 \leq 64$ Ry
- Brillouin zone integration mesh of 0.003 bohr^{-3}
- Ion migration energies estimated with Nudged Elastic Band (NEB) method. (Hinkleman et al. *JCP* **113**, 9901 & 9978 (2000))
- Visualization software: ***Xcrysden, VESTA***
- X-ray powder diffraction simulated using ***Mercury***

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Thank You