

SUPPORTING INFORMATION

Computational investigation of halogen-substituted Na argyrodites as solid-state superionic conductors

Bin Ouyang^{ab}, Yan Wang^c, Yingzhi Sun^{ab}, Gerbrand Ceder^{ab*}

^a Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA

^b Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c Advanced Materials Lab, Samsung Research America, 3 Van de Graaff Drive, Burlington, MA 01803, USA

* Email: gceder@berkeley.edu

SUPPORTING INFORMATION

S1: R-square fitting errors of MSD for Na–Sb–S–I system and Na–P–Se–Cl system.

Tab. 1: Calculated R-square fitting errors of MSD for Na–Sb–S–I system and Na–P–Se–Cl system

	600K	800K	900K	1000K	1100K	1200K
Na ₆ SbS ₅ I (4a)	0.994	0.990	0.996	0.954	0.987	0.999
Na ₆ SbS ₅ I (4c)	0.987	0.989	0.999	0.997	0.991	0.999
Na ₆ SbS ₅ I (Mixed)	0.995	0.989	0.999	0.995	0.998	0.998
Na ₅ SbS ₄ I ₂ (4a_4c)	0.999	0.998	0.999	0.998	0.999	0.999
Na ₆ PSe ₅ Cl (4a)	0.994	0.999	0.998	0.998	0.999	0.996
Na ₆ PSe ₅ Cl (4c)	0.972	0.995	0.997	0.979	0.986	0.992
Na ₆ PSe ₅ Cl (Mixed)	0.985	0.989	0.999	0.993	0.989	0.976
Na ₆ PSe ₅ Cl (4a_4c)	0.994	0.998	0.999	0.990	0.991	0.995

S2: Number of inter-cluster jumps for Na–Sb–S–I system and Na–P–Se–Cl system.

Tab. 2: Number of inter-cluster jumps for Na–Sb–S–I system for 200 ps and Na–P–Se–Cl system for 100 ps.

	600K	800K	900K	1000K	1100K	1200K
Na ₆ SbS ₅ I (4a)	40	104	143	257	403	1368
Na ₆ SbS ₅ I (4c)	64	113	128	309	467	1673
Na ₆ SbS ₅ I (Mixed)	166	490	729	733	1017	1724
Na ₅ SbS ₄ I ₂ (4a_4c)	247	642	919	972	1263	1368
Na ₆ PSe ₅ Cl (4a)	135	328	413	557	1000	1159
Na ₆ PSe ₅ Cl (4c)	104	241	530	849	1042	1194
Na ₆ PSe ₅ Cl (Mixed)	107	285	331	594	792	916
Na ₆ PSe ₅ Cl (4a_4c)	145	206	377	447	867	973

S3: Arrhenius plot for all sodium argyrodite considered

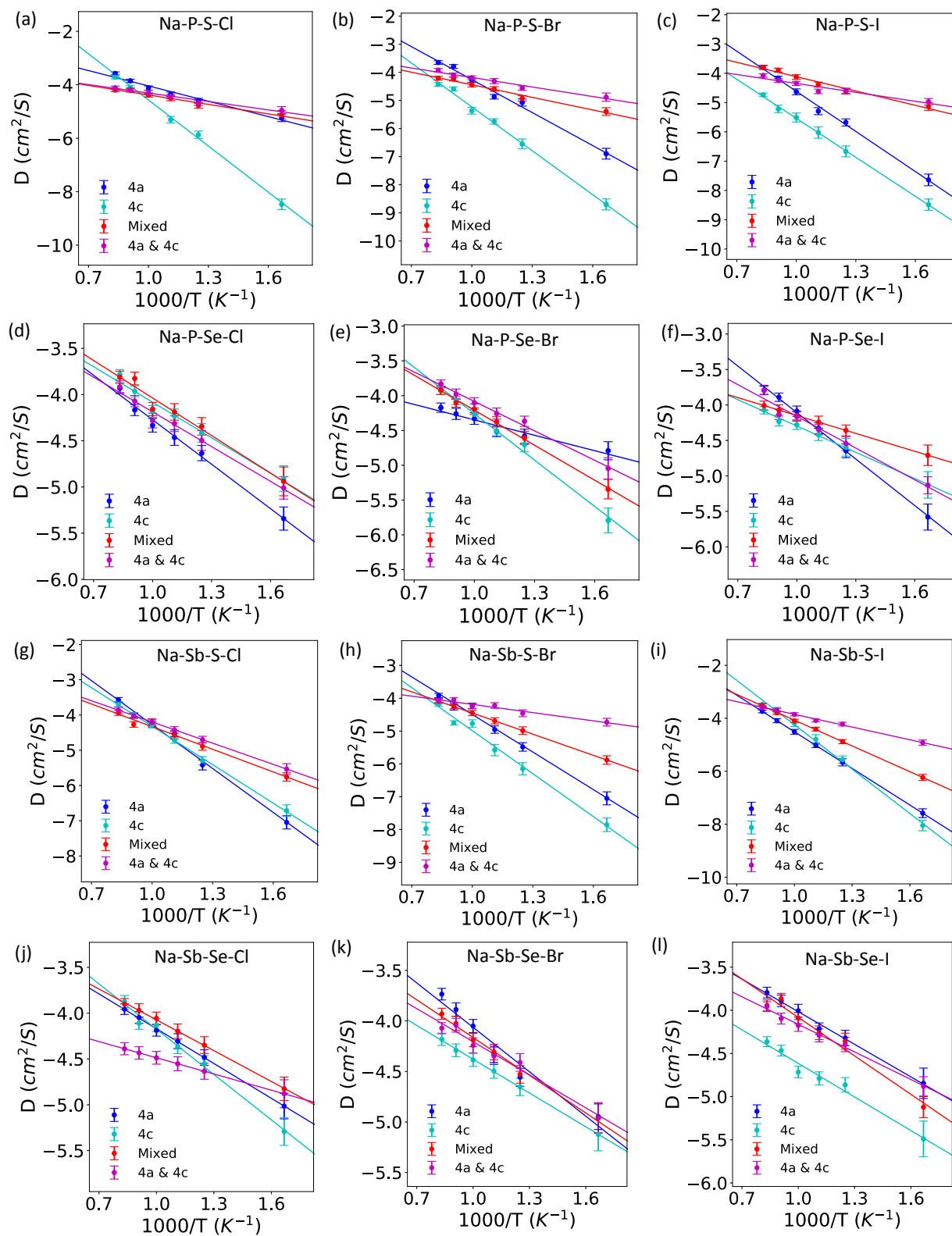


Fig. S 1: Arrhenius plot of all sodium argyrodites with different chalcogens, pnictogens and halogens.

S4: Room temperature Na⁺ conductivity for all sodium argyrodite considered

System	Conductivity (300K)	System	Conductivity (300K)
Na ₆ PS ₅ Cl (4a)	0.35 mS/cm	Na ₆ PSe ₅ Cl (4a)	0.98 mS/cm
Na ₆ PS ₅ Cl (4c)	< 1e-8 mS/cm	Na ₆ PSe ₅ Cl (4c)	8.46 mS/cm
Na ₆ PS ₅ Cl (Mixed)	8.28 mS/cm	Na ₆ PSe ₅ Cl (Mixed)	6.61 mS/cm
Na ₅ PS ₄ Cl ₂ (4a_4c)	17.42 mS/cm	Na ₅ PSe ₄ Cl ₂ (4a_4c)	7.28 mS/cm
Na ₆ PS ₅ Br (4a)	4e-6 mS/cm	Na ₆ PSe ₅ Br (4a)	83.30 mS/cm
Na ₆ PS ₅ Br (4c)	< 1e-8 mS/cm	Na ₆ PSe ₅ Br (4c)	0.03 mS/cm
Na ₆ PS ₅ Br (Mixed)	1.30 mS/cm	Na ₆ PSe ₅ Br (Mixed)	0.74 mS/cm
Na ₅ PS ₄ Br ₂ (4a_4c)	14.36 mS/cm	Na ₅ PSe ₄ Br ₂ (4a_4c)	3.68 mS/cm
Na ₆ PS ₅ I (4a)	< 1e-8 mS/cm	Na ₆ PSe ₅ I (4a)	0.06 mS/cm
Na ₆ PS ₅ I (4c)	< 1e-8 mS/cm	Na ₆ PSe ₅ I (4c)	6.08 mS/cm
Na ₆ PS ₅ I (Mixed)	1.26 mS/cm	Na ₆ PSe ₅ I (Mixed)	73.40 mS/cm
Na ₅ PS ₄ I ₂ (4a_4c)	16.54 mS/cm	Na ₅ PSe ₄ I ₂ (4a_4c)	1.83 mS/cm
Na ₆ SbS ₅ Cl (4a)	1e-6 mS/cm	Na ₆ SbSe ₅ Cl (4a)	7.19 mS/cm
Na ₆ SbS ₅ Cl (4c)	1.7e-5 mS/cm	Na ₆ SbSe ₅ Cl (4c)	0.91 mS/cm
Na ₆ SbS ₅ Cl (Mixed)	0.022 mS/cm	Na ₆ SbSe ₅ Cl (Mixed)	19.90 mS/cm
Na ₅ SbS ₄ Cl ₂ (4a_4c)	0.126 mS/cm	Na ₅ SbSe ₄ Cl ₂ (4a_4c)	119.90 mS/cm
Na ₆ SbS ₅ Br (4a)	4e-6 mS/cm	Na ₆ SbSe ₅ Br (4a)	2.53 mS/cm
Na ₆ SbS ₅ Br (4c)	< 1e-8 mS/cm	Na ₆ SbSe ₅ Br (4c)	9.22 mS/cm
Na ₆ SbS ₅ Br (Mixed)	3.6e-2 mS/cm	Na ₆ SbSe ₅ Br (Mixed)	8.08 mS/cm
Na ₅ SbS ₄ Br ₂ (4a_4c)	63.64 mS/cm	Na ₅ SbSe ₄ Br ₂ (4a_4c)	14.53 mS/cm
Na ₆ SbS ₅ I (4a)	< 1e-8 mS/cm	Na ₆ SbSe ₅ I (4a)	9.99 mS/cm
Na ₆ SbS ₅ I (4c)	< 1e-8 mS/cm	Na ₆ SbSe ₅ I (4c)	2.02 mS/cm
Na ₆ SbS ₅ I (Mixed)	2.3e-4 mS/cm	Na ₆ SbSe ₅ I (Mixed)	2.56 mS/cm
Na ₅ SbS ₄ I ₂ (4a_4c)	2.1 mS/cm	Na ₅ SbSe ₄ I ₂ (4a_4c)	16.90 mS/cm