Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

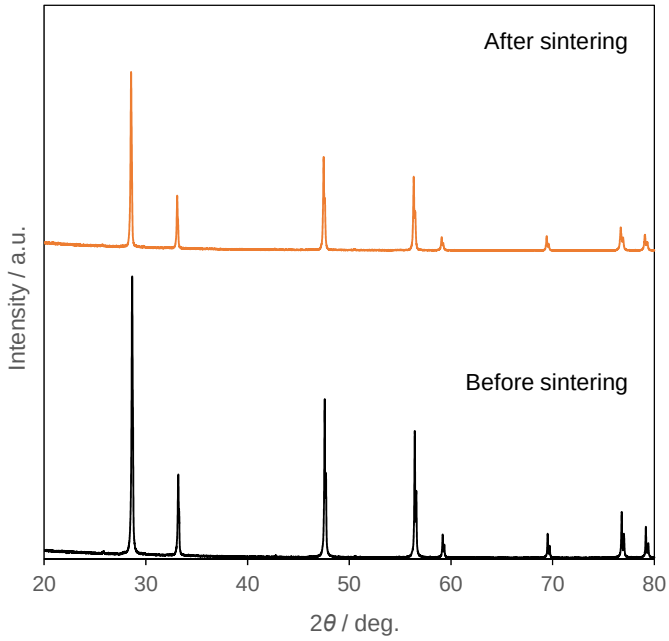

Figure S1. X-ray powder diffraction patterns of ceria: (bottom) before sintering, and (upper) after sintering for 8 h at 1000 ºC.

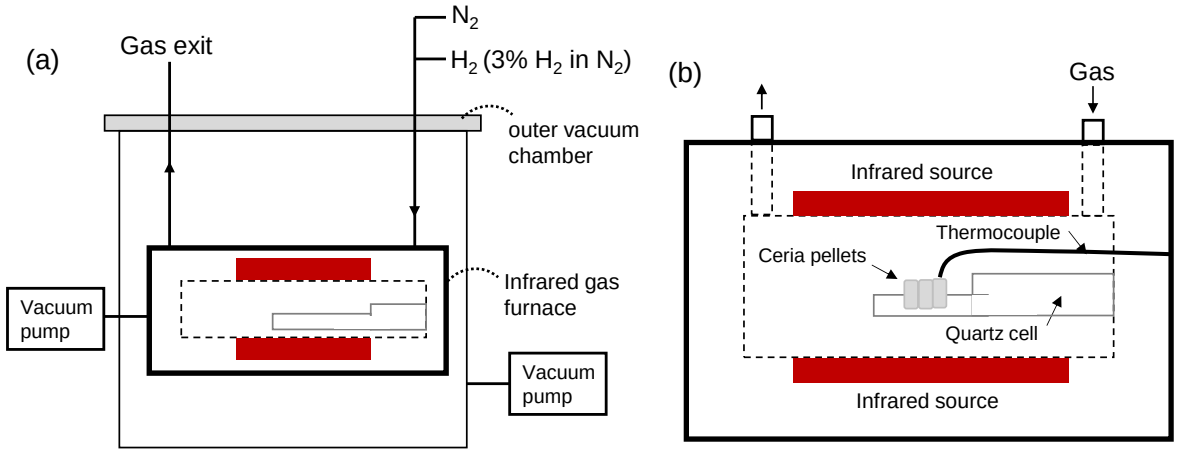

Figure S2. Schematic of a high-temperature gas furnace: (a) the set-up view of the high temperature gas furnace, (b) the section view of sample room.

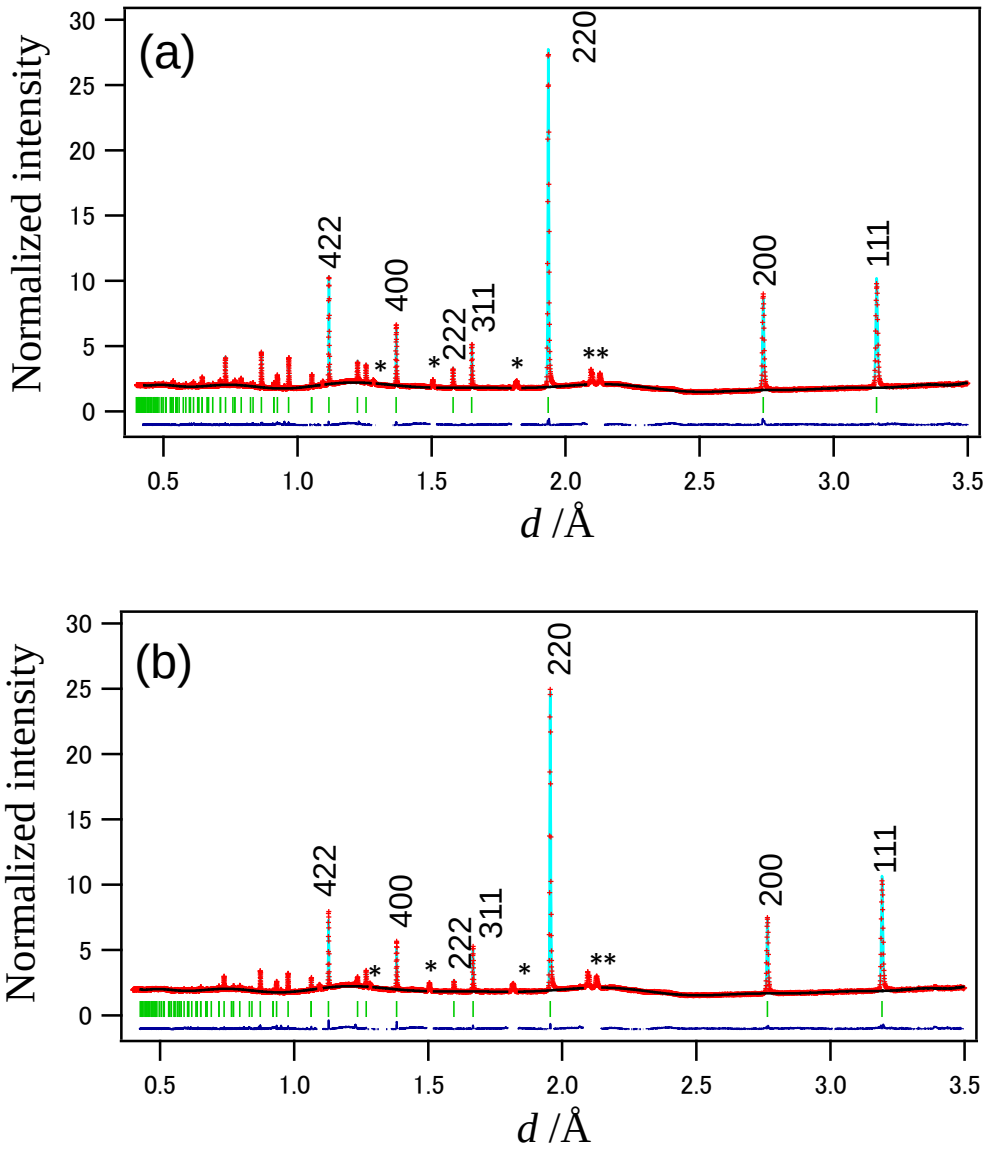

Figure S3. Rietveld refinement patterns of long-holding time ceria powder at 800ºC: (a) time sliced PND patterns after 1 hour. The red "+" marks, the solid light-blue line, the green tick marks, and the lower solid blue line indicate the experimental data, calculated data, Bragg-peak positions of CeO_2, and the difference between the experimental and calculated intensities, respectively. The asterisk denotes the peaks of the thermocouple, which are deselected in the refinement. The final *R* factor was R_{wp} = 2.28%. (b) time sliced PND patterns after 20 hour. The red "+" marks, the solid light-blue line, the green tick marks, and the lower solid blue line indicate the experimental data, calculated data, Bragg-peak positions of $CeO_{1.91}$, and the difference between the experimental and calculated intensities, respectively. The asterisk denotes the peaks of the thermocouple, which are deselected in the refinement. The final *R* factor was R_{wp} = 2.58%.

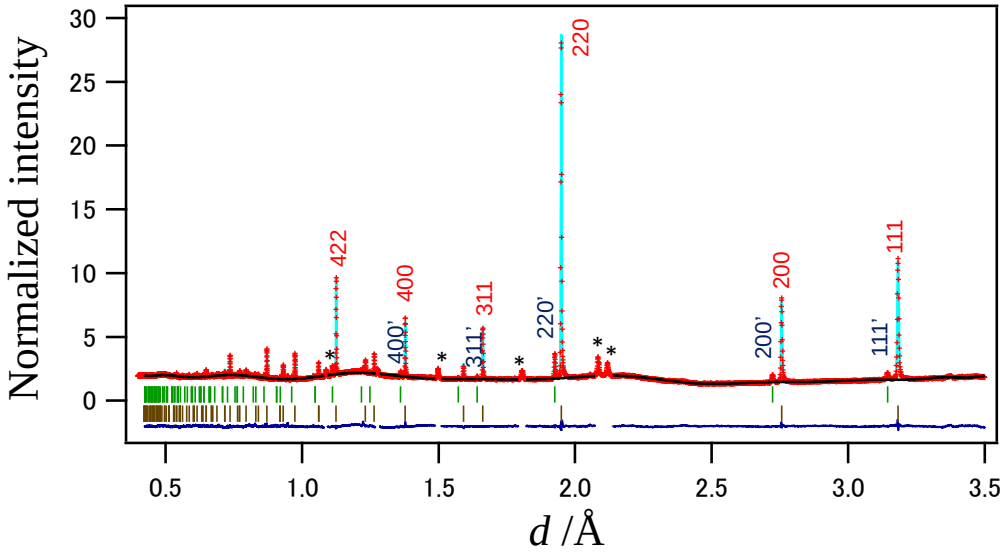

Figure S4. Rietveld refinement patterns of long-holding time ceria powder at 500ºC. The red "+" marks, the solid light-blue line, the green tick marks, the brown tick marks and the lower solid blue line indicate the experimental data, calculated data, Bragg-peak positions of cubic $CeO_{1.94(2)}$, Bragg-peak positions of cubic $CeO_{1.892(1)}$, and the difference between the experimental and calculated intensities, respectively. The asterisk denotes the peaks of the thermocouple, which are deselected in the refinement. The final *R* factor was R_{wp} = 2.67%.

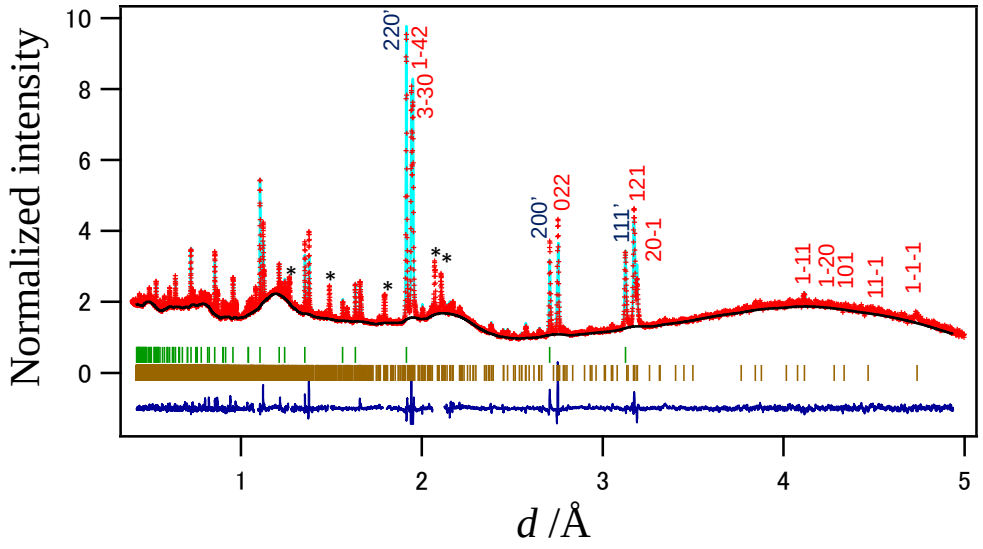

Figure S5. Rietveld refinement patterns of long-holding time ceria powder at 25ºC. The red "+" marks, the solid light-blue line, the green tick marks, the brown tick marks, and the lower solid blue line indicate the experimental data, calculated data, Bragg-peak positions of cubic CeO_2, Bragg-peak positions of triclinic $Ce_{11}O_{20}$, and the difference between the experimental and calculated intensities, respectively. The asterisk denotes the peaks of the thermocouple, which are deselected in the refinement. The final *R* factor was R_{wp} = 3.50%.

S1. The crystal structure parameters of ceria during 20 hour at 800°C

Time (hour)	1	2	3	4	5	6	7	8	9	10
Chemical formula	CeO_2	CeO_2	$CeO_{1.983(1)}$	$CeO_{1.970(1)}$	$CeO_{1.972(1)}$	$CeO_{1.970(1)}$	$CeO_{1.950(1)}$	$CeO_{1.946(1)}$	$CeO_{1.950(1)}$	$CeO_{1.954(1)}$
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	*Fm* -3*m*	*Fm* -3*m*	*Fm* -3*m*	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m
a (Å)	5.474672(2)	5.481775(2)	5.486796(3)	5.491102(3)	5.494990(3)	5.498596(4)	5.501970(4)	5.505198(4)	5.508218(4)	5.510985(4)
V (Å^3)	164.08	164.72	165.18	165.57	165.92	166.25	166.55	166.85	167.12	167.37
Z	4	4	4	4	4	4	4	4	4	4
R_{wp} (%)	2.28	3.48	2.73	2.5	2.58	2.53	2.41	2.41	2.45	2.51

Time (hour)	11	12	13	14	15	16	17	18	19	20
Chemical formula	$CeO_{1.931(1)}$	$CeO_{1.939(1)}$	$CeO_{1.927(1)}$	$CeO_{1.927(1)}$	$CeO_{1.917(1)}$	$CeO_{1.910(1)}$	$CeO_{1.906(1)}$	$CeO_{1.909(1)}$	$CeO_{1.909(1)}$	$CeO_{1.909(1)}$
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m	*Fm* -3m
a (Å)	5.513555(4)	5.515998(3)	5.518298(3)	5.520369(3)	5.522331(3)	5.524136(3)	5.525846(3)	5.527422(3)	5.528899(3)	5.530314(3)
V (Å^3)	167.61	167.83	168.04	168.23	168.41	168.57	168.73	168.88	169.01	169.14
Z	4	4	4	4	4	4	4	4	4	4
R_{wp} (%)	2.34	2.43	2.3	2.49	2.36	2.42	2.33	2.33	2.42	2.58

Time (h)			site	*g*	*x*	*y*	*z*	B_{iso} (Å^2)
1	CeO_2	Ce	4*a*	1	0	0	0	1.245(3)
		O	8*c*	1	1/4	1/4	1/4	1.905(2)
2	CeO_2	Ce	4*a*	1	0	0	0	1.125(3)
		O	8*c*	1	1/4	1/4	1/4	2.007(3)
3	$CeO_{1.983(1)}$	Ce	4*a*	1	0	0	0	1.151(4)
		O	8*c*	0.9917(8)	1/4	1/4	1/4	1.896(3)
4	$CeO_{1.970(1)}$	Ce	4*a*	1	0	0	0	1.415(8)
		O	8*c*	0.9849(8)	1/4	1/4	1/4	2.106(3)
5	$CeO_{1.972(1)}$	Ce	4*a*	1	0	0	0	1.391(8)
		O	8*c*	0.9860(8)	1/4	1/4	1/4	2.157(3)
6	$CeO_{1.970(1)}$	Ce	4*a*	1	0	0	0	1.376(8)
		O	8*c*	0.9849(7)	1/4	1/4	1/4	2.227(3)
7	$CeO_{1.950(1)}$	Ce	4*a*	1	0	0	0	1.393(8)
		O	8*c*	0.9748(7)	1/4	1/4	1/4	2.285(4)
8	$CeO_{1.946(1)}$	Ce	4*a*	1	0	0	0	1.494(8)
		O	8*c*	0.9730(8)	1/4	1/4	1/4	2.436(4)
9	$CeO_{1.950(1)}$	Ce	4*a*	1	0	0	0	1.335(8)
		O	8*c*	0.9749(8)	1/4	1/4	1/4	2.460(4)
10	$CeO_{1.954(1)}$	Ce	4*a*	1	0	0	0	1.308(8)
		O	8*c*	0.9770(7)	1/4	1/4	1/4	2.500(4)
11	$CeO_{1.931(1)}$	Ce	4*a*	1	0	0	0	1.404(8)
		O	8*c*	0.9654(7)	1/4	1/4	1/4	2.575(4)
12	$CeO_{1.939(1)}$	Ce	4*a*	1	0	0	0	1.366(8)
		O	8*c*	0.9697(7)	1/4	1/4	1/4	2.632(4)
13	$CeO_{1.927(1)}$	Ce	4*a*	1	0	0	0	1.432(8)
		O	8*c*	0.9636(7)	1/4	1/4	1/4	2.707(4)
14	$CeO_{1.927(1)}$	Ce	4*a*	1	0	0	0	1.268(8)
		O	8*c*	0.9638(7)	1/4	1/4	1/4	2.601(4)
15	$CeO_{1.917(1)}$	Ce	4*a*	1	0	0	0	1.409(8)
		O	8*c*	0.9588(7)	1/4	1/4	1/4	2.765(4)
16	$CeO_{1.910(1)}$	Ce	4*a*	1	0	0	0	1.400(8)
		O	8*c*	0.9550(8)	1/4	1/4	1/4	2.773(4)
17	$CeO_{1.906(1)}$	Ce	4*a*	1	0	0	0	1.395(8)
		O	8*c*	0.9533(7)	1/4	1/4	1/4	2.837(4)
18	$CeO_{1.909(1)}$	Ce	4*a*	1	0	0	0	1.440(8)
		O	8*c*	0.9547(7)	1/4	1/4	1/4	2.914(4)
19	$CeO_{1.909(1)}$	Ce	4*a*	1	0	0	0	1.400(8)
		O	8*c*	0.9549(7)	1/4	1/4	1/4	2.864(3)
20	$CeO_{1.909(1)}$	Ce	4*a*	1	0	0	0	1.324(8)
		O	8*c*	0.9547(7)	1/4	1/4	1/4	2.852(3)

Table S2. The crystal structure parameters of ceria between 800°C and 25°C

Temp. (℃)	700	600	500		400		300		200		100		25	
Chemical formula	$CeO_{1.885(1)}$	$CeO_{1.907(1)}$	$CeO_{1.94(2)}$	$CeO_{1.892(1)}$	CeO_2	$Ce_{11}O_{20}$	CeO_2	$Ce_{11}O_{20}$	CeO_2	$Ce_{11}O_{20}$	CeO_2	$Ce_{11}O_{20}$	CeO_2	$Ce_{11}O_{20}$
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Triclinic	Cubic	Triclinic	Cubic	Triclinic	Cubic	Triclinic	Cubic	Triclinic
Space group	*Fm* -3*m*	*Fm* -3*m*	*Fm* -3m	*Fm* -3m	*Fm* -3m	*P* -1	*Fm* -3m	*P* -1	*Fm* -3m	*P* -1	*Fm* -3m	*P* -1	*Fm* -3m	*P* -1
a (Å)	5.523542(3)	5.516127(3)	5.44648(2)	5.513235(3)	5.436850(8)	6.79527(4)	5.429537(8)	6.78592(3)	5.423211(8)	6.77997(4)	5.417536(8)	6.77204(3)	5.414097(7)	6.76711(3)
b (Å)						10.31916(8)		10.30890(8)		10.29544(9)		10.28306(8)		10.27862(3)
c (Å)						6.75486(4)		6.74908(4)		6.74418(8)		6.73730(3)		6.73367(3)
α (°)						89.8157(8)		89.8293(4)		89.8274(7)		89.8264(8)		89.8041(4)
β (°)						99.8279(8)		99.8262(3)		99.8261(9)		99.8252(7)		99.8177(4)
γ (°)						96.3049(4)		96.3056(4)		96.3077(8)		96.3094(4)		96.3349(3)
V (Å^3)	168.52	167.84	161.56	167.58	160.71	437.66	160.06	472.13	159.5	470.76	159	469.16	158.7	468.37
Z	4	4	4	4	4	1	4	1	4	1	4	1	4	1
R_{wp} (%)	2.54	2.56	2.67		2.73		2.87		3.37		3.25		3.5	

Temp. (℃)			site	*g*	*x*	*y*	*z*	B_{iso} (Å^2)
700	$CeO_{1.885(1)}$	Ce	4*a*	1	0	0	0	1.379(8)
		O	8*c*	0.9426(9)	1/4	1/4	1/4	2.748(8)
600	$CeO_{1.907(1)}$	Ce	4*a*	1	0	0	0	1.284(7)
		O	8*c*	0.9536(9)	1/4	1/4	1/4	2.674(8)
500	$CeO_{1.94(2)}$	Ce	4*a*	1	0	0	0	2.64(7)
		O	8*c*	0.970(8)	1/4	1/4	1/4	1.19(3)
	$CeO_{1.892(1)}$	Ce	4*a*	1	0	0	0	1.373(7)
		O	8*c*	0.9459(9)	1/4	1/4	1/4	2.615(8)
400	CeO_2	Ce	4*a*	1	0	0	0	1.06(1)
		O	8*c*	1	1/4	1/4	1/4	1.210(7)
	$Ce_{11}O_{20}$	Ce (1)	1*a*	1	0	0	0	1.03(2)
		Ce (2)	2*i*	1	0.1018(9)	0.3614(8)	0.176(1)	1.03(2)
		Ce (3)	2*i*	1	0.557(1)	0.1764(8)	0.115(1)	1.03(2)
		Ce (4)	2*i*	1	0.6348(9)	0.5287(8)	0.2689(9)	1.03(2)
		Ce (5)	2*i*	1	0.1423(8)	0.7236(8)	0.3607(8)	1.03(2)
		Ce (6)	2*i*	1	0.7370(9)	0.9180(8)	0.465(1)	1.03(2)
		O (1)	2*i*	1	0.6523(9)	0.9605(9)	0.142(1)	1.07(1)
		O (2)	2*i*	1	0.1658(8)	0.7972(9)	0.0451(9)	1.07(1)
		O (3)	2*i*	1	0.4399(9)	0.3723(8)	0.0435(9)	1.07(1)
		O (4)	2*i*	1	0.9324(8)	0.5647(9)	0.1653(8)	1.07(1)
		O (5)	2*i*	1	0.0339(7)	0.9271(8)	0.3551(8)	1.07(1)
		O (6)	2*i*	1	0.2360(8)	0.1508(8)	0.2138(8)	1.07(1)
		O (7)	2*i*	1	0.7948(8)	0.3341(8)	0.3128(8)	1.07(1)
		O (8)	2*i*	1	0.3411(8)	0.5455(8)	0.3711(9)	1.07(1)
		O (9)	2*i*	1	0.8117(8)	0.7028(8)	0.4513(9)	1.07(1)
		O (10)	2*i*	1	0.5967(9)	0.1240(9)	0.4697(9)	1.07(1)
		Vo	2*i*	0	0.5	0.75	0.25	
300	CeO_2	Ce	4*a*	1	0	0	0	0.457(9)
		O	8*c*	1	1/4	1/4	1/4	0.467(8)
	$Ce_{11}O_{20}$	Ce (1)	1*a*	1	0	0	0	0.98(2)
		Ce (2)	2*i*	1	0.1012(8)	0.3624(8)	0.1777(9)	0.98(2)
		Ce (3)	2*i*	1	0.555(1)	0.1752(9)	0.1157(9)	0.98(2)
		Ce (4)	2*i*	1	0.6389(8)	0.5261(8)	0.2713(8)	0.98(2)
		Ce (5)	2*i*	1	0.1440(8)	0.7240(8)	0.3573(8)	0.98(2)
		Ce (6)	2*i*	1	0.7339(8)	0.9175(8)	0.4707(9)	0.98(2)
		O (1)	2*i*	1	0.6523(9)	0.9583(9)	0.1452(8)	1.00(1)
		O (2)	2*i*	1	0.1690(8)	0.7968(8)	0.0460(8)	1.00(1)
		O (3)	2*i*	1	0.4409(8)	0.3715(8)	0.0401(8)	1.00(1)
		O (4)	2*i*	1	0.9384(8)	0.5648(9)	0.1650(8)	1.00(1)
		O (5)	2*i*	1	0.0348(7)	0.9275(8)	0.3538(8)	1.00(1)
		O (6)	2*i*	1	0.2360(7)	0.1510(8)	0.2118(8)	1.00(1)
		O (7)	2*i*	1	0.7925(8)	0.3346(9)	0.3157(8)	1.00(1)
		O (8)	2*i*	1	0.3391(9)	0.5482(9)	0.3668(8)	1.00(1)
		O (9)	2*i*	1	0.8106(8)	0.7040(9)	0.4502(8)	1.00(1)
		O (10)	2*i*	1	0.5929(8)	0.1252(9)	0.4748(8)	1.00(1)
		Vo	2*i*	0	0.5	0.75	0.25	

Temp. (℃)			site	*g*	*x*	*y*	*z*	B_{iso} (Å^2)
200	CeO_2	Ce	4*a*	1	0	0	0	0.494(8)
		O	8*c*	1	1/4	1/4	1/4	0.607(4)
	$Ce_{11}O_{20}$	Ce (1)	1*a*	1	0	0	0	0.94(2)
		Ce (2)	2*i*	1	0.102(1)	0.3625(8)	0.178(1)	0.94(2)
		Ce (3)	2*i*	1	0.554(1)	0.1760(8)	0.114(1)	0.94(2)
		Ce (4)	2*i*	1	0.6387(9)	0.5268(8)	0.2715(9)	0.94(2)
		Ce (5)	2*i*	1	0.1441(9)	0.7246(8)	0.3581(9)	0.94(2)
		Ce (6)	2*i*	1	0.7326(9)	0.9171(9)	0.470(1)	0.94(2)
		O (1)	2*i*	1	0.652(1)	0.9595(8)	0.143(1)	0.96(1)
		O (2)	2*i*	1	0.1681(9)	0.7966(8)	0.045(1)	0.96(1)
		O (3)	2*i*	1	0.440(1)	0.3724(7)	0.0402(9)	0.96(1)
		O (4)	2*i*	1	0.9389(9)	0.5655(8)	0.1643(9)	0.96(1)
		O (5)	2*i*	1	0.0354(9)	0.9283(8)	0.3524(9)	0.96(1)
		O (6)	2*i*	1	0.2357(9)	0.1520(9)	0.2111(9)	0.96(1)
		O (7)	2*i*	1	0.7924(9)	0.3351(9)	0.3143(9)	0.96(1)
		O (8)	2*i*	1	0.339(1)	0.5469(9)	0.368(1)	0.96(1)
		O (9)	2*i*	1	0.8111(9)	0.7037(8)	0.451(1)	0.96(1)
		O (10)	2*i*	1	0.592(1)	0.1246(8)	0.4738(9)	0.96(1)
		Vo	2*i*	0	0.5	0.75	0.25	
100	CeO_2	Ce	4*a*	1	0	0	0	0.560(8)
		O	8*c*	1	1/4	1/4	1/4	0.587(4)
	$Ce_{11}O_{20}$	Ce (1)	1*a*	1	0	0	0	0.98(2)
		Ce (2)	2*i*	1	0.0997(8)	0.3589(8)	0.1808(9)	0.98(2)
		Ce (3)	2*i*	1	0.5566(9)	0.1774(8)	0.1094(8)	0.98(2)
		Ce (4)	2*i*	1	0.6316(8)	0.5293(8)	0.2723(8)	0.98(2)
		Ce (5)	2*i*	1	0.1479(7)	0.7241(4)	0.3591(7)	0.98(2)
		Ce (6)	2*i*	1	0.7373(7)	0.9162(8)	0.4604(9)	0.98(2)
		O (1)	2*i*	1	0.6559(8)	0.9552(8)	0.1425(8)	0.99(1)
		O (2)	2*i*	1	0.1587(8)	0.7959(8)	0.0414(8)	0.99(1)
		O (3)	2*i*	1	0.4336(7)	0.3750(8)	0.0426(8)	0.99(1)
		O (4)	2*i*	1	0.9331(8)	0.5634(8)	0.1670(7)	0.99(1)
		O (5)	2*i*	1	0.0365(7)	0.9253(4)	0.3517(8)	0.99(1)
		O (6)	2*i*	1	0.2345(7)	0.1480(8)	0.2104(8)	0.99(1)
		O (7)	2*i*	1	0.7938(8)	0.3340(8)	0.3086(7)	0.99(1)
		O (8)	2*i*	1	0.3432(8)	0.5458(9)	0.3702(8)	0.99(1)
		O (9)	2*i*	1	0.8171(8)	0.7017(8)	0.4548(8)	0.99(1)
		O (10)	2*i*	1	0.5961(8)	0.1225(8)	0.4685(9)	0.99(1)
		Vo	2*i*	0	0.5	0.75	0.25	
25	CeO_2	Ce	4*a*	1	0	0	0	0.452(7)
		O	8*c*	1	1/4	1/4	1/4	0.451(4)
	$Ce_{11}O_{20}$	Ce (1)	1*a*	1	0	0	0	0.86(2)
		Ce (2)	2*i*	1	0.0998(8)	0.3577(8)	0.1833(9)	0.86(2)
		Ce (3)	2*i*	1	0.5592(9)	0.1739(8)	0.101(1)	0.86(2)
		Ce (4)	2*i*	1	0.6308(8)	0.5276(8)	0.2775(8)	0.86(2)
		Ce (5)	2*i*	1	0.1465(7)	0.7292(8)	0.3657(8)	0.86(2)
		Ce (6)	2*i*	1	0.7357(8)	0.9185(8)	0.4655(8)	0.86(2)
		O (1)	2*i*	1	0.6542(8)	0.9532(8)	0.144(1)	0.94(1)
		O (2)	2*i*	1	0.1538(8)	0.7947(8)	0.0374(9)	0.94(1)
		O (3)	2*i*	1	0.4297(8)	0.3711(9)	0.0374(9)	0.94(1)
		O (4)	2*i*	1	0.9328(8)	0.5596(3)	0.1651(8)	0.94(1)
		O (5)	2*i*	1	0.0444(7)	0.9211(3)	0.3467(8)	0.94(1)
		O (6)	2*i*	1	0.2313(8)	0.1469(8)	0.2053(8)	0.94(1)
		O (7)	2*i*	1	0.7947(7)	0.3329(8)	0.3029(8)	0.94(1)
		O (8)	2*i*	1	0.3509(8)	0.5431(8)	0.3643(8)	0.94(1)
		O (9)	2*i*	1	0.8144(7)	0.7031(8)	0.4471(8)	0.94(1)
		O (10)	2*i*	1	0.5936(8)	0.1174(8)	0.4672(8)	0.94(1)
		Vo	2*i*	0	0.5	0.75	0.25	