Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Doping Strategy and Mechanism for Oxide and Sulfide Solid Electrolytes with High Ionic Conductivity

Yue Wang,[1-5] Yujing Wu,[1-4] Zhixuan Wang, [1-4] Liquan Chen,[1-4] Hong Li,[1-5] and Fan Wu[1-5*]*

[1]Tianmu Lake Institute of Advanced Energy Storage Technologies, Liyang 213300, Jiangsu, China;
[2]Yangtze River Delta Physics Research Center, Liyang 213300, Jiangsu, China;
[3]Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices,
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of
Sciences, Beijing, 100190, China;
[4]University of Chinese Academy of Sciences, Beijing, 100049, China
[5]Nano Science and Technology Institute, University of Science and Technology of China, Suzhou 215123, China

[*]Corresponding authors:
hli@iphy.ac.cn; fwu@iphy.ac.cn

Materials Synthesis: All the synthesis process was performed in a dry argon-filled glove box. For the synthesis of Li_6PS_5I (LPSI), starting materials Li_2S, P_2S_5, and LiCl were weighed based on the stoichiometric ratio and ball-milled at 600 rpm using a planetary ball-mill apparatus. Following the ball-milling process, the as-prepared precursor was finally loaded into a sealed quartz tube and subsequently annealed at 550 °C to obtain the LPSI SE, which was grounded in an agate mortar for further use.

Material Characterization :X-ray diffraction (XRD) patterns were carried out on a Bruker AXS D8 Advance with a Cu Kα radiation of λ = 1.54178 Å over the range of $10° \leq 2\theta \leq 80°$.

Ionic Conductivity Measurements: Ionic conductivity of prepared sulfide SEs was measured by EIS measurements in the frequency range of 0.1 Hz to 8 MHz and the amplitude of 10 mV, using a Zennium-pro electrochemical workstation.

Table S1. ^{71}Ga NMR Parameters of the Octahedral (Ga^{Oh}) and Tetrahedral (Ga^{Td}) Positions Measured for the $Y_3Ga_5O_{12}$ (YGG) Garnet by Vosegaard et al. and the Parameters Obtained for the LZLGO Material in the Present Work.

compound/site	∂_{iso}(ppm)	C_Q (MHz)	η_Q
YGG[29]/ Ga^{Oh}	5.6 ± 1.2	4.1 ± 0.06	0.03 ± 0.04
YGG[29]/ Ga^{Td}	219 ± 19	13.1 ± 0.2	0.05 ± 0.03
LZLGO/ Ga^{Td}	207 ± 10	12.7 ± 0.3	0.05 ± 0.05

Table S2. NPD data of Ge0.10-LLZO determined by Rietveld refinement. Space group: Ia3d (no. 230); lattice parameter: a=b=c=12.963 5 (1) Å. R-factors: R=7:91, χ^2=12.9. Biso is the isotropic atomic displacement parameter; the constraint on this parameter is such that Biso (Li1) = Biso (Ge). The density of the Ge0.10-LLZO powder phase is refined as 5.143 g cm^{-3}.

Spices	Site	x/α，y/b,z/c	Biso	Occupancy
Li1	24d	0.375,0,0.25	2.58(5)	2.83(2)
Li2	96h	0.0997(2),0.6865(2),0.5770(2)	0.500	3.78(2)
La	24c	0.125,0,0.25	0.748(6)	3.000
Zr	16a	0,0,0	0.724(6)	2.000
Ge	24d	0.375,0,0.25	2.58(5)	0.100
O	96h	-0.03226(2),0.05363(2),014945(2)	1.142(6)	12.000

Table S3. T1 relaxation times for ^{7}Li extracted from saturation recovery experiments of $Li_{6.55+y}Ga_{0.15}La_3Zr_{2-y}Sc_yO_{12}$

y	Component	Contribution(%)	T1(s)
0	A	100	0.38
0.10	A	50	0.36
	B	50	0.15
0.20	A	50	0.42
	B	50	0.17

Table S4. E_a and ionic conductivities of $Li_{6+x}P_{1-x}Si_xS_5I$ ($0 \leq x \leq 0.5$) samples

$Li_{6+x}P_{1-x}Si_xS_5I$	Ionic Conductivity (S cm^{-1})	Activation Energy(eV)
X=0	3.13×10^{-6}	0.248
X=0.1	3.10×10^{-5}	0.264
X=0.25	8.68×10^{-4}	0.167
X=0.5	7.34×10^{-3}	0.112