Supplementary Information for

Hierarchical Approach to Designing a Na-Rich Phosphide Solid-State Electrolyte for Na-Ion Batteries

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The optimized structures of Na_7TaP_4 in A, B, and C phases.

data_A_phase
_chemical_formula_structural 'Na7 (Ta P4)'
_chemical_formula_sum 'Na7 P4 Ta1'
_cell_length_a 13.16471
_cell_length_b 13.16471
_cell_length_c 13.16471
_cell_angle_alpha 90.
_cell_angle_beta 90.
_cell_angle_gamma 90.
_cell_volume 2281.57
_cell_formula_units_Z 8
_space_group_name_H-M_alt 'P a -3'
_space_group_IT_number 205
loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Ta1 0.130600   0.130600   0.130600
P1   0.236556   0.236556   0.236556
P2   0.517956   0.238517   0.469815
Na1 0.364811   0.364811   0.364811
Na2 0.121372   0.397025   0.138964
Na3 0.368911   0.372121   0.111649
#End of data_A_phase

data_B_phase
_chemical_formula_structural 'Na7 (Ta P4)'
_chemical_formula_sum 'Na7 P4 Ta1'
_cell_length_a 13.17179
_cell_length_b 13.17179
_cell_length_c 13.17179
_cell_angle_alpha 90.
_cell_angle_beta 90.
_cell_angle_gamma 90.
_cell_volume 2285.25
_cell_formula_units_Z 8
_space_group_name_H-M_alt 'P -4 3 n'
_space_group_IT_number 218
loop_
_atom_site_label
_atom_site_fract_x

_atom_site_fract_y
_atom_site_fract_z
Na1 0 0.5 0.5
Na2 0.25 0 0.5
Na3 0.233639   0.233639   0.233639
Na4 0.249838   0.235910   -0.017060
Na5 0.265248   0.000000   0.000000
Ta1 0.5 0 0.25
Ta2 0 0 0
P1 0.352354   0.385702   0.103696
P2 0.106383   0.106383   0.106383
#End of data_B_phase

data_C_phase
_chemical_formula_structural 'Na7 (Ta P4)'
_chemical_formula_sum 'Na7 P4 Ta1'
_cell_length_a 9.25166
_cell_length_b 9.25166
_cell_length_c 6.71076
_cell_angle_alpha 90
_cell_angle_beta 90
_cell_angle_gamma 90
_cell_volume 574.40
_cell_formula_units_Z 2
_space_group_name_H-M_alt 'P 42/n m c Z'
_space_group_IT_number 137
loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Ta1 0.750000   0.250000   0.750000
P1 0.750000   0.469320   0.548894
Na1 0.985466   0.014534   0.250000
Na2 0.750000   0.750000   0.829034
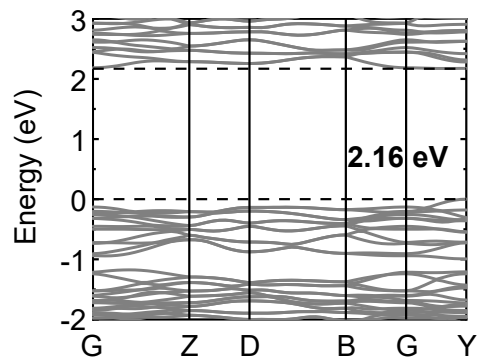Na3 0.250000   0.750000   0.750000
#End of data_C_phase

Figure S1. Calculated band structure of experimental phase of Na_7TaP_4 using the HSE06 hybrid functional.
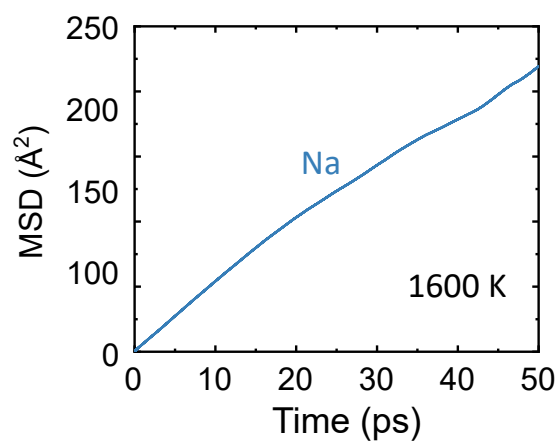

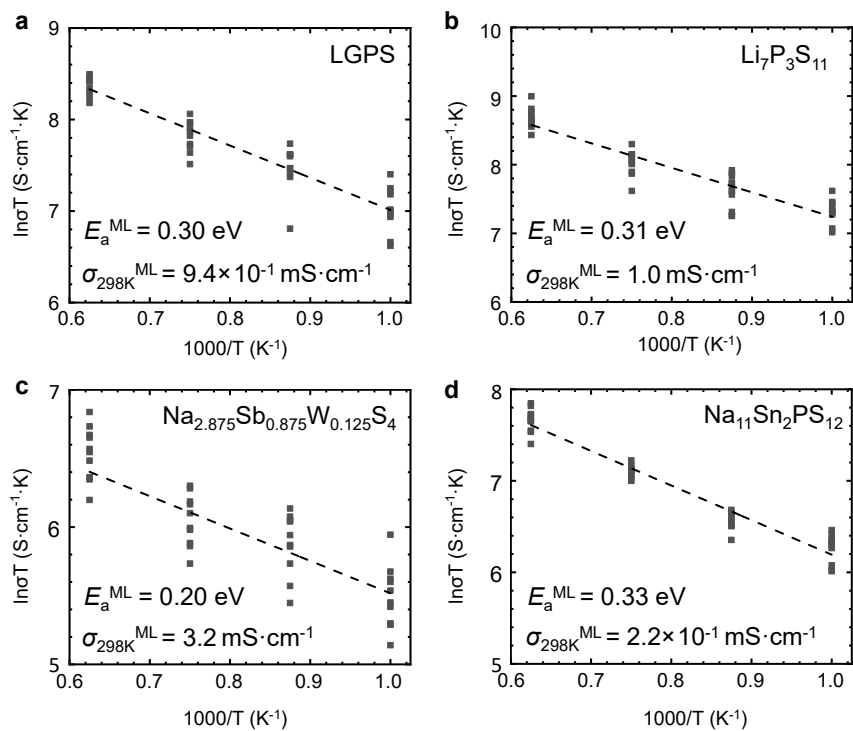**Figure S2.** MSD of Na ions in A phase of Na_7TaP_4 from ML-MD simulation at 1600 K.

Figure S3. The activation energies of some well-known solid-state electrolytes using ML-MD simulations.
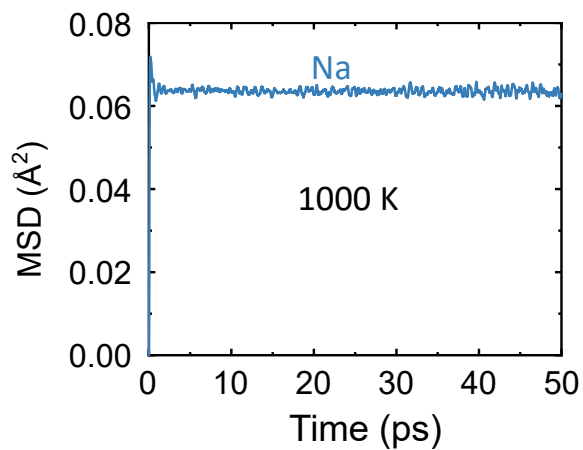

Figure S4. MSD of Na ions in the 96-atom supercell of the experiment phase of Na_7TaP_4 from ML-MD simulation at 1000 K.
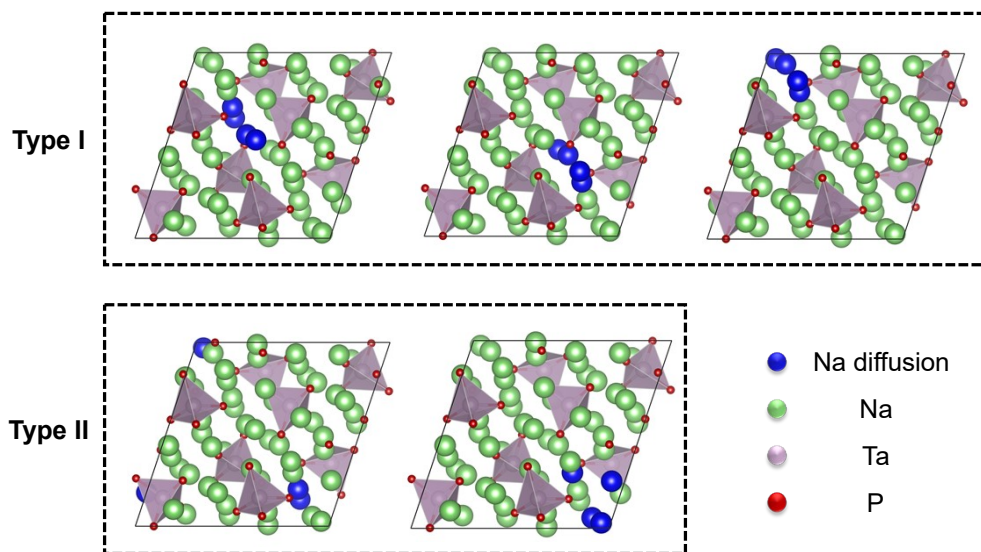
Figure S5. Five different diffusion events when performing MD at high temperatures from 1550 K to 1650 K with 10 K as the sample interval to find the very first step of Na diffusion in experimental phase, classified into two diffusion types according to their diffusion energy barriers. The Na atoms shaded blue engage in the very first step of Na diffusion, changing positions but still maintaining the original crystal structure.
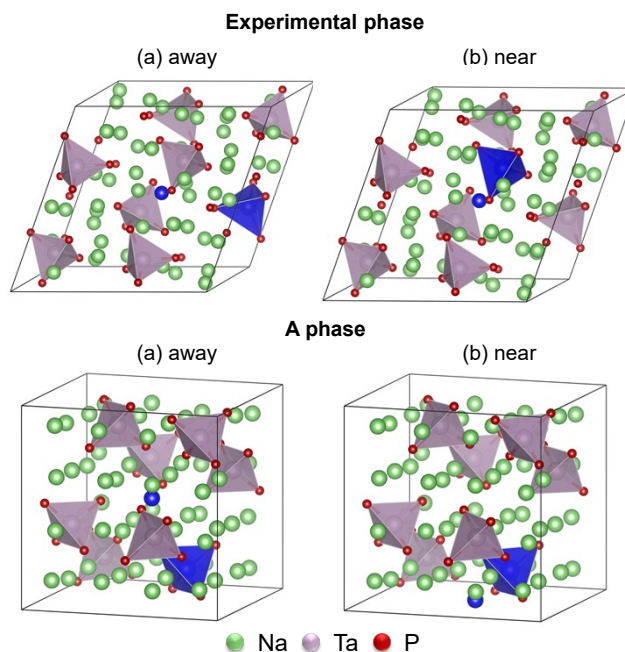
Experimental phase

(a) away (b) near

A phase

(a) away (b) near

Na Ta P

Figure S6. Crystal structures of experimental and A phase of Na_7TaP_4 doping with tetravalent elements (Zr, Hf, Sn, Ti, Ge, Si). A Ta atom is substituted with the tetravalent element and a Na atom is introduced for charge conversation (both highlighted in blue). For experimental and A phase of Na_7TaP_4, two crystal models that (a) the tetravalent element is away from the Na atom and (b) the tetravalent element is near the Na atom are considered.
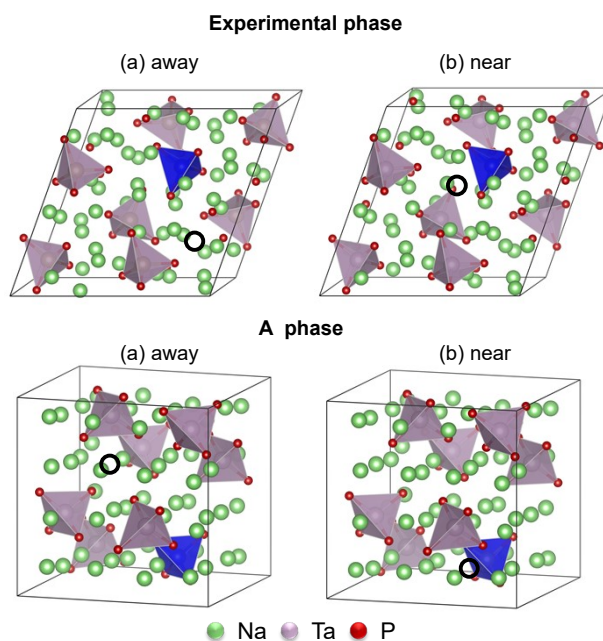
Experimental phase

(a) away (b) near

A phase

(a) away (b) near

Na Ta P

Figure S7. Crystal structures of experimental and A phase of Na_7TaP_4 doping with hexavalent elements (W, Mo). A Ta atom is substituted with the hexavalent element (highlighted in blue) and a Na vacancy is introduced for charge conversation (highlighted in black). Two cases are discussed: (a) The hexavalent element is away from the Na vacancy. (b) The hexavalent element is near the Na vacancy.