Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018



Figure S1. Rietveld analysis of pristine LuFe₂O₄ at RT



Figure S2. Rietveld analysis of pristine YbFe₂O₄ at RT



Figure S3. Rietveld analysis of pristine YFe₂O₄ at RT



Figure S4. Rietveld analysis of pristine $InFe_2O_4$ at RT





Figure S6. Lebail fit of maximally oxidized (ex situ) YbFe_2O_{4+\delta} at RT



Figure S7. Lebail fit of maximally oxidized (ex situ) $YFe_2O_{4+\delta}$ at RT



Figure S8. Lebail fit of maximally oxidized (ex situ) $InFe_2O_{4+\delta}$ at RT



Figure S9. The evolution of unit cell volume as a function of temperature in He and Air. Even though thermal expansion is observed under He, an anisotropic lattice parameter change is observed under air. Both atmospheres give rise to a similar net cell volume change as the 'a' parameter expansion rate in air was higher than that in He, compensating for the decrease in the 'c' parameter in air



Figure S10. To get a better understanding of oxygen insertion mechanism, $LuFe_2O_4$ was heated from RT to 250 °C in He, then exposed to O_2 /He for 15 min, and finally ramped up to 700 °C at 10°C/min under H₂. The *in-situ* diffraction patterns are illustrated here. Upon exposure to O_2 at 250°C the R2 supercell structure formed. However, when the temperature reached 500 °C, the fully oxidized R3 phase formed even under the fully reducing atmosphere of H₂. This indicates that the mechanism for oxygen insertion faces a low activation barrier as it easily incorporates into the layered structure at the relatively low temperature of 250 °C.



Figure S11. Rietveld analysis done for $InFe_2O_4$ a) The pristine compound at RT b) regenerated compound at the end of the 1st cycle at 600 °C c) regenerated compound at the end of the 2nd cycle at 600 °C. InFe₂O₄ degrades under H₂ and the degradation products are indicated at the top right corner with phase percentages by weight.



Figure S12. The change of oxygen non-stoichiometry (δ) with temperature calculated using thermogravimetric analysis done for the four *A*-site analogues using three ramp rates a) 5 °C/min b) 10 °C/min c) 25 °C/min. The sample were equilibrating every 100 °C for 10 minutes d) Heated at 10 °C/min till 600 °C and then held at 600 °C for 3 hours. The δ value changed slightly across the different ramp rates.

Lattice parameter	LuFe ₂ O ₄	YbFe ₂ O ₄
<i>a</i> (Å)	5.95313 (4)	5.98747 (3)
<i>b</i> (Å)	3.44019 (3)	3.46233 (2)
<i>c</i> (Å)	8.65173 (4)	8.60957 (5)
beta (°)	103.269 (1)	103.402° (1)

Table S1. Lattice parameters for Lu and Yb in the C2/m space group

Table S2. Structural parameters from Rietveld refinement using 6c site and isotropic ADPs for the *A* cation

	LuFe ₂ O ₄	R-3m		a = 3.43748(1) Å	<i>c</i> = 25.2567(1) Å	R_{wp} = 13.68%
Aton	n Site	х	у	Z	Occ.	B_{eq} (Å ²)
Lu	6 <i>c</i>	0	0	0.00676(2)	0.5	0.0019(71)
Fe	6 <i>c</i>	0	0	0.21529(2)	1	0.3131(11)
01	6 <i>c</i>	0	0	0.12900(11)	1	0.803(42)
02	6 <i>c</i>	0	0	0.29227(11)	1	0.803(42)
	YbFe ₂ O ₄	R-3m		<i>a</i> = 3.45879(1) Å	<i>c</i> = 25.1205(1) Å	R_{wp} = 14.044%
Yb	6 <i>c</i>	0	0	0.00715(2)	0.5	0.0221(79)
Fe	6 <i>c</i>	0	0	0.21496(3)	1	0.491(13)
01	6 <i>c</i>	0	0	0.29182(11)	1	1.107(44)
02	6 <i>c</i>	0	0	0.12830(11)	1	1.107(44)
	YFe ₂ O ₄	R-3m		<i>a</i> = 3.51093(1) Å	<i>c</i> =24.8356(1) Å	$R_{wp} = 14.14\%$
Y	6 <i>c</i>	0	0	0.00844(1)	0.5	0.413(11)
Fe	6 <i>c</i>	0	0	0.21450(2)	1	0.990(9)
01	6 <i>c</i>	0	0	0.29228(11)	1	1.611(33)
02	6 <i>c</i>	0	0	0.12786(7)	1	1.611(33)
	InFe ₂ O ₄	R-3m		a = 3.33898(1) Å	<i>c</i> = 26.07193(1)	<i>R_{wp}</i> 11.528%
In	6 <i>c</i>	0	0	0.00218(6)	0.5	0.2281(79)
Fe	6 <i>c</i>	0	0	0.21651(1)	1	0.539(11)
01	6 <i>c</i>	0	0	0.12861(6)	1	0.734(23)
02	6c	0	0	0.29291(7)	1	0.734(23)

Table S3. Values of R_0 and B adopted for the calculation of BVS

	R ₀	В	Reference
Fe ²⁺	1.658	0.447	Gagné, O. C.; Hawthorne, F. C. Acta Crystallogr. Sect. B
Fe ³⁺	1.766	0.36	Struct. Sci. Cryst. Eng. Mater. 2015 , 71 (5), 562–578.