Supplementary material

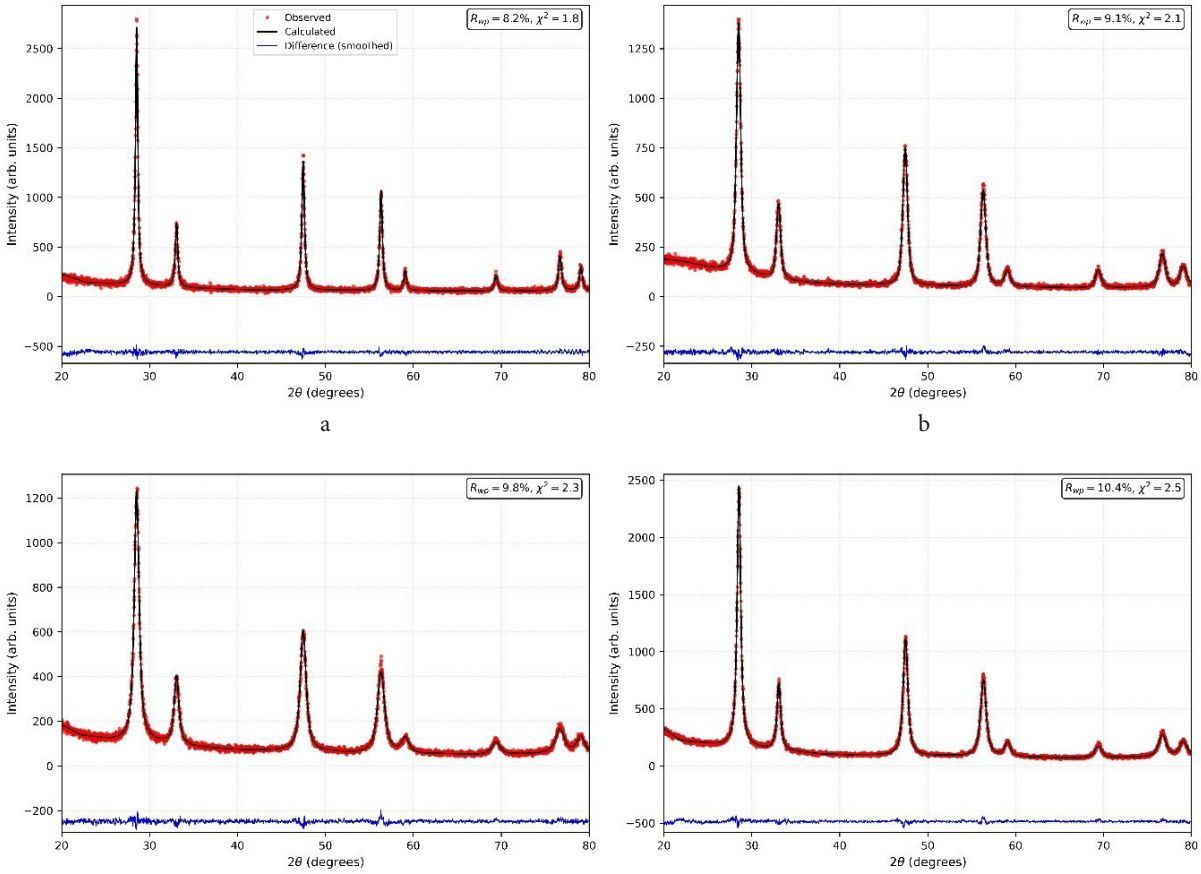

Fig. S1. (Color online) Rietveld refinement plots for all morphologies: CeO_2-25 nm (a), CeO_2-AA (b), CeO_2-BB (c), and CeO_2-MM (d) samples. Observed data (red dots), calculated pattern (black line), and difference curve (blue line) are shown in the 20 – 80° 2θ range.

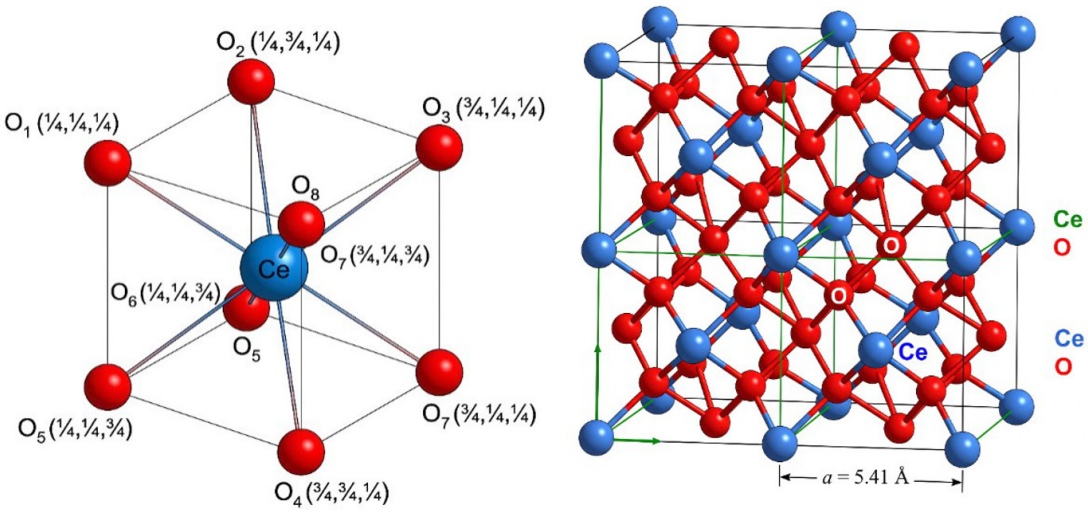

Fig. S2. (Color online) Labelling scheme of Ce-O bonds used in the bond valence sum calculations (Table S9) (a). A central Ce atom (blue sphere) is coordinated by its eight nearest-neighbour O atoms (red spheres) located at the corners of a cube. The O atoms are labelled O_1 to O_8 according to their fractional coordinates: O_1 (¼, ¼, ¼), O_2 (¼, ¾, ¼), O_3 (¾, ¼, ¼), O_4 (¾, ¾, ¼), O_5 (¼, ¼, ¾), O_6 (¼, ¾, ¾), O_7 (¾, ¼, ¾), O_8 (¾, ¾, ¾). In the ideal fluorite structure, all Ce-O distances are equal (≈2.34 Å). The numbering is arbitrary and only serves to distinguish individual bonds in the table. Crystal structure of CeO_2 in the fluorite type (space group $Fm\bar{3}m$, No. 225) (b). Ce atoms (blue spheres) occupy the 4a Wyckoff positions (0, 0, 0) and face centers with 8-fold cubic coordination, while O atoms (red spheres) occupy the 8c positions (¼, ¼, ¼) with 4-fold tetrahedral coordination. The lattice parameter is a = 5.41 Å. The axes correspond to the crystallographic directions [100], [010], and [001]. This structure is common to all samples studied, as confirmed by Rietveld refinement (Fig. S1).

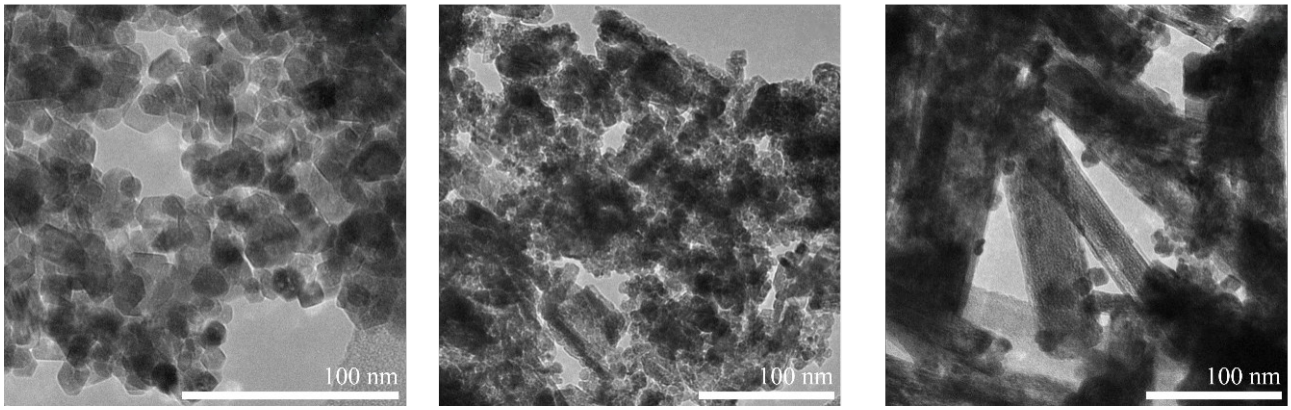

Fig. S3. Representative TEM images confirming the morphology of all samples: CeO_2-AA spherulites (a), CeO_2-BB intermediate rods (b), CeO_2-MM long rods (c). Scale bars: 100 nm.

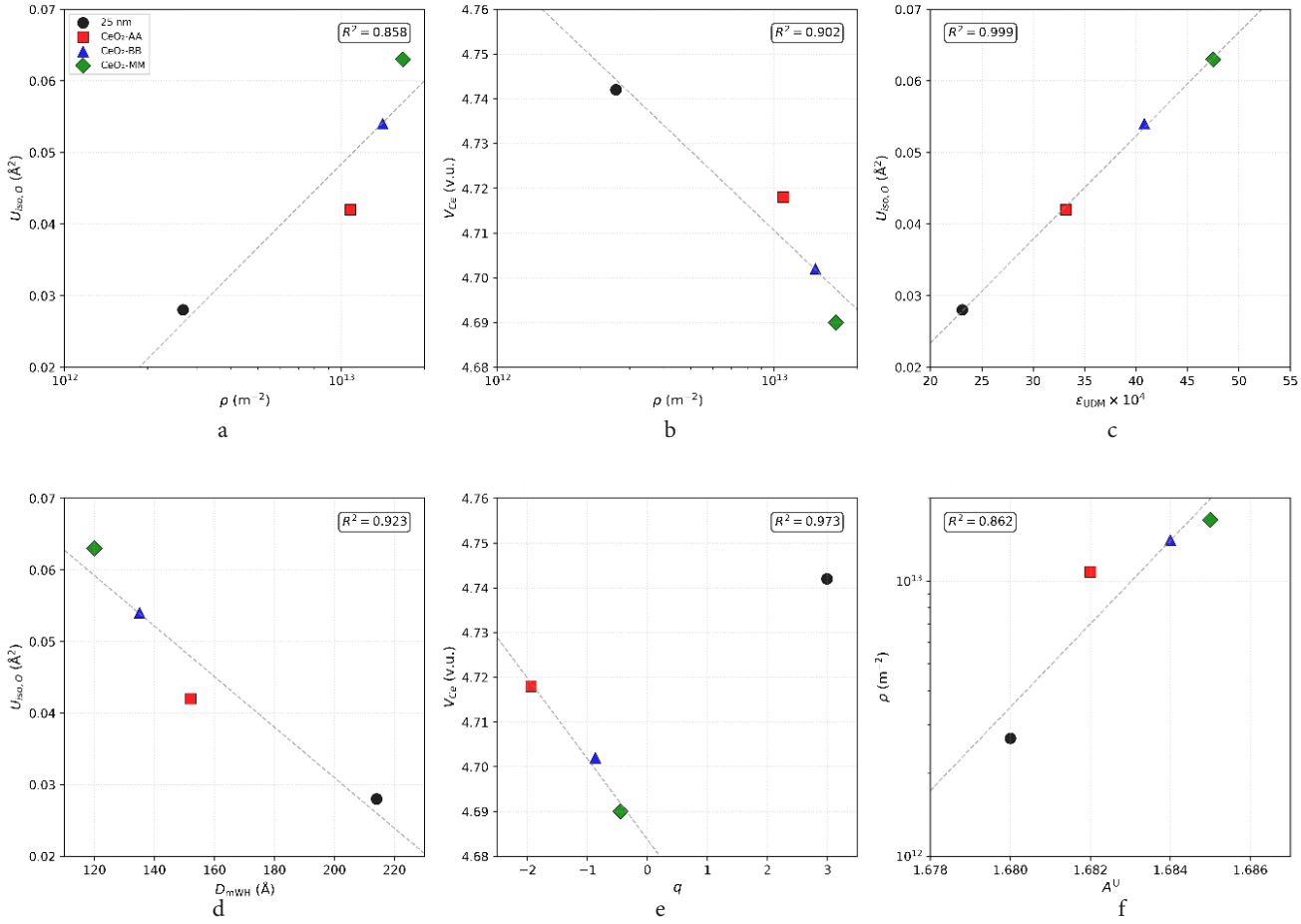

Fig. S4. (Color online) Correlation plots between microstructural and bonding parameters. Dislocation density ρ vs. $U_{iso,O}$ (a); ρ vs. V_{Ce} (b); Microstrain ε vs. $U_{iso,O}$ (c); Crystallite size D vs. $U_{iso,O}$ (d); Dislocation character q vs. V_{Ce} (e); Anisotropy index A^U vs. ρ (f). The R^2 values for each sample are indicated in the corresponding panels.

Table S1. Synthesis conditions for CeO_2 nanostructures.

Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
ODA (M)	-	0.2	0.05	0.01
α	-	3	1	0.3
Morphology	Nanoparticles	Spherulites	Rods (intermediate aspect ratio)	Long rods (high aspect ratio)

Table S2. Rietveld refinement parameters.

Parameters		CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
Lattice parameter	a (Å)	5.41208(1)	5.42011(1)	5.41630(1)	5.41491(1)
Unit cell volume	V (Å^3)	158.523	159.230	158.894	158.772
Atomic displacement parameters	$U_{iso,Ce}$ (Å^2)	0.0095(3)	0.0027(2)	0.0008(2)	0.0074(3)
	$U_{iso,O}$ (Å^2)	0.0479(8)	0.0136(5)	0.0669(12)	0.0458(10)
Agreement factors	R_p (%)	6.2	5.8	6.5	6.1
	R_{wp} (%)	8.2	7.5	9.1	8.7
	R_{exp} (%)	4.6	4.3	5.0	4.8
	χ^2	1.8	1.7	1.8	1.8
Bragg R-factor	R_{Bragg} (%)	3.2	2.9	3.5	3.3

Note: Values in parentheses represent estimated standard deviations in the last digit. All refinements were performed in space group $Fm\bar{3}m$ (No. 225) with Ce at 4a (0,0,0) and O at 8c (¼, ¼, ¼) positions.

Table S3. Integral breadths.

Sample	*hkl*	2θ (°)	*d* (Å)	*s* (Å^{-1})	β* (10^{-3} Å^{-1})	β_G* (10^{-3} Å^{-1})	β_L* (10^{-3} Å^{-1})
CeO_2-25 nm (a = 5.41208 Å)	111	28.544	3.1247	0.3200	0.3187	0.0840	0.2347
	200	33.077	2.7060	0.3695	0.3405	0.0847	0.2558
	220	47.478	1.9135	0.5226	0.3575	0.0879	0.2696
	311	56.335	1.6318	0.6128	0.3613	0.0906	0.2707
	222	59.082	1.5623	0.6401	0.3568	0.0916	0.2652
	400	69.405	1.3530	0.7391	0.3991	0.0960	0.3031
	331	76.691	1.2416	0.8054	0.4098	0.0999	0.3099
	420	79.065	1.2102	0.8263	0.4258	0.1013	0.3245
CeO_2-AA (a = 5.42011 Å)	111	28.500	3.1293	0.3196	0.5690	0.3174	0.2516
	200	33.027	2.7101	0.3690	0.5466	0.3230	0.2236
	220	47.403	1.9163	0.5218	0.6100	0.3470	0.2630
	311	56.244	1.6342	0.6119	0.6806	0.3669	0.3137
	222	58.985	1.5647	0.6391	0.7189	0.3740	0.3449
	400	69.288	1.3550	0.7380	0.7431	0.4050	0.3381
	331	76.556	1.2435	0.8042	0.8202	0.4316	0.3886
	420	78.925	1.2120	0.8251	0.8209	0.4412	0.3797
CeO_2-BB (a = 5.41630 Å)	111	28.521	3.1271	0.3198	0.6497	0.2613	0.3884
	200	33.050	2.7082	0.3692	0.6186	0.2675	0.3511
	220	47.438	1.9150	0.5222	0.7813	0.2937	0.4876
	311	56.287	1.6331	0.6123	0.9427	0.3152	0.6275
	222	59.031	1.5636	0.6395	1.0256	0.3227	0.7029
	400	69.343	1.3541	0.7385	1.0901	0.3554	0.7347
	331	76.619	1.2426	0.8048	1.2559	0.3830	0.8729
	420	78.991	1.2111	0.8257	1.2589	0.3930	0.8659
CeO_2-MM (a = 5.41491 Å)	111	28.528	3.1263	0.3199	0.4710	0.1106	0.3604
	200	33.059	2.7075	0.3693	0.4739	0.1336	0.3403
	220	47.451	1.9145	0.5223	0.6153	0.2075	0.4078
	311	56.303	1.6327	0.6125	0.7328	0.2557	0.4771
	222	59.048	1.5631	0.6398	0.7840	0.2713	0.5127
	400	69.364	1.3537	0.7387	0.8742	0.3340	0.5402
	331	76.643	1.2423	0.8050	0.9944	0.3828	0.6116
	420	79.016	1.2108	0.8259	1.0133	0.3997	0.6136

Note: Integral breadths β, β_G, β_L are instrumental-corrected values in 10^{-3} Å^{-1}.

Table S4. Convergence of total energy and elastic constants with respect to plane-wave cutoff energy for CeO_2 (representative morphology, 3-atom fluorite cell).

Cutoff (eV)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	Bulk modulus (GPa)	ΔE (eV/atom) vs. 800 eV
700	319.71	93.65	36.76	169.00	8×10^{-5}
800	315.78	90.79	35.69	165.79	–

Note: Calculations were performed with GGA-PBE+U (U = 4.5 eV on Ce 4f), ultrasoft pseudopotentials, and a fixed 5 × 5 × 5 k-point grid. SCF tolerance: 1×10^{-7} eV per cell (≈3.3×10^{-8} eV/atom). Final SCF convergence reached <1×10^{-9} eV/atom. The changes in elastic constants are within 1.2% (C_{11}), 3.1% (C_{12}), 2.9% (C_{44}), and 1.9% (bulk modulus), well within typical DFT+U uncertainty.

Table S5. Convergence of total energy with respect to k-point grid for CeO_2 (cutoff fixed at 700 eV).

k-point grid	Total energy (eV)	ΔE (eV/atom) vs. previous	ΔE (eV/atom) vs. 6×6×6
3×3×3	−2129.21145	–	1.0×10^{-3}
4×4×4	−2129.21447	1.0×10^{-3}	1.0×10^{-5}
5×5×5	−2129.21451	1.3×10^{-5}	1.3×10^{-5}
6×6×6	−2129.21450	3.3×10^{-6}	–

Note: Same computational parameters as in Table S4. The difference between 5×5×5 and 6×6×6 grids is 1.3×10^{-5} eV/atom, two orders of magnitude below the 0.001 eV/atom convergence criterion.

Table S6. Lattice parameters from Rietveld refinement and DFT.

Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
a (XRD) (Å)	5.4122(1)	5.4201(1)	5.4162(1)	5.4149(1)
a (DFT) (Å)	5.509	5.509	5.510	5.510

Note: Values in parentheses represent estimated standard deviations in the last digit.

Table S7. TEM particle dimensions.

Parameters	CeO_2-AA	CeO_2-BB	CeO_2-MM
Width (nm)	14.33 ± 3.62	17.21 ± 6.01	32.58 ± 7.04
Length (nm)	13.47 ± 3.44	79.12 ± 47.71	307.66 ± 91.33
Aspect Ratio	0.96 ± 0.18	5.39 ± 4.14	9.98 ± 4.07
Number of particles	265	194	232

Note: Values are mean ± standard deviation. CeO_2-25 nm nanoparticles are commercial; nominal size (25 nm) provided by the supplier.

Table S8. Microstructural and bonding parameters.

Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
D_{UDM} (Å)	221.0 ±11.2	152.2 ± 8.5	208.1±10.8	317.6 ±15.8
ε_{UDM} ($\times10^{-4}$)	1.148 ± 0.12	18.28 ±1.45	67.98 ± 4.82	56.37 ± 4.21
q_{mWH}	2.99 ± 0.14	−1.94 ± 0.09	−0.87 ± 0.06	−0.45 ± 0.05
D_{mWH} (Å)	199.6 ±10.5	137.7 ± 8.2	189.9 ±10.4	288.6 ±14.5
ρ_{mWH} (m^{-2})	$(8.46\pm1.2)\times10^{11}$	$(4.42\pm0.6)\times10^{13}$	$(7.03\pm0.9)\times10^{14}$	$(5.14\pm0.7)\times10^{14}$
R^2_{mWH}	0.624	0.905	0.973	0.991
a (Å)	5.41208	5.42011	5.4163	5.41491
$d_{(Ce\text{-}O)}$ (Å)	2.3435	2.347	2.3453	2.3447
V_{pol} (Å³)	19.8154	19.9037	19.8618	19.8465
$U_{iso,Ce}$ (Å²)	0.0095	0.0027	0.0008	0.0074
$U_{iso,O}$ (Å²)	0.0479	0.0136	0.0669	0.0458
V_{Ce} (v.u.)	4.7549	4.7101	4.7318	4.7395
BVD_{Ce} (v.u.)	0.7549	0.7101	0.7318	0.7395

Note: Uncertainties for *D*, ε, *q*, and ρ are given in Table S6. U_{iso} values are in Å²; V_{Ce} in valence units.

Table S9. Complete Williamson–Hall parameters.

Model	Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
UDM	*D* (Å)	221.0 ±11.2	152.2 ± 8.5	208.1±10.8	317.6 ±15.8
	ε ($\times10^{-4}$)	1.148 ± 0.12	18.28 ±1.45	67.98 ± 4.82	56.37 ± 4.21
	R^2	0.097	0.827	0.949	0.984
USDM	*D* (Å)	210.4 ±12.5	135.5 ± 9.8	117.7 ±10.2	154.5 ±12.1
	σ (GPa)	−0.0103 ± 0.005	0.1646 ± 0.021	0.5328 ± 0.045	0.4109 ± 0.038
	R^2	0.078	0.665	0.579	0.520
UDEDM	*D* (Å)	213.5 ±11.8	146.9 ± 9.2	160.5 ±11.5	220.1±14.2
	u (GPa)	$(1.83\pm0.25)\times10^{-8}$	$(1.95\pm0.22)\times10^{-4}$	$(2.31\pm0.28)\times10^{-3}$	$(1.47\pm0.19)\times10^{-3}$
	R^2	0.0024	0.854	0.840	0.806
mWH	*D* (Å)	199.6 ±10.5	137.7 ± 8.2	189.9 ±10.4	288.6 ±14.5
	q	2.99 ± 0.15	−1.94 ± 0.12	−0.87 ± 0.08	−0.45 ± 0.05
	ρ (m^{-2})	$(8.46\pm1.2)\times10^{11}$	$(4.42\pm0.6)\times10^{13}$	$(7.03\pm0.9)\times10^{14}$	$(5.14\pm0.7)\times10^{14}$
	R^2	0.624	0.905	0.973	0.991
Williamson–Smallman	ρ_{screw} (m^{-2})	$(1.30\pm0.2)\times10^{12}$	$(3.28\pm0.4)\times10^{14}$	$(4.54\pm0.6)\times10^{15}$	$(3.12\pm0.4)\times10^{15}$
	ρ_{edge} (m^{-2})	$(1.45\pm0.2)\times10^{12}$	$(3.66\pm0.5)\times10^{14}$	$(5.07\pm0.7)\times10^{15}$	$(3.49\pm0.5)\times10^{15}$

Note: Uncertainties represent standard deviations from linear regression.

Table S10. Bond valence sum calculations.

	Bond	d_i (Å)	$\exp[(R_0 - d_i)/b]$	V_{Ce} contribution
CeO_2-25	$Ce\text{-}O_1$	2.3435	0.594359	0.594359
	$Ce\text{-}O_2$	2.3435	0.594359	0.594359
	$Ce\text{-}O_3$	2.3435	0.594359	0.594359
	$Ce\text{-}O_4$	2.3435	0.594359	0.594359
	$Ce\text{-}O_5$	2.3435	0.594359	0.594359
	$Ce\text{-}O_6$	2.3435	0.594359	0.594359
	$Ce\text{-}O_7$	2.3435	0.594359	0.594359
	$Ce\text{-}O_8$	2.3435	0.594359	0.594359
	V_{Ce} (sum)			4.7549
	V_O (4 × 0.594359)			2.3774
	BVD_{Ce}			0.7549
	BVD_O			0.3774
CeO_2-AA	$Ce\text{-}O_1$	2.3470	0.588764	0.588764
	$Ce\text{-}O_2$	2.3470	0.588764	0.588764
	$Ce\text{-}O_3$	2.3470	0.588764	0.588764
	$Ce\text{-}O_4$	2.3470	0.588764	0.588764
	$Ce\text{-}O_5$	2.3470	0.588764	0.588764
	$Ce\text{-}O_6$	2.3470	0.588764	0.588764
	$Ce\text{-}O_7$	2.3470	0.588764	0.588764
	$Ce\text{-}O_8$	2.3470	0.588764	0.588764
	V_{Ce} (sum)			4.7101
	V_O (4 × 0.588764)			2.3551
	BVD_{Ce}			0.7101
	BVD_O			0.3551
CeO_2-BB	$Ce\text{-}O_1$	2.3453	0.591475	0.591475
	$Ce\text{-}O_2$	2.3453	0.591475	0.591475
	$Ce\text{-}O_3$	2.3453	0.591475	0.591475
	$Ce\text{-}O_4$	2.3453	0.591475	0.591475
	$Ce\text{-}O_5$	2.3453	0.591475	0.591475
	$Ce\text{-}O_6$	2.3453	0.591475	0.591475
	$Ce\text{-}O_7$	2.3453	0.591475	0.591475
	$Ce\text{-}O_8$	2.3453	0.591475	0.591475
	V_{Ce} (sum)			4.7318
	V_O (4 × 0.591475)			2.3659
	BVD_{Ce}			0.7318
	BVD_O			0.3659
CeO_2-MM	$Ce\text{-}O_1$	2.3447	0.592435	0.592435
	$Ce\text{-}O_2$	2.3447	0.592435	0.592435
	$Ce\text{-}O_3$	2.3447	0.592435	0.592435
	$Ce\text{-}O_4$	2.3447	0.592435	0.592435
	$Ce\text{-}O_5$	2.3447	0.592435	0.592435
	$Ce\text{-}O_6$	2.3447	0.592435	0.592435
	$Ce\text{-}O_7$	2.3447	0.592435	0.592435
	$Ce\text{-}O_8$	2.3447	0.592435	0.592435
	V_{Ce} (sum)			4.7395
	V_O (4 × 0.592435)			2.3697
	BVD_{Ce}			0.7395
	BVD_O			0.3697

Note: Calculations performed with $R_0 = 2.151$ Å and $b = 0.37$ Å.

Table S11. Single-crystal elastic constants.

Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
C_{11}	319.708 ± 0.774	319.700 ± 0.767	319.652 ± 0.756	319.641 ± 0.753
C_{12}	93.652 ± 0.399	93.632 ± 0.390	93.550 ± 0.397	93.541 ± 0.396
C_{44}	36.755 ± 0.113	36.746 ± 0.124	36.728 ± 0.131	36.722 ± 0.133

Note: Uncertainties are derived from the finite strain method calculations.

Table S12. Polycrystalline elastic properties (Hill averages).

Parameters	CeO_2-25	CeO_2-AA	CeO_2-BB	CeO_2-MM
K (GPa)	169.004	168.988	168.918	168.908
G (GPa)	58.804	58.798	58.787	58.781
E (GPa)	158.077	158.062	158.028	158.013
ν	0.34411	0.34411	0.34408	0.34408
A^U	1.68046	1.6814	1.68349	1.68404

Note: Hill averages of bulk modulus K, shear modulus G, Young's modulus E, Poisson's ratio ν, and universal anisotropy index A^U.