Ab initio Simulations Of A Novel Sodium Superionic Conductor

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MOTIVATION & OBJECTIVE

- Solid electrolytes can enable safer and high-energy density batteries than liquid electrolytes
- Sodium solid electrolytes can help in reducing the shuttling effect , which causes capacity loss in the newly emerging room-temperature Na-S batteries

In the current study, using first-principles simulations, we present a case for a novel composition: $Na_{10}GeP_2S_{12}$ (NGPS), for application in room-temperature Na-S batteries
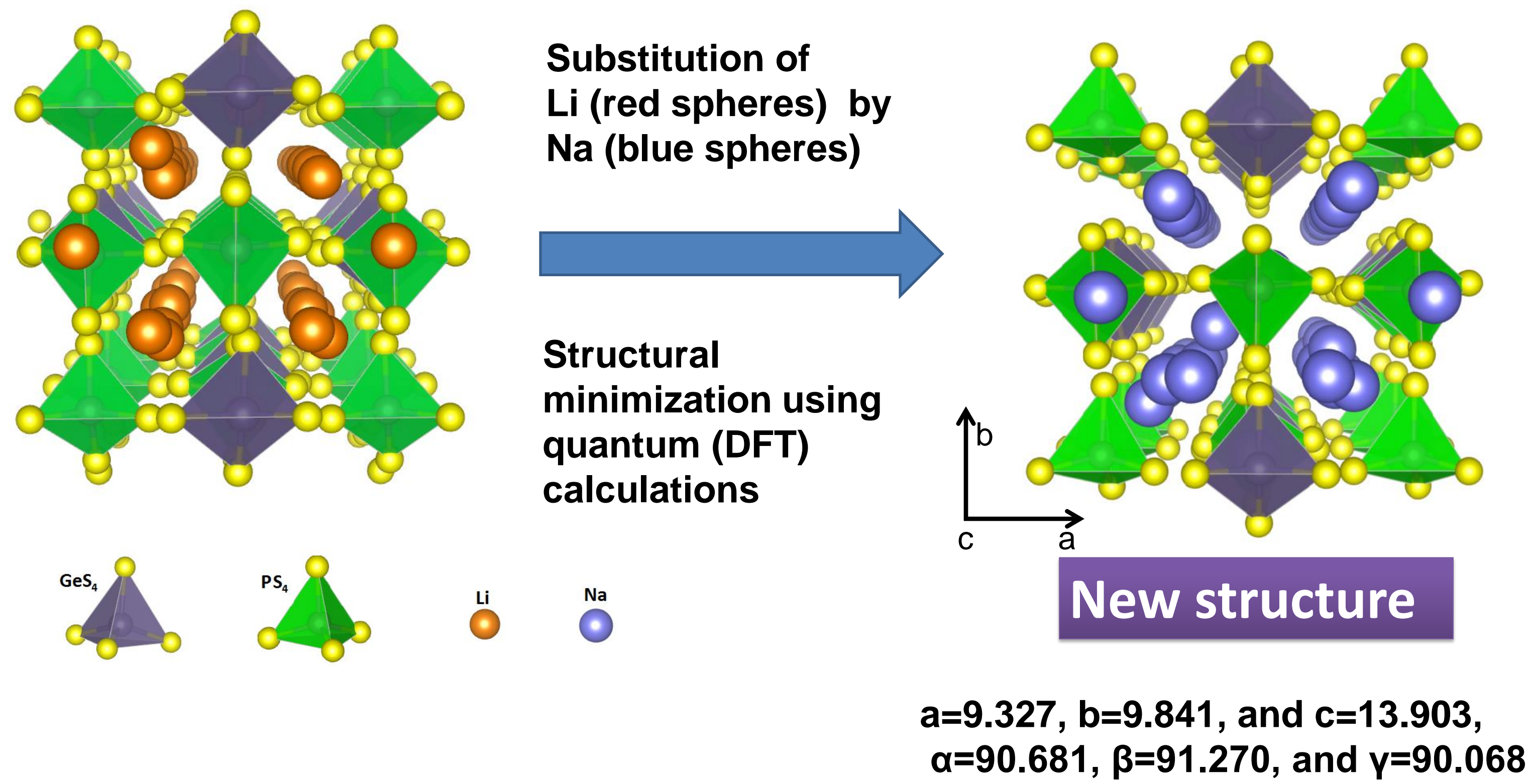
METHODOLOGY

- The structure and Na ion diffusivities in NGPS are determined using quantum Density Functional Theory (DFT) calculations.
- Projector Augmented Wave (PAW)[1,2] method with Perdew-Burke-Ernzerhof (PBE)[3,4] exchange correlation functional as implemented in the Vienna Ab initio Simulation Package (VASP)[5-7] program is used in all the calculations.

I. STRUCTURE AND PHASE STABILITY

What is the structure of the new material?

$Li_{10}GeP_2S_{12}$: A lithium superionic conductor reported in literature[9]

$Na_{10}GeP_2S_{12}$: A potential novel sodium superionic conductor

Substitution of Li (red spheres) by Na (blue spheres)

Structural minimization using quantum (DFT) calculations

New structure

a=9.327, b=9.841, and c=13.903,
α=90.681, β=91.270, and γ=90.068

Is the new material stable?

1. Phonon (vibrational modes) calculations:

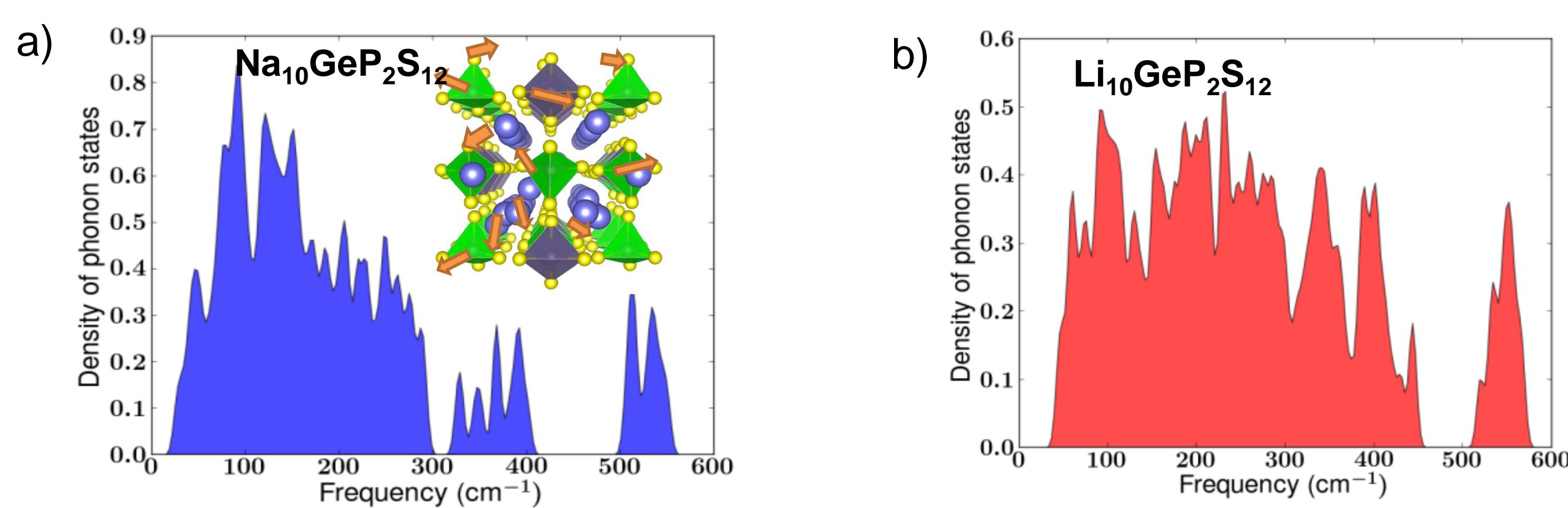**Figure 1.:** Density of states of Γ-point phonons for a) the novel material: $Na_{10}GeP_2S_{12}$, and b) the reported $Li_{10}GeP_2S_{12}$. Vibrational entropies for both materials are further calculated from these phonon density of states (see below).

2. Decomposition reaction energies

	Possible decomposition Reactions of NGPS and LGPS	ΔU_{rexn} Energy (eV/f.u.)
1	$Na_{10}GeP_2S_{12} \longrightarrow 2Na_3PS_4 + Na_4GeS_4$	-0.147
2	$Li_{10}GeP_2S_{12} \longrightarrow 2Li_3PS_4 + Li_4GeS_4$	-0.625 (Ref. 10)

Table 1.: Calculated energies of possible route of decomposition of the predicted material $Na_{10}GeP_2S_{12}$ and $Li_{10}GeP_2S_{12}$

For solids, the free energy can be written as, $\Delta G = \Delta U_{rexn} - T(\Delta S_{config.} + \Delta S_{vib.})$

ΔU_{rexn} : is the decomposition reaction energy (as in Table 1), $\Delta S_{config.}$ is the configurational entropy

$\Delta S_{vib.}$: is the vibrational entropy, and T : is the temperature

From Fig. 1a and 1b, we find that, $\Delta S_{vib.}^{NGPS} > \Delta S_{vib.}^{LGPS}$
$\Delta S_{config.}^{NGPS} \approx \Delta S_{config.}^{LGPS}$

Due to similar structures, $\Delta G^{NGPS} < \Delta G^{LGPS}$

From Table 1., $\left| \Delta U_{rexn}^{NGPS} \right| < \left| \Delta U_{rexn}^{LGPS} \right|$

Since LGPS is stable at room temperature, NGPS can also be stable at same temperature

III. Ab initio molecular dynamics: calculation of Na-ion conductivity

How fast does Na+ ion diffuse?

- Ab initio molecular dynamics calculations were carried out at four different temperatures: 800,1000,1200 and 1400 K to calculate Na-ion diffusivities
- The mean-squared displacements converged in a time interval of 50 ps
- Room temperature Na-ion diffusivity and hence conductivity values are obtained from Arrhenius plot (Fig. 3) by extrapolation.
- The following equations are used for diffusivity and conductivity calculations:

$$D = \frac{1}{2d} \frac{< (r(t+t_0))^2 - (r(t_0))^2 >}{t}$$

$$\sigma = \frac{c_i z_i^2 F^2 D}{RT}$$

$$\sigma = \sigma_0 \exp\left(-\frac{E_A}{R}\right)$$

Where c_i is the Na-ion concentration in the compound z_i is the magnitude of charge on Na ion, F is the Faraday's constant; R is the gas constant T is the temperature, D is the diffusivity coefficient, σ is the conductivity, E_A is the activation energy and Δt denotes a timestep in MD simulation.

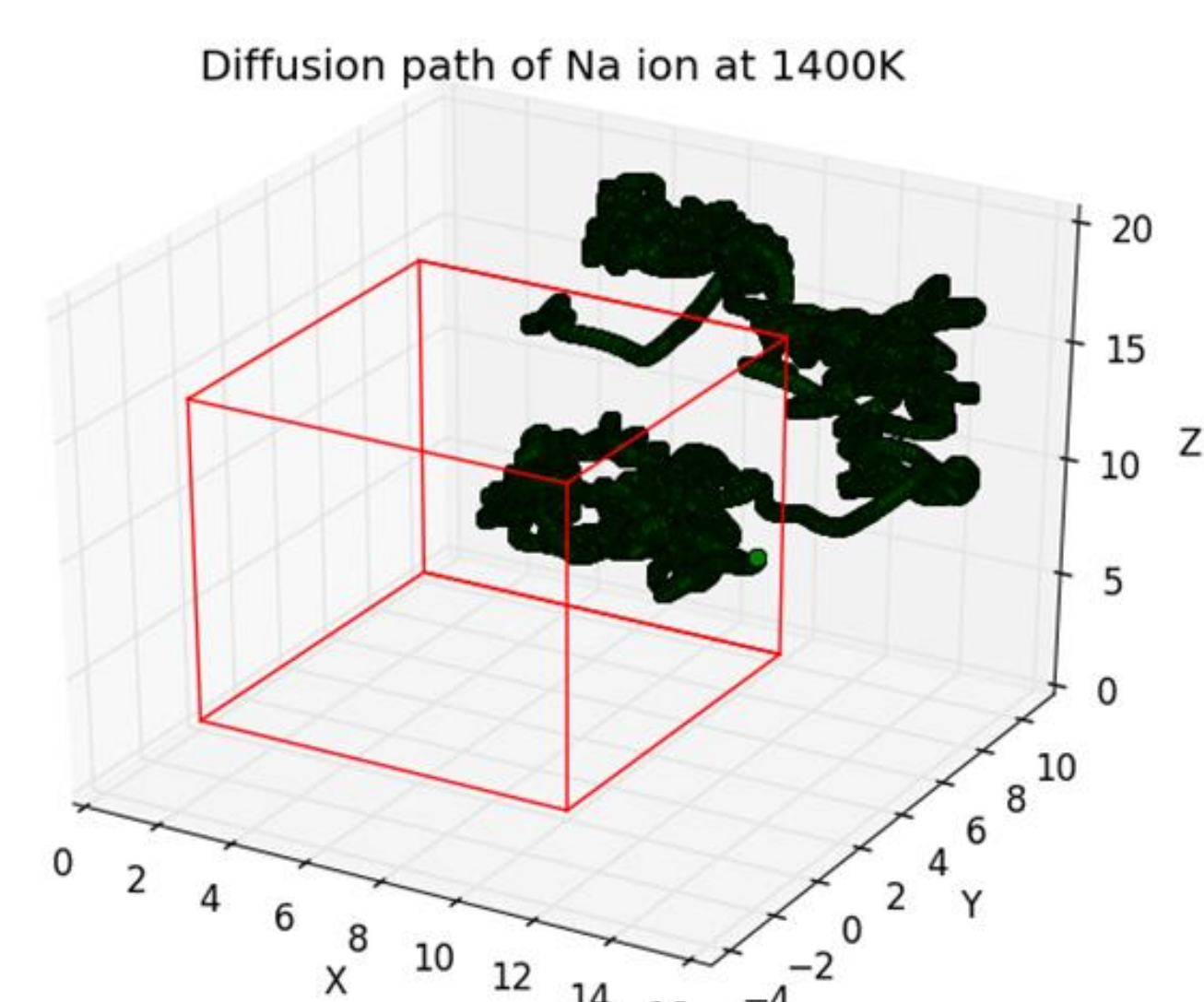Diffusion path of Na ion at 1400K

Figure 2: Trajectory of diffusion of a Na-ion as calculated from ab initio MD at 1400 K. The box represents the simulation cell.
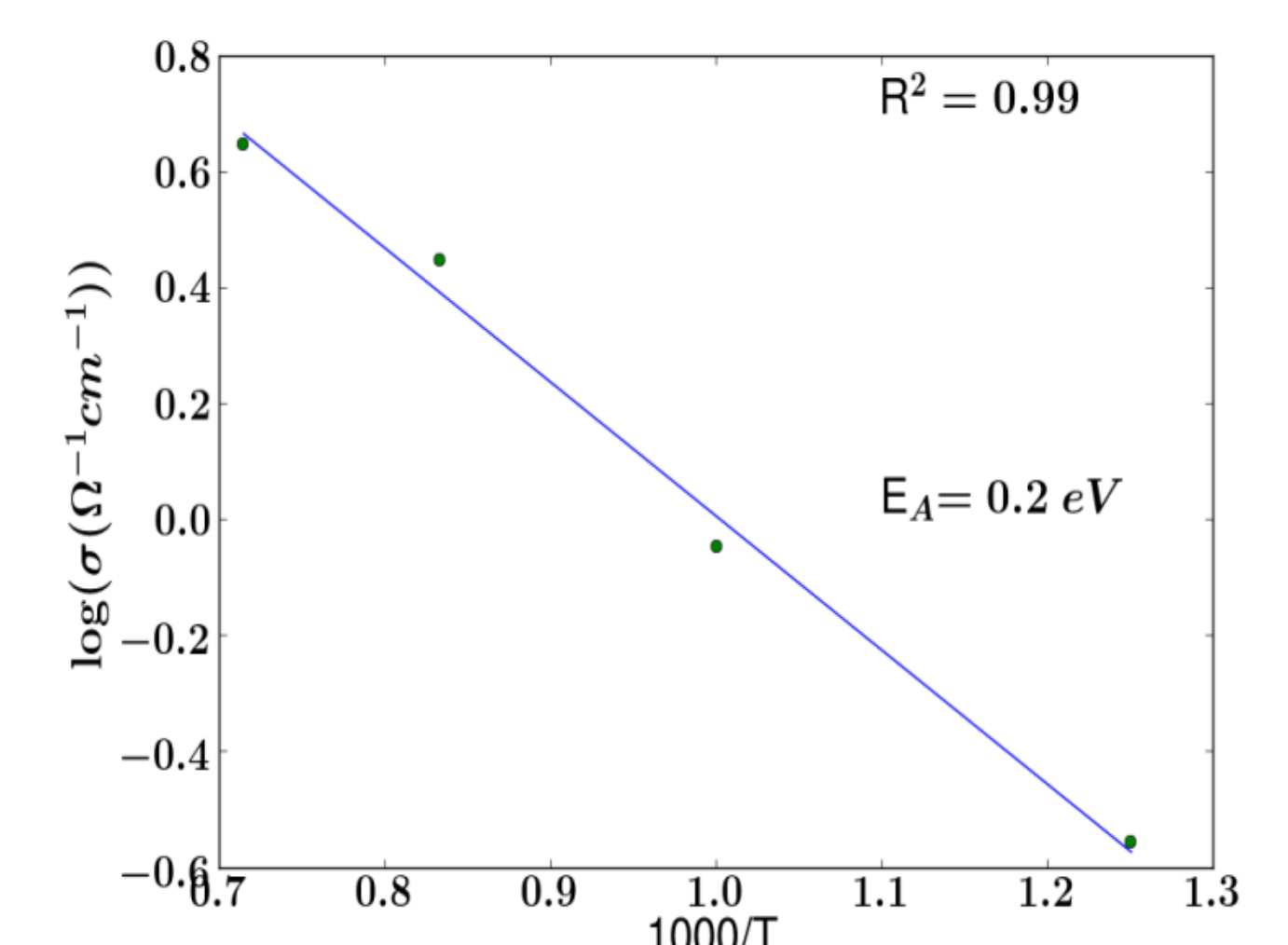
Figure 3: Arrhenius plot of Na-ion conductivity as a function of temperature

Name of the sodium conductor	Conductivity mS cm⁻¹ 25 ˚C	Activation energy (eV)	Comment	Reference
Polycrystalline β''-alumina	2	0.15 – 0.26	Used in high-temperature Na-S battery	11
		0.113 (<150 ˚C)		10
$Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (0<x<3) NASICON	3.4	0.32 – 0.38 (< 157 ˚C)	Used in high-temperature Na-S battery	12
		0.13 – 0.24 (> 157 ˚C)		
		0.2 (527 – 1127 ˚C)		13
$Na_{10}GeP_2S_{12}$ (current study)	4.7	0.2 (> 527 ˚C)		
$94Na_3PS_4 . 6NaSiS_4$	0.74	0.28	Highest reported conductivity for a sulfide electrolyte	14
Na_3PS_4 (glass ceramic)	0.2	0.416	Enabled all-solid-state room-temperature Na-S battery	15

Table 2. : Comparison of room temperature conductivities of NGPS with other sodium electrolytes currently being used/studied. NASICON stands for sodium (NA) Super Ionic CONductor.

Conclusion:

- Our calculations show that the new material can be stable, has an electrochemical window of 2.7 V and exhibit high Na-ion conductivity
- The room-temperature conductivity value of 4.7 mScm⁻¹ is higher than other superionic solid electrolytes such as β''-alumina and $Na_3Zr_2Si_2PO_{12}$, currently used in practical high-temperature Na-S batteries
- Hence the predicted material is worth pursuing for experimental studies

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