SUPPLEMENTARY INFORMATION FOR

Reversible Oxygen Intercalation in Hexagonal Y_{0.7}Tb_{0.3}MnO_{3+δ}: Toward Oxygen Production by Temperature-Swing Absorption in Air

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Table. S1. Structural parameters of the as-synthesized $Y_{0.7}Tb_{0.3}MnO_3$ samples. The parent Hex0 ($\delta = 0$) *P*6₃*cm* phase was used in the Rietveld refinements.

Sample	a [Å]	c [Å]	V[Å ³]	χ^2	R_{wp} [%]
Y _{0.7} Tb _{0.3} MnO ₃ SS	6.1576(1)	11.4022(1)	374.41(1)	2.122	2.4
Y _{0.7} Tb _{0.3} MnO ₃ SG	6.1612(1)	11.4143(2)	375.12(1)	1.519	6.5



Figure S1. (b-e) Elemental mappings registered at 10,000 magnification for the $Y_{0.7}Tb_{0.3}MnO_3$ SS powder grain shown in a). Data for: b) Y, c) Tb, d) Mn and e) oxygen.



Figure S2. (b-e) Elemental mappings registered at 10,000 magnification for the $Y_{0.7}Tb_{0.3}MnO_3$ SG powder grain shown in a). Data for: b) Y, c) Tb, d) Mn and e) oxygen.



Figure S3. Room temperature XRD patterns and the Rietveld refinements for the oxygen annealed samples during thermogravimetric analysis experiments: top - $Y_{0.7}Tb_{0.3}MnO_{3.45}$ SG; bottom - $Y_{0.7}Tb_{0.3}MnO_{3.37}$ SS. Oxygen content was determined from TG data. Small amounts of other hexagonal phases are denoted by asterisk

Table. S2. Structural parameters for the oxidized samples shown in Fig S3. Newly described Hex3 $P6_{3}mc$ structure was used in the Rietveld refinements.

Sample	a [Å]	c [Å]	V [Å3]	χ2	Rw_p [%]
Y0.7Tb0.3MnO3.45 SS	7.1507(1)	11.1463(2)	493.58(1)	4.982	3.4
Y0.7Tb0.3MnO3.45 SG	7.1449(1)	11.1486(2)	492.88(1)	5.563	3.8



Figure S4. a) Bright field TEM image of the Y_{0.7}Tb_{0.3}MnO_{3.45} SG (Hex3) material b) high resolution image at 500k magnification and c) the corresponding reduced FFT image. The calculated *d*-spacing ($d_{TEM} = 3.0947$ Å) corresponds very well to (200) plane of Hex3 structure ($d_{XRD} = 3.0938$ Å).



Figure S5. Time dependence of the a) oxidation and b) reduction processes during temperature swing experiment recorded for $Y_{0.7}Tb_{0.3}MnO_{3+\delta}$ SG sample in O₂ between 300 °C and 350 °C. Data was recorded for 10 consecutive cycles by using rapid heating and cooling of 100 °C min⁻¹ during temperature change.

Table. S3. Oxygen content change in $Y_{0.7}Tb_{0.3}MnO_{3+\delta}$ during temperature swing between 300 °C and 350 °C in oxygen atmosphere.

	δ change during heating	δ change during cooling
1 st cycle	0.339	0.160
2 nd cycle	0.191	0.156
3 rd cycle	0.165	0.157
4 th cycle	0.160	0.156
5 th cycle	0.160	0.158
6 th cycle	0.158	0.156
7 th cycle	0.157	0.160
8 th cycle	0.160	0.155
9 th cycle	0.155	0.154
10 th cycle	0.157	0.158



Figure S6. Isothermal reduction of $Y_{0.7}Tb_{0.3}MnO_{3+\delta}$ SG sample registered at 330 °C after initial oxidation at 265 °C in air for 45 h (see text for details).



Figure S7. XRD pattern together with Rietveld analysis for $Y_{0.7}Tb_{0.3}MnO_{3+\delta}$ SS samples after heating in oxygen at 300 °C and 275 °C for 7 days.

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