Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Enhancing sodium ionic conductivity in tetragonal-Na_3PS_4 by halogen doping: A first principle investigation

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Table S1. The probability of Na vacancy near Br atom in the t-$Na_{47}P_{16}S_{63}Br$ at 600 K, 800 K, 1000 K, 1200 K and 1400 K. The last 2000 steps of AIMD simulation are chosen for the statistic. The distribution of Na vacancy at the cubic region near Br atom (~ 3.1 Å) and remote from Br atom, and the distribution of Na vacancy at other 46 cubic regions are considered. The distribution has been normalized to each cubic region when the Na vacancy is located at other 46 cubic regions. The distribution is averaged to each cubic region when the Na vacancy is located at other 46 cubic regions.

Na vacancy statistics in t-$Na_{47}P_{16}S_{63}Br$ from 600 K to 1400 K						
	Region near Br atom		Region remote to Br atom		Other cubic regions	
	Frequency	Distribution	Frequency	Distribution	Frequency	Distribution
600 K	248	12.40%	12	0.60%	1740	46×1.89%
800 K	152	7.60%	28	1.40%	1820	46×1.98%
1000 K	70	3.50%	38	1.90%	1892	46×2.06%
1200 K	48	2.40%	41	2.05%	1911	46×2.08%
1400 K	43	2.15%	42	2.10%	1925	46×2.09%

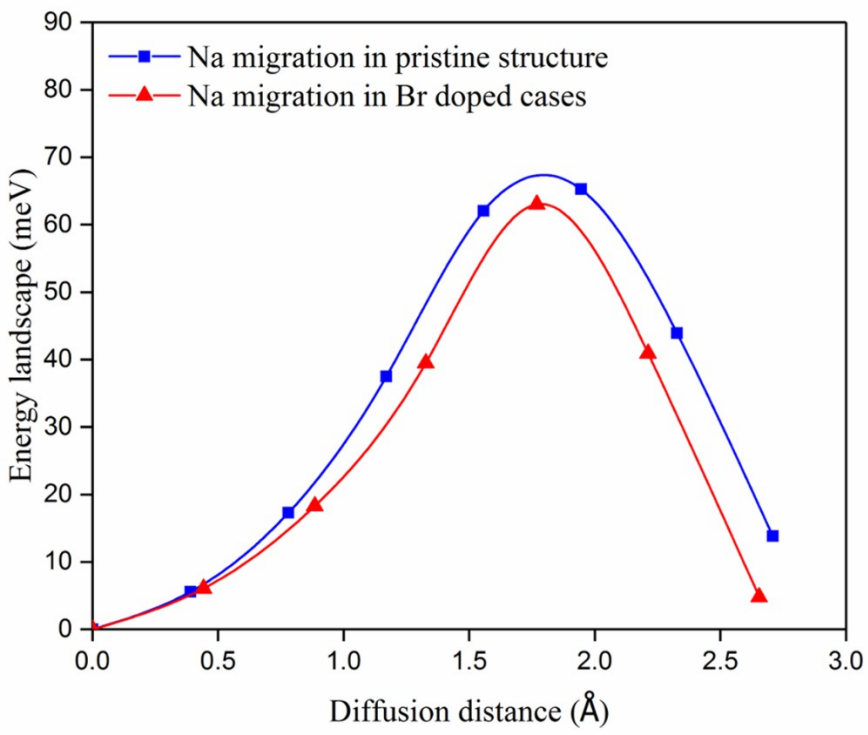

Figure S1. The energy barrier of Na ion diffusion along the a or b-axis direction in the pristine structure and Br doped structure. The Na vacancy is chosen 7 Å far from the Br atom in the unit cell. It shows little difference between the migration energy of Na ion in the t-Na3PS4 and the one in the Br doped pristine structure. In brevity, it is convenient to study the Na ion migration by omitting the effect of different kind of halogen elements when the Na ions are remote from those halogen atoms.

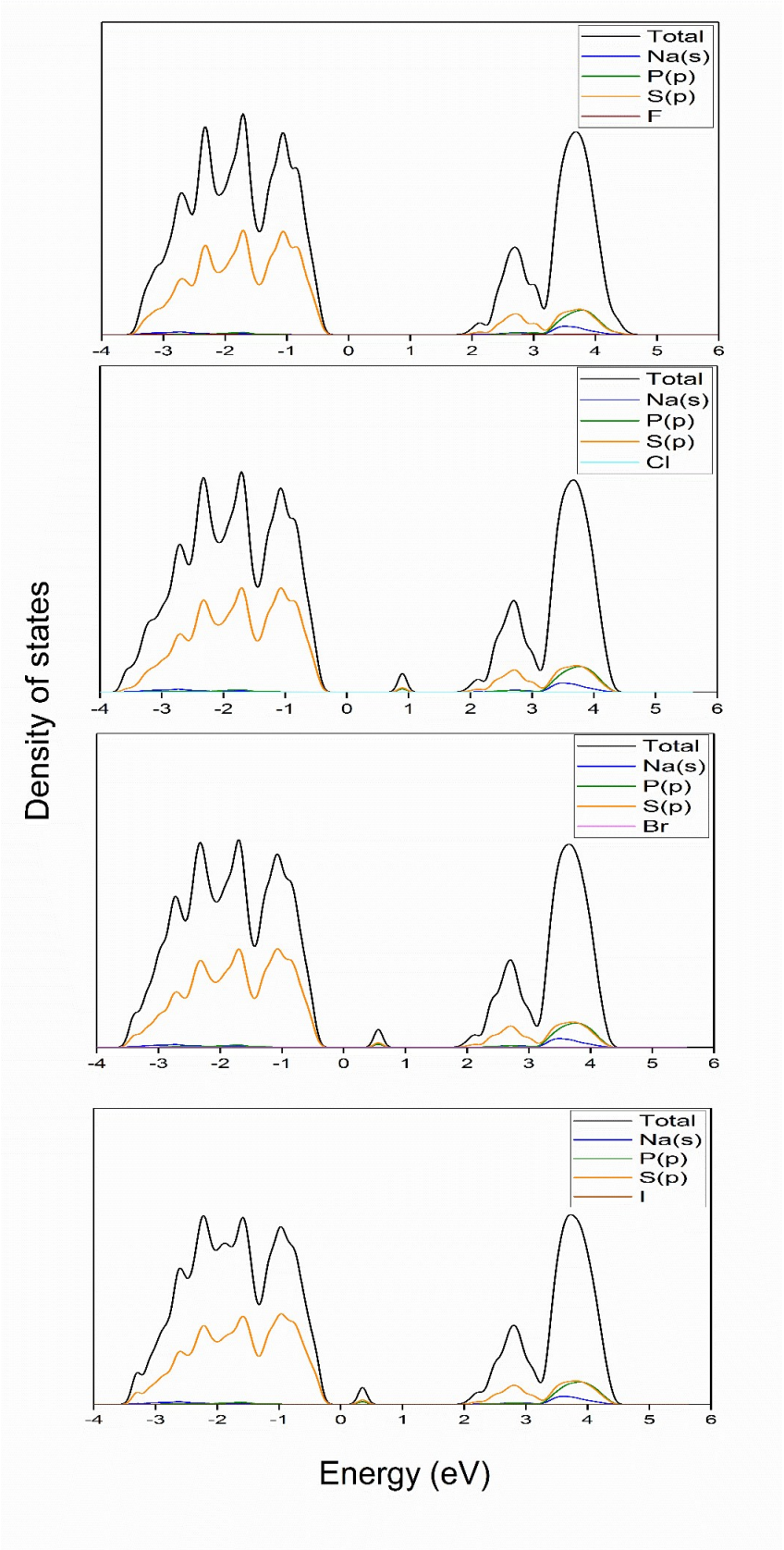

Figure S2. The electron density of states (DOS) of halogen doped t-Na_3PS_4 structure and partial DOS Corresponding to each element orbit. It indicates that the band gaps of

all cases are larger than 2 eV. The s orbitals of Na atoms, and p orbitals of P and S atoms contribute to the conduction bands, while the valance bands existence is mainly from the effect of p orbitals of S atoms. The intrinsic defect DOS are ascribed to the local defect pairs in halogen doped t-Na_3PS_4. While the left shift of the intrinsic defect DOS is because of smaller electron negativity of larger atomic number halogen dopants.

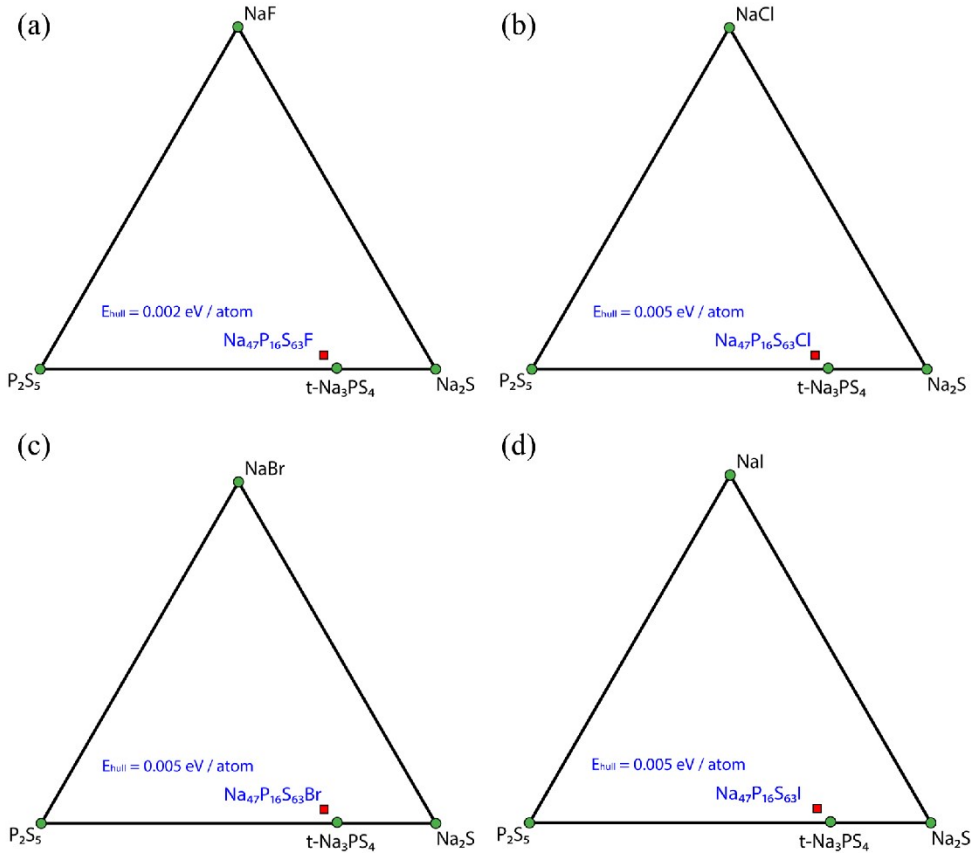

Figure S3. Compound phase diagram of (a) NaF-P_2S_5-Na_2S, (b) NaCl-P_2S_5-Na_2S, (c) NaBr-P_2S_5-Na_2S and (d) NaI-P_2S_5-Na_2S. All green points represent the stable state at 0 K, while red points represent unstable state.

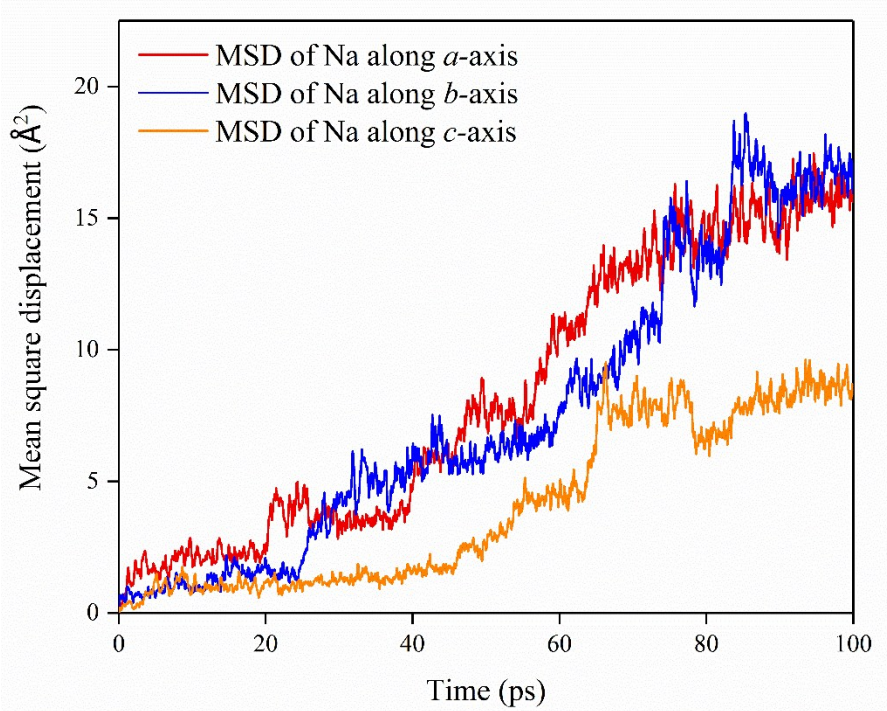

Figure S4. Mean square displacement of Na ions along *a*-, *b*- and *c*-axis for the Na vacancy contained $Na_{47}P_{16}S_{64}$ at 1000 K.