SUPPORTING INFORMATION

Phase stability, electrochemical stability and ionic conductivity in the $Li_{10\pm1}MP_2X_{12}$ (M = Ge, Si, Sn, Al or P, and X = O, S or Se) family of superionic conductors

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Relaxed Structures

As the refined LGPS structure ($P4_2/nmc$) has partial occupancies on Li sites as well as Ge/P sites, we ordered the arrangement of Li, Ge, and P atoms in LGPS using an electrostatic energy criterion. All ions were assigned "idealized" charges based on their valence states, *i.e.*, +1 for Li, +4 for Ge, +5 for P and -2 for S. We then selected the 30 structures with the lowest electrostatic energy and

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relaxed them using density functional theory (DFT). The structure that minimizes the electrostatic energy is not the lowest energy structure based on DFT calculations. While the lowest electrostatic energy ordered structure still has a tetragonal $P4_2/mc$ spacegroup, the lowest DFT energy structure has a $P1$ spacegroup with a unit cell that is slightly distorted from the tetragonal cell. The coordinates of the lowest DFT energy P1 structure and lowest electrostatic energy $P4_2/mc$ structure are provided in Tables 1 and 2 respectively.

Table 1: Relaxed ordered P1 $Li_{10}GeP_2S_{12}$ structure.

Lattice parameters							
	a	b	c	α	β	γ	
	8.561	8.847	12.929	91.97	90.63	90.24	
Atomic positions							
Element	a	b	c	Element	a	b	c
Li	0.989	0.517	0.952	S	0.989	0.177	0.444
Li	0.964	0.517	0.426	S	0.005	0.793	0.389
Li	0.510	0.965	0.549	S	0.295	0.531	0.901
Li	0.497	0.996	0.051	S	0.685	0.530	0.899
Li	0.260	0.289	0.158	S	0.496	0.696	0.097
Li	0.744	0.747	0.282	S	0.487	0.309	0.060
Li	0.216	0.818	0.754	S	0.196	0.947	0.589
Li	0.230	0.757	0.252	S	0.801	0.946	0.590
Li	0.754	0.220	0.352	S	0.007	0.295	0.065
Li	0.462	0.516	0.751	S	0.001	0.711	0.103
Li	0.229	0.228	0.366	S	0.213	0.486	0.601
Li	0.734	0.256	0.857	S	0.814	0.491	0.589
Li	0.245	0.761	0.006	S	0.485	0.800	0.375
Li	0.741	0.263	0.131	S	0.496	0.180	0.423
Li	0.764	0.728	0.689	S	0.283	0.989	0.906
Li	0.222	0.259	0.919	S	0.715	0.999	0.922
Li	0.748	0.761	0.008	S	0.993	0.664	0.788
Li	0.244	0.720	0.485	S	0.003	0.281	0.761
Li	0.783	0.214	0.625	S	0.778	0.466	0.274
Li	0.241	0.212	0.650	S	0.203	0.478	0.292
Ge	0.997	0.488	0.183	S	0.517	0.202	0.721
Ge	0.509	0.991	0.816	S	0.492	0.791	0.702
P	0.993	0.965	0.502	S	0.687	0.016	0.221
P	0.493	0.516	0.993	S	0.291	0.031	0.219
P	0.008	0.483	0.684				
P	0.488	0.009	0.311				

Table 2: Relaxed ordered P42/mc $Li_{10}GeP_2S_{12}$ structure

Lattice parameters							
	a	*b*	*c*	α	β	γ	
	8.758	8.758	12.626	90	90	90	
Atomic positions							
Element	*a*	*b*	*c*	Element	*a*	*b*	*c*
Li	0.228	0.773	0.294	S	0.000	0.195	0.412
Li	0.772	0.227	0.294	S	0.000	0.805	0.412
Li	0.273	0.272	0.794	S	0.305	0.500	0.912
Li	0.727	0.728	0.794	S	0.695	0.500	0.912
Li	0.228	0.227	0.294	S	0.500	0.691	0.097
Li	0.772	0.773	0.294	S	0.500	0.309	0.097
Li	0.273	0.728	0.794	S	0.191	0.000	0.597
Li	0.727	0.272	0.794	S	0.809	0.000	0.597
Li	0.000	0.500	0.940	S	0.000	0.304	0.094
Li	0.000	0.500	0.440	S	0.000	0.696	0.094
Li	0.500	0.000	0.548	S	0.196	0.500	0.594
Li	0.500	0.000	0.048	S	0.804	0.500	0.594
Li	0.256	0.225	0.037	S	0.500	0.789	0.404
Li	0.744	0.775	0.037	S	0.500	0.211	0.404
Li	0.275	0.756	0.537	S	0.289	0.000	0.904
Li	0.725	0.244	0.537	S	0.711	0.000	0.904
Li	0.275	0.244	0.537	S	0.000	0.693	0.777
Li	0.725	0.756	0.537	S	0.000	0.307	0.777
Li	0.256	0.775	0.037	S	0.807	0.500	0.277
Li	0.744	0.225	0.037	S	0.193	0.500	0.277
Ge	0.500	0.000	0.801	S	0.500	0.209	0.698
Ge	0.500	0.000	0.301	S	0.500	0.791	0.698
P	0.000	0.500	0.686	S	0.709	0.000	0.198
P	0.000	0.500	0.186	S	0.291	0.000	0.198
P	0.000	0.000	0.504				
P	0.500	0.500	0.004				

For aliovalently substituted structures (Al^{3+} or P^{5+} for Ge^{4+} with corresponding changes in Li^+ concentration), we performed a similar electrostatic ordering of the structure and then performed DFT calculations on the lowest electrostatic energy structure only, *i.e.*, we did not perform DFT calculations on multiple possible orderings, given the significant computational time involved in exploring many orderings. These structures are provided in Tables 3 and 4.

Table 3: Relaxed ordered $Li_{11}AlP_2S_{12}$ structure.

Lattice parameters							
	a	*b*	*c*	α	β	γ	
	8.722	8.567	13.662	90.686	89.194	89.473	
Atomic positions							
Element	*a*	*b*	*c*	Element	*a*	*b*	*c*
Li	0.252	0.270	0.146	S	0.001	0.192	0.430
Li	0.744	0.736	0.165	S	0.015	0.799	0.427
Li	0.761	0.247	0.682	S	0.301	0.517	0.914
Li	0.275	0.746	0.291	S	0.687	0.512	0.890
Li	0.729	0.257	0.367	S	0.510	0.696	0.081
Li	0.234	0.214	0.329	S	0.510	0.302	0.065
Li	0.766	0.786	0.341	S	0.191	-0.006	0.601
Li	0.286	0.726	0.797	S	0.801	-0.013	0.597
Li	0.752	0.265	0.161	S	-0.005	0.289	0.063
Li	0.227	0.209	0.722	S	-0.021	0.716	0.076
Li	0.773	0.788	0.737	S	0.214	0.486	0.621
Li	0.212	0.250	-0.056	S	0.817	0.504	0.611
Li	0.765	0.746	-0.032	S	0.500	0.787	0.418
Li	0.268	0.740	0.524	S	0.474	0.215	0.423
Li	0.245	0.246	0.519	S	0.308	-0.014	0.897
Li	0.721	0.736	0.529	S	0.708	-0.010	0.887
Li	0.241	0.767	0.035	S	0.012	0.692	0.790
Li	0.773	0.258	-0.054	S	-0.012	0.302	0.783
Li	-0.007	0.515	0.946	S	0.786	0.503	0.274
Li	-0.008	0.496	0.396	S	0.197	0.478	0.269
Li	0.506	0.010	0.542	S	0.498	0.212	0.740
Li	0.513	-0.001	0.089	S	0.503	0.821	0.709
Al	-0.005	0.499	0.170	S	0.713	0.006	0.231
Al	0.494	0.005	0.321	S	0.298	0.004	0.213
P	0.008	0.500	0.698				
P	0.506	0.004	0.810				
P	0.000	-0.004	0.515				
P	0.506	0.507	-0.014				

Table 4: Relaxed ordered $Li_9P_3S_{12}$ structure.

Lattice parameters							
	a	*b*	*c*	α	β	γ	
	8.817	8.817	12.660	90.000	90.000	89.780	
Atomic positions							
Element	*a*	*b*	*c*	Element	*a*	*b*	*c*
Li	0.261	0.277	0.181	S	0.008	0.189	0.401
Li	0.772	0.236	0.710	S	0.011	0.807	0.413
Li	0.236	0.772	0.290	S	0.307	0.511	0.913
Li	0.277	0.261	0.819	S	0.689	0.508	0.901
Li	0.761	0.777	0.319	S	0.508	0.689	0.099
Li	0.272	0.736	0.790	S	0.511	0.307	0.087
Li	0.736	0.272	0.210	S	0.189	0.008	0.599
Li	0.777	0.761	0.681	S	0.807	0.011	0.587
Li	0.739	0.739	0.000	S	-0.014	0.312	0.100
Li	0.236	0.759	0.526	S	-0.007	0.701	0.095
Li	0.759	0.236	0.474	S	0.201	0.493	0.595
Li	0.239	0.239	0.500	S	0.812	0.486	0.600
Li	0.259	0.736	0.026	S	0.486	0.812	0.400
Li	0.736	0.259	-0.026	S	0.493	0.201	0.405
Li	0.002	0.497	0.944	S	0.312	-0.014	0.900
Li	-0.003	0.502	0.444	S	0.701	-0.007	0.905
Li	0.502	-0.003	0.556	S	0.001	0.687	0.777
Li	0.497	0.002	0.056	S	0.009	0.307	0.788
P	0.009	0.492	0.689	S	0.807	0.509	0.288
P	-0.008	0.509	0.189	S	0.187	0.501	0.277
P	0.509	-0.008	0.811	S	0.501	0.187	0.723
P	0.492	0.009	0.311	S	0.509	0.807	0.712
P	0.005	0.005	0.500	S	0.687	0.001	0.223
P	0.505	0.505	0.000	S	0.307	0.009	0.212

Stable phases

Tables 5-7 list the spacegroup and formation energies per atom of all the **stable** compounds in the Li-M-P-X systems investigated in this work. The $Li_{10\pm1}MP_2X_{12}$ are metastable in the calculated phase diagrams, and the structures are reported in the previous sections.

Table 5: Stable binary compounds in the Li-M-P-X systems.

Formula	Spacegroup	Form. energy / atom (eV)	Formula	Spacegroup	Form. energy / atom (eV)
Li_9Ge_4	Cmcm	-0.343	$Li_{13}Sn_5$	$P\bar{3}m1$	-0.395
$Li_{15}Ge_4$	$I\bar{4}3d$	-0.321	Li_5Sn_2	$R\bar{3}m$	-0.395
LiGe	$I4_1/a$	-0.28	Li_2Sn_5	P4/mbm	-0.202
GeO_2	$P4_2/mnm$	-2.054	Li_7Sn_2	Cmmm	-0.367
Li_2O	$Fm\bar{3}m$	-2.078	$Li_{17}Sn_4$	$F\bar{4}3m$	-0.346
Li_2O_2	$P6_3/mmc$	-1.766	SnO_2	Immm	-2.543
LiP	$P2_1/c$	-0.526	Sn_4P_3	$R\bar{3}m$	-0.066
LiP_7	$I4_1/acd$	-0.163	SnS	Pnma	-0.445
Li_3P_7	$P2_12_12_1$	-0.364	SnS_2	$P\bar{3}m1$	-0.379
Li_3P	$P6_3/mmc$	-0.698	$SnSe_2$	$P\bar{3}m1$	-0.337
P_2O_5	Pnam	-2.433	SnSe	Pcmn	-0.436
GeS	Pbnm	-0.266	$Li_{13}Si_4$	Pbam	-0.244
GeS_2	Pc	-0.315	$Li_{21}Si_5$	$F\bar{4}3m$	-0.215
Li_2S	$Fm\bar{3}m$	-1.341	$Li_{12}Si_7$	Pnma	-0.248
P_4S_9	$P2_1/c$	-0.17	SiO_2	$I\bar{4}2d$	-3.267
P_4S_3	Pmnb	-0.152	SiP	$Cmc2_1$	-0.159
P_2S_5	$P\bar{1}$	-0.164	SiP_2	Pbam	-0.131
P_4S_7	$P2_1/c$	-0.181	SiS_2	$P\bar{1}$	-0.680
Ge_4Se_9	$Pca2_1$	-0.248	$SiSe_2$	Imcb	-0.453
GeSe	Pcmn	-0.236	LiAl	$Fd\bar{3}m$	-0.175
$GeSe_2$	$P2_1/c$	-0.266	Li_3Al_2	C2/m	-0.179
Li_2Se	$Fm\bar{3}m$	-1.263	$LiAl_3$	$Pm\bar{3}m$	-0.090
PSe	$P2_1/c$	-0.081	AlP	$F\bar{4}3m$	-0.612
LiSn	P2/m	-0.326	Al_2S_3	$P6_1$	-1.053

Table 6: Stable ternary compounds in the Li-M-P-X systems.

Formula	Spacegroup	Form. energy / atom (eV)	Formula	Spacegroup	Form. energy / atom (eV)
Li_2GeO_3	$Ccm2_1$	-2.295	Li_4SnS_4	Pnma	-1.055
Li_4GeO_4	Cmcm	-2.288	$SnPS_3$	Pc	-0.348
$Li_4Ge_5O_{12}$	$P\bar{1}$	-2.198	Li_2SnSe_3	Cc	-0.831
GeP_2O_7	$P\bar{1}$	-2.473	Li_4SnSe_4	Pnma	-0.977
$Li_4P_2O_7$	$P2_1/c$	-2.753	$SnPSe_3$	Pc	-0.248
$LiPO_3$	$P2_1/c$	-2.708	$Li_2Si_2O_5$	Ccc2	-3.022
Li_3PO_4	$Pmn2_1$	-2.764	Li_2SiO_3	$Ccm2_1$	-2.893
Li_2GeS_3	$Ccm2_1$	-0.891	Li_4SiO_4	$P\bar{1}$	-2.685
Li_4GeS_4	Pnma	-1.061	Li_8SiO_6	$P6_3cm$	-2.450
Li_2PS_3	$P\bar{3}1m$	-0.876	SiP_2O_7	$P2_1/c$	-2.781
Li_3PS_4	$Pmn2_1$	-0.941	$Si_5P_6O_{25}$	$R\bar{3}$	-2.873
Li_2GeSe_3	$Ccm2_1$	-0.786	Li_2SiS_3	$Ccm2_1$	-1.061
Li_4GeSe_4	Pnma	-0.957	Li_4SiS_4	Pnma	-1.185
Li_2PSe_3	$P\bar{3}1m$	-0.724	Li_4SiSe_4	Pnma	-1.026
SnP_4O_{11}	$P2_1/c$	-2.456	Li_5AlS_4	Pmmn	-1.324
$Sn(PO_3)_2$	Pbca	-2.432	$LiAlS_2$	$Pna2_1$	-1.284
SnP_2O_7	$P\bar{1}$	-2.528	$AlPS_4$	P222	-0.582
Li_2SnS_3	Cc	-0.903			

Table 7: Stable quarternary compounds in the Li-M-P-X systems.

Formula	Spacegroup	Form. energy / atom (eV)
$LiSn_2(PO_3)_5$	Pc	-2.500