Supplementary Information

Investigation of the effect of O doping on the Li-ion mobility of Li_3PS_4 solid-state electrolytes: an *ab initio* molecular dynamics study

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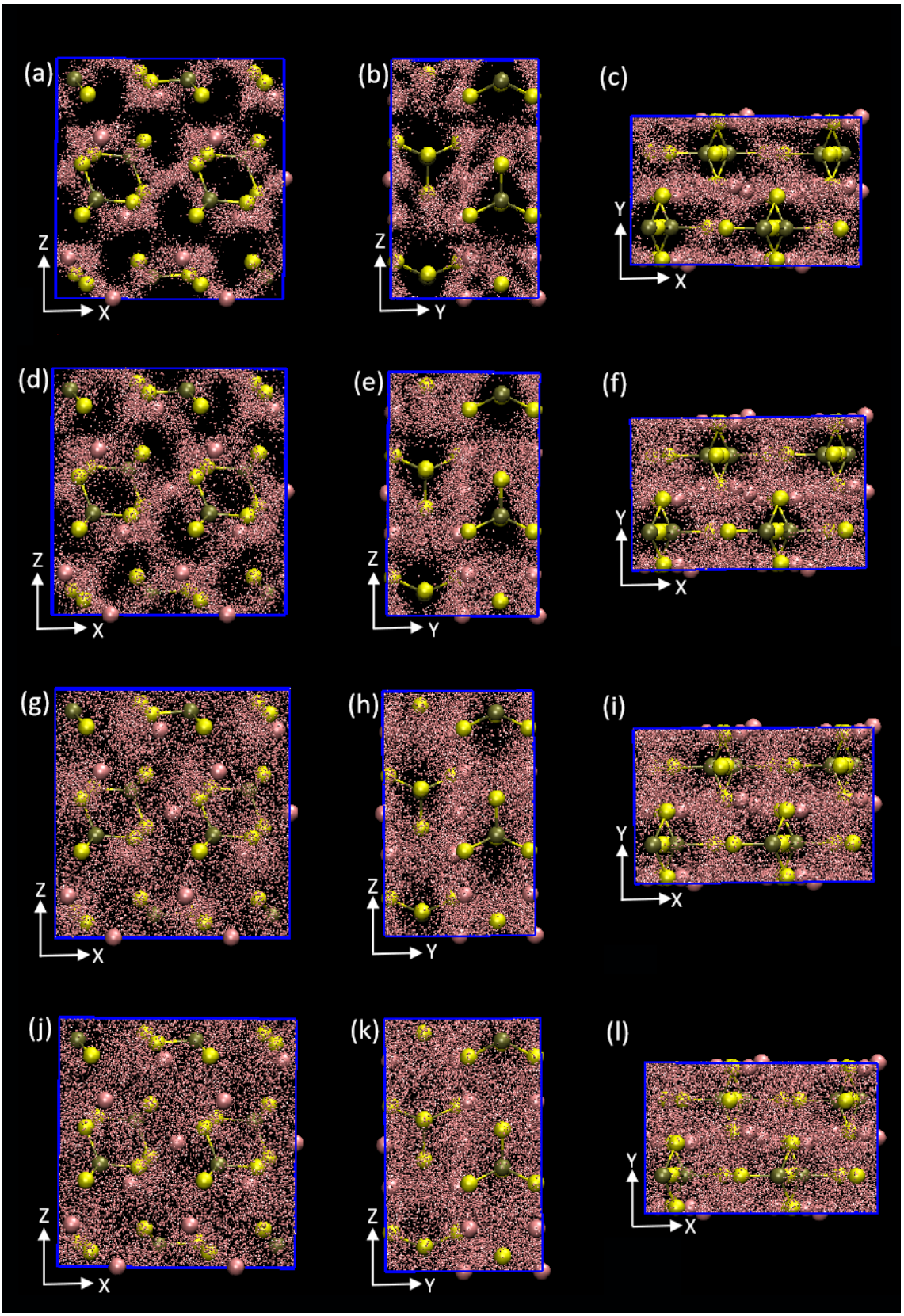

Figure S1. Trajectories (small pink balls) of Li ions (large pink balls) during AIMD simulations of Li_3PS_4. (a-c) 600 K, (d-f) 900 K, (g-i) 1200 K, and (j-l) 1500 K.

Colour set: brown, phosphorus; yellow, sulfur; pink, lithium; red, oxygen.

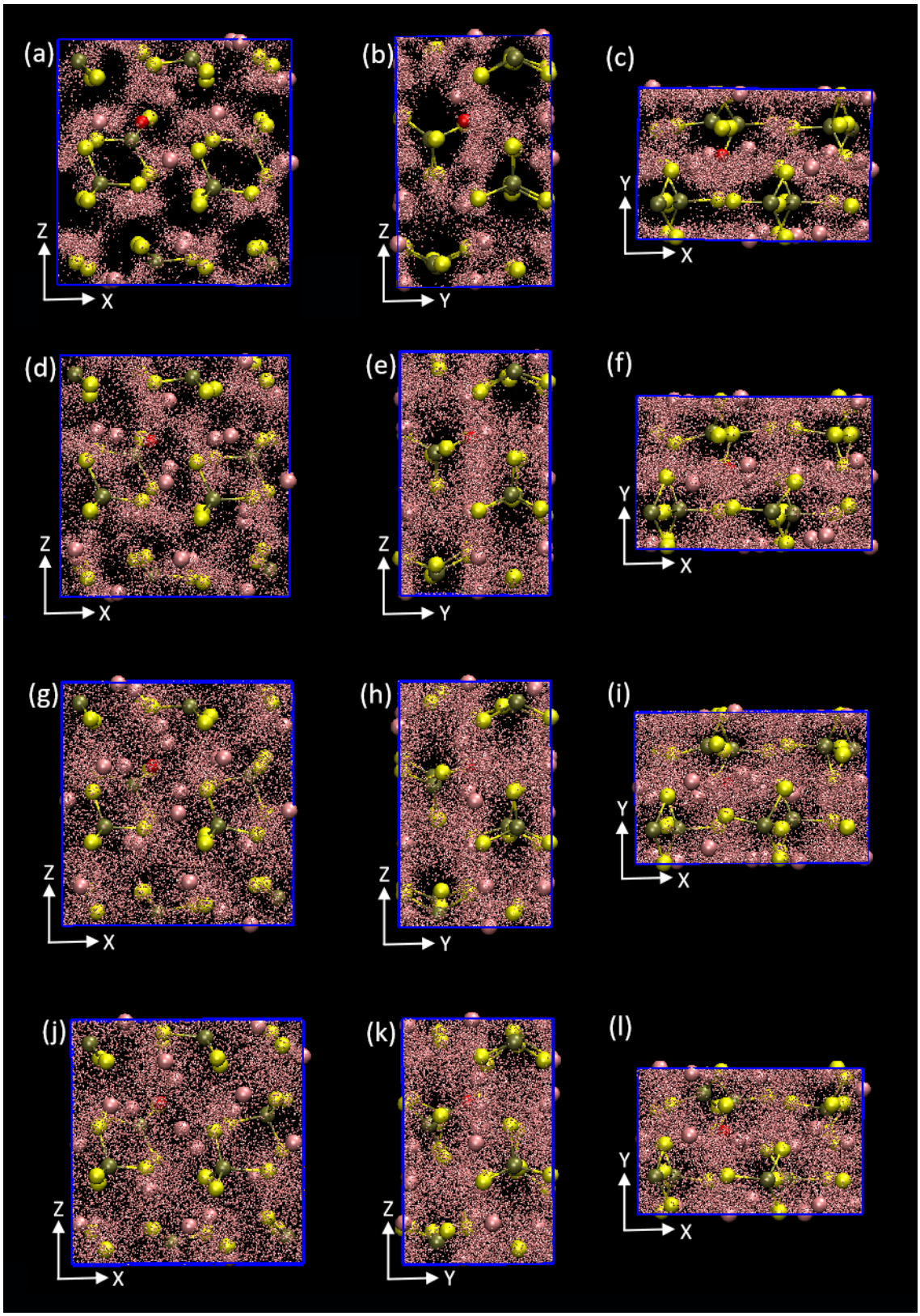

Figure S2. Trajectories (small pink balls) of Li ions (large pink balls) during AIMD simulations of O-doped Li_3PS_4. (a-c) 600 K, (d-f) 900 K, (g-i) 1200 K, and (j-l) 1500 K.

1 Procedure to obtain the diffusion coefficient using VASPKIT

VASPKIT → 722 (Mean Squared Displacement (MSD) Using FFT Method) → Li → 1000 (Skip the initial 1000 frames) → 1 (Every frame is used to calculate MSD) → MSD.dat

VASPKIT → 723 (Diffusion Coefficient and Ion Mobility from MSD.dat File) → 40000 (40,000 time steps were used to fit) → 1 (Ionic valency) → Diffusion coefficient

Table S1 The data of diffusion coefficient (*D*) of Li-ions of undoped Li_3PS_4 (unit:$cm^2 \cdot S^{-1}$)

Temperature	600 K	900 K	1200 K	1500 K
D in x direction	0.1599E-04	0.5526E-04	0.1402E-03	0.1746E-03
D in y direction	0.6425E-05	0.3008E-04	0.8425E-04	0.2680E-03
D in z direction	0.1110E-04	0.4778E-04	0.1023E-03	0.2186E-03
Average D	0.1117E-04	0.4437E-04	0.1089E-03	0.2204E-03

Table S2 The data of diffusion coefficient (*D*) of Li-ions of O-doped Li_3PS_4 (unit:$cm^2 \cdot S^{-1}$)

Temperature	600 K	900 K	1200 K	1500 K
D in x direction	0.1559E-04	0.4359E-04	0.1129E-03	0.1528E-03
D in y direction	0.1113E-04	0.5810E-04	0.1322E-03	0.1935E-03
D in z direction	0.9798E-05	0.3191E-04	0.1164E-03	0.1265E-03
Average *D*	0.1217E-04	0.4453E-04	0.1205E-03	0.1576E-03

2 The calculation process of ionic conductivity

Diffusion Coefficient $$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

Ionic Mobility $$\mu = \frac{Dq}{k_B T}$$

Ionic Conductivity $$\sigma = \frac{NDq^2}{k_B T}$$

Arrhenius' formula $$\log D = \log D_0 - \frac{E_a}{2303 k_B}\left(\frac{1000}{T}\right)$$

where D is the diffusion coefficient, μ is the ionic mobility, σ is the ionic conductivity, D_0 is the pre-exponential factor, E_a is migration barriers, T is the temperature, k_B is Boltzmann constant, q is the ionic charge and N is the number of mobile ions per unit volume.

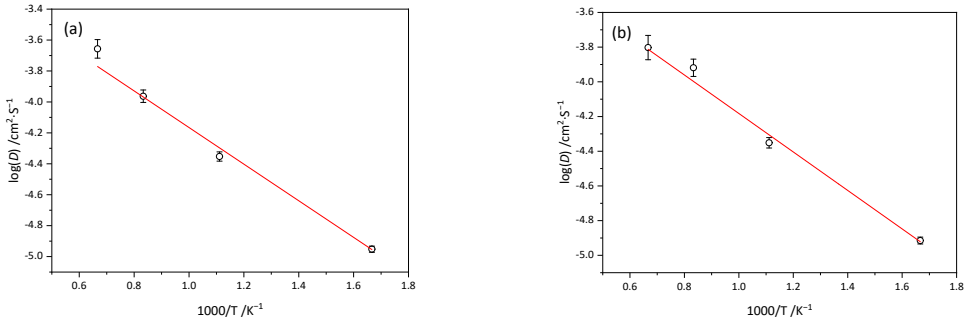

Figure S3. Arrhenius plots of Li_3PS_4 (a) and O-doped Li_3PS_4 (b).

(a) Li_3PS_4

$$\log D = -1.1837 \times \left(\frac{1000}{T}\right) - 2.9819 \qquad r^2=0.9914$$

T = 300 K

$$D = 10\text{^}(-1.1837 \times \left(\frac{1000}{300}\right) - 2.9819) = 1.1815 \times 10^{-7}\ cm^2 \cdot S^{-1}$$

$$\sigma = \frac{24 \times (1.1815 \times 10^{-7}) \times 1^2}{8.6173 \times 10^{-5} \times 300} = 1.10 \times 10^{-4}\ S \cdot cm^{-1}$$

(b) O-doped Li_3PS_4

$$\log D = -1.1090 \times \left(\frac{1000}{T}\right) - 3.0734 \qquad r^2=0.9883$$

T = 300 K

$$D = 10\text{^}(-1.1090 \times \left(\frac{1000}{300}\right) - 3.0734) = 1.6980 \times 10^{-7}\ cm^2 \cdot S^{-1}$$

$$\sigma = \frac{24 \times (1.6980 \times 10^{-7}) \times 1^2}{8.6173 \times 10^{-5} \times 300} = 1.58 \times 10^{-4}\ S \cdot cm^{-1}$$

Table S3 The experimental data of ionic conductivity of O-doped Li_3PS_4 (unit: $S \cdot cm^{-1}$)

Composition	Ionic conductivity	Ref
β-Li_3PS_4	1.60×10^{-4}	1
$Li_{3.06}P_{0.98}Zn_{0.02}S_{3.98}O_{0.02}$	1.12×10^{-3}	2
$75Li_2S\cdot23P_2S_5\cdot2P_2O_5$	2.72×10^{-4}	3
90-Li_3PS_4 -10$Li_6ZnNb_4O_{14}$	2.44×10^{-4}	4
98-Li_3PS_4 - 2Al_2O_3	2.28×10^{-4}	4
98-Li_3PS_4 - 2SiO_2	1.84×10^{-4}	4

References

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