

Supporting Information

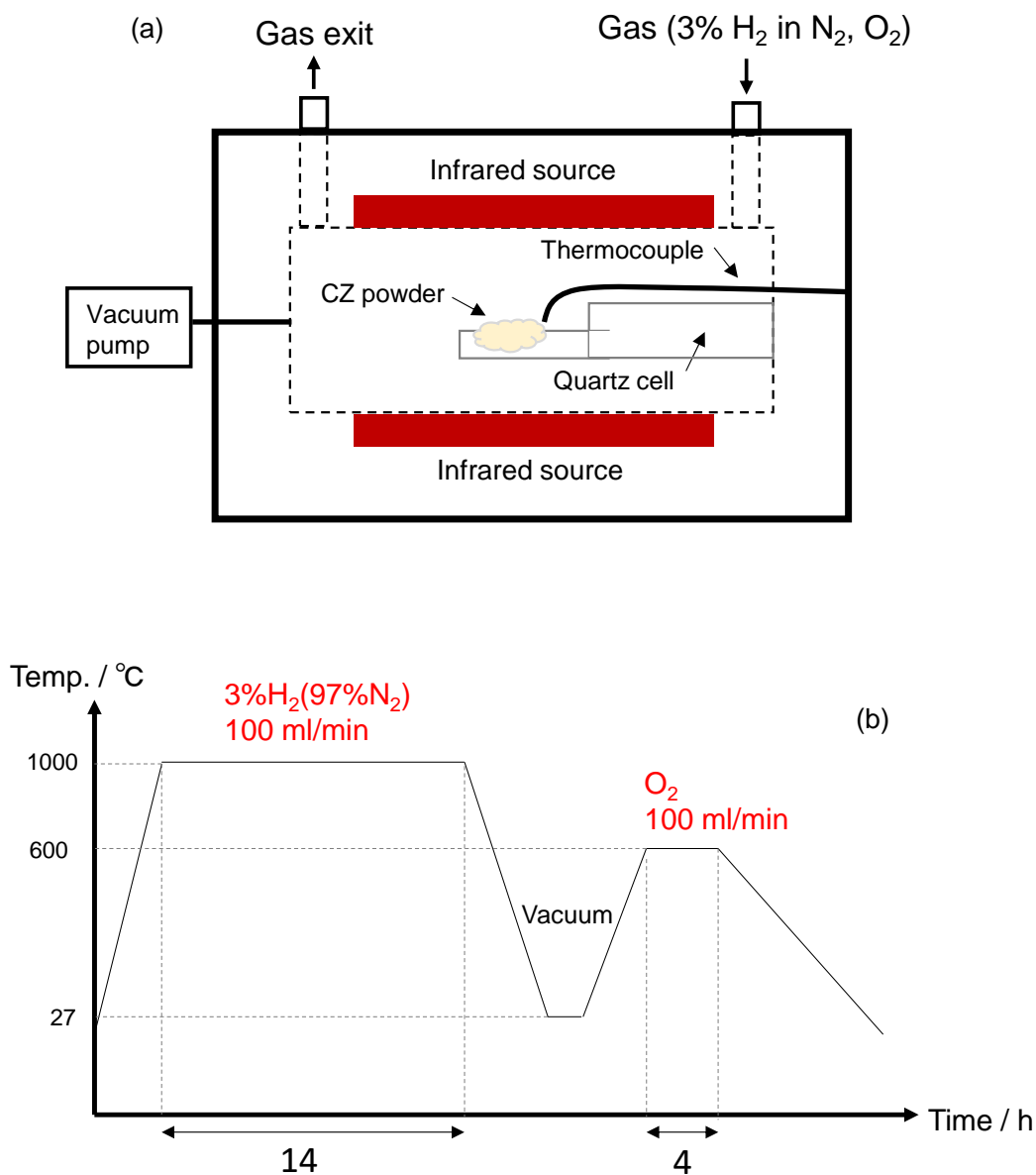


Figure S1. (a) Set-up view of the high-temperature gas furnace, (b) Schematic description of temperature program for redox treatment.

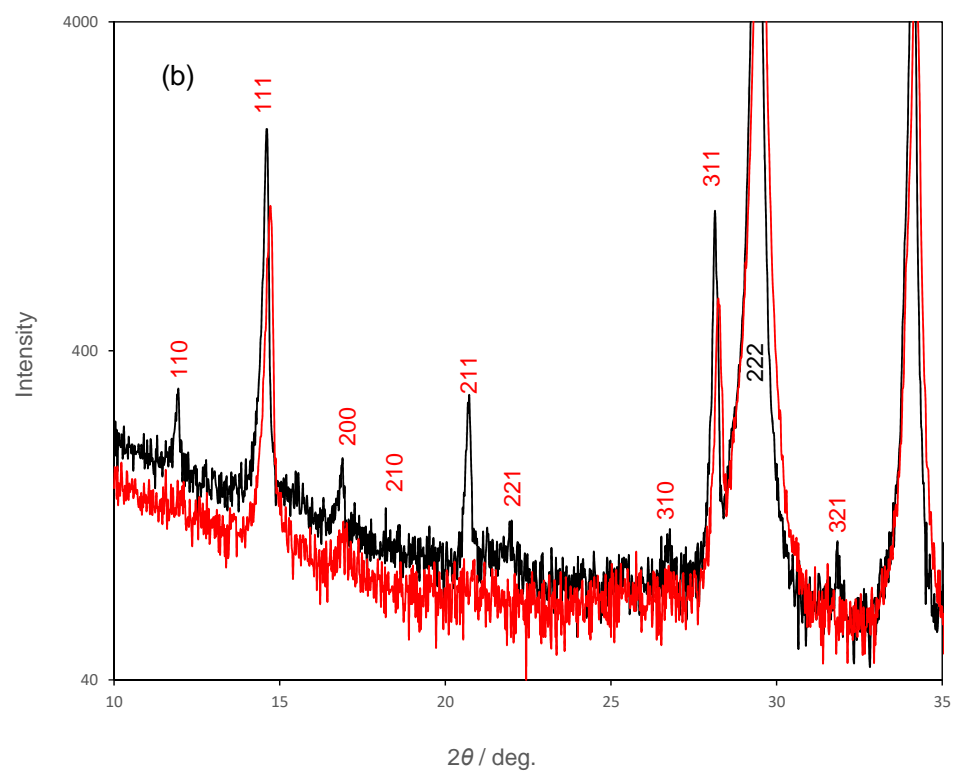
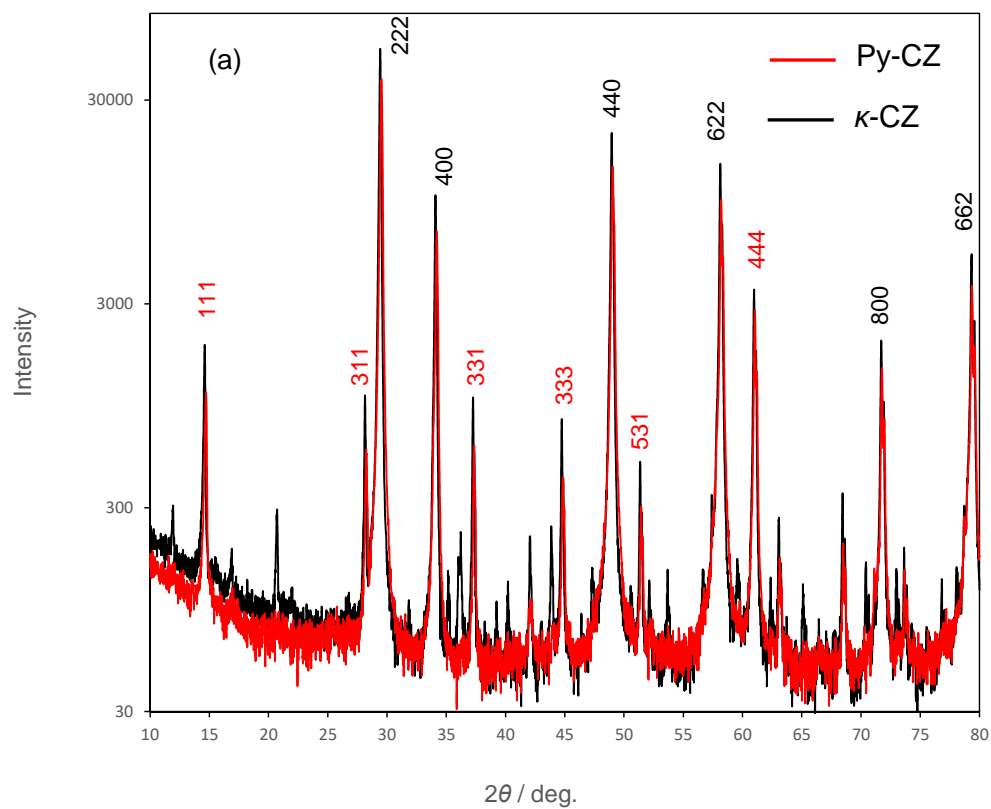


Figure S2. XRD patterns of κ -CZ and pyrochlore-type CZ as a reference: (a) $10 \leq 2\theta \leq 80^\circ$ (linear scale), (b) $10 \leq 2\theta \leq 35^\circ$ (log scale).

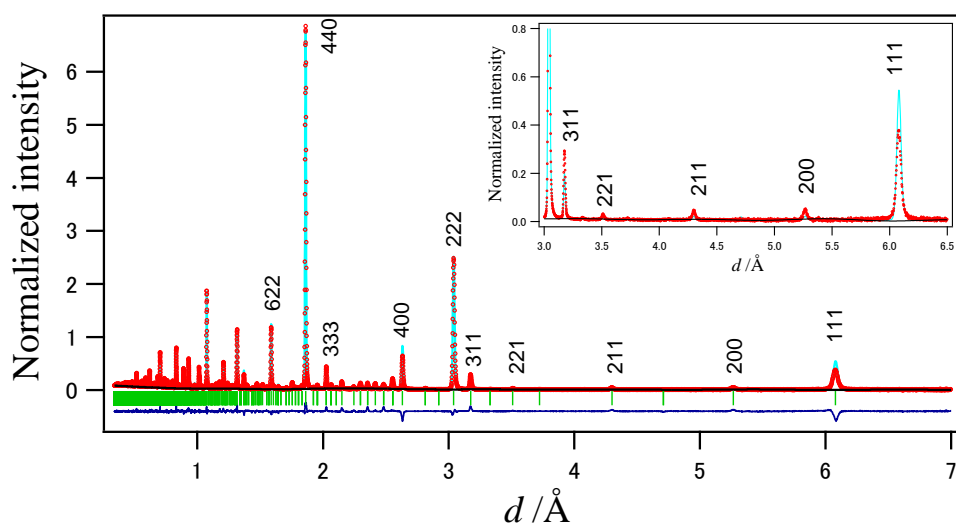


Figure S3. Rietveld refinement patterns of κ -CZ, which was refined by cubic structure (space group $P2_13$). The red “o” marks, solid light-blue line, green tick marks, and lower solid blue line indicate experimental data, calculated data, Bragg-peak positions of cubic κ -CZ, and the difference between experimental and calculated intensities, respectively. The final R factor and chi-square were $R_{wp} = 11.9\%$ and $S^2 = 42.4$, respectively.

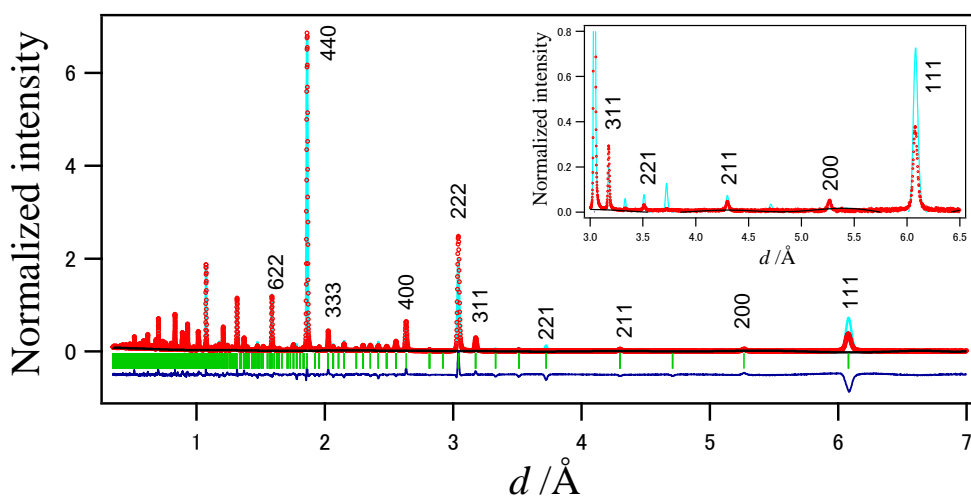


Figure S4. Rietveld refinement patterns of κ -CZ, which was refined by trigonal structure (space group $R-3m$). The red “o” marks, solid light-blue line, green tick marks, and lower solid blue line indicate experimental data, calculated data, Bragg-peak positions of cubic κ -CZ, and the difference between experimental and calculated intensities, respectively. Lattice parameters were $a=10.534199(8)$ Å, $\alpha=90.05^\circ$. The final R factor and chi-square were $R_{wp} = 16.2\%$ and $S^2 = 78.6$, respectively. Inset: The diffracted patterns for the d -spacing between 3.0 and 6.5 Å.

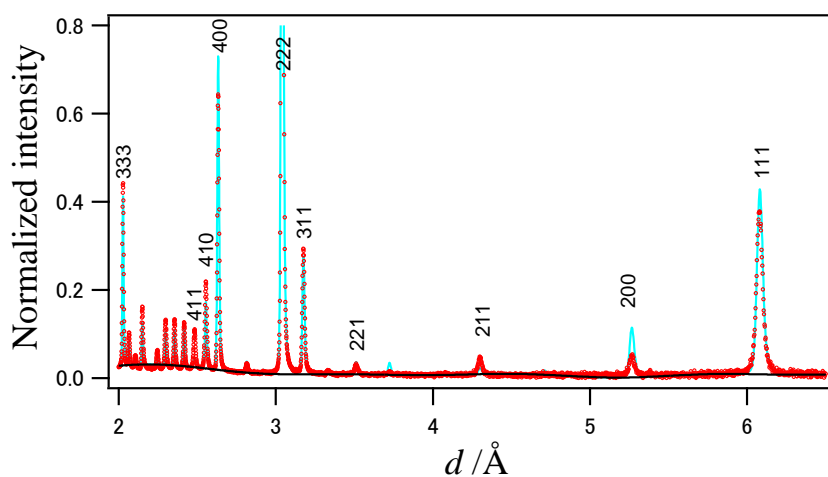


Figure S5. Rietveld refinement patterns of oxygen-deficient cubic κ -CZ ($\text{CeZrO}_{3.773(1)}$). The diffracted patterns for the d -spacing between 2.0 and 6.5 Å.

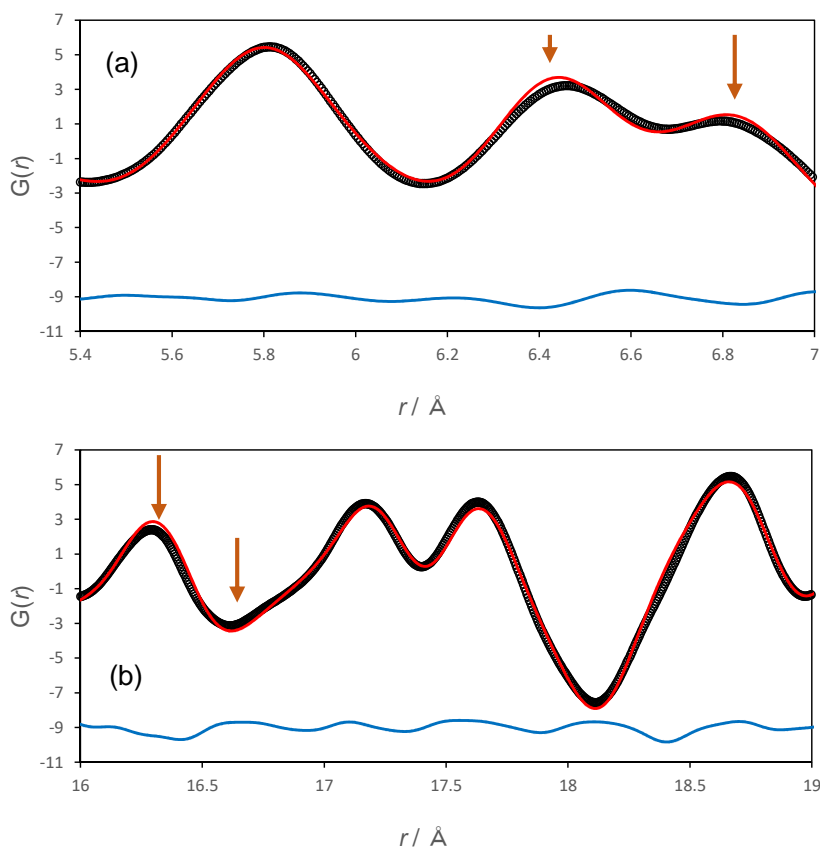


Figure S6. Neutron PDF spectra of oxygen-deficient cubic κ -CZ ($\text{CeZrO}_{3.773(1)}$) in the r range (b) $5.4 < r < 7.0$ Å and $16 < r < 19$ Å. The black “o” marks, solid red line, and lower solid blue line indicate experimental $G(r)$ data, calculated data, and the difference between experimental and calculated intensities, respectively. Arrows indicate that the differences (miss fits) were observed by the cubic phase.

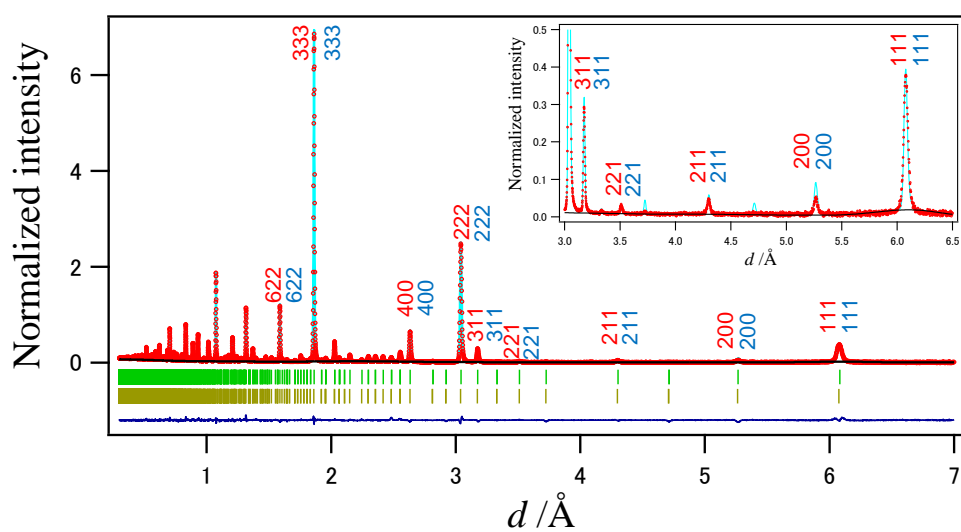


Figure S7. Rietveld refinement patterns of κ -CZ, which was refined by double-phases of cubic structure (space group $P2_13$). The red “o” marks, solid light-blue line, green tick marks, and lower solid blue line indicate experimental data, calculated data, Bragg-peak positions of cubic κ -CZ, and the difference between experimental and calculated intensities, respectively. The final results gave the following crystallographic parameters: (1) $\text{CeZrO}_{3.82(2)}$ belonging to space group $P2_13$ with $a=10.53803(4)$ \AA and (2) $\text{CeZrO}_{3.96(3)}$ belonging to space group $P2_13$ with $a=10.52825(2)$ \AA . The final R factor and chi-square were $R_{\text{wp}} = 8.17\%$ and $S^2 = 20.0$, respectively. Inset: The diffracted patterns for the d -spacing between 3.0 and 6.5 \AA .

Table S1. Crystal structure parameters of κ -CZ: (a) $P2_13$, (b) $R-3m$

Sample	κ -CZ	
Chemical formula	CeZrO _{3.82(2)}	CeZrO ₄
Crystal system	Cubic	Trigonal
Space group	$P2_13$ (#198)	$R-3m$ (#166_2)
a (Å)	10.534324(7)	10.53270(8)
$\alpha=\beta=\gamma$ (°)	90	90.012(2)
V (Å ³)	1169	1168.5
Z	16	16

(a)	site	g	x	y	z	B_{iso} (Å ²)
Ce1	4a	1	0.3814(1)	0.3814(1)	0.3814(1)	0.115(8)
Ce2	12b	1	0.1262(1)	0.1209(1)	0.3716(1)	0.115(8)
Zr1	4a	1	0.8676(1)	0.8676(1)	0.8676(1)	0.492(8)
Zr2	12b	1	0.1283(1)	0.1293(1)	0.8689(1)	0.492(8)
O1	4a	1	0.2523(1)	0.2523(1)	0.2523(1)	0.573(3)
O2	4a	0.865(2)	0.4944(1)	0.4944(1)	0.4944(1)	0.573(3)
O3	4a	1	0.7467(2)	0.7467(2)	0.7467(2)	0.573(3)
O4	4a	0.417(2)	0.0133(2)	0.0133(2)	0.0133(2)	0.573(3)
O5	12b	1	0.0049(1)	-0.0027(1)	0.79536(5)	0.573(3)
O6	12b	1	-0.0023(1)	0.0018(1)	0.23930(8)	0.573(3)
O7	12b	1	0.2523(2)	0.2506(2)	0.5074(1)	0.573(3)
O8	12b	1	0.2540(2)	0.2514(1)	0.0018(1)	0.573(3)

(b)	site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}} (\text{\AA}^2)$
Ce1	1 <i>a</i>	1	0	0	0	1.44(8)
Ce2	3 <i>e</i>	1	0	1/2	1/2	1.44(8)
Ce3	6 <i>h</i>	1	0.2013(8)	0.2013(8)	-0.0133(9)	1.44(8)
Ce4	6 <i>g</i>	1	0.2667(8)	0.7332(8)	1/2	1.44(8)
Zr1	1 <i>b</i>	1	1/2	1/2	1/2	0.38(5)
Zr2	3 <i>d</i>	1	1/2	0	0	0.38(5)
Zr3	6 <i>f</i>	1	0.2601(4)	0.7398(4)	0	0.38(5)
Zr4	6 <i>h</i>	1	0.2282(3)	0.2282(3)	0.5744(8)	0.38(5)
O1	2 <i>c</i>	1	0.1444(9)	0.1444(9)	0.1444(9)	0.49(3)
O2	6 <i>h</i>	1	0.3511(9)	0.3511(9)	0.147(1)	0.49(3)
O3	2 <i>c</i>	1	0.4118(7)	0.4118(7)	0.4118(7)	0.49(3)
O4	6 <i>h</i>	1	0.9249(8)	0.9249(8)	0.4610(8)	0.49(3)
O5	6 <i>h</i>	1	0.3085(7)	0.1049(4)	0.1049(4)	0.49(3)
O6	12 <i>i</i>	1	0.4300(8)	0.1126(8)	0.6424(8)	0.49(3)
O7	12 <i>i</i>	1	0.1544(8)	0.8548(8)	0.3568(8)	0.49(3)
O8	6 <i>h</i>	1	0.166(1)	0.361(1)	0.361(1)	0.49(3)
O9	6 <i>h</i>	1	0.3129(8)	0.6256(8)	0.6256(8)	0.49(3)
O10	6 <i>h</i>	1	0.7900(7)	0.0550(8)	0.0550(8)	0.49(3)