Electronic supplementary information (ESI)

Lattice expansion and oxygen non-stoichiometry of nanocrystalline ceria

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No	Precipitation conditions	Additional treatment		Particle size, nm
		Type of treatment	Temperature and duration	
1[a]	0.08 M aqueous solution of $Ce(NO_3)_3$ + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	4.7
2[a]		Annealing[b]	200°C, 2h	4.8
3[a]		Annealing	300°C, 2h	5.4
4[a]		Annealing	400°C, 2h	6.4
5[a]		Annealing	500°C, 2h	8.9
6[a]		Annealing	600°C, 2h	12.9
7[a]		Annealing	700°C, 2h	23.5
8[a]	0.08 M aqueous solution of $Ce(NO_3)_3$ + 3 M NH_4OH; freeze-drying -30…30°C, 48 h	–	–	4.8
9[a]		Annealing	200°C, 2h	4.6
10[a]		Annealing	300°C, 2h	5.3
11[a]		Annealing	400°C, 2h	6.0
12[a]		Annealing	500°C, 2h	8.1
13[a]		Annealing	600°C, 2h	10.9
14[a]		Annealing	700°C, 2h	17.6
15	0.02 M $Ce(NO_3)_3$ in H_2O/*i*-PrOH (1/19 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	4.8
16		Annealing	200°C, 2 h	5.1
17		Annealing	400°C, 2 h	7.8
18		Annealing	500°C, 2h	14.0
19		Annealing	700°C, 2h	33.8
20	0.08 M $Ce(NO_3)_3$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	4.5
21		Annealing	200°C, 2 h	4.9
22		Annealing	400°C, 2 h	6.4
23		Annealing	600°C, 2h	14
24[c]		Annealing	700°C, 2h	21.8
25[c]	0.02 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH	Drying	50°C, 24 h	2.6
26[c]	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH	Drying	50°C, 24 h	2.6
27[c]	0.3 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH	Drying	50°C, 24 h	3.1
28	0.8 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH	Drying	50°C, 24 h	3.3
29	0.02 M aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + 3 M NH_4OH	Drying	50°C, 24 h	2.7
30	0.08 M aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + 3 M NH_4OH	Drying	50°C, 24 h	2.5
31	0.3 M aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + 3 M NH_4OH	Drying	50°C, 24 h	3.1
32[c]	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH at 50°C	Drying	50°C, 24 h	3.9

Table S1. Particle size of ceria samples synthesized by various methods.

[a] See also: V. K. Ivanov, O. S. Polezhaeva, A. E. Baranchikov, A. B. Shcherbakov, *Inorg. Mater.*, 2010, **46**, 43.

[b] Annealing was performed under ambient atmosphere

[c] See also V. K. Ivanov, A. E. Baranchikov, Yu. D. Tretyakov, *Khimicheskaya Tekhnologiya*, 2010, **11**, 139 (in Russian).

33[c]	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH at 80°C	Drying	50°C, 24 h	4.2
34[c]	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/19 v/v) + 3 M NH_4OH at 50°C	Drying	50°C, 24 h	2.7
35	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/19 v/v) + 3 M NH_4OH at 80°C	Drying	50°C, 24 h	4.4
36	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/19 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	2.3
37		Annealing	300°C, 2 h	5.8
38		Annealing	300°C, 4 h	5.8
39		Annealing	300°C, 8 h	6.1
40		Annealing	400°C, 2 h	7.7
41		Annealing	400°C, 4 h	7.8
42		Annealing	400°C, 8 h	8.1
43		Annealing	500°C, 2 h	9.8
44		Annealing	500°C, 4 h	10.1
45		Annealing	500°C, 8 h	10.2
46		Annealing	600°C, 2 h	13.6
47		Annealing	600°C, 4 h	14.7
48		Annealing	600°C, 8 h	15.9
49	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,2344 M, respectively), 60°C, 12 h	Drying	50°C, 24 h	4.4
50	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA[d] (0.0059 and 0,0586 M, respectively), 60°C, 1 h	Drying	50°C, 24 h	4.6
51	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,1406 M, respectively), 60°C, 1 h	Drying	50°C, 24 h	4.8
52	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,2344 M, respectively), 50°C, 1 h	Drying	50°C, 24 h	2.4
53	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,0176 M, respectively), 90°C, 1 h	Drying	50°C, 24 h	7.0
54	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,1406 M, respectively), 90°C, 1 h	Drying	50°C, 24 h	4.4
55	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,2344 M, respectively), 90°C, 1 h	Drying	50°C, 24 h	4.0
56	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,0586 M, respectively), 30°C, 1 h	Drying	50°C, 24 h	4.1
57	Aqueous solution of $(NH_4)_2Ce(NO_3)_6$ + HMTA (0.0059 and 0,1416 M, respectively), 180°C (HTMW), 1 h	Drying	50°C, 24 h	7.9
58[e]	0.08 M $Ce(NO_3)_3$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	HTMW[f]	120°C, 15 min	4.9
59[e]		HTMW	120°C, 3 h	5.0
60[e]		HTMW	150°C, 3 h	5.0
61[e]		HTMW	180°C, 3 h	5.2
62[e]		HTMW	210°C, 15 min	5.1
63[e]		HTMW	210°C, 3 h	6.0
64	0.08 M $Ce(NO_3)_3$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH; precipitate was not dried	HTMW	210°C, 3 h	11.0
65		HTMW	230°C, 6 h	11.2
66		HTMW	230°C, 1 h	10.2
67		HTMW	190°C, 1 h	10.0
68		HTMW	180°C, 3 h	12.0
69		Hydrothermal	180°C, 6 h	15.0

Table S1 (contd.). Particle size of ceria samples synthesized by various methods.

[d] Hexamethylenetetramine

[e] See also V. K. Ivanov, G. P. Kopitsa, A. E. Baranchikov, S. V. Grigor'ev, V. V. Runov, V. M. Haramus, *Russ. J. Inorg. Chem.*, 2009, **54**, 1857.

[f] Hydrothermal-microwave treatment in aqueous media

70	0.08 M $Ce(SO_4)_2$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	2.4
71		HTMW	120°C, 3 h	2.3
72		HTMW	150°C, 3 h	2.6
73		HTMW	180°C, 3 h	4.9
74		HTMW	210°C, 15 min	4.0
75		HTMW	210°C, 3 h	4.5
76[c]	0.08 M $(NH_4)_2Ce(NO_3)_6$ in H_2O/*i*-PrOH (1/6 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	2.2
77		HTMW	120°C, 3 h	3.3
78		HTMW	150°C, 3 h	3.6
79		HTMW	180°C, 3 h	4.7
80		HTMW	210°C, 3 h	6.3
81	0.08 M $CeCl_3$ in H_2O/*i*-PrOH (1/1 v/v) + 3 M NH_4OH; precipitate was dried in air at 50°C for 24 h	–	–	4.5
82		Hydrothermal	120°C, 3 h	4.6
83		Hydrothermal	150°C, 3 h	4.5
84		Hydrothermal	180°C, 3 h	4.7
85		Hydrothermal	210°C, 3 h	7.4
86	0.08 M aqueous solution of $Ce(NO_3)_3$ + 3 M NH_4OH at pH 7	Drying	50°C, 24 h	2.2
87[g]	Aqueous solution of $Ce(NO_3)_3$ + HMTA (0.0059 M and 0.0586 M, respectively), 60°C, 1 h	Drying	50°C, 24 h	7.0
88[g]	Aqueous solution of $Ce(NO_3)_3$ + HMTA (0.0039 M and 0,0117 M, respectively), 60°C, 1 h	Drying	50°C, 24 h	12.0
89[g]	Aqueous solution of $Ce(NO_3)_3$ + HMTA (0.0039 M and 0,1576 M, respectively), 60°C, 1 h	Drying	50°C, 24 h	9.0
90[h]	0.01 M aqueous solution of $Ce(NO_3)_3$ + Amberlite IRA 410 CL (in OH-form) at pH 10, precipitate was dried in air at 50°C for 24 h	HTMW	130°C, 3 h	5.4
91[h]		HTMW	150°C, 3 h	6.0
92[h]		HTMW	190°C, 2 h	5.8

Table S1 (contd.). Particle size of ceria samples synthesized by various methods.

[g] See also O. S. Polezhaeva, N. V. Yaroshinskaya, V. K. Ivanov, *Inorg. Mater.*, 2008, **44**, 51.
[h] See also V. K. Ivanov, O. S. Polezhaeva, A. B. Shcherbakov, D. O. Gil', Yu. D. Tret'yakov, *Russ. J. Inorg. Chem.*, 2010, **55**, 1.

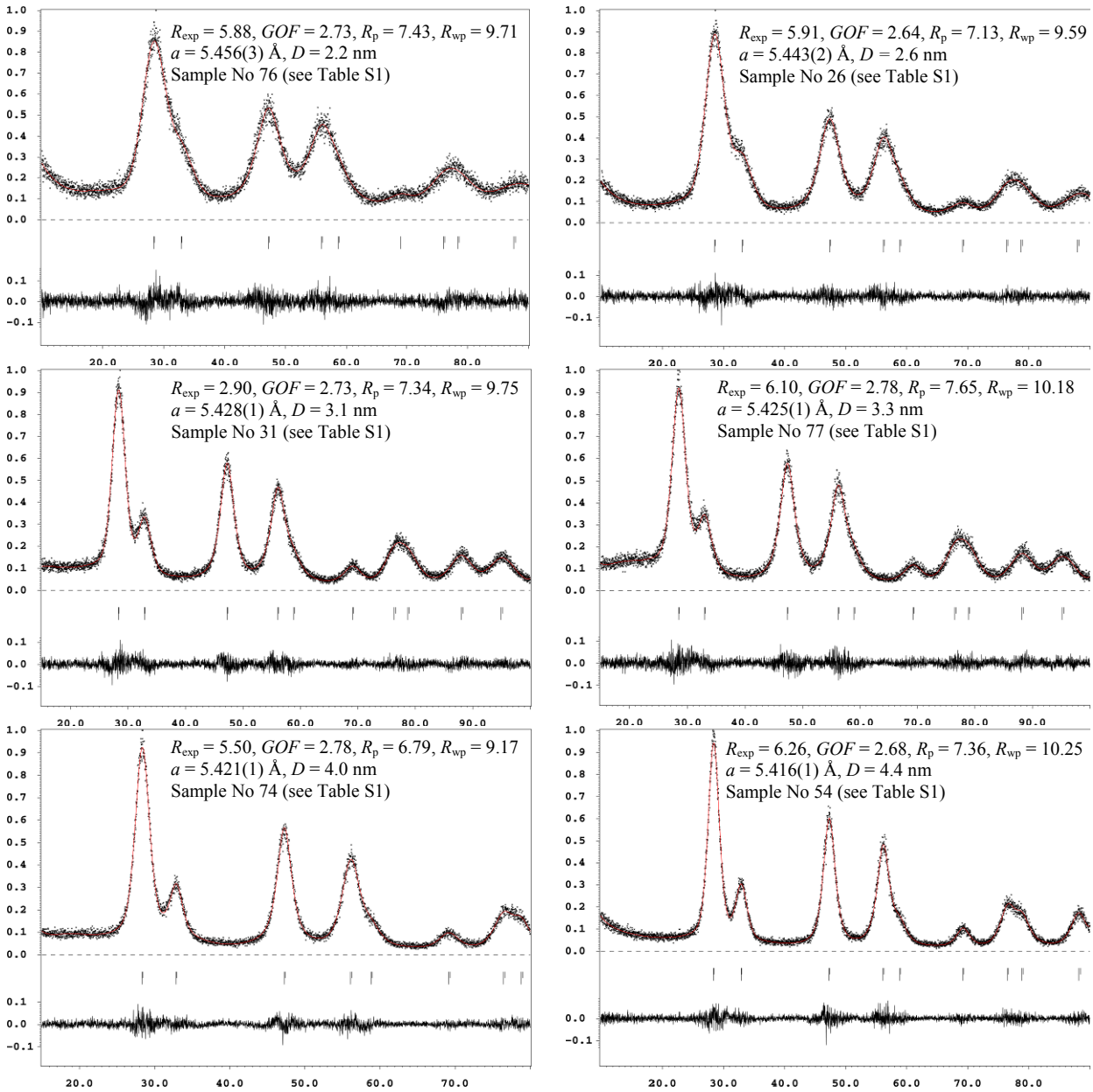


Figure S1. Rietveld refinement of selected ceria samples (particle size 2.2–23.5 nm).

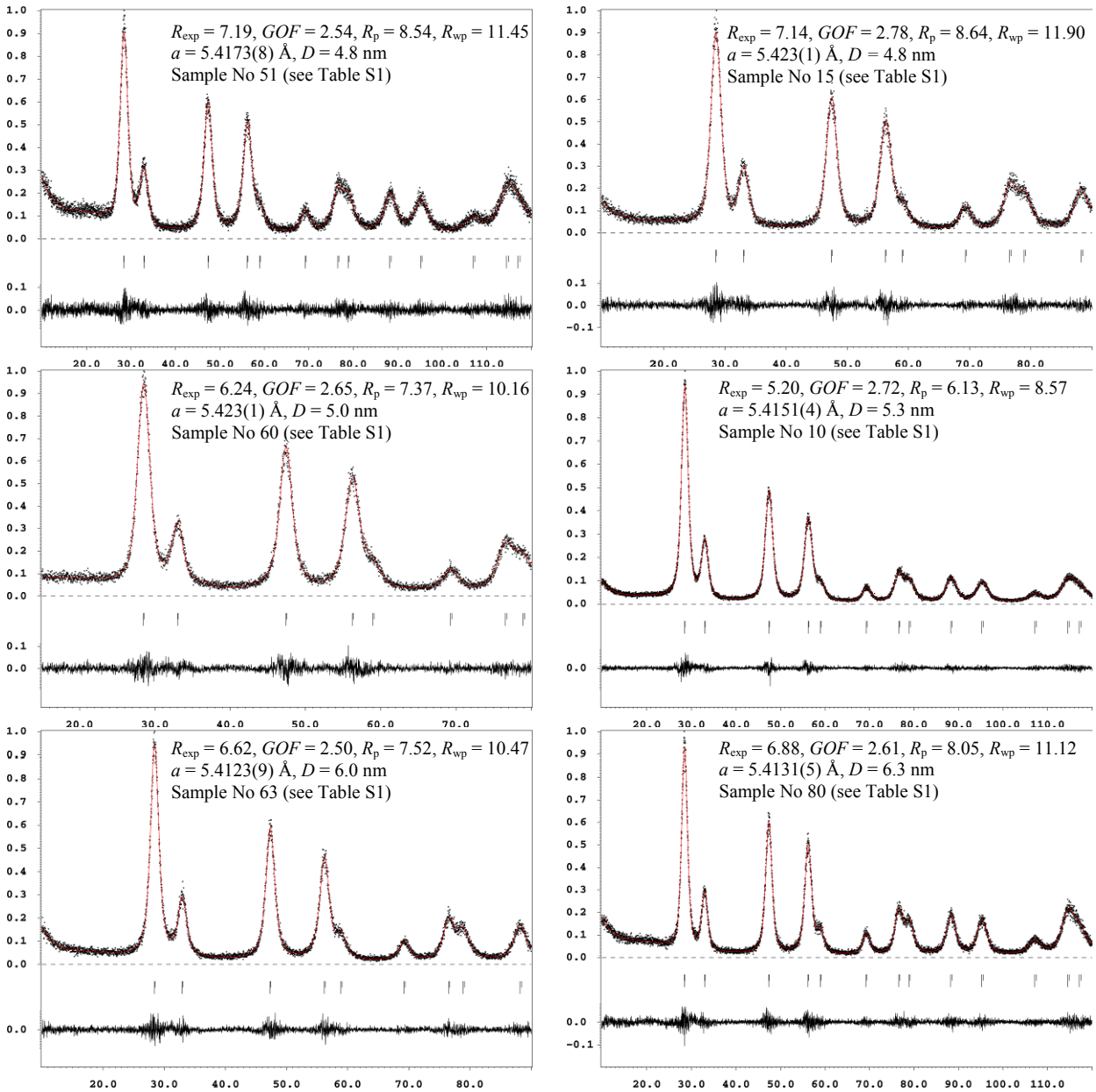


Figure S1 (contd.). Rietveld refinement of selected ceria samples (particle size 2.2–23.5 nm).

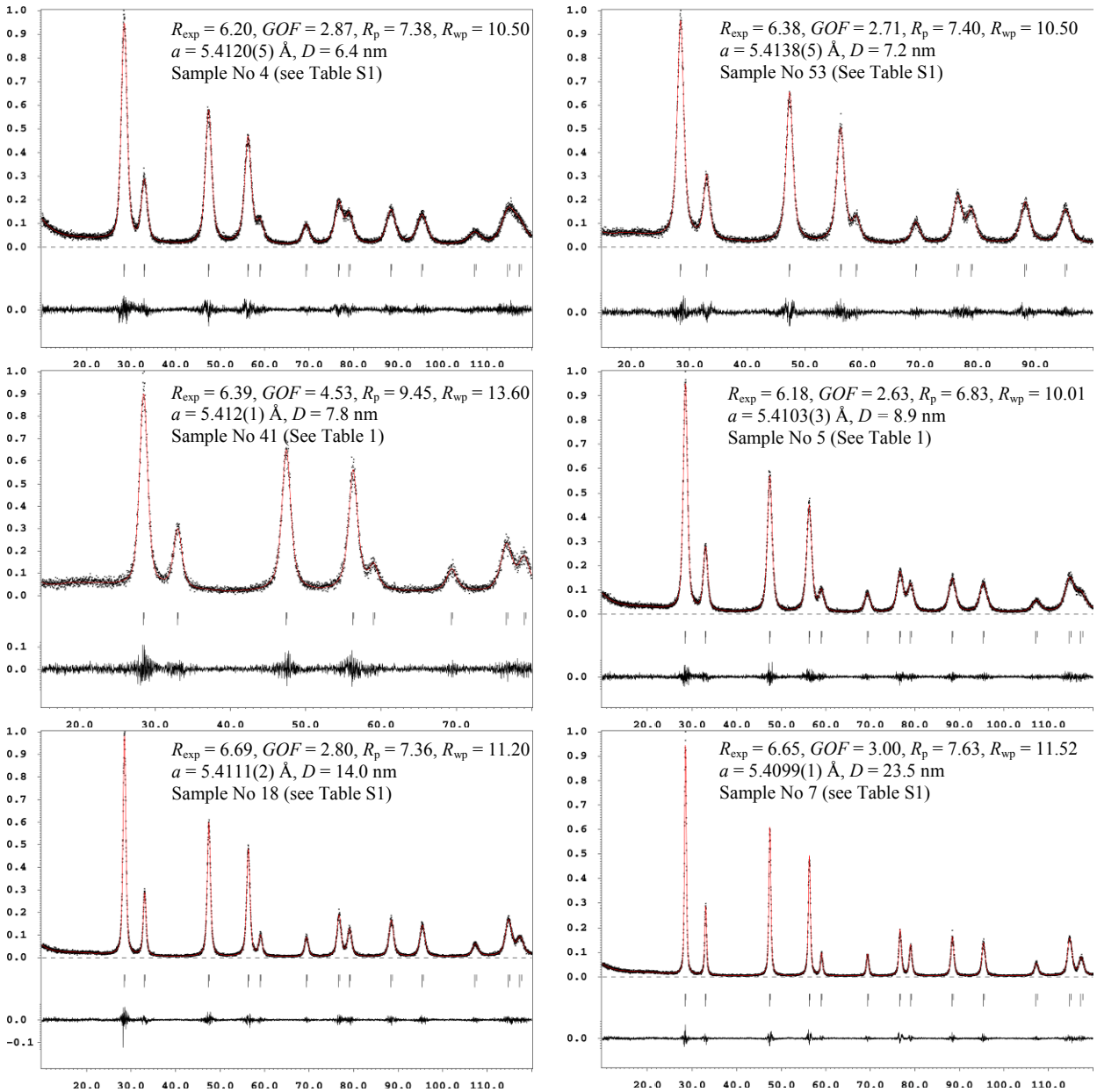
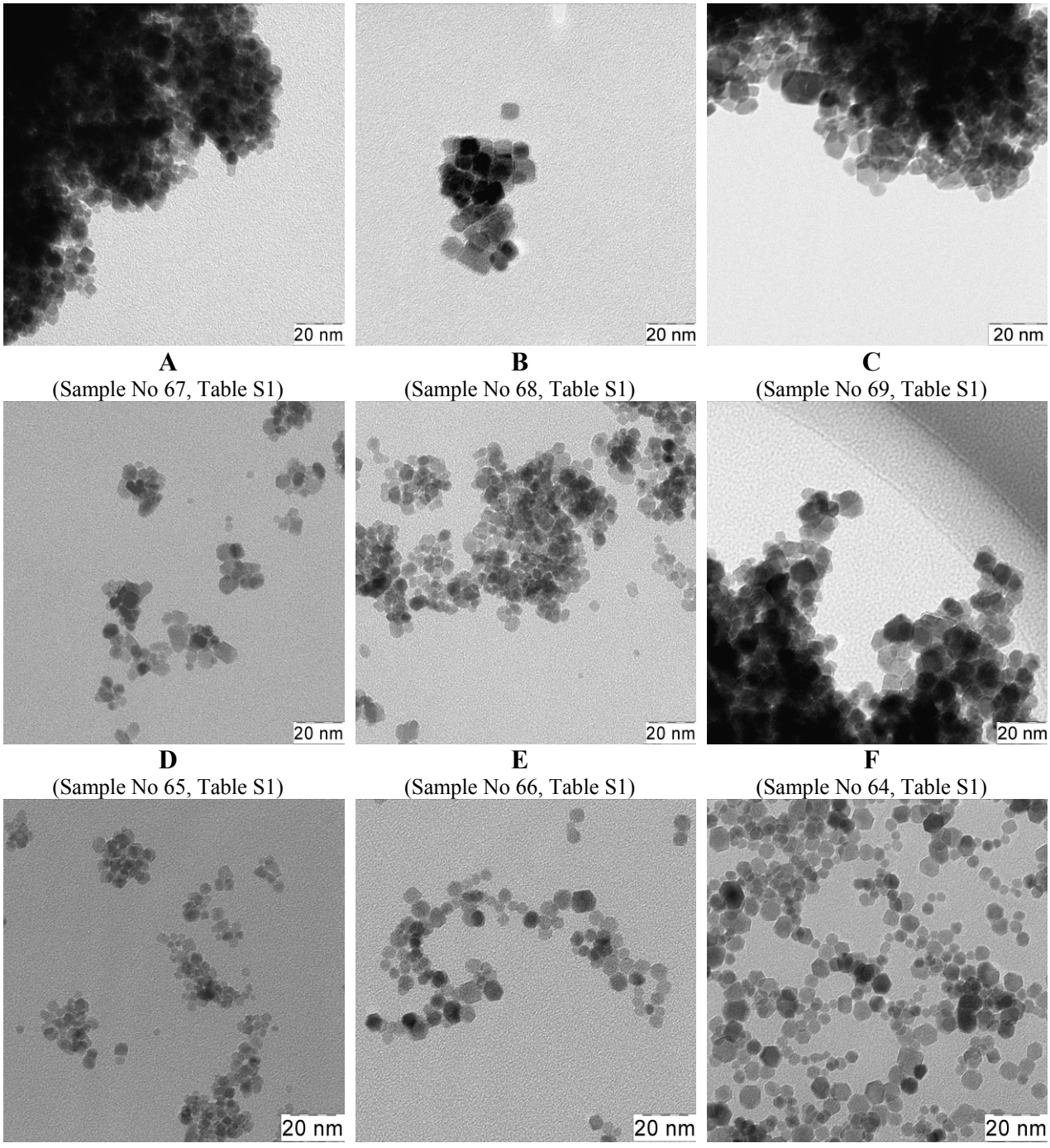


Figure S1 (contd.). Rietveld refinement of selected ceria samples (particle size 2.2–23.5 nm).

Sample No (See Table S1)	Ceria particle size, nm	Raman peak position, cm^{-1}	*a*, Å	
			Raman spectroscopy data	Rietveld refinement data
26	2.6	452.5	5.442	5.443
28	3.3	458.3	5.426	5.425
20	4.5	459.4	5.423	5.422
87	7.0	461.2	5.418	5.414

Table S2. Comparison of Raman spectroscopy and Rietveld refinement data.

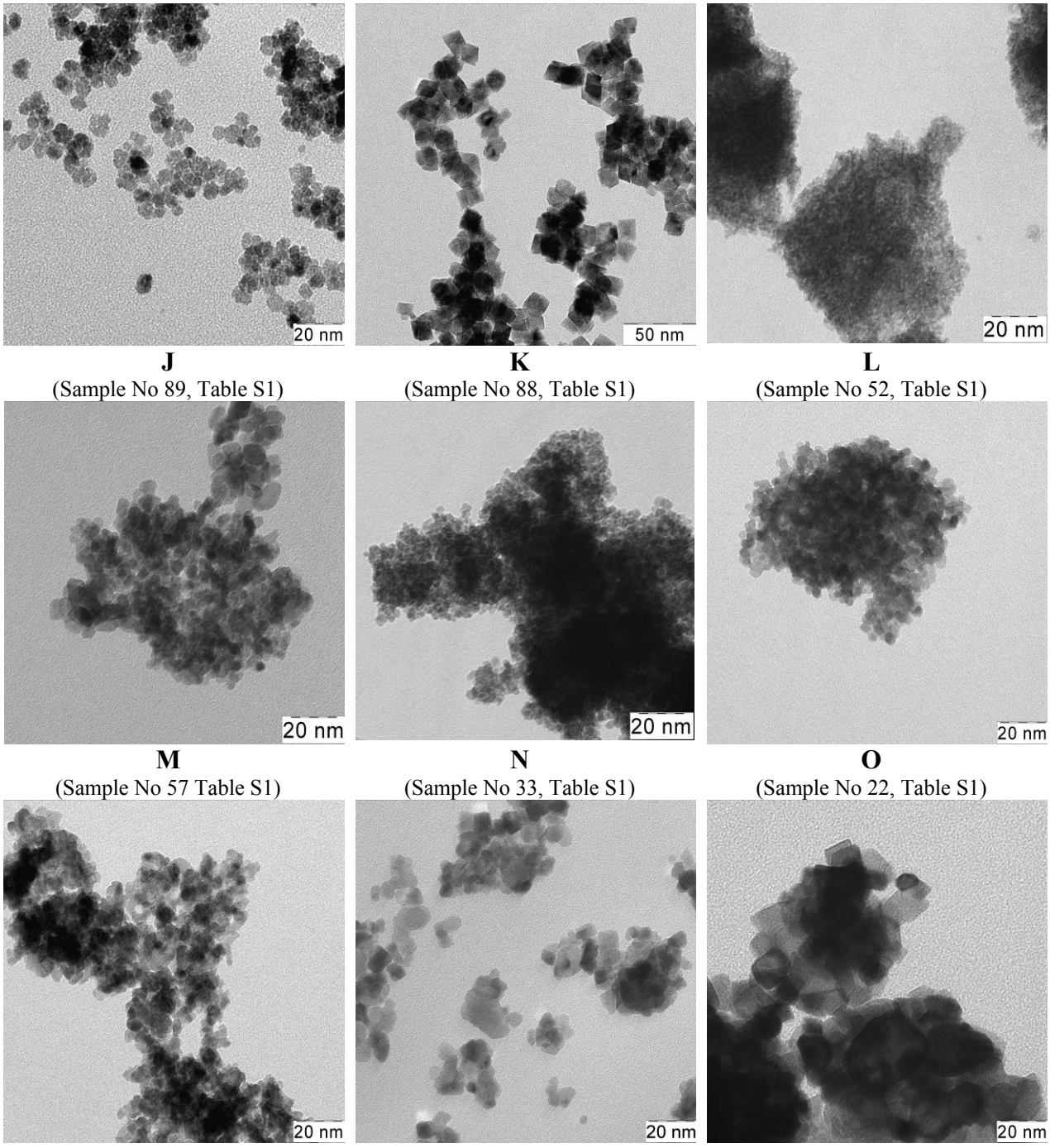


A (Sample No 67, Table S1) **B** (Sample No 68, Table S1) **C** (Sample No 69, Table S1)

D (Sample No 65, Table S1) **E** (Sample No 66, Table S1) **F** (Sample No 64, Table S1)

G (Sample No 63, Table S1) **H** (Sample No 91, Table S1) **I** (Sample No 92, Table S1)

Figure S2. Transmission electron microscopy images illustrating various shape of particles in different CeO_{2-x} samples prepared by (A–I) hydrothermal and hydrothermal-microwave treatment at 150–210°C for 15 min–3 h, (J–M) homogeneous precipitation from $Ce(NO_3)_3$ and $(NH_4)Ce(NO_3)_6$ solutions in the presence of hexamethylenetetramine, and (N–R) annealing of CeO_{2-x} nanopowders obtained by rapid precipitation from $Ce(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$ solutions in water/isopropanol.



J (Sample No 89, Table S1) **K** (Sample No 88, Table S1) **L** (Sample No 52, Table S1)

M (Sample No 57 Table S1) **N** (Sample No 33, Table S1) **O** (Sample No 22, Table S1)

P (Sample No 12, Table S1) **Q** (Sample No 18, Table S1) **R** (Sample No 24, Table S1)

Figure S2 (contd.). Transmission electron microscopy images illustrating various shape of particles in different CeO_{2-x} samples prepared by (A–I) hydrothermal and hydrothermal-microwave treatment at 150–210°C for 15 min–3 h, (J–M) homogeneous precipitation from $Ce(NO_3)_3$ and $(NH_4)Ce(NO_3)_6$ solutions in the presence of hexamethylenetetramine, and (N–R) annealing of CeO_{2-x} nanopowders obtained by rapid precipitation from $Ce(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_6$ solutions in water/isopropanol.