## Supporting Information:

# Anisotropic Vacancy-Mediated Phonon Mode Softening in Sm and Gd Doped Ceria

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## S1. STRUCTURAL OPTIMIZATION

In this study, we derive the ground-state energy/volume for the considered materials system by fitting the calculated DFT total energies, E (as a function of its volume, V) to the third order Birch Murnaghan equation of state (as shown in Figure S1):

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[ \left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1 \right]^2 \left[ 6 - 4 \left(\frac{V_0}{V}\right)^{\frac{2}{3}} \right]^3 \right\} \quad . \tag{1}$$

Here, the coefficients,  $B_0$  and  $B'_0$ , are the bulk modulus and its derivative, respectively. Details of the calculated values are tabulated in Table S1.

Table S1. Calculated lattice constant  $(a_0)$ , bulk modulus  $(B_0)$ , and formation energy  $(E_{\text{form}})$  for the pristine CeO<sub>2</sub>, vacany only model CeO<sub>2-x</sub>, Sm-doped Ceria (SDC), and Gd-doped Ceria (GDC).

	$CeO_2$	$CeO_{2-x}$	SDC	GDC
$ \begin{array}{c}     a_0 (\text{\AA}) \\     B_0 (\text{GPa}) \\     E_{\text{form}} (\text{eV/atom}) \end{array} $	5.494	5.511	5.508	5.498
	182	168	169	170
	-6.69	-6.69	-6.71	-6.72

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Figure S1. The energy-volume curves of (a)  $\text{CeO}_x$  (x = 2 or 1.97) (b) SDC, and (c) GDC. The markers represent the DFT total energies and the solid lines are fitted to the 3<sup>rd</sup> order Birch-Murnaghan equation-of-state.

For the molecular dynamics, we optimize the structure by using a total energy minimization and quenching process by using a parameters tabulated in Table S2. Here, all structures are exposed to total energy minimization and the quenching process. Firstly, each initial configuration has been optimized by the conjugate gradient energy minimization, which allows the position of ions to move to a lower energy configuration. After the energy minimization process, a quenching process is set

Table S2. Short range potential parameters for O–O, Ce–O, Gd–O, and Sm–O used in the Buckingham-type interatomic potential with a long-range Coulombic term.

Ion Pair	$A_{ij}$ (eV)	$\rho_{ij}$ (Å)	$C_{ij}~(\mathrm{eV}\mathrm{\AA}^6)$
O–O Ce–O	22746.3 1986.8	$0.149 \\ 0.3511$	$\begin{array}{c} 45.83\\ 20.40\end{array}$
Gd–O Sm–O	$1885.75 \\ 1944.44$	$0.3399 \\ 0.3414$	$20.34 \\ 21.49$

to accelerate the equilibration process for each system under a temperature gradient, which also allows the positions of vacancies and ions to equilibrate, and to avoid the formation of artificial defects. The quenching process is performed as follows: The system is firstly heated to 2,000 K with a constant pressure and temperature ensemble (NPT) to ensure thermal equilibrium at the desired temperature is reached. After that, the constant volume and energy ensemble (NVE) is enforced and the NVE MD simulation runs for 500 ps to reach equilibrium. Subsequently, the system is then rapidly cooled down (hence, quenched) from 2,000 to 300 K with now the NPT ensemble for 50 ps, and then further relaxed for another 200 ps with the NVE ensemble. Finally, the system is equilibrated with NPT and NVE ensembles at 300 K temperature. With this quenching process, the quenched atomic structures for a given target temperature are then used for further analysis.

During MD calculation, we investigate the influence of ordering in given structures used in DFT by building a set of structures including randomly distributed ions and defects (so called inhomogeneous structures) as represented in Figure S2(b)-(i).

Here, the distribution of dopants are investigated and depicted in Figure S3.



Figure S2. The atomic structures of  $Ce_{0.875}M_{0.125}O_{1.9375}$  used in the molecular dynamics (MD) calculations. Here, we expand the ordered structures used in DFT and construct the ordered structure at (a). From (b) to (i), we randomly exchange the white Ce atoms into blue dopants atoms (Sm or Gd) and the red oxygen atoms are replaced by vacancy (represented as black atoms) to model the series of randomly distributed doped ceria structures. The composition for each structures from (b) to (i) is identical.



Figure S3. The illustration of doped ion distribution of considered models. Here, red and blue bars indicate the distribution of homogeneous (ordered) and inhomogeneous doped ions along the [001] with 1 Å interval of distance, respectively, and red and blue spheres represent the ordered and randomly doped ions, respectively. The illustration of doped ion distribution of considered models. Here, red and blue bars indicate the distribution of homogeneous (ordered) and inhomogeneous doped ions along the [001] direction with 1 Å interval of distance, respectively, and red and blue spheres represent the ordered and randomly doped ions, respectively.

#### S2. STRUCTURAL ANALYSIS

Based on those optimized structures from DFT as well as MD, we perform the radial distribution function (RDF). Here, the averaged number of target atoms ( $\alpha$ ) are counted when they are positioned within a distance range of r to  $r + \delta r$ , centering each given  $\alpha$  atoms. Here,  $\delta r$  is taken as a small perturbation to the distance, r. In another words, the RDF ( $g_{\alpha\beta}(r)$ ) is a mathematically rigorous approach to describe the density probability for an atom of the  $\alpha$  species to have a neighboring  $\beta$  species atom at a given distance r. This can be elegantly expressed as,

$$g_{\alpha\beta}(r) = \frac{dn_{\alpha\beta}(r)}{4\pi r^2 dr} \frac{N_{\alpha}}{V} \quad .$$
<sup>(2)</sup>

Here, V represents as the volume of the periodic simulation cell and  $N_{\alpha}$  is equal to  $c_{\alpha}N$ , where  $c_{\alpha}$  is the concentration of species  $\alpha$  and N the total number of atoms in the cell. Additional structural information is provided via the simulated X-ray diffraction plots (based on Bragg's law) as implemented in the RIETAN-FP [1] code in the VESTA visualization program [2]. Here the XRD results are represented in Figure S4 and RDF results are in Figure 2 in main text.



Figure S4. Simulated X-ray diffraction (XRD) plots for both DFT and MD optimized ceria-based structures –  $CeO_2$ ,  $CeO_{2-x}$ , SDC and GDC. For the MD simulations, the SDC and GDC structures are optimized considering finite temperatures (from 1 to 1,000 K).

## S3. ELECTRONIC STRUCTURE

From the calculated Kohn-Sham DFT orbitals,  $\phi_i$ , we calculate the electron localization function (ELF). Here, the ELF is calculated as a grid in the three-dimensional space where,

$$ELF = \frac{1}{1 + (D/D_h)^2}$$
, (3)

when

$$D = \frac{1}{2} \sum_{i} |\nabla \phi_i|^2 - \frac{|\nabla \epsilon|^2}{8\epsilon} \quad , \tag{4}$$

and

$$D_h = \frac{3(3\pi^2)^{5/3}\epsilon^{5/3}}{10} \quad . \tag{5}$$

Here  $\epsilon$  is the electron density and the ELF must take values between 0 and 1. For instance, when ELF is 1, it corresponds to perfect localization of the electron density [3].



Figure S5. Electron localization function (ELF) plots of the (100) *bc*-plane, the (010) *ca*-plane, and the (001) *ab*-plane for  $\text{CeO}_{2-x}$ , GDC, and SDC, respectively. O, (Gd or Sm), and Ce atoms are presented as red, blue, and white spheres, respectively.





Figure S6. The electronic density-of-states (DOS) for the oxygen ions around the oxygen vacancy (V<sub>1</sub> represented in Figure 6 of the main text and the nearest cations bound to each oxygen. For instance, in (a), the  $O_{a\uparrow}^{V_1}$  ( $O_{ab}^{V_2}$ ) refers to the oxygen positioned above the oxygen vacancy (V<sub>1</sub>) along the *a*-direction and diagonally positioned to the other oxygen vacancy (V<sub>2</sub>) with 3 Ce and 1 Sm cations bound. The pale-shaded pink, skyblue, gray and light green regions represent the partial DOS in pristine CeO<sub>2</sub> (i.e. for O 2*p*, Ce 5*p*, Ce 5*d*, and Ce 4*f*, respectively). The solid red, black, blue, green lines then represent the partial DOS for O 2*p*, Ce 5*d*, and Ce 4*f* in SDC, respectively. Here, the dot-dashed black and blue lines are the partial DOS for Sm 5*p* and Sm 5*d*, respectively. We note that the partial DOS of GDC is very similar to that for SDC.

## S4. VIBRATIONAL PROPERTY ANALYSIS



Figure S7. Phonon vDOS (without neutron weighting corrections) for  $\text{CeO}_2$ ,  $\text{CeO}_{2-x}$ , SDC, and GDC. Here, the green region, red line, blue line and black line represent vDOS of the total system, oxygen, cerium, and dopants (Sm or Gd), respectively.



Figure S8. Direction-dependent partial vDOS for each oxygen atoms around the vacancy  $(V_1)$  in GDC are represented with comparing the pure CeO<sub>2</sub> (grey region). The total and direction dependent contribution of each oxygen atoms along *a* direction, contribution along *b* direction, and contribution along *c* direction are presented as black solid line, the other three different colored dotted line (red, blue and orange), respectively. With respect to the target vacancy  $(V_1)$ , the oxygens at 1NN sites are shown in left two column (a), (b), (e), (f), (i) and (j), the oxygens in 2NN sites are shown in third column (c), (g), (k), and the oxygens in 4NN sites are (d), (h) and (l). Detail labels for each case follow that in Figure 4. At (a), (b), (d), and (e), oxygens are standing 2NN or 4NN position with respect to another vacancy  $(V_2)$  as labelled within bracket.

Table S3. The averaged values for the center of the phonon vibrational density-of-states (vDOS) ( $\bar{\nu}$ , in meV) of various oxygens classified with respect to vacancies are calculated. There are 12 1NN oxygens, 20 2NN oxygens, 4 4NN oxygens, and 26 other oxygens. The *n*NN refers to the location of the oxygen ions at the *n* th nearest neighbor position with respect to each oxygen vacancy. For example, 1NN will then refer to the first nearest neighbor oxygen atoms found near the oxygen vacancy. The values in brackets below are the standard deviation measured for each case.

$(\mathrm{meV})$	1NN	2NN	4NN	others
SDC	41.34 $(0.78)$	46.42 $(1.21)$	43.29 (0.06)	45.28 $(1.25)$
GDC	41.49 (0.85)	46.67 (1.31)	43.44 (0.01)	45.59 $(1.31)$
VAC	39.64 $(1.28)$	45.45 (1.09)	41.01 (1.56)	44.25 $(1.21)$



Figure S9. Direction-dependent partial vDOS for each oxygen atoms around the vacancy  $(V_1)$  in CeO<sub>2-x</sub> are represented with comparing the pure CeO<sub>2</sub> (grey region). The total and direction dependent contribution of each oxygen atoms along a direction, contribution along b direction, and contribution along c direction are presented as black solid line, the other three different colored dotted line (red, blue and orange), respectively. With respect to the target vacancy  $(V_1)$ , the oxygens at 1NN sites are shown in left two column (a), (b), (e), (f), (i) and (j), the oxygens in 2NN sites are shown in third column (c), (g), (k), and the oxygens in 4NN sites are (d), (h) and (l). Detail labels for each case follow that in Figure 4. At (a), (b), (d), and (e), oxygens are standing 2NN or 4NN position with respect to another vacancy  $(V_2)$  as labelled within bracket.

(%)	$\Delta \nu_{\rm tot}$	$\Delta \nu_a$	$\Delta \nu_b$	$\Delta \nu_c$
$O_{a^{\uparrow}}^{V_1}$	-11.11	-26.92	-0.97	-5.46
$O_{a}^{\widetilde{V}_{1}}$	-11.11	-26.92	-0.97	-5.46
$O_{h\uparrow}^{\widetilde{V}_1}$	-16.90	-16.98	-29.47	-4.26
$O_{h}^{V_1}$	-8.30	-1.92	-21.18	-1.81
$O_{c\uparrow}^{V_1}$	-14.33	-5.78	-5.88	-31.34
$O_{c}^{V_1}$	-14.33	-5.78	-5.88	-31.34
$O_{2NN}^{V_1}$	-1.95	-1.49	-0.70	-3.66
$O_{2NN}^{2NN}$	-1.95	-1.49	-0.70	-3.66
$O_{b2}^{V_1}$	-13.10	-3.03	-30.93	-5.33
$O_{c2}^{\widetilde{V}_1}$	-6.24	-2.12	-2.10	-14.52
$O_{a\uparrow}^{V_1}$	-6.68	-23.58	+2.21	+2.20
$O_{a}^{\tilde{V}_{1}}$	-9.21	-27.26	-0.13	+0.77
$O_{h\uparrow}^{U_1}$	-9.86	-7.66	-22.25	+1.25
$O_{h}^{V_1}$	-6.95	2.05	-22.80	+0.77
$O_{a^{\uparrow}}^{V_1}$	-9.23	-0.86	-1.26	-24.73
$O_{al}^{V_1}$	-11.68	-2.09	-2.34	-29.71
$O_{2NN}^{V_1}$	-0.34	-1.22	+0.33	+0.73
$O_{2NN}^{2NN}$	-0.37	-0.47	+1.07	-0.86
$O_{c2}^{V_1}$	-4.78	-0.70	-0.77	-12.06
$O_{b2}^{\widetilde{V}_1}$	-4.53	-0.17	-11.57	-0.99
$\mathrm{O}_{a\uparrow}^{\mathrm{V}_1}$	-6.52	-24.55	+2.64	+2.64
$\mathrm{O}_{a\perp}^{\mathrm{V}_1}$	-8.80	-27.19	+0.82	+0.82
$\mathrm{O}_{b\uparrow}^{\mathrm{V}_1}$	-10.77	-8.99	+0.47	+0.47
$O_{b}^{V_1}$	-5.79	+2.72	+2.02	+2.02
$O_{c^{\uparrow}}^{\breve{V}_1}$	-9.36	-0.96	-25.94	-25.94
$O_{c^{\perp}}^{\widetilde{V}_{1}}$	-10.40	-1.36	-28.73	-28.73
$O_{2NN}^{V_1}$	-0.29	-1.28	+0.72	+0.72
$O_{2NN}^{\tilde{V}_1}$	+0.49	+0.20	+0.17	+0.17
$O_{h2}^{V_1}$	-4.31	+0.04	-0.73	-0.73
$\mathrm{O}_{c2}^{\mathrm{V}_1}$	-4.32	-0.38	-12.38	-12.38-

Table S4. The relative center of vDOS,  $\nu$ , for CeO<sub>2-x</sub>, SDC, and GDC, taken with respect to the  $\nu$  of O in  $CeO_2$  (45.40 meV) and expressed in %. Here,  $\nu_{tot}$ ,  $\nu_a$ ,  $\nu_b$ , and  $\nu_c$  are represent the total  $\nu$ , its decomposed contributions along a-direction, b-direction, and c-direction, respectively. By definition, a negative value will indicate phonon softening.

 $CeO_{2-x}$ 

SDC

GDC

#### **S5. DIFFUSION PROPERTIES**

The calculated ion diffusion coefficient (D) for all ceria-based models is computed for the quenched structures, and is obtained through the post-processing of the mean square displacement (MSD),  $\langle R^2 \rangle$  data. The  $\langle R^2 \rangle$  is calculated and collected throughout each MD run as a function of the simulation time (t). The D for each system is subsequently determined according to the Einstein relation [4], following,

$$D = \sum \frac{\langle R^2 \rangle}{6t} \quad , \tag{6}$$

where the brackets and  $\sum$  represent taking an average over all simulation time, and the summation over all ions, respectively.

The  $\langle R^2 \rangle$  of the anion and cations are separately calculated using 500 ps under various finite temperatures ranging from 600 and 1,800 K, with an increment of 100 K. Extending the diffusion analysis, the activation energy barrier,  $E_a$ , of oxygen ions are computed from the Arrhenius equation [5],

$$D = D_0 \exp(-\frac{E_{\rm a}}{k_{\rm B}T}) \quad , \tag{7}$$

where T corresponds to the target temperature,  $k_B$  the Boltzmann constant, and  $D_0$  for the temperature-independent pre-factor. This can linearlized to the following,

$$\log D = -\frac{E_{\rm a}}{k_{\rm B}} \frac{1}{T} + \log D_0 \quad . \tag{8}$$

Table S5. Diffusion coefficient (in unit of  $m^2/s$ ) for the DFT-derived ordered and five randomized models (notated as R1, R2, R3, R4 and R5) for SDC and GDC at 1,200 K.

$D \ ({\rm m^2/s}) \ge 10^{-12}$						
	Order	R1	R2	R3	R4	R5
SDC	0.97	1.59	1.55	1.08	1.28	1.07

- F. Izumi, K. Momma. Three-Dimensional Visualization in Powder Diffraction. Solid State Phenom. 2007, 130, 15–20.
- [2] K. Momma, F. Izumi. VESTA: A three-dimensional visualization system for electronic and structural analysis. J. Appl. Cryst. 2008, 41, 653–658.
- B. Silvi, A. Savin. Classification of chemical bonds based on topological analysis of electron localization functions. *Nature* 1994, 371, 683–686.
- [4] A. Einstein. On The Motion Of Small Particles Suspended In Liquids At Rest Required By The Molecular-kinetic Theory Of Heat. Ann. Phys. 1905, 17, 549–560.
- [5] S. Arrhenius. Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. Z. Phys. Chem. 1889, 4, 226–248.