Supplementary Information

The Effect of Doping on the Mechanical Properties of Rare-Earth Oxides – An Atomistic Study

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Figure S1(a) shows a sharp first coordination peak at ~2.34 Å in Ce–O RDF in stoichiometric CeO_2, which is expected for the stable fluorite structure. This peak broadens and subtly shifts upon doping with $YO_{1.5}$, indicating heightened static disorder about Ce^{4+} due to the creation of oxygen vacancies and associated local lattice relaxations induced by Y^{3+} substitution. The decrease in peak magnitude with broadened distribution reflects weakened and diversified Ce–O bond length, emphasizing the structural perturbation accompanying heterovalent doping.

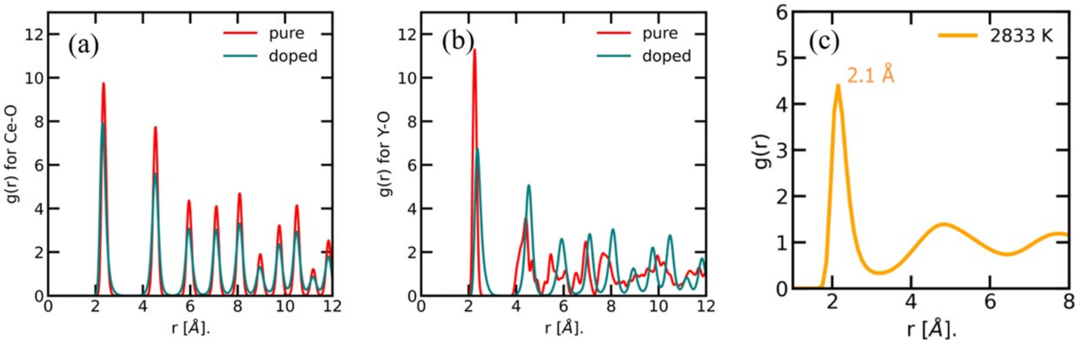

Figure S1. The RDFs for (a) Ce – O in pure CeO_2 and (b) Y – O in pure $YO_{1.5}$ simulated at 300 K are shown. (c) The all-pairs RDF for pure $YO_{1.5}$ simulated at 2833 K is presented.

Figure S1(b) compares the Y-O RDF in doped CeO_2 with that of pure $YO_{1.5}$. The Y-O coordination shell in the doped system has a markedly broader peak than in the ordered $YO_{1.5}$ crystal, showing

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that Y^{3+} ions incorporated into the CeO_2 lattice see a significantly less symmetric oxygen coordination environment. This broadening reflects both the mismatch in ionic radii between Ce^{4+} and Y^{3+} and the presence of charge-compensating oxygen vacancies, distorting the local fluorite network. The comparison with the pure $YO_{1.5}$ reference underlines how dopant ions in ceria assume a much more disordered arrangement than in their native host lattice.

The all-pairs RDF of pure $YO_{1.5}$ at 2833 K is shown in Fig. S1(c) and affirms known high-temperature behavior of the fully substituted oxide. At high temperatures, the peaks are broader and less pronounced, which is representative of the transition towards higher thermal disorder. Such a high temperature benchmark is of relevance for interpreting the structural state of Y^{3+} sites in doped CeO_2, since the broadened environment resembles, at least to some extent, the thermally agitated configuration of $YO_{1.5}$, but occurring here at room temperature due to defect-driven distortions rather than thermal motion.

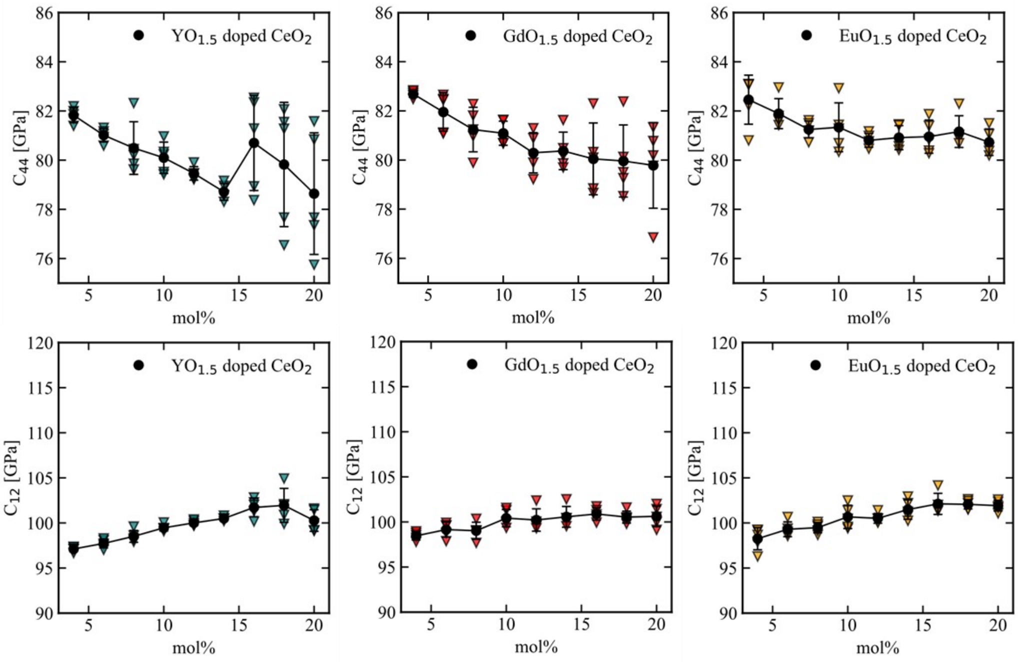

Figure S2. The figure presents the variation of elastic constants C_{44} and C_{12} for CeO_2 doped with $YO_{1.5}$, $GdO_{1.5}$, and $EuO_{1.5}$ across a dopant concentration range of approximately 4 to 20 mol%.

For all three dopants, a general decreasing trend in C_{44} is observed with increasing dopant concentration, indicating a reduction in shear rigidity. This softening effect is most pronounced in $YO_{1.5}$-doped CeO_2, while $EuO_{1.5}$-doped CeO_2 shows the least variation, suggesting a more stable shear response. In contrast, the C_{12} values exhibit a modest increasing trend for all dopants, which reflects a slight enhancement in the material's resistance to volumetric deformation. This increase of C_{12} has been reported previously. [1] In fluorite-structured CeO_2, the elastic constant C_{12} reflects transverse strain response under uniaxial stress and is sensitive to angular lattice flexibility. Doping with trivalent cations and the associated oxygen vacancies enhance this angular compliance, leading to an increase in C_{12}. This behavior arises from local bond-angle softening and elastic dipole interactions that amplify off-diagonal stress–strain coupling. $YO_{1.5}$- and $EuO_{1.5}$-doped systems show a more noticeable increase in C_{12} with concentration compared to $GdO_{1.5}$-doped systems. The error bars indicate some degree of variability, particularly in C_{44}, emphasizing sensitivity to dopant type and concentration. The clustering of data points around smooth curves for C_{12} suggests a consistent trend within each dopant series. Overall, these results provide insights into dopant-dependent tuning of elastic properties in doped CeO_2, relevant for its mechanical stability in functional applications.

Per-ion potential energy calculation

Within LAMMPS, the potential energy of an individual ion *i* is determined using the *compute pe/atom* command, which partitions the total potential energy into contributions for each ion. [2] The per-atom potential energy is expressed as

$$E_i = \frac{1}{2}\sum_{j \neq i} U_{ij}^{Short} + E_i^{long,\,coul} , \tag{S1}$$

where, U_{ij}^{Short} represents short-range pairwise interactions (e.g., Buckingham terms and Columbic attraction), and $E^{long,coul}_{i}$ is the long-range Coulombic contribution. For systems employing PPPM summation, the total Coulombic energy is decomposed as

$$U_{Coul} = U^{real}_{Coul} + U^{recip}_{Coul} - U^{self}_{Coul} \tag{S2}$$

with the real-space term given by

$$U^{real}_{Coul} = \frac{1}{4\pi\varepsilon_o}\sum_{i}\sum_{j<i}\frac{q_i q_j\, erfc\left(\alpha r_{ij}\right)}{r_{ij}} . \tag{S3}$$

The reciprocal-space contribution is evaluated in Fourier space. Per-atom Coulombic energies are obtained by assigning each ion a contribution corresponding to its interaction with all other ions in both real and reciprocal space, along with a per-atom self-energy correction:

$$U^{self}_{i} = -\frac{\alpha}{\sqrt{\pi}\,4\pi\varepsilon_o}q^{2}_{i} \tag{S4}$$

In classical molecular dynamics simulations, the total potential energy is calculated as the sum of predefined interatomic interactions specified by the force field. The per-ion potential energy is determined by consistently partitioning this total energy among individual ions. In contrast, density functional theory explicitly incorporates electronic structure and provides an absolute ground-state total energy for each ion. Since classical molecular dynamics does not attribute for electronic degrees of freedom, it omits the intrinsic ground-state energy of isolated ions. Therefore, per-ion energies obtained from molecular dynamics represent relative measures of local energetic environments within the condensed system. These values are best suited for comparative analysis across different compositions or defect configurations, rather than for determining absolute binding or formation energies.

References

[1] N. Swaminathan and J. Qu, “Evaluation of thermomechanical properties of non-stoichiometric gadolinium doped ceria using atomistic simulations,” *Model. Simul. Mater. Sci. Eng.*, vol. 17, no. 4, p. 045006, Jun. 2009, doi: 10.1088/0965-0393/17/4/045006.

[2] “compute pe/atom command — LAMMPS documentation.” Lammps.org, 2025. Accessed: Jan. 19, 2026. [Online]. Available: https://docs.lammps.org/compute_pe_atom.html