Supporting Information for:

Charge-fluctuation Drives the Anion Rotor Enhance the Conductivity of Na₁₁M₂PS₁₂ (M= Si, Ge, Sn) Superionic Conductors

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Figure S1. (a) One dimensional free energy profiles along the distance between the Na⁺-ion and the PS_4^{3-} anion in Na₁₁M₂PS₁₂; (b) and (c) is the result of 300K; (d)Na₁₁Si₂PS₁₂, (e) Na₁₁Ge₂PS₁₂, and (f) Na₁₁Sn₂PS₁₂ is the Helmholtz free energy surface as a function of θ and R.



Figure S2. (a) and (b) one-dimensional entropy contribution along the distance between the Na+-ion and the MS_4/PS_4 ligand in $Na_{11}M_2PS_{12}(M=Si, Ge, Sn)$; (c) and (d) is the 2D entropy contribution surface as a function of θ and R.



Figure S3. (a) Structure for Symmetry-Adapted Perturbation Theory. R is the distance from Na to M. The results of SAPT are shown in (b);



Figure S4. Shown for (a) and (e) is the structure of PS_4^{3-} and MS_4^{4-} . The angle between the P-S/M-S bond and the z axis is defined as θ and the angle φ is the angle between the x axis and the projection of the P-S/M-S vector in the xy plane. Shown in (b) $Na_{11}Si_2PS_{12}$; (c) $Na_{11}Ge_2PS_{12}$ and (d) $Na_{11}Sn_2PS_{12}$ is the Helmholtz free energy surface as a function of angle θ and φ for PS_4^{3-} and (f)-(h) are for MS_4^{4-} . The Helmholtz free energy A was computed as $A = -k_BTln[\rho(\theta, \varphi)]$, where k_B is the Boltzman constant, T is temperature, $\rho(\theta, \varphi)$ is the probability density distribution of the S ligands of PS_4^{3-} or MS_4^{4-} anions from the AIMD simulations.



Figure S5. The angle (a) θ and (b)-(c) ϕ of the four S atoms bond to P3 is shown as a function of the simulation time in Na₁₁Si₂PS₁₂.



Figure S6. (a) Residence time correlation functions for Na+-cations nearest to the polyhedral anion at 300K; (b)Na₁₁Si₂PS₁₂; (c)Na₁₁Ge₂PS₁₂ and (d)Na₁₁Sn₂PS₁₂. We present the bond vector correlation function, $\langle P_l P_l(t) \rangle$, to measure the relative orientation between the P-Na and P-S, or the relative position of Na away from PS³⁻₄/MS⁴⁻₄. Here, P_l is a Legendre Polynomial of degree l = 1, 2. P_l takes the cosine form for the P-Na and P-S bond vectors.



Figure S7. Na⁺-ion isosurface of sodium probability density distribution. (The isosurface level is 0.000226). From the AIMD Na⁺-ion trajectories, we calculate the Na⁺-ion probability density, defined as the time-averaged Na⁺-ion occupancy, allowing visualization of the Na⁺-ion diffusion mechanism. Note that although the probability density of Na⁺-ions provides an intuitive picture of the diffusion path, this analysis is insufficient to obtain a quantitative understanding of the diffusion path. In particular, the low probability density value does not necessarily indicate the inactiveness of the sites because intermediate sites for ion migration are less frequently occupied but actively participate in the diffusion.



Figure S8. Number of Na⁺-cations around the MS_4^{4-} anion and PS_4^{3-} anion.



Figure S9. Number of Na^+ -ions around MS_4 and PS_4 group (a)and (d) for $Na_{11}Si_2PS_{12}$, (b) and (e) for $Na_{11}Ge_2PS_{12}$, (c) and (f) for $Na_{11}Sn_2PS_{12}$.



Figure S10. Number of Na⁺-ion around the M7 anion. (a) for Si7; (b) for Ge7; (c) for Sn7.



Figure S11. The charge density is shown (a) $Na_{11}Si_2PS_{12}$, (b) $Na_{11}Ge_2PS_{12}$,(c) $Na_{11}Sn_2PS_{12}$. (The isosurface level is 0.0764.)

List of Supporting Tables

| Material | MS_{4}^{4-} | PS_{4}^{3-} |
|---|------------------|------------------|
| Na ₁₁ Si ₂ PS ₁₂ | 15.64 ± 1.07 | 15.53 ± 1.15 |
| $Na_{11}Ge_2PS_{12}$ | 15.85 ± 0.98 | 15.75 ± 1.06 |
| $Na_{11}Sn_2PS_{12} \\$ | 16.06 ± 0.96 | 16.00 ± 1.08 |

Table 1. The number of Na around the MS_4^{4-} and PS_4^{3-} anions.

Table 2. Charge-fluctuation of MS_4^{4-} .

| Material | 1050K | 300K |
|----------------------|--------------------|--------------------|
| $Na_{11}Si_2PS_{12}$ | -3.153 ± 0.027 | -3.169 ± 0.008 |
| $Na_{11}Ge_2PS_{12}$ | -3.162 ± 0.025 | -3.180 ± 0.01 |
| $Na_{11}Sn_2PS_{12}$ | -3.164 ± 0.020 | -3.186 ± 0.01 |

| Table 3. The differentia | l capacitance of | MS_{4}^{4-} . | (Bader charge) |
|--------------------------|------------------|-----------------|----------------|
|--------------------------|------------------|-----------------|----------------|

| MS^{4-}_4 | 1050K | 300K |
|----------------------|-------|-------|
| SiS_4 | 18.83 | 18.38 |
| GeS ₄ | 18.66 | 18.44 |
| SnS_4 | 18.62 | 18.51 |

Table 4. The differential capacitance of MS_4^{4-} -Na. (Bader charge)

| MS ₄ ⁴ _Na | 1050K | 300K |
|----------------------------------|-------|-------|
| SiS ₄ | 17.90 | 17.64 |
| GeS ₄ | 17.87 | 17.68 |
| SnS_4 | 17.77 | 17.74 |

| MS^{4-}_4 | 1050K | 300K |
|----------------------|-------|-------|
| SiS_4 | 19.10 | 18.73 |
| GeS ₄ | 19.03 | 19.04 |
| SnS_4 | 18.79 | 19.37 |

Table 5. The differential capacitance of MS_4^{4-} . (Hirshfeld charge)

Table 6. The differential capacitance of MS_4^{4-} -Na. (Hirshfeld charge)

| MS ₄ ⁴⁻ -Na | 1050K | 300K |
|-----------------------------------|-------|-------|
| SiS_4 | 18.59 | 18.28 |
| GeS ₄ | 18.51 | 18.43 |
| SnS_4 | 18.46 | 18.87 |