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Article

$Sr_3Co_2O_{4.33}H_{0.84}$: An Extended Transition Metal Oxide-Hydride

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Reaction of the *n* = 2 Ruddlesden–Popper oxide $Sr_3Co_2O_{5.80}$ with CaH_2 yields an extended oxide-hydride phase: $Sr_3Co_2O_{4.33}H_{0.84}$. Neutron powder diffraction data reveal the material adopts a body-centered orthorhombic structure (*Immm*: *a* = 3.7551(5) Å, *b* = 3.7048(4) Å, *c* = 21.480(3) Å) in which the hydride ions are accommodated within disordered $CoO_{1.16}H_{0.46}$ layers. Low temperature neutron powder diffraction data show no evidence for long-range magnetic order, suggesting the chemical disorder in the anion lattice of the material leads to magnetic frustration.

Introduction

Extended solids containing transition metal centers can exhibit a diverse range of correlated electronic behavior arising from electrons in partially filled metal d-states.[1] The exchange interactions which lead to these cooperative phenomena are generally mediated via bridging ligands which link neighboring metal centers within solids, be they single atom ligands such as oxide or fluoride ions or more complex molecular ligands such as those found in metal–organic frameworks. Building on this observation, an obvious strategy for preparing new functional materials, or tuning the behavior of existing phases, is the modification of these intermetal exchange interactions by changing the identity of the bridging ligands. In the widely studied field of complex transition metal oxides this requires the preparation of mixed anion phases such as oxy-halides, oxy-chalcogenides, and oxy-pnictides.[2-4]

The synthesis of mixed oxy-anion phases presents a number of challenges. For example, it is generally true that ternary mixed oxy-anion systems are less thermodynamically stable than the all-oxide equivalent (oxy-nitrides are an obvious example[5]) so care has to be taken to limit the availability of oxygen during syntheses. In addition the strong oxidizing potential of oxygen can lead to the formation of oxo-acid salts such as sulfates and arsenates rather than the desired oxy-sulfide or oxy-arsenide products.

A further complication which tends to restrict the possibilities offered by mixed oxy-anion systems is the tendency for the different anions within a phase to segregate on the basis of size and polarizability. As a result mixed anion phases have a strong preference for adopting layered structures in which the different anions are isolated in separate layers. Furthermore the non-oxide heteroanions tend to be located outside the transition metal containing layers and thus do not bridge between transition metal centers and so do not play a large role in electronic exchange pathways in these phases, as exemplified by the oxy-chloride and oxy-sulfide phases shown in Figure 1.[6,7]

Soft chemical processes which exploit the topotactic nature of low-temperature solid state reactions can be utilized to overcome this problem by inserting heteroanions into the coordination spheres of transition metal ions within preformed complex oxides. Such a process led to the formation of a series of complex $LnSrCoO_{3+x}H_y$ (Ln = La, Nd, Pr) oxide–hydride phases in which hydride ions are located within the equatorial $Co_{1+x}H_y$ layers of the host $n = 1$ Ruddlesden–Popper phase (Figure 1) facilitating strong superexchange between cobalt centers, as demonstrated by high-temperature antiferromagnetic order ($380 < T_N/K < 445$).[8-10] Here we report the preparation of a related oxide-hydride phase $Sr_3Co_2O_{4.33}H_{0.84}$ prepared by the low-temperature reaction of the $n = 2$ Ruddlesden–Popper oxide $Sr_3Co_2O_{5.80}$ with CaH_2.

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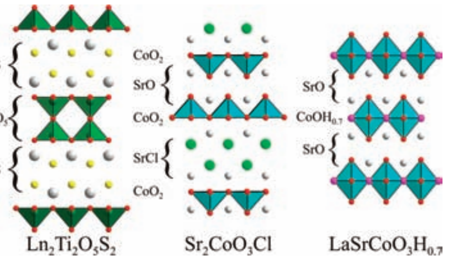

Figure 1. Structures of the oxy-anion phases $Ln_2Ti_2O_5Cl_2$ (Ln = Pr, Nd, Sm), Sr_2CoO_3Cl, and $LaSrCoO_3H_{0.7}$.

Experimental Section

Synthesis of $Sr_3Co_2O_{7-x}$. Five gram samples of $Sr_3Co_2O_{7-x}$ were prepared by a ceramic method previously described by Hill et al.[11] Suitable stoichiometric ratios of $SrCO_3$ (99.999%) and Co_3O_4 (99.9985%) were ground together in an agate pestle and mortar before being heated to 1000 °C in air to decompose the carbonate. The resulting mixture was then pressed into pellets and heated at 1100 °C, for two periods of 40 h, under flowing argon which had been passed over titanium wire heated to 800 °C. X-ray powder diffraction data collected from samples prepared in this manner were consistent with a single phase and could be indexed on the basis of a body-centered orthorhombic cell: $a = 3.926(1)$ Å, $b = 3.687(1)$ Å, $c = 20.666(1)$ Å in agreement with the reported lattice parameters of $Sr_3Co_2O_{5.80}$ ($a = 3.92741(4)$ Å, $b = 3.68277(4)$ Å, $c = 20.6587(2)$ Å).[11] Thermogravimetric reduction under an atmosphere of 5% H_2 in N_2 revealed a 9.50% mass loss (Supporting Information) consistent with an overall composition of $Sr_3Co_2O_{5.81(3)}$.

Reaction of $Sr_3Co_2O_{5.80}$ with CaH_2. Small samples (~300 mg) of $Sr_3Co_2O_{5.80}$ were ground with two mole equivalents of CaH_2 in an argon filled glovebox (O_2 and $H_2O < 1$ ppm). The resulting mixtures were then sealed under vacuum within Pyrex tubes (volume ~15 cm^3) and heated at temperatures between 200 and 300 °C to determine reactivity as a function of temperature.

Because of the hazards associated with the production of hydrogen gas when using calcium hydride as a reducing agent, large samples suitable for neutron powder diffraction studies were prepared by means of a spring loaded venting apparatus which limits the pressure over the sample to less than 5 mbar above atmospheric pressure, as described previously.[12] Approximately 5 g of $Sr_3Co_2O_{5.80}$ was combined with 1.5 mol equivalents of CaH_2 and heated for 24 h at 240 °C, 2 periods of 24 h at 250 °C, and one period of 24 h at 255 °C with regrinding between heating periods.

Characterization. Room temperature X-ray powder diffraction data were collected from samples contained within homemade air sensitive sample holders utilizing a Panalytical X'pert diffractometer incorporating an X'celerator position sensitive detector (monochromatic Cu $K_{\alpha 1}$ radiation). Neutron powder diffraction data were collected using the POLARIS diffractometer (ISIS neutron source, UK) from samples contained within vanadium cans sealed under an argon atmosphere with an indium washer. Rietveld profile refinement was performed using the GSAS suite of programs.[13]

Thermogravimetric measurements were performed by heating powder samples under a 5% H_2 in N_2 atmosphere and measuring the mass change as a function of temperature using a Netzsch STA 409PC balance.

Solid state ^{1}H MAS spectra were obtained at 399.9 MHz (9.4 T) on a Varian/Chemagnetics Infinity spectrometer, using a 4 mm double resonance probe and a sample rotation rate of 14 kHz. Each spectrum resulted from 500 scans separated by a 20 s delay. The ^{1}H chemical shifts were externally referenced to TMS at 0 ppm.

Results

Reactivity of $Sr_3Co_2O_{5.80}$. X-ray powder diffraction data collected from the products of reaction between $Sr_3Co_2O_{7-x}$ and CaH_2 reveal that at temperatures below 240 °C no reaction occurs. Reactions performed at temperatures above 270 °C result in the decomposition of the ternary oxide phase and the formation of SrO, CoO, elemental cobalt, and CaO. In the temperature range $250 < T/°C < 270$ reactions resulted in the formation of a body-centered orthorhombic phase $a = 3.75(1)$ Å, $b = 3.70(1)$ Å, $c = 21.44(1)$ Å consistent with a topotactic reaction.

Attempts to remove the calcium containing phases (CaO, CaH_2) from the reaction mixture using a dilute solution of NH_4Cl in methanol, in a manner used previously for reactions of this type,[8] resulted in the decomposition of the sample to SrO and other amorphous products. A similar decomposition was observed on contact with pure, dry methanol demonstrating the extreme reactivity of the sample with acids. To reduce the quantity of CaH_2 and CaO within the sample to facilitate neutron diffraction studies, a density separation method was employed. The sample was stirred in 100 mL of dry chloroform (99%) under inert atmosphere. On the cessation of stirring the dense ternary oxide phase settled from suspension more rapidly than the CaO and CaH_2 allowing a mechanical separation to be performed once the chloroform had been drawn off and the sample pumped to dryness. As can be seen from the X-ray powder diffraction data shown in Figure 2 this procedure led to a reduction in the quantity of CaH_2 and CaO within the sample, but not the complete removal of these phases.

Structural Characterization. Neutron powder diffraction data, collected at room temperature from a sample which had undergone the density separation process described above, were used to refine a structural model consisting of three phases: $Sr_3Co_2O_x$, CaO, and CaH_2. The reported structure of $Sr_3Co_2O_{5.80}$ (with adjusted lattice parameters) was used as a starting model for the $Sr_3Co_2O_x$ phase,[11] and structural models for CaO and CaH_2 were obtained from the literature.[14,15] After a few refinement cycles it became clear that there were a number of diffraction features which were not accounted for by the three phases in the structural model. These additional peaks were consistent with the presence of a small amount of $Sr_3Co_2O_{5.80}$ starting material within the sample, so this was added to the model as a fourth phase. During the refinement, only the lattice parameters and a global thermal parameter for each of the three minority phases (CaO, CaH_2, and $Sr_3Co_3O_{5.80}$) were allowed to vary from literature values.

The structural refinement of the bulk $Sr_3Co_2O_x$ phase was performed by varying the positional and thermal

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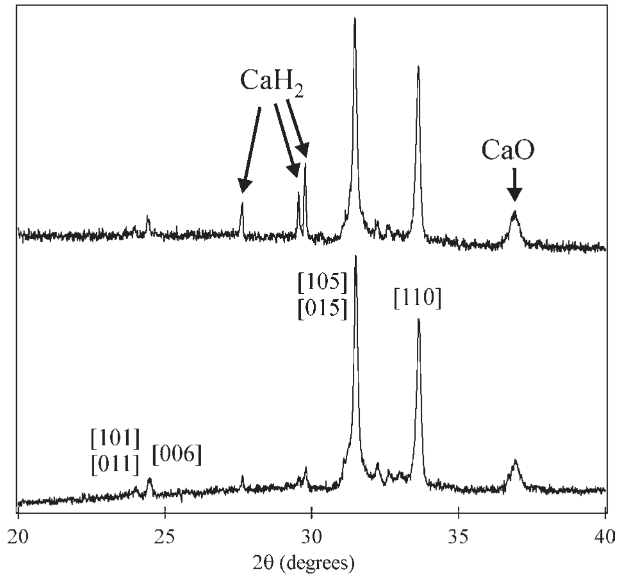

Figure 2. X-ray powder diffraction data collected from the products of reaction between $Sr_3Co_2O_{5.80}$ and CaH_2 at 255 °C before (top) and after (bottom) a density separation process.

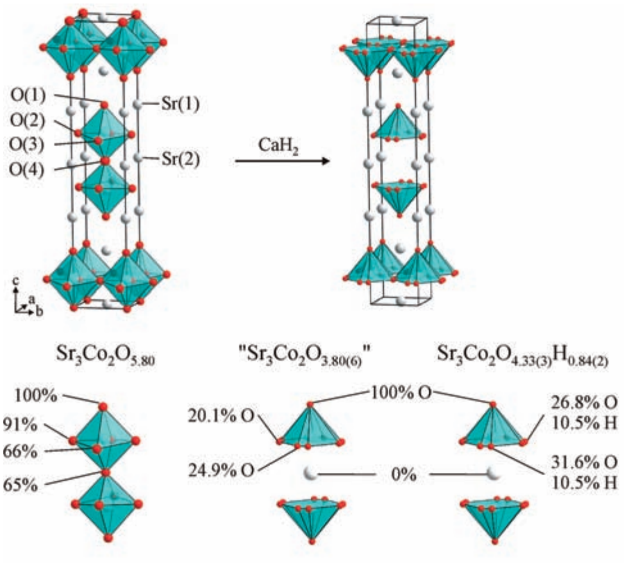

Figure 3. Structure of $Sr_3Co_2O_{5.80}$ and the two candidate structures for the majority phase produced by the reaction of $Sr_3Co_2O_{5.80}$ and CaH_2: "$Sr_3Co_2O_{3.80}$" and $Sr_3Co_2O_{4.33}H_{0.84}$.

Table 1. Selected Structural and Chemical Parameters from $Sr_3Co_2X_n$ Phases

	$Sr_3Co_2O_{5.8}$	"$Sr_3Co_2O_{3.8}$"	$Sr_3Co_2O_{4.33}H_{0.84}$
cobalt oxidation state	+2.8	+0.8	+1.75
cobalt coordination number	4.79	2.80	4.16
equatorial layer composition	$CoO_{1.57}$	$CoO_{0.9}$	$CoO_{1.16}H_{0.42}$
Sr(1) coordination number	8.88	6.8	8.16
Sr(2) coordination number	8.14	3.6	6.35

parameters of all the atoms within the model. In addition the occupancies of the anion sites were also refined to account for the change in anion stoichiometry. The refinement proceeded smoothly, and it was observed that the occupancy of the O(4) "central axial" anion site declined to zero, and so this atom was removed from the model. In addition the occupancy of the O(2) and O(3) "equatorial" anion sites declined dramatically, while that of the O(1) "external axial" anion site remained at full occupancy as shown in Figure 3.

Examination of the structural model refined for the $Sr_3Co_2O_x$ phase revealed that the thermal parameters for the two equatorial anion sites (O(2) and O(3)) were significantly larger than those of the other atoms within the structure. This was taken as a sign of static disorder resulting from the disordered twisting of the CoO_x polyhedra around the *z*-axis. To model this the equatorial anions were moved from *4j* ($^1/_2$, 0, *z*) and *4j* (0, $^1/_2$, *z*) sites to lower symmetry *8l* ($^1/_2$, *y*, *z*) and *8m* (*x*, $^1/_2$, *z*) sites with halved occupancy. This lead to an improvement in the fit ($\chi^2 = 1.489$) and the refinement of a phase of stoichiometry $Sr_3Co_2O_{3.80(6)}$ as shown in Figure 3 and described fully in the Supporting Information.

Examination of the refined structure of "$Sr_3Co_2O_{3.80}$" reveals a number of physically unreasonable features. First, the average local coordination number of the cobalt cations is 2.8 (1 × 100% O(1) + 4 × 20.1% O(2) + 4 × 24.9% O(3)) (Figure 3, Table 1). While there are reports of 3-coordinate transition metal centers in topotactically reduced oxides[16] there are none for the preparation of phases with only two oxide ions in the transition metal coordination sphere. Furthermore, if the strontium cations are considered, it can be seen that they have coordination numbers Sr(1) = 6.8 and Sr(2) = 3.6 (Table 1) compared to 8.14 and 8.88, respectively, in the structure of $Sr_3Co_2O_{5.80}$.[11] These extremely low coordination numbers for the strontium cations, particularly Sr(2), have no chemical precedent. A second unreasonable feature of "$Sr_3Co_2O_{3.80}$" is that the stoichiometry implies an average cobalt oxidation state of Co +0.8. There are reports of Co+1 oxide phases (e.g., CsK_2CoO_2 or K_3CoO_2)[17,18] and even phases with cobalt oxidation states less than Co+2 prepared by topotactic reduction (e.g., $LaSrCoO_{3.38}$ and $LaBaCo_2O_{4.25}$).[19,20] There is however no precedent for an extended oxide phase with an average cobalt oxidation state less than Co +1. Combined together these observations suggest the refined structure and chemical formulation of "$Sr_3Co_2O_{3.80}$" are incorrect.

An alternative and more physically reasonable description of the majority phase produced by the reaction of $Sr_3Co_2O_{5.80}$ and CaH_2 can be formulated by considering the analogous reaction between $LnSrCoO_4$ (Ln = La, Pr, Nd) and CaH_2 to form the oxide-hydride phases $LnSrCoO_{3+x}H_y$.[8-10] Naturally abundant isotopic ratios of hydrogen have a negative neutron scattering length (H = −3.739 fm).[21] If an anion site contained a mixture of oxide and hydride ions, the observed neutron scattering power of this site would be the weighted average of the neutron scattering lengths of the two anions (O = 5.803 fm).[21] Thus we could account for the observed

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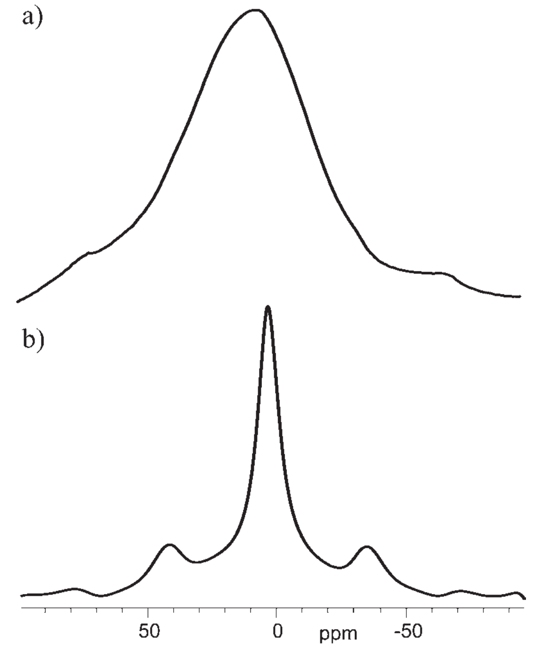

Figure 4. Solid State Proton NMR collected from (a) the products of reaction between $Sr_3Co_2O_{5.80}$ and CaH_2: ($\delta(^1H)$ = 7.3 ppm, $\Delta\nu_{1/2}$ = 22000 Hz) and (b) CaH_2:($\delta(^1H)$ = 4.2 ppm, $\Delta\nu_{1/2}$ = 4990 Hz).

scattering power of the equatorial anion sites as being due to either oxide ions and vacancies alone (giving the physically unreasonable $Sr_3Co_2O_{3.8}$ model and stoichiometry) or a combination of oxide ions, hydride ions, and vacancies, to yield an oxide-hydride structural model with a higher, more physically reasonable anion content.

To confirm the presence of hydride ions in the majority phase, ^1H MAS NMR spectra were collected from the "neutron sample" and from a sample of CaH_2. As shown in Figure 4 the spectrum collected from CaH_2 has resonance centered at $\delta(^1H)$ = 4.2 ppm with a relatively narrow line width ($\Delta\nu_{1/2}$ = 4990 Hz) and a weak progression of spinning side bands. In contrast the spectrum collected from the "neutron sample" is centered at $\delta(^1H)$ = 7.3 ppm and is significantly broader than the CaH_2 spectrum ($\Delta\nu_{1/2}$ = 22000 Hz). The large differences between the two spectra demonstrate that although the "neutron sample" does contain CaH_2 (as demonstrated by diffraction data) the ^1H MAS spectrum of this sample cannot be accounted for by the presence of CaH_2 alone, demonstrating the presence of another hydrogen containing phase. Furthermore, the broad resonance observed for the "neutron sample" is consistent with the paramagnetic broadening expected for a $Sr_3Co_2O_xH_y$ phase. Thus, the NMR data support the description of the bulk cobalt containing phase as an oxide-hydride rather than a reduced oxide.

Considering the neutron scattering lengths of oxygen and hydrogen stated above, we can define the O:H ratios consistent with the refined neutron scattering powers of the two equatorial anion sites as: O(2) = $O_{(0.201+n)}$-$H_{(1.55n)}$; O(3) = $O_{(0.249+m)}H_{(1.55m)}$. To deduce the values of *n* and *m* and hence the overall stoichiometry of the majority phase, thermogravimetric data were collected. To avoid complications due to the presence of minority phases, reductive thermogravimetric measurements were performed. The measurement proceeded according to the reaction in (1), confirmed by X-ray powder diffraction data collected from the products.

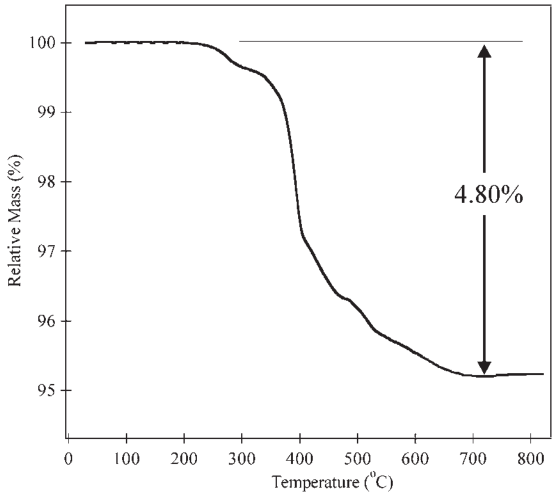

Figure 5. Data collected as a function of temperature during the thermogravimetric reduction of the products of the reaction between $Sr_3Co_2O_{5.80}$ and CaH_2.

$$p\mathrm{Sr_3Co_2O}_x\mathrm{H}_y + q\mathrm{Sr_3Co_2O_{5.80}} + r\mathrm{CaO} + s\mathrm{CaH_2} \rightarrow 3(p+q)\mathrm{SrO} + 2(p+q)\mathrm{Co} + r\mathrm{CaO} + s\mathrm{CaH_2} \quad (1)$$

The observed relative mass loss of 4.80(3)% shown in Figure 5 is considerably larger than the 3.46% expected if the bulk phase was $Sr_3Co_2O_{3.8}$. This larger value is consistent with a stoichiometry of $Sr_3Co_2O_{4.34}H_{0.84}$ for the majority phase when the phase fractions of the minority phases are taken into account (Table 2). Assuming the hydride ions are distributed evenly over the O(2) and O(3) anion sites, as suggested by the similar *a* and *b* lattice parameters, this gives values of $n = m = 0.067$ to give site occupations of O(2) = $O_{0.268}H_{0.105}$ and O(3) = $O_{0.316}H_{0.105}$. Note that complete occupation of the of the equatorial anion sites corresponds to a fractional occupancy of 0.5 because of the shift from the high symmetry *4j* sites to the lower symmetry *8l* and *8m* sites for these anions, described above.

A final structural model in which the equatorial anion sites of the majority phase are occupied by this combination of oxide and hydride ions was refined against the neutron diffraction data. This model converged rapidly with a good statistical fit (χ^2 = 1.489). A complete description of the refined structure of $Sr_3Co_2O_{4.34}H_{0.84}$ is given in Table 2 with selected bond lengths in Table 3. Observed, calculated, and difference plots from the structural refinement are shown in Figure 6.

Neutron powder diffraction data collected from the sample at 5 K show no evidence of long-range magnetic order and could be readily modeled using the same 4-phase structural description employed for the ambient temperature data. Full details of this low temperature structural refinement are given in the Supporting Information.

Discussion

Structure and Composition of $Sr_3Co_2O_{4.33}H_{0.84}$. A combination of neutron diffraction analysis, ^1H MAS NMR, and thermogravimetric data reveal that the majority

Table 2. Refined Structural Parameters of $Sr_3Co_2O_{4.33}H_{0.84}$ at 298 K

atom	symmetry	x	y	z	fraction	U_{iso} (Å^3)
Sr(1)	2c	$^1/_2$	$^1/_2$	0	1	0.0293(10)
Sr(2)	4i	0	0	0.3134(1)	1	0.0087(3)
Co(1)	4i	0	0	0.1017(2)	1	0.0075(4)
O(1)	4i	0	0	0.1958(1)	1	0.0044(4)
O/H(2)	8 L	$^1/_2$	0.089(1)	0.0892(2)	0.268(3)/0.105(3)	0.0074(8)
O/H(3)	8 m	0.089(1)	$^1/_2$	0.0892(2)	0.316(4)/0.105(4)	0.0074(8)

$Sr_3Co_2O_{4.33(3)}H_{0.84(2)}$

space group *Immm*: a = 3.7551(5) Å, b = 3.7048(4) Å, c = 21.480(3) Å, weight fraction = 65.2(2)%

$Sr_3Co_2O_{5.80}$

space group *Immm*: a = 3.944(1) Å, b = 3.687(1) Å, c = 20.652(3) Å, weight fraction = 16.6(2)%

CaO

spacegroup $Fm\bar{3}m$, a = 4.8209(6) Å, weight fraction = 12.1(2)%

CaH_2

spacegroup *Pnma*: a = 5.9650(8) Å, b = 3.6024(4) Å, c = 6.821(1) Å, weight fraction = 6.2(2)%

χ^2 = 1.489, wRp = 1.95%, Rp = 2.83%

Table 3. Selected Bond Lengths from the Refined Structure of $Sr_3Co_2O_{4.33}H_{0.84}$

cation	anion	bond length (Å)
Co(1)	O(1)	2.021(5)
	O/H(2)	1.925(1)
	O/H(3)	1.901(1)
Sr(1)	O(1)	2.526(3)
	O(1)	2.645(1)
	O/H(2)	2.588(4)/3.023(4)
	O/H(3)	2.600(4)/3.044(4)
Sr(2)	O/H(2)	2.447(4)/2.904(4)
	O/H(3)	2.460(4)/2.926(4)

phase formed in the reaction between $Sr_3Co_2O_{5.80}$ and CaH_2 is the oxide-hydride phase $Sr_3Co_2O_{4.33}H_{0.84}$. The chemical composition determined for this oxide-hydride phase is dependent on a number of assumptions. Principally that the mass fractions determined for the four phases in the sample are correct (Table 2) and that the composition of the $Sr_3Co_2O_{7-x}$ oxide impurity is $Sr_3Co_2O_{5.80}$. Studies by Hill et al. have revealed that the lattice parameters of Sr_3CoO_{7-x} phases are not very sensitive to the anion content in the composition range $Sr_3Co_2O_{5.64}$−$Sr_3Co_2O_{5.80}$.[11] However, when allowed to vary, the anion content of the $Sr_3Co_2O_{7-x}$ impurity phase within the 4-phase structural refinement against neutron diffraction data, did not vary from the values published for $Sr_3Co_2O_{5.80}$ within error. Given that the major diffraction peaks from $Sr_3Co_2O_{5.80}$ are well separated from those of the other phases in the sample this provides strong support for the composition of the oxide-hydride phase stated.

The refined structure of $Sr_3Co_2O_{4.33}H_{0.84}$ contains cobalt coordination polyhedra with an average composition of $CoO_{3.33}H_{0.84}$. As shown in Figure 7 this average environment can be deconvoluted into three distinct coordination environments: CoO_3H (68%), CoO_4 (16%), and CoO_4H (16%). Bond valence sums (BVS)[22] calculated for these sites are consistent with the average cobalt oxidation state of Co +1.75 derived from the stoichiometry of the phase. The observed Co−(O/H) bond lengths within the structure of $Sr_3Co_2O_{4.33}H_{0.84}$ (Table 3) are consistent with a weighted average of the Co−O and Co−H bond lengths observed in $LnSrCoO_{3+x}H_y$ phases.[8,10] The two strontium coordination sites within the structure of $Sr_3Co_2O_{4.33}H_{0.84}$ have average coordinations of Sr(1): $SrO_{7.32}H_{0.84}$ and Sr(2):$SrO_{4.64}H_{1.68}$. As shown in Figure 7 the coordination polyhedra derived by deconvoluting these averages are consistent with strontium coordination polyhedra observed in other topotactically reduced phases.[12] Thus it can be seen that the refined structure and stoichiometry of $Sr_3Co_2O_{4.33}H_{0.84}$ are both plausible and consistent with previously observed $LnSrCoO_{3+x}H_y$ phases.

The mechanism proposed for the formation of the previously reported $LnSrCoO_{3+x}H_y$ oxide-hydride phases proceeds initially via the topotactic reduction of $LnSrCoO_4$ substrates with CaH_2, to form phases of composition $LnSrCoO_{3.5+\delta}$. These isolatable Co+2 intermediate phases then undergo an essentially redox neutral anion exchange reaction with CaH_2 to form phases of composition $LnSrCoO_{3+x}H_y$.[8,9] The degree of anion exchange in this second step has been observed to be dependent on the pressure of hydrogen gas over the sample, allowing phases in the composition range $LnSrCoO_3H_{0.7}$ to $LnSrCoO_{3.21}H_{0.58}$ to be prepared by varying this parameter.[9,10]

The synthesis of $Sr_3Co_2O_{4.33}H_{0.84}$, via the reaction of the n = 2 Ruddlesden−Popper oxide $Sr_3Co_2O_{5.80}$ with CaH_2, has many features consistent with this mechanism. $Sr_3Co_2O_{4.33}H_{0.84}$ has an average cobalt oxidation state of Co+1.75, which lies within the range of oxidation states observed for $LnSrCoO_{3+x}H_y$ phases (Co+1.7 to Co+2).[8,10] The preparation of $Sr_3Co_2O_{4.33}H_{0.84}$ from $Sr_3Co_2O_{5.80}$ therefore requires both a reduction (Co+2.8 to Co+1.75) and an anion exchange (oxide for hydride) in common with the synthesis of $LnSrCoO_{3+x}H_y$ phases described above. However unlike the reported syntheses of $LnSrCo_{3+x}H_y$ phases it has not been possible to observe separate reduction and anion exchange reaction steps during the preparation of $Sr_3Co_2O_{4.33}H_{0.84}$ as the expected "$Sr_3Co_2O_{4.75}$" intermediate has not been observed. The presence of both unreduced $Sr_3Co_2O_{5.80}$ and anion exchanged $Sr_3Co_2O_{4.33}H_{0.84}$ in the

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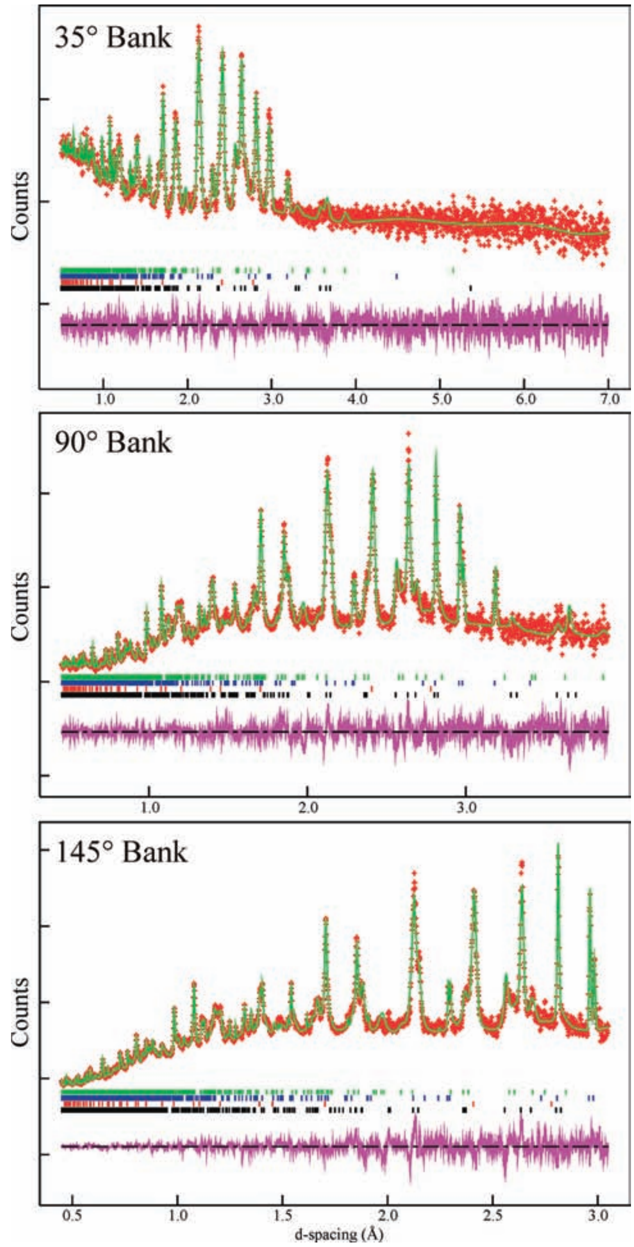

Figure 6. Observed, calculated, and difference plots for the 4-phase structural refinement of the products from the reaction between $Sr_3Co_2O_{5.80}$ and CaH_2 against neutron powder diffraction data. Tick marks show reflection positions for $Sr_3Co_2O_{4.34}H_{0.84}$ (bottom), CaO (lower middle), CaH_2 (upper middle), and $Sr_3Co_2O_{5.80}$ (top).

sample analyzed by neutron diffraction suggests that if a reduced intermediate phase is produced either it is very short-lived so that it does not accumulate in the reaction mixture or it is amorphous. Attempts to prepare such an intermediate by the low temperature reduction of $Sr_3Co_2O_{5.80}$ with dilute hydrogen, in an analogy to the synthesis of $LnSrCoO_{3.5+\delta}$ phases,[10,19] led to decomposition of the ternary oxide phase. Likewise attempts to isolate an intermediate reduced phase via reduction with other reducing agents, such as sodium hydride, have been unsuccessful to date.

The degree of hydride substitution that occurs during the formation of $Sr_3Co_2O_{4.33}H_{0.84}$ (0.42 H^- per cobalt center) is significantly lower than that observed in the $LnSrCoO_{3+x}H_y$ phases, which ranges from 0.7 H^- per cobalt center in $LaSrCoO_3H_{0.7}$ to 0.58 H^- per cobalt center in $NdSrCoO_{3.21}H_{0.58}$. This low level of anion exchange is consistent with the much lower hydrogen pressure under which $Sr_3Co_2O_{4.33}H_{0.84}$ is prepared (~ 1 atm in venting system, < 2 atm for small scale samples in sealed tubes) compared with that reported for the synthesis of $LnSrCoO_{3+x}H_y$ phases (9−18 atm). Attempts to prepare $Sr_3Co_2O_xH_y$ phases under increased hydrogen pressure by the reaction of 1.5 g of $Sr_3Co_2O_{5.8}$ with a 1.5 stoichiometric excess of CaH_2 at 250 °C in sealed Pyrex ampules (expected hydrogen pressure ~9 atm) led to decomposition of the ternary phase.

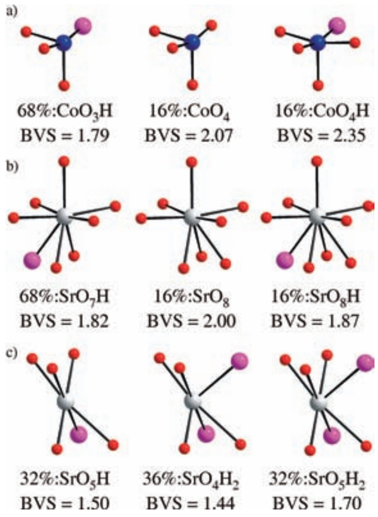

Figure 7. Deconvoluted coordination polyhedra of (a) cobalt, (b) Sr(1), and (c) Sr(2) within the structure of $Sr_3Co_2O_{4.33}H_{0.84}$. Red spheres represent oxide ions, purple spheres hydride ions.

Magnetic Behavior. The lack of long-range magnetic order in $Sr_3Co_2O_{4.33}H_{0.84}$ is surprising given relatively high ordering temperatures ($380 < T_N/K < 445$) exhibited by the $LnSrCoO_{3+x}H_y$ phases.[9,10] These high magnetic ordering temperatures have been attributed to superexchange interactions mediated by strong hybridization between cobalt 3d, hydrogen 1s, and oxygen 2p states.[9] These strong magnetic coupling interactions should also exist in $Sr_3Co_2O_{4.33}H_{0.84}$ so the lack of long-range order in the phase is a little unexpected. It should be noted that the separation between CoO_xH_y equatorial layers within the structure of $LaSrCoO_3H_{0.7}$ is 6.50 Å[8] compared with 6.37 Å for $Sr_3Co_2O_{4.33}H_{0.84}$, indicating that it is unlikely that weak interlayer coupling is responsible for the suppression of long-range magnetic order in the later phase.

One explanation for the lack of long-range magnetic order comes from the observation that the hydride ions in $Sr_3Co_2O_{4.33}H_{0.84}$ appear to be disordered statistically over the different anion sites within the $CoO_{1.16}H_{0.42}$ equatorial layers (Figure 3). This anion disorder would be expected to introduce competition between antiferromagnetic σ-superexchange interactions between electrons in cobalt "e_g" orbitals and the ferromagnetic π-superexchange interactions between electrons in cobalt "t_{2g}" orbitals, potentially suppressing long-range magnetic order. This idea is supported by the observation that the anion distribution in the magnetically ordered $LnSrCoO_{3+x}H_y$ phases is itself more ordered with the ($^1/_2$, 0, 0) site occupied exclusively by oxide ions and the (0, $^1/_2$, 0) site occupied by hydride ions or a mixture of hydride and oxide ions in phases with lower levels of hydride substitution.[8] The more ordered anion arrangement would be expected to limit the competition between magnetic exchange pathways, resulting in strong magnetic coupling and magnetic order.[9] Unfortunately because of the mixture of phases in the sample and the presence of small amounts of ferromagnetic elemental cobalt (undetectable by diffraction) it was not possible to collect meaningful magnetization data from $Sr_3Co_2O_{4.33}H_{0.84}$.

Thermal and Chemical Stability of Oxide-Hydride Phases. Observations described above reveal that $SrCo_2O_{4.33}H_{0.84}$ decomposes at a lower temperature than the $LnSrCoO_{3+x}H_y$ phases in the presence of CaH_2 (270 °C compared with >500 °C) and in addition $Sr_3Co_2O_{4.33}H_{0.84}$ reacts rapidly with weak acids such as methanol, in contrast to the $LnSrCoO_{3+x}H_y$ phases.[8,10] This indicates that while the oxide-hydride phases derived from both $n = 1$ and $n = 2$ Ruddlesden−Popper oxide phases are thermodynamically unstable, the $LnSrCoO_{3+x}H_y$ phases have much greater kinetic stability than $Sr_3Co_2O_{4.33}H_{0.84}$. This reduced kinetic stability is attributable to the high level of anion deficiency in $Sr_3Co_2O_{4.33}H_{0.84}$ (-0.91 anions per cobalt center compared to an ideal $Sr_3Co_2X_7$ formulation) compared with the most anion deficient $LnSrCo_{3+x}H_y$ phases ($LaSrCoO_3H_{0.7}$: -0.3 anions per cobalt center compared to $LaSrCoX_4$). Such a high concentration of anion vacancies will lead to the lowering of the lattice energy of that phase, which will in turn lower the energetic barriers preventing long-range cation diffusion thus lowering the kinetic stability of the anion deficient phase.

While the relative thermal stabilities of $Sr_3Co_2O_{4.33}H_{0.84}$ and the $LnSrCoO_{3+x}H_{0.84}$ phases can be readily explained, the observation that they are stable at all is surprising considering the facile and thermodynamically advantageous decomposition of transition metal oxide-hydride phases to binary metal oxides, elemental transition metals, and water. Indeed transition metal oxide-hydrides are so reactive and thermally unstable that, to our knowledge, $Sr_3Co_2O_{4.33}H_{0.84}$ and the $LnSrCo_{3+x}H_y$ phases are the only structurally characterized materials of this type, as the extreme reactivity of other transition metal oxide-hydrides, such as $BaMnO_3H_3$,[23] prevent their detailed characterization.

The dearth of well characterized transition metal oxide-hydride phases is not for the want of trying. Numerous complex transition metal oxides have been reacted with calcium hydride and other binary hydrides; however, these reactions have yielded only topotactically reduced oxides with no sign of the subsequent anion exchange reactions required for the formation of oxide-hydride phases. Taking the reactivity of Ruddlesden−Popper type transition metal oxides as examples, it has been observed that on reaction with CaH_2, $LaAMnO_4$ (A = Sr, Ba) is reduced to $LaAMnO_{3.5}$,[24] $Sr_3Fe_2O_{7-x}$ is reduced to $Sr_3Fe_2O_5$,[25] and $La_3Ni_2O_7$ is reduced to $La_2Ni_2O_6$[26] with no sign of any oxide-hydride phases observed in any of these reactions. The lack of any anion exchange behavior in Ruddlesden−Popper oxides containing manganese, iron, or nickel indicates the formation of oxide-hydride phases from Ruddlesden−Popper cobaltates is anomalous and requires some explanation. As noted above, analysis of the electronic structure of $LaSrCoO_3H_{0.7}$ reveals strong hybridization between cobalt 3d, oxygen 2p, and hydrogen 1s states within the $CoOH_{0.7}$ layers of the phases.[9] It is plausible that this strong hybridization not only supports strong magnetic superexchange, but also strengthens the bonding interactions within CoO_xH_y layers helping to kinetically stabilize the cobalt oxide-hydride phases formed, by providing a larger energetic barrier to their decomposition. This strong hybridization requires an effective energy match between metal and anion orbitals. The failure to date to prepare analogous manganese, iron, or nickel oxide-hydride phases suggests that, unlike cobalt, the orbital energy match between hydride ions and these metals is not sufficiently good to stabilize the highly metastable oxide-hydride phases. Thus if new, non-cobalt, transition metal oxide-hydride phases are to be prepared additional stabilizing interactions, possibly of structural origin, will be required.

In conclusion, reaction of the $n = 2$ Ruddlesden−Popper phase $Sr_3Co_2O_{5.80}$ with CaH_2 yields the oxide-hydride phase $Sr_3Co_2O_{4.33}H_{0.84}$. Extreme anion deficiency leads to low thermal and chemical stability in this phase, while anion disorder within the $CoO_{1.16}H_{0.42}$ planes appears to suppress long-range magnetic order.

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Supporting Information Available: Thermogravimetric data from the reduction of $Sr_3Co_2O_{5.81(3)}$. Full structural details from the refinement of "$Sr_3Co_2O_{3.8}$" at room temperature and $Sr_3Co_2O_{4.33}H_{0.84}$ at 5 K. Comparison of the observed, calculated and difference plots from the 4-phase refinements of $Sr_3Co_2O_{4.33}H_{0.84}$ against neutron diffraction data collected at 298 K and 5 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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