Mapping Temperature–Dependent Energy–Structure–Property Relationships for Solid Solutions of Inorganic Halide Perovskites Supporting Information

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S1. ERROR ESTIMATION FOR FREE ENERGY COMPUTATIONS

When calculating the partition function for $Cs(Pb_xSn_{1-x})X_3$ at a given composition:

$$Z(x,T) = \sum_{n=1}^{N} g_n \exp\left(-\frac{E_n}{k_B T}\right),\tag{1}$$

one can either use the 0 K DFT-derived lattice energies $E_n(x)$ or with extra contribution from the vibrational free energy $F_{vib}^n(x,T)$ for a given dopant configuration, denoted by n. However, calculating $F_{vib}^n(x,T)$ for every dopant configuration at each composition x will be extremely computational demanding. Therefore, it will be desirable if $F_{vib}^n(x,T)$ can be approximated by $F_{vib}^{\min}(x,T)$, i.e. the Helmholtz free energy for the configuration with lowest $E_n(x)$ at a given x. For this purpose, it is necessary to estimate the errors associated with such an approximation.

We denote the error introduced into the approximated free-energy for the *n*-th configuration as $\Delta F_{vib}^n(x,T) = F_{vib}^n(x,T) - F_{vib}^{\min}(x,T)$. In this case, the true partition function is

$$Z(x,T) = \sum_{n=1}^{N} g_n Z_n(x,T) = \sum_{n=1}^{N} g_n \exp\left[-\frac{E_n + F_{vib}^n(x,T)}{k_B T}\right]$$

with

$$Z_n(x,T) = \exp\left[-\frac{E_n + F_{vib}^n(x,T)}{k_B T}\right]$$
(2)

From here, the error associated with each term when $F_{vib}^{\min}(x,T)$ being used given by:

$$\frac{|\Delta Z_n(x,T)|}{Z_n(x,T)} = 1 - \exp\left[-\frac{\Delta F_{vib}^n(x,T)}{k_BT}\right].$$

Defining $\Delta F_{vib}^{\max}(x,T) = \max\{\Delta F_{vib}^n(x,T)|n \in N\}$, this means that the maximum error in the partition function should be

$$\Delta Z(x,T) = Z(x,T) \left\{ 1 - \exp\left[-\frac{\Delta F_{vib}^{\max}(x,T)}{k_B T}\right] \right\}.$$
(3)

The free energy is related to the partition function as

$$G(x,T) = -k_B T \ln Z(x,T), \qquad (4)$$

meaning that the error associated with G due to uncertainty in Z can be obtained via applying the chain rule as

$$\left|\Delta G(x,T)\right| = \left|\frac{\partial G(x,T)}{\partial Z(x,T)}\Delta Z(x,T)\right| = \left|\frac{k_B T \Delta Z(x,T)}{Z(x,T)}\right|$$

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Substituting (3) into (5), we see that the relative error in the mixing free energy is:

$$\left|\frac{\Delta G(x,T)}{G(x,T)}\right| = \frac{1}{\ln Z(x,T)} \left\{ 1 - \exp\left[-\frac{\Delta F_{vib}^{\max}(x,T)}{k_B T}\right] \right\},\tag{5}$$

which, with (4), it is also possible to estimate the error as:

$$\left|\frac{\Delta G(x,T)}{G(x,T)}\right| \approx -\frac{k_B T}{G_{mix}(x,T)} \left\{ 1 - \exp\left[-\frac{\Delta F_{vib}^{\max}(x,T)}{k_B T}\right] \right\},\tag{6}$$

where $G_{mix}(x,T)$ is the mixing free energies estimated solely based on the 0 K DFT total energies for all configurations.



FIG. S1: Temperature dependent Helmholtz free energy profile for all 48 configurations of $Cs(Pb_{0.375}Sn_{0.625})Br_3$ across all demonstrating that the variance in the Helmholtz free energies across all 48 configurations are generally small within the range of temperatures considered.

In Fig. S1, the temperature dependent Helmholtz free energies $F_{vib}(T)$ for Cs(Pb_{0.375}Sn_{0.625})Br₃ across all 48 configurations are compared. It can be seen here that, generally, the differences in F_{vib} energies across two different dopant configurations are generally very small. At 800 K, if we use the difference between the highest and lowest F_{vib} as a proxy for $\Delta F_{vib}^{\text{max}}$, then we have $\Delta F_{vib}^{\text{max}} \approx 0.026 \text{ eV}/\text{atom}$, and $G_{mix}(x,T) \approx 0.25 \text{ eV}/\text{atom}$. According to Eq. 6, the error introduced will be around **9**% for using $F_{vib}^{\text{min}}(x,T)$ to approximate $F_{vib}^n(x,T)$ for all meta–stable dopant configurations.



FIG. S2: Temperature dependent Helmholtz free energies for $Cs(Pb_xSn_{1-x})X_3$ (X=Cl, Br and I) for the lowest energy configurations cross all different concentrations of Sn being sampled.

Fig. S2 show the Helmholtz free energy curves for the lowest energy configurations for $Cs(Pb_xSn_{1-x})X_3$ (X=Cl, Br and I) across all different concentrations of Sn dopants. It can be seen from Fig. S2 that, generally there is no clear trend of the Helmholtz free energies with respect to the Pb/Sn ratio in $Cs(Pb_xSn_{1-x})X_3$. Nevertheless, by comparing Fig. S2 with Fig. S1, it can be seen that the Helmholtz free energies are more sensitive to the chemical change (governed by the Sn dopant concentration), rather than the structural change (differences in the Sn dopant positions at a given concentration). The above findings thus provide a solid support for using $F_{vib}^{\min}(x,T)$ to approximate $F_{vib}^{n}(x,T)$ in expediting the process of (free) energy landscape samplings for alloys of halide perovskites.

S2. PHONON DENSITY-OF-STATES UNDER HARMONIC APPROXIMATION



FIG. S3: Comparison between the phonon density-of-states (DOS) for $Cs(Pb_xSn_{1-x})X_3$ with different Sn concentrations and halide anions.

S3. CORRELATION BETWEEN ANHARMONIC SCORES AND STRUCTURAL SIMILARITIES AT DIFFERENT TEMPERATURES



FIG. S4: Time dependent anharmonic scores and structural similarities (measured by the SOAP–REMatch kernel with respect to the 0 K static structure) for the MD trajectory of $CsSnI_3$ at two different temperatures of 100 and 300 K. It shows that although at 100 K, the structural similarities are higher than those in 300 K, the crystal is more anharmonic at lower temperature. However, within each trajectory, high kernel similarities generally lead to lower anharmonic scores.