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In situ diffraction studies on reversible oxygen uptake and release in $AFe_2O_{4+\delta}$ (A= Lu, Yb, Y, In).

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We have studied the reversible uptake and release of oxygen in the layered metal oxide system AB_2O_4 for A= Lu, Yb, Y, and In to understand their suitability as oxygen storage materials. We first examined their structures in their pristine state of AFe_2O_4 with high-resolution synchrotron X-ray diffraction. To emulate chemical looping conditions, we then monitored their structures and reactivity under H₂ and O₂ atmospheres utilizing *in situ* synchrotron X-ray diffraction and thermogravimetric analysis (TGA) measurements. The nature of the trivalent *A* cation affects the oxidation kinetics, thermal cycling stabilities, and oxygen storage capacities, which varied between 2.20-3.13 wt.% (0.7-0.98 O₂ mmol/g), corresponding an oxygen nonstoichiometry (δ) of ~0.5. These layered oxides underwent various phase transitions above 200 °C that included the creation of a superstructure as oxygen incorporates until the maximally oxidized phase is established above ~400 °C. Bond valence sum analysis of the Fe-O bonding across the series reveals that the more underbonded the Fe cation, the more facile the oxygen insertion. During the cycling experiments all samples exhibited stable reversible oxygen insertion at 600 °C with the exception of *A*=In, which degraded under H₂. The Y analogue displayed the fastest kinetics for oxidation, which may make it the most suitable for oxygen storage and sensing applications.

1.Introduction

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In addition to their unique optical, magnetic and electronic properties,¹ oxides of transition metals in mixed valence states also display important functions in energy storage and conversion.^{2,3} In particular, their ability to reversibly uptake and release oxygen renders them relevant for key energy applications such as oxygen storage, energy conversion and oxygen gas sensing.^{4,5} Mixed valence metal oxides can act as oxygen storage materials (OSMs) releasing (or gaining) oxygen under reducing (or oxidizing) environments, which is often correlated to their oxygen non-stoichiometries. A challenge in this field is to design materials whereby oxygen is released and incorporated topotactically and efficiently as the redox active metal cycles between two oxidation states.

Chemical looping combustion (CLC) and chemical looping reforming (CLR) are two applications that utilize OSMs to thermochemically deliver oxygen from air to fuels. These OSMs can either completely oxidize a fuel in CLC (to generate CO_{2+} H₂O) or partially oxidize a fuel in CLR (to generate CO+ H₂).⁶ OSMs eliminate the need to purify and isolate oxygen by the costly process of cryogenic distillation. Furthermore, it enables easy product separation and prevents product contamination by NOx gas formation.^{6,7} Long term stability, fast and reversible

redox kinetics, low operational temperatures, and high oxygen storage capacities are all metrics for designing new OSMs. ^{6,8}

The materials first studied as OSMs include the binary oxides of Mn, Fe, Co, Ni, and Cu due to their natural abundance and variable oxidation states.⁹ However, their agglomeration from sintering under the thermal work conditions have been a major drawback. As alternatives to binaries, ternary metal oxides such as perovskites and spinels have been researched as OSMs owing to their high structural stability and oxygen storage capacities (OSCs).^{10–13} Two types of oxygen species in these oxides take part in the oxidation process: 1) weakly bound lattice oxygen that completely oxidizes the fuel at lower temperatures 2) strongly bound lattice oxygen that partially oxidizes the fuel (chemical reforming) at higher temperatures.^{10,11} Hence by fine tuning the type of ternary metal oxide and the reaction conditions, a well-designed OSM could achieve specific product selectivity.

The layered oxide LuFe₂O₄ has drawn recent attention as an OSM and a conductometric gas sensor owing to its 1:1 mixed valence states of Fe²⁺ and Fe³⁺.^{14–16} LuFe₂O₄ does not adopt the typical AB_2O_4 spinel or ferrite aristotypes but instead a structure consisting of bilayers where edge-sharing BO_5 trigonal bipyramids alternate with edge-sharing AO_6 octahedra (Fig 1a). Typically, the *A* cation is trivalent such as a lanthanide (Ln^{3+}) and *B* is a transition metal in a mixed valence state. LuFe₂O₄ is the second member of the homologous $[AO_2]_m[BO]_n$ series with m=1 and n=2,¹⁷ and its unit cell has the centrosymmetric space group *R*-3m¹⁸ (Fig. 1b). However, a lowering of symmetry to *P*1 or *C*2/*m* has been reported due to the structural distortion arising from charge ordering below 330K that breaks the 3-fold

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Figure 1. a) The crystal structure of AB₂O₄ and its unit cell in b) R-3m and c) C2/m space groups. While R-3m is standard, C2/m is used for LuFe₂O₄ due to its charge order driven monoclinic distortion below 330 K. The relation between their lattice parameters is also shown where β_M is the monoclinic angle.¹⁴

rotational symmetry.^{19,20} Through electron diffraction studies, Hervieu et al. reported the monoclinic space group C2/m to describe the charge ordered phase and its relationship to the hexagonal unit cell (Fig. 1c).14 However, R-3m is the most commonly reported space group for the isostructural YbFe₂O₄²¹, YFe₂O₄²² and InFe₂O₄.²³

The AB₂O₄-type oxides have been heavily researched for their physical properties such as multiferroicity, magnetism, and linear/non-linear electronic conduction.^{24–30} However, oxygen storage properties have not been explored as much in this system. Hervieu et al. found that $LuFe_2O_4$ can be successfully cycled between its reduced (Fe^{2.5+}) and oxidized (Fe ³⁺) states at 500 °C under hydrogen and dynamic vacuum.¹⁴ Reversible oxygen intercalation was confirmed through X-ray diffraction and thermogravimetric analysis. Despite the AFe₂O₄ family having the same structure type, their physical properties vary depending on the A-site cation. For instance, LuFe₂O₄ exhibits charge ordering below 330 K14 and ferrimagnetism at 240 K,³¹ YFe₂O₄ displays two metal-insulator transitions at 240 K and 220 K with antiferromagnetic spin ordering,³² while InFe₂O₄ exhibits both charge and magnetic orderings below room temperature.³³ This study is the first to explore the impact of elemental substitution in the AB2O4-system on two properties: 1) kinetics of reduction/oxidation and 2) overall oxygen storage capacity.

We first report the effects of A-site substitution on the structure of the four analogues, A= Lu, Yb, Y and In from room temperature to 700 °C. Next, we relate their reactivity and suitability as OSMs as determined by cycling experiments carried out at 600 °C in oxidizing and reducing atmospheres emulating both CLC and CLR conditions. The rapid data collection of *in situ* synchrotron X-ray powder diffraction (sXPD) allows to monitor the kinetics of the redox reactions by analyzing unit cell volume and lattice parameter changes with time. Using thermogravimetric analysis (TGA) experiments we further investigate their oxygen storage capacities (OSCs) and the suitability as OSMs in related oxygen-sensitive applications.

2.1 Materials synthesis

All samples were prepared using solid-state reactions. 99.9% (Alfa Aesar) A₂O₃ (A=Yb, Lu, In, Y), 99% (Sigma Aldrich) Fe₂O₃ and 99.5% (Sigma Aldrich) Fe powder were ground in an agate mortar and pestle in 1/2: 5/6: 1/3 ratio respectively to prepare 0.25 g of the target compound, and pressed into pellets of 13-mm diameter. The pellets were placed in a 2 ml alumina crucible and sealed inside evacuated 8 mm diameter quartz ampoules. Before sealing, the ampoules were flushed with N₂ gas and evacuated several times to obtain the required oxygen partial pressure (P₀₂).³⁴ These compounds are highly sensitive to the P_{02} , and $A_2Fe_3O_7$ often forms as an impurity if the P_{02} is not below approximately 10-7 Torr. The samples were sintered at 1180 °C (850 °C for In) for 12 hours and then quenched to room temperature. To make the oxidized phases, $AFe_2O_{4+\delta}$ (ex situ), the as synthesized samples were oxidized at 500 °C under air and cooled to room temperature.

2.2 Ex situ high-resolution sXPD

Ex situ experiments with high-resolution synchrotron X-ray powder diffraction (sXPD) were performed on the 11 BM beam line at the Advance Photon Source (APS) at Argonne National Laboratory. An average wavelength of 0.41458 Å was used, covering a *Q*-range of approximately ~0.7 Å⁻¹ to 10 Å⁻¹. Powder patterns were collected at ambient temperature and pressure for both the pristine compounds (AFe₂O₄) and their oxidized phases (AFe₂O_{4+δ}) prepared ex situ. The powder patterns were analysed by Rietveld refinements for the pristine phases and Le Bail fits for the oxidized phases using TOPAS 5.35

2.3 In situ sXPD

In situ sXPD experiments were performed in transmission geometry on the 17 BM beam line at the APS. A 2D PerkinElmer Si flat panel detector was used with an average wavelength of 0.45336 Å. We collected diffraction patterns every 0.33 seconds and integrated the diffraction images with GSAS-II³⁶ to yield patterns with a Q-range of approximately 0.30 Å⁻¹ to 6.6 Å⁻¹. A constant gas flow was maintained at a rate of 15 mL/min through a quartz capillary sample holder which was loaded with the sample, and a residual gas analyzer (RGA) was used to monitor the gaseous products.

Two types of experiments were carried out for all the A-site analogues. First, we ramped the temperature of the sample environment up to 700 °C under 20% O₂/He (air), holding at every 100 °C for 20 minutes. We repeated this temperature profile in pure helium to differentiate between temperature and oxidation driven changes. Second, we performed cycling experiments to emulate a chemical looping reactor, by

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switching the atmosphere between 20 % O₂/He and 3.5 % H₂/He. The samples were heated to 600 °C in He and held at 600 °C while cycling between the two atmospheres. Automated sequential refinements³⁷ were carried out using TOPAS 5 to study the lattice volume evolution with time.

2.4 Thermogravimetric analysis (TGA)

TGA was conducted using a SDT Q600 equipped with a TA Discovery MKS104-S0212004 Micron Vision 2 Mass Spectrometer. The instrument was calibrated prior to the experiment using alumina standards for each ramp rate. Ramp rates of 5 °C/min, 10 °C/min, and 25 °C/min were used with a flow rate of 100 ml/min. Samples were heated to 700 °C in air, holding at every 100 °C for 10 minutes to allow for maximum weight gain. An experiment was also done by heating samples up to 600 °C in air at 10 °C/min and holding the temperature for 3 hours at 600 °C to monitor the stability in the weight gained.

3. Results

3.1 Structures of AFe_2O_4 and AFe_2O_{4+\delta} from high-resolution sXPD

We successfully fitted a structural model¹⁸ for pristine AFe_2O_4 phases (before oxidation) to the high-resolution sXPD pattern collected at room temperature (Fig. 2). A Pseudo-Voight function was used for the peak shape profile and the intensities were corrected for Lorentz-polarization and absorption effects. The refined structural parameters are listed in Table 1. All four

A-site analogues are isostructural with relative/iechanges. Line intensities, predominantly for the (003). (006)^{9/and/0}(009) reflections, due to the difference in the A-site atomic scattering factors. We observed the characteristic splitting of the (015) reflection in R-3m symmetry to the (1-1-2) and (201) reflections in C2/m symmetry for the Yb and Lu compounds but not the Y and In analogues as shown in Fig. 2e. However, since our focus is to compare A-site substitution effects, R-3m (No. 166) was used as the space group for all four compounds. The lattice parameters for Lu and Yb in the C2/m space group are included in the supplementary information (Table S1).

During the Rietveld analysis, we introduced anisotropic atomic displacement parameters (ADPs) for the A-site, which we found to significantly improve the fit (for $A=Yb R_{wp}$ from 18.17% to 14.04 %). Table 1 shows the refinement results when anisotropic ADPs were used with the A cation occupying the 3a special position with 100% occupancy. However, we could similarly improve the fit when we employed isotropic ADPs for the A-site while it occupied the 6c site (0, 0, z) at 50% occupancy (Table S2). The site occupancy of A=In slightly deviated from unity, which likely occurred due to the high volatility of In. We therefore sintered $InFe_2O_4$ at a lower temperature than the rest. We performed Le Bail fits for the high-resolution sXPD patterns of the maximally oxidized phase $AFe_2O_{4+\delta}$ prepared *ex situ* (Fig. S5-S8). P-3 was used for A = Yb, Lu and Y^{38} , and C2/m was used for $A = \ln^{39}$ as the space group, and the refined lattice parameters are shown as an inset



Figure 2. Observed, calculated, and difference curves of the AFe_2O_4 crystal structures at room temperature (RT) with high-resolution synchrotron X-ray powder diffraction patterns for A = a) Lu, b) Yb, c) Y, and d) In. A wavelength of 0.41458 Å was used. e) Monoclinic distortion observed in the high resolution sXPD patterns of Lu and Yb analogues as evidenced by the splitting of the (0 1 5) reflection of *R*-3*m* symmetry in to the (1-1-2) and (2 0 1) reflections of *C*2*/m* symmetry.

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Table 1. Structural parameters from Rietveld refinement with the high resolution (11-BM) synchrotron X-ray powder diffraction data for the AFe₂O₄ series at 298 King Article Opling

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LuFe ₂ O ₄		R-3m	<i>a</i> = 3.43731 (1) Å	<i>c</i> = 25.2556 (1) Å	<i>R_{wp}</i> = 13.57 %				
Atom	Site	х	У	Z	Occ.	B _{eq} /U _{ii} (Ų)			
Lu	3a	0	0	0	1	$U_{11} = U_{22} = 0.00006$ (9)	U33 = 0.03407 (23)	<i>U</i> ₁₂ = 0.00003 (9)	
Fe	6c	0	0	0.21530 (2)	1	0.357 (11)			
01	6c	0	0	0.12902 (11)	1	0.837 (42)			
02	6c	0	0	0.29206 (11)	1	0.837 (42)			
YbFe ₂ O ₄			R-3m	<i>a</i> = 3.45879 (1) Å	<i>c</i> = 25.1205 (1) Å	<i>R_{wp}</i> = 14.39 %			
Yb	3a	0	0	0	1	$U_{11} = U_{22} = 0.00013$ (10)	U33 = 0.03791 (27)	U ₁₂ = 0.00007 (10)	
Fe	6c	0	0	0.21497 (3)	1	0.537 (13)			
01	6c	0	0	0.29179 (11)	1	1.102 (44)			
02	6c	0	0	0.12837 (11)	1	1.102 (44)			
YFe ₂ O ₄			R-3m	<i>a</i> = 3.51188 (1) Å	<i>c</i> =24.84257 (7) Å		<i>R_{wp}</i> = 12.03 %		
Y	3a	0	0	0	1	$U_{11} = U_{22} = 0.00230$ (8)	<i>U</i> ₃₃ = 0.06285 (26)	U ₁₂ = 0.00115 (8)	
Fe	6c	0	0	0.21454 (1)	1	1.059 (7)			
01	6c	0	0	0.29193 (6)	1	1.557 (20)			
02	6c	0	0	0.12828 (5)	1	1.557 (20)			
InFe ₂ O ₄		R-3m		<i>a</i> = 3.33899 (1) Å	<i>a</i> = 3.33899 (1) Å <i>c</i> = 26.07201 (1) Å		<i>R_{wp}</i> = 13.31 %		
In	3a	0	0	0.00218(6)	0.970 (1)	$U_{11} = U_{22} = 0.00350$ (8)	<i>U</i> ₃₃ = 0.00716 (13)	U ₁₂ = 0.00175 (8)	
Fe	6c	0	0	0.21653 (1)	1	0.516(9)			
01	6c	0	0	0.12861 (6)	1	0.758 (20)			
02	6c	0	0	0.29290 (6)	1	0.758 (20)			

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3.2 Structural evolution with temperature: In situ sXPD

With *in situ* sXPD, we explored the thermal stability, optimal operating temperatures and associated structural phase transitions of the title compounds. Fig. 3 shows the contour plots of the *in situ* sXPD patterns of AFe_2O_4 as they are heated under air up to 700 °C. Below 200 °C we did not observe any new reflections, and the room temperature phases of AFe_2O_4 ,

which we label R1, were retained. Upon further heating, extra satellite reflections appeared around 230 °C for all compounds except for In, which indicated the formation of the supercell structure (R2 phase). These supercell reflections gradually disappear around 350 °C for Y and 480 °C for Lu and Yb. In the 250 °C - 450 °C region, the diffraction peaks are not well defined,



Figure 3. Contour plots of the sXPD data as AFe_2O_4 is heated in air (20% O_2 in He) from 100 °C to 700 °C. a) The Lu, b) Yb, c) Y and d) In analogues. The yellow labels and blue dash lines indicate phase co-existence. The white arrows and asterisks mark some of the reflections: (0 0 6) belongs to the R1 phase (AFe_2O_4) in *R*-3*m* symmetry, (0 2 4) is one of the supercell reflections in the R2 phase that develops above 230 °C, (0 0 2) belongs to the R3 oxidized phase ($AFe_2O_{4+\delta}$). The asterisks mark the satellite peaks which belong to the R2 supercell, and are observed for the Lu, Yb and Y analogues. e) The supercell satellite reflections in the isolated powder patterns of the R2 super cell structure at the end of the 20 min hold at 300 °C for Lu, Yb and Y analogues.

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Figure 4. Contour plots of synchrotron x-ray diffraction patterns of the AFe₂O₄ series during cycling between oxidizing (20% O₂ in He) and reducing (3.5% H₂ in He) atmospheres at 600 °C. a) LuFe₂O₄ b) YbFe₂O₄ c) YFe₂O₄ and d) InFe₂O₄. Three consecutive cycles were carried out for Lu and Yb and two cycles for Y and In. The Lu, Yb and Y analogues show stable cyclability. The degradation of InFe₂O₄ under H₂ is clearly evidenced by the diminishing intensities of the Bragg reflections.

and the patterns display a large amount of phase co-existence, most apparently for Y. Upon further heating, a major structural phase transition occurs and the maximally oxidized phase (same as the *ex situ* structure in Fig. S5-S8) is reached, which we label the R3 phase. This transition is complete by 430 °C for Y, 500 °C for Lu and Yb, and 600 °C for In (Fig. 3). Evidently, the A-site substitution has an impact on the oxidation temperatures, controlling the window of stability for the high-temperature R3 phase. All four compounds were stable until 700 °C. The *in situ* diffraction experiments performed in air were repeated in He to isolate temperature driven changes from those driven by oxidation. We observed different trends in the lattice parameter evolution under the two atmospheres (discussed in section 4.2). DOI: 10.1039/C7TA09823E

3.3 Cycling experiments with in situ sXPD

The optimal operational temperature for OSMs in chemical looping reactions is a trade-off between fast redox kinetics of oxygen release/uptake and prolonged structural stability. To achieve fast reaction rates while preserving the structural stability, we chose 600 °C as the cycling temperature for the *in situ* sXPD experiment. To this end, cycling experiments were performed under oxidizing (20% O₂ /He) and reducing (3.5 % H₂/He) atmospheres. Fig. 4 shows the structural evolutions observed in this experiment as a contour plot of some major reflections. The cycling stability and reactivity was almost identical for the Lu and Yb analogues (Fig. 4a, 4b). The In analogue, however, started to degrade once it was exposed to the H₂ (Fig. 4d).

3.4 Thermogravimetric analysis (TGA)

To correlate oxidation driven weight changes to crystallographic changes, we performed TGA mimicking the *in situ* sXPD experiment (Fig. 3). Fig. 5 displays the TGA curves where samples were heated up to 700 °C, equilibrating every 100 °C for 10 minutes. The R2 supercell structure that formed above 200 °C in the *in situ* sXPD corresponds to a weight gain of 0.80-1.0 % (for Lu, Yb, Y). The total weight gain, once the R3 phase is formed, varies from 2.2 % to 2.6 % among the four oxides. The derivative of the weight change is also plotted in Fig. 5 (black curve), and the highest weight gain due to oxidation occurs between the 300 °C - 400 °C region for all samples. This rapid weight gain, however, is most pronounced for the Y analogue, indicating that this analogue displays the fastest kinetics for oxide insertion. The derivative curve also



Figure 5. Thermogravimetric analysis (TGA) depicting the weight change % as a function of time and temperature for a) LuFe2O4 b) YbFe2O4 c) YFe2O4 and d) InFe2O4. The corresponding synchrotron powder diffraction patterns are shown on the left of each TGA

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Figure 6. a). The linear dependence of *a*- and *c*-lattice parameters on the radii of the *A* cations. The size of the spheres is to scale. b) Displacement of Fe from the center of the trigonal bipyramid towards the AO_6 octahedral layer. As a result, there are three distinctive Fe—O bond lengths which are denoted as Q, R and S.

demonstrates that the In analogue is the most sluggish of the series, which corroborates our *in situ* sXPD data. Calculations of OSCs based on all TGA experiments are presented in section 4.4.

4. Discussion

4.1 A-site substitution effects on structure, bond valence of Fe and kinetics of oxidation

In the AFe₂O₄ series, the transition metal is the redox active centre while the A-site cation does not directly participate in the reaction. While this is the case in many OSM's consisting of ternary metal oxides, the A-site cation has shown to play key roles in determining the stability of the compound, concentration of oxygen vacancies, and the oxidation state of the transition metal.²⁸ Shen et al. compared A-site substitution effects of several AFeO₃ perovskites and found that the oxygen desorption capability varies on the A cation's radius.⁴⁰ In this study Ba and Sr were used as the A-site cations, and the Ba analogues showed higher oxygen desorption amounts due to the larger lattice volumes. In a similar study of three hexagonal AMnO₃ perovskites, Abughayada et al. demonstrated that the oxygen storage capacity is highly sensitive to the A cation's radius,⁴¹ where the adsorption/desorption of the oxygen content increased with larger A cations. Hence, we anticipated comparable results for the AFe₂O₄ series.

Based on our Rietveld refinements, both structural and cell parameters are affected by the nature of the A-site in the title compounds. The *a*-lattice parameters follow the order Y^{3+} Yb³⁺> Lu³⁺> In³⁺, while the *c*-lattice parameters behave conversely. The ionic radii of the A-site cation clearly determine these trends (Fig. 6a). Rietveld refinements of the R1 phase also revealed significant A-site disorder from the special position 3a. This characteristic disorder has been reported previously for LuFe₂O₄.^{18,13} Infrared spectroscopy has also revealed a splitting of the Lu-O vibrational modes,42 which arises from the interactions between the polar \mbox{FeO}_5 bilayers with the \mbox{LuO}_6 octahedral layers. The polarity in FeO₅ bilayers is attributed to charge ordering of the Fe³⁺ (electron-deficient) and Fe²⁺ (electron-rich) cations. In our study, we observed this anisotropic disorder along the z axis for the A cations in all four compounds.

Upon heating in air, we observed the supercell structure of the R2 phase around 250 °C (Fig.3a-c). Hervieu et al. found the



Figure 7. Isolated *in situ* sXPD patterns of LuFe₂O₄, collected while ramping under air from RT to 700 °C shown with the refined unit cell parameters. **a)** The structure of LuFe₂O₄ at RT **b)** The super cell structure at 300 °C. The satellite reflections marked with red arrows are due to the O₂ driven modulations. **c)** The maximally oxidized structure of LuFe₂O_{4+ $\delta}$} at 600 °C

same supercell reflections by X-ray and electron diffraction, indexed them in the rhombohedral R-3m space group,¹⁴ and attributed their appearance to oxygen insertion in a manner commensurate to the metal sublattice. The refined powder pattern of the R2 phase for LuFe₂O₄, isolated at 300 °C, is shown in Fig. 7b along with the refined unit cell parameters. Interestingly, we observed the formation of the R2 phase for the Lu, Yb and Y analogues but not for the case of A = In.

To extend our understanding of the A-site substitution effects on the structure of the title compounds, we carried out bond valence (BV) calculations using bond lengths from the Xray diffraction results. BVs were calculated using the formula of Brown and Altermatt,⁴³ and the empirical values R₀ and B were adopted from Gagné et al. (Used R₀ and B values are listed in Table S3).44 Bond lengths and BVs of the Fe—O bonds are tabulated alongside the A-site ionic radii in Table 2. In the FeO₅ trigonal bipyramidal polyhedron, the Fe atoms are off-centre and shifted towards the AO₆ octahedral layers to create two unequal Fe—O axial bond lengths (Fig. 6b). While the axial Fe— O bonds showed no significant trend with the choice of A-site cation, the equatorial Fe-O bond lengths showed a direct correlation to the A cationic radii. This is also reflected in the overall bond valence sum (BVS) of Fe-O bonds. The BVS of Fe-O in the Y and In analogues depict the highest and lowest deviation from the average valence state of 2.5 in Fe. Hence, in the Y analogues, iron is the most under-bonded, and in the case of In, it is the most over-bonded before the oxidation step.

The mixed valence state (+2.5) of the R1 phase has been observed by Fe-2*p*, O-1*s* X-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy,^{31,45} and other studies have confirmed that when forming the R3 phase, the mixed valence state goes fully to Fe³⁺.^{46,38} One noticeable difference across our series is the temperature at which oxidation to the R3 phase is

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Figure 8. The evolution of lattice parameters as a function of temperature in He and Air obtained from sequential refinements for Lu and Yb. While thermal expansion is observed under He, an anisotropic lattice parameter change is observed under air due to oxidation driven effects. The error bars are shown and are smaller than the marker

completed. As mentioned in section 3.2 (Fig. 3), Y is the first to fully transform to the R3 phase (~ 430 °C) while In is the last (~600 °C). This difference in reactivity towards oxidation clearly reflects the difference in the deviation in the BVS of Fe from the mixed valence (+2.5) state. In the Y analogue, Fe is found in the most under-bonded environment, and hence oxidizes the fastest. The reverse is found for the In analogue, where the sluggish kinetics of oxygen insertion is likely due to Fe being over-bonded.

4.2 Lattice expansion from oxygen insertion vs thermal expansion

Upon heating the samples in He, we did not observe any of the above discussed phase transitions, confirming that they are completely driven by oxygen insertion. To further isolate the thermal expansion effects from oxidation ones, the evolution of refined unit cell parameters with time was analyzed in air versus He. Fig. 8 depicts the evolution of cell parameters for Lu and Yb in both atmospheres. In air, anisotropic cell volume changes were observed as opposed to the isotropic thermal expansion under He. The *a*-lattice parameter gradually increased as a function of temperature while the *c*-lattice parameter decreased. A similar temperature dependence for lattice parameters was reported previously for the Yb and Tm analogues in the temperature range of 50-400 K.47 In our samples, the overall cell volume change was almost equal in both environments as the *a*-parameter expansion rate in air was higher than that in He, compensating for the decrease in the cparameter in air (Fig. S9). The increase in the *a*-parameter can be attributed to the bilayer shift mechanism in the *ab*-plane due to O^{2⁻} insertion, which has been evidenced from electron diffraction experiments.¹⁴ The decrease in *c*-parameter can be



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Figure 9. Comparison of unit cell volume change of the Lu and Yb analogues for 3 consecutive cycles. Refined unit cell volumes from sequential refinements are plotted with the error bar. Both compounds exhibit a similar stability and reversibility throughout the three cycles. Error bars are smaller than the markers.

attributed to the decreasing ionic radii of iron upon oxidation. Approximately 35-44% of Fe-sites are already oxidized at 300 °C (in air) in the Lu and Yb compounds based on the ionic radii change (~0.1 Å) and c-lattice parameter change (0.035-0.044 Å).

4.3 Thermochemical cycling capability and stability

The only study¹⁴ to test the oxygen storage capacity and cycling stability of LuFe₂O₄ utilized 500 °C as the cycling temperature where the reaction kinetics were slow. Hence, we chose 600 °C as the cycling temperature, which did in fact increase the reaction rate, noticeably for the reduction step. Fig. 9 depicts the refined cell volume change with time for the Lu and Yb analogues under air and H₂. The rate of cell volume change in air is relatively faster than that in H₂ illustrating the faster reaction kinetics for oxidation. This is a clear indication of the difference in the thermodynamic stability of the two phases. We also found the rate of cell volume change for both compounds to be nearly the same. This is promising since Yb is less expensive than Lu, and the Yb analogue could therefore be proposed as a cost-effective alternative to Lu. While YFe2O4 appeared stable towards cycling (Fig. 4c), it was rather difficult to calculate the accurate cell volume change due to highly disordered oxidized phases.

Under air, we observed that these layered oxides were quite stable but started to decompose above 700 °C. This observation agrees with the report by Hervieu et al.¹⁴ However, the stability under H₂ at 600 °C was not the same for all the samples. The In analogue started to degrade once it was exposed to the reducing atmosphere. Although the A-site cation typically does not take part in the redox reaction in many OSMs, In³⁺ reacts with H₂ to destabilize the structure and therefore leads to phase degradation (Fig. S11).

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Table 2. Comparison of bond lengths, unit cell volume and A³⁺ cationic radii of the A-site analogues at RT. Q, R and S are labels for the Fe-O bond lengths as shown in Figure 6b.

A-site cation			Fe-O			Shannon radii ⁴⁸ of A
		Q	R	S	sum Fe	site cation (Å)
In ³⁺	BL (Å)	1.9521 (2)	2.294 (2)	1.991 (2)		
	BV (v.u)	0.5515 (3)	0.237 (1)	0.501 (2)	2.392 (3)	1.06
Lu ³⁺	BL (Å)	2.0079 (5)	2.155 (4)	1.936 (4)		
	BV (v.u)	0.4803 (6)	0.334 (3)	0.574 (6)	2.349 (7)	1.117
Yb ³⁺	BL (Å)	2.0164 (5)	2.155 (4)	1.919 (4)		
	BV (v.u)	0.4703 (6)	0.333 (3)	0.599 (6)	2.343 (7)	1.125
Y^{3+}	BL (Å)	2.0392 (2)	2.153 (2)	1.985 (2)		
	BV (v.u)	0.4445 (2)	0.335 (2)	0.508 (3)	2.177 (3)	1.159

BV = bond valence, BL = bond length, v.u = valence unit

4.4 Comparison of oxygen storage capacity

The maximum oxygen non-stoichiometry (δ) that has been reported in this series is ~0.5 for $LuFe_2O_{4+\delta}.^{14}\,$ Fig. S12 a-c shows the change of δ with temperature, calculated with TGA measurements performed with three different ramp rates. The maximum δ obtained is close to ~0.5, which is reached by 400 °C for Y and by 600 °C for the rest of the oxides. Furthermore, across all ramp rates, the maximum OSCs vary between 2.20-3.13 wt.% (0.7-0.98 O2 mmol/g) at 600 °C, which are listed in Table 3. Taylor et al. has reported the OSC of the La_{1-x}Sr_xFeO₃ perovskite system together with OSCs of other metal oxides from literature.⁴⁹ In these oxide systems the OSCs range from 1.7-3.7 wt. %. Therefore, AFe₂O₄ compounds in this study have comparable OSCs to these perovskites, and structural modifications could be explored to further increase their OSCs. Figure S12d shows that once the maximum oxygen gain is reached at 600 °C, the OSCs remain stable over a time span of 3 hours. While oxidation kinetics do correlate with A-site ionic radii, the final OSCs do not. However, variations between OSCs could be complicated by other parameters such as particle size and surface area. While beyond the scope of this study, these parameters should be analyzed to better understand how to improve OSCs in the AFe₂O₄ system.

Ramp rate	5 °C/min		10 °C/min		25 °C/min	
OSC	wt.%	O ₂	wt.%	O ₂	wt.%	O ₂
		mmol/g		mmol/g		mmol/g
$LuFe_2O_4$	2.29	0.72	2.20	0.69	2.25	0.70
YbFe ₂ O ₄	2.41	0.75	2.36	0.73	2.21	0.69
YFe ₂ O ₄	2.99	0.93	3.07	0.96	3.13	0.98
InFe ₂ O ₄	2.64	0.82	2.60	0.81	2.38	0.74

Conclusions

We have studied four A-site analogues of AFe_2O_4 (A=Lu, Yb, Y, In) as OSMs. The Y and In compounds have never been explored as OSMs before, and we have found that Y and In express the fastest and the slowest kinetics, respectively, for oxygen uptake across all ramp rates. This study affords us the

ability to understand how the non-redox active metal center can affect important properties such as oxygen insertion kinetics and cycling stability. The A-site cationic radii demonstrate a clear correlation to the lattice parameter change of the pristine structures and to the iron valence state as evidenced by the BVS analysis. The deviation of the BVS of Fe from the ideal 2.5 state is directly proportional to the A-cationic radii, while the lattice parameters show an anisotropic correlation. When heated under air all four analogues undergo a phase transition above ~400 °C from R-3m (R1 phase) to P-3 or C2/m symmetry (R3-phase). For Lu, Yb and Y, the formation of a supercell structure is observed around 250 °C as evidenced by satellite reflections in sXPD data. Sequential refinements of in situ diffraction data indicate an anisotropic cell volume change in air contrary to the isotropic thermal expansion under He. As the deviation of the BVS of Fe increases, the temperature at which the phase transition from $R1 \rightarrow R3$ completes in air, decreases due to the more under-bonded Fe.

These layered oxides exhibit reversible oxygen insertion at 600 °C in alternating 20% O₂/He and 3.5% H₂/He atmospheres transitioning between the two phases (R1 and R3). Increasing cycling temperature from 500 °C to 600 °C increased the rate of reaction, and the rate of oxidation was faster than that of reduction. While Lu, Yb and Y showed stable cycling, the In analogue showed signs of degradation under H₂. OSCs calculated based on thermogravimetric analysis with different ramp rates vary in the range of 2.20-3.13 wt.% at 600 °C, but no clear trend with A-cation size could be established for this metric. However, the oxidation kinetics showed a direct correlation to the ionic radii across all ramp rates. Based on these gathered metrics, the Yb and Lu analogues have comparable reaction rates, cycling stability and OSCs, making Yb a cost-effective alternative for Lu. Considering the fast oxidation kinetics of the Y analogue at low temperatures along with its ability to cycle, it could be a suitable candidate for applications such as gas sensing in addition to chemical looping.

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