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Supporting information for:

On the energetics of cation ordering in tungsten-bronze-type oxides

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Derivation of thermodynamic equations

Here we give a more detailed derivation of equation (3) in the main text. We start by explicitly evaluating the free energy expression:

$$\Delta G_{\text{int}} = \alpha x + \beta x^2 + RT \sum_s b_s \sum_i x_{i,s} \ln x_{i,s}, \tag{S.1}$$

where x is the degree of cation interchange, b_s is the multiplicity of site (or sublattice) s, and $x_{i,s}$ is the fractional occupancy of species i (cations or vacancies) on site s. For the chemical equilibrium in equation (1) in the main text, we write out the entropy part as follows:

$$\begin{aligned}\Delta S_{\text{int}} &= -R \sum_s b_s \sum_i x_{i,s} \ln x_{i,s} \\ &= -R \left\{ 2 \left[\frac{1+x}{2} \ln \frac{1+x}{2} + \frac{1-x}{2} \ln \frac{1-x}{2} \right] + 4 \left[\frac{4-x}{4} \ln \frac{4-x}{4} + \frac{x}{4} \ln \frac{x}{4} \right] \right\}\end{aligned} \tag{S.2}$$

Differentiating (S.2) gives

$$\frac{\partial \Delta S_{\text{int}}}{\partial x} = -R \ln \frac{(1+x)x}{(1-x)(4-x)} \tag{S.3}$$

For equilibrium conditions,

$$\frac{\partial \Delta G_{\text{int}}}{\partial x} = 0, \tag{S.4}$$

which, using the above results, evaluates to

$$\alpha + 2\beta x + RT \ln \frac{(1+x)x}{(1-x)(4-x)} = 0, \tag{S.5}$$

which gives equation (3) in the main text when rearranged.

Energetics in numbers

Table S1 gives the calculated energies for different configurations of BN, SN and PN. The numbers are plotted in Figure 2 in the main text. Energies are given for experimental lattice parameters (initial), relaxed atomic positions and relaxed unit cell volume. All energies are given relative to the highest initial energy for each composition. The unit is eV per unit cell ($A_5Nb_{10}O_{30}$), and can be converted to kJ mol^{-1} by multiplication by 96.485.

Structural data

Tables S2, S3 and S4 give the structural data (space group symmetry, lattice parameters and atomic positions) for the most stable configuration of BN, SN and PN, respectively, after full geometry optimization by DFT calculations. All structures are given in the standard setting (ITA) of the relevant space group (space groups are listed in Table 1 in the main text). Table S5 gives the lattice parameters for all 30 cases (compositions and configurations) considered in the main text, in a pseudo-tetragonal setting which better facilitates direct comparison between cases with different symmetry.

Table S1: Calculated energies for BN in different configurations.

Configuration	Energy (eV)		
	Initial	+ Ionic relax.	+ Volume relax.
$BaNb_2O_6$			
PP[100]	−0.794	−1.987	−2.459
PP[110]	−0.828	−1.882	−2.190
PP[101]	−0.825	−1.967	−2.444
PP[111]	−0.860	−1.882	−2.207
PP[001]	0.000	−1.784	−2.217
SS[110]	−1.605	−2.131	−2.322
SS[111]	−1.607	−2.228	−2.395
SS[001]	−0.631	−2.227	−2.531
SP[110]	−0.959	−2.157	−2.498
SP[111]	−1.022	−2.101	−2.473
$SrNb_2O_6$			
PP[100]	−0.906	−3.678	−3.803
PP[110]	−0.946	−2.757	−3.074
PP[101]	−0.931	−3.655	−3.791
PP[111]	−0.973	−3.282	−3.359
PP[001]	−0.062	−3.068	−3.219
SS[110]	−1.040	−2.431	−2.486
SS[111]	−1.041	−2.809	−2.883
SS[001]	0.000	−2.546	−2.592
SP[110]	−0.728	−3.513	−3.573
SP[111]	−0.775	−3.551	−3.623
$PbNb_2O_6$			
PP[100]	−0.882	−3.254	−3.410
PP[110]	−0.892	−2.654	−2.664
PP[101]	−0.900	−3.254	−3.452
PP[111]	−0.916	−2.628	−2.727
PP[001]	−0.160	−3.100	−3.421
SS[110]	−0.884	−2.965	−3.187
SS[111]	−0.886	−3.021	−3.229
SS[001]	0.000	−2.986	−3.267
SP[110]	−0.676	−3.363	−3.485
SP[111]	−0.710	−3.298	−3.506

Table S2: Lattice parameters and atomic positions of lowest-energy configuration for BN. The WP column gives the Wyckoff position in the relevant space group.

Configuration		SS[001]		
Space group		$P4/m$ (83)		
a		12.6130 Å		
c		3.9356 Å		
Atom	WP	x	y	z
Ba	1d	½	½	½
	4k	0.6744	0.1669	½
Nb	2e	0	½	0
	4j	0.2054	0.0691	0
	4j	0.7159	0.4199	0
O	2f	0	½	½
	4j	0.7818	0.2838	0
	4j	0.0709	0.1497	0
	4j	0.5737	0.3620	0
	4j	0.3444	0.9999	0
	4j	0.8436	0.5131	0
	4k	0.2077	0.0842	½
	4k	0.7104	0.4313	½

Table S3: Lattice parameters and atomic positions of lowest-energy configuration for SN. The WP column gives the Wyckoff position in the relevant space group.

Configuration		PP[100]		
Space group		$Pmc2_1$ (26)		
a		7.7000 Å		
b		12.5263 Å		
c		12.5099 Å		
Atom	WP	x	y	z
Sr	2a	0	0.9445	0.8442
	2a	0	0.2515	0.0040
	2b	½	0.9499	0.8673
	2b	½	0.5681	0.1764
	2b	½	0.2556	0.0032
Nb	4c	0.7482	0.2460	0.5060
	4c	0.7473	0.4658	0.9291
	4c	0.7497	0.0407	0.0872
	4c	0.7535	0.3258	0.2209
	4c	0.7547	0.1770	0.7929
O	2a	0	0.2604	0.5109
	2a	0	0.4610	0.9308
	2a	0	0.0520	0.1067
	2a	0	0.3269	0.1835
	2a	0	0.1542	0.7572
	2b	½	0.2205	0.4710
	2b	½	0.4316	0.8918
	2b	½	0.0460	0.0445
	2b	½	0.3217	0.2104
	2b	½	0.1620	0.8209
	4c	0.7193	0.0174	0.7255
	4c	0.7465	0.4648	0.2808
	4c	0.7740	0.3090	0.8629
	4c	0.7382	0.1903	0.1213
	4c	0.7238	0.3954	0.0628
	4c	0.7966	0.1029	0.9263
	4c	0.7025	0.5995	0.9956
	4c	0.7756	0.9111	0.9978
	4c	0.7809	0.2353	0.3386
	4c	0.6995	0.2506	0.6548

Table S4: Lattice parameters and atomic positions of lowest-energy configuration for PN. The WP column gives the Wyckoff position in the relevant space group.

Configuration		SP[111]							
Space group		*Pm* (6)							
a		12.6188 Å							
b		7.7282 Å							
c		12.7657 Å							
β		91.1498°							
Atom	WP	x	y	z	Atom	WP	x	y	z
Pb	1a	0.2970	0	0.8660	O	1b	0.9988	½	0.5089
	1a	0.6420	0	0.2139		1b	0.4800	½	0.9740
	1a	0.8279	0	0.7263		1b	0.8156	½	0.9193
	1a	0.1893	0	0.3854		1b	0.2333	½	0.0685
	1a	0.4943	0	0.5102		1b	0.9126	½	0.1885
	1b	0.2975	½	0.8850		1b	0.0641	½	0.7791
	1b	0.6471	½	0.2140		1b	0.3051	½	0.5615
	1b	0.1448	½	0.3522		1b	0.7320	½	0.4124
	1b	0.9958	½	0.0162		1b	0.4060	½	0.2895
	1b	0.4944	½	0.5116		1b	0.5607	½	0.6964
Nb	2c	0.9966	0.7534	0.5076		2c	0.2207	0.7369	0.7177
	2c	0.4993	0.7491	0.0022		2c	0.7825	0.7660	0.2759
	2c	0.7896	0.7485	0.9374		2c	0.7138	0.7472	0.7834
	2c	0.2055	0.7549	0.0807		2c	0.2916	0.7842	0.2063
	2c	0.9194	0.7539	0.2190		2c	0.9296	0.7794	0.8463
	2c	0.0662	0.7512	0.7972		2c	0.0749	0.7255	0.1417
	2c	0.2832	0.7466	0.5898		2c	0.8688	0.7630	0.0622
	2c	0.7103	0.7476	0.4320		2c	0.1439	0.7146	0.9286
	2c	0.4213	0.7493	0.2884		2c	0.4311	0.7676	0.6273
	2c	0.5791	0.7509	0.7218		2c	0.5749	0.7082	0.3439
O	1a	0.0263	0	0.4708		2c	0.3639	0.7763	0.4211
	1a	0.5124	0	0.0111		2c	0.6369	0.7375	0.5564
	1a	0.7813	0	0.9091		2c	0.6564	0.7244	0.9967
	1a	0.1966	0	0.0458		2c	0.3445	0.7708	0.9873
	1a	0.9416	0	0.2121		2c	0.0027	0.7138	0.3418
	1a	0.1067	0	0.8055		2c	0.0086	0.7919	0.6504
	1a	0.2729	0	0.5613		2c	0.1599	0.7294	0.4869
	1a	0.6819	0	0.4029		2c	0.8474	0.7895	0.4938
	1a	0.4652	0	0.2801		2c	0.5073	0.7191	0.1497
	1a	0.5896	0	0.6844		2c	0.4999	0.7753	0.8397

Table S5: Lattice parameters for all the 30 structures considered in this work, as obtained by full structural optimization by DFT calculations. PP configurations are orthorhombic, SS tetragonal and SP monoclinic, and to make it easier to compare between structures of different symmetry, all parameters are given for a pseudo-tetragonal supercell. Structures with a base-centered orthorhombic lattice are given as primitive monoclinic cells with $a = b$ and $\gamma \neq 90°$ (denoted by an asterisk next to the monoclinic angle). A blank space for b means $a = b$, while a blank space for γ means 90°.

Configuration	a	b	c	γ
$BaNb_2O_6$				
PP[100]	12.7695	12.6857	7.8450	
PP[110]	12.6389		7.9012	89.8007*
PP[101]	12.7653	12.7082	7.8448	
PP[111]	12.6356		7.8903	89.7461*
PP[001]	12.7051		7.8778	90.4811*
SS[110]	12.5686		7.9049	
SS[111]	12.5681		7.9128	
SS[001]	12.6130		7.8712	
SP[110]	12.6658	12.6338	7.8571	89.4534
SP[111]	12.6925	12.6583	7.8504	90.3003
$SrNb_2O_6$				
PP[100]	12.5099	12.5263	7.7000	
PP[110]	12.4580		7.8006	90.1746*
PP[101]	12.5534	12.5078	7.7002	
PP[111]	12.4843		7.7299	89.7364*
PP[001]	12.5884		7.8007	91.0520*
SS[110]	12.4010		7.8279	
SS[111]	12.4218		7.8492	
SS[001]	12.4445		7.7987	
SP[110]	12.4648	12.4247	7.6931	89.8807
SP[111]	12.4269	12.4776	7.6917	89.8320
$PbNb_2O_6$				
PP[100]	12.8174	12.6034	7.7896	
PP[110]	12.5686		7.8450	90.0184*
PP[101]	12.7857	12.6279	7.7292	
PP[111]	12.6110		7.7511	90.7487*
PP[001]	12.7843		7.7939	91.5995*
SS[110]	12.7396		7.7644	
SS[111]	12.7327		7.7682	
SS[001]	12.7575		7.7586	
SP[110]	12.7791	12.5556	7.7663	90.0961
SP[111]	12.7657	12.6188	7.7282	91.1498