Supporting Information for 'Prediction of ternary alkaline-earth metal Sn(II) and Pb(II) chlorides with potential applications as *p*-type transparent conductors'

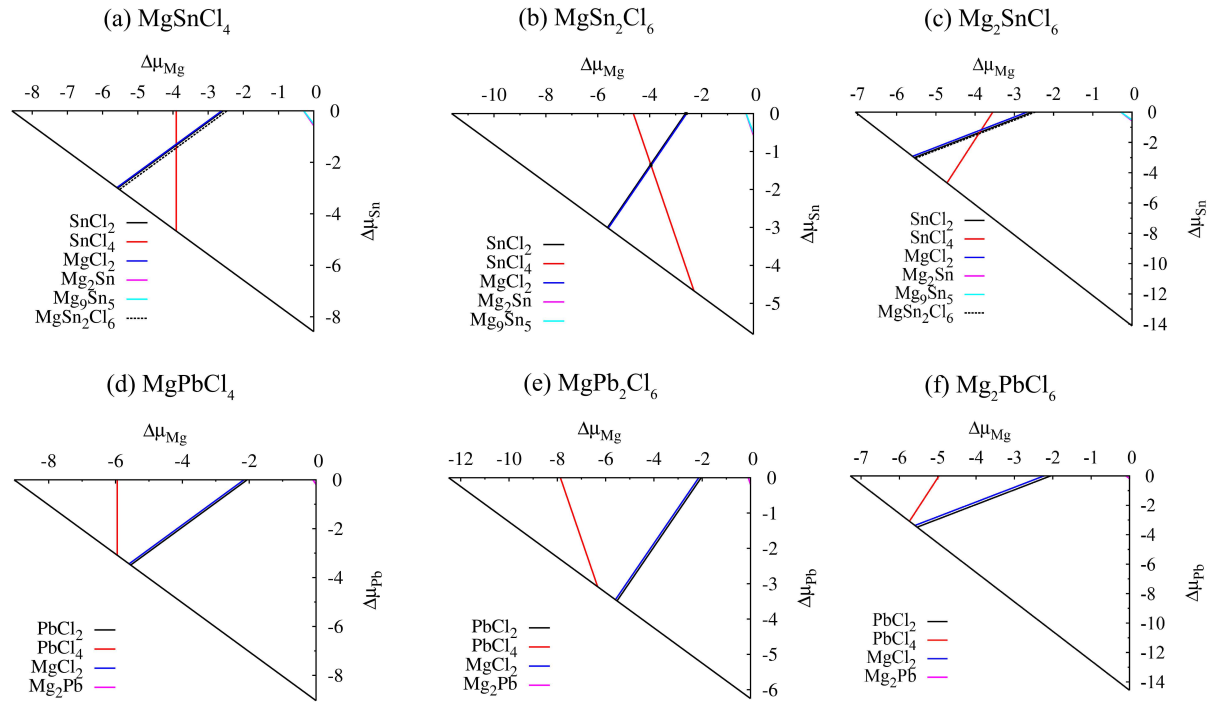

Figure S1: The entire phase stability diagrams for $MgSnCl_4$ (a), $MgSn_2Cl_6$ (b), Mg_2SnCl_6 (c), $MgPbCl_4$ (d), $MgPb_2Cl_6$ (e), and Mg_2PbCl_6 (f). Each line represents a known competing phase, and the stable region is indicated in green (same below). The stable chemical region exists only for $MgSn_2Cl_6$.

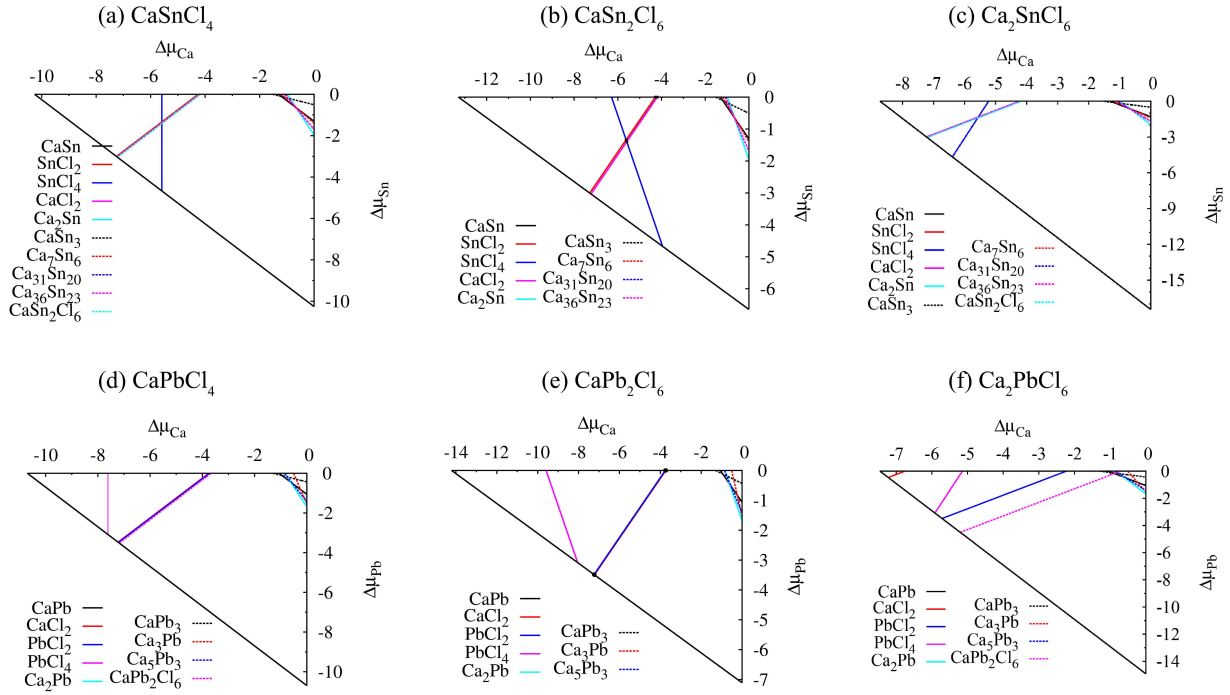

Figure S2: The entire phase stability diagrams for $CaSnCl_4$ (a), $CaSn_2Cl_6$ (b), Ca_2SnCl_6 (c), $CaPbCl_4$ (d), $CaPb_2Cl_6$ (e), and Ca_2PbCl_6 (f). The stable chemical region exists only for $CaSn_2Cl_6$ and $CaPb_2Cl_6$.

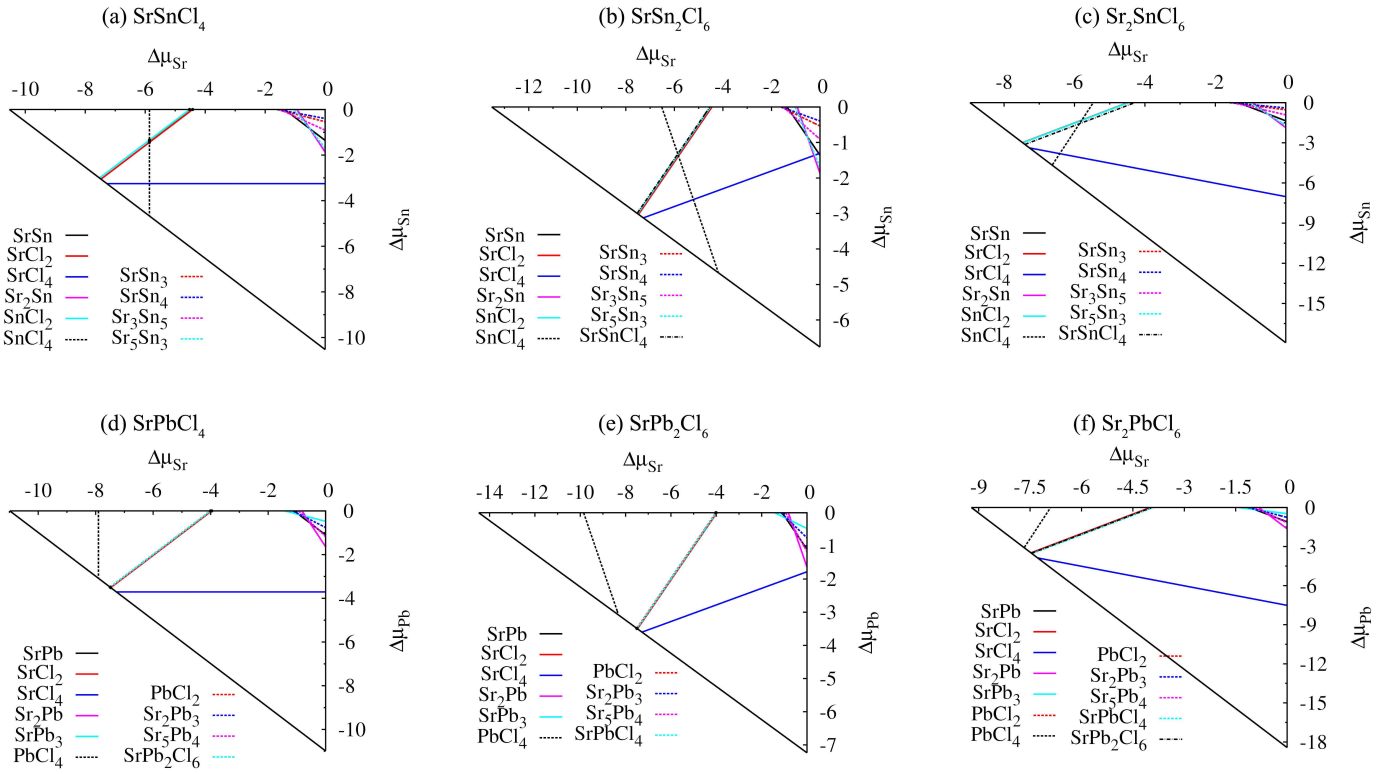

Figure S3: The entire phase stability diagrams for $SrSnCl_4$ (a), $SrSn_2Cl_6$ (b), Sr_2SnCl_6 (c), $SrPbCl_4$ (d), $SrPb_2Cl_6$ (e), and Sr_2PbCl_6 (f). The stable chemical region exists in $SrSnCl_4$, $SrPbCl_4$ and $SrPb_2Cl_6$.

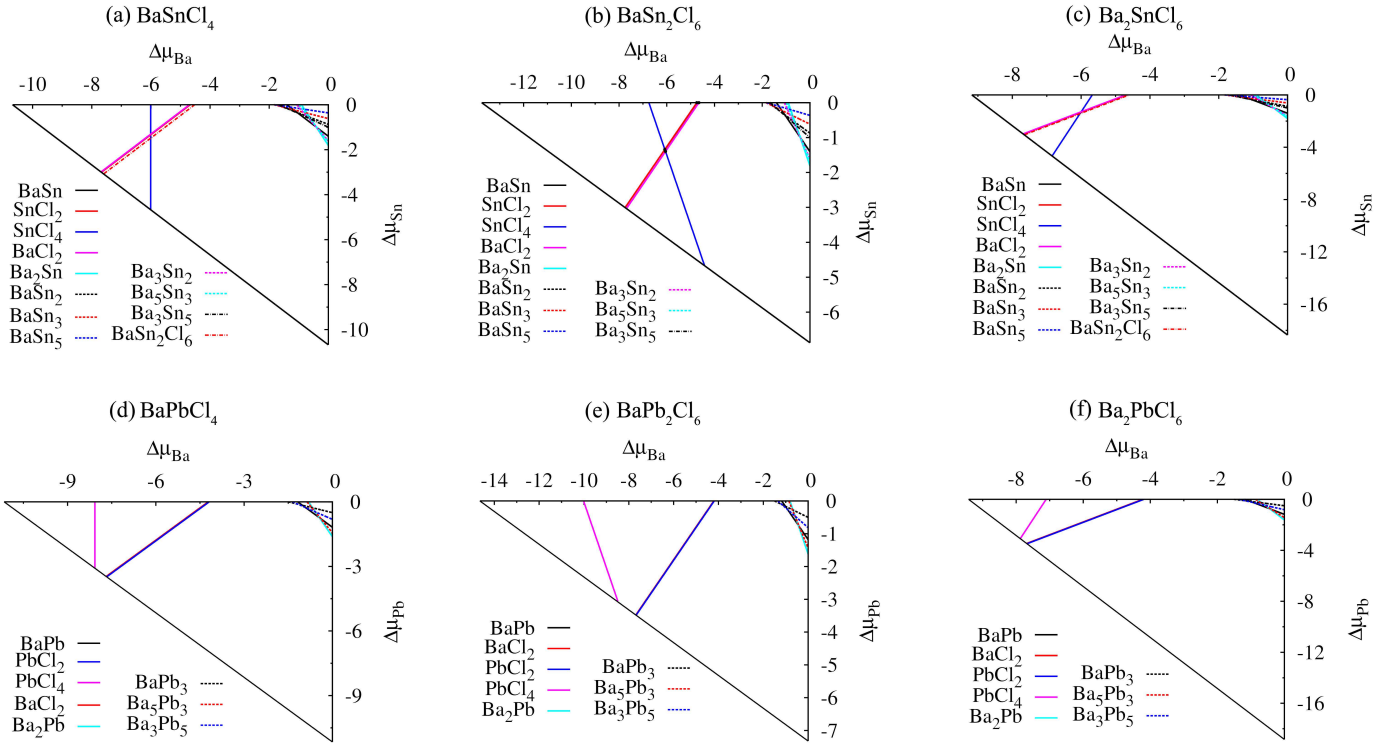

Figure S4: The entire phase stability diagrams for $BaSnCl_4$ (a), $BaSn_2Cl_6$ (b), Ba_2SnCl_6 (c), $BaPbCl_4$ (d), $BaPb_2Cl_6$ (e), and Ba_2PbCl_6 (f). The stable chemical region exists only for $BaSn_2Cl_6$.

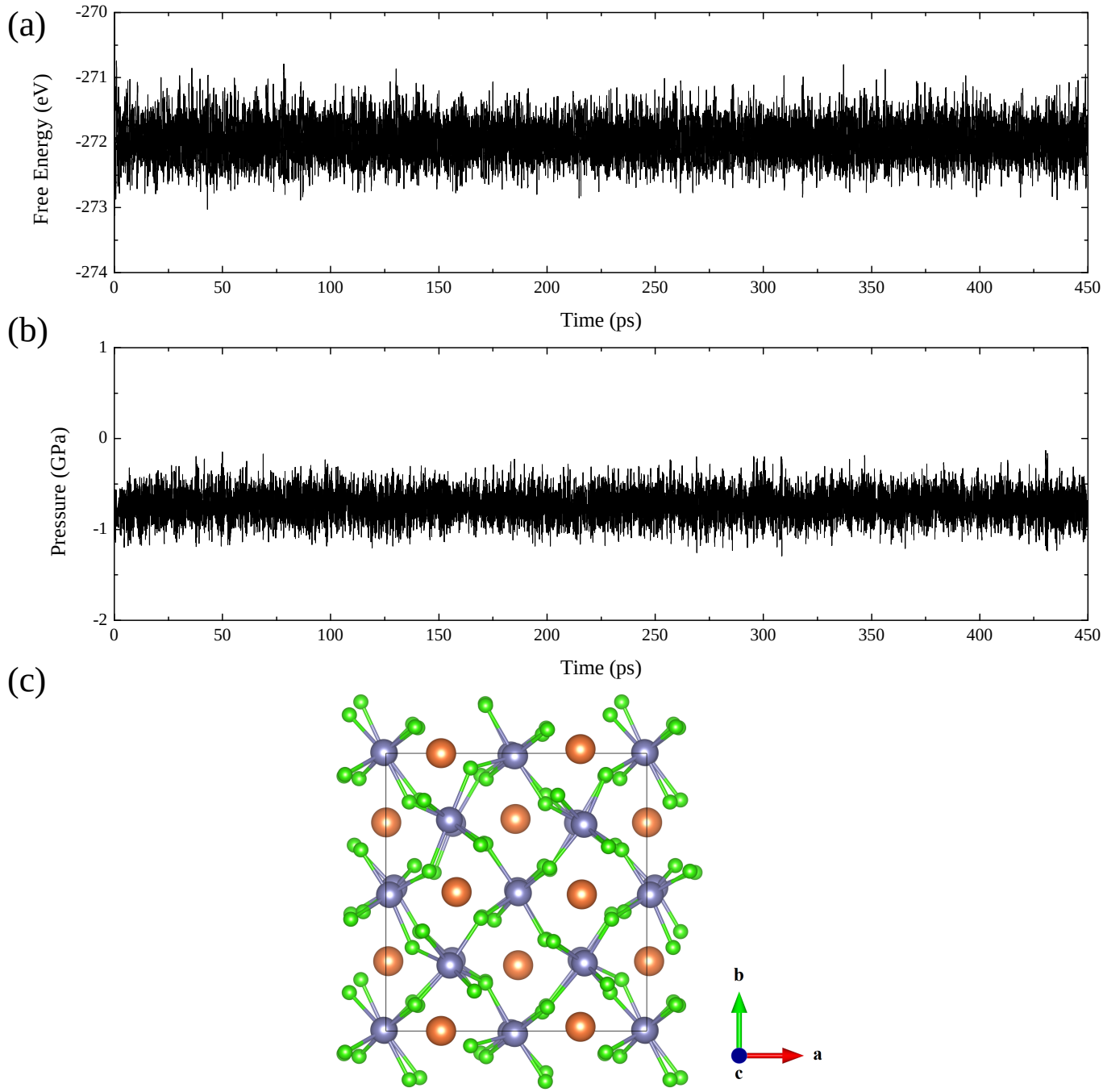

Figure S5: The free energy (a) and pressure (b) evolutions of $CaPb_2Cl_6$ during molecular dynamics at 300 K of a 450 ps simulation are presented. The ultimate structural configuration of this evolutionary process is illustrated in (c).

Table S1: The Single Crystal Elastic Constants C_{ij} (in GPa) of $P2_1/c$-$MgSn_2Cl_6$, $P2_1/c$-$CaSn_2Cl_6$, $Pnnm$-$CaPb_2Cl_6$, $P2_12_12_1$-$SrSnCl_4$, $P2_12_12_1$-$SrPbCl_4$, $P2_1/m$-$SrPb_2Cl_6$, and $P2_1/m$-$BaSn_2Cl_6$. The strikethrough indicates that there is no this constant.

Structure	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}	Mechanically stablity
$P2_1/c$-$MgSn_2Cl_6$	29.35	4.71	3.93	4.32	13.14	7.27	2.57	14.52	2.93	9.59	0.96	4.06	5.66	
$P2_1/c$-$CaSn_2Cl_6$	34.32	9.12	7.14	-2.08	14.93	6.87	-1.73	13.49	-4.49	10.29	1.25	8.00	6.14	
$Pnnm$-$CaPb_2Cl_6$	12.27	12.12	15.42	-	38.15	17.30	-	32.98	-	7.46	-	3.41	5.58	
$P2_12_12_1$-$SrSnCl_4$	30.80	15.31	14.59	-	24.01	10.15	-	31.59	-	6.87	-	12.85	10.45	stable
$P2_12_12_1$ -$SrPbCl_4$	41.60	22.08	20.30	-	24.42	12.61	-	36.08	-	6.88	-	13.66	12.29	
$P2_1/m$-$SrPb_2Cl_6$	36.16	17.97	19.04	2.07	34.49	15.80	-0.31	40.83	1.11	11.64	2.68	6.09	11.16	
$P2_1/m$-$BaSn_2Cl_6$	14.41	8.32	5.49	-0.83	26.89	6.87	1.44	16.86	1.28	1.25	0.72	4.78	5.48	

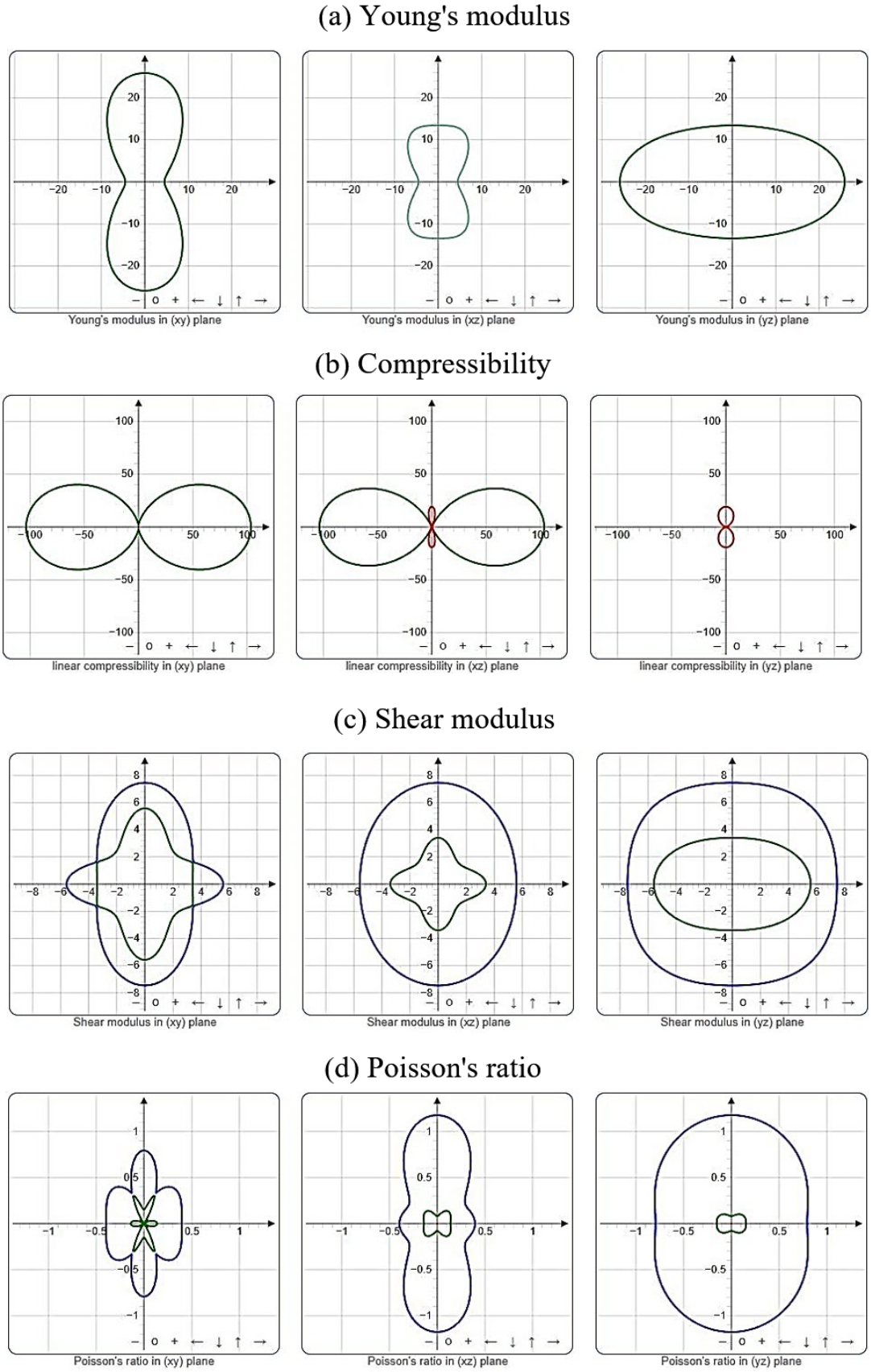

Figure S6: Two-dimensional (2D) plots of Young's moduli (a), compressibility (b), Shear moduli (c) and Poisson ratios (d) of $CaPb_2Cl_6$ at 0GPa. The green line and red line in (b) show the positive and negative values, respectively.

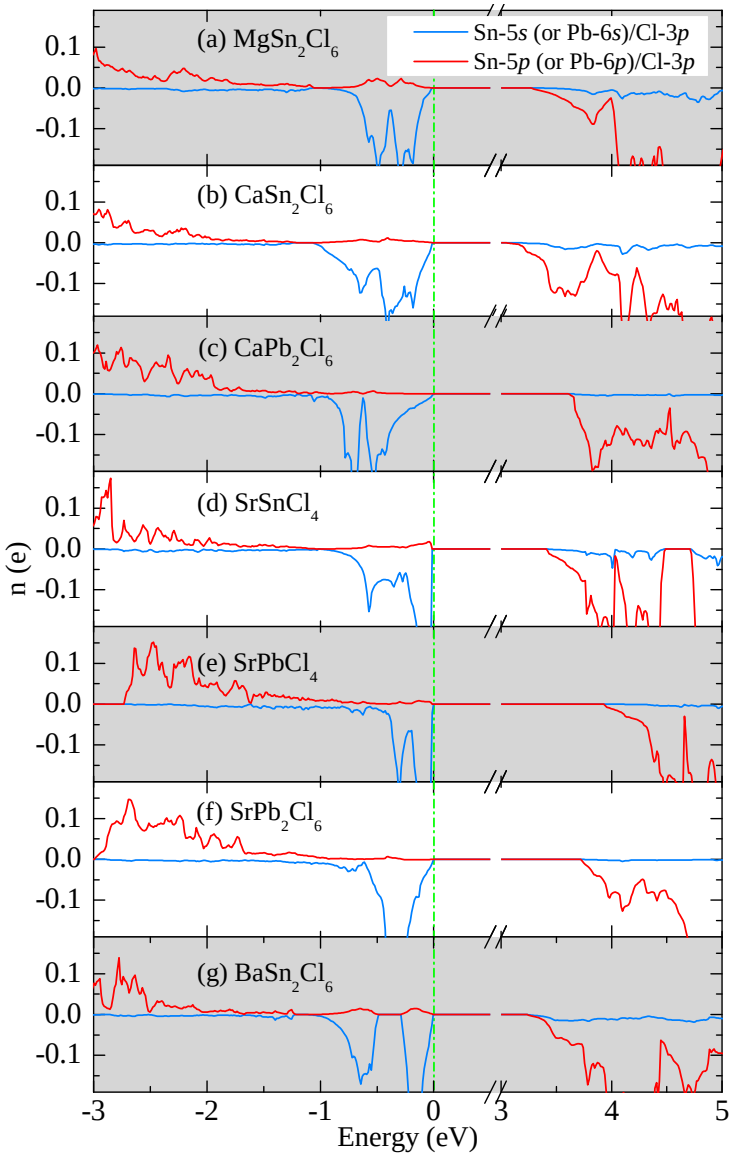

Figure S7: Crystal orbital overlap population (COOP) between the Sn-5s (or Pb-6s) and Cl-3p orbitals (blue lines), and the Sn-5p (or Pb-6p) and Cl-3p orbitals (red lines) for $MgSn_2Cl_6$ (a), $CaSn_2Cl_6$ (b), $CaPb_2Cl_6$ (c), $SrSnCl_4$ (d), $SrPbCl_4$ (e), $SrPb_2Cl_6$ (f), and $BaSn_2Cl_6$ (g). Positive n(e) represents bonding states and negative n(e) represents antibonding ones. The VBM is set to energy zero. (dash dot line).

The 2D plots of elastic properties of $CaPb_2Cl_6$ obtained using the online tool ELATE[1] are depicted in Figure S5. Table S3 provides a summary of the variations in elastic moduli with respect to different crystallographic directions. As illustrated in Figure S5 and Table S2, $CaPb_2Cl_6$ exhibits a notable anisotropy in Young's moduli and shear moduli, with even negative values observed for compressibility and Poisson ratios. The distinctive wine-rack-like structure in the $CaPb_2Cl_6$ crystal is responsible for the observed anisotropy and negative values of elastic properties.

References

[1] R. Gaillac, P. Pullumbi and F.-X. Coudert, *J. Phys.: Condens. Matter*, 2016, **28**, 275201.

Table S2: Structural data for the structures of $MgSnCl_4$, Mg_2SnCl_6, $MgPbCl_4$, $MgPb_2Cl_6$, Mg_2PbCl_6, $CaSnCl_4$, Ca_2SnCl_6, $CaPbCl_4$, Ca_2PbCl_6, $SrSn_2Cl_6$, Sr_2SnCl_6, Sr_2PbCl_6, $BaSnCl_4$, Ba_2SnCl_6, $BaPbCl_4$, $BaPb_2Cl_6$, and Ba_2PbCl_6 identified from our structure predictions. *Aea*2-$BaPb_2Cl_6$ and *Pbcn*-$BaPb_2Cl_6$ have indistinguishable enthalpy and are both listed.

Space group and pressure	Lattice parameters (Å)	Wyckoff positions	Atoms	x	y	z
		4b	Mg	0.0000	0.5000	0.5000
$MgSnCl_4$	$a = 8.5908$		Sn	0.3145	0.7500	0.6936
Pnma	$b = 7.4541$	4c	Cl1	0.1839	0.7500	0.4542
	$c = 11.3987$		Cl2	0.8059	0.7500	0.5604
		8d	Cl3	0.8975	0.5023	0.2932
			Mg1	0.8885	0.7255	0.7133
			Mg2	0.8850	0.4252	0.7113
			Sn	0.9308	0.1063	0.6499
Mg_2SnCl_6	$a = 7.1637$		Cl1	0.1411	0.9700	0.5018
$Pca2_1$	$b = 18.9368$	4a	Cl2	0.6759	0.8031	0.9157
	$c = 6.5831$		Cl3	0.1328	0.5033	0.8828
			Cl4	0.1200	0.3438	0.5496
			Cl5	0.1263	0.6463	0.5385
			Cl6	0.6625	0.1939	0.8134
			Mg	0.0000	0.9388	0.2500
$MgPbCl_4$	$a = 6.4840$	4c	Pb	0.0000	0.6735	0.2500
Pbcn	$b = 15.6617$		Cl1	0.7816	0.9518	0.5632
	$c = 6.5518$	8d	Cl2	0.7757	0.1803	0.6066
		2a	Mg	0.0000	0.0000	0.0000
$MgPb_2Cl_6$	$a = 11.6045$	4f	Pb	0.3107	0.5000	0.0000
Pmnn	$b = 7.0624$	4g	Cl1	0.0000	0.8080	0.3058
	$c = 6.9806$	8h	Cl2	0.6536	0.7100	0.3512
		2d	Mg	0.3333	0.6667	0.5000
Mg_2PbCl_6	$a = 6.5393$	1a	Pb	0.0000	0.0000	0.0000
P-31*m*	$c = 6.2576$	6k	Cl	0.0000	0.6364	0.2739
			Ca	0.6221	0.0074	0.1746
	$a = 13.9790$		Sn	0.8644	0.0258	0.8646
$CaSnCl_4$	$b = 6.7483$	4e	Cl1	0.5509	0.8003	0.8736
$P2_1/c$	$c = 7.6337$		Cl2	0.7027	0.2844	0.9581
	$\beta = 93.62°$		Cl3	0.7930	0.6786	0.6265
			Cl4	0.0229	0.7736	0.9000
			Ca1	0.9003	0.7402	0.7022
			Ca2	0.8992	0.4205	0.7025
			Sn	0.9108	0.0952	0.6867
Ca_2SnCl_6	$a = 7.6735$		Cl1	0.1476	0.9776	0.5100
$Pca2_1$	$b = 19.8135$	4a	Cl2	0.6644	0.8199	0.8950
	$c = 7.0485$		Cl3	0.1388	0.5043	0.8751
			Cl4	0.1320	0.3330	0.5359
			Cl5	0.1352	0.6539	0.5312
			Cl6	0.6663	0.1769	0.8377
			Ca	0.6206	0.5046	0.1677
	$a = 14.1853$		Pb	0.8655	0.5200	0.8436
$CaPbCl_4$	$b = 6.6841$	4e	Cl1	0.5468	0.2906	0.8784
$P2_1/c$	$c = 7.7058$		Cl2	0.7014	0.7725	0.9379
	$\beta = 92.50°$		Cl3	0.7863	0.1929	0.6228
			Cl4	0.0260	0.2630	0.9014
		4e	Ca	0.0000	0.0000	0.3329
Ca_2PbCl_6	$a = 6.5645$	2a	Pb	0.5000	0.5000	0.5000
$P4_2/mnm$	$c = 12.8307$	4f	Cl1	0.6875	0.6875	0.0000
		8j	Cl2	0.7006	0.7006	0.6742
			Sr	0.4262	0.7844	0.4491
			Sn1	0.7632	0.2208	0.4386
			Sn2	0.1310	0.2862	0.3724
$SrSn_2Cl_6$	$a = 11.1152$		Cl1	0.6595	0.4276	0.1401
Pc	$b = 7.2045$	2a	Cl2	0.2459	0.0034	0.6255
	$c = 7.4450$		Cl3	0.9124	0.0683	0.2597
	$\beta = 107.95°$		Cl4	0.5827	0.0403	0.7367
			Cl5	0.3247	0.4987	0.6509
			Cl6	0.9977	0.5704	0.0808

Space group and pressure	Lattice parameters (Å)	Wyckoff positions	Atoms	x	y	z
			Sr1	0.2710	0.7007	0.9725
			Sr2	0.8398	0.8187	0.3083
	$a = 7.2410$		Sn	0.3925	0.2407	0.3577
Sr_2SnCl_6	$b = 7.5060$		Cl1	0.7657	0.0487	0.5133
P-1	$c = 10.8994$	2i	Cl2	0.2385	0.4335	0.4927
	$\alpha = 90.68°$		Cl3	0.4692	0.0052	0.8347
	$\beta = 104.02°$		Cl4	0.9560	0.8630	0.8102
	$\gamma = 102.84°$		Cl5	0.5134	0.5031	0.1660
			Cl6	0.9863	0.3655	0.8550
		4f	Sr	0.6731	0.0832	0.2804
	$a = 5.5372$	2e	Pb	0.6683	0.7500	0.2654
Sr_2PbCl_6	$b = 13.9148$	4f	Cl1	0.2411	0.4149	0.9331
$P2_1/m$	$c = 7.4812$		Cl2	0.7636	0.9191	0.5571
	$\beta = 107.14°$	2e	Cl3	0.2342	0.7500	0.4461
			Cl4	0.7596	0.2500	0.0668
			Ba	0.1399	0.6350	0.3775
	$a = 7.9937$		Sn	0.4910	0.0714	0.6993
$BaSnCl_4$	$b = 9.2560$	4e	Cl1	0.3713	0.3645	0.3619
$P2_1/c$	$c = 12.4240$		Cl2	0.7834	0.0378	0.6308
	$\beta = 126.10°$		Cl3	0.2337	0.7889	0.6571
			Cl4	0.7601	0.5986	0.3982
			Ba1	0.4945	0.7589	0.6756
			Ba2	0.5023	0.5864	0.1857
			Sn	0.0200	0.9269	0.7341
Ba_2SnCl_6	$a = 7.3463$		Cl1	0.3104	0.8527	0.9735
$Pca2_1$	$b = 21.5074$	4a	Cl2	0.2486	0.0313	0.0228
	$c = 7.4150$		Cl3	0.2492	0.6743	0.9275
			Cl4	0.2487	0.5011	0.4359
			Cl5	0.8532	0.8215	0.8106
			Cl6	0.7562	0.6711	0.4372
			Ba	0.3703	0.5016	0.7208
	$a = 14.3632$		Pb	0.8914	0.4634	0.7443
$BaPbCl_4$	$b = 7.3183$	4e	Cl1	0.7327	0.6648	0.6384
$P2_1/c$	$c = 7.3718$		Cl2	0.4946	0.7464	0.9911
	$\beta = 94.70°$		Cl3	0.9710	0.7445	0.4882
			Cl4	0.7734	0.2010	0.5072
		4a	Ba	0.0000	0.5000	0.3083
$BaPb_2Cl_6$	$a = 21.2630$		Pb	0.3243	0.5370	0.3897
*Aea*2	$b = 7.2840$	8b	Cl1	0.9042	0.8004	0.1106
	$c = 7.3463$		Cl2	0.5717	0.6779	0.4821
			Cl3	0.2670	0.2419	0.6517
		4c	Ba	0.5000	0.1539	0.7500
$BaPb_2Cl_6$	$a = 7.2661$		Pb	0.0366	0.2378	0.5741
Pbcn	$b = 7.3548$	8d	Cl1	0.8216	0.3283	0.6782
	$c = 21.2620$		Cl2	0.7446	0.0080	0.5176
			Cl3	0.7008	0.5436	0.3460
			Ba1	0.5000	0.7564	0.6738
			Ba2	0.5006	0.5856	0.1820
			Pb	0.0376	0.9285	0.7462
Ba_2PbCl_6	$a = 7.3606$		Cl1	0.3000	0.8501	0.9683
$Pca2_1$	$b = 21.7343$	4a	Cl2	0.2408	0.0179	0.0086
	$c = 7.3770$		Cl3	0.2490	0.6731	0.9253
			Cl4	0.2489	0.5009	0.4323
			Cl5	0.8340	0.8252	0.8330
			Cl6	0.7554	0.6692	0.4333

Table S3: Variations of the elastic moduli of $CaPb_2Cl_6$ at 0 GPa.

Elastic moduli	Young's modulus (GPa)		Linear compressibility (TPa^{-1})		Shear modulus (GPa)		Poisson's ratio	
	E_{min}	E_{max}	β_{min}	β_{max}	G_{min}	G_{max}	ν_{min}	ν_{max}
Value	4.5	25.9	-19.2	103.6	2.1	8.0	-0.06	1.18
Anisotropy	5.7		-5.4		3.8		-21.6	
Axis	1.0	0.0	0.0	1.0	0.7	0.0	-0.7	0.0
	0.0	1.0	0.0	0.0	0.0	0.7	0.7	0.0
	0.0	0.0	1.0	0.0	0.7	0.7	0.0	1.0