CeO2			Ce1-xSmxO2-x/2			Sm2O3		
F structure cF12 Fm-3m Z=4 a=5.4097(1) Å [8]			Hybrid (H) model used for Rietveld refinement of samples with <i>x</i> =0.4, 0.5 and 0.6 <i>c1</i> 96 <i>Ia</i> -3 Z=32			C structure cI80 Ia-3 Z=16 a=10.929 Å		
Atom	Wyckoff site	Coordinates	Atom	Wyckoff site	Coordinates	Atom	Wyckoff site	Coordinates
			Ce/Sm1	24 <i>d</i>	<i>x</i> , 0, 1/4	Sm1	24 <i>d</i>	x, 0, 1/4
Ce	4 <i>a</i>	0, 0, 0			<i>x</i> = 0.25			x = 0.2796
			Ce/Sm	8a	0, 0, 0	Sm2	8a	0, 0, 0
			O1	48 <i>e</i>	<i>x, y, z</i>	0	48 <i>e</i>	<i>x, y, z</i>
					x = 0.125			x = 0.1011
					<i>y</i> = 0.375			<i>y</i> = 0.3551
Ο	8 <i>c</i>	1/4, 1/4, 1/4			<i>z</i> = 0.125			<i>z</i> = 0.1343
			O2	16 <i>c</i>	<i>x, x, x</i>			
					<i>x</i> = 0.125			

**Table S1** – Hybrid (H) structural model compared to the F structure typical of CeO<sub>2</sub> and to the C structure typical of sesquioxides of heavy rare earths; data of Sm<sub>2</sub>O<sub>3</sub> are taken from M. Mitric *et al., J. Alloy Compd.* **2009**, *485*, 473-477.

## Rietveld refinement plots

In this file all the Rietveld plots obtained after the last refinement cycle are reported. The dotted and the continuous line are the experimental and the calculated diffractogram, respectively; the lower line is the difference curve; the vertical lines indicate the position of the expected peaks.

According to the RE content and to the applied pressure (in GPa), samples are named Sm20\_5, Sm30\_7, and so on.



**Figure S1** – Rietveld refinement plot for sample Sm20\_room pressure. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S2** – Rietveld refinement plot for sample Sm20\_2.75. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S3** – Rietveld refinement plot for sample Sm20\_3.45. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S4** – Rietveld refinement plot for sample Sm20\_4.20. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S5** – Rietveld refinement plot for sample Sm20\_4.88. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S6** – Rietveld refinement plot for sample Sm20\_7.54. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S7** – Rietveld refinement plot for sample Sm30\_room pressure. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S8** – Rietveld refinement plot for sample Sm30\_1.15. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S9** – Rietveld refinement plot for sample Sm30\_1.85. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S10** – Rietveld refinement plot for sample Sm30\_1.95. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S11** – Rietveld refinement plot for sample Sm30\_2.18. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S12** – Rietveld refinement plot for sample Sm30\_2.63. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S13** – Rietveld refinement plot for sample Sm30\_2.99. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S14** – Rietveld refinement plot for sample Sm30\_4.18. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S15** – Rietveld refinement plot for sample Sm30\_5.23. Excluded regions are placed in correspondence of Bragg peaks of Cu, which was used to calibrate the applied pressure.



**Figure S16** – Rietveld refinement plot for sample Sm40\_2.42.



Figure S17 – Rietveld refinement plot for sample Sm40\_3.00.



**Figure S18** – Rietveld refinement plot for sample Sm40\_3.17.



Figure S19 – Rietveld refinement plot for sample Sm40\_3.73.



**Figure S20** – Rietveld refinement plot for sample Sm40\_4.11.



**Figure S21** – Rietveld refinement plot for sample Sm40\_4.67.



Figure S22 – Rietveld refinement plot for sample Sm50\_room pressure.



Figure S23 – Rietveld refinement plot for sample Sm50\_0.20.



Figure S24 – Rietveld refinement plot for sample Sm50\_1.11.



Figure S25 – Rietveld refinement plot for sample Sm50\_1.86.



Figure S26 – Rietveld refinement plot for sample Sm50\_2.60.



Figure S27 – Rietveld refinement plot for sample Sm50\_3.92.



Figure S28 – Rietveld refinement plot for sample Sm50\_5.05.



Figure S29 – Rietveld refinement plot for sample Sm50\_6.94.



Figure S30 – Rietveld refinement plot for sample Sm50\_7.32.



Figure S31 – Rietveld refinement plot for sample Sm60\_0.74.



Figure S32 – Rietveld refinement plot for sample Sm60\_1.58.



Figure S33 – Rietveld refinement plot for sample Sm60\_2.98.



Figure S34 – Rietveld refinement plot for sample Sm60\_4.11.



Figure S35 – Rietveld refinement plot for sample Sm60\_4.86.



Figure S36– Rietveld refinement plot for sample Sm60\_5.43.



Figure S37–Rietveld refinement plot for sample Sm60\_6.00.



Figure S38– Rietveld refinement plot for sample Sm60\_6.56.