Supporting Information for "Entropic stabilization plays a key role in the non-uniform distribution of oxygen ions and vacancy defects in gadolinium-doped ceria"

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S1. Statistical mechanics basis for $\pi_{O-V}(\epsilon)$ and associated free energy

The periodic YSZ and GDC system is composed of M anion sites. N O^{2-} ions and $M-N$ vacancy defects are distributed among the M sites. All ion configurations that satisfy this constraint are of interest to us. We write the canonical partition function for the system as

$$Q(T,V,N,M)=\sum_{s\in\sigma}\exp\left(-\beta U_s\right) \tag{S1}$$

where $\beta=(k_BT)^{-1}$, k_B is the Boltzmann constant, T is absolute temperature, U_s is the system energy associated with the particular (all ion) configuration or state s, and σ is the set of states that satisfy the above constraint.

Let us now focus on a pair of sites with environment ϵ. The pair can be occupied by O-O, O-V, V-O and V-V (four cases). The set of states associated with each case is denoted as σ_{O-O}, σ_{O-V}, σ_{V-O} and σ_{V-V}, such that

$$\sigma_{O-O}\cup\sigma_{O-V}\cup\sigma_{V-O}\cup\sigma_{V-V}=\sigma. \tag{S2}$$

Accordingly, the partition function can be written as

$$Q(T,V,N,M)=\sum_{s\in\sigma_{O-O}}\exp\left(-\beta U_s\right)+\sum_{s\in\sigma_{O-V}}\exp\left(-\beta U_s\right)+\sum_{s\in\sigma_{V-O}}\exp\left(-\beta U_s\right)+ \tag{S3}$$

The probability of being in σ_{O-V} is given by

$$\pi_{O-V}(\epsilon) = \frac{\sum_{s \in \sigma_{O-V}} \exp(-\beta U_s)}{Q}. \tag{S4}$$

Let us write the numerator in Equation (S4) in terms of the energy levels possible with $s \in \sigma_{O-V}$

$$\pi_{O-V}(\epsilon) = \frac{1}{Q}\left(\sum_E \omega(E)\exp(-\beta E)\right)_{s \in \sigma_{O-V}}. \tag{S5}$$

Here E is the energy level and $\omega(E)$ is the degeneracy. The subscript $s \in \sigma_{O-V}$ on the right hand side of Equation (S5) reminds us that only states in set σ_{O-V} are considered. We should also remember that the analysis is being done with environment ϵ. We define the partition function for O^{2-}-vac pair as

$$q_{O-V} = \left(\sum_E \omega(E)\exp(-\beta E)\right)_{s \in \sigma_{O-V}}. \tag{S6}$$

The free energy for the O^{2-}-vac pair in environment ϵ is defined as

$$F_{O-V}(T,V,N,M;\epsilon) = -k_B T \ln q_{O-V} \tag{S7}$$

The free energy can be written as a sum of energy and entropy terms as $F_{O-V} = E_{O-V} - TS_{O-V}$. $E_{O-V}(\epsilon)$ is the average energy and $S_{O-V}(\epsilon)$ is the entropy for the O^{2-}-vac pair in environment ϵ. E_{O-V} and S_{O-V} can be calculated in the standard manner [1] using the F_{O-V} dependence on T, i.e., $E_{O-V}(\epsilon) = -T^2\left(\frac{\partial F_{O-V}(\epsilon)/T}{\partial T}\right)_{V,N,M}$ and $S_{O-V}(\epsilon) = -\left(\frac{\partial F_{O-V}(\epsilon)}{\partial T}\right)_{V,N,M}$. Note that only relative values of F_{O-V}, E_{O-V} and S_{O-V} can be evaluated, and not their absolute values. Similar equations can be written for σ_{O-O}, σ_{V-O} and σ_{V-V}. Accordingly, the probability of observing ξ, $\xi = \sigma_{O-O}$, σ_{O-V}, σ_{V-O} or σ_{V-V}, is

$$\pi_\xi(T,V,N,M;\epsilon) = \frac{\exp(-\beta F_\xi(T,V,N,M;\epsilon))}{Q}. \tag{S8}$$

The free energy F_ξ contains contributions arising from energetic interactions, vibrational entropy and configurational entropy. The vibrational terms arise from the motion of ions around their lattice positions, whereas the configurational terms arise from the arrangement of ions outside of ϵ. For conciseness, we write $\pi_\xi(\epsilon)$ although the T,V,N,M dependence remains.

Consider O-V and O-O in environment ϵ. From Equation (S8)

$$\frac{\pi_{O-V}(\epsilon)}{\pi_{O-O}(\epsilon)} = \exp\left(-\beta \Delta F_{O-V}(\epsilon)\right). \tag{S9}$$

Here, $\Delta F_{O-V}(\epsilon) = F_{O-V}(\epsilon) - F_{O-O}(\epsilon)$. We write $\Delta F_{O-V} = \Delta E_{O-V} - T\Delta S_{O-V}$.

We can now study the effect of temperature. Suppose ΔE_{O-V} is large compared to k_BT in Equation (S9), $\pi_{O-V}(\epsilon)$ and $\pi_{O-O}(\epsilon)$ would be functions of temperature. In YSZ, $\pi_{O-V}(\epsilon)$ and $\pi_{O-O}(\epsilon)$ are found to depend on temperature (see Figure S1 later), and both energetic and entropic contributions to ΔF_{O-V} are significant. However, from our MD simulations of GDC, for all environments π_{O-V} and π_{O-O} are found to be practically independent of temperature. This suggests that in GDC $\Delta E_{O-V}(\epsilon)$ must be small compared to k_BT.

The free energy term ΔF_{O-V} can be understood in a more intuitive manner, namely, in terms of O^{2-} ion movement in the YSZ/GDC structure. During the MD simulation, oxygen ions are exchanged between environments. Consider two environments ϵ and ϵ'. From Equation (S9)

$$\frac{\pi_{O-V}(\epsilon)}{\pi_{O-V}(\epsilon')} = \frac{\pi_{O-O}(\epsilon)\exp\left(-\beta\Delta F_{O-V}(\epsilon)\right)}{\pi_{O-O}(\epsilon')\exp\left(-\beta\Delta F_{O-V}(\epsilon')\right)}. \tag{S10}$$

Suppose we are performing a Metropolis Monte Carlo experiment [2] wherein an O^{2-} ion is transferred from an O-O pair in environment ϵ to an O-vac pair in ϵ' (the two environments considered can be anywhere in the structure), as well as the backward move. We write this type of a move as

$$O-O[\epsilon] + O-V[\epsilon'] \rightleftharpoons O-O[\epsilon'] + O-V[\epsilon]. \tag{S11}$$

Next, we write detailed balance equation for the move. The probability of finding $O-O[\epsilon]$ in the structure is $\theta(\epsilon)\pi_{O-O}(\epsilon)$. Here $\theta(\epsilon)$ is the probability of finding a pair of sites with environment ϵ in the YSZ/GDC structure (see Figure 4c for $\theta(\epsilon)$ in GDC). At equilibrium, the detailed balance equation is given by

$$\theta(\epsilon)\pi_{O-O}(\epsilon)\theta(\epsilon^{'})\pi_{O-V}(\epsilon^{'})\langle\min(\exp(-\beta\Delta U),1)\rangle_f = \theta(\epsilon)\pi_{O-V}(\epsilon)\theta(\epsilon^{'})\pi_{O-O}(\epsilon^{'})\langle \mathrm{mi} \quad \text{(S12)}$$

Here $\langle\min(\exp(-\beta\Delta U),1)\rangle_f$ is the Metropolis acceptance probability averaged over all ionic arrangements (beyond C1-C6 positions around the two pairs of sites with environments ϵ and $\epsilon^{'}$). The subscript f indicates that the averaging is done for the move in the forward direction. Subscript b is used for the backward move. ΔU is the change in system energy during the move. Rearranging the equation yields

$$\frac{\pi_{O-V}(\epsilon)}{\pi_{O-V}(\epsilon^{'})} = \frac{\pi_{O-O}(\epsilon)\langle\min(\exp(-\beta\Delta U),1)\rangle_f}{\pi_{O-O}(\epsilon^{'})\langle\min(\exp(-\beta\Delta U),1)\rangle_b}. \quad \text{(S13)}$$

Compare Equations (S10) and (S13). The above equation provides a recipe for the calculation of the free energy difference using the interaction energies. The configurational entropy arises from effect of the ionic arrangement beyond the first cation neighbors (C1-C6 positions) on $\langle\min(\exp(-\beta\Delta U),1)\rangle_m$, $m = f,b$. Specifically,

$$\delta F_{O-V}(\epsilon) = \frac{\langle\min(\exp(-\beta\Delta U),1)\rangle_f}{\langle\min(\exp(-\beta\Delta U),1)\rangle_b}. \quad \text{(S14)}$$

The quantity $\delta F_{O-V}(\epsilon) = \Delta F_{O-V}(\epsilon) - \Delta F_{O-V}(\epsilon^{'})$ in Equation (S14) is the excess free energy associated with the O-V pair (calculated with respect to environment $\epsilon^{'}$; we take $\epsilon^{'}$ to be host environment like CCCCCC or ZZZZZZ).

Note that a variation of Equation (S13) is used in studies on segregation [3]. In this context, Equation (S13) is called the Langmuir-McLean model [3,4]. Using the excess free energy, one can calculate the distribution of A and B species between interfaces and bulk in an $A-B$ alloy [3].

Suppose we want to separate the vibrational and configurational contributions analogous to cluster expansion framework [5]. q_{O-V} can be written as

$$q_{O-V} = q_{O-V}^{vib} q_{O-V}^{config}. \tag{S15}$$

Here q_{O-V}^{config} accounts for ion arrangement at different lattice sites, while q_{O-V}^{vib} accounts for the vibrations of each ion around its equilibrium position. The vibrational and configurational free energy follow from q_{O-V}^{vib} and q_{O-V}^{config}, such that

$$F_{O-V}(T,V,N,M;\epsilon) = F_{O-V}^{vib}(T,V,N,M;\epsilon) + F_{O-V}^{config}(T,V,N,M;\epsilon). \tag{S16}$$

A procedure to calculate the frequency distribution $g(\nu)$ from MD data is given in Ref. [6]. F_{O-V}^{vib} can be calculated as [1]

$$F_{O-V}^{vib}(\epsilon) = \int_0^\infty \left[k_B T \ln\left(1 - \exp\left(\frac{h\nu}{k_B T}\right)\right) + \frac{h\nu}{2}\right] g_{O-V}(\nu,\epsilon) d\nu. \tag{S17}$$

Here $g_{O-V}(\nu,\epsilon)$ is the frequency distribution when the pair of sites is occupied with oxygen anion and vacancy defect in environment ϵ.

The vibrational contribution involving $\Delta F_{O-V}(\epsilon)$ in Equation (S9) becomes

$$\Delta F_{O-V}^{vib}(\epsilon) = \int_0^\infty \left[k_B T \ln\left(1 - \exp\left(\frac{h\nu}{k_B T}\right)\right) + \frac{h\nu}{2}\right] \left(g_{O-V}(\nu,\epsilon) - g_{O-O}(\nu,\epsilon)\right) d\nu. \tag{S18}$$

For large system size, $g_{O-V}(\nu,\epsilon) \approx g_{O-O}(\nu,\epsilon)$. According to Equation (S10) one needs to calculate $\delta F_{O-V}(\epsilon)$. The vibration term involved is

$$\delta F_{O-V}^{vib}(\epsilon) = \Delta F_{O-V}^{vib}(\epsilon) - \Delta F_{O-V}^{vib}(\epsilon'). \tag{S19}$$

The vibrational terms cancel each other, i.e., $\delta F_{O-V}^{vib}(\epsilon) \approx 0$. Thus, the configurational terms determine the excess entropy for the O^{2-}-vac pair in environment ϵ (see discussion around Equations (S12)-(S14)).

S2. Additional figures

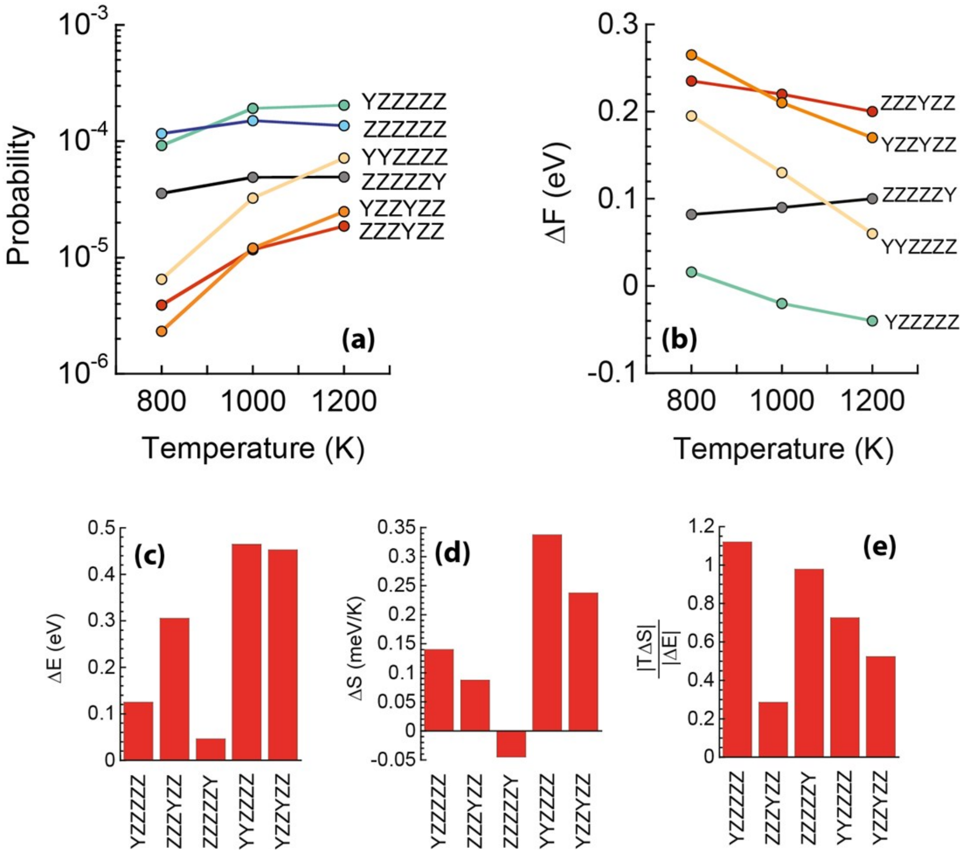

Figure S1. (a) Probability of observing a pair of oxygen ion and vacancy defect in a local environment in YSZ. Corresponding (b) free energy (see discussion below), (c) energy, and (d) entropy differences with respect to Zr-only environment. (e) Ratio of $|T\Delta S|/|\Delta E|$.

From Ref. [7], we find that for YSZ $\pi_{O-O} \approx 1$ and π_{O-V} can have values between 10^{-9} to 10^{-2} depending on the cation environment. Therefore, we assume $\frac{\pi_{O-O}(T,V,x,\epsilon)}{\pi_{O-O}(T,V,x,\epsilon^{'})} \approx 1$ for the analysis used with YSZ. We write Equation (S2) as

$$\pi_{O-V}(\epsilon) = \exp\left(-\beta\Delta F_{O-V}(\epsilon)\right). \tag{S20}$$

and

$$\frac{\pi_{O-V}(\epsilon)}{\pi_{O-V}(\epsilon^{'})} = \frac{\exp\left(-\beta\Delta F_{O-V}(\epsilon)\right)}{\exp\left(-\beta\Delta F_{O-V}(\epsilon^{'})\right)}. \tag{S21}$$

Equation (S21) is used to calculate $\delta F_{O-V} = \Delta F_{O-V}(\epsilon) - \Delta F_{O-V}(ZZZZZZ)$ in Figure S1b.

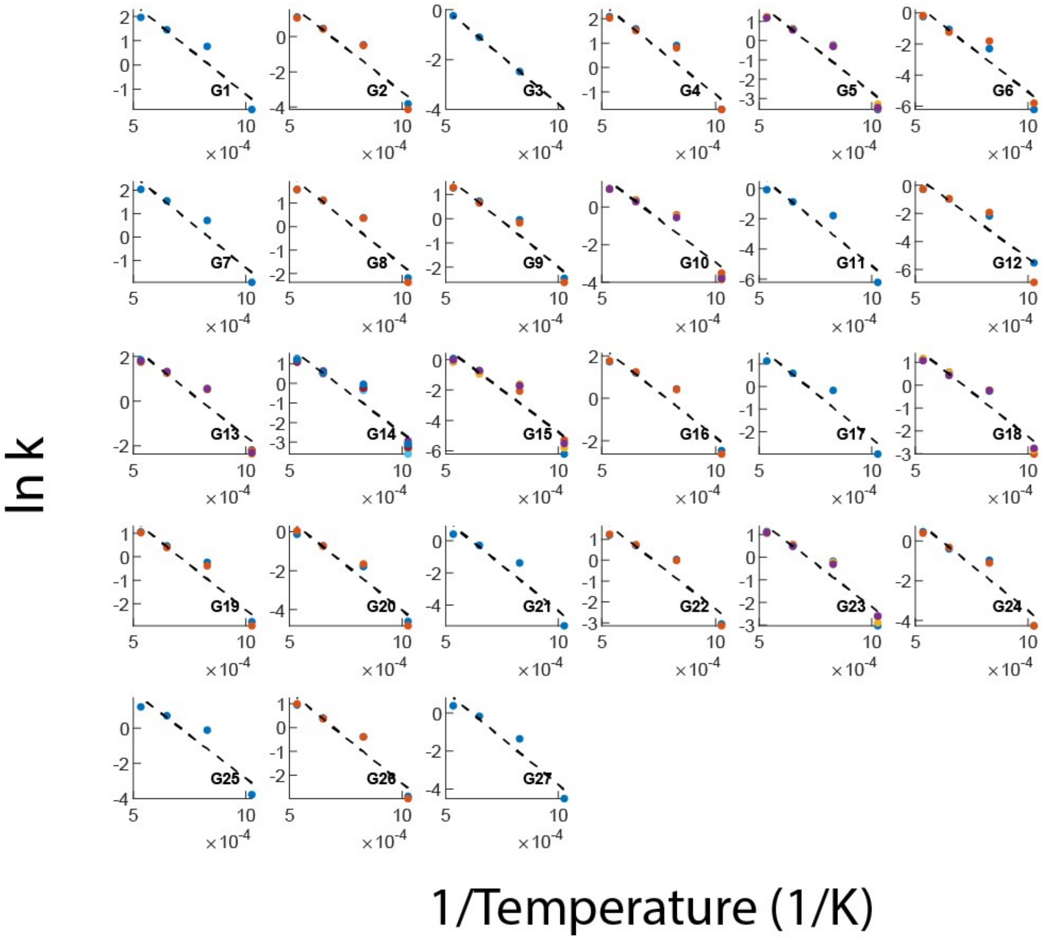

Figure S2. Arrhenius rate law fitted to rate constants from MD. Here, rate constant has units of ns^{-1}.

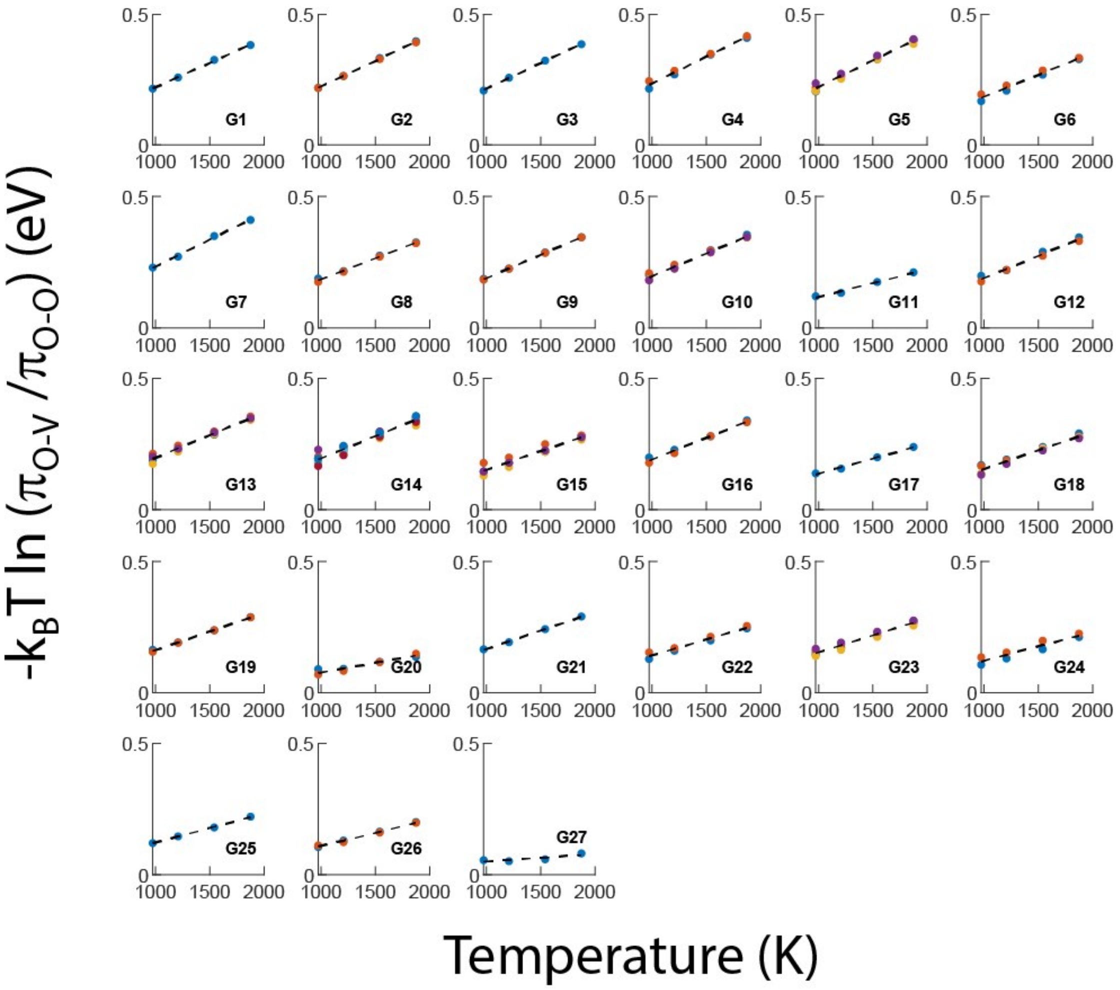

Figure S3. Thermodynamic model (Equation (S9) and Equation (6) from main manuscript) fitted to free energy of a pair of oxygen ion and vacancy defect.

References

1 T. L. Hill, *An introduction to statistical thermodynamics*, Dover, New York, 1986.

2 D. Frenkel and B. Smit, *Understanding molecular simulation: From algorithms to applications*, Academic Press, New York, 1996.

3 P. Lejcek, *Grain Boundary Segregation in Metals*, Springer-Verlag, Berlin, Heidelberg, New York, 2010.

4 S. Divi and A. Chatterjee, Generalized nano-thermodynamic model for capturing size-dependent surface segregation in multi-metal alloy nanoparticles, *RSC Adv.*, 2018, **8**,

10409.

5 A. van de Walle and G. Ceder, The effect of lattice vibrations on substitutional alloy thermodynamics, *Rev. Mod. Phys.*, 2002, **74**, 11–45.

6 D. J. Cooke, S. C. Parker and D. J. Osguthorpe, Calculating the vibrational thermodynamic properties of bulk oxides using lattice dynamics and molecular dynamics, *Phys. Rev. B*, 2003, **67**, 134306.

7 M. Jaipal and A. Chatterjee, Relative Occurrence of Oxygen-Vacancy Pairs in Yttrium-Containing Environments of Y2O3-Doped ZrO2Can Be Crucial to Ionic Conductivity, *J. Phys. Chem. C*, 2017, **121**, 14534–14543.