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1 **Defining chemical expansion: the choice of units for the stoichiometric expansion**
2 **coefficient**

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13
14 **Abstract**

15
16 *Chemical expansion refers to the spatial dilation of a material that occurs upon changes in its*
17 *composition. When this dilation is caused by a gradual, iso-structural increase in the lattice parameter*
18 *with composition, it is related to the composition change by the stoichiometric expansion coefficient. In*
19 *this work, three different approaches to defining the stoichiometric expansion coefficient (α_s) are*
20 *discussed. While all three definitions of α_s given here are legitimate, we show that there are advantages to*
21 *selecting certain ones for comparison across different crystal structures. Examples are provided for*
22 *changes in oxygen content in fluorite, perovskite, and Ruddlesden-Popper (K_2NiF_4) phase materials used*
23 *in solid oxide fuel cells.*

24
25 **Introduction**

26 Chemical expansion refers to the spatial dilation of a material that occurs upon
27 changes in its composition. The dilation can be either associated with a gradual increase in
28 lattice parameter upon change in composition (*stoichiometric expansion*) or with the formation
29 of a new phase and increase in its molar fraction (*phase change expansion*)⁽¹⁻⁵⁾. Examples are
30 the expansion upon *phase change* of Ni to NiO in a solid oxide fuel cell (SOFC) anode or the
31 gradual change in lattice parameter upon oxygen *stoichiometry* change of a (La,Sr)(Co,Fe)O_{3- δ}
32 SOFC cathode^(6,7). In the latter case, a stoichiometric expansion coefficient, relating the

33 expansion to the change in chemical species content (e.g. δ : oxygen non-stoichiometry), is
34 commonly defined, though often generically called the chemical expansion coefficient^(1,4). For
35 instance, cerium oxide ($\text{CeO}_{2-\delta}$), with a particularly large stoichiometric expansion coefficient,
36 undergoes volumetric expansion of $\sim 3\%$ under typical operating conditions in SOFC anodes and
37 related catalysis applications as well as in thermochemical water splitting⁽⁸⁻¹³⁾. In such ceramic
38 materials and composite devices, this expansion can often lead to mechanical instabilities⁽¹⁴⁻¹⁷⁾.
39 Similarly, chemical expansion is known to limit significantly the performance of certain
40 promising anode and cathode materials for Li-ion batteries, e.g. Sn, Si and LiCoO_2 ^(18,19).

41 Spurred by the above-mentioned issues, a significant research effort has been
42 performed to uncover the origins of chemical expansion^(6,20-24) in order to guide research on
43 developing new materials, compositions, and morphologies with reduced chemical expansion,
44 as recently summarized by the authors^(1,25). In this article, caution is drawn to the generally
45 accepted way the stoichiometric expansion coefficient is defined. As will become apparent,
46 there are a number of slightly different approaches to defining this coefficient, resulting in
47 different values and units, which, in turn, impact comparisons between different structures. To
48 demonstrate this point, a case study of SOFC electrode materials showing stoichiometric
49 expansion with different crystalline structures (fluorite, perovskite, and Ruddlesden-Popper
50 [K_2NiF_4]) is presented. These conclusions will be of use in chemo-mechanical coupling studies
51 of materials that present stoichiometric expansion, such as, batteries and the many SOFC
52 electrode compounds with rapid oxygen reduction reaction (ORR) kinetics at relatively low
53 temperatures (400 - 600 °C), for example, perovskite (e.g. $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$)⁽²⁶⁻²⁸⁾, double
54 perovskite $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ ⁽²⁹⁾, and Ruddlesden-Popper (e.g. $\text{La}_2\text{NiO}_{4\pm\delta}$)^(6,30-32)
55 structured materials.

57 **Alternative definitions and choice of units for the stoichiometric expansion coefficient (α_S)**

58 For a change in oxide ion content (C_O), the isothermal stoichiometric expansion (ε_S) is
59 in general described by the following equation.

$$61 \quad \varepsilon_S = \alpha_S (C_O^\circ - C_O) \quad (1)$$

62
63 where α_S is the stoichiometric expansion coefficient and C_O° is the initial oxide ion content at
64 the initial state. In equation 1, the final value of the oxygen content is subtracted from the initial
65 value in order to follow the general convention in the literature where, for a positive α_S , loss of
66 oxygen results in expansion of the material. C_O , in turn, may be defined in three ways, as

67 discussed in this manuscript: i) in terms of concentration ($\#/cm^3$), ii) moles of oxide ions with
 68 respect to the moles of oxide (molar fraction), and iii) moles of oxide ions with respect to the
 69 total oxide ion content in the stoichiometric material. In the following, the different oxide ion
 70 content representations and their impact on α_s are discussed.

71 Since the role of point defects in materials properties are generally defined in terms of
 72 the concentration of those point defects (e.g. oxide ion vacancies (V_O^\bullet) and oxide ion interstitials
 73 (O_i'') in the non-stoichiometric oxides discussed here), it is more convenient to report C_O as
 74 the equivalent oxide ion vacancy (V_O^\bullet) or interstitial content (O_i''). V_O^\bullet and O_i'' thus replace
 75 C_O in equation 1 and, as typically performed in the literature, are expressed as molar fraction δ
 76 (e.g. δ in $CeO_{2-\delta}$), where δ is defined as

$$78 \quad \delta = \frac{[V_O^\bullet]}{[\text{oxide}]} \quad (2a)$$

79
 80 for oxide ion vacancies or

$$82 \quad \delta = -\frac{[O_i'']}{[\text{oxide}]} \quad (2b)$$

83
 84 for oxide ion interstitials, where brackets denote concentration in terms of number per volume
 85 (e.g. $\#/cm^3$) and $[\text{oxide}]$ is the concentration of formula units for the studied oxide (e.g.
 86 $[CeO_2]$). The corresponding stoichiometric expansion coefficient is denoted as α_s^δ and is
 87 unitless. Alternatively, V_O^\bullet and O_i'' can be expressed directly as concentration (i.e. $[V_O^\bullet]$ or
 88 $[O_i'']$). In this case, the corresponding stoichiometric expansion coefficient is denoted as $\alpha_s^{[]}$
 89 and has units of volume (i.e. cm^3). A third possibility is to express V_O^\bullet and O_i'' as the molar
 90 fraction δ , normalized to the molar fraction of oxide ions in the stoichiometric composition, N_O
 91 (i.e. 2 for fluorites, 3 for perovskites, and 4 for K_2NiF_4 oxides). This latter molar fraction is
 92 shown by X_V or X_i for vacancies and interstitials, respectively, in equation 3.

$$94 \quad X_V = \frac{\delta}{N_O} \quad (3a)$$

$$96 \quad X_i = \frac{\delta}{N_O} \quad (3b)$$

97

98 The corresponding stoichiometric expansion coefficient is in this case denoted as α_s^X and is
 99 again unitless. As discussed in the next section, α_s^X and $\alpha_s^{[]}$ facilitate comparison of
 100 stoichiometric expansion coefficients between materials with different crystal structure.

101

102 **Implications of the different definitions and choice of units for the stoichiometric** 103 **expansion coefficient**

104 In table 1, the stoichiometric expansion coefficients defined above are presented for
 105 three materials that are commonly used in SOFC applications. It should be noted that each of
 106 these materials belongs to a different crystal structure, possessing a different molar fraction of
 107 oxide ions in the stoichiometric material. Also, α_s reported for the K_2NiF_4 structured materials is
 108 the volume expansion coefficient equivalent to expansion in a polycrystalline material, as these
 109 materials have very anisotropic stoichiometric expansion ⁽¹⁾.

110

111 *Table 1: Chemical (stoichiometric) expansion coefficients according to the three definitions introduced in*
 112 *the text for three materials, each belonging to a different crystal structure with a different molar fraction*
 113 *of oxide ions in the stoichiometric material (N_O). “vac.” and “int.” denote whether δ is accommodated by*
 114 *oxide ion vacancies or interstitials.*

Composition	N_O	[oxide] x 10 ⁻²² at ~23 °C [cm ⁻³]	α_s^δ	$\alpha_s^{[]}$, [cm ³]	α_s^X	$\frac{\alpha_s^\delta}{\alpha_{s,ceria}^\delta}$	$\frac{\alpha_s^{[]}}{\alpha_{s,ceria}^{[]}}$	$\frac{\alpha_s^X}{\alpha_{s,ceria}^X}$
CeO _{2-δ} (Fluorite, vac.)	2	2.52 ⁽³³⁾	0.105 ^(9,10)	4.16 x 10 ⁻²⁴	0.21	1	1	1
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (Perovskite, vac.)	3	1.72 ⁽³⁴⁾	0.033 ^(4,6,35)	1.92 x 10 ⁻²⁴	0.10	0.31	0.46	0.47
La _{0.98} Sr _{0.98} Co _{0.2} Fe _{0.8} O _{4-δ} (K ₂ NiF ₄ , vac.)	4	1.01 ⁽²²⁾	0.012 ^(6,22)	1.19 x 10 ⁻²⁴	0.048	0.11	0.29	0.23
La ₂ NiO _{4-δ} (K ₂ NiF ₄ , int.)	4	1.03 ⁽³⁶⁾	-0.002 ⁽³⁶⁾	-0.19 x 10 ⁻²⁴	-0.008	-0.019	-0.05	-0.038

115

116

117 A key finding from table 1 is that the apparent difference in expansion coefficients for vacancy
 118 formation between materials is less for $\alpha_s^{[]}$ and α_s^X as compared to the conventional α_s^δ term.
 119 For example, α_s^δ in CeO_{2- δ} is ~3x larger than in La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} whereas $\alpha_s^{[]}$ is only
 120 ~2x larger. This difference is illustrated in table 1 by the ratios of α_s^δ , $\alpha_s^{[]}$, and α_s^X to that of

121 ceria in the three far right columns. Similarly, the absolute values of $\alpha_s^{[1]}$ and α_s^X for loss of
 122 interstitials in $\text{La}_2\text{NiO}_{4-\delta}$ is closer to that for oxygen loss in the fluorite and perovskite examples
 123 as compared to α_s^δ . Another interesting point to note is that the ratios of $\alpha_s^{[1]}$ and α_s^X with
 124 respect to that of ceria are fairly similar. Taking the ratio of X_V to concentration, below,
 125 provides insight into this relationship:

$$127 \quad \frac{X_V}{[V_O^{\bullet\bullet}]} = \frac{1}{[\text{oxide}]N_O} \quad (4a)$$

$$128 \quad \frac{X_i}{[O_i^{\prime\prime}]} = \frac{1}{[\text{oxide}]N_O} \quad (4b)$$

129
 130 Inputting values for the oxides included in table 1 into the right hand side denominator of
 131 equation 4 yields $[\text{oxide}]N_O = 5.0 \times 10^{22} \text{ cm}^{-3}$ for $\text{CeO}_{2-\delta}$, $5.2 \times 10^{22} \text{ cm}^{-3}$ for
 132 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $4.0 \times 10^{22} \text{ cm}^{-3}$ for $\text{La}_{0.98}\text{Sr}_{0.98}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{4-\delta}$, and $4.1 \times 10^{22} \text{ cm}^{-3}$ for
 133 $\text{La}_2\text{NiO}_{4-\delta}$. The similarity of these values, results in the small aforementioned difference in the
 134 ratios of $\alpha_s^{[1]}$ and α_s^X in table 1. The reason behind this similarity is associated with the fact
 135 that $[\text{oxide}]$ and N_O are inversely correlated in oxides with similar cation size, e.g. the larger the
 136 N_O , the larger the molar volume as shown in table 1, and therefore the smaller the concentration
 137 of formula units, $[\text{oxide}]$.

138

139 Preferred definition and choice of units for the stoichiometric expansion coefficient

140 It should be emphasized that all three definitions of α_s given earlier are equally
 141 legitimate and the question of a preferred definition is therefore more a matter of convenience.
 142 α_s^δ is typically employed due to the convenience of measuring or computing vacancy content in
 143 terms of molar fraction (as it does not require the knowledge of the oxide's molar volume).
 144 Nevertheless, *it neglects the fact that materials with different structures contain different molar*
 145 *fractions of oxide ions or different volumes per formula unit.* For example, for the same increase
 146 in oxygen vacancy concentration in $\text{CeO}_{2-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, and $\text{La}_{0.98}\text{Sr}_{0.98}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{4-\delta}$,
 147 for instance, $0.1 \times 10^{22} \text{ cm}^{-3}$, $\Delta\delta$ is ~ 0.04 , ~ 0.06 , and ~ 0.1 , respectively. Clearly, although the
 148 oxygen vacancy concentration changes by the same amount, δ does not and α_s^δ will reflect this
 149 difference through a smaller α_s for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ relative to $\text{CeO}_{2-\delta}$. It can be argued
 150 that it is more "fair" to compare α_s among different structures on the basis of the same $\Delta[V_O^{\bullet\bullet}]$
 151 rather than $\Delta\delta$, and that therefore $\alpha_s^{[1]}$ is a more appropriate choice when comparing among

152 different structures since it offers a normalization to the formula unit volume. The
153 proportionality between $[V_{O}^{\bullet\bullet}]$ and X_V , with a more or less structure independent
154 proportionality factor (Eq. 4), renders X_V , and therefore α_S^X , an equally appropriate choice for
155 comparison among different structures. α_S^X retains the convenience of α_S^δ in terms of
156 computation (not requiring the oxide's molar volume) and is therefore a good compromise
157 between α_S^δ and $\alpha_S^{[1]}$.

158 As mentioned above, comparing the last two columns of table 1 to the column
159 $\alpha_S^\delta/\alpha_{S,\text{ceria}}^\delta$ shows that normalizing α_S to the formula unit volume or to the molar fraction of
160 oxide ions decreases the difference between the different structures. Nevertheless, the
161 differences remain quite significant as $\alpha_S^{[1]}$ for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and
162 $\text{La}_{0.98}\text{Sr}_{0.98}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{4-\delta}$ are 54% and 71% smaller than that of ceria, respectively. Recent studies
163 aiming at improving our understanding of the origin of stoichiometric expansion in the fluorite
164 ^(20,23,24) and perovskite structure ⁽²⁴⁾ have concluded that the expansion observed upon increasing
165 $V_{O}^{\bullet\bullet}$ content arises from the associated reduction of (some of) the cations, thereby adopting
166 increased ionic radii. The formation of oxide ion vacancies leads to contraction of the oxide's
167 molar volume in both cases. The different relative change of cation radii for the different
168 reducible cations present in the compounds of table 1 may therefore also account for part of the
169 observed differences, e.g. the relative change in ionic radius for Ce^{4+} to Ce^{3+} (18%) $\text{CeO}_{2-\delta}$ is
170 larger than that for Co^{4+} to Co^{3+} (15%, high spin) and Fe^{4+} and Fe^{3+} (10%, high spin) in
171 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.98}\text{Sr}_{0.98}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{4-\delta}$ ⁽³⁷⁾. Though, as recently shown, a significant
172 reason for the smaller α_S of perovskites (ABO_3) as compared to ceria is related to the restraining
173 action of the A-O sub-lattice to the expansion of the B-site cation upon reduction ⁽²⁴⁾. The fact
174 that such structural constraints play a major role in the value of α_S can also be inferred by the
175 substantially different α_S values found in the perovskite and K_2NiF_4 structured oxides for
176 vacancy formation (see table 1), despite the fact that they contain the same reducible cations. In
177 the case of the K_2NiF_4 structured oxide, the 2-3 times smaller stoichiometric expansion
178 coefficient along the a-direction versus the c-direction is attributed to the constraining action of
179 the rock-salt layers on the perovskite layers ⁽²²⁾. On the other hand, the perovskite layers can
180 expand freely along the c-direction, thereby yielding α_S values comparable to that of perovskites
181 with related compositions. The structural characteristics therefore and the limitations that they
182 impose are clearly the determining factor for the magnitude of the stoichiometric expansion
183 coefficient.

184

185 **Conclusions**

186 In this work, three different approaches to defining the stoichiometric expansion
187 coefficient were discussed. While all three definitions of α_S given here are equally legitimate,
188 there are advantages to selecting certain ones for comparison across different crystal structures.
189 Indeed, the commonly used definition based on mole fraction of vacancies (δ), α_S^δ , neglects the
190 fact that materials with different structures contain different molar fractions of oxide ions or
191 different volumes per formula unit. As a consequence, this definition is not adequate when
192 comparing among different crystalline structures. A second definition, $\alpha_S^{[1]}$, (obtained by using
193 vacancy or interstitial concentration rather than δ) solves this problem, though it requires the
194 a-priori knowledge of the oxide's molar volume. A third definition, α_S^X , (using δ normalized by
195 the molar fraction of oxide ions in the stoichiometric compound, i.e. 2 for ceria, 3 for
196 perovskites, and 4 for K_2NiF_4 oxides) is found to be an appropriate choice for comparison
197 among different structures, while retaining the convenience of being unitless. Although the
198 magnitude of the stoichiometric expansion coefficient depends on the chosen definition, the
199 crystallographic characteristics and the limitations they impose are clearly the determining
200 factor, at least for the cases examined here.

201

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207

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