

Control of Thermochemical Expansion in Perovskite Oxides via Octahedral Tilting and High-Entropy A-sites

Xiaolin Zheng

xlzheng@stanford.edu

Stanford University <https://orcid.org/0000-0002-8889-7873>

Adam Potter

Stanford University <https://orcid.org/0000-0002-7889-6180>

Igor Evangelista

Stanford University <https://orcid.org/0000-0003-2402-9484>

Yifan Wei

Stanford University

Mathias Kiefer

SLAC National Accelerator Laboratory

Dongjae Kong

Stanford University

Yuzhe Li

Stanford University

Andy Huynh

Stanford University

Michal Bajdich

SLAC National Accelerator Laboratory <https://orcid.org/0000-0003-1168-8616>

Nicholas Strange

SLAC National Accelerator Laboratory

Kirsten Winther

SLAC National Accelerator Laboratory <https://orcid.org/0000-0003-1254-1165>

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Control of Thermochemical Expansion in Perovskite Oxides via Octahedral Tilting and High-Entropy A-sites

Adam Potter, Igor Evangelista, Yifan Wei, Mathias Kiefer, Dongjae Kong, Yuzhe Li, Andy Huynh, Michal Bajdich, Nicholas Strange, Kirsten Winther, Xiaolin Zheng*

The durability of solid oxide cells is critically limited by the overall thermochemical expansion of perovskite electrodes, exacerbated by the formation of oxygen vacancies with increasing temperature. This creates a fundamental trade-off, where oxygen vacancies enhance electrochemical functionality at the cost of thermomechanical stability. We independently study thermal and chemical expansion of fifteen perovskite oxides with complex A-site cation mixtures using synchrotron X-ray diffraction, dilatometry, thermogravimetry, and density functional theory. We demonstrate that the Goldschmidt tolerance factor governs both thermal and chemical expansion through octahedral tilting dynamics, which offset bond-stretching vibrations and compensate for vacancy-induced strain. We identify that high-entropy A-site mixing also suppresses chemical expansion via "strain containment", where larger cobalt sites with increased bond covalency locally absorb vacancy-induced strain. This lowers the chemical expansion coefficient by up to 29% relative to the benchmark electrode. Together, these correlations and mechanistic insights map structural and compositional descriptors onto expansion behaviors, providing targeted design principles to tune thermochemical expansion without sacrificing functional defects.

I. INTRODUCTION

High-temperature solid oxide cells (SOCs) are a cornerstone technology for efficient electricity generation, reversible electrolysis, and chemical synthesis, but their deployment is constrained by materials integration at elevated temperature. In SOC stacks, layered electrodes must remain mechanically compatible with the electrolyte during fabrication and thermal cycling. This compatibility is governed by the coefficient of thermochemical expansion (CTE): even modest CTE mismatch generates interfacial stresses that can drive cracking, delamination, and long-term performance loss. Consequently, CTE limits the range of viable oxygen-electrode perovskites (formula $\text{ABO}_{3-\delta}$) [1, 2]. For example, while $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ exhibits excellent electronic conductivity and catalytic activity, its high CTE ($\bar{\alpha}_{25-800^\circ\text{C}} = 20 \times 10^{-6} \text{ K}^{-1}$) prevents its application. A persistent challenge for the SOC-relevant perovskites is the tradeoff between CTEs and ionic conductivity [2–5], as both depend on the oxygen vacancy formation. While a high concentration of oxygen vacancy leads to higher ionic conductivity, it also drives lattice expansion due to its coupling with the B-site redox chemistry. Consequently, perovskites with higher ionic conductivities exhibit undesirable larger CTEs. Mitigation strategies such as composite electrodes incorporating negative-thermal-expansion phases can reduce bulk expansion [2, 6], but they introduce additional interfaces and potential reactivity, underscoring the need for intrinsic approaches to tune CTE and decouple it from functional defect chemistry.

High-entropy perovskite oxides (HEPOs), which incorporate five or more cations into a crystallographic site, have been studied for SOC [1, 7, 8] and have emerged

as a new platform to tuning functional properties [9, 10]. High configurational entropy can stabilize complex compositions at elevated temperature and opens a much larger design space for tuning defect energetics, lattice geometry, and transport [1, 10]. Yet, the CTE in HEPOs remains poorly understood, complicated by the combined effects of thermal expansion α_{th} from anharmonic lattice vibrations and chemical expansion β due to oxygen vacancies. Although critical for device applications, these contributions are rarely studied independently, obscuring more mechanistic understandings.

In simple perovskites, current understandings of α_{th} emphasize B-site composition, including valence state [2], spin transitions in cations such as Co [3], or cation deficiency [11]. In contrast, A-site composition is typically assumed to exclusively impact chemical expansion by governing oxygen vacancy formation through charge compensation [3–5]. Moreover, the prevailing understanding of the chemical expansion coefficient β (the expansion per oxygen vacancy) is related to the change in B-site ionic radius upon reduction, implicitly relegating the role of A-site to mediating vacancy concentration [4, 5, 12]. Previous studies have observed that experimentally measured β can deviate from this prevailing model, attributing these discrepancies to local lattice distortions surrounding the oxygen vacancy identified in simulations [12–14]. Emerging studies, including connections between β and tolerance factor t [14–16] or charge delocalization [16–19], suggest that A-site chemistry and structure can also control β . A mechanistic framework that explains when and why these effects occur, and how they change under high-entropy mixing, is still lacking.

In this work, we establish a mechanistic framework explaining how A-site chemistry governs the thermal (α_{th}) and chemical expansion (β) terms in the CTE in perovskite electrodes across 15 low-entropy (LE) and high-entropy (HE) compositions benchmarked against $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$. Using *in situ* X-ray diffrac-

* Corresponding author: xlzheng@stanford.edu

tion (XRD), dilatometry, and thermogravimetric analysis (TGA), we show A-site composition tunes average CTE (100–800°C) by 30%, largely driven by A-site 2+ cation mole fraction via oxygen vacancy formation. In addition, we find lowering the Goldschmidt tolerance factor (t) reduces both thermal expansion α_{th} , through transverse octahedral tilting dynamics, and chemical expansion per vacancy β . Overall, HE mixing achieved β reductions up to 29% relative to LSCF6428. Density function theory (DFT) calculations reveal that while LE materials mitigate chemical expansion with octahedral tilting, HE materials lower β by an additional mechanism. In the HE structures, the Co sites that absorb charge from vacancies exhibit more covalent bonding and larger Bader volumes relative to the average B-site, allowing them to locally contain strain when reduced. Both tilting and strain confinement strategies lower β , weakening the couple between vacancy formation from mechanical expansion.

II. RESULTS

Thermochemical expansion is reported here as an average coefficient $\bar{\alpha}_{T_1-T_2}$ (Eq. 1) that combines a thermal term α_{th} , arising from anharmonic lattice vibrations, and an isothermal chemical term β , arising from oxygen vacancy formation and the corresponding reduction of B-site cations to larger ionic radii. Because A-site 2+ substitution (into a 3+ site) is charge-compensated by oxygen vacancies and electron holes, the A-site 2+ cation mole fraction X_{2+} controls the vacancy population available to drive chemical expansion. Definitions and governing equations for $\bar{\alpha}_{T_1-T_2}$, α_{th} , β , X_{2+} , t , and ΔS_{mix} are given in Section S1 of Supplemental Materials.

We first present the measured CTEs ($\bar{\alpha}_{T_1-T_2}$) across the composition library (Table I, Figure 1a) and identify which A-site compositional descriptors best correlate with the $\bar{\alpha}_{T_1-T_2}$ (Figure 2). We then decompose the $\bar{\alpha}_{T_1-T_2}$ into its three governing terms (Eq. 1): oxygen vacancy formation $\Delta\delta$ (Figure 2c-d), thermal expansion α_{th} (Figure 3), and chemical expansion per vacancy β (Figures 4-5), and further analyze the mechanisms controlling each term.

$$CTE = \bar{\alpha}_{T_1-T_2} = \frac{1}{\Delta T} \frac{\Delta L}{L_0} \approx \alpha_{\text{th}} + \beta \frac{\Delta\delta}{\Delta T} \quad (1)$$

Fifteen materials were chosen as A-site variants of the benchmark SOC air electrode LSCF6428 (labeled as LE-1), spanning three low-entropy (labeled LE) and twelve high-entropy (labeled HE) based on the definition by the mixing entropy criterion (Eq. 4). All samples have identical B-site compositions ($\text{Co}_{0.2}\text{Fe}_{0.8}$) to isolate the effects of the A-site chemistry. In addition to the common La and Sr, the A-site contains varying fractions of Ca, Y, Ba, Nd, Sm, and Gd (see Table I). The A-site of most HE samples contains equimolar mixtures of 5-7 elements, and two are non-equimolar but remain high-entropy.

A. Correlating $\bar{\alpha}_{T_1-T_2}$ with Composition

Thermochemical expansion was measured by *in situ* synchrotron X-ray diffraction (XRD) for all 15 materials and by pushrod dilatometry (DIL) for a subset of eight materials (5x HE and 3x LE). As shown in Figure 1a, the chosen compositions span a broad design space in both tolerance factor t (Eq. 3) and A-site 2+ cation mole fraction X_{2+} (Eq. 5).

Representative *in situ* XRD spectra for LE-1 from 25–800°C (Figure 1) reveal systematic peak shifts due to lattice expansion. All samples were identified as mixed phase perovskites, comprising varying fractions of cubic ($Pm3m$), rhombohedral ($R3c$), and orthorhombic ($Pnma$) phases. Phase compositions remain largely unchanged upon heating, with the notable exception of LE-1, which exhibits a transition of its rhombohedral phase fraction to cubic ($Pm3m$) around 500°C, consistent with literature [20]. Reitveld refinements, lattice parameters, phase fractions, and anisotropic expansion are described in Section S2 of Supplemental Materials. XRD- and DIL-derived effective length changes generally agree, with Figure 1c showing agreement between values of $\bar{\alpha}_{100-800^\circ\text{C}}$ (also reported in Table I).

We computed the Pearson correlations between $\bar{\alpha}_{100-800^\circ\text{C}}$ (Eq. 1, both XRD and DIL values) with three composition descriptors: X_{2+} (Eq. 5), t (Eq. 3), and ΔS_{mix} (Eq. 4). As shown in Figure 2a, $\bar{\alpha}_{100-800^\circ\text{C}}$ has the strongest correlation with X_{2+} (0.78), and modest correlations with t (0.57), and ΔS_{mix} (0.32). Plotting $\bar{\alpha}_{100-800^\circ\text{C}}$ against X_{2+} (Figure 2b) shows that $\bar{\alpha}_{100-800^\circ\text{C}}$ increases with X_{2+} for both LE and HE samples. This relation is reasonable as that more A-site 2+ dopants increase oxygen vacancy formation due to the charge balance (Eq. S6), therefore increasing the chemical expansion contribution (Eq. S4)[3, 12].

To test whether vacancy formation quantitatively explains the observed $\bar{\alpha}_{100-800^\circ\text{C}}$ variation among samples, we measured the change in oxygen vacancy $\Delta\delta_{300-800^\circ\text{C}}$ from 300–800°C using TGA, assuming that changes in δ below 300°C to be negligible [4]. A subset of data in Figure 2c was taken from our previous work [21]. For both LE and HE samples, $\Delta\delta_{300-800^\circ\text{C}}$ increases with increasing X_{2+} (Figure 2c). Notably, HE samples show a greater oxygen vacancy formation compared to LE samples, an effect we previously reported and attributed to the effects of lattice distortion on the distribution of vacancy energetics [21]. Finally, when we plot $\bar{\alpha}_{100-800^\circ\text{C}}$ against the change in oxygen vacancy $\Delta\delta_{300-800^\circ\text{C}}$ (Figure 2d), it shows a clear positive correlation, indicating that the chemical expansion accounts for a substantial fraction of the composition-to-composition variation in overall $\bar{\alpha}_{100-800^\circ\text{C}}$.

Notably, HE compositions display a shallower slope than LE variants (Figure 2d), indicating that HE samples may achieve a lower chemical expansion coefficient (β) than LE materials. Suppressing β is advantageous for achieving high oxygen vacancy concentrations without incurring additional expansion.

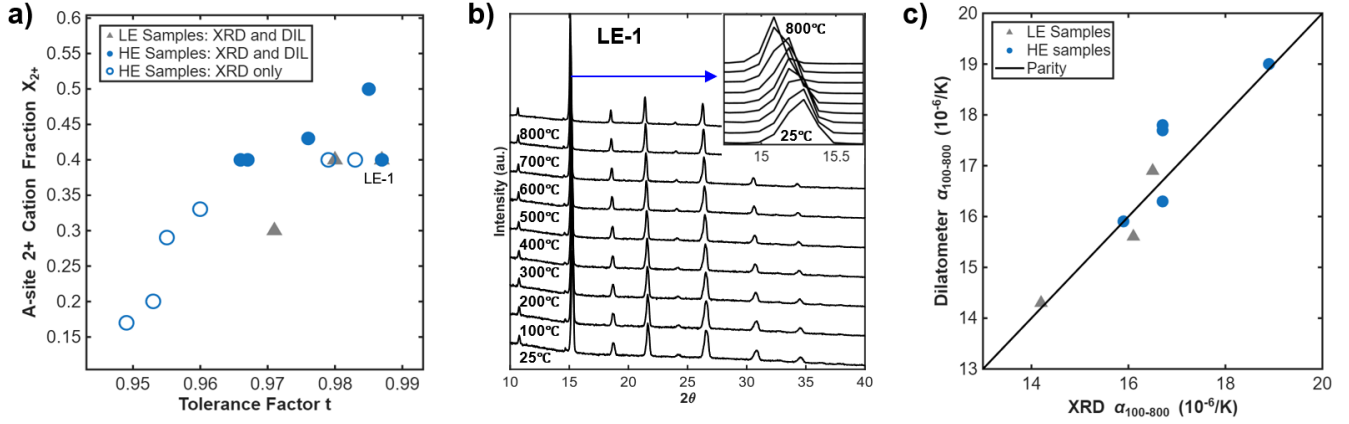


FIG. 1. a) Chosen LE and HE materials spanning a composition space of X_{2+} and t (see Table I). b) *in situ* XRD spectra at increasing temperatures for LE-1 with shifting peaks indicating lattice expansion. c) Comparison of CTEs $\bar{\alpha}_{100-800^\circ C}$ measured from XRD and dilatometry.

Label	A-site	t	X_{2+}	TGA $\Delta\delta_{300-800^\circ C}$	XRD $\bar{\alpha}_{100-800^\circ C}$ ($10^{-6} K^{-1}$)	DIL $\bar{\alpha}_{100-800^\circ C}$ ($10^{-6} K^{-1}$)	α_{th} ($10^{-6} K^{-1}$)	$\beta_{800^\circ C}$ ($10^{-3} \delta^{-1}$)
LE-1	$La_{0.6}Sr_{0.4}$	0.987	0.40	0.022	16.2	15.6	14.5	35.5
LE-2	$La_{0.6}Sr_{0.2}Ca_{0.2}$	0.980	0.40	0.031	16.5	16.9	15.5	32.6
LE-3	$La_{0.7}Ca_{0.3}$	0.971	0.30	0.012	14.2	14.3	13.5	25.6
HE-1	$(LaSrNdGdBa)_{1/5}$	0.987	0.40	0.082	16.7	17.8	15.5	29.2
HE-2	$(LaSrCaSmNdBa)_{1/6}$	0.985	0.50	0.113	18.9	19.0	15.7	28.5
HE-3	$(LaSrCaSmGdYBa)_{1/7}$	0.976	0.43	0.067	16.7	17.7	14.7	28.3
HE-4	$(LaSrCaNdGd)_{1/5}$	0.967	0.40	0.073	15.9	15.9	13.7	27.4
HE-5	$(LaSrCaNdY)_{1/5}$	0.966	0.40	0.081	16.7	16.3	13.1	25.1
HE-6	$La_{0.4}Sr_{0.2}Nd_{0.2}Ca_{0.1}Ba_{0.1}$	0.983	0.40	0.060	15.7			
HE-7	$La_{0.2}Ca_{0.3}Nd_{0.2}Y_{0.2}Ba_{0.1}$	0.979	0.40	0.062	16.5			
HE-8	$(LaSrCaSmNdGd)_{1/6}$	0.960	0.33	0.061	16.8			
HE-9	$(LaSrCaNdGdY)_{1/6}$	0.960	0.33	0.050	15.6			
HE-10	$(LaSrCaSmNdGdY)_{1/7}$	0.955	0.29	0.039	15.5			
HE-11	$(LaSrSmGdY)_{1/5}$	0.953	0.20	0.027	15.4			
HE-12	$(LaSrSmNdGdY)_{1/6}$	0.949	0.17	0.018	14.5			

TABLE I. Materials labels, A-site composition (all B-sites are $Co_{0.2}Fe_{0.8}$), tolerance factor t , A-site 2+ cation mole fraction X_{2+} , change in oxygen vacancy $\Delta\delta$, average expansion coefficients from XRD and dilatometry (DIL) $\bar{\alpha}$, thermal-only expansion coefficient from experimental model fitting α_{th} , and experimental chemical expansion coefficient β at $800^\circ C$.

A detailed analysis of β and its underlying mechanisms is presented in Section II C.

B. Thermal Expansion Portion α_{th} of CTE, Tolerance Factor and Octahedral Tilting

CTEs of perovskites have contributions from both thermal expansion and chemical expansions arising from more oxygen vacancy formation at higher temperatures (Eq. 1). This effect is clearly shown in the length expansion vs. temperature curves, $\frac{\Delta L}{L_0}(T)$, measured from dilatometry (Figure 3a), where the initial length expansion is linear but increases quickly at higher temperature. The onset of faster expansion matches the onset of the oxygen vacancy formation around $550^\circ C$. Fitting the dilatometry curves between $200-800^\circ C$ (avoiding low-temperature dilatometry artifacts)

and oxygen vacancy formation curves, $\Delta\delta(T)$, with Eq. 1 yields estimates of α_{th} and β (additional fitting details in Section S3 of Supplemental Materials). The fitted model attributes approximately 10-19% of the total $100-800^\circ C$ expansion in air to the vacancy-correlated (chemical) contribution, with the remainder arising from thermal expansion.

The extracted pure thermal expansion α_{th} varies greatly across the samples, ranging from 13.2 to $15.7 \times 10^{-6}/K$, i.e., a 17% spread to the mean. When we plot α_{th} against the various compositional descriptors evaluated in this study, both HE and LE samples show the strongest correlation with the tolerance factor t with a positive slope ($R^2 = 0.70$) in Figure 3b. To evaluate whether the α_{th} vs. t trend extends beyond our dataset, we compiled literature expansion data for perovskites with the same B-site, ($Co_{0.2}Fe_{0.8}$) and A-sites including La, Sr, Pr, Ca, Ce, Sm, and Ba [22–25].

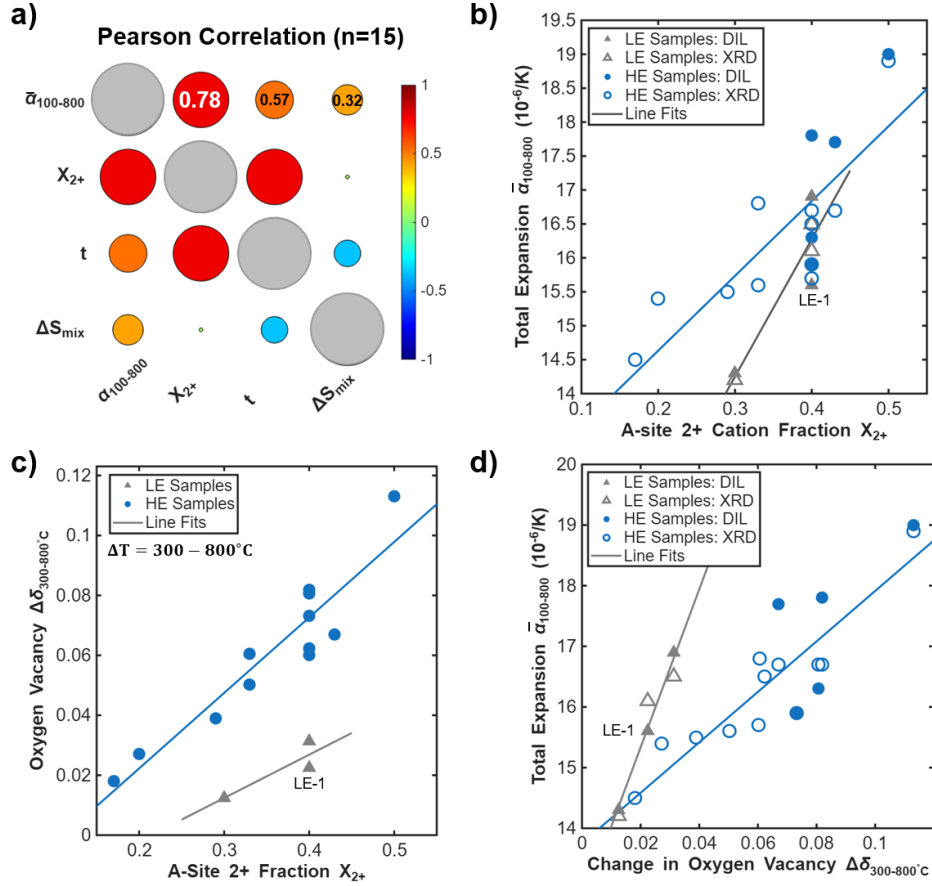


FIG. 2. a) Pearson correlation matrix of average expansion coefficients $\bar{\alpha}$ (combined XRD and DIL values) and three compositional descriptors for $n=15$ materials. b) $\bar{\alpha}$ plotted against X_{2+} with separate line fits for LE and HE data. c) Change in oxygen vacancy $\Delta\delta_{300-800^\circ\text{C}}$ from TGA as a function of X_{2+} . d) $\bar{\alpha}$ as a function of $\Delta\delta_{300-800^\circ\text{C}}$ with positive correlation due to chemical expansion.

We assumed α_{th} to be the average expansion coefficient $\bar{\alpha}_{100-500^\circ\text{C}}$, because oxygen vacancy formation below 500°C is negligible [3]. The compiled data (Figure 3c) also shows that higher tolerance factor correlates with higher thermal expansion α_{th} . This strong correlation establishes that the tolerance factor is an effective structural handle for tuning α_{th} in perovskite oxides.

We interpret this dependence through octahedral tilting dynamics. Tolerance factor t reflects the size mismatch between the A-site cations and the corner-sharing BO_6 octahedra (Eq. 3); lower t increases the equilibrium tilt of the relatively rigid octahedra and softens the librational modes that bend the B-O-B linkage [26, 27]. At elevated temperatures, larger-amplitude transverse octahedral librations act to reduce the average B-B distance, partially offsetting bond-stretching-driven expansion (Figure 3d-e; geometric model and derivation in Section S4 of Supplemental Materials).

Altogether, the extracted α_{th} values and the literature comparison indicate that A-site composition tunes the thermal component of CTE primarily by modifying tolerance factor and octahedral tilting dynamics. Lower t promotes higher amplitudes for octahedral librations

with the net effect of lowering α_{th} .

C. Chemical Expansion Portion β of CTE, Octahedral Tilting and Strain Confinement

The last section shows that A-site composition affects the thermal component α_{th} in Eq. 1 through tolerance factor, and this section will discuss the chemical expansion β contribution per vacancy, especially how the smaller slope in Figure 2d suggests lower β for HE samples.

We first measured β at 800°C for eight materials using isothermal, variable- pO_2 dilatometry ($\text{pO}_2 = 0.21 - 0.01\text{bar}$, see Section S5 in Supplemental Materials for method details), and the corresponding oxygen vacancy change $\Delta\delta$ was determined by TGA for a range of pO_2 . The β values reported in Figure 4a and Table I were calculated using Eq. S3 and range from 25.1 to $35.5 \times 10^{-3}\delta^{-1}$, consistent with prior reported values for similar materials [31, 34]. β of the benchmark LE-1 (LSCF6428) is $35.5 \times 10^{-3}\delta^{-1}$, consistent with values reported for LSCF6428 and related La-Sr ferrites [28, 31-33]. Among the measured subset, Figure 4a shows HE

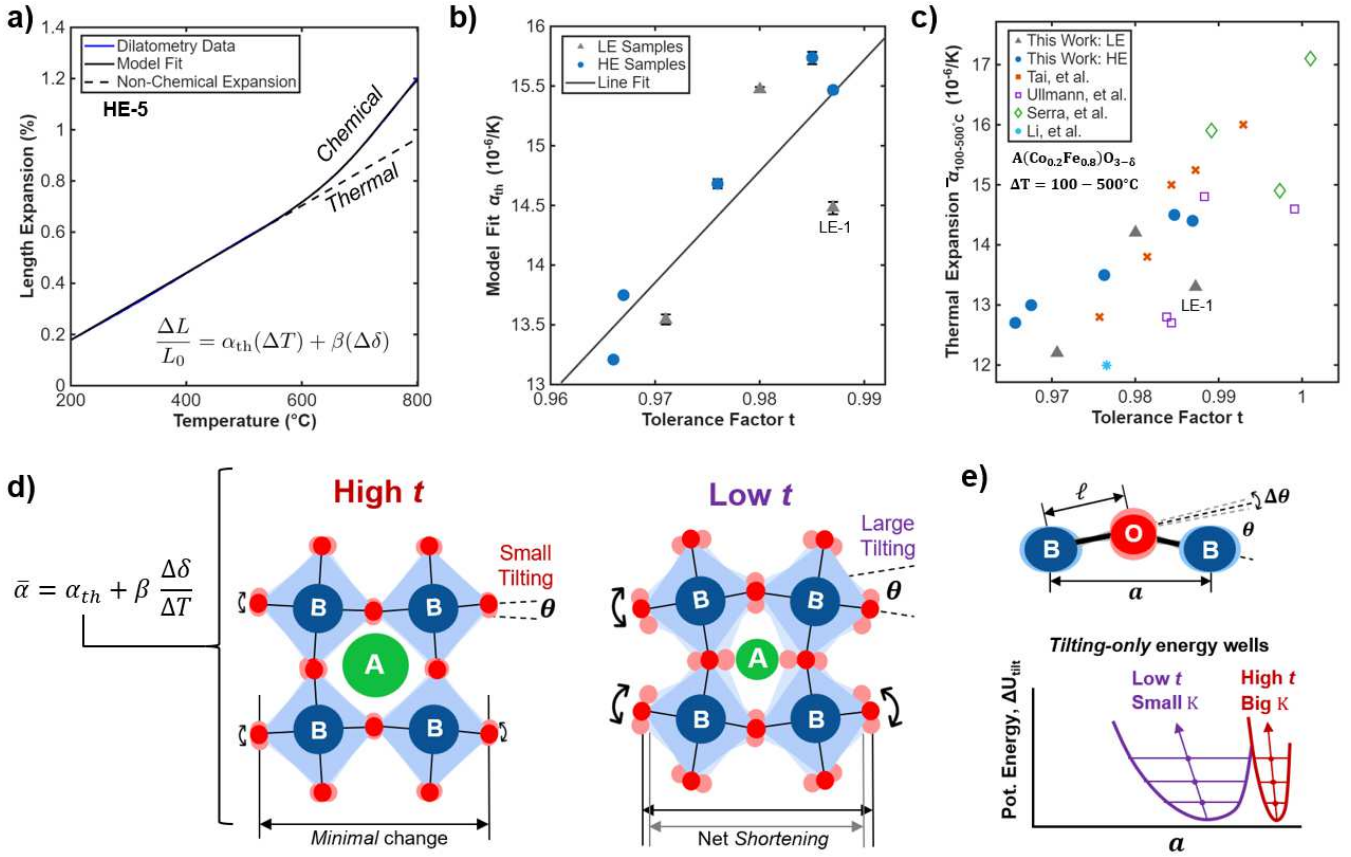


FIG. 3. a) Model fitting to HE-5 expansion curve from dilatometry with Eq. 1. b) Model fit pure thermal expansion coefficients α_{th} with uncertainties as a function of tolerance factor t . c) Low-temperature (100 – 500°C) average expansion coefficient $\bar{\alpha}$ from literature and this study [22–25] as a function of tolerance factor t . d) Schematic of a mechanism linking tolerance factor to thermal expansion where low t relaxes the octahedral tilting vibrational mode, which can shorten the distance between B-site cations at higher amplitudes. e) Geometric illustration of how bending vibrations in a potential well are biased toward B-B contraction over expansion.

samples exhibit noticeably smaller β than LE-1.

All compositions share the same B-site chemistry, so this cannot be explained based on previous models for predicting β using only the B-site chemistry [4, 5, 14]. Therefore, A-site composition must play a critical role. Figure 4a shows that similar to α_{th} , β increases with increasing the tolerance factor t with a weaker correlation among HE materials. To place this trend in context, we collected literature β values grouped by their redox-active B-site cations: Fe [4, 19, 28–33], Cr [31], Ni [17], and Mn [31], and plotted them together with our data against tolerance factor (Figure 4b). Across the broader dataset, β shows a positive dependence on t with an average slope of $0.40 \times \delta^{-1}$, consistent with a prior reported correlation between β and t across diverse SOC materials by Frade et al. (slope of $0.70 \times \delta^{-1}$) [14]. Our LE compositions follow a similar trend, but the HE subset exhibits a smaller slope of $0.14 \times \delta^{-1}$.

To elucidate why β depends on t and why this dependence is reduced in HE, we calculated vacancy-induced lattice responses using DFT. Simulations target the lattice response to introducing one (1v) and two (2v) oxygen vacancies into five structures of varying

phase and composition (see Section S6 of Supplemental Materials). All structures exhibit positive volume expansion upon vacancy formation, consistent with experiments. Building upon previous suggestions that B-O-B bending could mitigate chemical expansion [35], we quantify the initial tilt state using the average relaxed B-O-B bond angle θ (Figure 5a). As expected, lower t and lower symmetry phases correspond to larger tilting angle θ .

Accommodating an oxygen vacancy alters the overall length (a) of the B-O-B linkage (Figure 5a) through both bond stretching ($\Delta \ell$) and bond angle bending ($\Delta \theta$). In Eq. 2, we define a metric - tilt compensation, which describes the structural effect of tilting ($\Delta \theta$) on the relative B-B length expansion, derived from the partial derivative of a (Eq. S8) with respect to θ . This descriptor quantifies the ensemble-averaged fractional change in a across N B-O-B linkages resulting from a tilt angle change $\Delta \theta_i$ at initial angle θ_i . Equation 2 reveals that for an ideal cubic lattice ($\theta = 0^\circ$), small perturbations in θ have a negligible effect on expansion. In contrast, for an initially tilted structure ($\theta > 0^\circ$), an equivalent $\Delta \theta$ yields greater tilt compensation, scaling

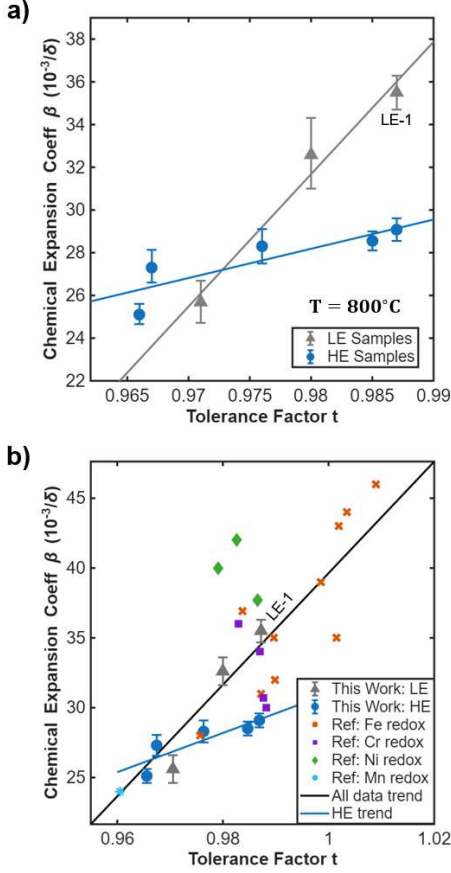


FIG. 4. a) Experimental β at 800°C with model-fit uncertainty plotted against tolerance factor t with separate best fit lines for LE and HE data. b) Values of β as a function of tolerance factor from this study and the literature, separated by redox active B-site: Fe [4, 19, 28–33], Cr [31], Ni [17], and Mn [31].

with $\tan \theta$.

$$\begin{aligned} \text{Tilt Comp.} &:= \left\langle \frac{\partial(a/a_0)}{\partial \theta} \right\rangle \\ &= \langle -\partial \theta \tan \theta \rangle = -\frac{1}{N} \sum_{i=1}^N \Delta \theta_i \tan \theta_i \end{aligned} \quad (2)$$

Figure 5b plots tilt compensation (Eq. 2) of relaxed structures averaged across the 0→1 and 1→2 oxygen vacancy transitions as a function of initial average θ . Among LE structures, the tilt compensation descriptor is negative, and becomes more negative at larger θ , suggesting contraction due to an overall increase in tilting (positive $\Delta \theta$). While the octahedra in LE structures tilt in response to oxygen vacancies, Figure 5b shows the HE structures exhibit little to no change in average tilt, suggesting their structures respond differently to vacancy strain, something noted later. Figure 5c shows that for LE structures, a greater magnitude of tilt compensation (more negative) is associated with suppressed chemical expansion for both experimentally-measured and for DFT-calculated

β . Through octahedral tilt compensation, t can affect β , explaining experimental trends in Figures 4a-b.

To understand why HE structures exhibit low β but negligible octahedral tilting (Figure 5b), we compared how vacancy formation is accommodated structurally and electronically. We first quantify the spatial extent of vacancy-induced lattice distortion by plotting the average oxygen displacement averaged between 0v→1v and 1v→2v transitions (Figure 5d). For all structures, displacements are largest near the defect. However, HE structures show smaller displacement amplitudes than LE structures both near and far from the vacancy. Vacancy-induced strain is minimized, or contained, in HE structures but has long-ranged effects in LE structures. This long-ranged distortion can be attributed to octahedral tilt-responses in LE structures (Figures 5b-c).

We next examine how the two electrons left by oxygen removal are accommodated by the B-site network. Because oxygen vacancies are compensated primarily by reducing B-site transition metals cations [3], we identify the primary “charge-host” B-sites using changes in local magnetic moments after each vacancy introduction (Figure S7). In all cases, the 1-3 charge hosts identified were cobalt. Next, we characterize the local electronic environment of each B-site cation using its Bader charge and Bader volume, descriptors previously employed to quantify structural distortion effects in high-entropy alloys [36]. Figure 5e shows the average Bader charge q_B on Fe and Co sites in the zero-vacancy structure, with error bars indicating the standard deviation of q_B . The average Bader charge on Fe, q_B^{Fe} , remains near constant across structures, deviating by less than $0.02 e^-$. In contrast, q_B^{Co} varied by over $0.15 e^-$, with greater q_B^{Co} in HE structures. This difference is most apparent comparing rhombohedral (rhom) structures. This suggests that in the HE structures, the Co cations acting as charge hosts have more covalent bonding with oxygen. This is consistent with previous work associating lower chemical expansion with greater metal-oxygen bond covalency [16, 18] and studies reporting enhanced bond covalency in high-entropy oxides [37–39].

The importance of bond covalency and structure on vacancy-induced strain is illustrated through Bader volume, which describes volume encapsulating charge attributed to an atom. Figure 5f shows the distribution of initial Bader volumes (zero-vacancy structure) across all B-sites for each structure, with averages marked for Co (dotted blue) and Fe (solid brown). The HE structures exhibit a broader distribution of Bader volumes than LE structures, reflecting a wider range of local environments produced by A-site disorder. For all structures, the average Co Bader volume was larger than that for Fe, but the difference is largest in the HE structures due to greater Bader charge (Figure 5e) and longer B-O bond lengths. HE structures also experience a more localized changes in Bader charge on B-site cations (Figure S8). We observe an inverse dependence where the larger the Bader volumes of

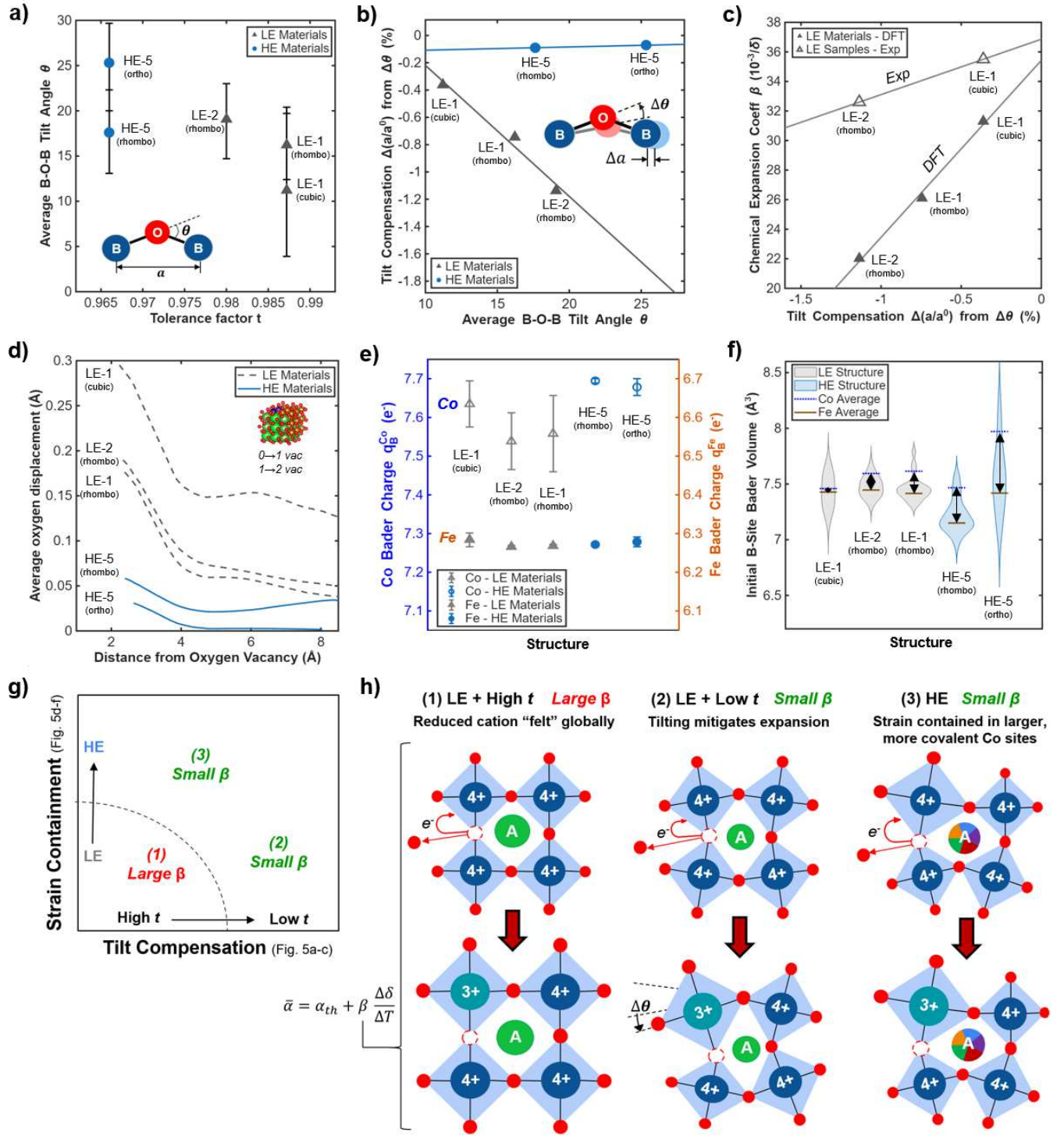


FIG. 5. a) Initial average B-O-B bond angle θ with error bars indicating standard deviations plotted against tolerance factor t . b) Tilt compensation (Eq. 2) as a function of average initial tilt angle θ . c) Experimental and DFT-measured chemical expansion coefficients β for LE samples plotted against tilt compensation calculated from DFT. d) Smoothed curve of average fractional oxygen displacement from DFT following an oxygen removal (combined $0v \rightarrow 1v$, $1v \rightarrow 2v$) as a function of distance from the vacancy defect. e) Average Bader charge q_B for Fe and Co in zero-vacancy structures, ordered by decreasing oxygen displacement. Error bars are standard deviations of q_B . f) Distributions of B-site Bader volumes in zero-vacancy structures, with lines indicating averages for Co (dotted blue) and Fe (solid brown). Differences between Co and Fe averages (black arrows) are larger in HE structures. g) Schematic of identified design space where β is a function of both tilt compensation (Fig. 5c) and strain containment (Fig. 5f). h) Schematic summarizing mechanisms affecting chemical expansion where LE materials compensate for strain depending on bond angles θ and HE materials minimize β by containing strain in Co sites with greater covalency.

Co compared to Fe, the lower the vacancy-induced oxygen displacement (Figure 5d). We interpret this as strain containment: when the vacancy charge is accommodated on B-sites with larger Bader volumes, the cation can reduce without transmitting large distortions into the surrounding lattice, and vice versa. This containment lowers β in the HE structures independent from tolerance factor t . In contrast, in LE structures, strain propagates because charge compensation is forced onto less accommodating B-sites, driving a collective lattice response via octahedral tilting (Figure 5b). This difference explains why experimentally, β is more sensitive to tolerance factor in LE compositions than HE compositions (Figure 4a-b).

Figure 5g summarizes the two mechanistic pathways identified for suppressing the chemical expansion coefficient (β) in structures studied in this section. LE structures reduce β via tilt compensation, which is enhanced at lower tolerance factors due to greater initial tilt angles (θ). HE compositions suppress β through local strain containment, enabled by greater cobalt bond covalency. The three labeled regimes in Figure 5g are expanded in Figure 5h, which details how these contrasting lattice architectures accommodate vacancy-induced charge and its associated strain.

III. CONCLUSION

We establish a comprehensive framework that decodes the influence of A-site cation composition on the thermochemical expansion of perovskite oxides, providing a mechanistic guide for tuning this critical property. We found the strongest compositional predictor of CTE from 100 – 800°C was the divalent doping fraction X_{2+} because it drives oxygen vacancy formation. We also identified strong correlations between tolerance factor and the thermal α_{th} and chemical β expansion coefficients and explained them mechanistically with octahedral tilting using DFT simulations. Furthermore, we observed key differences in the chemical expansion behavior of LE and HE compositions, including an increase in oxygen vacancy formation and reduction in per-vacancy-expansion (lower β) due to larger, more covalent Co-sites minimizing strain.

While this study is only performed on perovskites with B-site ($\text{Co}_{0.2}\text{Fe}_{0.8}$), compositional trends for α_{th} and β are consistent with a wide range of materials in the literature, suggesting the mechanisms proposed could be broadly applicable to other perovskite oxides. Through separate study of thermal and chemical expansion, this work provides fundamental design principles needed to mitigate the trade-off between electrochemical performance and thermomechanical stability that has long constrained material use in solid oxide cells.

IV. METHODS

A. Compositional Descriptors

In calculating X_{2+} it is assumed Sr, Ca, and Ba are divalent while La, Y, Nd, Sm, and Gd are trivalent resulting in Eq. 5. The Goldschmidt tolerance factor t is calculated with Eq. 3 where r_A , r_B , and r_O are the average ionic radii of the A-, B-, and O-sites, respectively.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (3)$$

Calculating tolerance factor required several assumptions about valency and spin state to determine relevant ionic radii. First, crystal radii were used which are simply the ionic radii from *Shannon* with an offset [40]. A-site cations assume coordination number (CN) 12, with a linear extrapolation used for CN12 Y and Pr. A-site valence states are assumed the same as above with tetravalent Ce and Pr. For B-site cations, CN6 was assumed with valency determined by charge balance with no oxygen vacancies. The $\delta = 0$ assumption sets the upper bound for t , while in reality non-zero δ will lower t . It is assumed that Fe, Co, Cr, Mn, and Ni were redox active while Ti, Ga, Al, and V were not with Fe assumed to oxidize preferentially to Co [41]. Finally, we assume high spin states for Fe^{3+} , Co^{3+} , Co^{4+} , Mn^{3+} , Ni^{3+} for high temperatures.

Configurational disorder on the A-site is quantified with the mixing entropy ΔS_{mix} , given by Eq. 4, where R is the universal gas constant and X_i is the mole fraction of the i -th cation in the A-site. High-entropy material is typically defined as $\Delta S_{\text{mix}} \geq 1.5R$.

$$\Delta S_{\text{mix}} = -R \sum_i X_i \ln X_i \quad (4)$$

The A-site 2+ fraction X_{2+} is defined in Eq. 5 as the sum of Ca, Sr, and Ba site fractions.

$$X_{2+} = X_{\text{Ca}} + X_{\text{Sr}} + X_{\text{Ba}} \quad (5)$$

B. Sample Preparation

Samples were synthesized using the solution combustion synthesis method using stoichiometric mixing of metal nitrate precursors from Thermo Fisher Scientific dissolved in 100 mL of deionized water: $\text{La}(\text{NO}_3)_3$ (99.9%), $\text{Sr}(\text{NO}_3)_2$ ($\geq 99\%$), $\text{Ca}(\text{NO}_3)_2$ ($\geq 99\%$), $\text{Ba}(\text{NO}_3)_2$ ($\geq 99\%$), $\text{Nd}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (99.9%), $\text{Sm}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (99.9%), $\text{Gd}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (99.9%), $\text{Y}(\text{NO}_3)_3 \cdot 6(\text{H}_2\text{O})$ (99.9%), $\text{Fe}(\text{NO}_3)_2 \cdot 9(\text{H}_2\text{O})$ ($\geq 98\%$), and $\text{Co}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ ($\geq 98\%$). Sucrose (Sigma-Aldrich Omnipur) is added as a fuel in a fuel-oxidizer ratio of 1.0 (1M sucrose) and stirred at 50°C on a hot plate for 12 hours or until solution forms a gel. The solution is ignited at 350°C until combustion is complete. Powders are annealed at 800°C for 180 minutes with a 4°C/min ramp rate and high-energy ball-milled at 10Hz in a Retsch Cryomill to reduce particle size. Rods for dilatometry were prepared by adding 2 g of milled electrode powder, 40 μL menhaden fish oil as a dispersant, 40 μL dibutyl phthalate as a platisizer (99%), and 40 mg Polyvinyl butyral as a binder (all additives from Sigma-Aldrich) to 50 mL IPA, then ball milling with 10 g of 3 mm YSZ media at 50 RPM for 12 hours. The well-mixed slurry was dried at 50–60 °C with stirring until the

IPA evaporated, then ground and sieved through $\sim 250 \mu\text{m}$ mesh. Powders were pressed into pellets at 15 kpsi in a $\frac{1}{4}$ inch die and sintered at 800°C for 2 hours followed by 1200°C for 6 hours at a constant $2^\circ\text{C}/\text{min}$ ramp rate.

C. Material Characterization

Synchrotron *in situ* X-ray diffraction was performed at beamline 2-1 of the Stanford Synchrotron Radiation Lightsource (SSRL) in transmission geometry, using an incident wavelength of $0.729 \text{ \AA}$. The absolute wavelength for the measurements was refined using a NIST 660c LaB_6 standard. Angle-dispersive XRD data were acquired stepwise using a Pilatus 100K area detector in portrait orientation. Two-dimensional diffraction images were normalized to the incident beam, stitched, and integrated into one-dimensional diffraction patterns using a Python script developed specifically for SSRL beamline 2-1. XRD measurements were performed using a capillary sample cell [42] equipped with Nichrome coil heaters. Powders were prepared in 1.0 mm outer diameter (o.d.) quartz capillaries (Hilgenberg) with a 0.01 mm wall thickness and an internally mounted type K thermocouple for regulating and measuring sample temperature. Measurements were performed in air between room temperature and 800°C , with approximately 4 minute equilibration times and temperature holds during data acquisition. Rietveld refinement details are provided in Section S2 of Supplemental Materials.

Bulk length expansion as a function of temperature was measured using a TA DIL801L pushrod dilatometer from $25\text{--}950^\circ\text{C}$ at $3^\circ\text{C}/\text{min}$. Data above 850°C is not reported as minor irreversible sintering effects were found to contaminate thermal expansion data. Dilatometry was also performed at a constant 800°C while varying partial pressure of oxygen ($p\text{O}_2$) with mixed dry air and argon. More details on dilatometry with variable $p\text{O}_2$ are provided in Section S5 of Supplemental Materials.

Thermogravimetric analysis (TGA) was performed on a Setaram LABSYS evo TGA-DSC to quantify the change in oxygen vacancy concentration ($\Delta\delta$) under varying conditions. The value of $\Delta\delta$ was calculated from the fractional mass loss ($\Delta m/m_0$) and the material's theoretical molar mass (M_W) per Eq. 6. A blank crucible run was subtracted from all measurements. Temperature Dependence ($\Delta\delta$ vs. T): To correlate with dilatometry, vacancy formation curves, $\Delta\delta(T)$, were measured on 200–250 mg of crushed sintered rod powder. The sample was heated to 800°C at a rate of $3^\circ\text{C}/\text{min}$. Separately, to determine the total change in vacancy concentration between 300°C and 800°C ($\Delta\delta_{300\text{--}800^\circ\text{C}}$), a 50–70 mg powder sample was held isothermally for 1–2 hours at 100°C intervals. Oxygen Partial Pressure Dependence ($\Delta\delta$ vs. $p\text{O}_2$): The isothermal dependence of $\Delta\delta$ on oxygen partial pressure ($p\text{O}_2$) was determined at 800°C . A 150–200 mg sample of a crushed sintered pellet was exposed to flowing mixtures of dry air and argon (100 SCCM total flow) to achieve $p\text{O}_2$ values of 0.21, 0.10, 0.05, 0.03, and 0.01 atm, with the system held at each step until equilibrium was reached. The resulting data was fit to a defect model (see Section S5 of Supplemental Materials Section) to confirm its physicality and to create a continuous map between δ and $p\text{O}_2$.

$$\Delta\delta = \frac{\Delta m}{m_0} \frac{M_W}{16} \quad (6)$$

D. DFT Simulation

DFT calculations were performed for five material-phase models, including cubic and rhombohedral (LE-1), rhombohedral (LE-2), and orthorhombic and rhombohedral (HE-5). Including two symmetries for LE-1 and HE-5 enables within-composition comparison of phase and octahedral-tilt effects, although the limited model set does not completely separate structural effects from compositional disorder. In LSCF, the relative energies of relaxed one-vacancy configurations were compared among candidate oxygen sites, and removing an oxygen bridging Co and Fe produced the lowest-energy configuration. Both successive vacancies were therefore introduced at Co-O-Fe linkages in all models to maintain the same nearest-neighbor B-site environment across compositions. This selection is consistent with previous studies showing that Co-containing environments facilitate oxygen-vacancy formation in Co-Fe perovskites [43, 44]. Each stoichiometric structure (0V) was fully relaxed before the first oxygen removal and subsequent relaxation of the 1V structure. A second oxygen bridging Co and Fe was then removed from the selected 1V configuration, followed by relaxation of the resulting 2V structure. Because vacancy sites were not independently screened in every model, these calculations represent consistently selected zero-temperature vacancy configurations rather than the lowest-energy or configurationally averaged vacancy states for every composition.

Our first-principles calculations were performed using density functional theory (DFT), as implemented in the Vienna *Ab initio* Simulation Package (VASP) [45]. The interaction between valence electrons and ionic cores was described using the projector augmented-wave (PAW) method [46]. Exchange-correlation effects were treated using the Perdew-Burke-Ernzerhof generalized gradient approximation. On-site corrections were applied to the transition-metal d states using the rotationally invariant Dudarev DFT+ U formulation, with $U_{\text{eff}} = U - J = 4.30 \text{ eV}$ for Fe and 3.32 eV for Co [47]. These values were selected based on established DFT+ U treatments of transition-metal oxides using linear-response calculations and oxide-formation-energy fitting [48, 49]. For Nd-containing structures, the Nd $4f$ electrons were treated as part of the frozen core. Spin-polarized calculations were initialized with ferromagnetically aligned Fe and Co moments of 5 and $2 \mu_B$, respectively. The spin density and site-resolved magnetic moments were then allowed to evolve self-consistently during structural relaxation.

Brillouin-zone integrations were performed using Γ -centered k -point meshes with a reciprocal-space spacing of approximately $0.05 \times 2\pi \text{ \AA}^{-1}$. A plane-wave kinetic-energy cutoff of 450 eV was used for all calculations. Gaussian smearing was applied with a width of 0.05 eV. Both atomic positions and cell vectors were relaxed until the maximum force was below $2 \times 10^{-2} \text{ eV \AA}^{-1}$. Electronic self-consistency thresholds of 10^{-6} eV and 10^{-5} eV were used for the LE and HE-5 structures, respectively.

Disordered cation configurations were represented using special quasirandom structures generated with the ATAT package [50]. One SQS realization was used for each material-phase model. The stoichiometric supercells contained 27 ABO_3 formula units and 135 atoms for cubic LE-1, 24 formula units and 120 atoms for rhombohedral LE-1, rhombohedral LE-2, and rhombohedral HE-5, and 16 formula units and 80 atoms for orthorhombic HE-5. Removal of

one and two oxygen atoms therefore produced δ values of 0.037 and 0.074, 0.042 and 0.083, or 0.063 and 0.125, depending on the model size. These cell sizes were selected to provide computationally tractable vacancy calculations while maintaining separation between periodic vacancy images.

Following each oxygen removal, both atomic positions and cell vectors were fully relaxed. The relaxed cell volume V_n was obtained for each vacancy state, where $n = 0, 1$, and 2. For a supercell containing N_{FU} ABO_3 formula units, the oxygen nonstoichiometry was calculated as $\delta_n = n/N_{\text{FU}}$. The corresponding linear strain was estimated using the pseudocubic approximation

$$\varepsilon_{\text{L},n} = \frac{1}{3} \frac{V_n - V_0}{V_0}. \quad (7)$$

An effective DFT chemical-expansion coefficient β_{DFT} was obtained from the slope of a linear least-squares fit constrained through the 0V reference

$$\varepsilon_{\text{L}} = \beta_{\text{DFT}} \delta. \quad (8)$$

The fit included the 0V, 1V, and 2V structures. The resulting coefficients represent zero-temperature estimates over the calculated vacancy-concentration range.

V. DATA AVAILABILITY

Processed thermal expansion, oxygen vacancy, lattice structure, and tolerance factor estimates have been deposited in a FigShare database (DOI TBD).

VI. CODE AVAILABILITY

Code for processing results of DFT calculations are available upon request to the authors.

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VII. AUTHOR CONTRIBUTIONS

A.P. lead conceptualization, experimental investigations, formal analysis, and supplied the initial draft. I.E. and Y.W. performed computational and experimental investigations respectively in addition to writing review and editing. M.K. performed experimental structural characterizations and analysis. D.J., Y.L., and A.H. performed synthesis or characterization for experimental investigations. M.B. and K.W. provided supervision for computational investigations and X.Z. lead project supervision, funding acquisition, and writing review and editing.

VIII. COMPETING INTERESTS

The authors declare no competing interests.

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