

Electronic Supplementary Information (ESI)

Redox properties of nanostructured lanthanide-doped ceria spheres prepared by microwave assisted hydrothermal homogeneous co-precipitation

Fernando F. Muñoz^a, Leandro M. Acuña^{a,b}, Cecilia A. Albornoz^c, A. Gabriela Leyva^{c,d},

Richard T. Baker^e and Rodolfo O. Fuentes^{b,c}

^a CINSO (Centro de Investigaciones en Sólidos), CONICET-CITEDEF, J.B. de La Salle 4397, 1603 Villa Martelli, Buenos Aires, Argentina.

^b CONICET, Buenos Aires, Argentina.

^c Departamento de Física, Centro Atómico Constituyentes, CNEA, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina.

^d Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín, Av. Gral. Paz 1499, (1650) San Martín, Buenos Aires, Argentina.

^e EaStChem, School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom.

* Corresponding author: rofuentes@conicet.gov.ar.

Table S1. Structural parameters and standard Rietveld agreement factors for nanostructured GDC10 spheres (HMW).

Atmosphere	Air*	5% H ₂ /He	5% H ₂ /He	Air*	Air*
<i>T</i> (°C)	25	300	500	500	25
<i>a</i> (Å)	5.4213(6)	5.4305(9)	5.4514(8)	5.4456(8)	5.4201(8)
<i>V</i> (Å ³)	159.336(3)	160.149(5)	162.004(4)	161.490(4)	159.233(4)
<i>R_p</i>	3.49	3.88	4.48	4.53	3.50
<i>R_{wp}</i>	4.11	4.61	4.99	5.11	4.34
<i>R_e</i>	2.67	2.64	2.72	2.78	2.57
χ^2	2.37	3.05	3.38	3.37	2.85

*Air corresponds to synthetic air (21% O₂/N₂).

Table S2. Structural parameters and standard Rietveld agreement factors for nanostructured GDC20 spheres (HMW).

Atmosphere	Air*	5% H ₂ /He	5% H ₂ /He	Air*	Air*
<i>T</i> (°C)	25	300	500	500	25
<i>a</i> (Å)	5.4238(4)	5.4336(6)	5.4560(5)	5.4462(8)	5.4219(7)
<i>V</i> (Å ³)	159.562(4)	160.424(5)	162.417(5)	161.548(3)	159.388(4)
<i>R_p</i>	3.47	3.40	4.14	3.70	3.73
<i>R_{wp}</i>	4.18	4.02	4.66	4.26	4.25
<i>R_e</i>	2.75	2.66	2.72	2.78	2.72
χ^2	2.32	2.29	2.93	2.34	2.45

*Air corresponds to synthetic air (21% O₂/N₂).

Table S3. Structural parameters and standard Rietveld agreement factors for nanostructured PrDC10 spheres (HMW).

Atmosphere	Air*	5% H ₂ /He	5% H ₂ /He	Air*	Air*
<i>T</i> (°C)	25	300	500	500	25
<i>a</i> (Å)	5.4214(6)	5.4384(9)	5.4661(8)	5.4456(8)	5.4158(8)
<i>V</i> (Å ³)	159.343(3)	160.851(5)	163.314(4)	161.490(4)	158.852(4)
<i>R_p</i>	2.88	2.93	3.74	3.69	3.07
<i>R_{wp}</i>	3.65	4.18	4.42	4.49	3.87
<i>R_e</i>	2.58	2.44	2.57	2.59	2.55
χ^2	2.00	2.93	2.97	3.00	2.30

*Air corresponds to synthetic air (21% O₂/N₂).

Table S4. Structural parameters and standard Rietveld agreement factors for nanostructured PrDC20 spheres (HMW).

Atmosphere	Air*	5% H ₂ /He	5% H ₂ /He	Air*	Air*
<i>T</i> (°C)	25	300	500	500	25
<i>a</i> (Å)	5.4278(6)	5.4493(9)	5.4887(8)	5.4508(8)	5.4177(8)
<i>V</i> (Å ³)	159.909(2)	161.819(5)	165.351(4)	161.951(4)	159.021(4)
<i>R_p</i>	2.95	3.05	3.08	3.29	2.89
<i>R_{wp}</i>	3.77	3.83	3.96	4.12	3.70
<i>R_e</i>	2.35	2.25	2.38	2.37	2.31
χ^2	2.57	2.89	2.76	3.03	2.57

*Air corresponds to synthetic air (21% O₂/N₂).

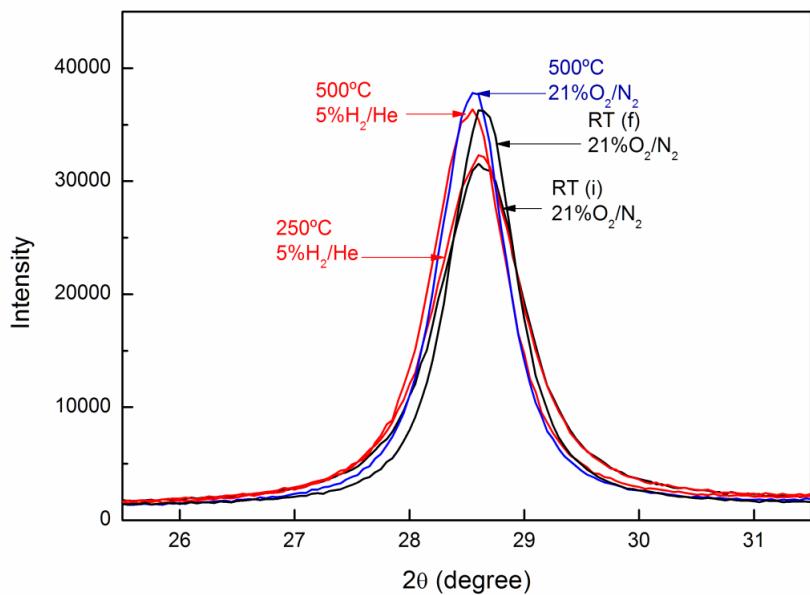


Figure S1. SR-XRD patterns in the vicinity of the 111 reflection for nanostructured GDC10 spheres. RT (i) and (f) indicate the initial state (fresh sample) and final state (after exposure to the different redox conditions described in the text) of the sample, respectively.

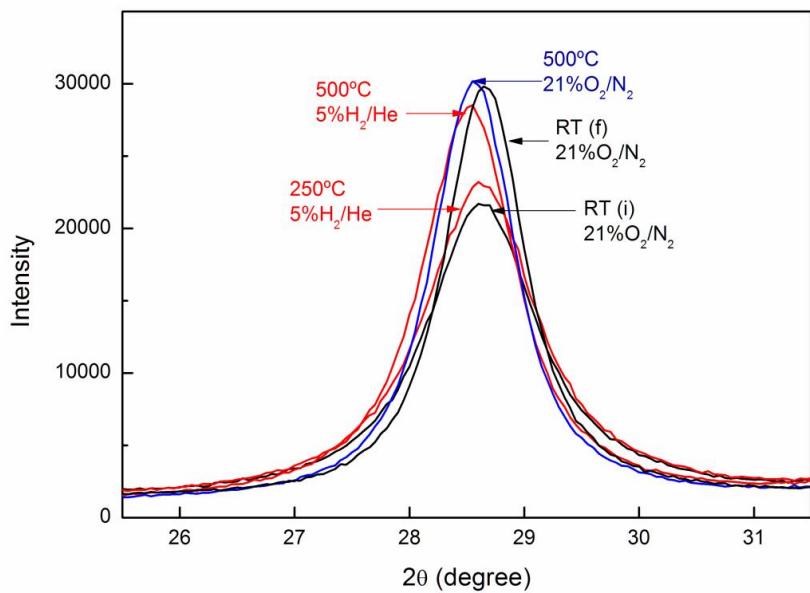


Figure S2. SR-XRD pattern in the vicinity of the 111 reflection for nanostructured GDC20 spheres. RT (i) and (f) indicate the initial state (fresh sample) and final state (after exposure to the different redox conditions described in the text) of the sample, respectively.

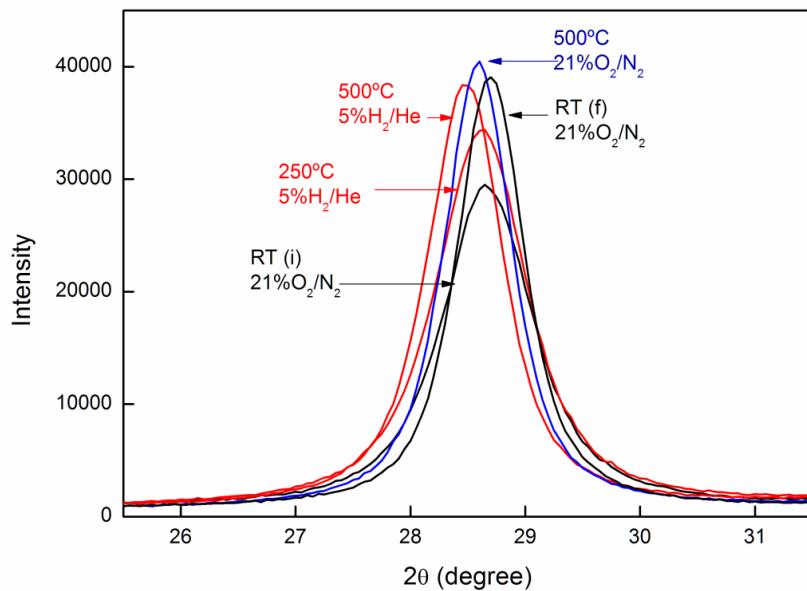


Figure S3. SR-XRD pattern in the vicinity of the 111 reflection for nanostructured PrDC10 spheres. RT (i) and (f) indicate the initial state (fresh sample) and final state (after exposure to the different redox conditions described in the text) of the sample, respectively.

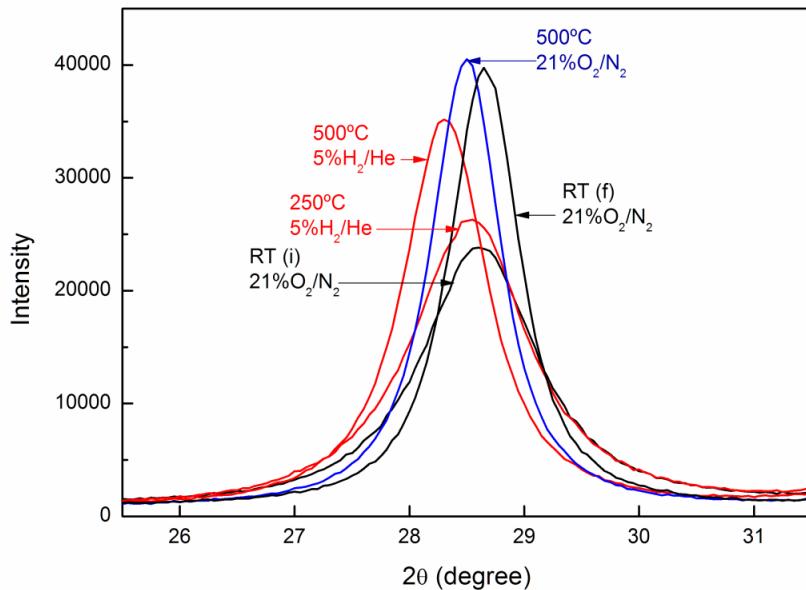


Figure S4. SR-XRD pattern in the vicinity of the 111 reflection for nanostructured PrDC20 spheres. RT (i) and (f) indicate the initial state (fresh sample) and final state (after exposure to the different redox conditions described in the text) of the sample, respectively.

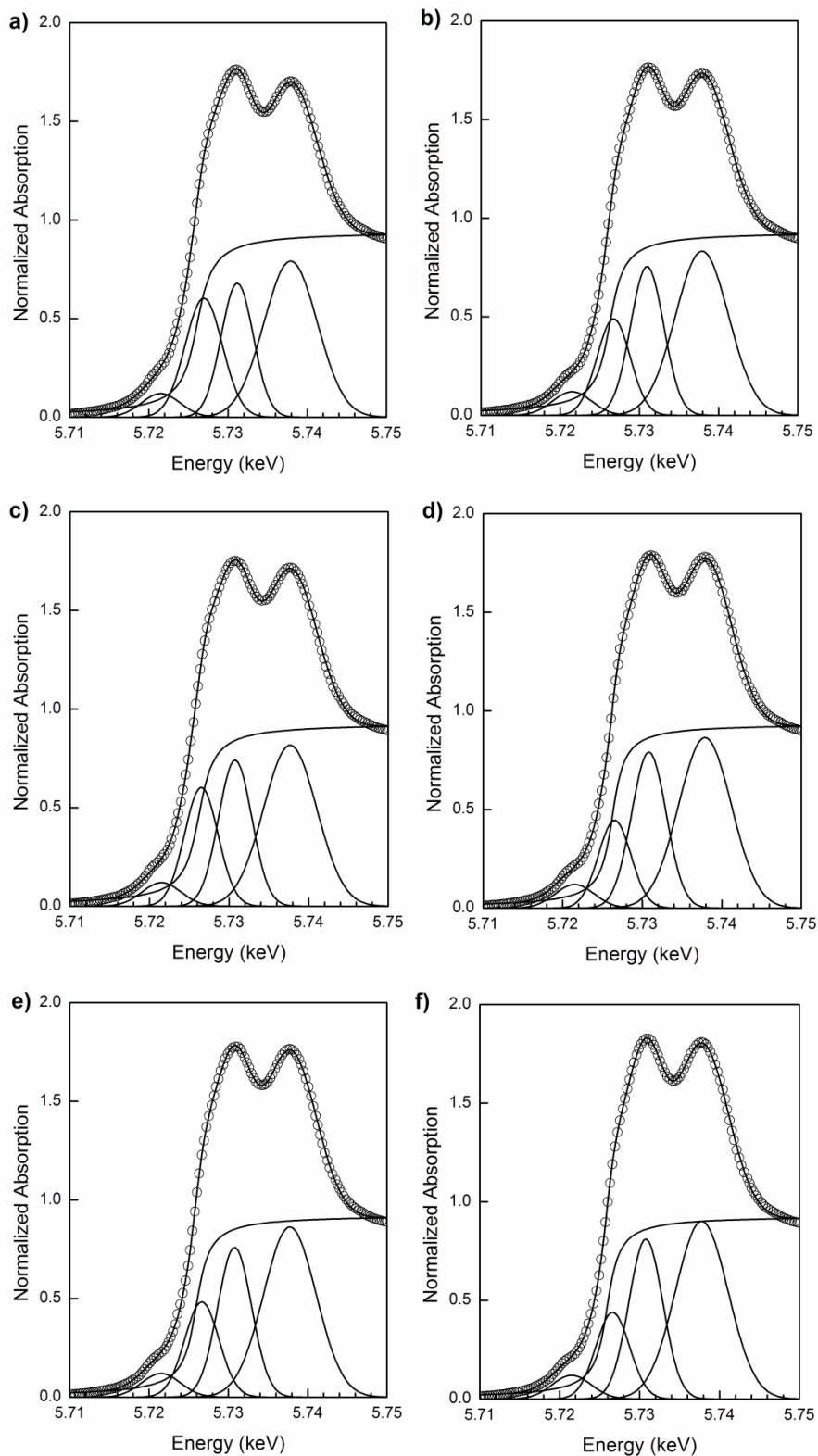


Figure S5. Normalized XANES spectra at the Ce L₃-edge for GDC10, GDC20 and PrDC20 at 500 °C under (a, c and e) reducing and (b, d and f) oxidizing conditions, respectively, showing the experimental data (empty circles), four Gaussian peaks (A–D), one arctangent function obtained by least-squares fitting and the sum of all five functions (continuous line).