SUPPLEMENTARY INFORMATION

Theoretical prediction of a highly conducting solid electrolyte for sodium battery: $Na_{10}GeP_2S_{12}$

Vinay S. Kandagal*[a], Mridula Dixit Bharadwaj[a] and Umesh V. Waghmare[b]

[a]*Center for Study of Science Technology and Policy, 10th cross Mayura street, Papanna Layout, Nagashettihalli, Bengaluru, Karnataka 560094, India. Email: vinayk@cstep.in*
[b]*Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru, Karnataka 560064, India.*

1. Structural optimization of $Na_{10}GeP_2S_{12}$

The convergence thresholds for energy and forces used in geometry optimization are 10^{-7} eV and 10^{-2} eV/ Å respectively.

Total energy of the system converged within 1 meV/atom at an energy cut-off of 600 eV.

A uniform mesh of 2x2x2 k-points is used for all calculations. The difference in total energy when a 3x3x3 mesh is used is of the order of only 10^{-4} eV/atom. Hence the former is used to reduce the computational cost. Furthermore, number of grid points in the FFT mesh is adjusted appropriately to reduce FFT related errors.

Γ-point phonons and electronic density of states of the optimized structure are calculated using the same energy cut-off (600 eV) and k-points as mentioned above.

2. Ab initio molecular dynamics

Initially, the MD simulations are carried out to calculate Li^+ diffusivities in $Li_{10}GeP_2S_{12}$. Noting that that our results are in good agreement with the values reported in the literature (Mo et al., *Chem. Mater.*, 2012, **24**, 15–17), the same methodology is then used for studying $Na_{10}GeP_2S_{12}$ (NGPS).

To reduce the computational cost, energy cut-off of 300 eV has been used which is lower than 600 eV – the cut-off used for structural optimization. It is seen that a structural distortion resulting from displacing an atom by 0.04 Å in each of the three axes directions results in similar change in total energy calculated with both energy cut-offs, and hence forms the basis for choosing the lower cut-off.

A uniform mesh of 2x2x2 k-points is used in all MD calculations.

All calculations have been performed with VASP program (version 4.6.36). The structure of NGPS, consisting of unit cell (50 atoms), is initially heated from 100 K to temperatures ranging from 800 to 1400 K, at a rate of 250 K/ps. With a time-step of 2 fs, the structure is later relaxed for 20 ps, and further run for 50 ps for calculation of diffusivities. Nose-Hoover thermostat is used for controlling temperature.

The error bars for Na-ion diffusivities and conductivities are evaluated by block averaging method.