Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary information for: Design of $Li_{1+2x}Zn_{1-x}PS_4$, a new lithium ion conductor

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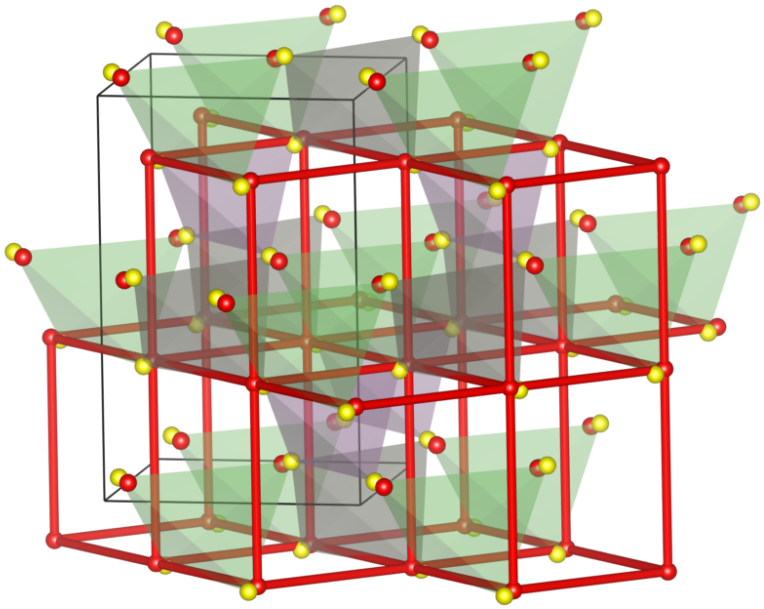
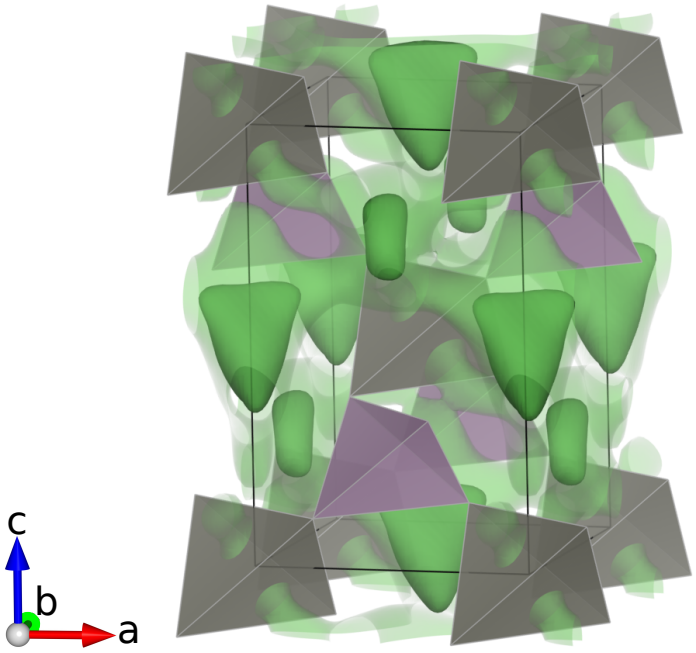
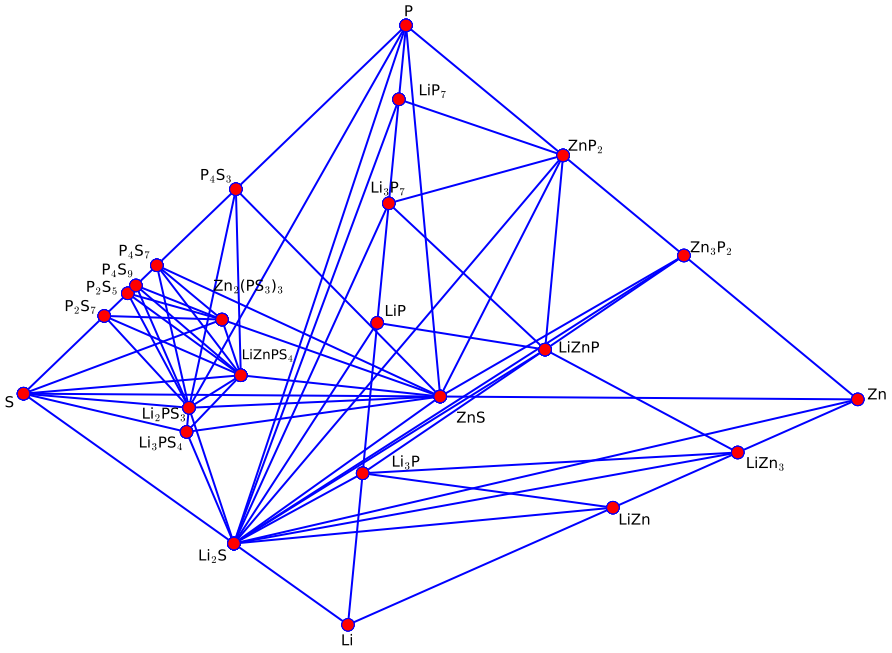


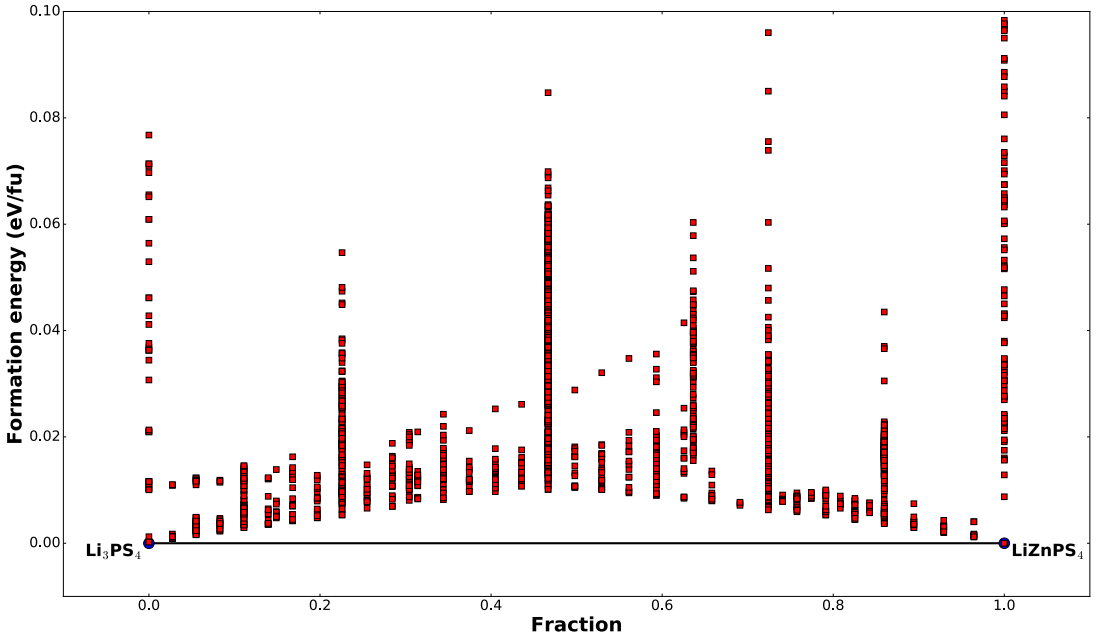
Supplementary Figure 1: Ideal body-centered-tetragonal (bct) lattice (red) with an a/c ratio of 0.90 overlaid on the sulfur framework (yellow) of $Li_{1+2x}Zn_{1-x}PS_4$. Transparent tetrahedra are: PS_4 (purple), ZnS_4 (grey), and LiS_4 (green). The sulfur atoms are each displaced 0.29 Å from the idealized bct position



Supplementary Figure 2: Representative Li-ion probability density isosurfaces in LZPS, calculated from AIMD of $Li_{1.25}Zn_{0.875}PS_4$ at 800 K and projected onto the conventional cell. Since there is some Li_{Zn} occupancy, some diffusion occurs through the Zn site (grey tetrahedra). The high-probability regions (dark green) correspond to the tetrahedral lithium sites shown in Figure 1b. The lower probability (lighter transparent green) regions show the Li-ion conducting pathways through the crystal structure.

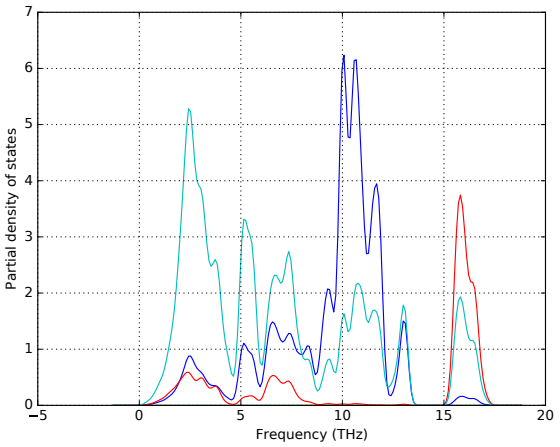


(a)

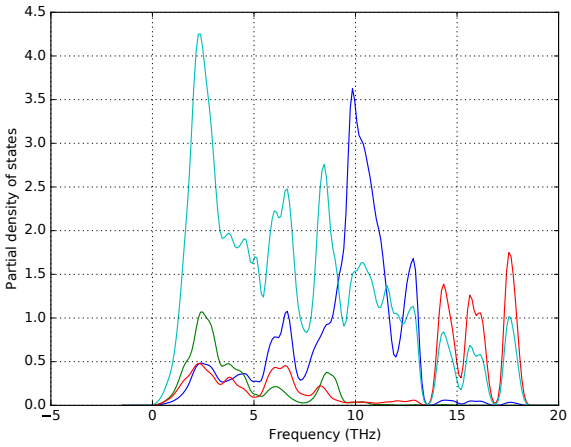


(b)

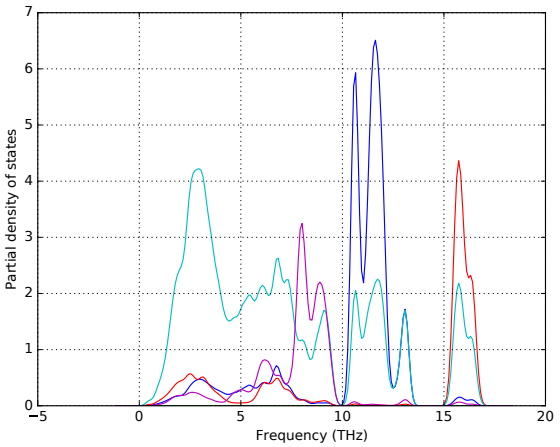
Supplementary Figure 3: a) DFT calculated 0 K phase diagram of the Li-Zn-P-S chemical system. Note the tieline between the $LiZnS_4$ and Li_3PS_4 compositions indicating their coexistence. b) DFT calculated formation energies of calculated structures along the $LiZnS_4$-Li_3PS_4 tieline. These structures were generated either with the cluster expansion Monte Carlo simulation or the ionic substitution algorithm from known materials in other chemical systems.



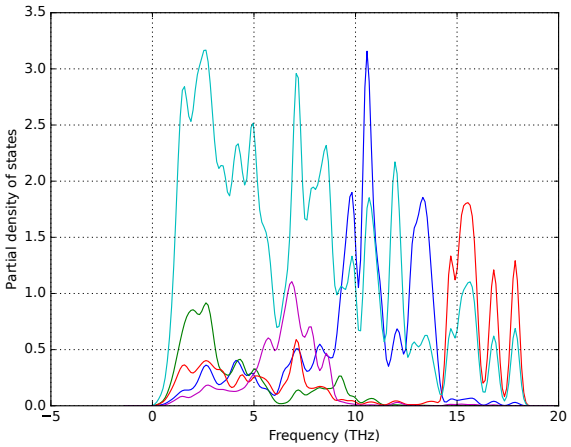
(a)



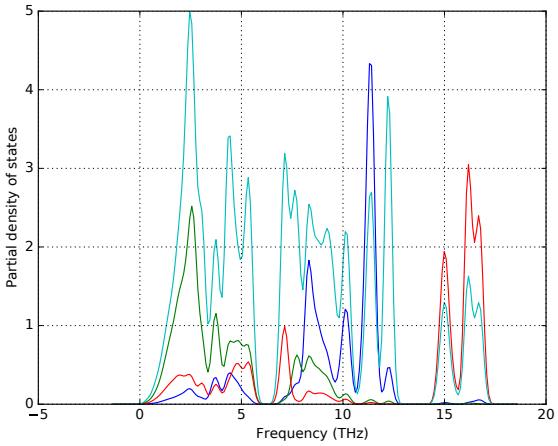
(b)



(c)

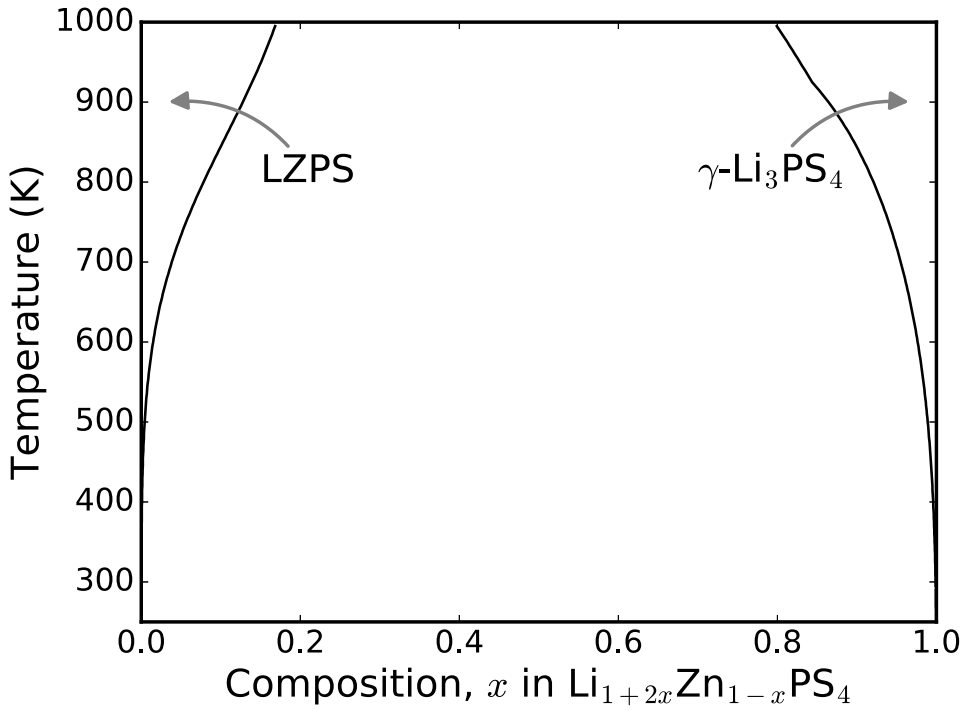


(d)



(e)

Supplementary Figure 4: Partial phonon densities of states for a) $Pmn2_1$ Li_3PS_4, b) $Pmn2_1$ $Li_2Zn_{0.5}PS_4$, c) $I\bar{4}$-Li_3PS_4, d) $I\bar{4}$ $Li_2Zn_{0.5}PS_4$, and e) $I\bar{4}$ $LiZnPS_4$. Blue – Li in the Li/Zn layer or in the $Pmn2_1$ structure. Green – Zn. Red – P. Teal – S. Purple – Li in the Li/P layer in the $I\bar{4}$ structure.



Supplementary Figure 5: Pseudo-binary phase diagram of the $LiZnPS_4$–γ-Li_3PS_4 system, generated from cluster expansion Monte Carlo calculations excluding the phonon contributions to the free energy.