

Supplementary material

Low temperature synthesis of mixed valence gold halide perovskites and exploration of their photoluminescence properties

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Thermodynamic calculations

We present here the thermodynamic calculations performed to obtain the values presented in the main text. Table S.1 presents a comparison of the standard enthalpies of formation for the gold HaPs as well as those of the relevant binaries. Values in bold are experimental data at 298 K and 1 bar. In the case of the halide ionic complexes, the standard state is the ideal solution in water at 1 mol.kg⁻¹, in both cases taken from Wagman et al.¹ Values not in bold were calculated at 0 K from the OQMD database².

$\Delta_f H_0$				
Chlorides				
	CsCl	AuCl	AuCl ₃	
	-2.20 (-2.15)	-0.18 (-0.40)	-0.31 (-0.52)	eV/atom
	CsCl _{aq}	AuCl ₂ ⁻	AuCl ₄ ⁻	
	-2.22	-0.58	-0.67	eV/atom
	Cs ₂ Au ^I Au ^{III} Cl ₆		CsAuCl ₄	
	-1.27		-1.19	eV/atom
Bromides				
	CsBr	AuBr	AuBr ₃	
	-2.18 (-1.96)	-0.07 (-0.28)	-0.14	eV/atom
	CsBr _{aq}	AuBr ₂ ⁻	AuBr ₄ ⁻	
	-1.98	-0.44	-0.40	eV/atom
	Cs ₂ Au ^I Au ^{III} Br ₆		CsAuBr ₄	
	-1.09		-1.00	eV/atom
Iodides				
	CsI	AuI	AuI ₃	
	-1.80 (-1.65)	0.0 (-0.13)	-0.18	eV/atom
	CsI _{aq}	AuI ₂ ⁻	AuI ₄ ⁻	
	-1.61	-	-	eV/atom
	Cs ₂ Au ^I Au ^{III} I ₆			
	-0.82			eV/atom

Table S.1: Enthalpy of formation of the ternaries compared with those of the relevant binaries.

Values in bold are data at 298 K and 1 bar. In the case of the halide ionic complexes, the standard state is the ideal solution in water at 1 mol.kg⁻¹, in both cases taken from Wagman et al¹. Values not in bold were calculated at 0 K from the OQMD database.



We can assume that the difference in temperature reported in the main text during the synthesis of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ comes from the way it is measured, viz. in the silicon heating bath rather than directly in solution. Taking an average temperature, one can say the precipitation point is reached around $91^\circ\text{C} \pm 3^\circ\text{C}$. It follows equation 1 in the main text that the associated solubility product for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ at $364 \text{ K} \pm 3\text{K}$ is:

$$K_s (T = 364 \text{ K}) = [\text{Cs}^+]^2 [\text{AuCl}_2^-] [\text{AuCl}_4^-]. \quad (\text{S.1})$$

Using the concentrations given in the methods section of the main text, $K_s (T = 364 \text{ K}) = 1.6 \cdot 10^{-9}$. Moreover, the dependence of K_s on the temperature is described by the equation:

$$K_s = \exp(-\Delta_d G / kT) = \exp(\Delta_p G / kT) \quad (\text{S.2})$$

with $\Delta_d G$ is the Gibbs free energy of the dissolution reaction and $\Delta_p G$ the Gibbs free energy for the precipitation reaction. This allows us to estimate a value for $\Delta_d G_{\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6} \approx 0.5 \text{ eV}$. From the Gibbs free energy of the precipitation reaction, it is possible to compute the formation energy of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$, since they are related through equation S.3:

$$\Delta_p G = 2\Delta_f G_{\text{CsCl}} + \Delta_f G_{\text{AuCl}_2} + \Delta_f G_{\text{AuCl}_4} - \Delta_f G_{\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6} \quad (\text{S.3})$$

However, these Gibbs free energies need to be taken all at the same temperature. We can use the relationship $\Delta_f G_0(T) = \Delta_f H_0 + T S_0$. Hence, from the data at 298 K, we can compute the Gibbs free energies of formation at 364 K. The results are summarized in Table S.1.

From equation S.3, $\Delta_f G_{\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6} (T = 364 \text{ K}) = -1.19 \text{ eV /atom}$. From Table S.1, it seems that the difference between the computed and experimental enthalpy of formation varies between -0.2 eV /atom in the case of AuCl and AuCl_3 and $+0.05 \text{ eV /atom}$ in the case of CsCl . To a first approximation, we will assume that the experimental standard enthalpy of formation is equal to the computed standard enthalpy of formation for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$. In this case, this would suggest that the standard entropy for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ is $0.19 \text{ meV} \cdot \text{atom}^{-1} \cdot \text{K}^{-1}$.

	CsCl_{aq}	AuCl_2^-	AuCl_4^-	
$\Delta_f H_0$				
	-2.22	-0.58	-0.67	eV/atom
$\Delta_f G_0(T = 298 \text{ K})$				
	-2.19	-0.52	-0.49	eV/atom
$\Delta_f G_0(T = 364 \text{ K})$				
	-2.18	-0.51	-0.45	eV/atom

Table S.1: Thermodynamic data of the chloride binaries. The standard state is the ideal solution in water at $1 \text{ mol} \cdot \text{kg}^{-1}$, taken from Wagman et al¹.



In the case of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$, a different experiment was performed to assess the Gibbs energy of formation and entropy of formation. The initial concentrations of AuCl , AuCl_3 and CsCl were kept unchanged compared to those detailed in the methods section of the main text, in a 20 mL solution. However, the concentration of HBr was initially of $10^{-3} \text{ mol.L}^{-1}$ and increased by addition of a 0.1 mol.L^{-1} solution by $10 \mu\text{L}$ increments. Upon adding $v_1 = 100 \mu\text{L}$ of the second solution, a black precipitate started to appear. The temperature of the solution was constant and kept at $297\text{K} \pm 1\text{K}$.

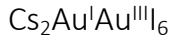
It follows from equation 2 in the main text that the associated solubility product for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$ at $297 \text{ K} \pm 1\text{K}$ is:

$$K_S (T = 364\text{K}) = [\text{Cs}^+]^2 [\text{AuBr}_2^-] [\text{AuBr}_4^-] \quad (\text{S.4})$$

with $[\text{AuBr}_2^-]$ and $[\text{AuBr}_4^-]$ dictated by the concentration of HBr in solution. With the concentration detailed above, $K_S (297\text{K}) = 7.29 \cdot 10^{-8}$. With the same process as described above for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Cl}_6$ through the use of equations S.2 and S.3, one obtains $\Delta_f G_{\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6} (T = 297 \text{ K}) = -1.07 \text{ eV/atom}$. From Table S.4, it seems that the difference between the computed and experimental enthalpy of formation varies between -0.2 eV/atom in the case of AuBr and $+0.2 \text{ eV/atom}$ in the case of CsBr . For a first approximation, we will assume that the experimental standard enthalpy of formation is equal to the computed standard enthalpy of formation for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$. In this case, this would suggest that the standard entropy for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$ is $0.07 \text{ meV.atom}^{-1}.\text{K}^{-1}$, less than half that of the chloride perovskite.

	CsBr_{aq}	AuBr_2^-	AuBr_4^-	
$\Delta_f H_0$				
	-2.10	-0.44	-0.40	eV/atom
$\Delta_f G_0(T = 298 \text{ K})$				
	-2.05	-0.40	-0.35	eV/atom

Table S.2: Thermodynamic data of the bromide binaries. The standard state is the ideal solution in water at 1 mol.kg^{-1} , taken from Wagman et al¹.



In the case of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$, an experiment based on the protocol described in the main text was performed to assess the Gibbs energy of formation and entropy of formation. A first solution of 20 mL containing HAuCl_4 in a $10^{-2} \text{ mol.L}^{-1}$ concentration was prepared. A second solution containing CsI in a 0.6 mol.L^{-1} concentration was then added to the first solution in $50 \mu\text{L}$ increments. Upon adding $v_1 = 700 \mu\text{L}$ of the second solution to the first, a black precipitate started to appear. The temperature of the solution was constant and kept at $297\text{K} \pm 1\text{K}$.

It follows from equation 3 in the main text that the associated solubility product for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$ at $297 \text{ K} \pm 1\text{K}$ is:

$$K_S (T = 364 \text{ K}) = [\text{Cs}^+]^2 [\text{AuI}_4^-]^2 [\text{I}^-] \quad (\text{S.4})$$

with $[Au_4^-]$ and $[I^-]$ dictated by the concentration of CsI in solution. With the concentration detailed above, $K_s(297\text{ K}) = 3.46 \cdot 10^{-7}$. With the same process as described above for $Cs_2Au^I Au^{III} Cl_6$ through the use of equations S.2 and S.3, one obtains $\Delta_f G_{Cs_2Au^I Au^{III} Cl_6}(T = 297\text{ K}) = -0.39\text{ eV/atom}$. Here again, in a first approximation, we will assume that the experimental standard enthalpy of formation is equal to the computed standard enthalpy of formation for $Cs_2Au^I Au^{III} I_6$. In this case, this would suggest that the standard entropy for $Cs_2Au^I Au^{III} Br_6$ is $1.4\text{ meV}\cdot\text{atom}^{-1}\cdot\text{K}^{-1}$.

	CsI_{aq}	AuI_2^-	AuI_4^-	
$\Delta_f H_0$				
	-1.79	-	-	eV/atom
$\Delta_f G_0(T = 298\text{ K})$				
	-1.78	-	-	eV/atom

Table S.3: Thermodynamic data of the iodide binaries. The standard state is the ideal solution in water at $1\text{ mol}\cdot\text{kg}^{-1}$, taken from Wagman et al¹.

Additional XRD pattern

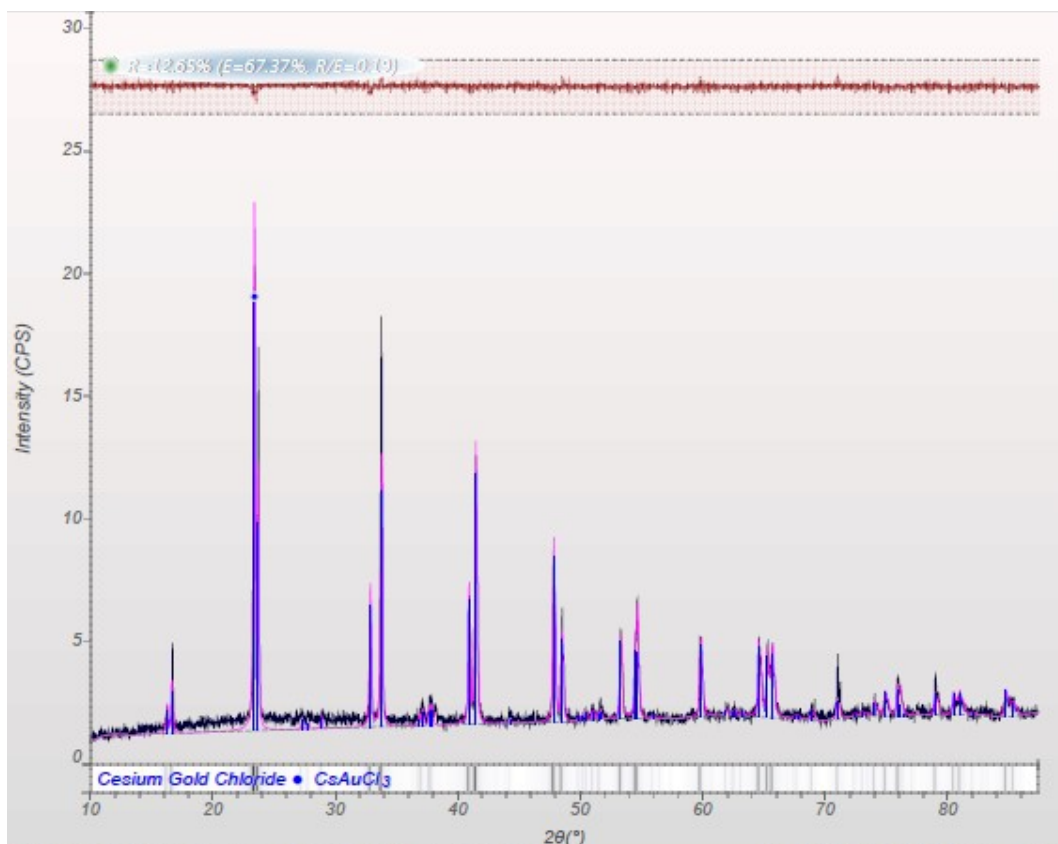


Figure S1: XRD pattern of a $Cs_2Au^I Au^{III} Cl_6$ powder sample

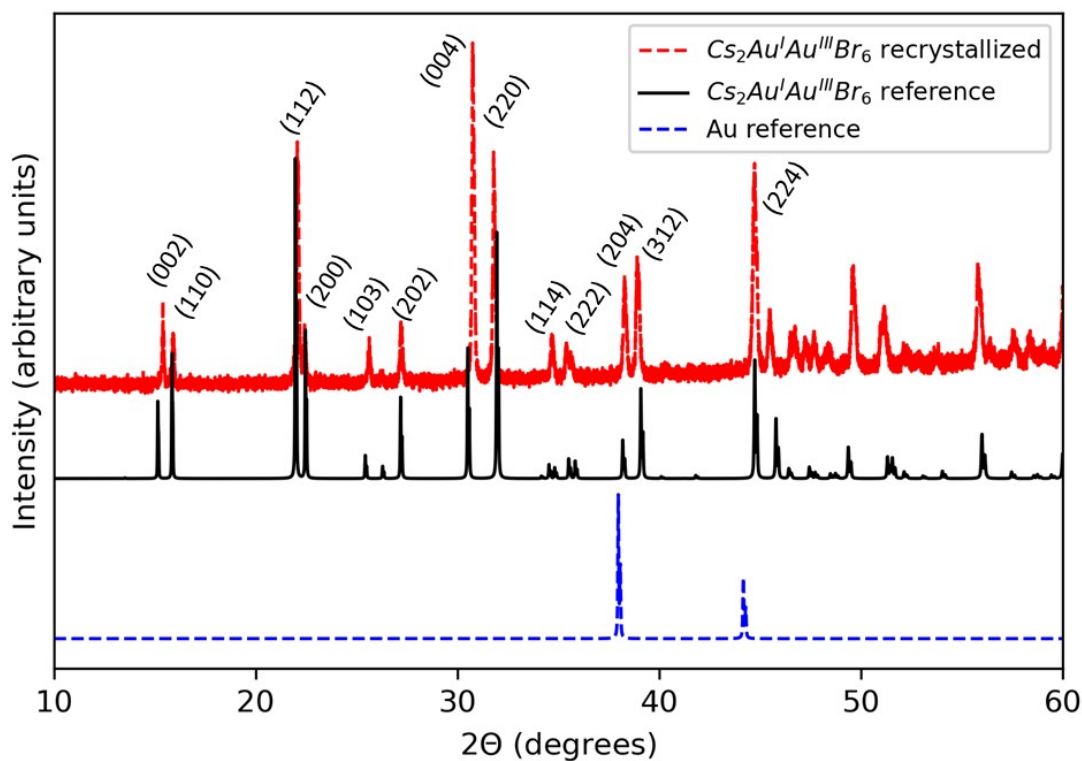


Figure S2: Measured XRD patterns of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$ powders, compared to the $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{Br}_6$ and Au reference patterns from the ICSD database.

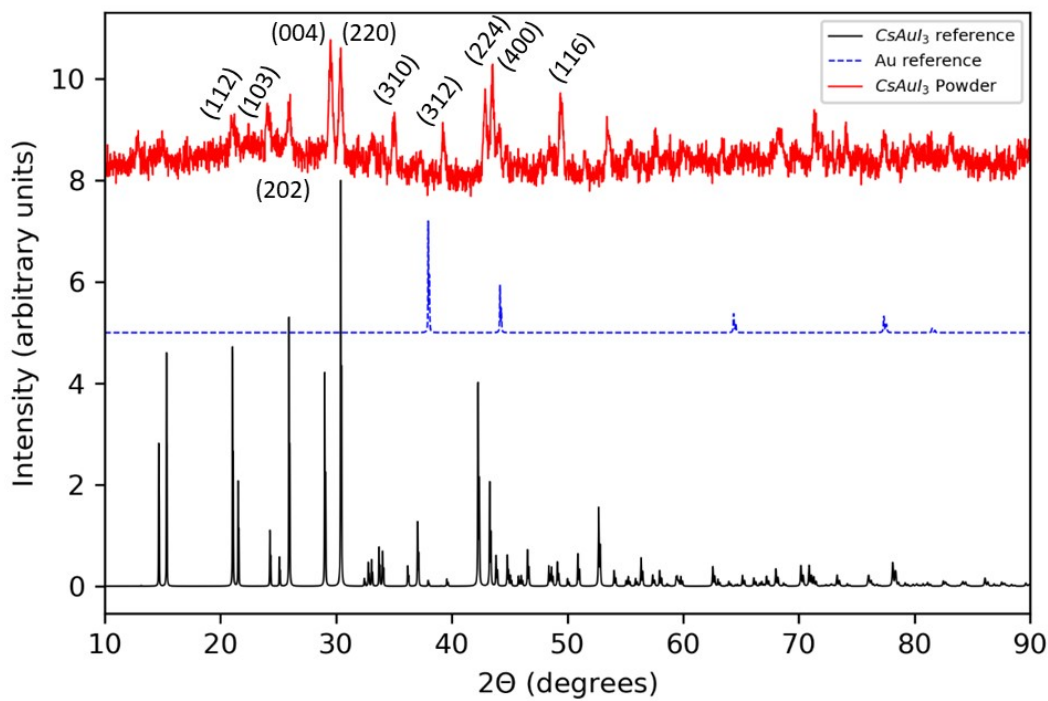


Figure S3: Measured XRD patterns of $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$ powders, compared to the $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$ and Au reference patterns from the ICSD database.

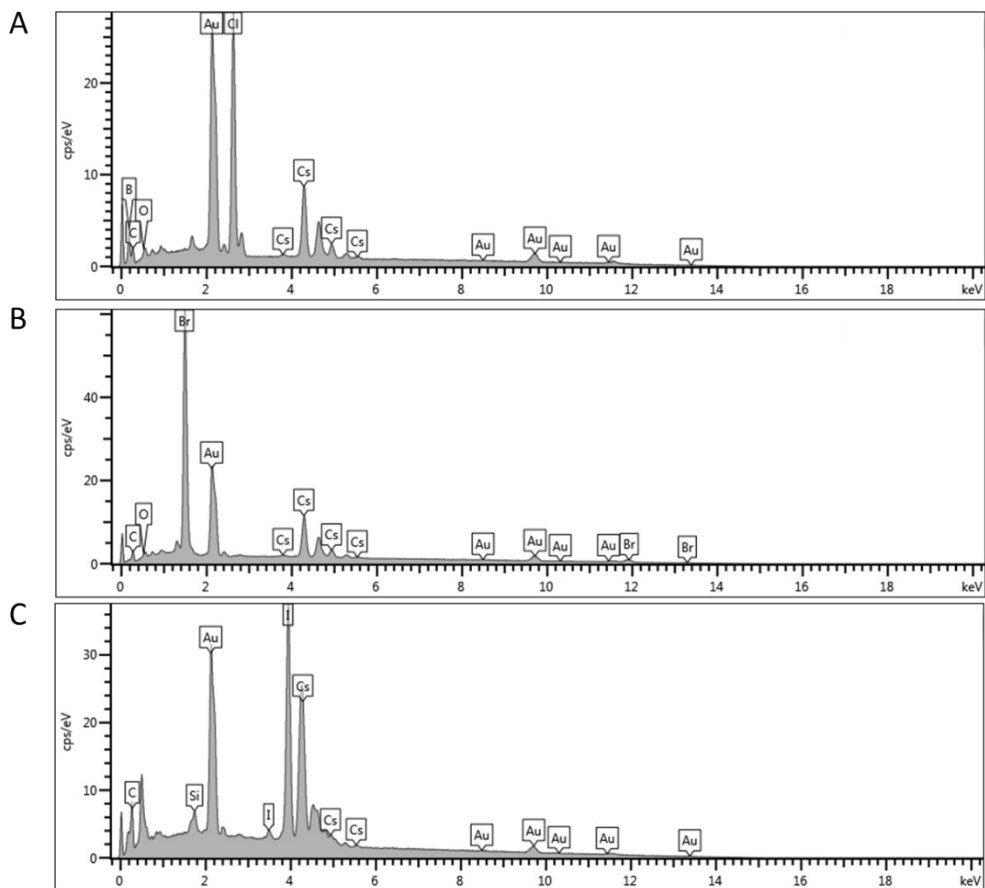


Figure S4: EDX spectra of $\text{Cs}_2\text{Au}_2\text{X}_6$ ($X = \text{Cl}, \text{Br}, \text{I}$), averaged over the entire SEM image.

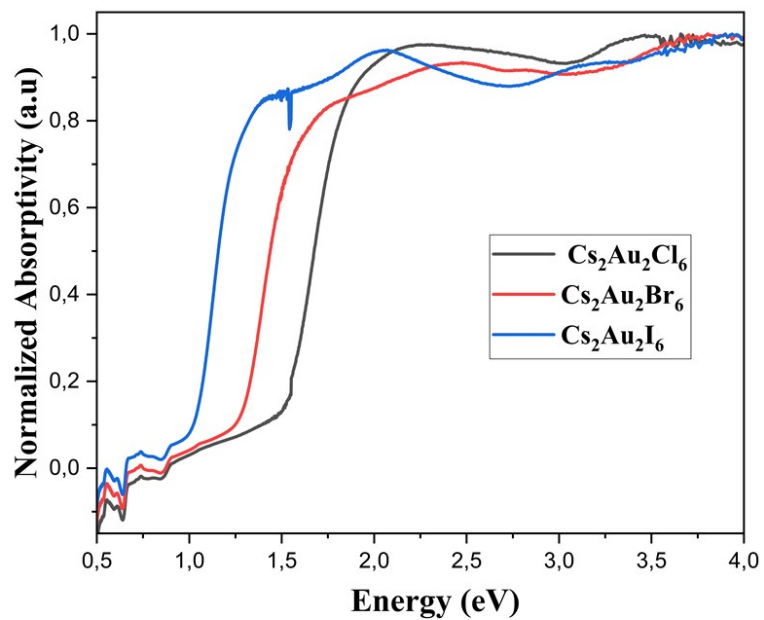


Figure S5: UV-Vis absorption spectra of $\text{Cs}_2\text{Au}_2\text{X}_6$ ($X = \text{Cl}, \text{Br}, \text{I}$), showing a redshift in the absorption onset with increasing halide atomic number.

References

¹ D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, and I. Halow, *The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units* (National Standard Reference Data System, 1982).

² J.E. Saal, S. Kirklin, M. Aykol, B. Meredig, and C. Wolverton, *JOM* **65**, 1501 (2013).