Supporting Information

Disorder by Design: High-Entropy Oxide as Next Generation Thermoelectric Materials

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S1. Mole fractions of precursor oxides and high entropy oxides:

Following Banerjee et al.'s[1] thermodynamic feasibility calculations, several authors[2–5] have used the same approach for their respective high entropy oxides. Table S1 presents the calculated coefficients (a-f and a_1-f_1) for Equation 16, governing the thermodynamic transition from precursor oxides to high entropy oxides.

Table S1: Mole fractions of precursor oxides (a_1, b_1,…,f_1) and high entropy oxides (a, b,…,f) as described in equation 16.

Final Product	Precursors											
HEO	$A_{a_1}O_x$	a/a_1	$B_{b_1}O_x$	b/b_1	$C_{c_1}O_x$	c/c_1	$D_{d_1}O_x$	d/d_1	$E_{e_1}O_x$	e/e_1	$F_{f_1}O_x$	f/f_1
$Sr(Ti_{0.2}Mo_{0.2}Fe_{0.2}Nb_{0.2}Cr_{0.2})O_3$[1]	$SrCO_3$	$0.2/1$	TiO_2	$0.2/1$	MoO_3	$0.2/1$	Fe_2O_3	$0.2/2$	Nb_2O_5	$0.2/2$	Cr_2O_3	$0.2/2$
$(Sr_{0.2}Ba_{0.2}La_{0.2}Eu_{0.2}Pb_{0.2})Nb_2O_6$[3]	$SrCO_3$	$0.2/1$	$BaCO_3$	$0.2/1$	La_2O_3	$0.2/2$	Eu_2O_3	$0.2/2$	PbO	$0.2/1$	Nb_2O_5	$2/2$
$Sr(Ce_{0.05}Sn_{0.08}Zr_{0.2}Ti_{0.16}Y_{0.3}Nb_{0.11}Al_{0.1})O_{2.9}$[4]	$SrCO_3$	$0.2/1$	CeO_2	$.05/1$	SnO_2	$.08/1$	ZrO_2	$0.2/1$	TiO_2	$.16/1$	Y_2O_3	$0.3/2$

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									Nb_2O_5	$.11/_2$	Al_2O_3	$0.1/_2$
$(Sr_{0.2}Ba_{0.2}Li_{0.2}K_{0.2}Na_{0.2})Nb_2O_6$[5]	$SrCO_3$	$0.2/_1$	$BaCO_3$	$0.2/_1$	Li_2CO_3	$0.2/_2$	K_2CO_3	$0.2/_2$	Na_2CO_3	$0.2/_2$	Nb_2O_5	$2/_2$
$(Sr_{1/3}Ba_{1/3}Ca_{1/3})TiO_3$[2]	$SrCO_3$	$.33/_1$	$BaCO_3$	$.33/_1$	$CaCO_3$	$.33/_1$	TiO_2	$1/_1$	Na_2CO_3	$0.2/_2$	Nb_2O_5	$0.2/_2$

S2. Mathematical proof of the fact that the possible high entropy alloys will be much more than lower component alloys (such as- binary, ternary alloys etc.):

Let's consider two alloys with the number of elements **r** and **r+1**. The elements will be selected from **n** number of chemical elements.

The formula to calculate the number of ways to choose **r** elements from a set of **n** elements will be, $N_1 = C(n,r) = \frac{n!}{r!(n-r)!} \ldots (S1)$

Similarly, when we select **r+1** elements from a possible set of **n** species, the number of selection will be, $N_2 = C(n,r+1) = \frac{n!}{(r+1)!(n-(r+1))!} \ldots (S2)$

Let's take the ratio of these two numbers and we obtain:

$$R = \frac{N_1}{N_2} = \frac{C(n,r)}{C(n,r+1)} = \frac{\frac{n!}{r!(n-r)!}}{\frac{n!}{(r+1)!(n-(r+1))!}} = \frac{(r+1)!(n-(r+1))!}{r!(n-r)!} \ldots (S3)$$

Now, applying the relations $(r+1)! = (r+1) \times r!$ and $(n-r)! = (n-r) \times (n-r-1)!$, we obtain,

$$R = \frac{(r+1)}{(n-r)} \ldots (S4)$$

If $\mathbf{r} \leq \boldsymbol{n/2}$, then (n-r) > (r+1), or in other words, $R = \frac{(r+1)}{(n-r)} < 1 \ldots$(S5)

This result indicates that for two alloys — one with **r** elements and another with **r+1** elements — the number of possible alloys will always be greater for the alloy containing **r+1** elements, provided that $\mathbf{r} \leq \boldsymbol{n/2}$**.**

Since at least 40 to 50 metallic elements can potentially form high-entropy alloys (HEAs) with 5, 6 or 7 components, the condition $\mathbf{r} \ll \boldsymbol{n/2}$ holds true in the case of HEAs. Consequently, the number of possible HEAs far exceeds that of lower-component alloys, highlighting the vast compositional space available for HEAs compared to traditional binary, ternary, or quaternary alloys.

References:

S1 R. Banerjee, S. Chatterjee, M. Ranjan, T. Bhattacharya, S. Mukherjee, S. S. Jana, A. Dwivedi and T. Maiti, *ACS Sustain. Chem. Eng.*, 2020, **8**, 17022–17032.

2 J. Bi, Y. Liang, Y. Bai, B. Cui, Z. Lu and B. Li, *J. Eur. Ceram. Soc.*, 2024, **44**, 2189–2197.

3 M. Zhu, D. Ma, N. Zhang, F. Zhan, Y. Zheng and P. La, *J. Eur. Ceram. Soc.*, 2024, **44**, 2198–2205.

4 R. Shishkin and V. Zhuravlev, *Ceram. Int.*, 2024, **50**, 15348–15355.

5 S. Sourav Jana and T. Maiti, *Mater. Horiz.*, 2023, **10**, 1848–1855.