Oxygen Trapping and Cation Site-Splitting in $Y_{(2-x)}Pr_xO_{3+\delta}$ ($0.0 \leq x < 2.0$ and $\delta \leq 1.0$)

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Abstract

The reduction and oxidation of the solid solution $Y_{2-x}Pr_xO_{3+\delta}$ ($0.0 \leq x < 2.0$ and $\delta \leq 1.0$) is investigated with emphasis on potential solid state electrolyte applications in solid oxide fuel cells. The fully reduced solid solution $Y_{2-x}Pr_xO_3$ ($0.0 \leq x < 2.0$) crystallizes in the bixbyite structure (*Ia-3*). The oxidized solid solution $Y_{2-x}Pr_xO_{3+\delta}$ ($0.0 \leq x < 1.4$) forms bixbyite phases (*Ia-3*) whereas $Y_{2-x}Pr_xO_{3+\delta}$ ($1.4 \leq x < 2$) compositions form fully disordered defect fluorite structures (*Fm-3m*) with variable oxide defect concentrations. The two cation positions are investigated in detail using synchrotron powder X-ray and time of flight neutron diffraction data. In the bixbyite structures the *8c* cation site splits into the *16c* cation site and the *24d* cation position migrates toward the ideal fluorite coordination upon oxidation. Reductive in-situ diffraction experiments reveal the co-existence of the fluorite and bixbyite structure only in a narrow temperature range. During oxidation of the bixbyite phase a new *16c* oxide anion site is populated. The impact of the *16c* oxide site population on the cation sublattice is being discussed.

1. Introduction

Transition metal and rare-earth oxide phases span a broad range of structural motives and extended structure types. Combining this structural diversity with redox active cations can be utilized for materials design. In addition, the chosen synthesis methods decide over the product structures. Oxide defect structures are widely employed for ion conductors and find applications as solid state oxide electrolytes in solid state oxide fuel cells (SOFCs).¹ Oxide ion conductors are ideally designed from high symmetry oxide structures with a sufficient amount of oxide defects that are fully disordered. The activation energies for oxide migration between equivalent sites needs to be minimized in order to increase ion mobility in these solid state electrolytes.² Ion mobility is inhibited by the presence of ordered oxide defects in extended solids through the introduction of non-equivalent oxide sites. A deeper understanding of the formation and annihilation of oxide defects can be gained from following oxidation and reduction of good defect host structures. The cubic bixbyite structure (figure 1) is an ordered defect oxide structure, with cations completely disordered on the fully occupied $8b$ and $24d$ sites with 25% oxide defects with respect to the oxide defect free fluorite parent structure.³ The oxide anions are found in the fully occupied $48e$ site. Commonly 5% to 10% oxide defects are expected to optimize oxide ion conduction in defect fluorite structures.² The cubic fluorite structure crystallizes in space group $Fm-3m$ with one cation site ($4a$) and one anion site ($8c$).³ Consequently a mixed cation system of composition $A'_{(2-x)}A''_xO_{4-y}$ must be cation disordered. Additionally the oxide defects must also be disordered to maintain $Fm-3m$ symmetry. If an initial bixbyite structure is oxidized to a defect fluorite structure an order/disorder transition is expected for the oxide/defect sublattice. Figure 1 illustrates the relation between the bixbyite structure and the fluorite structure.

This work explores the transition into the ordered and disordered defect structures as a function of reduction and oxidation, respectively. A sufficient amount of A''^{4+} cations is

required in order to reach a sufficient oxygen composition for the formation of the disordered defect fluorite structure.

The $Y_{(2-x)}Pr_xO_{3+\delta}$ system is an excellent candidate to follow the structural evolution as a function of A' and A'' cation ratio and addition of extra oxygen. Previously the $Y_{(2-x)}Pr_xO_3$ phases have been reported as thin films prepared by molecular beam epitaxy as fully reduced bixbyites.⁴⁻⁷ Kimmel et al. reported a biphasic gap for the $Y_{(2-x)}Pr_xO_{3+\delta}$ system for bulk materials with $1 \leq x \leq 1.33$.⁸ In a recent study $YPrO_{3+\delta}$ has been reported as a single phase bixbyite and it has been shown⁹ that oxygen addition to $YPrO_3$ causes the *8b* cation site to split from the ideal position into a half occupied *16c* position. The additional oxygen is added to a newly created *16c* site without affecting the occupancy of the original *48e* site. No order/disorder transition is seen during the oxidation from $YPrO_3$ to $YPrO_{3.43(2)}$. A schematic of the oxidation of the ABO_3 bixbyite to $ABO_{3+\delta}$ is shown in figure 2. The $Y_{(2-x)}Pr_xO_{3+\delta}$ ($0.0 \leq x \leq 2.0$, and $0 \leq \delta \leq 1.0$) system is ideal for the investigation of defect annihilation and formation. We are reporting here that the $Y_{(2-x)}Pr_xO_{3+\delta}$ system can be oxidized at low temperatures and forms a solid solution for $0 \leq x \leq 2$ for partially and fully oxidized samples without any biphasic region. The reduction – oxidation reactions are also fully reversible. Furthermore the synthesis of the $x = 1$ material reported by Lussier, et al.⁹ is well understood, employing a sol-gel synthesis utilizing the citrate method. Understanding the oxygen loss at high temperatures led to a reliable synthesis method for the full solid solution. Slow-cooling results in monophasic samples. In contrast quenching samples^{8,10,11} potentially result in multiphasic products with variable oxygen stoichiometries. *In-situ* powder X-ray diffraction experiments can follow the oxygen uptake and the associated increase in symmetry from bixbyite to fluorite structures. The following detailed structural analyses are only possible because of the beneficial neutron scattering lengths ($b(Y) = 7.75$ fm, $b(Pr) = 4.58$ fm and $b(O) = 5.803$ fm)¹² in conjunction with high resolution synchrotron based x-ray scattering with good form factor contrast. Our simultaneous neutron/x-ray

analysis reveals details of the cation and anion sublattices which leads to an in-depth understanding of oxygen distribution and possible cation site splitting.

2. Experimental

2.1. *Synthesis*

$Y_{2-x}Pr_xO_{3+\delta}$ samples were prepared from stoichiometric amounts of calcined Y_2O_3 (Cerac, 99.999% purity) and Pr_6O_{11} (Alfa Aesar, 99.996% purity). The starting materials were dissolved in concentrated nitric acid and slowly added to molten citric acid monohydrate (CA, Aldrich, 99% purity). The resulting gel was decomposed on a hotplate overnight, followed by heating to 600°C for 12 hours. The powder was then ground in an agate mortar and heated in air in an alumina crucible at 900°C and 1200°C for 12 hours each (with intermediate grinding), before being cooled slowly to room temperature.

$Y_{2-x}Pr_xO_3$ samples were prepared by reducing $Y_{2-x}Pr_xO_{3+\delta}$ in 5% H_2 (in N_2) flow for 12 hours between 800°C and 1000°C.

2.2. *Powder X-ray Diffraction*

2.2.1. *Room Temperature Laboratory Diffraction*

Room temperature powder X-Ray diffraction was carried out using a PANalytical X'Pert Pro diffractometer (PANalytical B.V., Almelo, the Netherlands) in Bragg-Brentano geometry using Cu-K α radiation ($\lambda(K\alpha_1) = 1.540598\text{\AA}$, and $\lambda(K\alpha_2) = 1.544426\text{\AA}$), a diffracted beam Ni-filter and a 128 microstrip X'Celerator detector. The samples were mounted as thin layers from acetone slurries onto zero background sample holders (Si(510)) and measured on a PW3040/60 sample spinner stage at 1 revolution per second. Rietveld refinement quality data were collected with 2 hour diffraction data sets in the range of $20^\circ \leq 2\theta \leq 145^\circ$ with 0.0167° steps and 120 seconds per step counting time. Incident beam optics were chosen with 0.04 radians soller slits, 1° divergence slit, 10 mm mask and 2° anti scatter slit. The diffracted beam optics included a 3.4 mm anti scatter slit, 0.04 radian soller slits and a nickel filter. Diffractometer line profiles and peak positions were calibrated using NIST standards LaB $_6$ SRM 660a and Si SRM 640b.

2.2.2. High Temperature In-Situ Powder X-ray Diffraction

In-situ powder X-ray diffraction experiments were carried out using the same PANalytical X'Pert Pro diffractometer as in 2.2.1 equipped with an Anton Paar HTK2000 high temperature furnace attachment. The self-masking furnace uses a 10 mm wide Pt-strip heater and is controlled with a Eurotherm 2604 controller. All data were collected with Cu-K α radiation ($\lambda(K\alpha_1) = 1.540598 \text{ \AA}$, and $\lambda(K\alpha_2) = 1.544426 \text{ \AA}$) using a diffracted beam Ni-filter. 37 minute diffraction data sets were collected over $15^\circ \leq 2\theta \leq 80^\circ$ in 0.0167° steps. The sample was mounted directly onto a platinum strip heater and heated from 25°C to 600°C under flowing 5% hydrogen gas (balance nitrogen). Diffraction patterns were collected every 50°C .

2.2.3. Synchrotron X-ray Diffraction

Room temperature high resolution synchrotron diffraction data were collected on $\text{Y}_{0.5}\text{Pr}_{1.5}\text{O}_{3+\delta}$, and $\text{Y}_{1.5}\text{Pr}_{0.5}\text{O}_{3+\delta}$ using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, in Argonne, Illinois. The instrument, which is described elsewhere¹³ was calibrated using a mixture of NIST standard reference materials; Si (SRM 640c) and Al_2O_3 (SRM 676). Data were collected with an average wavelength of $0.41385 \text{ \AA}$ using 0.001° steps and a scan rate of 0.01° per second. Diffraction data were collected in the range of $0.5^\circ \leq 2\theta \leq 50^\circ$ using a Kapton capillary ($\phi = 0.8\text{mm}$) sample holder plugged with wax.

2.3. Powder Neutron Diffraction

Time-of-flight neutron Diffraction data were collected on the POWGEN diffractometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. Approximately 0.7 grams of select samples ($\text{Y}_{0.5}\text{Pr}_{1.5}\text{O}_{3+\delta}$, and $\text{Y}_{1.5}\text{Pr}_{0.5}\text{O}_{3+\delta}$) were

loaded into an 8mm diameter cylindrical vanadium sample can. A center wavelength of 1.333 Å was used covering a d-spacing from 0.41 Å to 5.37 Å. A slit width of 20 mm and a slit height of 35 mm were used and data were collected for approximately 1 hour each.

2.4. Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) experiments were conducted using a Linseis Thermowaage L81/1550 thermal balance in vertical measurement arrangement. Samples with masses between 50 mg and 100 mg were placed in alumina crucibles and heated with a rate of 10°C per minute from 25°C to 1000°C in flowing 5% H₂ (balance N₂) in order to reduce them to Y_{2-x}Pr_xO₃. X-ray diffraction was used to confirm reduction and the mass change was used in order to determine oxygen content of each sample (δ). Experiments were all corrected for buoyancy and used an empty alumina crucible as the reference.

2.5. Rietveld Refinements

Rietveld refinements were carried out using the *FullProf.2k*¹⁴ software package. Simultaneous refinements against powder synchrotron x-ray and time-of-flight neutron data were carried out for Y_{1.5}Pr_{0.5}O_{3.19(2)} and Y_{0.5}Pr_{1.5}O_{3.53(2)} using equal weights for the x-ray and neutron data. Rietveld refinements against laboratory x-ray diffraction data were performed by first fixing parameters based on results from synchrotron/neutron refinements, allowing instrumental parameters to be established. In order to consistently refine unit cell parameters and atomic positions some parameters were fixed based on these results. Oxygen stoichiometries were not refined, the values determined using thermal gravimetric analysis results, and yttrium to praseodymium ratios were set to synthesized values.

3. Results and discussion

3.1. $Y_{2-x}Pr_xO_{3+\delta}$ for $0 \leq x < 2$ Solid Solution Structures

The solid solution of $Y_{2-x}Pr_xO_{3+\delta}$ for $0 \leq x < 2$ was synthesized in air in intervals of $x = 0.1$ based on Lussier et al⁹. All samples prepared in air with $x \geq 1.4$ were obtained as phase-pure (based on x-ray diffraction) cubic fluorite structures (space group: *Fm-3m*, #225). For $x < 1.4$ phase pure bixbyite structures (space group: *Ia-3*, #206) were formed in air. The powder x-ray diffractograms in figure 3 illustrate the gradual intensity losses for the (411), (332), (341) bixbyite (space group *Ia-3*) superstructure peaks as the praseodymium fraction is increased to $x=1.4$. For $x \geq 1.4$ the bixbyite superstructure peaks are no longer present thus indicating the formation of fluorite structures. The yttrium and praseodymium cations are fully disordered over the 2 cation sites (*8b* and *24d* sites) in the bixbyite phases.

Figure 4a shows the Rietveld plots of the synchrotron x-ray and time of flight neutron data for $Y_{1.5}Pr_{0.5}O_{3.19(2)}$. Table 1 summarizes the structural details of the bixbyite phase $Y_{1.5}Pr_{0.5}O_{3.19(2)}$ and the fluorite phase $Y_{0.5}Pr_{1.5}O_{3.53(2)}$. In agreement with the previously published $YPrO_{3.43(2)}$ structure⁹ the $Y_{1.5}Pr_{0.5}O_{3.19(2)}$ bixbyite phase (*Ia-3*) shows a fully occupied oxygen *48e* site and a partially filled oxygen *16c* site. Yttrium and praseodymium are fully disordered over the two cation sites, namely the *24d* site and the *16c* split site (splitting of the original *8b* site). $Y_{0.5}Pr_{1.5}O_{3.53(2)}$ is a fully yttrium/praseodymium cation and oxygen/vacancy disordered fluorite structure with no indication of any deviations from the high symmetry (*Fm-3m*) structure. In figure 4b representative Rietveld plots based on laboratory powder x-ray diffraction data for selected “as-prepared” and corresponding reduced $Y_{2-x}Pr_xO_{3+\delta}$ members are shown.

The volumes per formula unit, V/Z , as derived from Rietveld refinements for the solid solution $Y_{2-x}Pr_xO_{3+\delta}$ for $0 \leq x < 2$ are presented in figure 5. The volumes for the reduced samples ($Y_{2-x}Pr_xO_3$ for $0 \leq x < 2$) increases linearly with the praseodymium concentration as expected from the ionic radii of $Pr^{3+}(VI) = 0.99 \text{ \AA}$ and $Y^{3+}(VI) = 0.9 \text{ \AA}$ ¹⁵ in agreement with

Vegard's law. Y_2O_3 ¹⁶ is stable as a bixbyite phase but Pr_2O_3 ¹⁷ forms a trigonal structure. Since all reduced $\text{Y}_{2-x}\text{Pr}_x\text{O}_3$ samples were prepared from the oxidized bixbyite and fluorite phases by topotactic reduction in dilute hydrogen only reduced bixbyite phases were obtained.

The "as-prepared" samples are oxidized phases with +4 being the predominant oxidation state for praseodymium as determined by TGA and confirmed with magnetic measurements.⁹ The oxidized samples also show a linear increase of V/Z as a function of the praseodymium concentration for the bixbyite and fluorite structures. Notably no discontinuity is observed at the bixbyite – fluorite boundary which agrees with the structural similarities of the bixbyite and fluorite structures. The volume evolution for the oxidized phases $\text{Y}_{2-x}\text{Pr}_x\text{O}_{3+\delta}$ for $0 \leq x < 2$ depends on the cation sizes and ratios as well as the oxygen stoichiometry. Based on the cation sizes ($r(\text{Pr}^{4+}(\text{VI})) = 0.85 \text{ \AA} < r(\text{Y}^{3+}(\text{VI})) = 0.9 \text{ \AA}$ ¹⁵) a volume contraction would be expected for larger praseodymium concentrations. This contraction is compensated for by the simultaneously increasing oxygen concentrations. This formula unit volume decrease during oxidation for fixed praseodymium concentrations is in contrast to the volume expansion during oxidation of the 3d-transition metal analogues $\text{ScVO}_{3+\delta}$, $\text{InVO}_{3+\delta}$ and $\text{ScTiO}_{3+\delta}$.¹⁸⁻²⁰

3.2. Y/Pr 24d-site Relaxation in Oxidized Bixbyite Phases

The (411), (332), (341) bixbyite superstructure peaks highlighted in figure 3 are very sensitive to the x-parameter of the 24d site ($x, 0, \frac{1}{4}$). Figure 6 shows the refined x-coordinate for the 24d position as a function of praseodymium content in $\text{Y}_{2-x}\text{Pr}_x\text{O}_{3+\delta}$ for $0 \leq x < 2$ as obtained from Rietveld refinements. Since no bixbyite superstructure peaks are measurable for $\text{Y}_{2-x}\text{Pr}_x\text{O}_{3+\delta}$ samples with $x > 1.4$ the 24d cations are fixed to $(0,0,\frac{1}{4})$. The crystal structure for $x = 1.4$ was refined using both a bixbyite and a fluorite setting and both values are shown on figure 6. As expected, the 24d x-parameter increases towards the ideal fluorite position as Pr^{4+} replaces Y^{3+} which is accompanied by oxide addition to the 16c position. The 24d site x-coordinate increases nearly linearly from $\text{Y}_{1.9}\text{Pr}_{0.1}\text{O}_{3+\delta}$ to $\text{Y}_{0.8}\text{Pr}_{1.2}\text{O}_{3+\delta}$. From $\text{Y}_{0.8}\text{Pr}_{1.2}\text{O}_{3+\delta}$ to $\text{Y}_{0.6}\text{Pr}_{1.4}\text{O}_{3+\delta}$ a sudden shift of the 24d cations toward the ideal fluorite position is observed.

This indicates a large sensitivity of the $24d$ site close at the threshold between the bixbyite and the fluorite structure. It is noted that the unit cell dimension evolution does not show this behavior (figure 5). For comparison, the x-coordinates for the bixbyite $24d$ positions of all reduced samples are also included in the figure, and show only a very small change with respect to the Pr concentration. All reduced samples crystallize in the bixbyite structure.

3.3. Site Splitting on the $8b$ Cation Position

It has been shown that YPrO_3 is a bixbyite phase with Y/Pr disorder on the $8b$ and $24d$ sites; whereas, in the oxidized $\text{YPrO}_{3.43}$ the $8b$ site undergoes site splitting by moving the disordered cations off the fully occupied $8b$ position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ to the half occupied $16c$ position (x, x, x) , thus moving the cations closer to the additional oxide ions on the invoked $16c$ site.⁹ Here we are following the site splitting and quantify the shift from the $8b$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ to the $16c$ $(\frac{1}{4} + \Delta x, \frac{1}{4} + \Delta x, \frac{1}{4} + \Delta x)$ position as a function of Pr^{4+} concentration. The $8b$ cation position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, of all members of the solid solution up to $x=1.3$, were allowed to freely refine into the $16c$ position (x, x, x) . Figure 7 shows the atomic coordinates for the $16c$ split position against the Pr-stoichiometry. In pure Y_2O_3 yttrium is located at the ideal $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position. Site splitting is observed even with minimal praseodymium content ($\text{Y}_{1.9}\text{Pr}_{0.1}\text{O}_{3+\delta}$) with the largest site splitting being observed for $\text{Y}_{1.1}\text{Pr}_{0.9}\text{O}_{3+\delta}$. Addition of praseodymium beyond $\text{Y}_{1.1}\text{Pr}_{0.9}\text{O}_{3+\delta}$ results in less pronounced site splitting and at $\text{Y}_{0.6}\text{Pr}_{1.4}\text{O}_{3+\delta}$ and larger praseodymium fractions no site splitting is present. At $x = 1.4$ the cubic fluorite structure is formed. For a Y:Pr ratio of approximately 1:1 that the anion $16c$ position will be almost half filled, which will pull the cation towards the filled position, and away from the hole.⁹ For praseodymium richer samples more oxide anions are added which will fill the remaining vacancies on the $16c$ anion site therefore pulling the cation back towards the ideal $8b$ position. Therefore the shift back towards $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ is expected, due to the higher probability of the cation being found coordinated to 8 oxide anions rather than 7.

3.4. In-situ Reduction of $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_{3+\delta}$

A deeper understanding of the reduction of the fluorite phases can be gained from *in-situ* diffraction studies. The contour plot shown in figure 8 illustrates the structural changes of $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_{3+\delta}$ during reduction in 5% hydrogen (balanced with nitrogen) while heating in 50°C increments. The starting material ($x=1.9$) is a cubic defect fluorite structure with no bixbyite superstructure peaks. Up to 300°C only thermal expansion is observed. Above 300°C the diffraction peaks shift rapidly to higher d-spacings as the reduction occurs. Between 350°C and 500°C the defect fluorite structure is reduced to a bixbyite phase. Figure 9 emphasizes a temperature dependent diffraction peak clearly illustrating the coexistence of 2 phases at 400°C and 450°C, namely a defect fluorite and a bixbyite structure. This is supported by the growth of a single set of bixbyite superstructure peaks at these temperatures. In contrast the main peaks that are common to the bixbyite and fluorite structures are double peaks. The reduction is completed at 500°C and only thermal expansion is observed beyond that temperature. Focussing on the (440) bixbyite and (220) fluorite peak in figure 9 reveals the transition at 400°C and 450°C. From these diffraction peaks one can begin to understand the reduction in a more mechanistic sense. The minimum oxygen content for $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_{3+\delta}$ as a defect fluorite will first be realized, at which point the transition to a bixbyite structure will slowly commence. Once the defect fluorite structure is depleted, the new oxygen-rich bixbyite will begin to lose oxygen until fully reduced. Comparing the reduction temperature to that found for YPrO_3 ⁹ the onset and completion of the reduction occurs at similar temperatures. Because the bixbyite and fluorite structures are so closely related, despite a loss of symmetry and a slightly more pronounced structural change, the topotactic reduction can still occur at low temperatures.

4. Conclusions

The $Y_{(2-x)}Pr_xO_{3+\delta}$ ($0.0 \leq x < 2$ and $0 \leq \delta < 1$) solid solution is ideal for deciphering the bixbyite-fluorite oxidation and reduction mechanism. We have illustrated the cation site responses for the partially oxidized bixbyite phases $Y_{(2-x)}Pr_xO_{3+\delta}$ ($0.0 \leq x < 1.4$ and $0 \leq \delta < 0.53$) and the occurrence of fluorite phases for $Y_{(2-x)}Pr_xO_{3+\delta}$ ($1.4 \leq x < 2$ and $0.53 \leq \delta < 0.6$). The defect fluorite phases are fully disordered on the cation and anion sites. The bixbyite phases accommodate excess oxygen in the additionally invoked $16c$ anion site in space group $Ia-3$. In response to this site preference the $8b$ cation site splits into a $16c$ site in order to form 7 nearly equal and 1 elongated bond. It is suggested that this will inhibit the oxide ion mobility despite the presence of oxide defects. The $24d$ cation moves towards the ideal fluorite position as the samples get progressively more oxidized. It should be noted that all oxidized samples in the investigated series are single phase and that the formula unit volume increases linearly with the praseodymium content. The *in-situ* reductions only show coexisting fluorite and bixbyite phases in a narrow temperature range. $Y_{(2-x)}Pr_xO_{3+\delta}$ is an ideal model system for the investigation of oxide defect formation and annihilation.

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TABLES:

Table 1:

Composition		$\text{Y}_{1.5}\text{Pr}_{0.5}\text{O}_{3.19(2)}$	$\text{Y}_{0.5}\text{Pr}_{1.5}\text{O}_{3.53(2)}$
space group		$Ia\bar{3}$ (206)	$Fm\bar{3}m$ (225)
unit cell	a (Å)	10.68813(4)	5.42208 (3)
	V (Å ³)	1220.972(12)	159.404(3)
	Z	16	2
	V/Z (Å ³)	76.3107(7)	79.702(2)
Y/Pr (16c) (x, x, x)	x/a	0.2414(2)	
	$\beta(11)/\beta(22)/\beta(33)$	0.00142 (11)	
	$\beta(12)/\beta(13)/\beta(23)$	0.00083 (10)	
Y/Pr (24d) (x, 0, 1/4)	x/a	-0.02535 (23)	
	B _{iso} (Å ²)	0.746 (35)	
O (48e) (x, y, z)	x/a	0.38696 (94)	
	y/b	0.14926 (88)	
	z/c	0.38042 (99)	
	Occupancy (%)	101 (3)	
	B _{iso} (Å ²)	0.86 (12)	
O (16c) (x, x, x)	x/a	0.8899 (53)	
	Occupancy (%)	17 (3)	
	B _{iso} (Å ²)	0.86 (12)	
Y/Pr (4a) (0, 0, 0)	B _{iso} (Å ²)		1.21(7)
O (8c) (1/4, 1/4, 1/4)	Occupancy (%)		88

	$B_{\text{iso}} (\text{\AA}^2)$		2.33 (40)
χ^2 :	Neutron (T.O.F.) ^a	2.50	3.66
	X-ray ($\lambda=0.4138 \text{ \AA}$) ^b	1.36	4.76

^aNeutron T.O.F range: 13200 – 110417 μs , 2663 data points

^bX-ray $\lambda=0.41385 \text{ \AA}$, $3.75^\circ \leq 2\theta \leq 49.99^\circ$, $\Delta 2\theta = 0.001^\circ$, 46240 data points

FIGURES:

Figure 1: Relation between bixbyite and fluorite structures with fcc cation lattices and anions located in tetrahedral holes. (a) Cubic bixbyite structure in space group $Ia-3$. Dark blue = $8b$ cation site, light blue = $24d$ cation site, grey = $48e$ anion site. (b) Cubic fluorite structure in space group $Fm-3m$ with all cations (light and dark blue) on the $4a$ site and all anions (grey and white) on the $8c$ site. The white anions can be thought of as inserted into the bixbyite structure raising the cation coordination from 6 to 8. Note that the cations in the bixbyite structure form a slightly distorted fcc lattice.

Figure 2: Top: Illustration of the bixbyite structure emphasizing the *8b* (dark blue) and *24d* (light blue) cation sites and the oxide (grey) *48e* site. Bottom: Schematic relation between bixbyite A_2O_3 and its oxidized $A_2O_{3+\delta}$ structure. The oxygen positions are illustrated as an idealized cubic fluorite sublattice with the grey positions relating to the *48e* site. The white dashed positions show oxides and vacancies in the partially filled *16c* positions to accommodate the additional oxide anions. The splitting of the *8b* cation site into the *16c* (dark blue) positions and the migration of the *24d* cation position (light blue) towards the $0, 0, \frac{1}{4}$ coordinates are illustrated as well.

Figure 3: Room temperature powder X-ray diffractograms of $\text{Y}_{2-x}\text{Pr}_x\text{O}_{3+\delta}$. The insert emphasizes the disappearance of the bixbyite superstructure peaks with increasing praseodymium content.

Figure (4a): Rietveld plot of the simultaneous refinement of the $\text{Y}_{1.5}\text{Pr}_{0.5}\text{O}_{3.19(2)}$ structure using powder synchrotron x-ray (main) and time of flight neutron (insert) data.

Figure (4b): Example Rietveld refinement plots of $\text{Y}_{(2-x)}\text{Pr}_x\text{O}_{3+\delta}$ using laboratory based powder X-ray diffraction data.

Figure 5: Volume per formula unit as a function of Pr content and oxygen content in $\text{Y}_{2-x}\text{Pr}_x\text{O}_{3+\delta}$. The volume decreases during oxidation but the additional oxygen compensates for the expected volume contraction as a function of praseodymium content.

Figure 6: Evolution of the Y/Pr 24d site x-coordinate in the bixbyite structure (*Ia-3*) as a function of Pr content. Blue symbols = Y_{2-x}Pr_xO_{3+δ} bixbyite (as prepared in air), black symbols = Y_{2-x}Pr_xO_{3+δ} fluorite (as prepared in air), red symbols = Y_{2-x}Pr_xO₃ bixbyite (fully reduced). The solid lines are linear fits to guide the eye and the dotted line is an extrapolation. The open rectangle emphasizes the regime with the largest deviation from the linear relation for Y_{2-x}Pr_xO_{3+δ}. The insert illustrates the migration of the 24d site towards the fluorite equivalent position (0,0,¼) with increasing praseodymium concentrations.

Figure 7: *8b* site splitting into *16c* as a function of praseodymium concentration. The insert illustrates the migration from the fully occupied *8b* site into the half occupied *16c* site. The Pr rich $Y_{2-x}Pr_xO_{3+\delta}$ members with $x > 1.3$ crystallize in the fluorite structure with no site-splitting.

Figure 8: Contour plot of *in-situ* x-ray diffraction data during the reduction of $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_{3+\delta}$ (fluorite) to $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_3$ (bixbyite) in flowing 5% H_2 gas. The bixbyite phase starts to form at approximately 400°C as indicated by the occurrence of the bixbyite superstructure peaks.

Figure 9: Selected powder X-ray diffraction peaks during *in-situ* reduction of $Y_{0.1}Pr_{1.9}O_{3+\delta}$ (fluorite) to $Y_{0.1}Pr_{1.9}O_3$ (bixbyite) in flowing 5% H_2 gas. The 350 to 450 °C data clearly illustrate the coexistence of 2 phases at the reductive structural transition.

Graphical Abstract:

Graphical Abstract: In-situ powder diffraction surface and contour plot for the reduction of $\text{Y}_{0.1}\text{Pr}_{1.9}\text{O}_{3+\delta}$ in dilute hydrogen. The cubic fluorite (center) structure with 8 coordinated cations undergoes topotactic oxide elimination resulting in the bixbyite phase (right) with distorted octahedral cation coordination and 2 distinct cation sites.