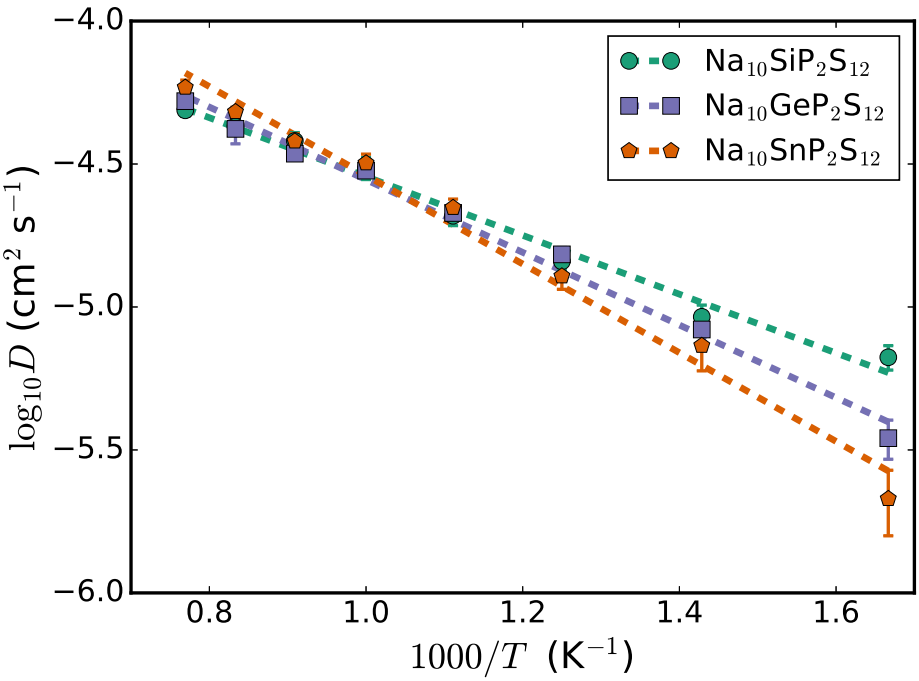
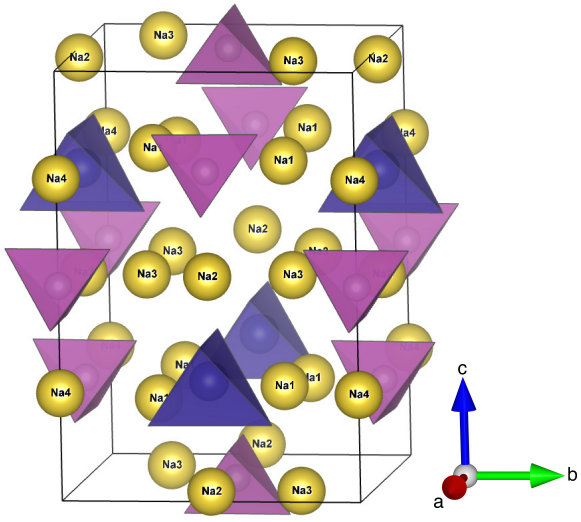
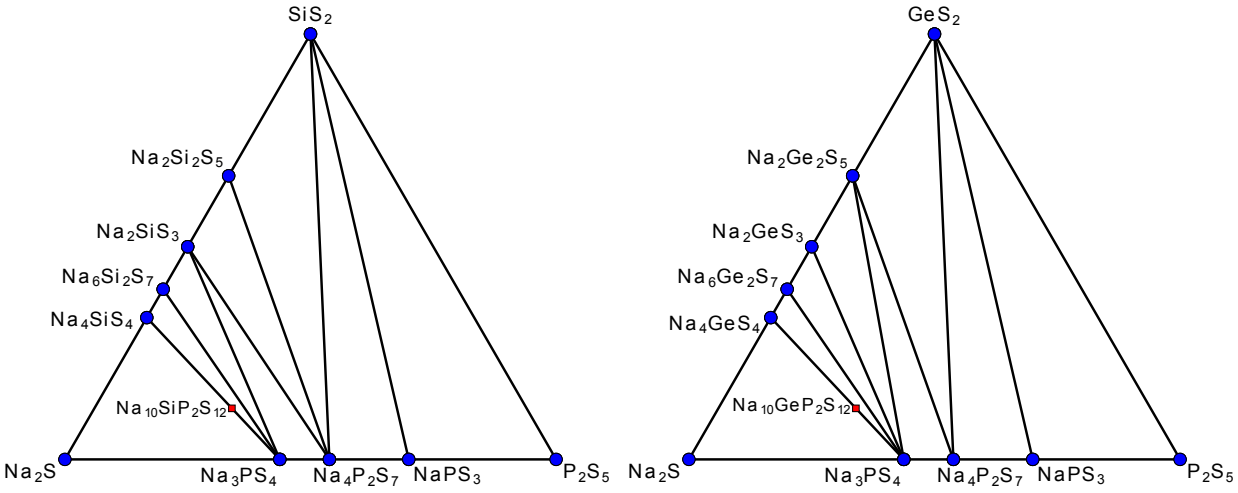
## Supplementary Figures




Supplementary Figure 1: Na self-diffusivity $D_{\text{self}}$ in $Na_{10}SiP_2S_{12}$, $Na_{10}GeP_2S_{12}$, and $Na_{10}SnP_2S_{12}$ from AIMD simulation

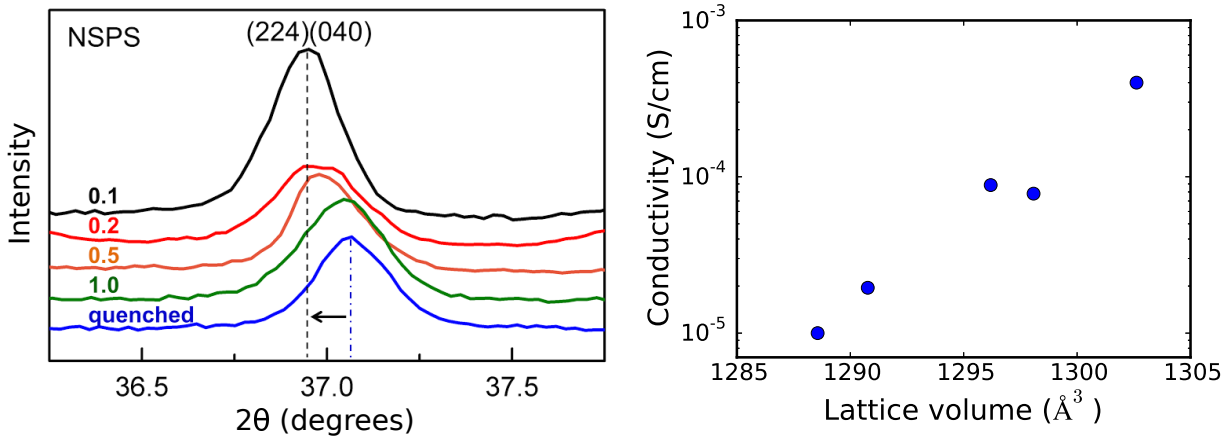



Supplementary Figure 2: $C222$ symmetry ground state ordering of Na atoms for the NMPS phases. Labels on the Na-atoms correspond to those of the $P4_2/nmc$ space group disordered structure.



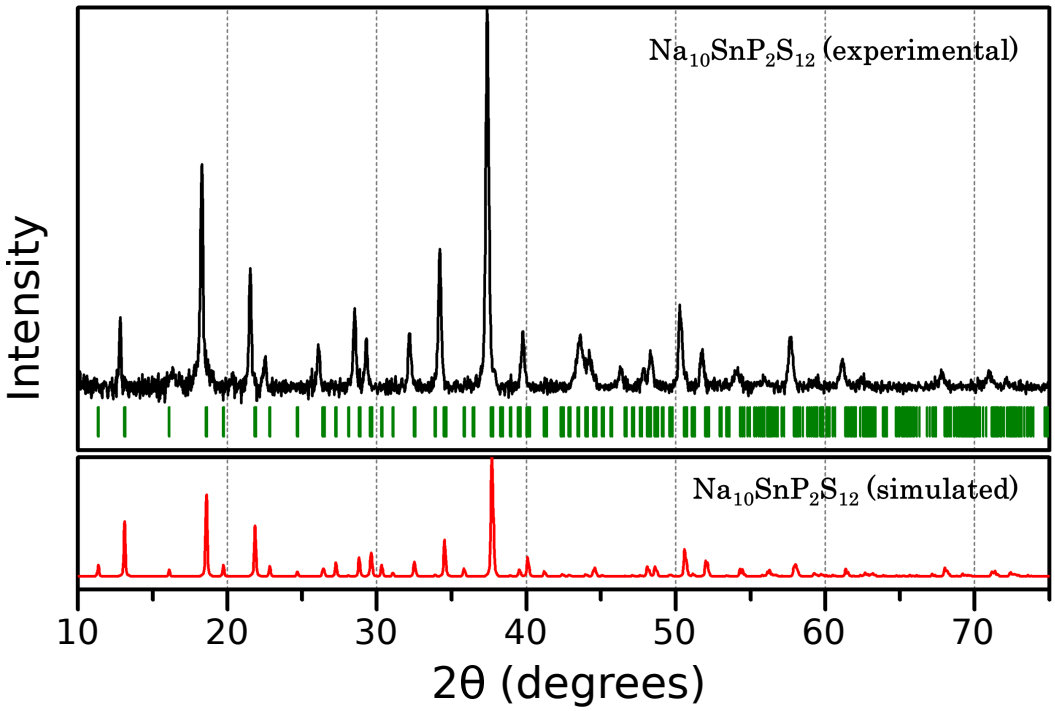

(a) (b)

Supplementary Figure 3: Pseudo-ternary 0K phase diagrams for the a) $Na_2S$-$SiS_2$-$P_2S_5$ and b) $Na_2S$-$GeS_2$-$P_2S_5$ chemical systems, computed from DFT energy calculations.




(a) (b)

Supplementary Figure 4: a) Main peak position for cooling rates of 0.1, 0.2, 0.5, and 1.0 K $min^{-1}$, and a quenched sample. Lattice volume increases as cooling rate is lowered b). Measured conductivity vs. lattice volume for these samples.




Supplementary Figure 5: Experimental and simulated XRD patterns of quenched $Na_{10}SnP_2S_{12}$.

## Supplementary Tables

| Compound | $E_a$ (eV) | Self diffusivity $D_{self}$ at 298 K ($cm^2$ $s^{-1}$) |
|---|---|---|
| $Na_{10}SiP_2S_{12}$ | 0.204 | $1.13 \times 10^{-7}$ |
| $Na_{10}GeP_2S_{12}$ | 0.252 | $2.97 \times 10^{-8}$ |
| $Na_{10}SnP_2S_{12}$ | 0.307 | $6.94 \times 10^{-9}$ |

Supplementary Table 1: Calculated self diffusivity $D_{self}$ of $Na_{10}MP_2S_{12}$ (M = Si, Sn, Al). Note that the differences between these activation energies and the activation energies of $D_{corr}$ listed in table 1 are not statistically significant.

| Cation (M) | a (Å) | c (Å) |
|---|---|---|
| Si | 9.60 | 13.53 |
| Ge | 9.62 | 13.59 |
| Sn | 9.68 | 13.63 |

Supplementary Table 2: DFT calculated lattice parameters for tetragonal $Na_{10}MP_2S_{12}$ (M = Si, Ge, Sn).