

# Supporting Information

## Tuning the Pr Valence State to Design High Oxygen Mobility, Redox and Transport Properties in the $\text{CeO}_2\text{-ZrO}_2\text{-PrO}_x$ Phase Diagram

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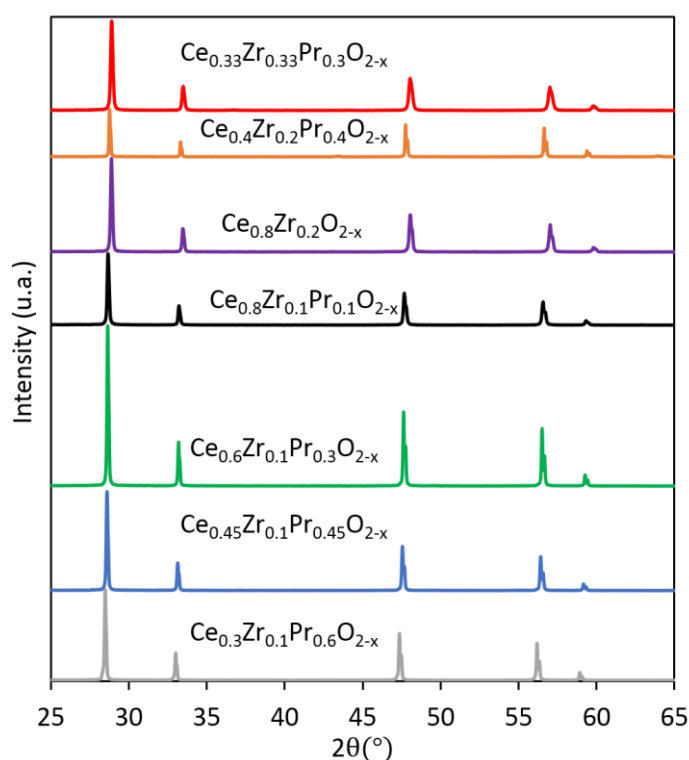
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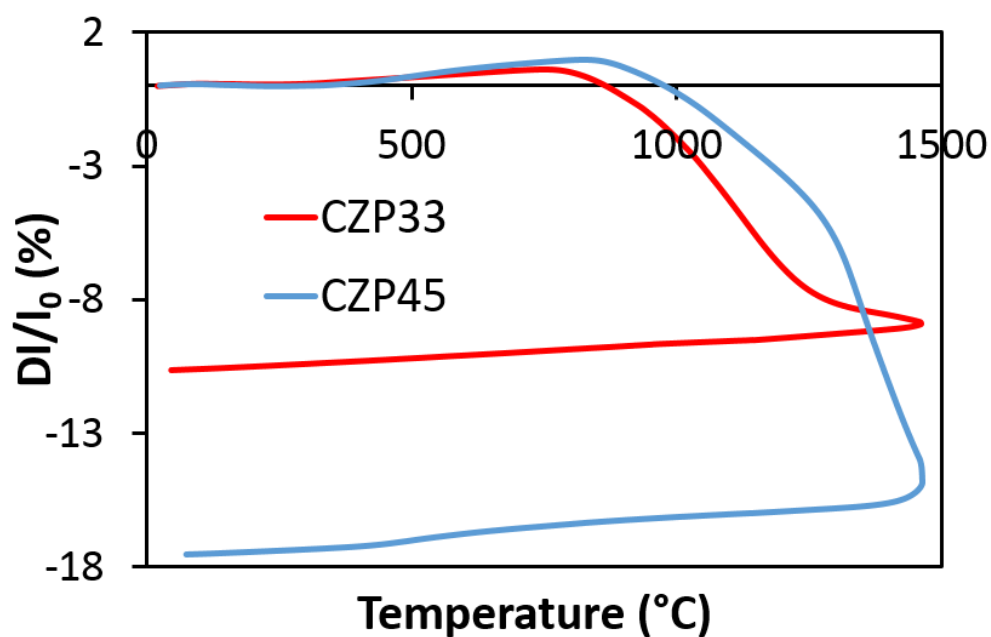
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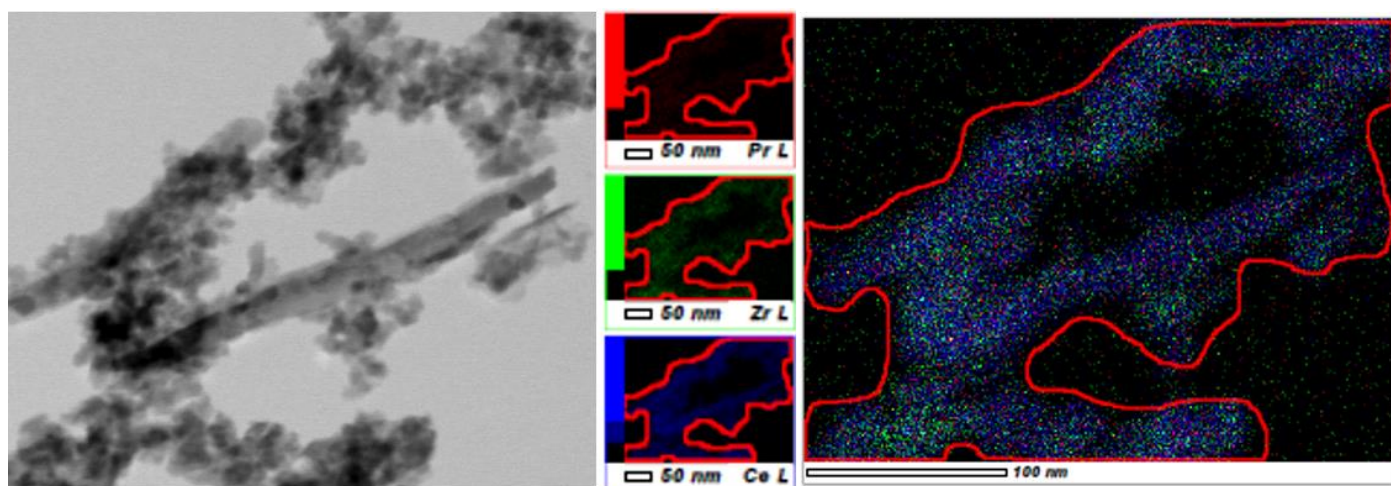
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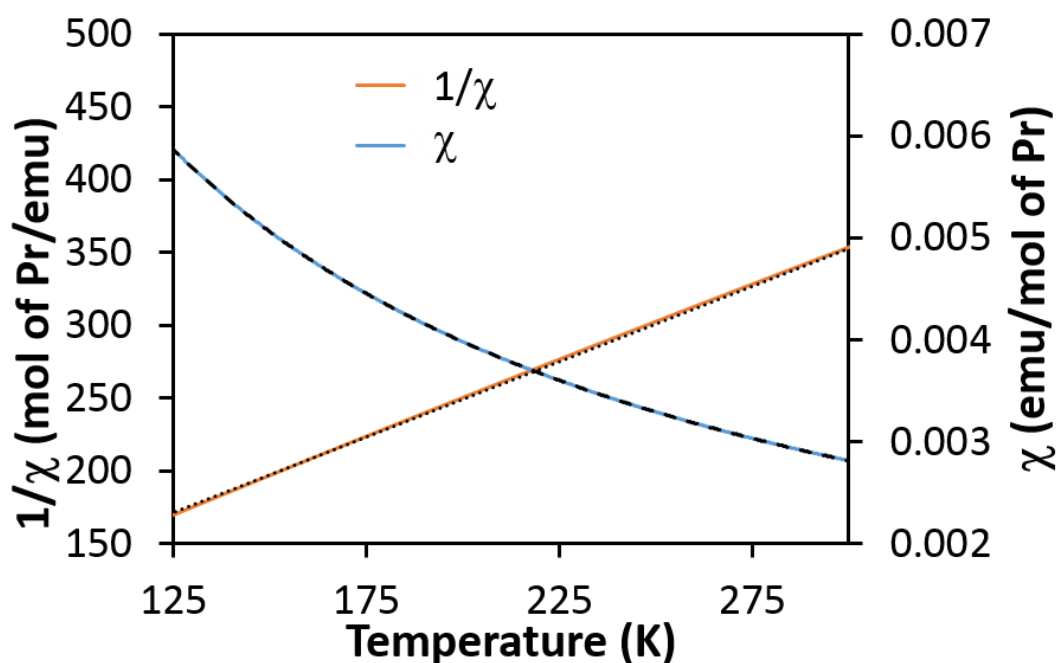
**Figure S1:** Powder XRD patterns of  $\text{Ce}_{1-x-y}\text{Zr}_x\text{Pr}_y\text{O}_{2-z}$  annealed at 1400°C under air.



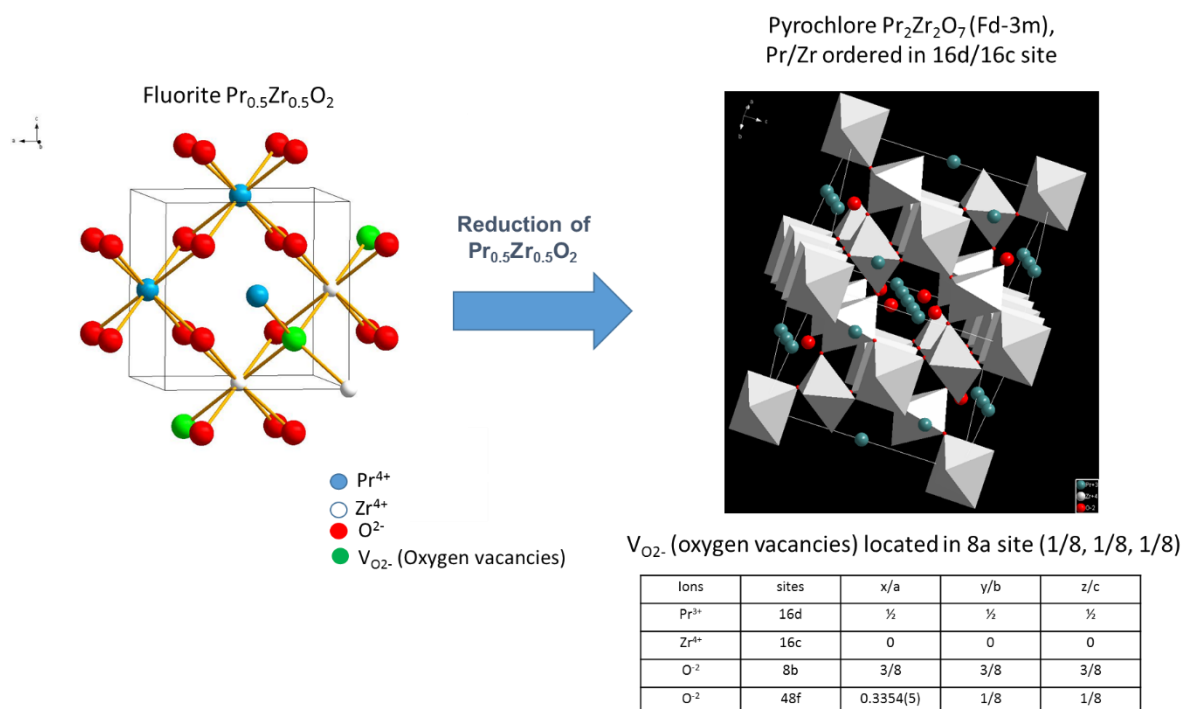
**Figure S2:** Thermal expansion behavior of CZP33 ( $\text{Ce}_{0.33}\text{Zr}_{0.33}\text{Pr}_{0.33}\text{O}_{2-x}$ ) and CZP45 ( $\text{Ce}_{0.45}\text{Zr}_{0.1}\text{Pr}_{0.45}\text{O}_{2-x}$ ) complex oxides (pellets from powders annealed at  $T=700^\circ\text{C}$  under air) from room temperature to  $T=1400^\circ\text{C}$  under air.



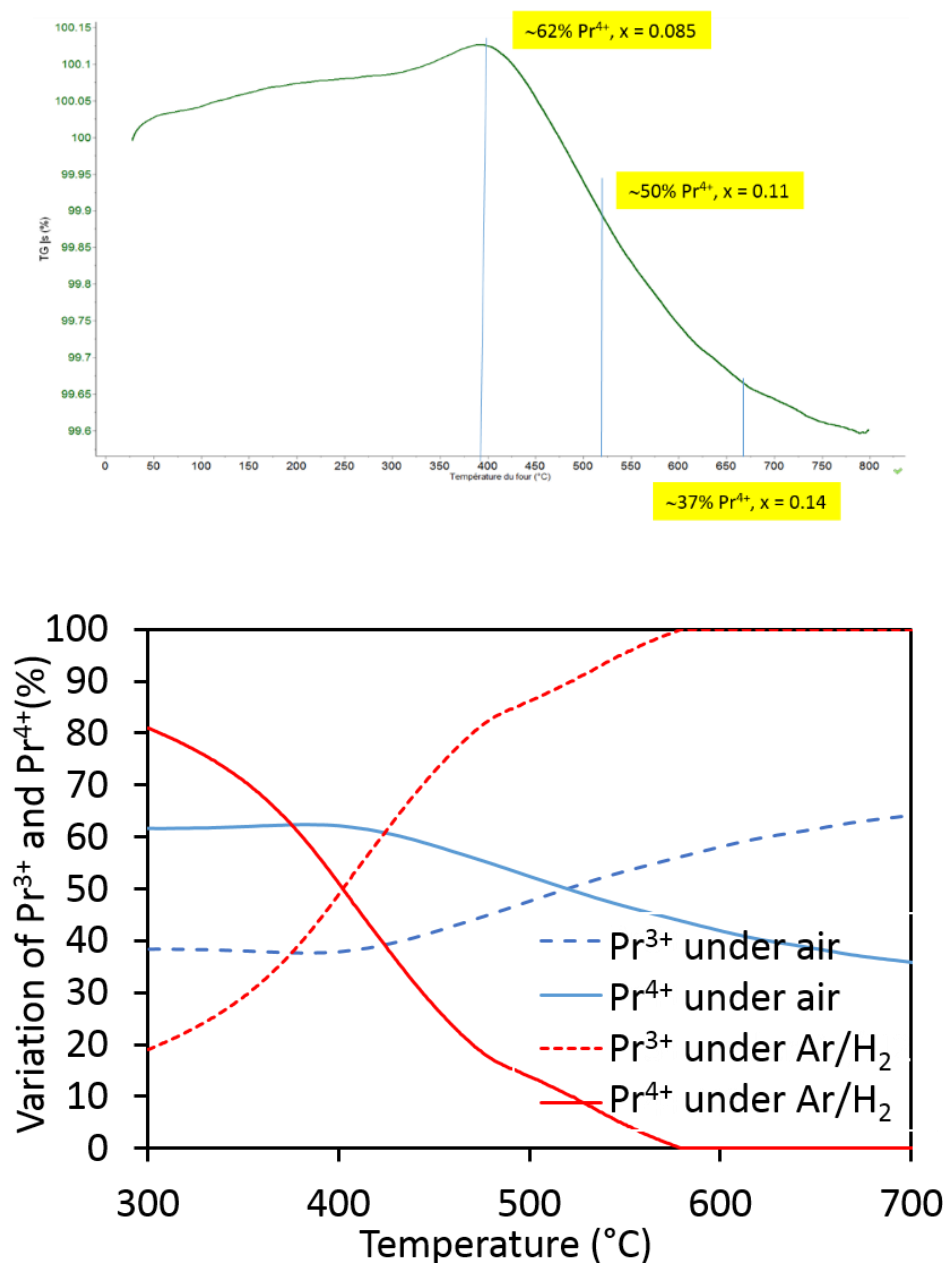
**Figure S3:** STEM light field image (left) analysis and EDX elementary analyses of CZP10 complex oxide (right, "three colors" images obtained by addition of the three elementary cartographies).



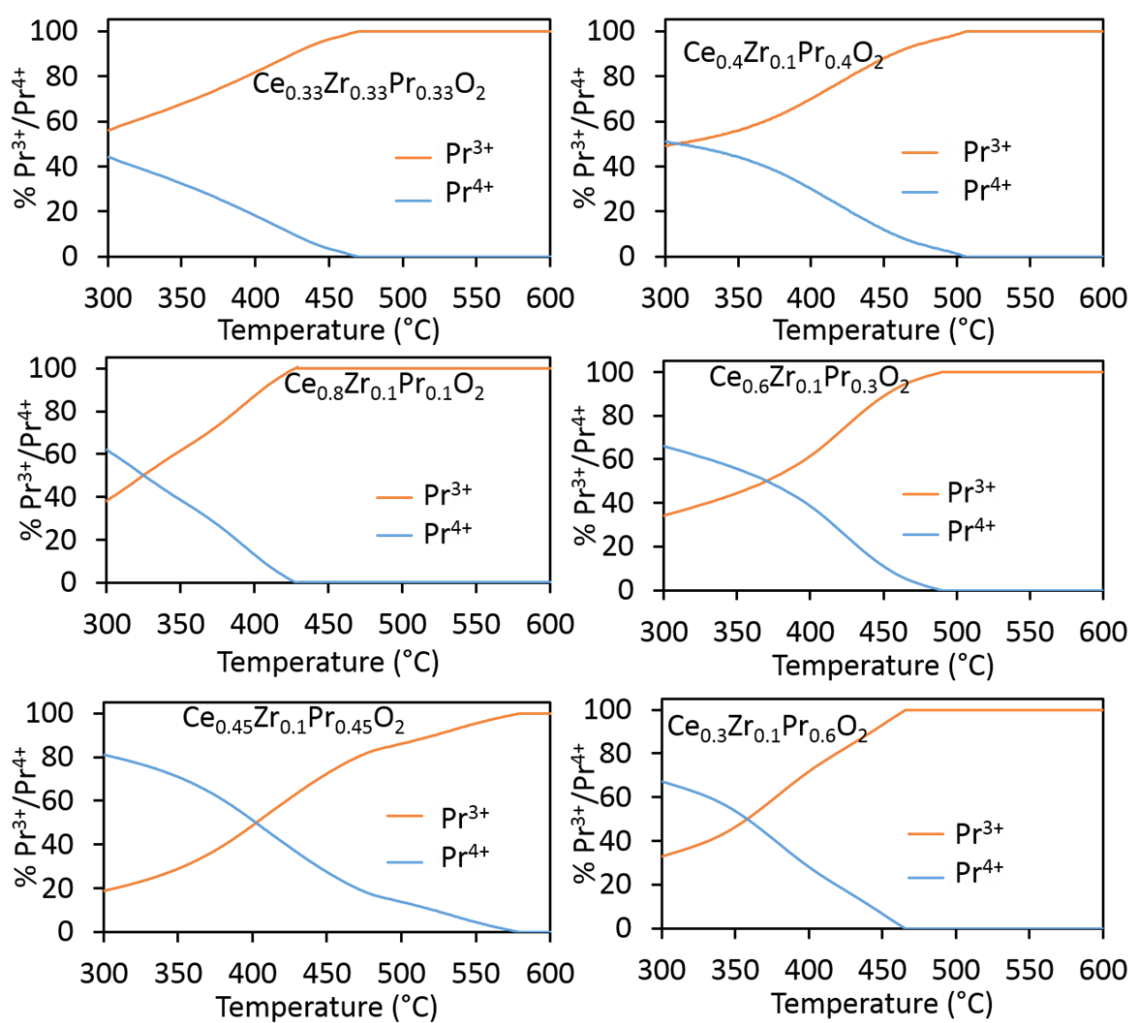
**Figure S4:** Temperature dependence of the magnetic susceptibility  $\chi$  and the inverse  $1/\chi$  for the  $\text{Ce}_{0.45}\text{Zr}_{0.1}\text{Pr}_{0.45}\text{O}_{2-z}$  compound annealed at  $700^\circ\text{C}$  under air (experiments and fittings with the Curie-Weiss law).



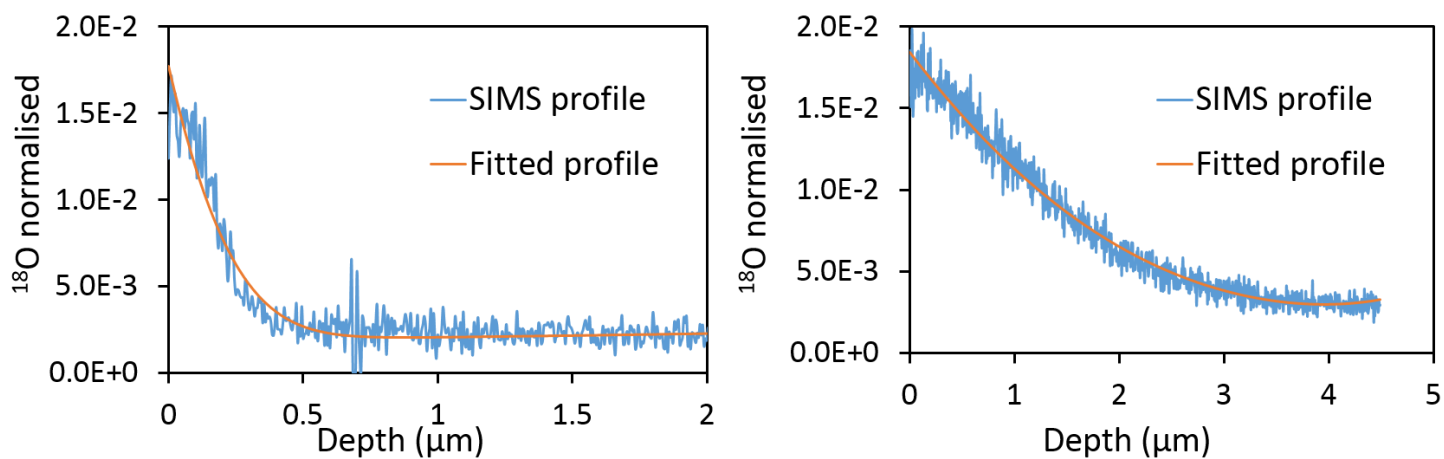
**Figure S5:** Oxygen vacancies ordering in  $\text{Pr}_2\text{Zr}_2\text{O}_7$  Pyrochlore-type structure and deduced oxygen vacancy environment ( $\text{V}_{\text{O}_2\text{-Zr}_3\text{Pr}}$  site) in the related Fluorite-type network.



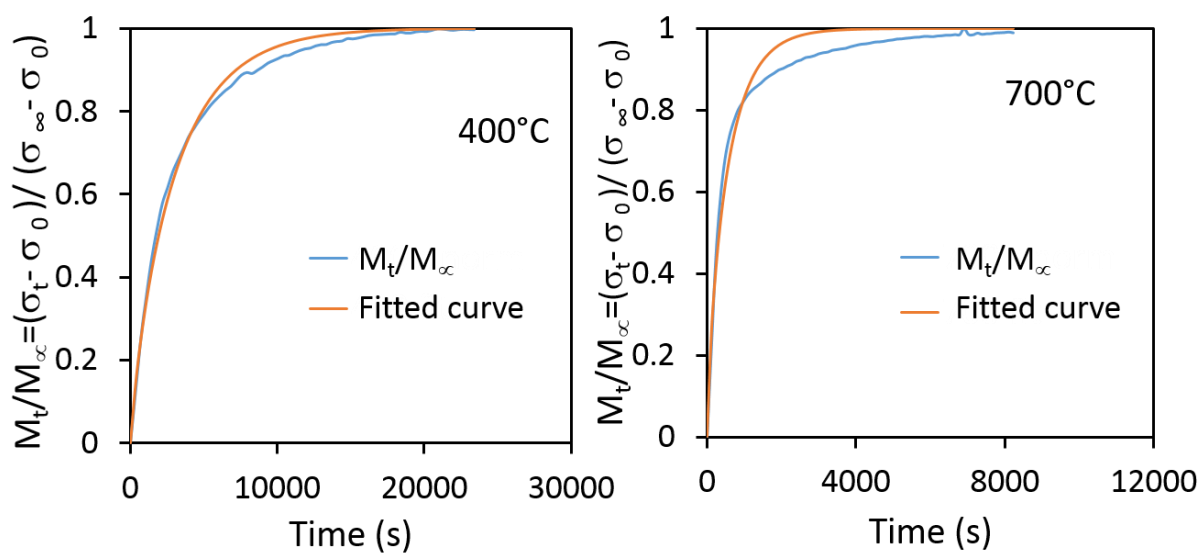
**Figure S6:** TGA under air (speed rate : 5°C/min) of  $\text{Ce}_{0.45}\text{Zr}_{0.1}\text{Pr}_{0.45}\text{O}_{2-x}$  pellet (sintered under air at 1400°C) and estimation of  $\text{Pr}^{4+}/\text{Pr}^{3+}$  molar concentration evolution versus temperature under air and  $\text{Ar}/\text{H}_2$ .



**Figure S7:** Estimation from TGA measurements under Ar/H<sub>2</sub> of  $\text{Pr}^{4+}/\text{Pr}^{3+}$  molar concentration evolution versus temperature.



**Figure S8:** Normalized oxygen concentration profiles recorded on dense pellets with CZ (left) and CZP10 (right) composition, after a preliminary  $^{18}\text{O}$  exchange performed at  $T=400^\circ\text{C}$  during 1h.



**Figure S9.:** Electronic conductivity relaxation profiles (experiments and fittings), recorded on CZP45 complex oxide and performed at  $400^\circ\text{C}$  and  $700^\circ\text{C}$ .

**Table S1:** Initial  $\text{Pr}^{4+}$  rates,  $\Delta m/m$ , deduced  $\Delta O$  exchanged oxygen and final  $\text{TR}^{4+}/\text{TR}^{3+}$  molar contents after reduction (TGA, Ar/5%  $\text{H}_2$ , or  $\text{H}_2$ /TPR, Ar/1% $\text{H}_2$ ) of complex oxides  $\text{Ce}_{1-x-y}\text{Zr}_x\text{Pr}_y\text{O}_{2-z}$  (see table 1 for oxides formulae) annealed at  $T = 700^\circ\text{C}$  under air.

Oxide	Initial Pr <sup>4+</sup> /Pr <sup>3+</sup> ratio	TGA					H <sub>2</sub> -TPR			
		T range (°C)	Δm/m (%)	ΔO	Pr <sup>4+</sup> /Pr <sup>3+</sup>	Ce <sup>4+</sup> /Ce <sup>3+</sup>	H <sub>2</sub> consumption (μmol H <sub>2</sub> /g)	ΔO	Pr <sup>4+</sup> /Pr <sup>3+</sup>	Ce <sup>4+</sup> /Ce <sup>3+</sup>
CZP33	44/56	320-470	-0.6	0.06	10/90	100/0	497	0.07	0/100	94/6
		470-700	-0.9	0.08	0/100	60/40				
		700-900	-0.4	0.04	0/100	37/63				
CZ	-	380-500	-0.4	0.04	-	90/10	497	0.08	-	80/20
		500-700	-0.8	0.09	-	69/31				
		700-900	-0.6	0.06	-	53/47				
CZP40	51/49	305-490	-0.9	0.09	3/97	100/0	-			
		490-700	-0.6	0.06	0/100	73/27				
		700-900	-0.4	0.04	0/100	56/44				
CZP10	62/38	310-460	-0.4	0.04	0/100	99/1	345	0.06	0/100	92/8
		460-700	-1.0	0.1	0/100	73/27				
		700-900	-0.6	0.06	0/100	57/43				
CZP30	66/34	305-490	-0.9	0.1	1/99	100/0	-			
		490-700	-0.8	0.08	0/100	73/27				
		700-900	-0.5	0.05	0/100	56/44				
CZP45	81/19	300-520	-1.5	0.16	11/89	100/0	1007	0.17	4/96	100/0
		520-700	-0.5	0.05	0/100	88/13				
		700-900	-0.4	0.04	0/100	72/29				
CZP60	67/33	290-430	-1.6	0.16	14/86	100/0	-			
		430-540	-0.9	0.09	0/100	69/31				
		540-700	-0.3	0.03	0/100	52/48				
		700-900	-0.3	0.03	0/100	30/70				

**Table S2:** Probabilities for various local O environments in CZP complex oxides deduced from multinomial law calculation (see table 1 for oxides formulae).

CZP33	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	1.23	4.95	7.4	4.95	1.23
1 Pr	4.95	14.8	14.8	4.95	-
2 Pr	7.4	14.8	7.4	-	-
3 Pr	4.95	4.95	-	-	-
4 Pr	1.23	-	-	-	-
CZ	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
	0.16	2.56	15.36	40.96	40.96
CZP40	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	0.16	1.28	3.84	5.12	2.56
1 Pr	1.28	7.68	15.36	10.24	-
2 Pr	3.84	15.36	15.36	-	-
3 Pr	5.12	10.24	-	-	-
4 Pr	2.56	-	-	-	-
CZP10	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	0.01	0.3	3.8	20.45	40.95
1 Pr	0.3	0.94	7.65	20.45	-
2 Pr	0.06	0.94	3.8	-	-
3 Pr	0.04	0.3	-	-	-
4 Pr	0.01	-	-	-	-
CZP30	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	0.01	0.24	2.16	8.64	12.96
1 Pr	0.12	2.16	12.96	25.92	-
2 Pr	0.54	6.48	19.44	-	-
3 Pr	1.08	6.48	-	-	-
4 Pr	0.81	-	-	-	-
CZP45	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	0.01	0.19	1.2	3.65	4.1
1 Pr	0.19	2.43	10.94	16.4	-
2 Pr	1.2	10.94	24.6	-	-
3 Pr	3.65	16.4	-	-	-
4 Pr	4.1	-	-	-	-
CZP60	0 Ce	1 Ce	2 Ce	3 Ce	4 Ce
0 Pr	0.01	0.12	0.5	1.08	0.81
1 Pr	0.24	2.16	6.48	6.48	-
2 Pr	2.16	12.96	19.44	-	-
3 Pr	8.68	25.92	-	-	-
4 Pr	12.96	-	-	-	-