

Supporting Information

Detection of hydride and hydroxyl functional groups in a ceria crystal under hydrogen reduction

Takeshi Matsukawa,^{1,*} Kazuki Iida,² Mitsutaka Nakamura,³ and Toru Ishigaki¹

¹ Frontier Research Center for Applied Atomic Sciences, Ibaraki University, 162-1 Shirakata, Tokai,
Ibaraki 319-1106, Japan,

² Neutron Science and Technology Center, Comprehensive Research Organization for Science and
Society, 162-1 Shirakata, Tokai, Ibaraki 319-1106, Japan,

³ J-PARC Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan.

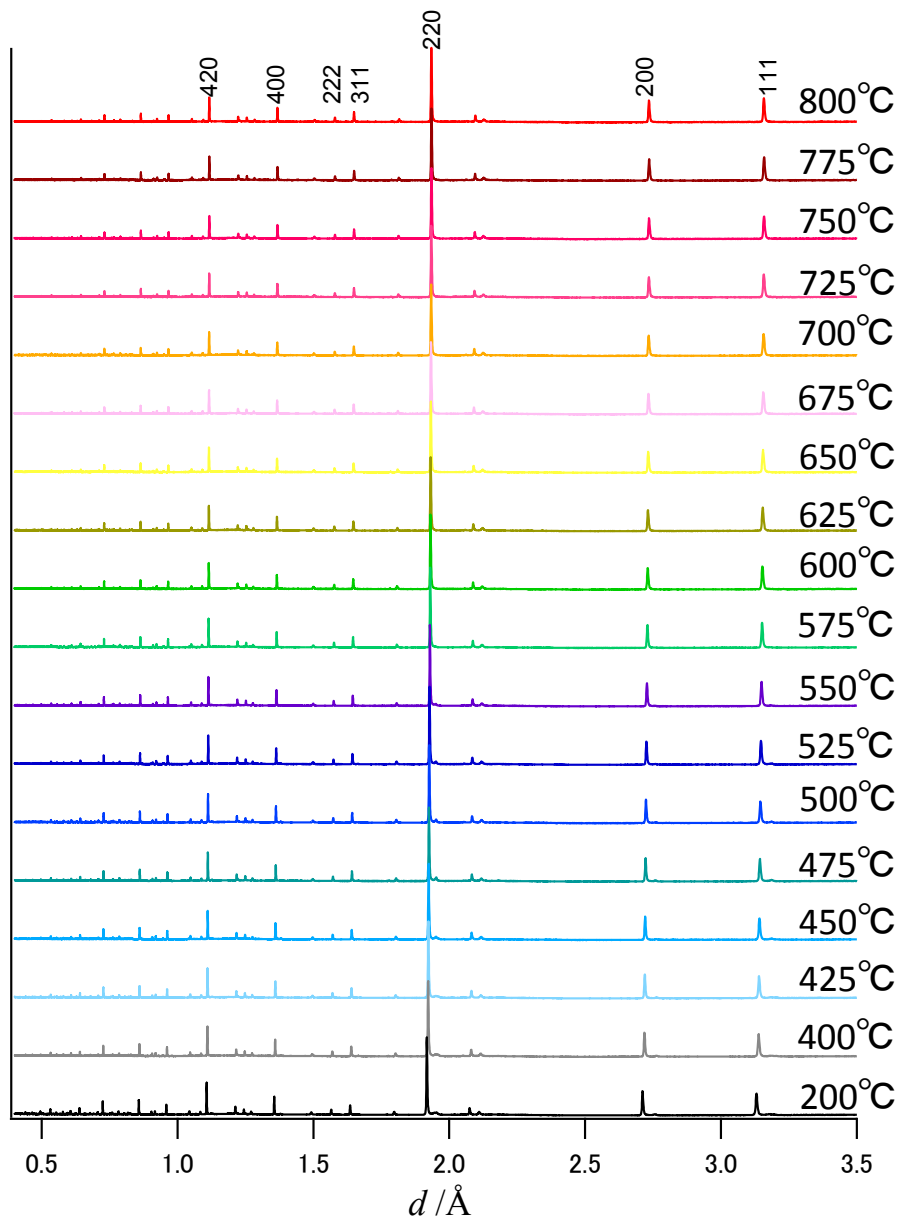


Figure S1. Neutron diffraction patterns of ceria crystal at temperature range 200-800°C.

Table S1. The crystal structure parameters of CeO_2H_y ($0 \leq y \leq 1$) and CeO_{2-x} ($0 \leq x \leq 0.5$) at 200 and 800°C

	500		475		450		425		400		200	
	$\text{CeO}_2\text{H}_0.030(7)$	CeO_2H	$\text{CeO}_2\text{H}_0.032(8)$	CeO_2H	$\text{CeO}_2\text{H}_0.035(6)$	CeO_2H	$\text{CeO}_2\text{H}_0.032(8)$	CeO_2H	$\text{CeO}_2\text{H}_0.031(1)$	CeO_2H	CeO_2	$\text{CeO}_{1.76(2)}$
C	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
S	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$	$Fm\text{-}3m$
a	5.448309(8)	5.51815(8)	5.445161(8)	5.51889(7)	5.442188(8)	5.5188(1)	5.439478(4)	5.5226(1)	5.437200(4)	5.5168(1)	5.423490(4)	5.5266(1)
V	161.7	161.4	161.2	168.1	161.2	168.1	160.9	167.9	160.7	167.8	159.5	168.6
Z	4	4	4	4	4	4	4	4	4	4	4	4
R	4.14	4.17	4.17	4.39	4.14	4.39	4.46	4.34	4.34	4.34	4.77	4.77
S	2.82	2.79	2.79	3.15	2.79	3.15	3.86	3.73	3.73	3.73	5.7	5.7

Temp. (°C)		site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)
800	CeO ₂ H _{0.032(8)}	Ce 4 <i>a</i>	1	0	0	0	1.21(1)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.912(9)
		H 32 <i>f</i>	0.004(1)	0.360(8)	0.360(8)	0.360(8)	2.0(2)
775	CeO ₂ H _{0.030(7)}	Ce 4 <i>a</i>	1	0	0	0	1.17(1)
		O 8 <i>c</i>	1	0.25	0.25	0.25	1.86(1)
		H 32 <i>f</i>	0.0037(9)	0.382(7)	0.382(7)	0.382(7)	1.0(1)
750	CeO ₂ H _{0.032(8)}	Ce 4 <i>a</i>	1	0	0	0	1.02(1)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.689(9)
		H 32 <i>f</i>	0.004(1)	0.357(8)	0.357(8)	0.357(8)	1.0(1)
725	CeO ₂ H _{0.032(8)}	Ce 4 <i>a</i>	1	0	0	0	1.08(1)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.78(1)
		H 32 <i>f</i>	0.004(1)	0.362(8)	0.362(8)	0.362(8)	1.4(1)
700	CeO ₂ H _{0.034(7)}	Ce 4 <i>a</i>	1	0	0	0	1.026(8)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.677(8)
		H 32 <i>f</i>	0.0042(9)	0.361(8)	0.361(8)	0.361(8)	1.0(1)
675	CeO ₂ H _{0.0032(8)}	Ce 4 <i>a</i>	1	0	0	0	0.945(9)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.572(8)
		H 32 <i>f</i>	0.004(1)	0.361(8)	0.361(8)	0.361(8)	1.1(1)
650	CeO ₂ H _{0.032(8)}	Ce 4 <i>a</i>	1	0	0	0	0.980(8)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.563(7)
		H 32 <i>f</i>	0.004(1)	0.359(8)	0.359(8)	0.359(8)	1.1(1)
625	CeO ₂ H _{0.038(7)}	Ce 4 <i>a</i>	1	0	0	0	0.979(9)
		O 8 <i>c</i>	1	0.25	0.25	0.25	1.538(8)
		H 32 <i>f</i>	0.0048(9)	0.359(8)	0.359(8)	0.359(8)	1.0(1)
600	CeO ₂ H _{0.024(8)}	Ce 4 <i>a</i>	1	0	0	0	0.874(8)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.402(7)
		H 32 <i>f</i>	0.003(1)	0.361(9)	0.361(9)	0.361(9)	1.0(1)
575	CeO ₂ H _{0.0032(6)}	Ce 4 <i>a</i>	1	0	0	0	0.892(8)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.416(8)
		H 32 <i>f</i>	0.0040(7)	0.361(8)	0.361(8)	0.361(8)	1.0(1)
575	CeO ₂ H	Ce 4 <i>a</i>	1	0	0	0	1.0(8)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.0(8)
		H 32 <i>f</i>	0.124(8)	0.35(1)	0.35(1)	0.35(1)	2.0(3)
550	CeO ₂ H _{0.035(5)}	Ce 4 <i>a</i>	1	0	0	0	0.891(9)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.437(8)
		H 32 <i>f</i>	0.0044(8)	0.359(4)	0.359(4)	0.359(4)	1.0(1)
550	CeO ₂ H	Ce 4 <i>a</i>	1	0	0	0	1.0(3)
		O 8 <i>c</i>	1	1/4	1/4	1/4	1.2(2)
		H 32 <i>f</i>	0.124(2)	0.359(8)	0.359(8)	0.359(8)	1.0(1)
525	CeO ₂ H _{0.033(5)}	Ce 4 <i>a</i>	1	0	0	0	0.892(8)
		O 8 <i>c</i>	1	0.25	0.25	0.25	1.330(8)
		H 32 <i>f</i>	0.0040(8)	0.361(8)	0.361(8)	0.361(8)	1.0(1)
525	CeO ₂ H	Ce 4 <i>a</i>	1	0	0	0	2.8(2)
		O 8 <i>c</i>	1	1/4	1/4	1/4	0.3(1)
		H 32 <i>f</i>	0.125(1)	0.359(2)	0.359(2)	0.359(2)	1.0(8)

Temp. (°C)		site	g	x	y	z	B_{iso} (Å ²)
500	CeO ₂ H _{0.030(7)}	Ce 4a	1	0	0	0	0.859(9)
		O 8c	1	1/4	1/4	1/4	1.271(9)
		H 32f	0.0038(8)	0.361(8)	0.361(8)	0.361(8)	0.9(1)
	CeO ₂ H	Ce 4a	1	0	0	0	1.1(1)
		O 8c	1	1/4	1/4	1/4	1.6(1)
		H 32f	0.124(9)	0.355(2)	0.355(2)	0.355(2)	1.2(8)
475	CeO ₂ H _{0.032(8)}	Ce 4a	1	0	0	0	0.824(8)
		O 8c	1	1/4	1/4	1/4	1.194(8)
		H 32f	0.004(1)	0.365(8)	0.365(8)	0.365(8)	0.8(1)
	CeO ₂ H	Ce 4a	1	0	0	0	2.3(1)
		O 8c	1	1/4	1/4	1/4	0.76(7)
		H 32f	0.124(9)	0.355(4)	0.355(4)	0.355(4)	1.4(8)
450	CeO ₂ H _{0.035(5)}	Ce 4a	1	0	0	0	0.789(8)
		O 8c	1	1/4	1/4	1/4	1.121(8)
		H 32f	0.0044(8)	0.355(4)	0.355(4)	0.355(4)	1.0(1)
	CeO ₂ H	Ce 4a	1	0	0	0	1.0(2)
		O 8c	1	1/4	1/4	1/4	1.0(1)
		H 32f	0.125(9)	0.359(2)	0.359(2)	0.359(2)	1.0(8)
	CeO ₂₍₀₎	Ce 4a	1	0	0	0	1.2(8)
		O 8c	1	1/4	1/4	1/4	1.1(3)
	425	CeO ₂ H _{0.032(8)}	Ce 4a	1	0	0	0
O 8c			1	1/4	1/4	1/4	1.082(4)
H 32f			0.0040(7)	0.360(4)	0.360(4)	0.360(4)	1.0(1)
CeO ₂ H		Ce 4a	1	0	0	0	1.4(2)
		O 8c	1	1/4	1/4	1/4	1.4(1)
		H 32f	0.124(1)	0.360(3)	0.360(3)	0.360(3)	1.0(1)
CeO _{1.88(8)}		Ce 4a	1	0	0	0	1.6(4)
		O 8c	0.94(4)	1/4	1/4	1/4	1.9(3)
400		CeO ₂ H _{0.03(1)}	Ce 4a	1	0	0	0
	O 8c		1	1/4	1/4	1/4	1.041(4)
	H 32f		0.036(7)(1)	0.359(8)	0.359(8)	0.359(8)	1.2(1)
	CeO ₂ H	Ce 4a	1	0	0	0	1.0(1)
		O 8c	1	1/4	1/4	1/4	1.02(8)
		H 32f	0.124(9)	0.354(2)	0.354(2)	0.354(2)	1.0(8)
	CeO _{1.78(8)}	Ce 4a	1	0	0	0	1.0(3)
		O 8c	0.89(4)	1/4	1/4	1/4	1.2(3)
	200	CeO ₂	Ce 4a	1	0	0	0
O 8c			1	1/4	1/4	1/4	0.714(3)
CeO ₂ H		Ce 4a	1	0	0	0	1.29(8)
		O 8c	1	1/4	1/4	1/4	1.34(8)
		H 32f	0.125(8)	0.359(1)	0.359(1)	0.359(1)	1.0(3)
CeO _{1.76(2)}		Ce 4a	1	0	0	0	1.8(2)
		O 8c	0.88(1)	1/4	1/4	1/4	1.6(1)

