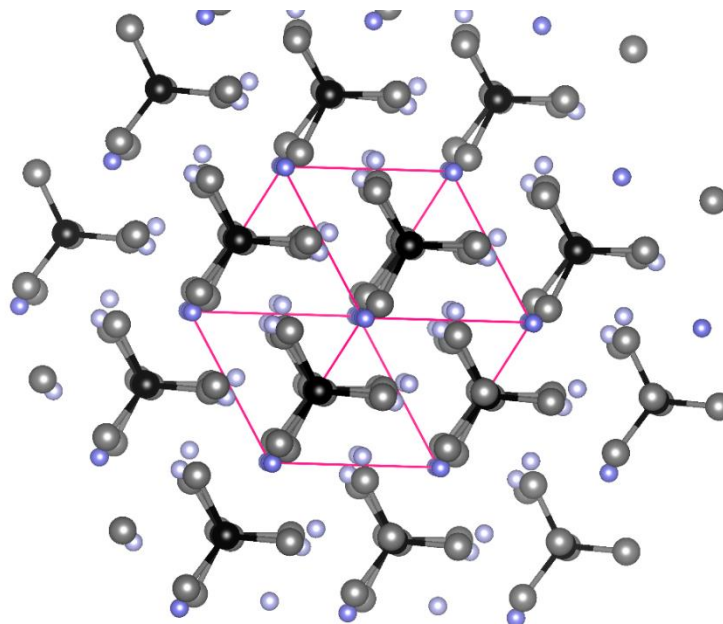


Computational Study of Ideal Electrolyte/Anode Interface for $\text{Na}_3\text{SbS}_4/\text{Na}$

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Outline

- I. Na-ion electrolytes for all-solid-state Na-ion batteries
- II. Motivation behind studying Na_3SbS_4
- III. Computational Methods
- IV. Results
- V. Conclusions

I. Na-ion Electrolytes

- i. Abundant (geopolitically-neutral & cheap)
- ii. \uparrow size of Na ions = \uparrow intercalation w.r.t. Li ions (higher reversibility)*
- iii. Cost-effective large-scale energy storage (option for Morocco's energy initiative?)
- iv. High energy density

* <https://ceder.berkeley.edu/research-areas/na-ion-battery-materials-design-and-discovery//>

II. Why Na_3SbS_4 ?

- i. Similar to Na_3PSe_4 ¹
- ii. Air-stable & high ionic conductivity^{2,3,4}
- iii. $E_a = 0.20 \text{ eV}$ at 25°C ⁴

1. Ceder et al., **Chem. Mater.**, **28**, pp. 252-258 (2016)
2. Wang et al., **Angew. Chem.**, **55**, pp. 8551-8555 (2016)
3. Zhang et al., **Adv. Sci.**, **3**, pg. 1600089 (2016)
4. Banerjee et al., **Angew. Chem.**, **55**, pp. 9634-9638 (2016)

III. Methodology

- i. Density functional theory with local-density approximation (LDA)
- ii. Projector Augmented Wave (PAW) formalism
- iii. PAW basis and projector functions generated by ATOMPAW¹
- iv. Quantum Espresso software package²
- v. Density of States calculations
- vi. Nudged Elastic Band (NEB) calculations³

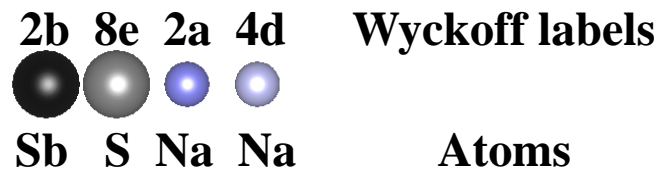
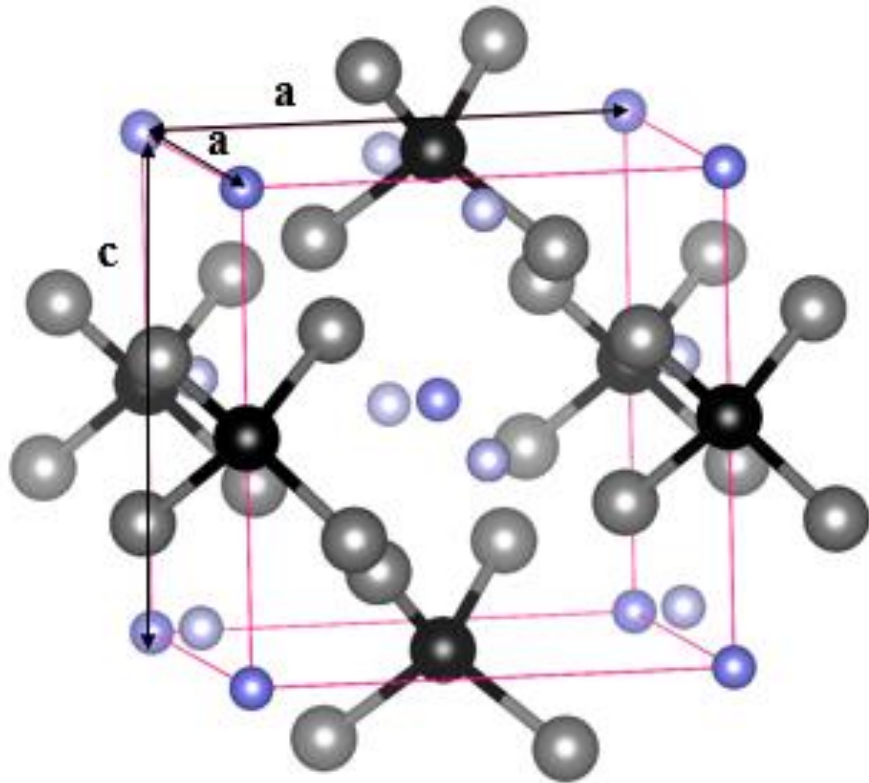
1. Holzwarth et al., **Computer Physics Communications**, **135**, pg. 329 (2001)

2. Giannozzi et al., **J. Phys.: Cond. Mat.**, **21**, pg. 395592 (2009)

3. Henkleman et al., **J. Chem. Phys.**, **113**, pp. 9901-9904 (2001)

IV. Results

Low temperature phase Na_3SbS_4 (space group $P\bar{4}2_1c$)



$$1 \quad x, y, z$$

$$2 \quad \bar{x}, \bar{y}, z$$

$$3 \quad y, \bar{x}, \bar{z}$$

$$4 \quad \bar{y}, x, \bar{z}$$

$$5 \quad \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$$

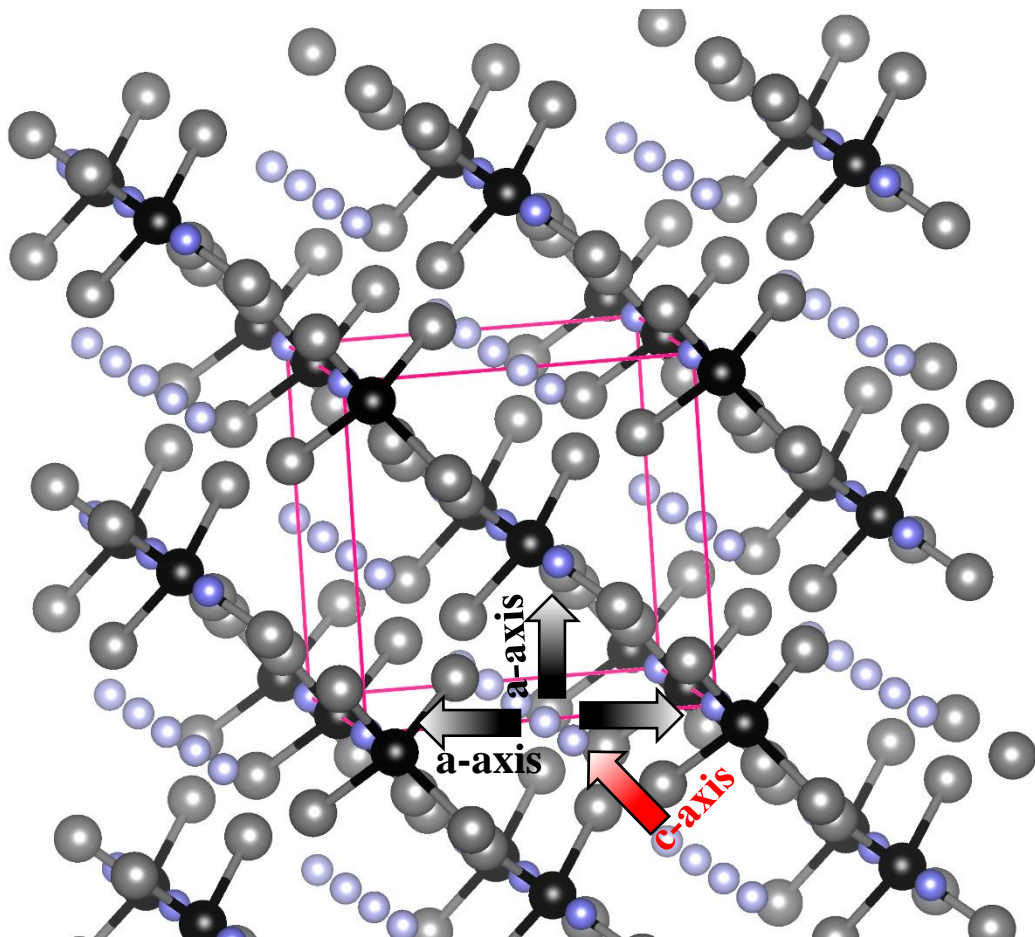
$$6 \quad \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$$





$$7 \quad \frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} + z$$

$$8 \quad \frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} + z$$

IV. Results

Ball-and-stick model for Na_3SbS_4

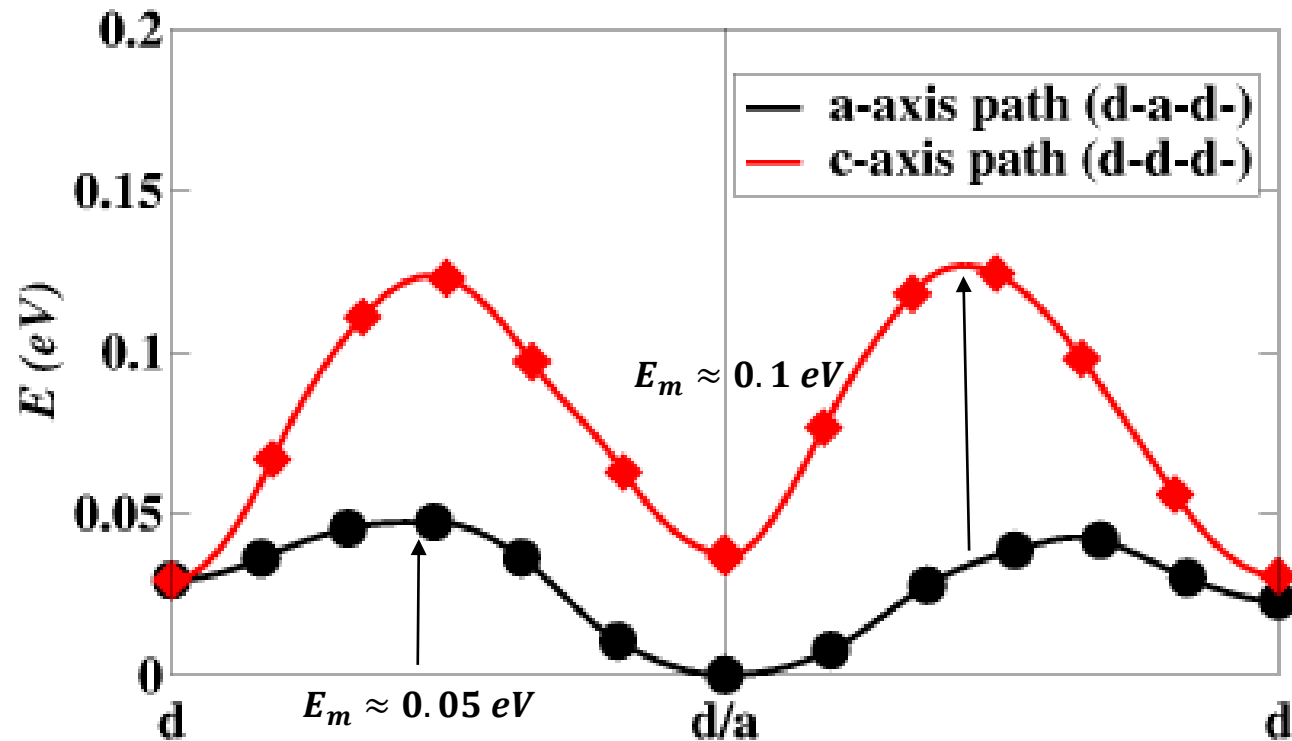


2b	8e	2a	4d	Wyckoff labels
				
Sb	S	Na	Na	Atoms

NEB calculations

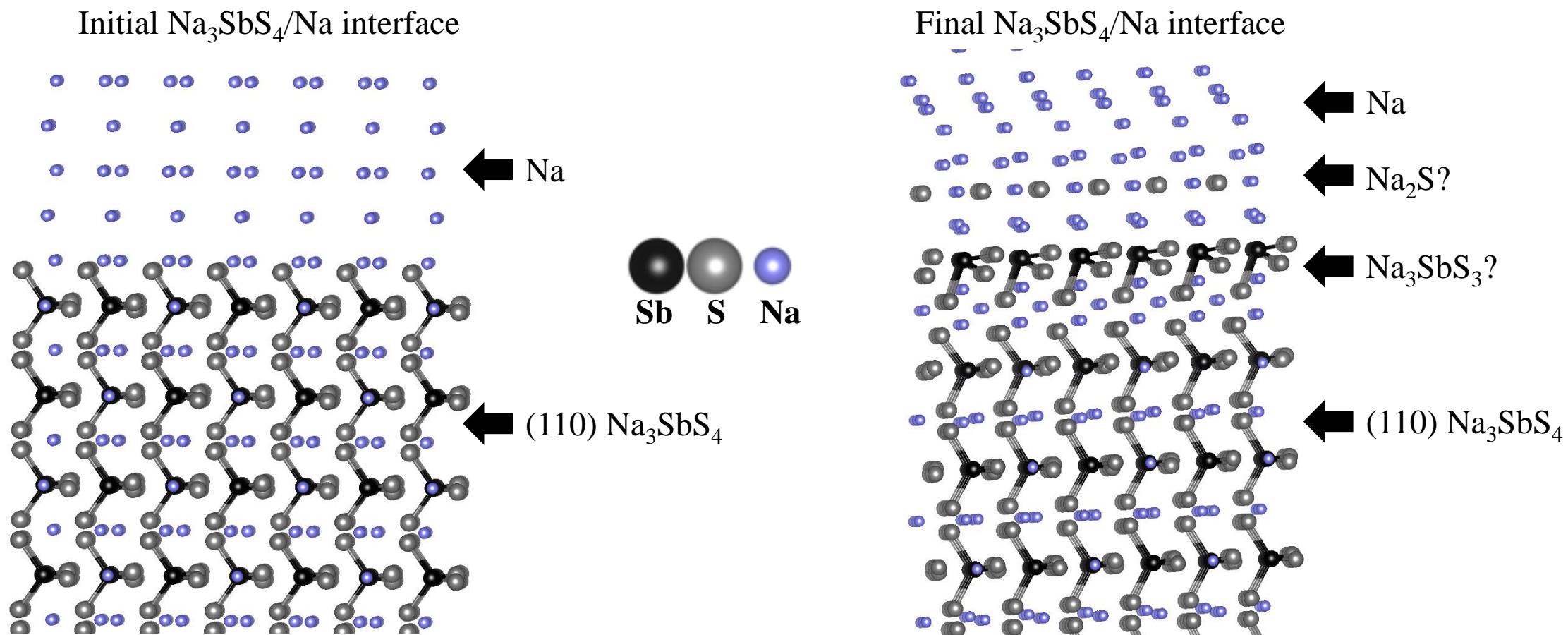
$$E_a \approx E_m$$

$$\sigma = \frac{c}{T} e^{-\frac{E_a}{kT}}$$



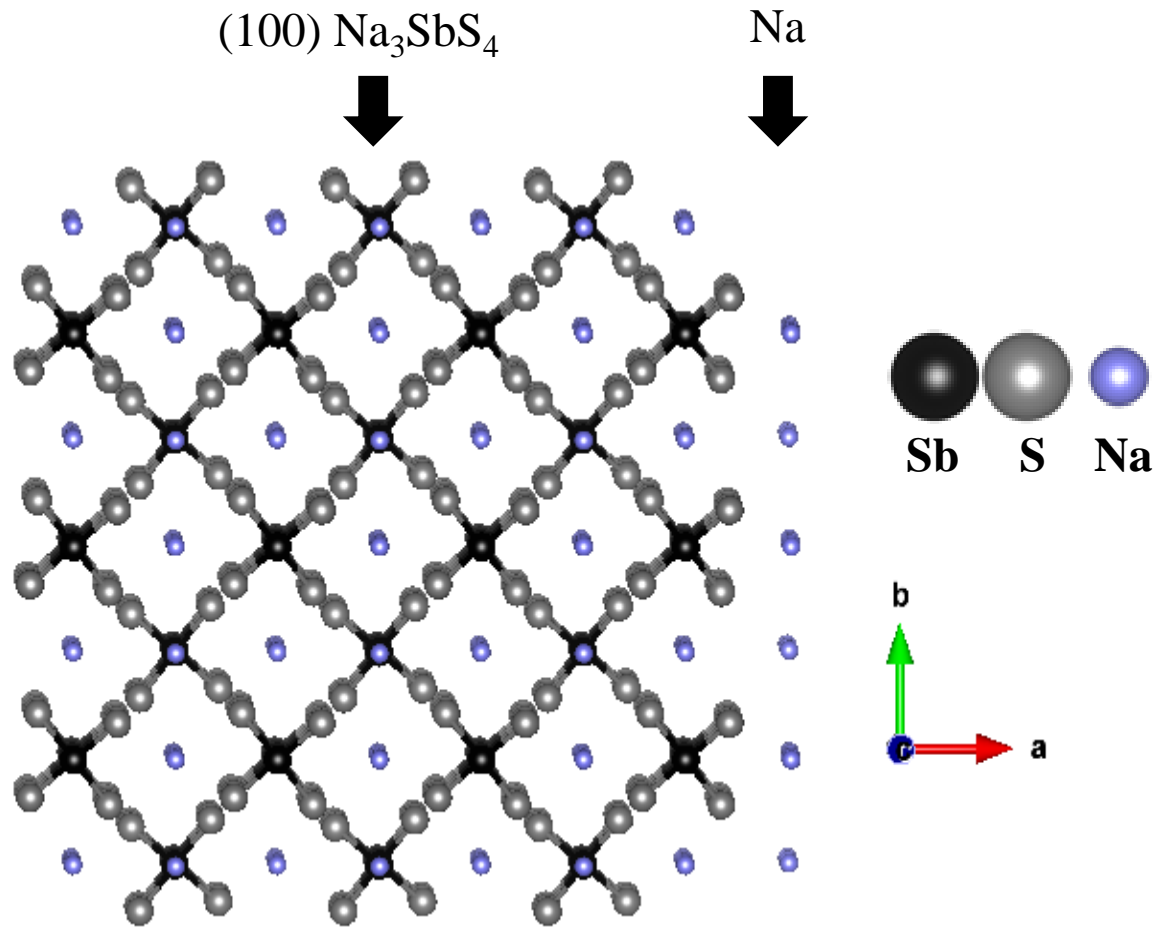
IV. Results

Interface Properties

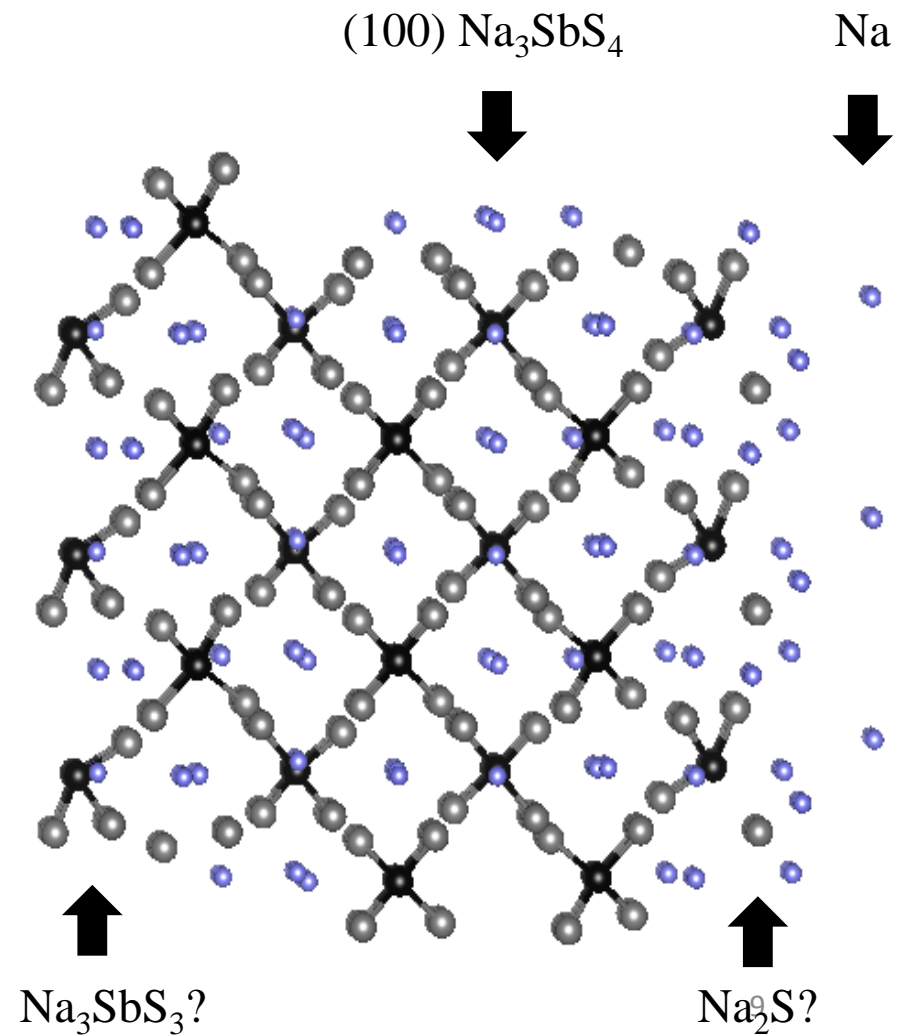


IV. Results

Initial $\text{Na}_3\text{SbS}_4/\text{Na}$ interface



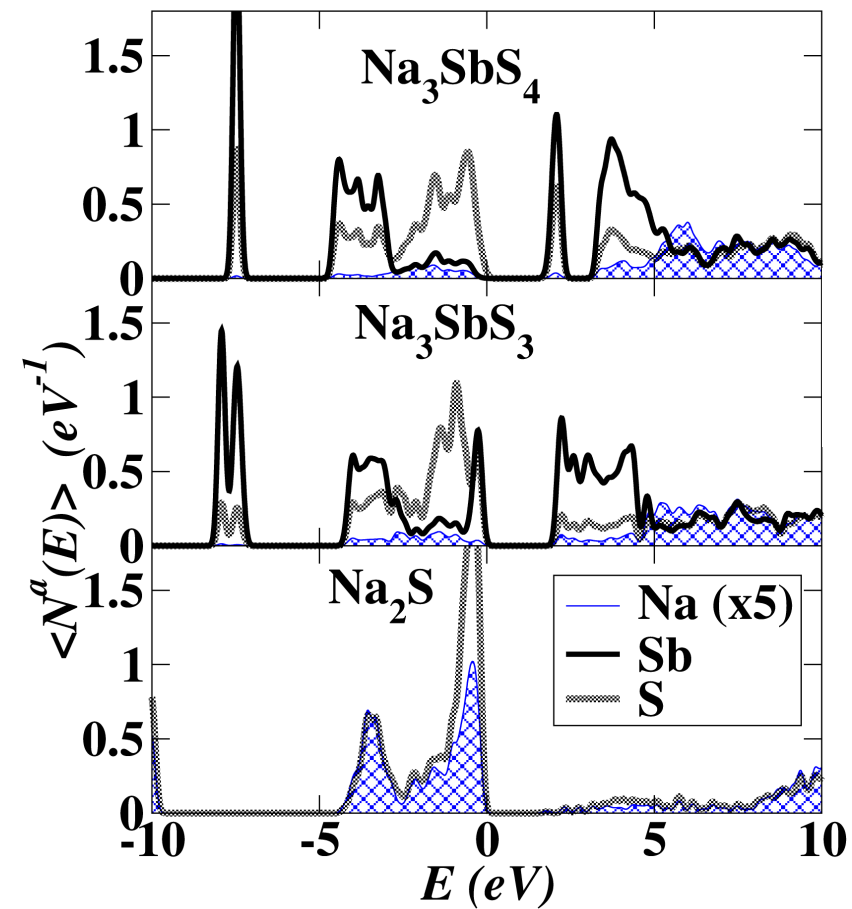
Final $\text{Na}_3\text{SbS}_4/\text{Na}$ interface



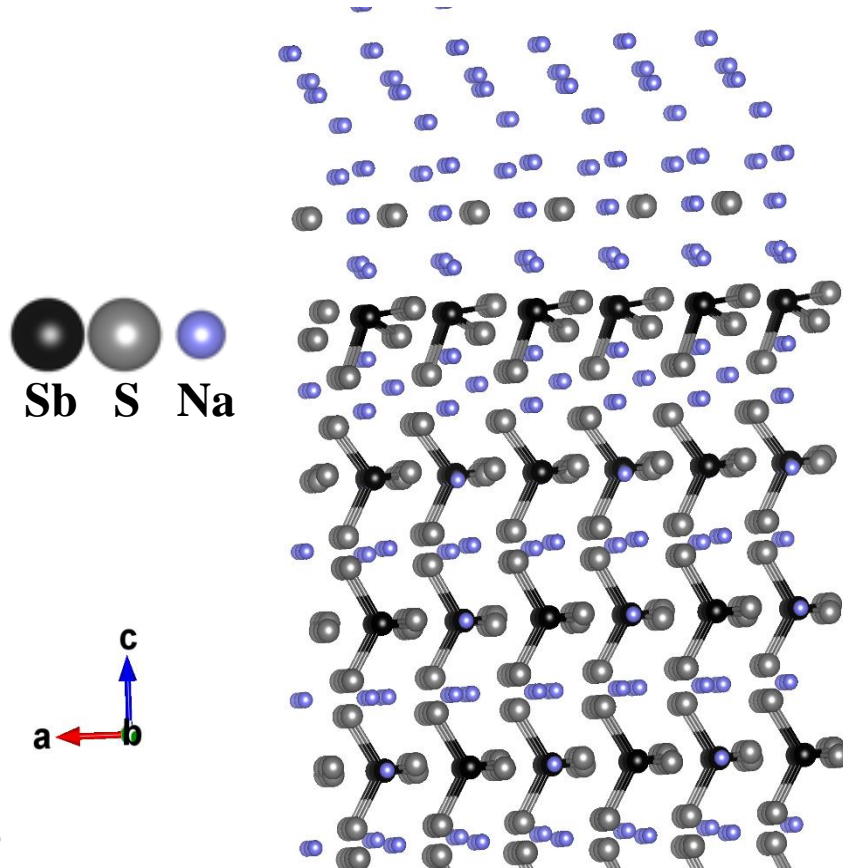
IV. Results

Density of States (DOS)

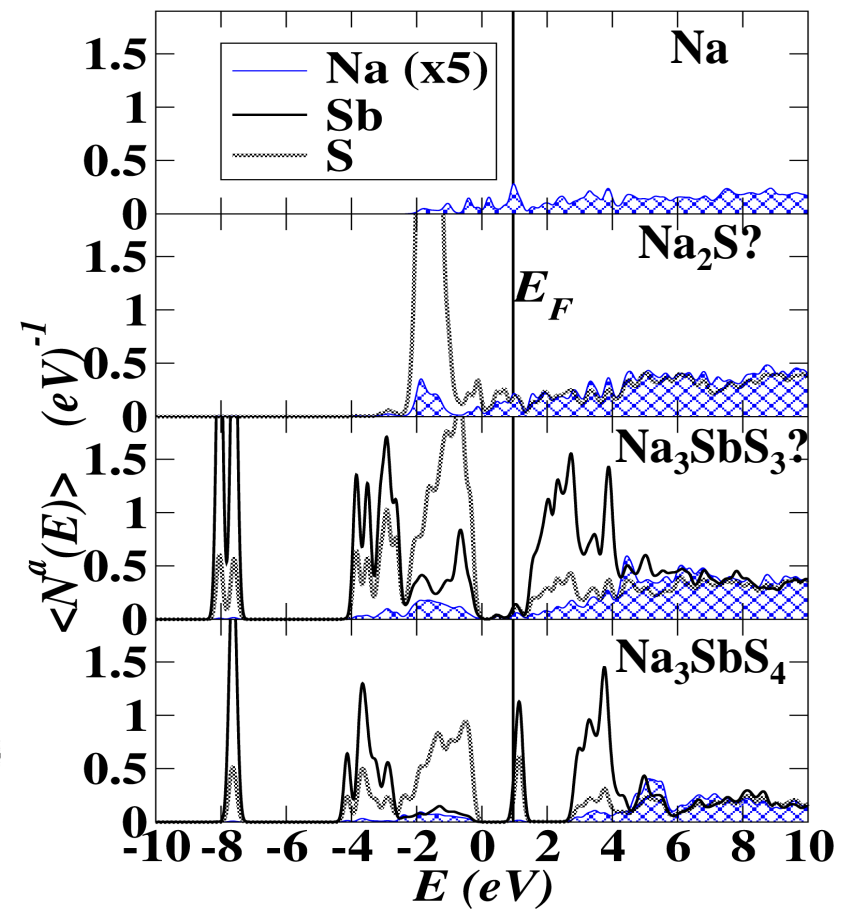
Bulk materials DOS



(110) $\text{Na}_3\text{SbS}_4/\text{Na}$ interface

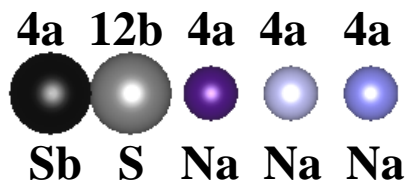
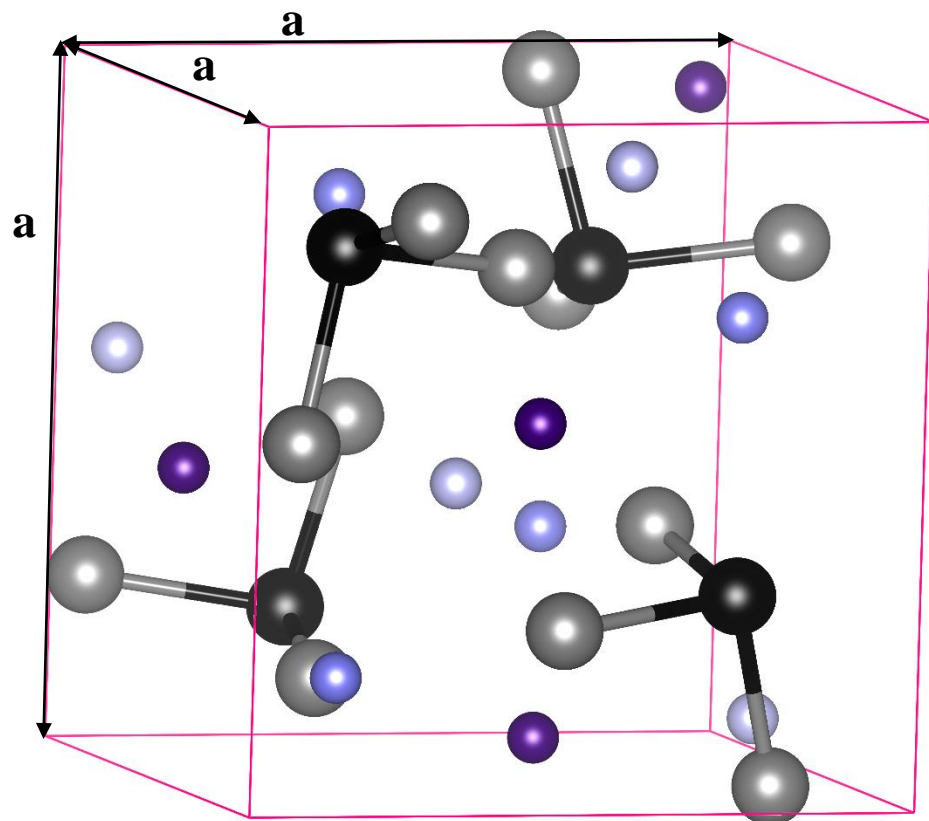


(110) $\text{Na}_3\text{SbS}_4/\text{Na}$ interface DOS



IV. Results

Bulk Na_3SbS_3 (space group $P 2_1 3$)



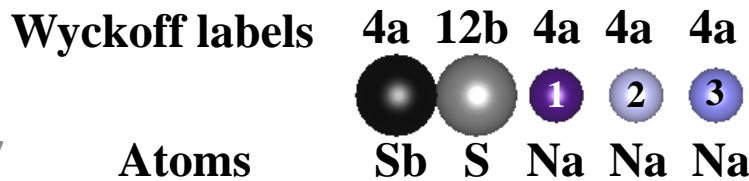
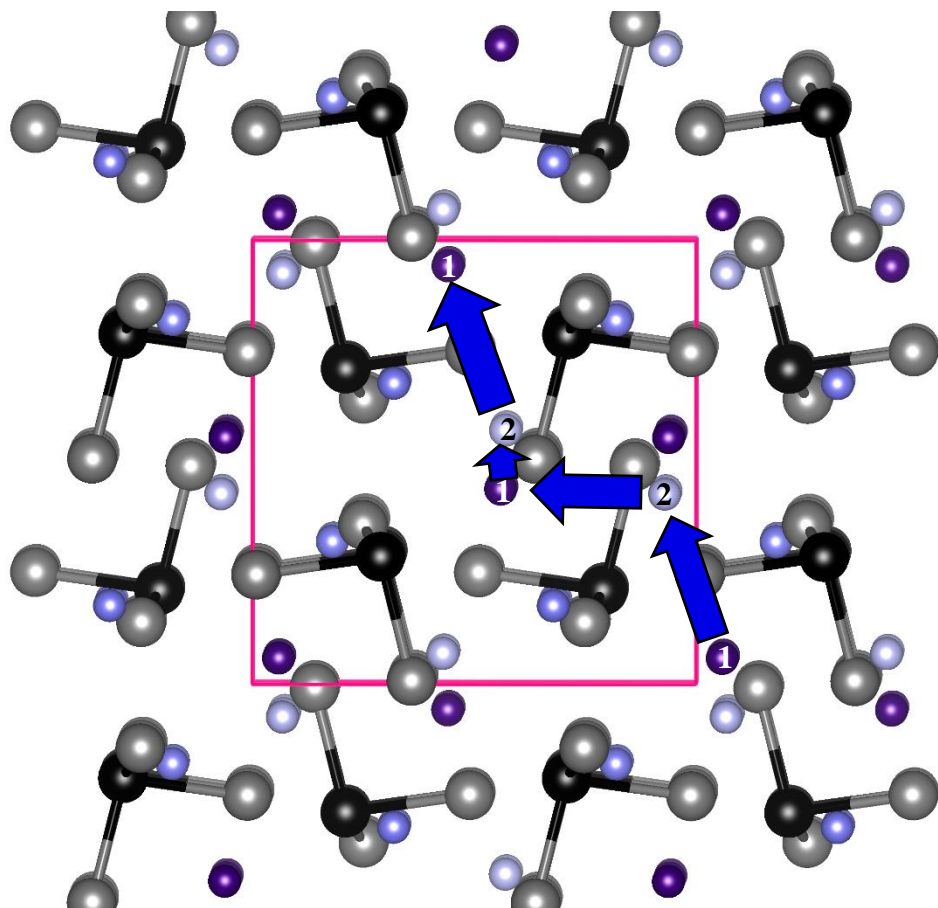
Wyckoff labels

Atoms

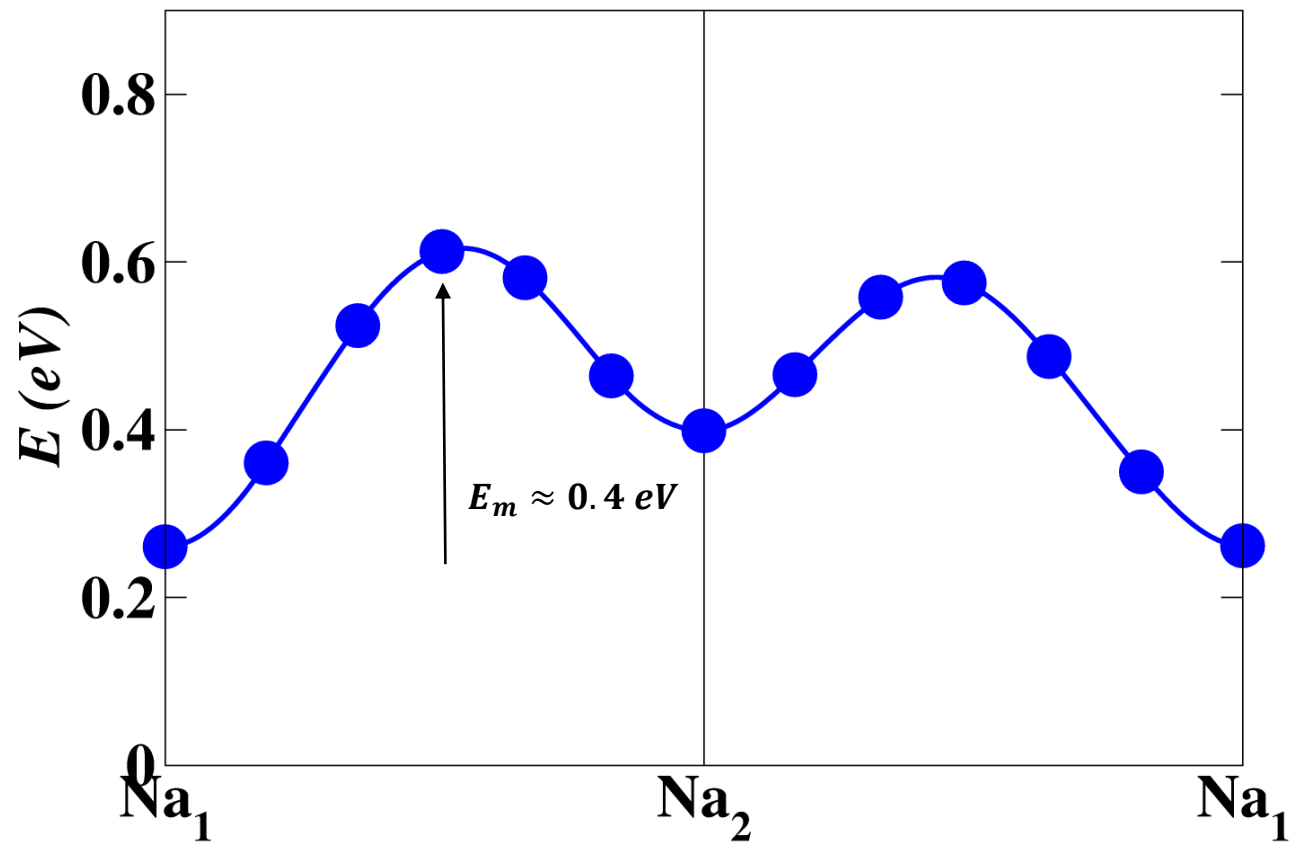
- | | | | |
|---|---|----|---|
| 1 | x, y, z | 5 | z, x, y |
| 2 | $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$ | 6 | $\frac{1}{2} - z, \bar{x}, \frac{1}{2} + y$ |
| 3 | $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ | 7 | $\frac{1}{2} + z, \frac{1}{2} - x, \bar{y}$ |
| 4 | $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ | 8 | $\bar{z}, \frac{1}{2} + x, \frac{1}{2} - y$ |
| | | 9 | y, z, x |
| | | 10 | $\bar{y}, \frac{1}{2} + z, \frac{1}{2} - x$ |
| | | 11 | $\frac{1}{2} - y, \bar{z}, \frac{1}{2} + x$ |
| | | 12 | $\frac{1}{2} + y, \frac{1}{2} - z, \bar{x}$ |

IV. Results

Ball-and-stick model for Na_3SbS_3



NEB calculations



V. Conclusions

- i. Na_3SbS_4 has $E_m \approx 0.05$ eV for a-axis migration
- ii. Na_3SbS_4 is reactive to Na
- iii. Na_3SbS_3 & Na_2S form at the $\text{Na}_3\text{SbS}_4/\text{Na}$ interface (based on DOS)
- iv. Pure Na_3SbS_3 has $E_m \approx 0.4$ eV



Acknowledgements

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Special thanks to Prof. Natalie Holzwarth

