Supplementary material

Li-ion site disorder driven superionic conductivity in solid electrolyts: A first-principles investigation of $\beta - Li_3PS_4$

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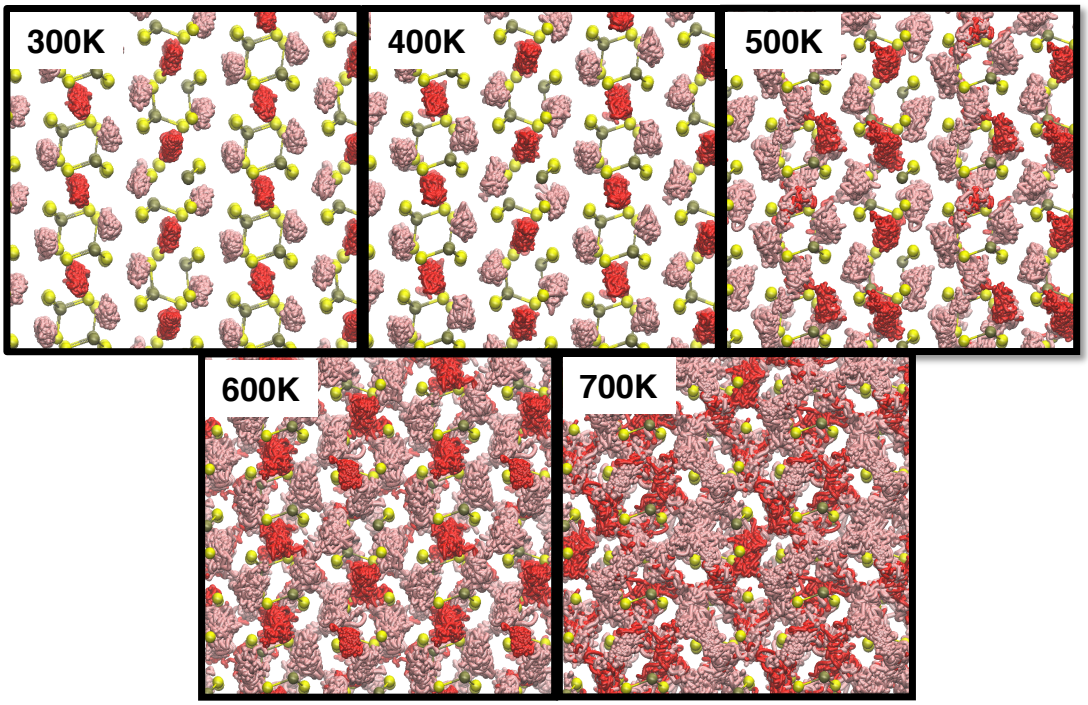

Figure S1: The figure shows the overlapped trajectories of lithium in the 4d (red) and the 2b/2c (pink) sites at different temperatures starting from the ground state lithium occupancies. A clear melting of the lithium sublattice is seen at 600K and above.

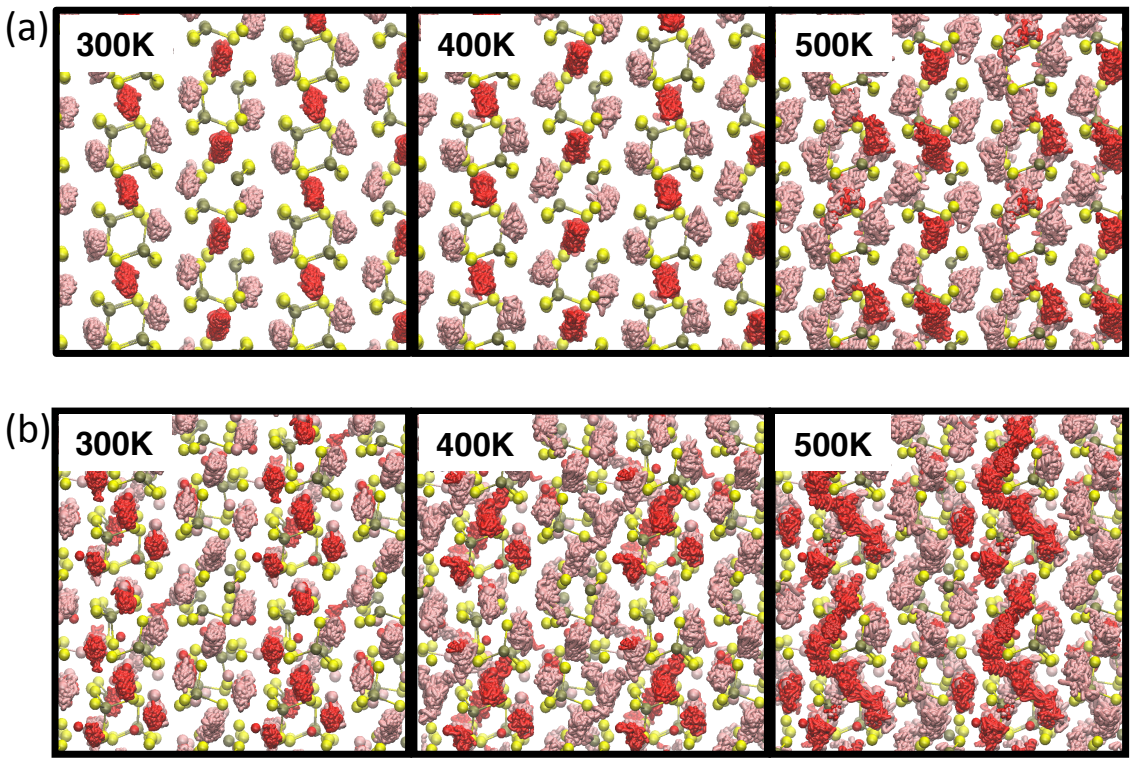

Figure S2: (a) The figure shows the overlapped trajectories of lithium in the 4d (red) and the 2b/2c (pink) sites at the lowest three different simulated temperatures starting from (top row) the ground state lithium occupancies and (bottom row) from a 900K temperature quenched structure with disordered liquid-like lithium positions. The simulations starting from disordered liquid-like lithium positions show increased diffusion over the same 60ps time interval. (b) This compares the total energy of the simulation at 300K starting from the two different configurations. The average energies and their fluctuations are very similar suggesting that the structure with increased lithium diffusion would have a lower free energy due to its increased entropy. This again underscores that the increased diffusivity in β - Li_3PS_4 is due to a liquid-like disordered lithium sublattice.

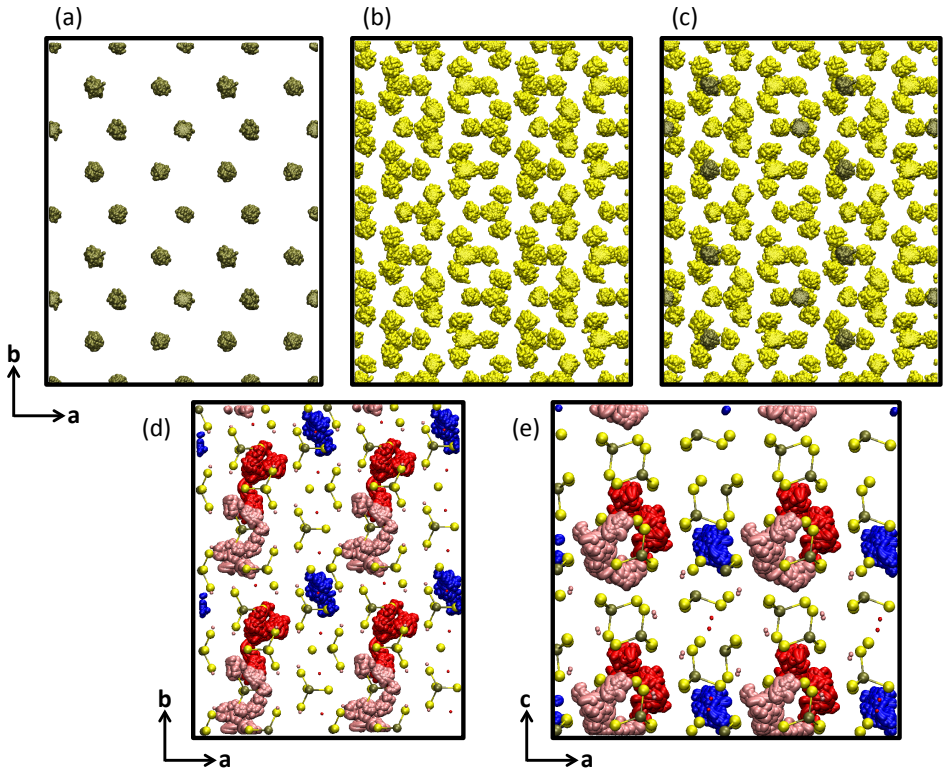

Figure S3: The figure shows only the overlapped trajectories of (a) phosphorous, (b) sulphur and (c) PS_4-anion atoms at 600K. The molecular unit is very much intact as the lithium atoms in (d) and (e) diffuse clearly suggesting a sublattice melted β - Li_3PS_4 phase.