

## **Supplementary Information**

### **Reducing the chemical expansion coefficient in ceria by addition of zirconium**

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#### **Experimental Methods**

PZCO powder was prepared using a modified Pechini-type sol gel method<sup>[1]</sup>. Powders for TGA and HTXRD were calcined in air at 1050 °C for two hours prior to measurement. Dense samples for TGA and dilatometry were prepared by sintering powder compacts >1400 °C. HTXRD was performed using CuK $\alpha$  radiation on a Bruker D8 Advance with LYNXEYE super speed detector (Bragg Brentano geometry) and an Anton Paar furnace model HTK2000. Lattice parameters were determined by plotting the lattice constant against the Nelson-Riley function and taking the intercept of the line fitted to the data<sup>[2]</sup>. An Orton dilatometer was used for bulk dilatometry. A Cahn 2000 microbalance and a homemade TGA system using a Mettler Toledo microbalance (model XP6V) were used for in-situ TGA measurements on bulk and powder specimens, respectively. Oxygen partial pressure was monitored using a Nernst-type zirconia based oxygen sensor in-situ for dilatometry and TGA, and ex-situ for HTXRD.

#### **Computational Methods**

The Density Functional Theory calculations were performed with the Vienna Ab-initio Simulation Package (VASP)<sup>[3]</sup>, with the Projector Augmented Wave (PAW) method. We used the Generalized Gradient Approximation (GGA) with the Perdew-Wang 91 (PW91) exchange-correlation functional and an energy cut-off of 500 eV. We also added a Hubbard term,  $U = 5$  eV, to properly describe the localized nature of the  $f$  electrons in cerium<sup>[4]</sup>. The calculations were carried out using the Brillouin zone sampled with a (2 x 2 x 2) Monkhorst-Pack mesh k-points grid. These settings are in line with those previously used in the literature

and convergence tests were performed to make sure that the results are well converged with respect to these parameters.

The DFT calculations were performed on a 2 x 2 x 2 unit cells box. A conjugate gradient minimization was employed with a force convergence criterion of 0.01 eV/Å. Chemical expansion coefficients were extracted from the lattice parameters of 9 Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2-δ</sub> compositions, corresponding to  $\delta = 0, 0.03125, 0.0625, 0.09375, 0.125, 0.15625, 0.1875, 0.21875$  and 0.25. We note here that the chemical expansion coefficient is effectively calculated at 0 K. Since this coefficient has been shown to be largely temperature-independent<sup>[5, 6]</sup> and previous DFT calculations of these coefficients in CeO<sub>2</sub> showed very good agreement with the experimental values<sup>[7]</sup>, we do not foresee a discrepancy between the 0 K computation and elevated temperature measurements.

## **Additional experimental results and discussion**

### *Structure and reversibility*

The structure of all powders and bulk samples was indexed to the cubic fluorite structure. Evidence for tetragonal distortions were found using Raman spectroscopy on powders<sup>[8]</sup>, but no significant change in the spectra before and after TGA measurements was observed. Dilatometry and TGA measurements on bulk samples took several days to reach equilibrium for each reduction step, and in the case of dilatometry (~30 days in reducing conditions at elevated T), an irreversible expansion of 0.2% was observed, possibly arising from an observed (by XRD) small amount of unidentified, second phase. No second phase was observed by XRD on all other specimens after testing. Due to the significantly more rapid equilibration, measurements on powders were performed within a few days, though it was found that reduction-oxidation-reduction treatments resulted in enhanced reducibility<sup>[9]</sup>. Therefore, the TGA and HTXRD measurements used to extract powder chemical expansion

coefficient were performed by measuring from oxidizing to reducing conditions, with the final measurement in oxidizing conditions showing reversible behavior.

### Thermal expansion of PZCO

Figure A shows the lattice parameter expansion vs temperature of PZCO measured by powder HTXRD, compared with other cubic fluorite structured oxides [with abbreviations used in the text defined as: GCO ( $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95-\delta}$ ), PCO ( $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ ), and YZO ( $\text{Y}_{0.16}\text{Zr}_{0.84}\text{O}_{1.92-\delta}$ )]. The first point to notice is the lattice expansion of all the oxides, except PCO, exhibits slightly non-linear behavior, typical of thermal expansion. PCO, on the other hand, exhibits a strong positive deviation above about 500 °C arising from formation of oxygen vacancies due to reduction of  $\text{Pr}^{4+}$  to  $\text{Pr}^{3+}$  and consequent chemical expansion [5, 10]. Despite containing Pr, PZCO does not exhibit such behavior, instead it follows the same trend as the other oxides, for which  $\delta \cong 0$  in the studied temperature and  $p\text{O}_2$ . This indicates that PZCO also exhibits no change in  $\delta$  for the studied range which is consistent with all Pr being trivalent, a result expected based on the decrease in reduction enthalpy typical upon addition of zirconia to ceria, as discussed in the manuscript.

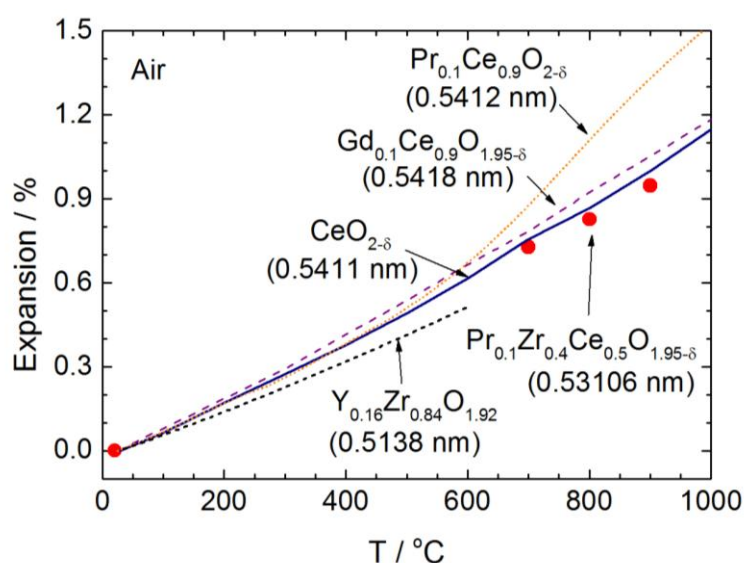


Figure A: Thermal expansion of different cubic fluorite oxides in air. Data for PZCO are from HTXRD of powder. Numbers in parenthesis are the respective lattice parameters at room temperature. Data are from: CeO<sub>2</sub> and GCO<sup>[11]</sup>, PCO<sup>[10]</sup>, and YZO<sup>[12]</sup>.

A second point to note from figure A is that PZCO exhibits thermal expansion greater than YSZ but less than both GCO and CeO<sub>2-δ</sub>. This behavior is consistent with stronger bonding, and hence reduced thermal expansion, due to a smaller lattice parameter (where radius of Zr < Ce < Gd<sup>[13]</sup>), with room temperature lattice constants reported in the figure.

#### Tables of experimental and computational data

Table 1: Experimental and computational chemical expansion coefficients ( $\alpha_c$ ) derived from linear fits to data in figure D.

Material	T / °C	$\alpha_c$
PZCO (pwd)	700	0.042
PZCO (pwd)	800	0.037
PZCO (pwd)	900	0.037
PZCO (bulk)	800	0.056
PZCO (bulk)	900	0.057
PZCO (avg)	-	0.046
CZO (DFT)	0	0.048
GCO	900	0.101

Table 2: Vacancy radius determined from the experimental and computational chemical expansion coefficients ( $\alpha_c$ ) reported in Table 1.

Material	T / °C	$r_v$
PZCO (pwd)	700	0.931
PZCO (pwd)	800	0.885
PZCO (pwd)	900	0.885
PZCO (bulk)	800	1.061
PZCO (bulk)	900	1.070
PZCO (avg)	-	0.966
CZO (DFT)	0	0.864
ZrO <sub>2</sub> (ref <sup>[7]</sup> )	-	0.988
CeO <sub>2</sub> (ref <sup>[7]</sup> )	-	1.169

Table 3: Lattice parameter measured by HTXRD of  $\text{Pr}_{0.1}\text{Zr}_{0.4}\text{Ce}_{0.5}\text{O}_{1.95-\delta}$  under different conditions

T / °C	Log(pO <sub>2</sub> / atm)	a <sub>0</sub> / nm	a <sub>0</sub> error / nm
20	-0.67	0.53106	0.00010
700	-0.67	0.53492	0.00017
700	-17.50	0.53603	0.00006
700	-19.49	0.53661	0.00009
700	-21.48	0.53728	0.00012
700	-0.67	0.53467	0.00016
800	-0.67	0.53545	0.00013
800	-15.03	0.53627	0.00011
800	-17.02	0.53707	0.00018
800	-19.01	0.53803	0.00010
800	-0.67	0.53538	0.00015
900	-0.67	0.53609	0.00012
900	-12.99	0.53704	0.00009
900	-14.97	0.53774	0.00009
900	-16.97	0.53908	0.00018
900	-0.67	0.53600	0.00022
20	-0.67	0.53101	0.0013

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