Effect of the chemical composition on the structural, thermodynamical and mechanical properties of all-inorganic Halide Perovskites

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SUPPLEMENTARY MATERIAL

APPENDIX 1 – SETS OF IONIC RADII.

Three different properties presented in this work depend directly on the ionic radii of the different atoms the perovskite is made of. Goldschmidt's and Sun's parameters and bonding strength are by definition, according to equations 1-3 (including related equations 2.1, 2.2 and 3.4), calculated mainly from the ionic radii. For all those calculations presented in the main body of this work, the Shannon's revised effective crystal radii,[1] as it is conventional in the field of crystallography, have been used, considering effective charges of the atoms (A=1, B=2, X=-1) and coordination environments (A=12, B=6, X=6) as those in the perovskite. Nevertheless, as there are also other sets which are also frequently used, other options have been explored, testing results with the Pauling's empirical crystal radii[2] and the Shannon's effective ionic radii,[1] besides different coordination environments for the different atoms.

In order to dismiss the bias based upon the specific used set, the knowledge and information extracted from the previously commented parameters has been checked with the other sets proposed before. In line with the purpose of those parameters, the stability limit defined by the Goldschmidt's parameter has been reevaluated, as well as the kindness of the correlation between Sun's parameter and formation enthalpy from fundamental elements (ΔH_f) and between bonding strength and formation enthalpy from binary competitor compounds (ΔH_s).

Below, two data tables are attached. The first one, Table S1,[1–5] presents the values for the different atoms of the studied perovskites within the different tested sets of radii. The second one, Table S2 shows, for every set, the minimal value of the Goldschmidt's parameter and the coefficient of determination and mean absolute error of the correlations between the other two parameters and the formation enthalpies.

The nomenclature for the different sets of radii is the following. SC corresponds to Shannon crystal, SI to Shannon ionic and P stands for Pauling's set. O and L stands for the correction of Sn^{2+} radius proposed by *Oku*[3] and *Li*[4] respectively, using Shannon ionic

radii for the rest of the atoms. Additionally, subindexes 1-4 correspond to different coordination environments tested, respectively A=12, B=6, X=6; A=6, B=6, X=6; A=12, B=6, X=2 and A=6, B=6, X=2.

TABLE S1. Tested sets of ionic radii [Å] for the different ions present in the studied perovskites.

[Å]	Cs^+	Pb^{2+}	Sn^{2+}	I^-	Br^-
SC_1	2.02	1.33	1.20	2.06	1.82
SC_2	1.81	1.33	1.20	2.06	1.82
P	1.69	1.22	1.03	2.16	1.95
SI_1	1.88	1.19	1.05	2.20	1.96
SI_2	1.67	1.19	1.05	2.20	1.96
SI_3	1.88	1.19	1.05	1.90	1.69
SI_4	1.67	1.19	1.05	1.90	1.69
O	1.88	1.19	0.93	2.20	1.96
L	1.88	1.19	1.10	2.20	1.96

TABLE S2. Results for the dependent properties: minimum Goldschmidt's tolerance factor t, Sun's parameter correlation $\zeta(R^2/MAE[meV/atom])$ and bonding strength correlation $S(R^2/MAE[meV/atom])$, with the different sets of radii.

	t	ζ (R^2/MAE[meV/atom])	S (R^2/MAE[meV/atom])
SC_1	0.85	0.993 / 6.8	0.896 / 4.5
SC_2	0.81	0.981 / 11.9	0.892 / 4.6
P	0.81	0.805 / 36.8	0.933 / 3.8
SI_1	0.85	0.994 / 6.1	0.916 / 4.1
SI_2	0.81	0.937 / 21.5	0.912 / 4.2
SI_3	0.87	0.995 / 6.1	0.915 / 4.1
SI_4	0.82	0.940 / 21.1	0.912 / 4.2
O	0.85	0.643 / 48.9	0.928 / 3.8
L	0.85	0.891 / 29.7	0.880 / 4.8

From the data in TABLE S2 can be clearly seen that there are no big differences in performance between different sets of radii, except for the case of Oku set which fails for Sun's parameter correlation. The rest of sets produce results with proper correlation indexes and with t parameters above the stability limit of 0.8, in addition trends are also maintained. This way non-reliability of the results on the chosen set can be considered proven. Beyond this, it can be seen how dodecahedral coordination environments for the Cesium atoms performs better than octahedral environments, the ones that are usual in bibliography.[3–6] In fact, SI_1 and SI_3 sets present better results than the finally chosen for the work SC_1, but crystalline structure of perovskites and comparison reasons decide towards the last one. It's also remarkable that Sun's parameter correlation performs better

with more covalent sets of radios while the bonding strength correlation works better with more ionic sets like the Pauling and Oku sets.

APPENDIX 2 – COMPLETE DATA

To complement all the information presented in the contour plots showed in the main body of this work, the numerical data used to fill those graphs is presented here in table format, making sure no piece of information is missed or deprecated. This way, for each property with a contour figure in the work, plus for the Poisson's ratio, there is a table with all the data in this section.

Lattice constant [Å]		X						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	6.238	6.227	6.214	6.185	6.157	6.143	6.132
	0.125	6.249	6.233	6.219	6.196	6.164	6.150	6.136
	0.25	6.258	6.241	6.227	6.201	6.174	6.160	6.145
	0.5	6.166	6.151	6.135	6.123	6.088	6.070	6.054
	0.75	5.870	5.858	5.845	5.817	5.788	5.774	5.759
	0.875	5.868	5.854	5.841	5.815	5.786	5.771	5.758
	1	5.871	5.856	5.841	5.812	5.785	5.773	5.756

Shape ratio		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	0.125	0.97	0.97	0.97	0.97	0.97	0.97	0.97
	0.25	0.94	0.94	0.94	0.93	0.93	0.93	0.93
	0.5	0.95	0.95	0.95	0.95	0.95	0.95	0.95
	0.75	1.07	1.07	1.07	1.07	1.07	1.07	1.07
	0.875	1.03	1.03	1.03	1.03	1.03	1.03	1.03
	1	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Volume [Å^3]		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	242.758	241.420	239.910	236.571	233.388	231.813	230.540
	0.125	236.315	234.534	232.912	229.977	226.656	225.092	223.461
	0.25	229.208	227.466	225.895	222.877	219.908	218.287	216.628
	0.5	222.555	221.051	219.440	217.320	213.869	212.180	210.369
	0.75	215.656	214.242	212.844	209.901	206.852	205.400	203.833
	0.875	208.816	207.422	205.956	203.268	200.261	198.789	197.370
	1	202.353	200.793	199.321	196.317	193.644	192.440	190.656

Goldschmidt's parameter		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	0.851	0.855	0.859	0.868	0.876	0.881	0.885
	0.125	0.853	0.857	0.861	0.870	0.878	0.883	0.887
	0.25	0.855	0.859	0.863	0.872	0.880	0.885	0.889
	0.5	0.856	0.861	0.865	0.874	0.883	0.887	0.892
	0.75	0.858	0.862	0.867	0.876	0.885	0.889	0.894
	0.875	0.860	0.864	0.869	0.878	0.887	0.892	0.897
	1	0.862	0.866	0.871	0.880	0.890	0.894	0.899

Sun's parameter		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	1.292	1.291	1.290	1.289	1.288	1.288	1.287
	0.125	1.295	1.295	1.294	1.293	1.292	1.291	1.291
	0.25	1.299	1.299	1.298	1.297	1.296	1.296	1.295
	0.5	1.303	1.303	1.302	1.299	1.299	1.299	1.299
	0.75	1.308	1.307	1.306	1.305	1.304	1.304	1.304
	0.875	1.313	1.312	1.312	1.310	1.309	1.309	1.309
	1	1.318	1.318	1.317	1.316	1.315	1.314	1.315

Bonding strength		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	0.220	0.222	0.223	0.225	0.229	0.230	0.231
	0.125	0.225	0.227	0.228	0.231	0.234	0.235	0.236
	0.25	0.229	0.231	0.232	0.235	0.238	0.239	0.240
	0.5	0.235	0.236	0.237	0.240	0.243	0.245	0.246
	0.75	0.239	0.240	0.242	0.245	0.248	0.249	0.250
	0.875	0.245	0.247	0.248	0.252	0.254	0.256	0.257
	1	0.249	0.251	0.253	0.255	0.259	0.260	0.261

Formation enthalpy ΔH_f [eV/atom]		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	-1.038	-1.031	-1.023	-1.009	-0.995	-0.988	-0.982
	0.125	-1.085	-1.078	-1.070	-1.055	-1.040	-1.034	-1.027
	0.25	-1.135	-1.126	-1.119	-1.104	-1.089	-1.082	-1.075
	0.5	-1.181	-1.174	-1.167	-1.146	-1.133	-1.126	-1.120
	0.75	-1.232	-1.224	-1.216	-1.200	-1.184	-1.177	-1.170
	0.875	-1.282	-1.274	-1.266	-1.249	-1.234	-1.226	-1.219
	1	-1.335	-1.327	-1.318	-1.302	-1.286	-1.279	-1.271

Formation enthalpy ΔH_s [meV/atom]		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	8.8	3.3	-1.9	-12.4	-23.3	-29.1	-35.7
	0.125	0.7	-3.4	-7.7	-17.0	-26.6	-31.7	-37.0
	0.25	-8.8	-12.3	-16.0	-24.3	-32.7	-37.0	-41.5
	0.5	-15.4	-19.8	-23.9	-25.1	-34.0	-38.7	-43.4
	0.75	-26.9	-29.7	-32.3	-38.0	-43.5	-46.7	-49.9
	0.875	-37.3	-39.6	-41.4	-45.6	-50.6	-53.1	-56.0
	1	-50.7	-52.1	-53.4	-56.5	-60.3	-62.8	-64.4

B-M Bulk modulus [GPa]		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	17.46	17.53	17.62	17.79	18.01	18.11	18.21
	0.125	18.08	18.09	18.20	18.41	18.62	18.73	18.85
	0.25	18.72	18.78	18.87	19.06	19.27	19.37	19.49
	0.5	18.69	18.82	18.89	19.31	19.62	19.66	19.91
	0.75	20.06	20.11	20.20	20.42	20.62	20.72	20.83
	0.875	20.85	20.90	21.01	21.20	21.42	21.52	21.64
	1	21.55	21.66	21.76	22.00	22.18	22.26	22.38

EC Bulk modulus [GPa]		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	20.29	15.36	19.76	19.88	20.05	17.71	19.75
	0.125	20.98	20.37	19.65	20.69	18.22	19.49	20.72
	0.25	22.14	20.85	21.64	21.64	21.77	20.98	21.64
	0.5	20.66	21.98	18.44	22.47	20.93	22.23	22.59
	0.75	24.09	23.10	23.48	23.29	23.78	23.47	23.54
	0.875	25.28	20.98	24.65	24.74	24.64	24.38	24.52
	1	26.50	25.06	25.82	25.98	26.12	25.29	25.65

Shear modulus [GPa]		x						
		0	**0.167**	**0.333**	**0.5**	**0.667**	**0.833**	**1**
b	**0**	9.49	9.13	9.19	9.49	9.69	9.78	9.79
	0.125	9.85	9.49	9.60	9.78	9.98	10.08	10.20
	0.25	10.34	9.94	10.05	10.23	10.41	10.49	10.52
	0.5	10.54	10.33	10.18	10.59	10.89	10.84	10.86
	0.75	11.29	10.71	10.83	10.94	11.15	11.19	11.19
	0.875	11.72	11.14	11.33	11.42	11.60	11.63	11.65
	1	12.34	11.68	11.84	11.95	12.07	12.06	11.95

Young's modulus [GPa]		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	24.63	22.87	23.88	24.55	25.03	24.77	25.21
	0.125	25.55	24.64	24.77	25.34	25.32	25.79	26.30
	0.25	26.85	25.72	26.11	26.51	26.94	26.97	27.17
	0.5	27.02	26.78	25.79	27.45	27.85	27.97	28.08
	0.75	29.29	27.84	28.16	28.39	28.94	28.97	28.98
	0.875	30.46	28.40	29.48	29.68	30.08	30.09	30.18
	1	32.05	30.34	30.80	31.07	31.39	31.22	31.03

Poisson's ratio		x						
		0	0.167	0.333	0.5	0.667	0.833	1
b	0	0.30	0.25	0.30	0.29	0.29	0.27	0.29
	0.125	0.30	0.30	0.29	0.30	0.27	0.28	0.29
	0.25	0.30	0.29	0.30	0.30	0.29	0.29	0.29
	0.5	0.28	0.30	0.27	0.30	0.28	0.29	0.29
	0.75	0.30	0.30	0.30	0.30	0.30	0.29	0.29
	0.875	0.30	0.27	0.30	0.30	0.30	0.29	0.29
	1	0.30	0.30	0.30	0.30	0.30	0.29	0.30

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