

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

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1 Background and Definitions

CTE is defined as the length change ΔL relative to an initial length L_0 in response to temperature fluctuations across $T_1 - T_2$ or ΔT , and is reported as an average expansion coefficient $\bar{\alpha}_{T_1-T_2}$ (Eq. 1) [1, 2, 3]. Perovskite SOC electrodes are mixed ionic–electronic conductors (MIECs) and their CTEs (Eq. 1) include both (i) a primary thermal expansion α_{th} (Eq. 2) driven by anharmonic lattice vibrations [4], and (ii) a secondary isothermal chemical expansion β (Eq. 3) driven by changes in oxygen nonstoichiometry δ (in $\text{ABO}_{3-\delta}$) [5]. Chemical expansion occurs because oxygen vacancy formation leaves two electrons behind to reduce transition metal cations [6]. For example, in $\text{La}_x\text{Sr}_{1-x}\text{FeO}_{3-\delta}$ (LSF), one oxygen vacancy formation leads to reduction of two Fe^{4+} atoms to Fe^{3+} per the reaction in Eq. 4 [3].

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

$$\alpha_{\text{th}} = \left. \frac{1}{L_0} \frac{dL}{dT} \right|_{\delta} \quad (\text{units } 10^{-6} \text{K}^{-1}) \quad (2)$$

$$\beta = \left. \frac{1}{L_0} \frac{dL}{d\delta} \right|_T \quad (\text{units } 10^{-3} \delta^{-1}) \quad (3)$$



The larger radius of Fe^{3+} (0.645 Å for high spin) in comparison to that of Fe^{4+} (0.585 Å for low spin) contributes to lattice expansion [7]. This is also true for other B-site transition metals used in SOC perovskite oxide electrodes, such as Co or Mn [6].

The chemical expansion portion of CTE (Eq. 1) in $\text{ABO}_{3-\delta}$ scales with the change in number of oxygen vacancies $\Delta \delta$, which is strongly influenced by the A-site 2+ cation mole fraction X_{2+} (Eq. 5). This is because since negative 2+ A-site defects are balanced by positive oxygen vacancies and electron hole p defects per Eq. 6 [8, 3]. Holes p tend to localize near the B-site cations, such as in the form Fe^{4+} in Eq. 4.

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

$$\delta = \frac{1}{2}(X_{2+} - p) \quad (6)$$

2 Sequential Refinements of in-situ XRD Data

Sequential Rietveld refinements were performed using TOPAS-Academic [9] to quantify structural evolution as a function of temperature using in-situ X-ray powder diffraction (XRD) data from Stanford Linear Accelerator Lab (SSRL). At room temperature, refinements shown in Figure S1 suggest samples are perovskite phases, with LE-1 and HE-2 being a mix of cubic (space group $Pm\bar{3}m$) and rhombohedral ($R\bar{3}c$) while

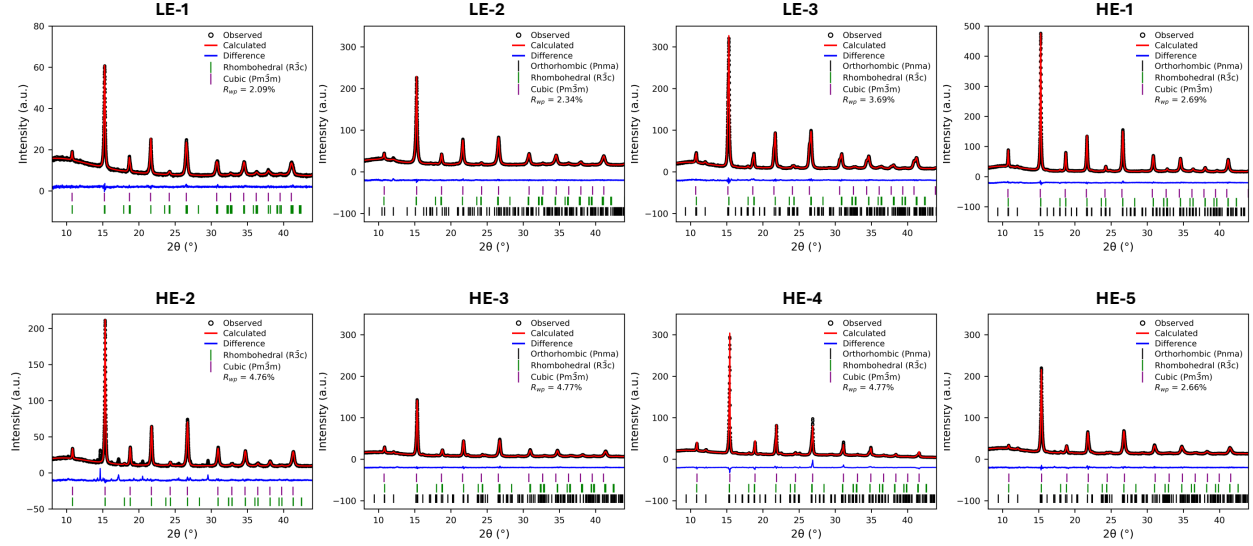


Fig. S 1: Rietveld refinements for eight powder XRD spectra at room temperature (25 °C). LE-1 and LE-2 are predominantly rhombohedral phases while the remaining structures are identified as orthorhombic.

other samples also include and orthorhombic (*Pnma*) phase. Fitting fewer phases typically resulted in the nearly equivalent volume expansion curves when applied to the same data sequence. Data for refined phase fractions, lattice parameters, cell volumes, and goodness-of-fit metrics are provided as a separate spreadsheet in this submission.

Anisotropic expansion can occur in perovskite oxides [10, 11] when the phase is not cubic. The main text focuses on volume expansion, since randomized grain orientation means anisotropy is not experienced in the bulk, however, it may still induce microstrain between crystals so we discuss it here. Directional expansion along each axis is reported in the supplied spreadsheet. LE-1 exhibited large expansion anisotropy with around 50% greater expansion along a-axis than the c-axis, consistent with large expansion anisotropy reported for the similar $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ [11]. In contrast, LE-2 expanded evenly on a- and c-axes. Among the orthorhombic structured samples (LE-3 and all HE samples) all exhibited 10-40% greater expansion in the b- and c- axes than the a-axis, with the exception of HE-5 which expanded more on the b-axis than either a- or c-axes. This anisotropy is indicative of the effects of octahedral tilting on expansion characteristics.

3 Two-parameter Model Fitting for Dilatometry

A two-parameter model (Eq. 7) is used to discriminate contributions of thermal versus chemical expansion in the overall expansion measured by dilatometry. In Eq. 7, dilatometer expansion curves ($\frac{\Delta L}{L_0}(\Delta T)$) are fit using oxygen vacancy formation curves ($\Delta\delta(T)$) with α_{th} and β as two parameters.

$$\frac{\Delta L}{L_0}(\Delta T) = \alpha_{\text{th}} \cdot \Delta T + \beta \cdot \Delta\delta(T) \quad (7)$$

Vacancy formation curves shown in Figure S2a are measured with thermogravimetry (TGA) using the same samples (crushed with mortar and pestle) from the corresponding dilatometry data under the same heating ramp rate (3°C/min). The onset of oxygen vacancy formation ranges from 450-650°C and generally aligns with the inflection point in expansion curves. Fitting was performed on data between 350-800°C to avoid low-temperature artifacts in the dilatometry and TGA curves, while low enough to precede the onset of vacancy formation. Figure S3 shows the model curve (black) fit to expansion data (blue) with a fit metric of $R^2 \geq 0.999$ indicated on each plot. The dashed line indicates the projected non-chemical expansion from α_{th} , similar to that in Figure 3a. A few points of model dependency are noted. For LE-1 and LE-3, an irregular bump around 500°C is not explained. For HE-2, the regions around 600°C show a model-fit discrepancy

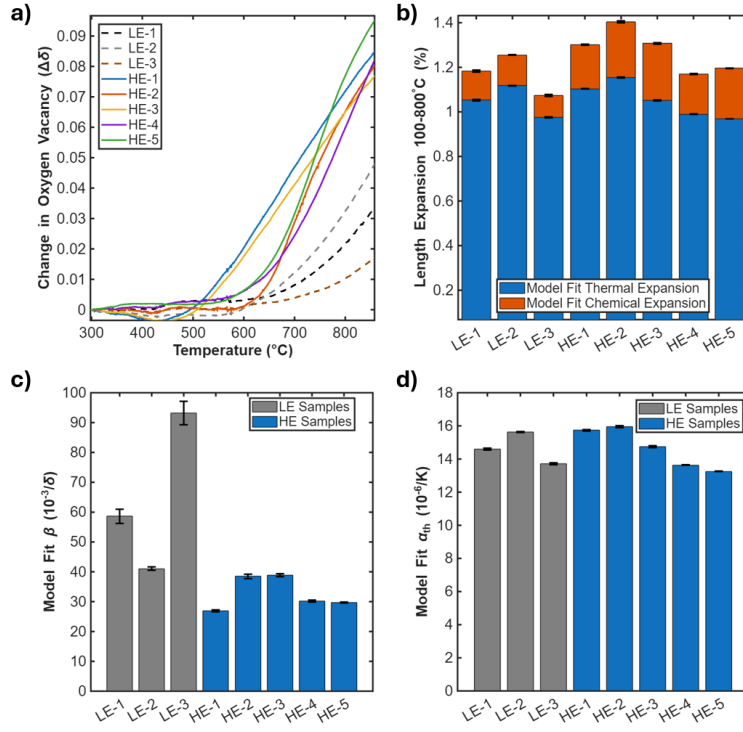


Fig. S 2: a) Change in oxygen vacancy from 300 $^{\circ}\text{C}$ from TGA. b) Thermal versus chemical expansion contributions from 100-800 $^{\circ}\text{C}$ estimated with model fitting. c) Model fit values of chemical expansion coefficient β and d) thermal expansion coefficient α_{th} . All error bars are model fit uncertainty.

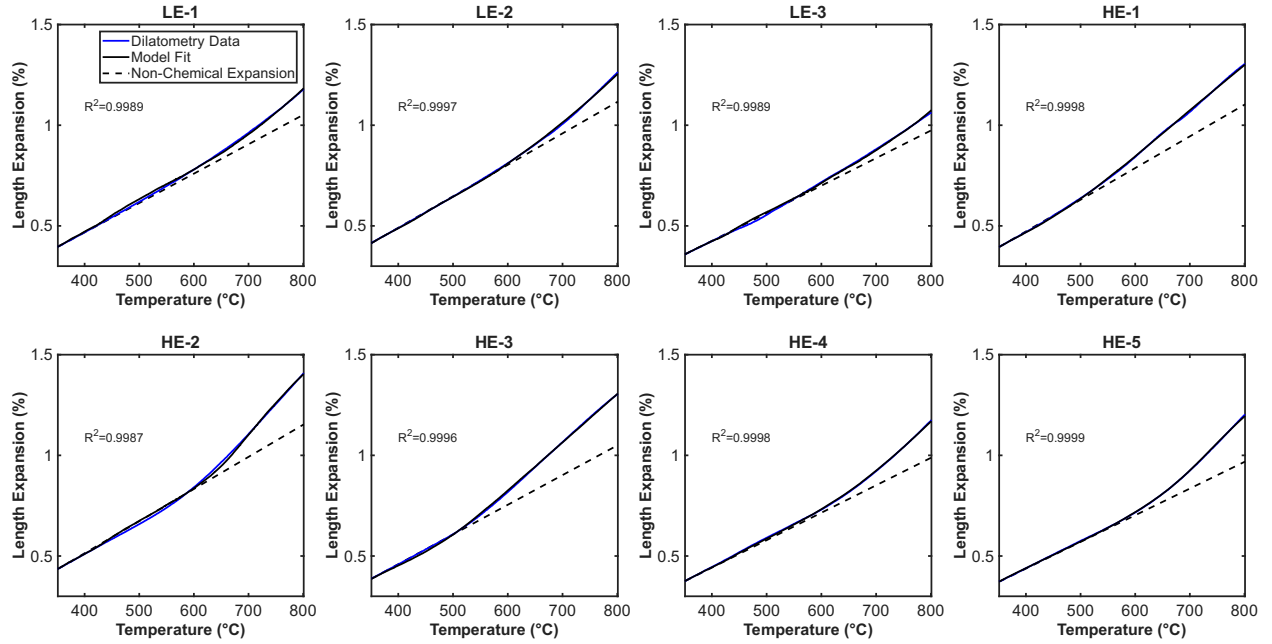


Fig. S 3: Two-parameter model fitting (black) to dilatometer expansion curves (blue) with the non-chemical expansion projected as a dashed line.

due to the expansion inflection point ($T=560^\circ\text{C}$) being earlier than the vacancy formation inflection point ($T=620^\circ\text{C}$, Figure S2a)

Notably, this model assumes α_{th} and β are invariant to temperature and oxygen vacancy concentration δ and independent of each other. In fact, α_{th} is expected to increase slightly with temperature, but in a small temperature range α_{th} can be averaged as a constant. Previous studies on chemical expansion found β to be largely invariant to temperature between $700\text{--}900^\circ\text{C}$ and constant for a small δ [8, 12, 13, 6]. Despite these assumptions, fitting in Figure S3 suggests the model effectively fits the data.

Based on model-fit parameters α_{th} and β , the contributions of chemical versus thermal expansion over $100\text{--}800^\circ\text{C}$ are illustrated in Figure S2b. Error bars in Figure S2b-d indicate model fit uncertainty is small, however, the oxygen vacancy formation curves ($\Delta\delta(T)$) may be another source of uncertainty, especially for β when $\Delta\delta$ is small. Figure S2c reports model-fit β , in agreement with isothermal dilatometry (Figure 4a) that β is smaller in HE samples than LE-1. However, LE-3 is unusually large, which can be attributed to uncertainty in small $\Delta\delta$ values and the irregular bump at 500°C in the expansion curve. In addition, model-fit values of β are around 50% higher than that measured with isothermal dilatometry at 800°C . This could be due to second order thermal expansion effects (slight increasing of α_{th} with temperature) attributed to chemical expansion. Overall, isothermal dilatometry is a more accurate method for measuring β than model-fitting. Values for α_{th} shown in Figure S2d should be more accurate than model-fit β as they are more resilient to uncertainty in $\Delta\delta(T)$.

4 Geometric Model of Octahedral Libration and Thermal Expansion

We interpret the dependence of α_{th} on the tolerance factor t through octahedral tilting dynamics (Figure 3d in main text). Tolerance factor t reflects the size mismatch between the A-site cations and the corner-sharing BO_6 octahedra. Lower t is known to cause more tilting of the relatively rigid BO_6 octahedra [14], and consequently, differences in phase [15, 3, 14]. The tilting effect on reducing the projected B–B separation at high temperature can be explained using a simplified geometric argument. Figure 3e in the main text shows that a , the distance between B-sites, can be calculated using the B–O bond lengths ℓ and tilt angle θ by Eq. 8.

$$a = 2\ell \cos \theta \quad (8)$$

At finite temperatures, octahedra oscillate about their equilibrium as a form of thermal vibration, called a libration [16, 17, 18, 14]. Since the oxygen atom oscillates perpendicular to the B-site cations, octahedral librations are transverse low-frequency phonon modes (0-2 THz), where B–O bond-stretching vibrations are longitudinal phonon modes (10-30 THz) [14]. As octahedra oscillate, the B–O–B linkage bends around its equilibrium tilt angle θ_{eq} . We assume that the corresponding potential is harmonic with an effective spring constant K . A lower tolerance factor t has been found to make octahedral libration phonon modes more compliant (lower K), in turn, lowering their frequency and increasing their amplitude [18]. The change of the potential energy ΔU_{tilt} due to the additional tilting is expressed by Eq. 9.

$$\Delta U_{\text{tilt}} \approx \frac{1}{2}K(\theta - \theta_{\text{eq}})^2 = \frac{1}{2}K \left(\cos^{-1}\left(\frac{a}{2\ell}\right) - \theta_{\text{eq}} \right)^2 \quad (9)$$

This potential correction function, plotted in Figure 3e of the main text, is anharmonic with respect to a . If bond lengths were held constant, increasing temperature decreases the average a . A lower K broadens the potential well (purple curve in Figure 3e of main text) making the contraction of a more pronounced. This tilting correction term reduces the normal thermal vibrations described by the Lennard-Jones potential[14].

In the extreme cases, this cancellation can lead to negative thermal expansion (NTE) [16]. A key finding from the study of NTE materials is that increasing the magnitude of octahedral librations, and their associated low-frequency phonon modes, can result in lattice contraction [14, 19, 16, 20], an effect referred to as the "tension" or "guitar string" effect [19]. This mechanism, and its connection to t , has been studied for the designing of NTE materials [20, 16], but to the best knowledge of the authors, has not been discussed in the context of mitigating positive thermal expansion in MIECs.

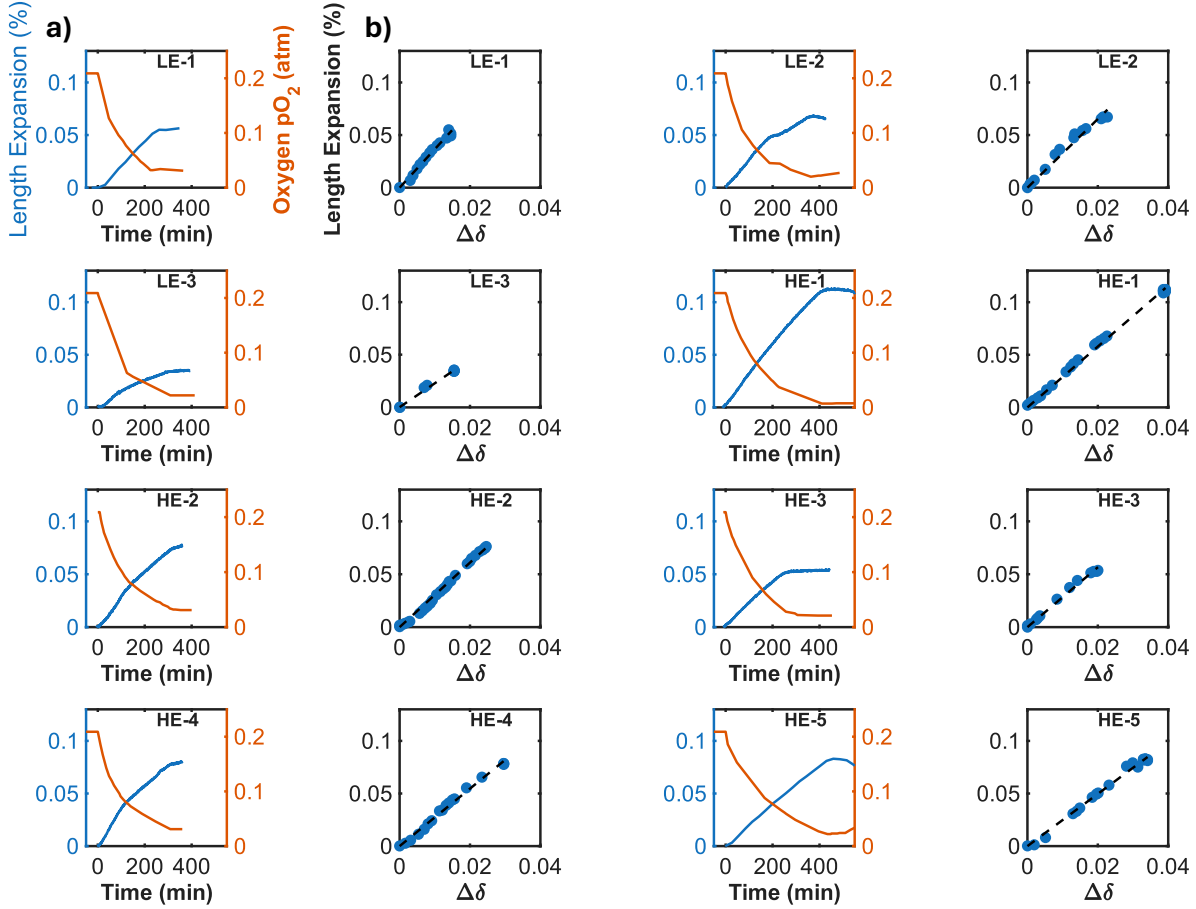


Fig. S 4: Two plots for each material: a) Chemical length expansion at 800°C from dilatometry (blue) and partial pressure of oxygen pO_2 as a function of experiment time (orange). b) Scatter plot of chemical length expansion versus change in oxygen vacancy for each pO_2 reading, with a proportional line fit (dashed) determining the slope β .

5 Chemical Expansion from Isothermal Dilatometry

Chemical expansion was measured isothermally with a TA DIL801L dilatometer on dense sintered rods (5mm diameter, 10-12mm length). The dilatometer was enclosed in a sealed acrylic chamber with cross-chamber gas flow and a fan for gas mixing. The sample is initially held at 800°C in air for at least 8 hours to achieve full equilibrium after which Argon is flowed into the chamber to lower pO_2 to 0.04-0.02 atm over the duration of 6-8 hours. The long experiment duration ensures effective gas mixing and chemical expansion is in pseudo-equilibrium. The pO_2 of the chamber is measured with a TOPTES Guard-722 O_2 Detector. While previous studies of chemical expansion probe a lower pO_2 region ($< 10^{-3}$ atm) [10, 21, 22], this reducing environment is not representative of that experience by air electrodes in solid oxide cells. At very low pO_2 , defects enter a new region of the Brouwer diagram, for example, due to polaron depletion, which results in different defect physics unrepresentative of behavior in oxidizing environments [8]. For this reason, a range of $pO_2=0.21-0.05$ atm was determined to be sufficient. Figures S4a for each material show increasing length expansion as the pO_2 decreases. Notably, the length expansion curve matches the inverse of the pO_2 curve, including during inflection points and plateaus near the end of the experiment. This suggests that chemical expansion was at near-equilibrium (or pseudo-equilibrium) conditions over the long (6-8 hour) experiment. This means that points collected during the pO_2 ramping are valid for estimating the β in equilibrium. Matching of the inflection points of dilatometry and pO_2 curves suggests chemical expansion lagged behind

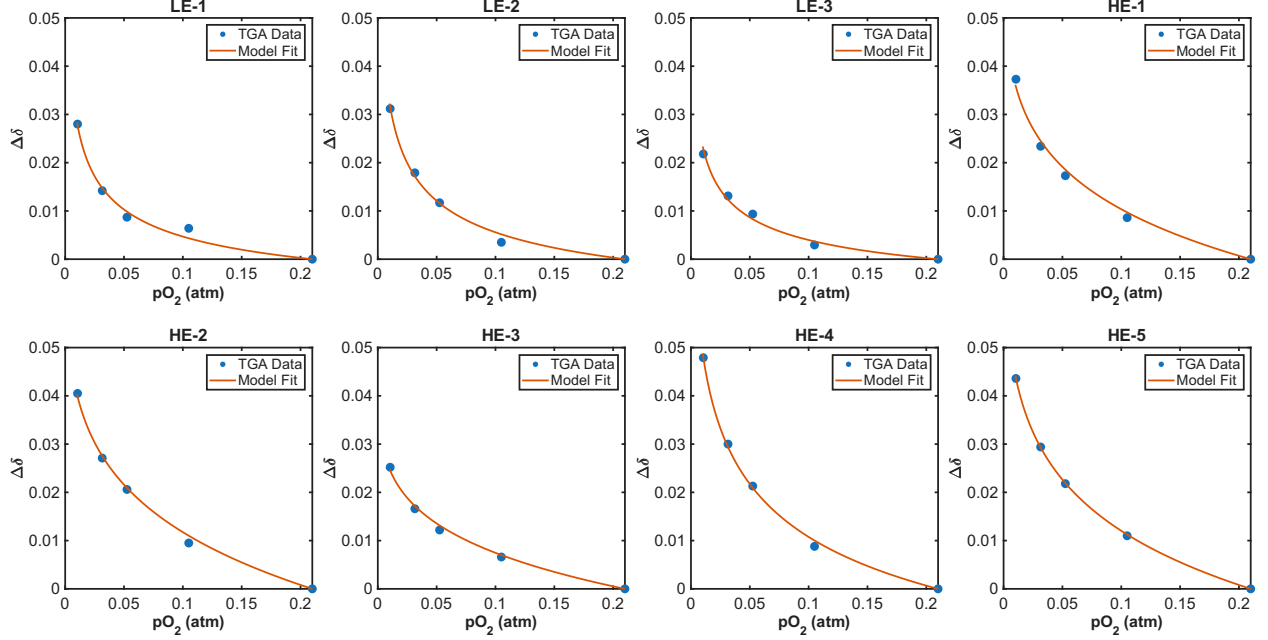


Fig. S 5: Change in oxygen vacancy $\Delta\delta$ relative to $pO_2=0.21$ atm from TGA with decreasing oxygen partial pressure (pO_2). Orange curves are the defect model fit using Eq. 11.

pO_2 in the chamber by about 20 minutes, which is adjusted accordingly when calculating β . This can be attributed to slow diffusion of gas from the chamber into the dilatometer, but it does not change the fact that chemical expansion of the samples is in pseudo-equilibrium with its environment.

In order to calculate β , changes in pO_2 must be mapped to change in oxygen vacancy ($\Delta\delta$) in each material. This is accomplished by measuring $\Delta\delta$ with TGA at $800^\circ C$ for $pO_2=0.21, 0.105, 0.05, 0.03$, and 0.01 atm by mixing dry air and argon (summing to a flow rate of 100 SCCM). Results for $\Delta\delta$ relative to $pO_2=0.21$ atm are shown in Figure S5. Samples consisted of 150-200mg of the sintered rod used for isothermal dilatometry. A blank crucible TGA run is subtracted and effects of changing gas density on sample buoyancy are considered. To validate and improve the physicality of δ - pO_2 curves, TGA data is fit to a defect model from previous work [23] for the oxygen vacancy formation reaction in Eq. 10. Eq. 11 describes equilibrium constant $K_{p,ox}$ for Eq. 10 in Kroger-Vink notation where $h^\cdot$ represents electron holes, O_O^x lattice oxygen, and $V_O^\cdot$ oxygen vacancies. The final expression is also a function of X_{2+} (Eq. 5 in main text) due to charge compensation of coupled defects. $K_{p,ox}$ is a constant for isothermal data.



$$K_{p,ox} = \frac{[V_O^\cdot] \left[\frac{pO_2}{pO_2^0} \right]^{1/2}}{[O_O^x][h^\cdot]^2} = \frac{\delta \sqrt{pO_2}}{(3-\delta)([X_{2+}] - 2\delta)^2} \quad (11)$$

To fit Eq. 11 to experimental data, an optimal $K_{p,ox}$ is determined by calculating δ for each pO_2 , and comparing $\Delta\delta$ to experiments. Orange curves in Figure S5 show effective model fits using just one parameter ($K_{p,ox}$) for five TGA data. Fit values of $K_{p,ox}$ ranged from $e^{-4.3}$ to $e^{0.95}$, consistent with those previously reported [23]. This proves the pO_2 -dependence of δ measured by TGA is physically valid. Model-fit curves are used to smoothly map pO_2 from isothermal dilatometry to $\Delta\delta$.

Using this pO_2 - δ mapping, β can be estimated by comparing length expansion to $\Delta\delta$, shown in Figures S4b for each material. The scatter plot reveals a linear relation, consistent with previous studies [11, 10, 24]. The linear fit slope is β with uncertainty determined by model fit uncertainty. Repeated experiments for LE-1 (same sample) revealed repeatable values for β : 35.1 vs. $35.5 \times 10^{-3} \delta^{-1}$.

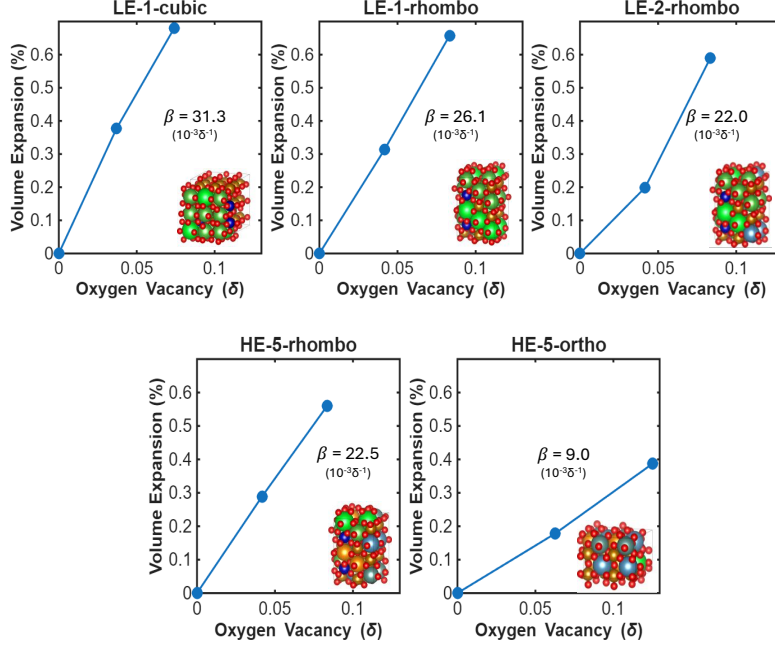


Fig. S 6: Volume expansion as a function of increasing oxygen vacancy δ for each structure, with the DFT supercell in the corner of each plot.

6 Structural Response to Vacancy Formation in DFT Simulations

The calculations used spin-polarized density functional theory as implemented in VASP [25], with the projector augmented-wave method [26] and the Perdew–Burke–Ernzerhof exchange–correlation functional [27]. On-site corrections to the Fe and Co d states were included using the Dudarev DFT+ U formulation [28]. Cation disorder was represented using special quasirandom structures [29]. Bader analysis was used to obtain atom-resolved electron populations and basin volumes from the calculated charge density [30]. Further computational settings are provided in the main-text Methods. Supercells used for DFT simulations are shown in Figure S6, where small red atoms are oxygen, blue are cobalt, dark orange are iron, dark green are lanthanum, light green are strontium, light blue are calcium, dark blue are neodymium, and light orange are yttrium. Figure S6 also shows volume expansion following each oxygen removal and the corresponding oxygen nonstoichiometry δ . The average length chemical expansion coefficient β is labeled, assuming the pseudo-cubic approximation (length expansion equals one third of volume expansion).

After introducing each oxygen vacancy and performing structural relaxation, changes in structure and magnetic moments are reported in Figure S7. Figure S7a shows that while most bonds between B-site cations (Fe and Co) and oxygen increase in length, some shorten due to distortion. The distribution of changing B-O lengths is illustrated with a swarm plot overlaid by a box plot for both the 0→1 vacancy and 1→2 vacancy transition. For all structures, the average is positive suggesting expansion, however, B-O bonds expand more in the low-entropy (LE) structures. Changes in B-O-B tilt angles ($\Delta\theta$) are reported in Figure S7b, where a positive values indicates more bending. HE structures show a narrower distribution of $\Delta\theta$ consistent with less vacancy-induced distortion. The average value of $\Delta\theta$ is positive for LE structures, suggesting a small average increase in tilting, while it is near zero for HE structures. Figure S7c shows the change in magnetic moment for B-site cations, where a few cations experience large changes but most are unaffected. These cation sites that experience a change in magnetic moment greater than a cutoff of $0.5 \mu_B$ are identified as charge hosts, as described in the main text. The data is separated by Co and Fe site making it clear that despite being only $\sim 20\%$ of the cations, results suggest the vacancy charge is compensated exclusively by Co. In the main text, the initial Bader volumes of Co sites are compared to that of the the average B-site (mostly Fe). Figure S7d provides a more detailed illustration of the distribution of Bader volumes for B-sites in no-vacancy structures. While the average Bader volume varies by $0.3\text{\AA}^3$ between structures, we hypothesize

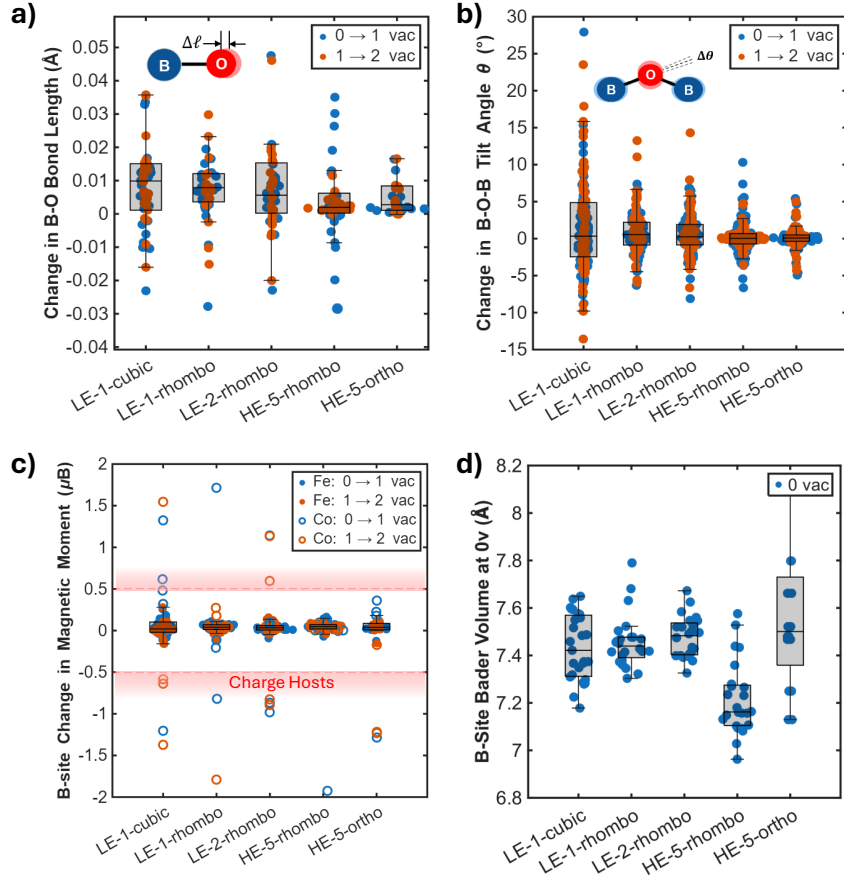


Fig. S 7: Overlaid box plots and swarm plots for each structure for: a) Changes in B-O bond length for $0 \rightarrow 1$ vacancy and $1 \rightarrow 2$ vacancy transitions. b) Changes in B-O-B bond angle for each transition. c) Changes in the magnetic moment of B-site cations for each transition with red lined indicating the cutoff used to identify charge hosts. d) Bader volumes for B-site cations in the initial no-vacancy structure.

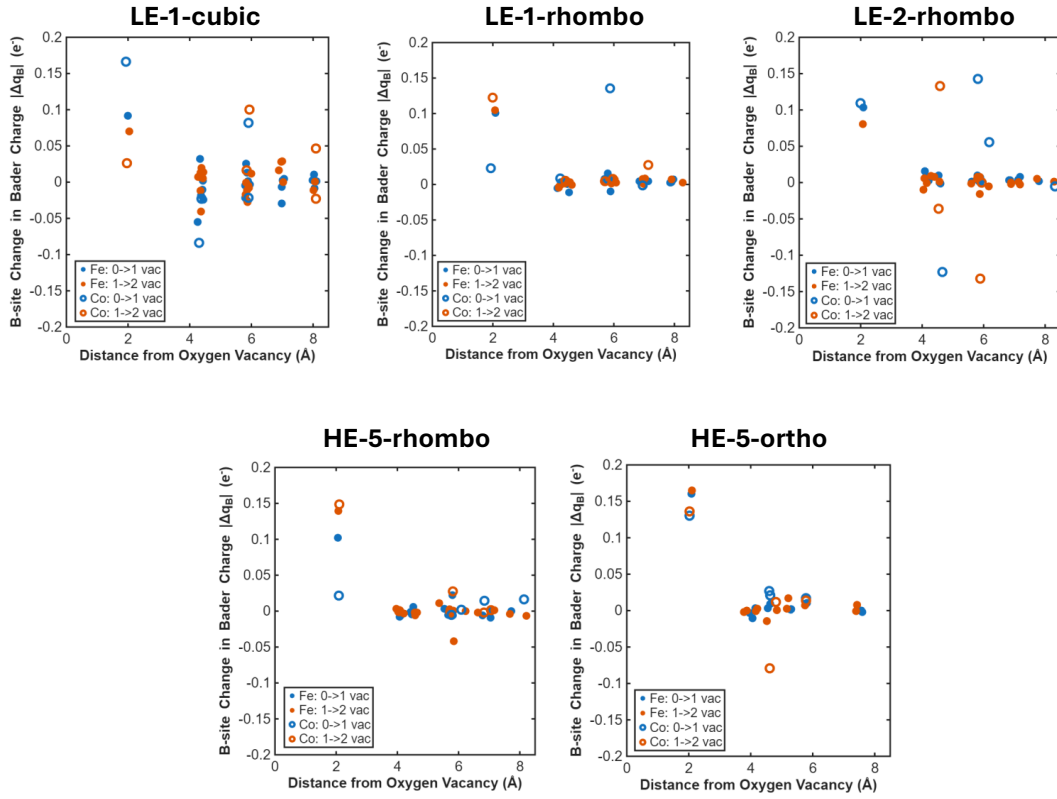


Fig. S 8: Change Bader charge on B-site cations after introduction of first (0→1 vac) and second (1→2 vac) oxygen vacancy plotted against distance from the vacancy.

that variance among sites is more important than the average for determining chemical expansion behavior.

Figure 5d in the main text shows that vacancy-induced lattice strain propagates throughout LE structures but is contained locally in HE structures. In the HE structures, not only is the structural response localized, but also electronic response. Figure S8 shows the changes in Bader charge on B-site cations after each vacancy addition plotted against the distance to the vacancy. As expected, the greatest change in Bader charge typically occurs on the two B-site cations adjacent to the vacancy ($2.1\text{\AA}$ from vacancy). However, the vacancy can also induce long-range electronic responses ($\Delta q_B > 0.05e^-$ further than $3\text{\AA}$ from the defect). Overall, the HE structures exhibit less long-range changes in Bader charge than the LE structures, suggesting their strain containment properties are accompanied by a localized electronic response.

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