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High-entropy alloy screening for halide perovskites†

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As the concept of high-entropy alloying (HEA) extends beyond metals, new materials screening methods are needed. Halide perovskites (HP) are a prime case study because greater stability is needed for photovoltaics applications, and there are 322 experimentally observed HP end-members, which leads to more than 10^{57} potential alloys. We screen HEAHP by first calculating the configurational entropy of 10^6 equimolar alloys with experimentally observed end-members. To estimate enthalpy at low computational cost, we turn to the delta-lattice parameter approach, a well-known method for predicting III–V alloy miscibility. To generalize the approach for non-cubic crystals, we introduce the parameter of unit cell volume coefficient of variation (UCV), which does a good job of predicting the experimental HP miscibility data. We use plots of entropy stabilization *versus* UCV to screen promising alloys and identify 10^2 HEAHP of interest.

New concepts

We demonstrate the new concept of using unit cell volume coefficient of variation to approximate the enthalpic penalty of a given high-entropy alloy candidate, and use it along with ideal sublattice configurational entropy to map promising high-entropy alloy halide perovskites. While lattice parameter differences have been used for 50 years to predict III–V alloy miscibility, we extend this approach to non-cubic crystals for the first time, and introduce it as a metric for high-entropy alloy materials screening. This new approach is particularly valuable for guiding the search for nonmetallic high-entropy alloys, which is in its infancy for covalent-bonded and semiconducting materials.

1. Introduction

Halide perovskites (HP) are a broad class of materials spanning 322 inorganic and hybrid organic–inorganic crystals. The prototypical ABX_3 HP has oxidation states of A^+, B^{2+} and X^-. The HP's divalent metal (B^{2+}) constituent is octahedrally coordinated to 6 halide ions (X^-). These octahedra share corners to form a three-dimensional inorganic framework that surrounds the weakly-bonded A^+ constituents in cuboctahedral sites.[1,2] Entropy stabilization (ES) is an emerging method[3–5] where components are added to a given material until its configurational entropy meaningfully alters its Gibbs free energy.

ES of HP is of interest for their many applications: for electrochemical energy storage materials, ES can enhance ion transport.[6,7] For thermoelectrics, ES reduces thermal conductivity.[8] For photovoltaics (PV), the enhanced stability of ES is desirable: the photoactive polytypes of the prototypical inorganic HP PV absorber $CsPbI_3$ are metastable below ~375 K.[9] However, the negative impact of ES on charge carrier transport or recombination may limit its use to non-absorbing PV functions such as buffer layers, transport layers or mechanical anchors.[10] For other HP applications such as light-emitting diodes (LEDs), lasers, neuromorphics, scintillators, *etc.*, the role of entropy is less clear, but such an extensively inhabited class of crystals make HEAHP of general interest for engineering, such that the boundaries of what is possible, feasible, and useful warrant exploration.

Density functional theory (DFT) is currently being used to screen HEA boride, carbide, and carbonitride ceramics.[11] We stress that computationally efficient *pre*screening methods are needed even for choosing alloys for DFT because HEA have large unit cells, and the 322 experimentally observed HP can combine to form 10^{57} alloys (considering equimolar compositions with up to 48 end-members). In our first screening, we report the 10^6 HEAHP consisting entirely of experimentally observed end-members. We then further screen by quantifying their ideal mixing ES and estimate enthalpic penalty using end-member unit cell volume coefficient of variation (UCV), identifying 10^2 alloys with promising UCV-ES tradeoffs.

2. Results

Metal alloys are the prototypical ES case because they commonly have single site lattice structures. This makes metals

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behave like ideal solid solutions, so their entropies increase dramatically as components are added: the configurational entropy of a 6-component equimolar mixture of (metal) elements on a single sublattice is −4.5 kJ mol^{-1} at 300 K.[12] ES of oxides has been demonstrated in $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$[13] and many other oxides.[14] Although MgO, NiO, CuO, and ZnO have different structures and a mean Gibbs energy of formation of −307 kJ mol^{-1},[15] the thermodynamics of $Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$ were predominated by entropy,[13] despite possessing ES of only −2.0 kJ mol^{-1} at 300 K. By comparison, HP ES should be relatively large and easy to measure. We find 282 inorganic HP that have been experimentally observed[16–24] and theory suggests that many more may exist,[23–27] so a staggeringly wide combinatorial chemical space can be drawn on to realize this potential. Moreover, weak bonding allows entropy to dominate HP Gibbs energies.[28]

A given alloy composition change can be net stabilizing if that change's configurational ES outweighs any enthalpic destabilization. In order to screen for promising alloy compositions, we assume each sublattice (A cation, B cation, and X anion) behaves like an ideal solid solution[12] to calculate the entropy of mixing (configurational entropy; S/R), as well as the ES term in the Gibbs energy equation at 300 K:

$$S/R = -\left(\frac{1}{5}\sum_i y_i^{\mathrm{A}} \ln\left(y_i^{\mathrm{A}}\right) + \frac{1}{5}\sum_j y_j^{\mathrm{B}} \ln\left(y_j^{\mathrm{B}}\right) + \frac{3}{5}\sum_k y_k^{\mathrm{X}} \ln\left(y_k^{\mathrm{X}}\right)\right) \quad (1)$$

$$\text{ES term} = -TS = RT\left(\frac{1}{5}\sum_i y_i^{\mathrm{A}} \ln\left(y_i^{\mathrm{A}}\right) + \frac{1}{5}\sum_j y_j^{\mathrm{B}} \ln\left(y_j^{\mathrm{B}}\right) + \frac{3}{5}\sum_k y_k^{\mathrm{X}} \ln\left(y_k^{\mathrm{X}}\right)\right) \quad (2)$$

R is the gas constant, T is temperature (K), and y_i^{A} is the mole fraction of the ith constituent on the A sublattice in ABX_3. Actual atomic distributions in (metal) HEA have been considered,[29,30] and simple scaling rules have been developed to predict HEA stability for metals.[31–37] Unlike metals, ABX_3 HP have covalent to ionic bonding and 3 distinct lattice sites (A, B, and X), which limits how much they can be stabilized with configurational entropy.[38]

In contrast to ES, estimating enthalpy for screening HEAHP is challenging, leading to a tradeoff between accuracy and computational (or experimental) cost. Experimentally screening HEA is most accurate and most expensive. The next most accurate and expensive method combines DFT with the special quasirandom structures approach.[39–44] Alternative approaches have been developed to screen alloys[45–48] and HEA,[49–53] but these are either too computationally expensive,[49,51] need too much experimental data,[53] or use experiment-free phase diagrams to predict HEA with machine learning, which has limited interpretability.[50,52] An approach with even lower computational cost is to estimate mixing enthalpy, which is proportional to the difference between the lattice parameters of a III–V alloy's constitutive end-members.[54] Based on the Hume–Rothery rules for metal alloying (minimize atomic radii differences, match crystal structures, keep valency constant, and keep electronegativity constant),[55] Foster showed that lattice parameter differences could be used to predict miscibility in III–Vs and II–VIs.[56] Foster and Stringfellow used this "delta-lattice parameter" approach to correctly group the miscibility of 9 ternary II–VI[56] and 9 quaternary III–V[57] alloy systems, respectively, and the method was recently extended to correctly group the miscibility of 18 ternary III–V alloy systems,[58] confirming broad accuracy in spite of its low computational cost. To extend the delta-lattice parameter method to non-cubic structures, we draw on Zen's law: there is an empirical linear relation between molar volume and composition of a solid solution.[59] (Zen's law simplifies to Vegard's law[60] for cubic structures with similar molar volumes.) Therefore, an HP alloy's unit cell volume is its weighted mean ($\bar{V}_{\mathrm{w}}$):

$$\bar{V}_{\mathrm{w}} = \sum_i \sum_j \sum_k y_i^{\mathrm{A}} y_j^{\mathrm{B}} y_k^{\mathrm{X}} V_{ijk_3} \quad (3)$$

Here V_{ijk_3} is the unit cell volume of the end-member with the ith, jth and kth constituent on the A, B and X sublattices, respectively. To reduce complexity, we consider only equimolar compositions, which have the greatest ES term. (A semiconductor alloy's density of states can shift its entropic minimum away from the equimolar composition,[61] so other compositions should be considered after the initial screening.) The equimolar unit cell volume's mean, standard deviation, and coefficient of variation are:

$$\bar{V} = \frac{\sum_i \sum_j \sum_k V_{ijk_3}}{N} \quad (4)$$

$$\sigma = \sqrt{\frac{\sum_i \sum_j \sum_k \left(V_{ijk_3} - \bar{V}\right)^2}{N}} \quad (5)$$

$$\mathrm{UCV} = \frac{\sigma}{\bar{V}} \quad (6)$$

Here $\bar{V}$ is equimolar unit cell volume, σ is equimolar alloy unit cell volume standard deviation, UCV is equimolar alloy unit cell volume coefficient of variation, and N is the number of end-members. Atomic radius differences,[62–64] lattice parameter differences,[65,66] and atomic position differences[67] have been previously parameterized to screen metal HEA. We instead parameterize unit cell volume to extend the approach to non-cubic crystals. Although perovskite lattice parameter was previously shown to correlate with ionic radii,[68,69] we use eqn (6) for enthalpic penalty in HEA for the first time. We confirm agreement with 42 out of 45 room temperature miscibility gap data from III–V (Fig. 1 and Table S1, ESI†)[57,58] and II–VI (Table S1, ESI†)[56] material systems. UCV correlates well with experimental III–V and II–VI mixing enthalpy (Table S1 and Fig. S1, ESI†), although future work using the elastic modulus or melting temperature are expected to improve the fit.[70] Using the phase

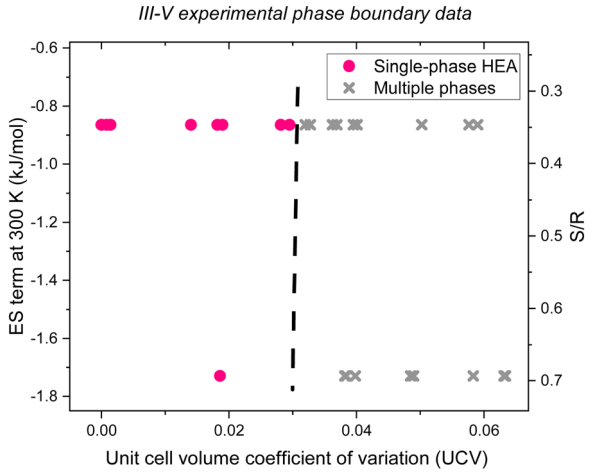

Fig. 1 Experimental III–V single-phase alloy (pink circles) and multiple phase (gray Xs) data,[57,58] confirming that plotting the ES term at 300 K (or *S*/*R*) as a function of UCV leads to a phase boundary near UCV of 0.03 (black dashed line) which is useful for screening HEA that have not yet been experimentally synthesized.

boundary for HP in Fig. 2,[71] 22 out of 26 experimental HEAHP data are grouped correctly. Mapping the boundary between single-phase and multiple phase alloys with UCV-ES plots also works for boride, carbide, and carbonitride ceramics: Fig. S2 and Tables S2, S3 (ESI†) show correct grouping of 56 out of the 64 miscibility data (88% accuracy). Good agreement with such broad experimental data and no fitting parameters suggests the UCV approach has sufficient accuracy despite its low computational cost. UCV allows us to directly compare cubic and hettotype perovskites—the latter have distortions that reduce symmetry, but are more common (*e.g.*, $CsPbI_3$'s metastable polymorphs).[1,2] There are more reports of single-phase inorganic HEAHP (Table S4, ESI†)[71–219] and hybrid organic–inorganic

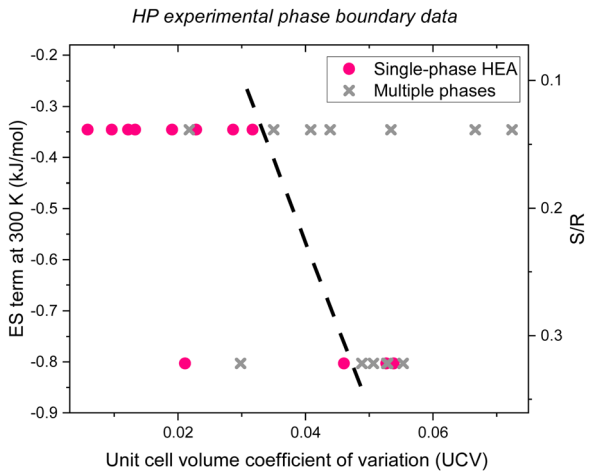

Fig. 2 Experimental HP single-phase alloy (pink circles) and multiple phase (gray Xs) data,[71] confirming that plotting the ES term at 300 K (or *S*/*R*) as a function of UCV leads to a phase boundary near UCV of 0.04 (black dashed line) which correctly groups 22 of the 26 data. Binary copper alloys are excluded because the synthesis method did not produce phase pure $KCuF_3$.[71]

HEAHP (Table S5, ESI†),[220–285] but more investigation into single-phase boundaries is needed to confirm the broadscale applicability of UCV for screening HEAHP.

Using DFT we calculate mixing enthalpy of 6 HEAHP compositions. To make the computations tractable we approximate a HEA's mixing enthalpy by calculating the energy of 8 distinct configurations of 40-atom unit cells and reference their mean to that alloy's constitutive end-members. The results in Fig. 3 and Table S6 (ESI†) confirm that UCV correlates with DFT mixing enthalpy for HEAHP.

It was argued that for thermoelectric devices ES can enhance crystal symmetry to preserve charge carrier transport despite the disordered nuclei that impede phonons and reduce thermal conductance.[8,286] In $CH_3NH_3PbI_3$ phonon lifetimes are shortened by the organic cation's entropy, which may improve charge carrier recombination properties.[287] HP's peculiar semiconductor physics have been attributed to dynamic disorder,[288] lattice softness and anharmonicity.[289]

Beyond PV absorbers, ES HP may be useful as oxygen evolution electrocatalysis,[71] electrochemical energy storage,[86] thermoelectrics,[8] light emitting diodes, photodetectors, PV buffers, contacts, solid state radiation detectors, scintillators, fuel cells, lasers, high temperature electronic components, barocaloric materials for use in refrigeration, ferroelectrics, and neuromorphic computers.

The disordered nuclei in ES HP may alter phonons, possibly reducing thermal conductance. Restricted phonons can result in slow cooling of hot charge carriers, similar to what is already observed in HP as a result of light-induced lattice distortions.[290,291] On the other hand, local bonding distortions in ES crystals should disrupt electron band energies, creating a distribution of local energy states similar to what was described for ion conductivity through ES materials.[7] Thus, bulk 3D carrier transport may suffer, but there may good charge carrier transport along specific crystal directions.

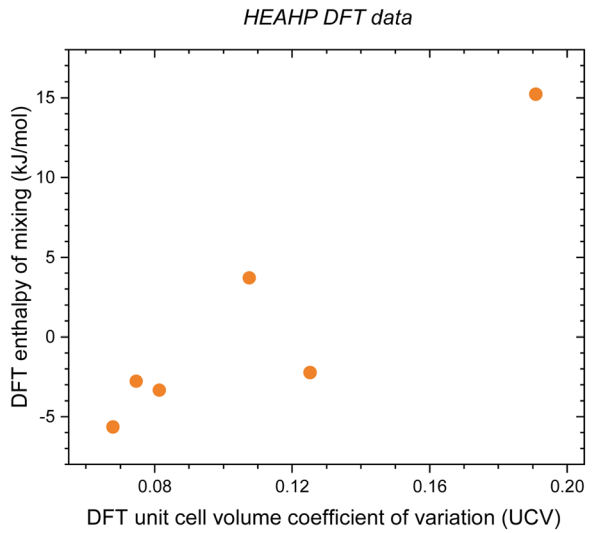

Fig. 3 DFT enthalpy of mixing as a function of UCV from DFT for the HEAHP in Table S6 (ESI†), showing that UCV correlates with DFT mixing enthalpy.

2.1 Mixing on all sublattices

Assuming equimolar compositions on each sublattice (A^+, B^{2+}, and X^- in ABX_3), we calculate the 1 340 752 possible combinations of the 282 experimentally observed inorganic HP with 5 or more components (Table S7, ESI†). The compositions with the greatest ES are in Table 1. HP are mostly composed of halides, so most of the compounds in Table 1 have 4 halide components. The greatest ES, −3.22 kJ mol^{-1}, is for $CsB(Br,Cl,F,I)_3$ with 10 B-site components. The next greatest ES, −3.17 kJ mol^{-1}, is for $(Cs,K,Rb)(Ca,Cd,Sn)(Br,Cl,F,I)_3$, as well as $CsB(Br,Cl,F,I)_3$ with 9 B-site components. $(Cs,Rb)(Ca,Cd,Pb,Sn)(Br,Cl,F,I)_3$ has ES of −3.11 kJ mol^{-1}. $CsB(Br,Cl,I)_3$ with 15 B-site components has ES of −3.00 kJ mol^{-1}.

Next, we calculate most of the combinations of the 282 inorganic HP with known lattice parameters in Fig. 4, where the ES term at 300 K is plotted as a function of UCV. As Fig. 4(b) and Table 2 show, HP are mostly composed of halides, so the greatest ES comes from X-site mixing. However, X-site mixing drives UCV higher: when all 4 halides are used, the ES term reaches −3.17 kJ mol^{-1} but has UCV of 0.283 for $Cs(Ca,Eu,Mg,Mn,Ni,Pb,Sn,Sr,Yb)(Br,Cl,F,I)_3$. When only 3 halides are used, an ES term of −2.96 kJ mol^{-1} is achieved at the much lower UCV of 0.156 for $Cs(Au,Ca,Eu,Ge,Mg,Mn,Ni,Pb,Sn,Sr,Ti,Tm,V,Yb)(Br,Cl,I)_3$. When only 2 halides are used, an ES term of only −2.28 kJ mol^{-1} is possible, but at UCV of only 0.106 for $(Cs,K,Rb,Tl)(Ca,Cd,Mn)(Br,Cl)_3$, while an ES term of −2.19 kJ mol^{-1} is reached at a UCV of only 0.073 for $(Cs,Rb)(Ca,Ge,Pb,Sn,Sr)(Br,Cl)_3$. We examine 1-halide compounds in the next section. Other compounds with attractive UCV-ES term tradeoffs are in Fig. 4(b) and Table 3. These specific compositions demonstrate that in general, mixing Br, Cl, and I on the X-site, Cs and Rb on the A-site and Ge, Pb, and Sn on the B-site are all promising. Less obvious constituents include F on the X-site, K and Tl on the A-site and Ca, Cd, Eu, and Sr on the B-site. Former work found the prospect of using hetero-valent substitutes on the B site to be promising.[292]

2.2 Mixing on only A and B sublattices (ordered valence band)

HP valence band maximum is dominated by (X) halide with minor B cation contributions, while the conduction band minimum is mostly determined by the B cation with small X contributions.[293] Therefore, to preserve order in the valence band and keep valence band energy constant to facilitate hole transport, A- and B-site cations can both be alloyed while the halide is kept pure (1 component on the X sublattice). In this case, the greatest ES term is only −1.68 kJ mol^{-1} for $CsBCl_3$ with 29 B-site components (Fig. 5). Other noteworthy compositions are shown in Fig. 5(b) and Table 4. As discussed in the previous section, less halide mixing translates to less ES but also lower UCV. Halide segregation is a known issue in HP[294] that could prevent the use of mixing on the X-site for ES. If that is a limitation, then the compounds in this section can still be used to achieve moderate ES at low enthalpic penalties (low UCV), all while maintaining an ordered valence band valuable for hole transport.

2.3 Mixing on only A and X sublattices (ordered conduction band)

To preserve order in the conduction band and conduction band energy alignment to facilitate electron transport, mixing on the A- and X-sites can be used. In this case, the greatest ES term is −2.77 kJ mol^{-1} for $(Cs,K,Rb,Tl)Cd(Br,Cl,F,I)_3$. Other noteworthy compositions are shown in Fig. 6(b) and Table 5. We note that 3 of the compounds are entirely composed of end-members whose experimental band gaps are known. The compounds' band gaps are estimated by averaging end-member values: 1.95 eV for CsSnBrClI, 2.31 eV for CsPbBrClI, and 2.48 eV for CsGeBrClI.

2.4 Mixing on only A sublattice (ordered valence and conduction bands)

To preserve order in the valence and conduction bands and prevent changes in the valence and conduction band energy as well as band gap, alloying on only the A-site should be used. In this case, the greatest ES term is only −0.97 kJ mol^{-1} with UCV of 0.063 for $(Cs,In,K,Li,Na,Rb,Tl)CaBr_3$. Other compositions of interest are shown in Fig. 7(b) and Table 6.

A-site and X-site segregation are both known issues in HP[295] that could prevent the use of mixing on the A- and X-sites for ES. If those are limitations, then the compounds in this section can still be used to achieve weak ES at low enthalpic penalties (low UCV), all while maintaining ordered valence and conduction bands valuable for both hole and electron transport.

Table 1 Inorganic HP compositions with the most negative ES term at 300 K whose end-members are all experimentally observed. We omit compositions with an ellipsis (...) that are analogous to the row above them and have the same A- and X-site occupation

Alloy composition	ES term (kJ mol^{-1})	S/R
$CsCa_{0.1}Cd_{0.1}Eu_{0.1}Mg_{0.1}Mn_{0.1}Ni_{0.1}Pb_{0.1}Sn_{0.1}Sr_{0.1}Yb_{0.1}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.22	1.29
$Cs_{0.33}K_{0.33}Rb_{0.33}Ca_{0.33}Cd_{0.33}Sn_{0.33}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.17	1.27
$CsCa_{0.11}Cd_{0.11}Eu_{0.11}Mg_{0.11}Mn_{0.11}Ni_{0.11}Pb_{0.11}Sn_{0.11}Sr_{0.11}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.17	1.27
...		
$Cs_{0.5}Rb_{0.5}Ca_{0.25}Cd_{0.25}Pb_{0.25}Sn_{0.25}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.11	1.25
$CsCa_{0.13}Cd_{0.13}Eu_{0.13}Mg_{0.13}Mn_{0.13}Ni_{0.13}Pb_{0.13}Sn_{0.13}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.11	1.25
...		
$CsCa_{0.14}Cd_{0.14}Eu_{0.14}Mg_{0.14}Mn_{0.14}Ni_{0.14}Pb_{0.14}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.05	1.22
...		
$CsAu_{0.07}Ca_{0.07}Cd_{0.07}Eu_{0.07}Ge_{0.07}Mg_{0.07}Mn_{0.07}Ni_{0.07}Pb_{0.07}Sn_{0.07}Sr_{0.07}Ti_{0.07}Tm_{0.07}V_{0.07}Yb_{0.07}BrClI$	−3.00	1.20
$Cs_{0.33}K_{0.33}Rb_{0.33}Ca_{0.5}Cd_{0.5}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19
...		
$Cs_{0.5}K_{0.5}Ca_{0.33}Cd_{0.33}Sn_{0.33}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19
$Cs_{0.5}Rb_{0.5}Ca_{0.33}Cd_{0.33}Pb_{0.33}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19
...		

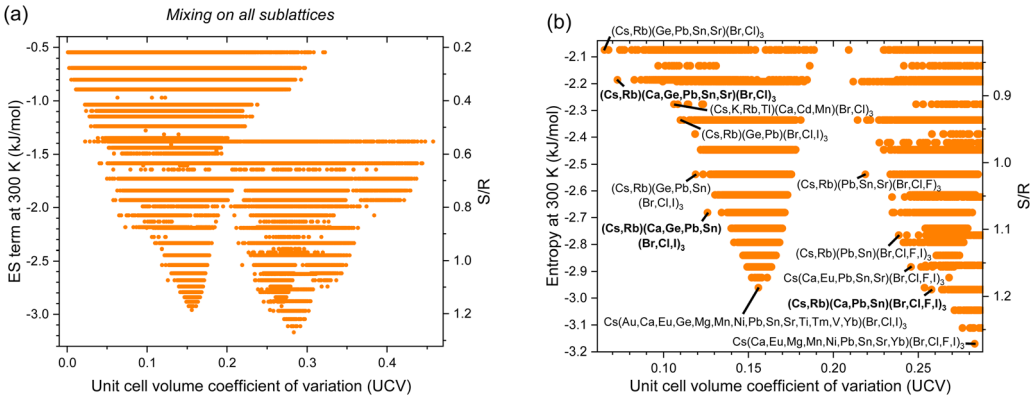

Fig. 4 Entropy stabilization (ES term at 300 K) as a function of enthalpic penalties, or unit cell volume coefficient of variation (UCV), for all equimolar inorganic HP compositions with experimentally observed constitutive end-members with mixing on all sublattices: (a) all data and (b) zoomed in, with promising alloys labeled and in bold.

Table 2 Inorganic HP compositions with the greatest ES term at 300 K whose lattice parameters are known and end-members are all experimentally observed with mixing on all sublattices. We omit compositions with an ellipsis (...) that are analogous to the row above them and have the same A- and X-site occupation

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV
$CsCa_{0.11}Eu_{0.11}Mg_{0.11}Mn_{0.11}Ni_{0.11}Pb_{0.11}Sn_{0.11}Sr_{0.11}Yb_{0.11}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.17	1.27	0.283
$CsCa_{0.13}Eu_{0.13}Mn_{0.13}Ni_{0.13}Pb_{0.13}Sn_{0.13}Sr_{0.13}Yb_{0.13}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.11	1.25	0.276
...			
$CsCa_{0.14}Eu_{0.14}Mn_{0.14}Pb_{0.14}Sn_{0.14}Sr_{0.14}Yb_{0.14}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−3.05	1.22	0.271
...			
$Cs_{0.5}Rb_{0.5}Ca_{0.33}Pb_{0.33}Sn_{0.33}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19	0.258
$CsCa_{0.17}Eu_{0.17}Pb_{0.17}Sn_{0.17}Sr_{0.17}Yb_{0.17}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19	0.264
...			
$Cs_{0.33}K_{0.33}Rb_{0.33}Ca_{0.5}Sn_{0.5}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19	0.273
$CsCa_{0.17}Eu_{0.17}Mn_{0.17}Sn_{0.17}Sr_{0.17}Yb_{0.17}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19	0.276
...			
$CsAu_{0.07}Ca_{0.07}Eu_{0.07}Ge_{0.07}Mg_{0.07}Mn_{0.07}Ni_{0.07}Pb_{0.07}Sn_{0.07}Sr_{0.07}Ti_{0.07}Tm_{0.07}V_{0.07}Yb_{0.07}BrClI$	−2.96	1.19	0.156
$Cs_{0.5}Rb_{0.5}Ca_{0.14}Cd_{0.14}Mn_{0.14}Ni_{0.14}Pb_{0.14}Sn_{0.14}Sr_{0.14}BrClF$	−2.96	1.19	0.254
$CsAu_{0.08}Ca_{0.08}Eu_{0.08}Ge_{0.08}Mg_{0.08}Mn_{0.08}Pb_{0.08}Sn_{0.08}Sr_{0.08}Ti_{0.08}Tm_{0.08}V_{0.08}Yb_{0.08}BrClI$	−2.92	1.17	0.152
...			
$CsCa_{0.08}Cd_{0.08}Eu_{0.08}Fe_{0.08}Hg_{0.08}Mg_{0.08}Mn_{0.08}Ni_{0.08}Pb_{0.08}Pd_{0.08}Sn_{0.08}Sr_{0.08}Yb_{0.08}BrClF$	−2.92	1.17	0.268
$CsAu_{0.08}Ca_{0.08}Eu_{0.08}Ge_{0.08}Mg_{0.08}Mn_{0.08}Pb_{0.08}Sn_{0.08}Sr_{0.08}Tm_{0.08}V_{0.08}Yb_{0.08}BrClI$	−2.88	1.16	0.149
...			
$Cs_{0.5}Rb_{0.5}Ca_{0.17}Ge_{0.17}Pb_{0.17}Sn_{0.17}Ti_{0.17}V_{0.17}BrClI$	−2.88	1.16	0.152
$CsAu_{0.08}Eu_{0.08}Ge_{0.08}Mg_{0.08}Mn_{0.08}Pb_{0.08}Sn_{0.08}Sr_{0.08}Ti_{0.08}Tm_{0.08}V_{0.08}Yb_{0.08}BrClI$	−2.88	1.16	0.152
...			
$Cs_{0.5}Rb_{0.5}Ca_{0.17}Cd_{0.17}Ni_{0.17}Pb_{0.17}Sn_{0.17}Sr_{0.17}BrClF$	−2.88	1.16	0.246
...			
$CsCa_{0.08}Cd_{0.08}Eu_{0.08}Fe_{0.08}Hg_{0.08}Mn_{0.08}Ni_{0.08}Pb_{0.08}Pd_{0.08}Sn_{0.08}Sr_{0.08}Yb_{0.08}BrClF$	−2.88	1.16	0.263
...			
$Cs_{0.33}K_{0.33}Rb_{0.33}Ca_{0.25}Cd_{0.25}Mn_{0.25}Sn_{0.25}BrClF$	−2.88	1.16	0.265
$CsCa_{0.08}Cd_{0.08}Eu_{0.08}Hg_{0.08}Mg_{0.08}Mn_{0.08}Ni_{0.08}Pb_{0.08}Pd_{0.08}Sn_{0.08}Sr_{0.08}Yb_{0.08}BrClF$	−2.88	1.16	0.266
...			
$CsCa_{0.2}Eu_{0.2}Pb_{0.2}Sn_{0.2}Sr_{0.2}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.88	1.16	0.254
...			

2.5 Organic A-site components (hybrid organic–inorganic HP)

The previous sections have only considered inorganic compounds, but there are at least 22 organic cations that can substitute on the A-site: methylammonium (MA; CH_3NH_3), formamidinium (FA; $HC(NH_2)_2$), guanidinium (GA; $C(NH_2)_3$), dimethylammonium (DMA; $(CH_3)_2NH_2$), ethylammonium (EA; $CH_3CH_2NH_3$), acetamidinium (ACA; $CH_3C(NH_2)_2$), ammonium (NH_4), hydrazinium (HA; N_2H_5), azetidinium (AZ; $C_3H_6NH_2$), imidazolium (IM; $C_3N_2H_5$), trimethylammonium (TMA; $(CH_3)_3NH$), tetramethylammonium (TEMA; $(CH_3)_4N$), arsonium, methylarsonium, methylphosphonium, aziridine, hydroxylammonium, phosphonium, antimonium, PF_4, NH_2CHPH_2, and NH_2CHAsH_2.[296] Therefore, hybrid organic–inorganic halide perovskites have an even larger chemical space that can be tapped for ES than the pure inorganics.

Previous work found ES in $(Cs,FA)PbI_3$,[297] $(FA,GA)PbBr_3$,[298] $(Cs,FA,MA)PbI_3$,[299] $(Cs,FA,MA)Pb(Br,I)_3$,[221,300] and $(Cs,FA,MA,Rb)PbI_3$,[220,222] and ES was also recently demonstrated in double HP[28,301] and "hollow" HP.[302] Long anneals of $CH_3NH_3PbI_3$ were argued to maximize configurational entropy of the organic cation, which was found to stabilize the cubic polytype and improve

Table 3 Inorganic HP compositions with attractive UCV-ES term at 300 K tradeoffs whose lattice parameters are known and end-members are all experimentally observed with mixing on all sublattices

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV
$Cs_{0.5}Rb_{0.5}Ca_{0.33}Pb_{0.33}Sn_{0.33}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.97	1.19	0.258
$CsCa_{0.2}Eu_{0.2}Pb_{0.2}Sn_{0.2}Sr_{0.2}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.88	1.15	0.254
$Cs_{0.5}Rb_{0.5}Pb_{0.5}Sn_{0.5}Br_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.77	1.11	0.239
$Cs_{0.5}Rb_{0.5}Ca_{0.25}Ge_{0.25}Pb_{0.25}Sn_{0.25}BrClI$	−2.68	1.08	0.126
$Cs_{0.5}Rb_{0.5}Ge_{0.33}Pb_{0.33}Sn_{0.33}BrClI$	−2.54	1.02	0.119
$Cs_{0.5}Rb_{0.5}Pb_{0.33}Sn_{0.33}Sr_{0.33}BrClF$	−2.54	1.02	0.219
$Cs_{0.5}Rb_{0.5}Ge_{0.5}Pb_{0.5}BrClI$	−2.34	0.94	0.112
$Cs_{0.25}K_{0.25}Rb_{0.25}Tl_{0.25}Ca_{0.33}Cd_{0.33}Mn_{0.33}Br_{1.5}Cl_{1.5}$	−2.28	0.91	0.106
$Cs_{0.5}Rb_{0.5}Ca_{0.2}Ge_{0.2}Pb_{0.2}Sn_{0.2}Sr_{0.2}Br_{1.5}Cl_{1.5}$	−2.19	0.88	0.073
$Cs_{0.5}Rb_{0.5}Ge_{0.25}Pb_{0.25}Sn_{0.25}Sr_{0.25}Br_{1.5}Cl_{1.5}$	−2.07	0.83	0.065

electrical properties.[303] Entropy stabilization of HP nanocrystals was recently demonstrated: Pb was substituted for Mg, Zn, and Cd in $CH_3NH_3PbBr_3$ to enhance stability, while narrow band emission was retained.[304] Unlike former reports,[297,298] here we consider the maximum feasible configurational ES, which restricts our focus to alloys with a minimum of 5 components.

Mixing the 40 organic and 282 inorganic HP end-members, we find 14 270 hybrid organic–inorganic HEAHPs consisting of 5 or more experimentally observed end-members (Fig. 8 and Table S8, ESI†). Attractive UCV-ES term tradeoffs are in Table 7. In general, smaller ES are possible at a given UCV, relative to the inorganic HEAHPs in the previous sections. Table 7 mostly consists of well-studied alloys based on Cs, MA, and FA, but the less-studied Rb and K are also present. For PV-related Br, Cl, and I systems, the B-site constituents are Ge, Sn and Pb. The F systems are of interest for electrochemical applications and have smaller unit cells, so NH_4 and Na are allowed, Cd, Fe, and Mn are prevalent while Tl, Co, Cu Fe, Mg, Ni and Zn are possible. $(Cs,K,NH_4,Rb,Tl)(Cd,Fe,Mn)(Cl,F)_3$ and $(K,NH_4,Rb,Tl)(Cd,Co,Cr,Cu,Fe,Mg,Mn,Ni,Sn,Zn)F_3$ have ES terms at 300 K of −2.39 and −1.84 kJ mol^{-1}, respectively. While inorganic HEAHP have more negative ES terms as temperature increases, the organic components' volatility may limit this effect for organic HEAHP.

2.6 Non-equimolar compositions

For non-equimolar compositions, weighted standard deviation (σ_w) and weighted coefficient of variation (UCV_w) are:

$$\sigma_w = \sqrt{\frac{\sum_i \sum_j \sum_k y_i^A y_j^B y_k^X \left(V_{ijk_3} - \bar{V}_w\right)^2}{\sum_i \sum_j \sum_k y_i^A y_j^B y_k^X}} = \sqrt{\sum_i \sum_j \sum_k y_i^A y_j^B y_k^X \left(V_{ijk_3} - \bar{V}_w\right)^2} \quad (7)$$

$$UCV_w = \frac{\sigma_w}{\bar{V}_w} \quad (8)$$

The boundary between single-phase and multiple phase

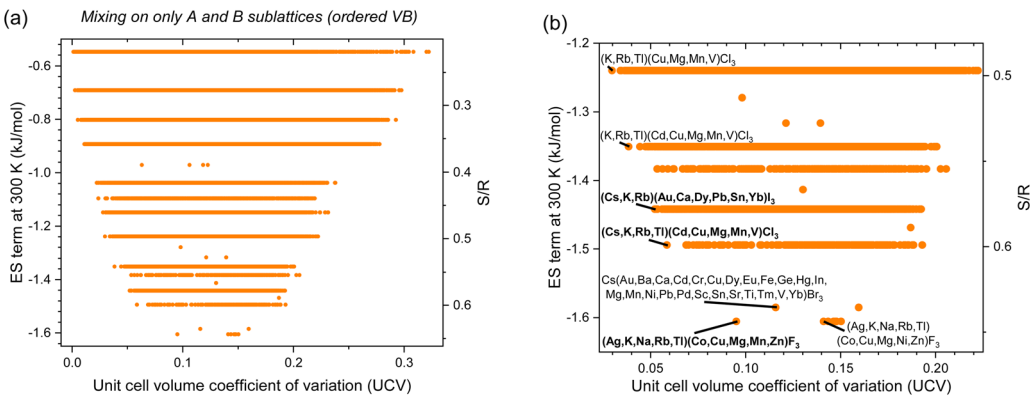

Fig. 5 Entropy stabilization (ES term at 300 K) as a function of enthalpic penalties, or unit cell volume coefficient of variation (UCV), for equimolar inorganic HP compositions with experimentally observed constitutive end-members with mixing on only A and B sublattices (ordered valence band): (a) all data and (b) zoomed in, with promising alloys labeled and in bold.

Table 4 Inorganic HP compositions with attractive UCV-ES term at 300 K tradeoffs whose lattice parameters are known and end-members are all experimentally observed with mixing on only A and B sublattices (ordered valence band)

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV
$Ag_{0.2}K_{0.2}Na_{0.2}Rb_{0.2}Tl_{0.2}Co_{0.2}Cu_{0.2}Mg_{0.2}Mn_{0.2}Zn_{0.2}F_3$	−1.61	0.64	0.095
$Ag_{0.2}K_{0.2}Na_{0.2}Rb_{0.2}Tl_{0.2}Co_{0.2}Cu_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}F_3$	−1.61	0.64	0.141
$CsAu_{0.04}Ba_{0.04}Ca_{0.04}Cd_{0.04}Cr_{0.04}Cu_{0.04}Dy_{0.04}Eu_{0.04}Fe_{0.04}Ge_{0.04}Hg_{0.04}In_{0.04}Mg_{0.04}Mn_{0.04}Ni_{0.04}Pb_{0.04}Pd_{0.04}Sc_{0.04}Sn_{0.04}Sr_{0.04}Ti_{0.04}Tm_{0.04}V_{0.04}Yb_{0.04}Br_3$	−1.59	0.64	0.116
$Cs_{0.25}K_{0.25}Rb_{0.25}Tl_{0.25}Cd_{0.2}Cu_{0.2}Mg_{0.2}Mn_{0.2}V_{0.2}Cl_3$	−1.49	0.60	0.059
$Cs_{0.33}K_{0.33}Rb_{0.33}Au_{0.17}Ca_{0.17}Dy_{0.17}Pb_{0.17}Sn_{0.17}Yb_{0.17}I_3$	−1.44	0.58	0.052
$K_{0.33}Rb_{0.33}Tl_{0.33}Cd_{0.2}Cu_{0.2}Mg_{0.2}Mn_{0.2}V_{0.2}Cl_3$	−1.35	0.54	0.038
$K_{0.33}Rb_{0.33}Tl_{0.33}Cu_{0.25}Mg_{0.25}Mn_{0.25}V_{0.25}Cl_3$	−1.24	0.50	0.030

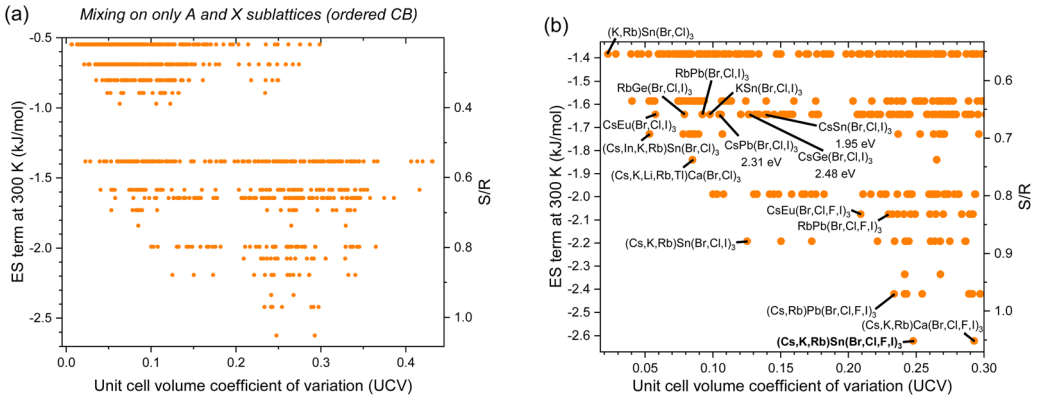

Fig. 6 Entropy stabilization (ES term at 300 K) as a function of enthalpic penalties, or unit cell volume coefficient of variation (UCV), for equimolar inorganic HP compositions with experimentally observed constitutive end-members with mixing on only A and X sublattices (ordered conduction band): (a) all data and (b) zoomed in, with promising alloys labeled and in bold.

Table 5 Inorganic HP compositions with attractive UCV-ES term at 300 K tradeoffs whose lattice parameters are known and end-members are all experimentally observed with mixing on only A and X sublattices (ordered conduction band)

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV
$Cs_{0.33}K_{0.33}Rb_{0.33}SnBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.62	1.05	0.248
$Cs_{0.33}K_{0.33}Rb_{0.33}CaBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.62	1.05	0.293
$Cs_{0.5}Rb_{0.5}PbBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.42	0.97	0.234
$K_{0.5}Rb_{0.5}SnBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.42	0.97	0.242
$Cs_{0.33}K_{0.33}Rb_{0.33}SnBrClI$	−2.19	0.88	0.125
$CsEuBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.07	0.83	0.209
$RbPbBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.07	0.83	0.230
$RbSnBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.07	0.83	0.232
$CsPbBr_{0.75}Cl_{0.75}F_{0.75}I_{0.75}$	−2.07	0.83	0.236
$Cs_{0.2}K_{0.2}Li_{0.2}Rb_{0.2}Tl_{0.2}CaBr_{1.5}Cl_{1.5}$	−1.84	0.74	0.085
$Cs_{0.25}In_{0.25}K_{0.25}Rb_{0.25}SnBr_{1.5}Cl_{1.5}$	−1.73	0.69	0.053
CsEuBrClI	−1.64	0.66	0.058
RbGeBrClI	−1.64	0.66	0.079
RbPbBrClI	−1.64	0.66	0.092
KSnBrClI	−1.64	0.66	0.098
CsPbBrClI (2.31 eV)	−1.64	0.66	0.105
CsGeBrClI (2.48 eV)	−1.64	0.66	0.127
CsSnBrClI (1.95 eV)	−1.64	0.66	0.138
$K_{0.5}Rb_{0.5}SnBr_{1.5}Cl_{1.5}$	−1.38	0.55	0.023

compositions has been mapped experimentally for MAPb(Br,Cl,I)$_3$.[223] We calculate ES term at 300 K and UCV$_w$ for MAPb(Br,Cl,I)$_3$ in Fig. 8(a) and (b). While UCV$_w$ predicts the general shape of the data, multiplying UCV$_w$ by a constant (C) and adding it to ES term accurately predicts 52 out of the 56 data (93%; Fig. 9(c)). ES′ combined effect on Gibbs energy (G_{ES}) is:

$$G_{ES} = \text{ES term} + \text{UCV}_w C = RT\left(\frac{1}{5}\sum_i y_i^A \ln\left(y_i^A\right) + \frac{1}{5}\sum_j y_j^B \ln\left(y_j^B\right) + \frac{3}{5}\sum_k y_k^X \ln\left(y_k^X\right)\right) + \left(\frac{\sqrt{\sum_i\sum_j\sum_k y_i^A y_j^B y_k^X \left(V_{ijk_3} - \bar{V}_w\right)^2}}{\sum_i\sum_j\sum_k y_i^A y_j^B y_k^X V_{ijk_3}}\right) C \quad (9)$$

This new equation is Calphad with crystal structure inputs. Empirically fitting C to the MAPb(Br,Cl,I)$_3$ data yields C of 23 kJ mol^{-1}. On the other hand, a C value of 40 kJ mol^{-1} matches the experimental data for CsPb(Br,Cl,I)$_3$ (Fig. S3, ESI†), suggesting

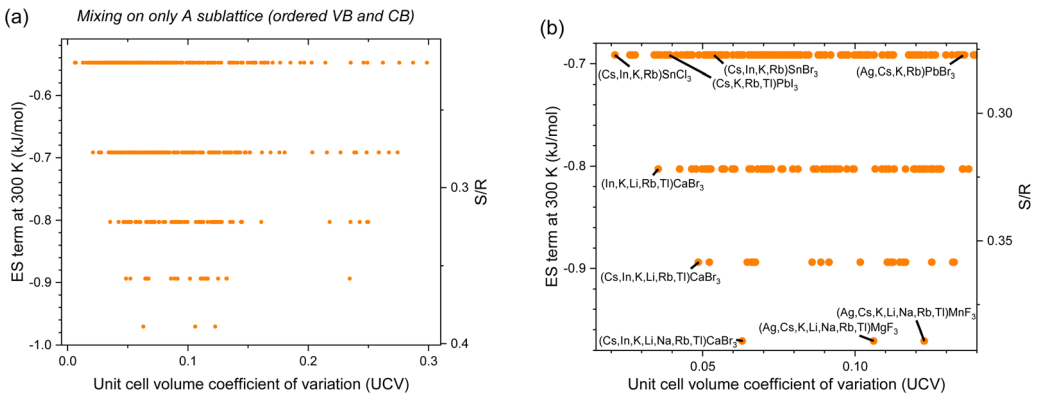

Fig. 7 Entropy stabilization (ES term at 300 K) as a function of enthalpic penalties, or unit cell volume coefficient of variation (UCV), for equimolar inorganic HP compositions with experimentally observed constitutive end-members with mixing on only the A sublattice (ordered valence and conduction bands): (a) all data and (b) zoomed in, with promising alloys labeled and in bold.

Table 6 Inorganic HP compositions with attractive UCV-ES term at 300 K tradeoffs whose lattice parameters are known and end-members are all experimentally observed with mixing on only the A sublattice (ordered valence and conduction bands)

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV
$Cs_{0.14}In_{0.14}K_{0.14}Li_{0.14}Na_{0.14}Rb_{0.14}Tl_{0.14}CaBr_3$	−0.97	0.39	0.063
$Ag_{0.14}Cs_{0.14}K_{0.14}Li_{0.14}Na_{0.14}Rb_{0.14}Tl_{0.14}MgF_3$	−0.97	0.39	0.106
$Ag_{0.14}Cs_{0.14}K_{0.14}Li_{0.14}Na_{0.14}Rb_{0.14}Tl_{0.14}MnF_3$	−0.97	0.39	0.123
$Cs_{0.17}In_{0.17}K_{0.17}Li_{0.17}Rb_{0.17}Tl_{0.17}CaBr_3$	−0.89	0.36	0.049
$In_{0.2}K_{0.2}Li_{0.2}Rb_{0.2}Tl_{0.2}CaBr_3$	−0.80	0.32	0.035
$Cs_{0.25}In_{0.25}K_{0.25}Rb_{0.25}SnCl_3$	−0.69	0.28	0.021
$Cs_{0.25}K_{0.25}Rb_{0.25}Tl_{0.25}PbI_3$	−0.69	0.28	0.039
$Cs_{0.25}In_{0.25}K_{0.25}Rb_{0.25}SnBr_3$	−0.69	0.28	0.053
$Ag_{0.25}Cs_{0.25}K_{0.25}Rb_{0.25}PbBr_3$	−0.69	0.28	0.135

enthalpic penalty plays more of a role in the latter. Altogether we accurately predict 75 out of the 83 ternary data (91%), showing that UCV-ES maps can rank alloys with different constituents *and* different compositions.

2.7 Known experimental band gaps

Of the 282 experimentally observed inorganic HP compounds, we find experimental band gaps for 19. Of the 1 340 752 alloy compositions we consider, 73 are entirely composed of end-members whose experimental band gaps are known. Fig. S4 and Table S9 (ESI†) show that they all contain Cs, most have Ge, Pb or Sn, and most band gaps are wider than 2 eV. Bowing can shift these band gap values, and experimental bowing data is in Table 7 and Fig. S9 (ESI†).

2.8 Overall accuracy

Finally, we note the high accuracy of UCV separating experimental miscibility data across crystal systems with a spectrum of bonding character: from *weak ionic* HP (89% of 109 data) to *weak covalent* II–VIs (83% of 18 data), *covalent* III–Vs (100% of 27 data), and finally to *strong covalent* boride, carbide, and carbonitride ceramics (88% of 64 data). Overall accuracy for the 218 data is 89.4%. For comparison, the accuracy of Materials Project DFT unit cell volumes relative to experiment is 92.6%.[305] There are exceptions to UCV predicting miscibility: $KCo_{0.2}Fe_{0.2}Mg_{0.2}Ni_{0.2}Zn_{0.2}F_3$ in Fig. 2, $Hf_{0.2}Mo_{0.2}Nb_{0.2}Ta_{0.2}W_{0.2}C_{0.5}N_{0.5}$ in Fig. S2 (ESI†), and $CsPb_{0.5}Zn_{0.5}Cl_3$, $CsPb_{0.5}Zn_{0.5}Br_3$, and $CsPb_{0.5}Zn_{0.5}I_3$ in Table S4 (ESI†). These exceptions show that crystal structure and Gibbs energy are more nuanced than a single parameter can describe, but UCV captures 89% of HEA mixing behavior.

3. Conclusions

We take a low computational cost approach to screening HEA and employ it to identify promising inorganic and hybrid organic–inorganic HEAHP. Drawing from the pool of 322 experimentally observed HP, we compute configurational entropy stabilization (ES) of equimolar HEA. Starting with the delta-lattice parameter approach for predicting III–V miscibility, we introduce the more generally applicable unit cell volume coefficient of variation (UCV) to estimate enthalpic penalty of HEA. UCV predicts the existing experimental III–V, II–VI, boride, carbide, carbonitride, and HP data well. We screen the 10^{57} possible HEAHP to report the 10^6 alloys consisting entirely of experimentally observed end-members, then identify 10^2 HEAHP with promising UCV-ES tradeoffs. These results can serve as a first screen for guiding more costly calculations and experiments.

4. Methods

Throughout the literature, the boundary between what is considered perovskite and not considered perovskite is ambiguous.[1,2] We limit our search to the 282 inorganic and 40 organic ABX_3 compounds that have been experimentally observed and previously labeled as "perovskites" (Tables S10[18–20,27,111,112,115,123,179,306–539] and S11 (ESI†),[315,466,524,526,540–558] respectively). We exclude the 90 inorganic HP that have been proposed but not synthesized (Table S12, ESI†).[23,24,307,430] In order to use a self-consistent database, where possible we use lattice parameters from the Materials Project[559] for the *Pnma*

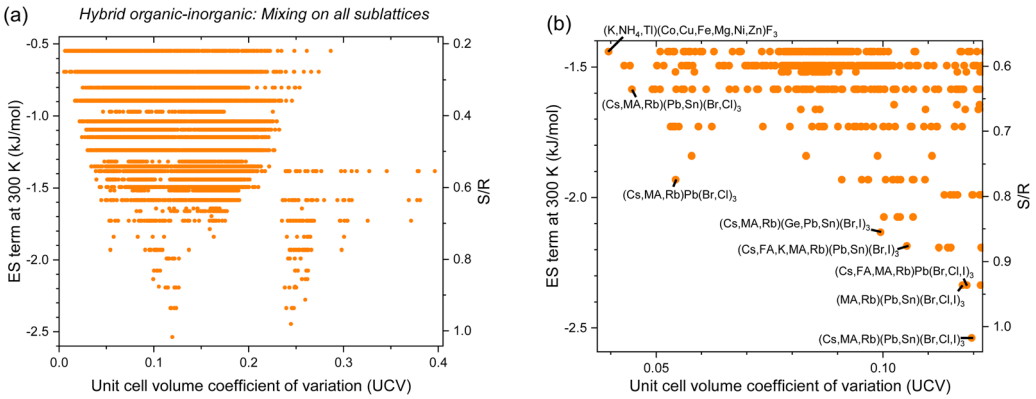

Fig. 8 Entropy stabilization (ES term at 300 K) as a function of enthalpic penalties, or unit cell volume coefficient of variation (UCV), for all equimolar hybrid organic–inorganic HP compositions with experimentally observed constitutive end-members with mixing on all sublattices: (a) all data and (b) zoomed in, with promising alloys labeled and in bold.

Table 7 Hybrid organic–inorganic HP compositions with the greatest ES term at 300 K whose lattice parameters are known and end-members are all experimentally observed with mixing on all sublattices. Calculated band gaps are included along with the maximum experimental band gap bowing (the difference between the linearly-interpolated-band gap and the actual band gap) and references

Alloy composition	ES term (kJ mol^{-1})	S/R	UCV	Band gap (eV)	Exp. bowing (eV)
$Cs_{0.33}MA_{0.33}Rb_{0.33}Pb_{0.5}Sn_{0.5}BrClI$	−2.54	1.02	0.120	—	—
$Cs_{0.2}K_{0.2}(NH_4)_{0.2}Rb_{0.2}Tl_{0.2}CdBrClF$	−2.45	0.98	0.245	—	—
$MA_{0.5}Rb_{0.5}Pb_{0.5}Sn_{0.5}BrClI$	−2.34	0.94	0.118	—	—
$Cs_{0.25}FA_{0.25}MA_{0.25}Rb_{0.25}PbBrClI$	−2.34	0.94	0.119	—	—
$Cs_{0.5}MA_{0.5}Pb_{0.5}Sn_{0.5}BrClI$	−2.34	0.94	0.122	2.24	$MA(Pb,Sn)(Br,I)_3 \leq 0.11$;[243] $(Cs,MA)(Pb,Sn)I_3 \leq 0.11$;[243] $(Cs,FA)PbI_3 \leq 0.02$;[249] $MAPb(Br,Cl)_3 \leq 0.17$[242]
$Cs_{0.25}K_{0.25}MA_{0.25}Rb_{0.25}SnBrClI$	−2.34	0.94	0.124	—	—
...					
$Cs_{0.25}K_{0.25}(NH_4)_{0.25}Rb_{0.25}Cd_{0.33}Fe_{0.33}Mn_{0.33}Cl_{1.5}F_{1.5}$	−2.28	0.91	0.260	—	—
$Cs_{0.33}FA_{0.33}Rb_{0.33}PbBrClI$	−2.19	0.88	0.112	2.31	$(Cs,Rb)PbBr_3 = 0$;[125] $(Cs,Rb)PbCl_3 = 0$[125]
...					
$Cs_{0.33}FA_{0.33}MA_{0.33}PbBrClI$	−2.19	0.88	0.122	2.28	$(FA,MA)Pb(Br,I)_3 \leq 0.10$;[230,243,245,261] $MAPb(Br,Cl)_3 \leq 0.17$[242]
...					
$Cs_{0.2}FA_{0.2}K_{0.2}MA_{0.2}Rb_{0.2}Pb_{0.5}Sn_{0.5}Br_{1.5}I_{1.5}$	−2.19	0.88	0.105	—	—
...					
$Cs_{0.33}MA_{0.33}Rb_{0.33}Ge_{0.33}Pb_{0.33}Sn_{0.33}Br_{1.5}I_{1.5}$	−2.13	0.86	0.099	—	—
...					
$Cs_{0.5}FA_{0.5}PbBrClI$	−1.99	0.80	0.115	2.27	—
...					
$MAPb_{0.5}Sn_{0.5}BrClI$	−1.99	0.80	0.120	2.34	$MA(Pb,Sn)(Br,I)_3 \leq 0.11$;[243] $MAPb(Br,Cl)_3 \leq 0.17$[242]
...					
$Cs_{0.5}MA_{0.5}PbBrClI$	−1.99	0.80	0.121	2.31	$MAPb(Br,I)_3 \leq 0.07$;[243,245] $MAPb(Br,Cl)_3 \leq 0.17$[242]
$Cs_{0.5}MA_{0.5}SnBrClI$	−1.99	0.80	0.122	2.16	$MASn(Br,I)_3 \leq 0.03$[243]
$FA_{0.5}MA_{0.5}PbBrClI$	−1.99	0.80	0.127	2.27	$MAPb(Br,I)_3 \leq 0.07$;[243,245] $MAPb(Br,Cl)_3 \leq 0.17$;[242] $(FA,MA)PbI_3 \leq 0.02$[261]
...					
$Cs_{0.33}MA_{0.33}Rb_{0.33}Pb_{0.5}Sn_{0.5}Br_{1.5}Cl_{1.5}$	−1.93	0.77	0.054	—	—
...					
$K_{0.25}Na_{0.25}(NH_4)_{0.25}Tl_{0.25}Co_{0.14}Cu_{0.14}Fe_{0.14}Mg_{0.14}Mn_{0.14}Ni_{0.14}Zn_{0.14}F_3$	−1.66	0.67	0.082	—	—
...					
$Cs_{0.33}MA_{0.33}Rb_{0.33}PbBr_{1.5}Cl_{1.5}$	−1.59	0.64	0.045	—	—

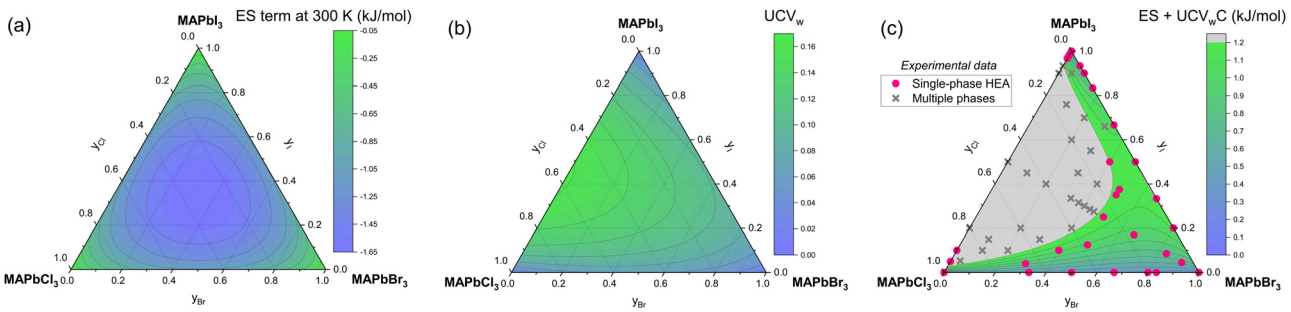

Fig. 9 (a) ES term at 300 K contours, (b) UCV_w contours, and (c) ES + UCV_wC contours for $MAPb(Br,Cl,I)_3$. Experimental HP single-phase alloy (pink circles) and multiple phase (gray Xs) data are in (c),[223] confirming that C = 23 kJ mol^{-1} leads to a phase boundary at G_{ES} = 1.22 kJ mol^{-1} that correctly groups 52 of the 56 data (93%).

orthorhombic perovskite structure (space group #62; 20 constituents per unit cell; 4 formula units per unit cell). Many HP have different structural symmetry (*e.g.*, $Pm\bar{3}m$ cubic with 5 constituents per unit cell or 1 formula unit per unit cell), and in such cases we consider the unit cell volume for which the number of atoms would be 20 (for $Pm\bar{3}m$ the unit cell volume is

multiplied by 4). Materials Project[559] unit cell volumes are well correlated with Inorganic Crystal Structure Database (ICSD) values.[305,560] We find lattice parameters for 265 of the inorganic HP. We also tabulate experimental band gaps where available. We first consider all possible equimolar alloys with 3 end-members, then check if a possible HEA consists entirely of experimentally observed end-members. If it does then we tabulate it after calculating the ES term at 300 K, UCV (if available), and mean band gap (if available). We provide example code with extensive comments as an ESI† file (Mathematica notebook). We execute the notebook on a personal computer using a built-in parallel do statement and consider alloys with up to 48 end-members. There are 10^{57} ways to combine 48 of the 322 end-members (322!/(48! (322-48)!) $\sim 10^{57}$), so to avoid checking every combination of the 9 A-site, 32 B-site and 4 X-site inorganic constituents and 10 additional A-site organic constituents, we examine the simpler alloy systems first to determine which complex alloys can possibly be built from the existing results. In other words, the computation can be simplified by only checking a higher order system's potential constituents if their constitutive lower order systems exist. Eventually, the number of constituents on a sublattice reaches a maximum, beyond which no more can be added without including an end-member that has not been experimentally observed, and then the search can stop. Here we examine only HP, but our approach has value for the closely related double perovskites[301] and the 76 experimentally observed chalcogenide (sulfur, selenium, and tellurium) perovskites,[24] although chalcogenide perovskites are less developed than the halides.[561]

DFT calculations: in order to verify that compositions with small (large) UCV are stable (unstable), we carry out geometric relaxations for the selected compositions in Table S6 (ESI†). We carry out these DFT calculations using the Vienna Ab initio Software Package (VASP, version 5.4),[562,563] in the framework of the generalized gradient approximation (GGA), with the Perdew, Burke and Ernzerhof (PBE) functional.[564] We use a plane wave energy cutoff of 400 eV and the following Brillouin zone grids, depending on the size of the supercell: $2 \times 2 \times 2$ k-point grids (8 irreducible k points) for $2 \times 2 \times 2$ supercells (40 atoms), $1 \times 2 \times 2$ k-point grids for $4 \times 2 \times 2$ supercells (80 atoms), and $1 \times 1 \times 1$ k-point grids for $3 \times 3 \times 3$ supercells (135 atoms). All the relaxations are started from ideal cubic perovskite structures and are fully relaxed (unit cell shape and atomic coordinates) using the conjugate-gradient algorithm until residual forces become smaller than 0.004 eV Å^{-1}. The electronic relaxations at each ionic step are stopped when the energy difference between consecutive self-consistency iterations reaches 10^{-7} eV. In order to improve convergence to equilibrium, we scale the displacement steps by 0.1 and declare 180 bands (20 more than the default). To assess mixing effects of various ions on the A-, B-, and X-sites, we include 8 distinct configurations for each composition, and average the final energy and final cell volume across these configurations. The DFT mixing enthalpy is the mean DFT energy of the 8 HEA configurations referenced to the DFT energy of the HEA's end-members:

$$H_{\mathrm{mix,DFT}} = \frac{E_{\mathrm{HEA,conf.1}}}{8} + \frac{E_{\mathrm{HEA,conf.2}}}{8} + \frac{E_{\mathrm{HEA,conf.3}}}{8} + \frac{E_{\mathrm{HEA,conf.4}}}{8} + \frac{E_{\mathrm{HEA,conf.5}}}{8} + \frac{E_{\mathrm{HEA,conf.6}}}{8} + \frac{E_{\mathrm{HEA,conf.7}}}{8} + \frac{E_{\mathrm{HEA,conf.8}}}{8} - \frac{\sum_i \sum_j \sum_k E_{ijk_3}}{N} \quad (10)$$

Conflicts of interest

There are no conflicts to declare.

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