Supporting Information

Synergy of non-lithium cation doping and lithium concentration affecting lithium ion transport in solid electrolyte

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Table S1. Calculated lattice parameters of $Li_{16-2x}Zn_xGe_4O_{16}$ and $Li_{16-2x}Mg_xGe_4O_{16}$ from DFT.

Composition	cell	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Unit cell Volume (Å^3)
$Li_{12}Mg_2Ge_4O_{16}$	supercell	10.57	12.71	10.99	90.00	90.51	89.29	1477.03
$Li_{14}MgGe_4O_{16}$	supercell	10.50	12.58	10.97	90.02	90.12	90.68	1448.86
$Li_{15}Mg_{0.5}Ge_4O_{16}$	supercell	10.94	12.60	10.43	89.90	89.90	90.17	1437.76
$Li_{15.5}Mg_{0.25}Ge_4O_{16}$	supercell	10.93	12.58	10.45	89.96	89.95	90.09	1435.30
$Li_{12}Zn_2Ge_4O_{16}$	supercell	10.58	12.62	10.99	90.04	91.08	89.85	1467.29
$Li_{14}ZnGe_4O_{16}$	supercell	10.50	12.60	10.95	90.01	89.94	90.52	1449.85
$Li_{15}Zn_{0.5}Ge_4O_{16}$	supercell	10.91	12.56	10.43	89.95	90.27	89.93	1429.10

Table S2. The phase stability and diffusional properties of $Li_{16-2x}Zn_xGe_4O_{16}$ and $Li_{16-2x}Mg_xGe_4O_{16}$.

Composition	E_{hull} (meV/atom)	σ_{300K}(mS/cm)	E_a (eV)
$Li_{12}Zn_2Ge_4O_{16}$	15	0.16	0.34
$Li_{14}ZnGe_4O_{16}$	23	2.50	0.27
$Li_{15}Zn_{0.5}Ge_4O_{16}$	27	1.16	0.30
$Li_{12}Mg_2Ge_4O_{16}$	17	0.01	0.42
$Li_{14}MgGe_4O_{16}$	24	0.15	0.35
$Li_{15}Mg_{0.5}Ge_4O_{16}$	28	4.55	0.25
$Li_{15.5}Mg_{0.25}Ge_4O_{16}$	28	3.20	0.27

Table S3. Calculated lattice parameters of $Li_{16-2x}M_{x/2}Cd_{x/2}Ge_4O_{16}$ (M = Zn, Mg) from DFT.

Composition	cell	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Unit cell Volume (Å^3)
$Li_{12}MgCdGe_4O_{16}$	supercell	10.62	12.69	11.15	90.22	90.99	89.89	1502.16
$Li_{14}Mg_{0.5}Cd_{0.5}Ge_4O_{16}$	supercell	10.53	12.64	11.03	89.86	89.89	90.58	1466.96
$Li_{15}Mg_{0.25}Cd_{0.25}Ge_4O_{16}$	supercell	10.95	12.60	10.50	89.90	90.43	89.83	1449.10
$Li_{12}ZnCdGe_4O_{16}$	supercell	10.65	12.67	11.14	90.23	90.92	90.03	1503.62
$Li_{14}Zn_{0.5}Cd_{0.5}Ge_4O_{16}$	supercell	10.55	12.65	11.03	89.89	89.88	90.60	1471.75
$Li_{15}Zn_{0.25}Cd_{0.25}Ge_4O_{16}$	supercell	10.96	12.61	10.50	89.90	90.36	89.86	1451.04

Table S4. The phase stability and diffusional properties of $Li_{16-2x}M_{x/2}Cd_{x/2}Ge_4O_{16}$ (M = Zn, Mg).

Composition	E_{hull} (meV/atom)	σ_{300K}(mS/cm)	Ea(eV)
$Li_{12}ZnCdGe_4O_{16}$	22	1.36	0.27
$Li_{14}Zn_{0.5}Cd_{0.5}Ge_4O_{16}$	28	2.48	0.27
$Li_{15}Zn_{0.25}Cd_{0.25}Ge_4O_{16}$	30	1.20	0.30
$Li_{12}MgCdGe_4O_{16}$	23	0.23	0.34
$Li_{14}Mg_{0.5}Cd_{0.5}Ge_4O_{16}$	28	3.70	0.25
$Li_{15}Mg_{0.25}Cd_{0.25}Ge_4O_{16}$	30	3.33	0.26

Table S5. The impact of cation (Cd and Mg) on ΔE_{site} in $Li_{14}Zn_{0.5}Cd_{0.5}Ge_4O_{16}$.

Zn_impact	E(eV)	Cd_impact	E(eV)
E site	-770.623	F site	-770.258
E' site	-769.497	F' site	-769.506
ΔE_{site}	1.126	ΔE_{site}	0.752

Table S6. The phase stability and diffusional properties of $Li_{15}Zn_{0.25}Mg_{0.25}Ge_4O_{16}$ and $Li_{12}MgZnGe_4O_{16}$.

Composition	E_{hull} (meV/atom)	σ_{300K}(mS/cm)	Ea(eV)
$Li_{15}Zn_{0.25}Mg_{0.25}Ge_4O_{16}$	27	3.00	0.26
$Li_{12}MgZnGe_4O_{16}$	16	0.09	0.37

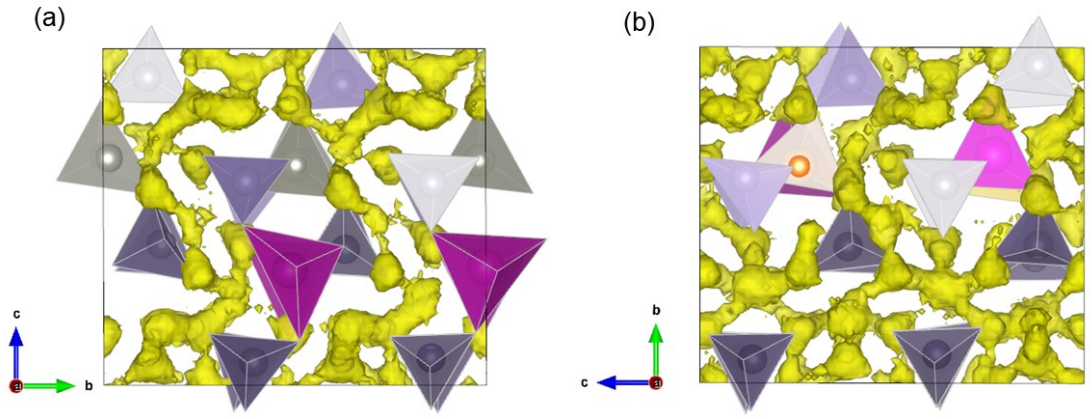

Figure S1. The probability densities of Li ions that was calculated by AIMD simulations at 900 K (a) in $Li_{12}ZnCdGe_4O_{16}$ and (b) in $Li_{12}MgCdGe_4O_{16}$ (yellow dots are used to represent the possible positions of lithium ions).

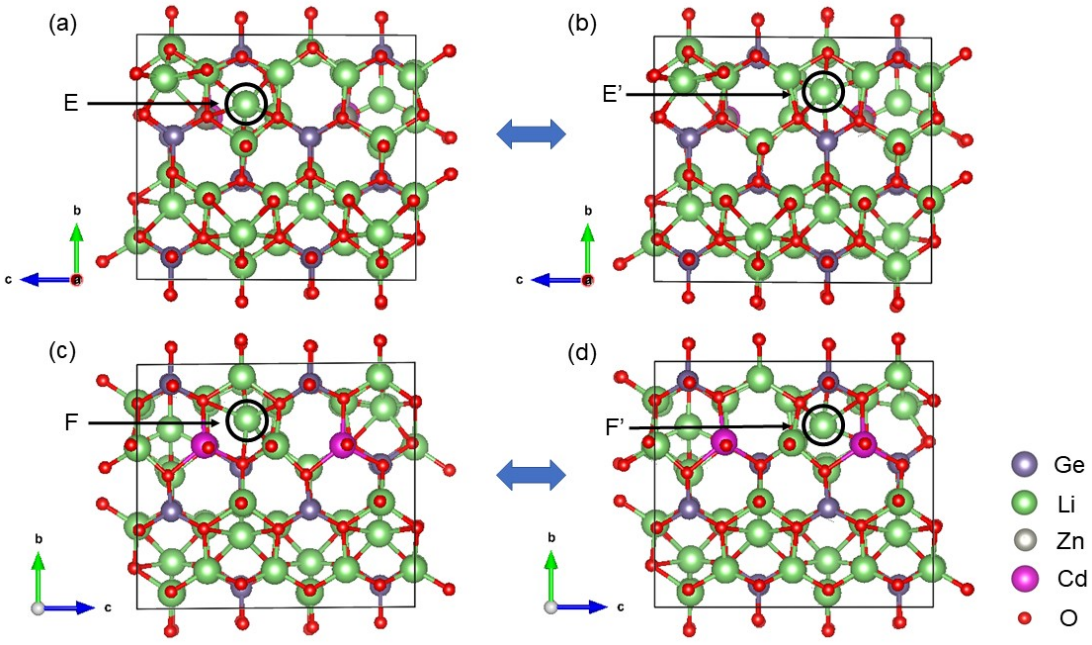

Figure S2. The comparison of Cd and Zn impacts in $Li_{14}Zn_{0.5}Cd_{0.5}Ge_4O_{16}$. E site in (a), E' site in (b), F site in (c), F' site in (d).

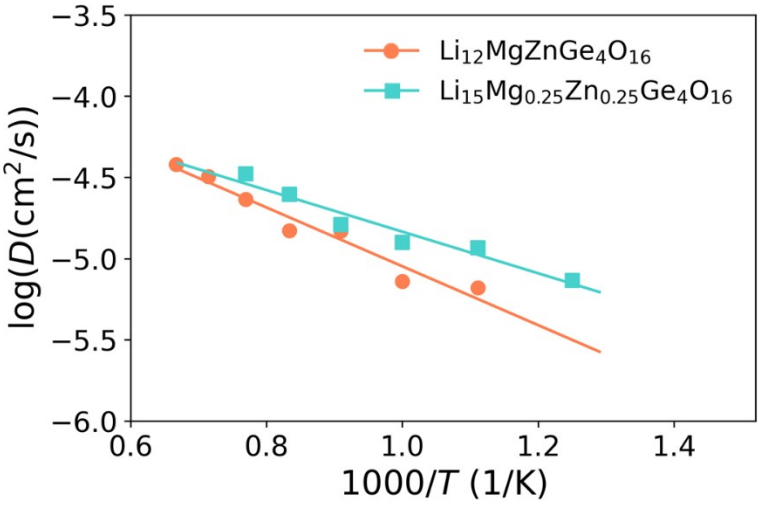

Figure S3. Arrhenius plots of Li ions diffusion in $Li_{12}MgZnGe_4O_{16}$ and $Li_{15}Mg_{0.25}Zn_{0.25}Ge_4O_{16}$ from AIMD simulation.

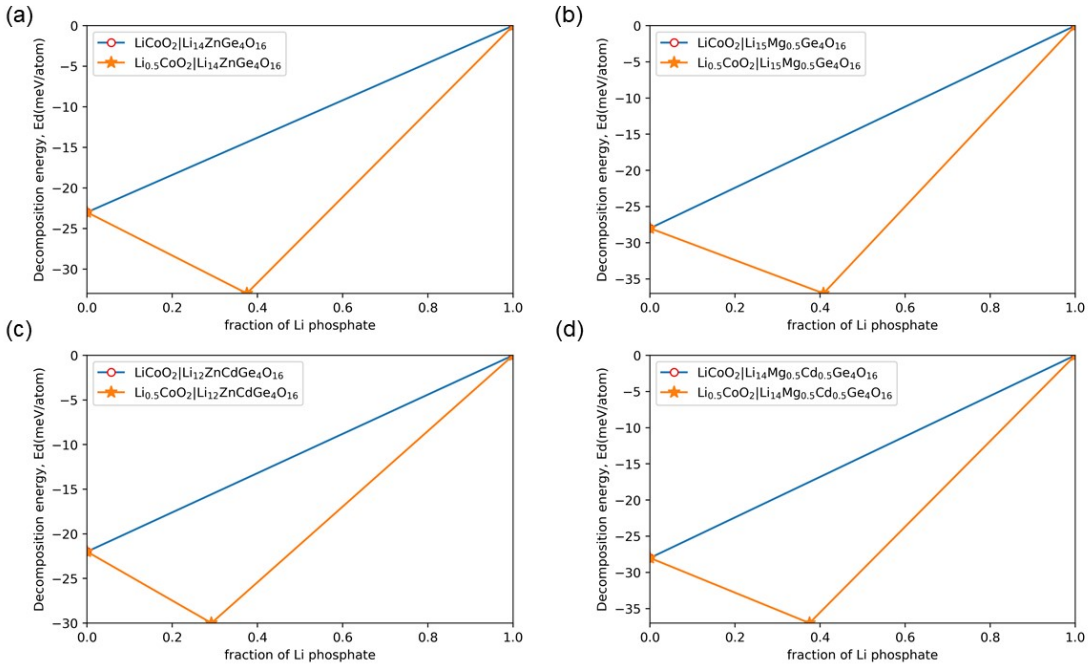

Figure S4. Decomposition energy of between (a) LCO and $Li_{14}ZnGe_4O_{16}$ ($LiCoO_2$ represents discharging status, $Li_{0.5}CoO_2$ represents charging state); (b) LCO and $Li_{15}Mg_{0.5}Ge_4O_{16}$; (c) LCO and $Li_{12}ZnCdGe_4O_{16}$; (d) LCO and $Li_{14}Mg_{0.5}Cd_{0.5}Ge_4O_{16}$.

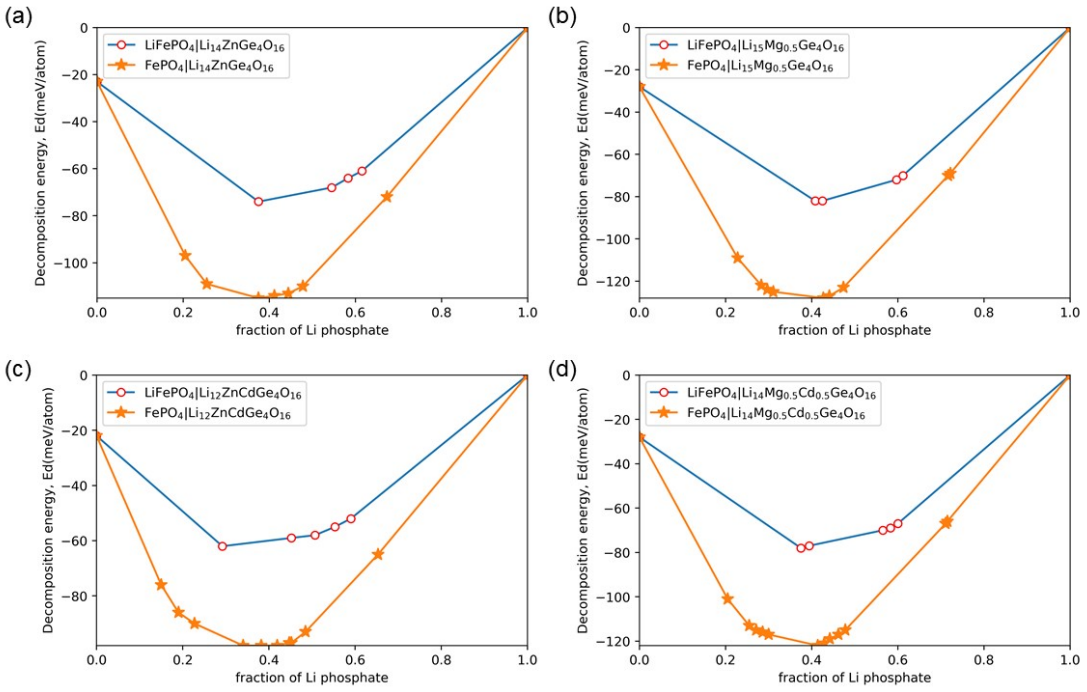

Figure S5. Decomposition energy of between (a) LFPO and $Li_{14}ZnGe_4O_{16}$ ($LiFePO_4$ represents discharging status, $FePO_4$ represents charging state); (b) LFPO and $Li_{15}Mg_{0.5}Ge_4O_{16}$; (c) LFPO and $Li_{12}ZnCdGe_4O_{16}$; (d) LFPO and $Li_{14}Mg_{0.5}Cd_{0.5}Ge_4O_{16}$.

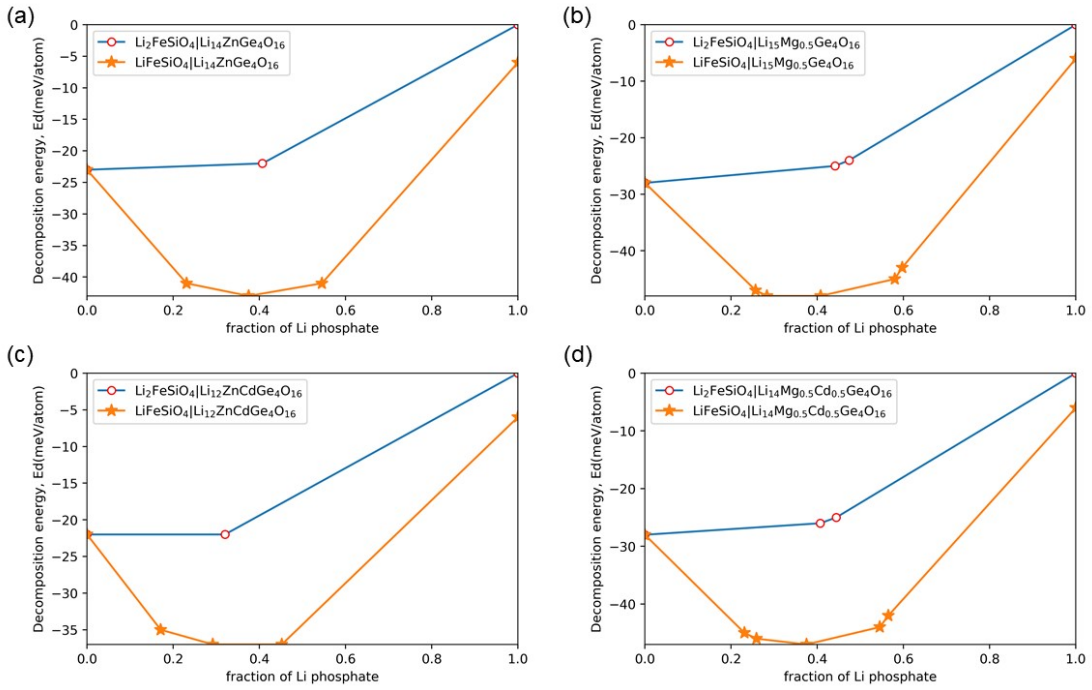

Figure S6. Decomposition energy of between (a) LFSO and $Li_{14}ZnGe_4O_{16}$ (Li_2FeSiO_4 represents discharging status, $LiFeSiO_4$ represents charging state); (b) LFSO and $Li_{15}Mg_{0.5}Ge_4O_{16}$; (c) LFSO and $Li_{12}ZnCdGe_4O_{16}$; (d) LFSO and $Li_{14}Mg_{0.5}Cd_{0.5}Ge_4O_{16}$.

Note 1:

In the studies of thio-LISICON type solid electrolyte, when the solid solution member x = 0.75 $Li_{4-x}Ge_{1-x}P_xS_4$ shows the highest conductivity, namely $Li_{9.75}Ge_{0.75}P_{2.25}S_{12}$.[1] Therefore, in theory the lithium-ion concentration of $Li_{10}GeP_2S_{12}$ exceeds the optimal value possibly. If further improving the lithium-ion conductivity of $Li_{10}GeP_2S_{12}$, according to we proposed doping theory, it should be doped with cations with smaller radii. In the study of $Li_{10}(Ge_{1-x}M_x)P_2S_{12}$ (M = Si, Sn), $Li_{10}Ge_{0.95}Si_{0.05}P_2S_{12}$ possess slightly higher lithium-ion conductivity than $Li_{10}GeP_2S_{12}$ at 300 K. However, doping with large-radius non-lithium cations would cause the decrease in Li-ion conductivity. Interestingly, in all Sn-doped materials their lithium-ion conductivity all are lower than that of $Li_{10}GeP_2S_{12}$.[2] Similarly, in experimental studies of $Li_{10}Ge_{1-x}Sn_xP_2S_{12}$ the similar results were also observed.[3] Furthermore, based on first-principles calculations, the order of Li-ion conductivity of these materials is $Li_{10}GeP_2S_{12}$ > $Li_{10}SnP_2S_{12}$.[4] Therefore, based on the above observations, our proposed doping strategies probably also are applicable to thio-LISICON type solid electrolyte.

References

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