Solid-State Structures

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High-Pressure Synthesis of Manganese Oxyhydride with Partial Anion Order

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Abstract: *The high-pressure synthesis of a manganese oxyhydride* $LaSrMnO_{3.3}H_{0.7}$ *is reported. Neutron and X-ray Rietveld analyses showed that this compound adopts the* K_2NiF_4 *structure with hydride ions positioned exclusively at the equatorial site. This result makes a striking contrast to topochemical reductions of* $LaSrMnO_4$ *that result in only oxygen-deficient phases down to* $LaSrMnO_{3.5}$*. This suggests that high* H_2 *pressure plays a key role in stabilizing the oxyhydride phase, offering an opportunity to synthesize other transition-metal oxyhydrides. Magnetic susceptibility revealed a spin-glass transition at 24 K that is due to competing ferromagnetic* (Mn^{2+}–Mn^{3+}) *and antiferromagnetic* (Mn^{2+}–Mn^{2}, Mn^{3+}–Mn^{3+}) *interactions.*

Over the past decades, transition-metal (TM) perovskite-based mixed-anion systems, such as oxynitrides and oxyhalides, have been intensively investigated with various novel phenomena, including a non-toxic pigment $La_{1-x}Sr_xTaO_{2-x}N_{1+x}$, a high T_c superconductor $Ca_{2-x}Na_xCuO_2Cl_2$, and a visible-light catalyst $Sm_2Ti_2O_5S_2$.[1–3] TM oxyhydrides are a relatively new class of mixed-anion systems. $LaSrCoO_3H_{0.7}$ was the first example, reported in 2002,[4] which was followed by $Sr_3Co_2O_{4.33}H_{0.84}$.[5] These compounds were prepared by a topochemical reaction of $n=1$ and 2 Ruddlesden–Popper (RP) perovskite oxides using CaH_2. Subsequently, $ATiO_{3-x}H_x$ (A = Ba, Sr, Ca) and $Sr_{n+1}V_nO_{2n+1}H_n$ ($n=1, 2, \infty$) were obtained from $ATiO_3$ and $Sr_{n+1}V_nO_{3n}$.[6] More recently, a high-pressure (HP) reaction has been shown as an alternate approach to access TM oxyhydrides. $SrCrO_2H$ and $Sr_2VO_{4-x}H_x$ were stabilized by reacting a mixture of binary oxides and hydrides under 5 GPa.[7,8] Interestingly, the cobalt and vanadium oxyhydrides display H/O ordering, which is however absent in the chromium and titanium cases. The origin of anion (H/O) order–disorder has been discussed but not yet fully understood.

The TM oxyhydrides exhibit remarkable properties. First, $LaSrCoO_3H_{0.7}$, $SrCrO_2H$, and $SrVO_2H$ exhibit magnetic order far above room temperature (RT),[4,7,9] which is rationalized in $LaSrCoO_3H_{0.7}$ by strong hybridizations between Co 3d e_g and H 1s orbitals, and in $SrCrO_2H$ by relieved octahedral tilting (vesrus isoelectronic $ACr^{3+}O_3$). The high T_N in $SrVO_2H$ is surprising, given the orthogonality of V 3d t_{2g} and H 1s orbitals, and calls for further investigations. Second, titanium oxyhydrides show a metallic conductivity with carrier density widely tuned by H^- content.[10] The last but not least is high mobility of hydride ions in $LaSrCoO_3H_{0.7}$[11] and an H/D exchangeability of $BaTiO_{2.4}H_{0.6}$ with D_2 gas,[6a] both occurring at moderate temperatures.

So far, only four TMs (Cr, Co, Ti, V) are known to afford oxyhydrides, a fact which significantly limits our understanding and rationalization of their stability, structures, and functions. Herein, we present the HP synthesis of a manganese analogue $LaSrMnO_{4-x}H_x$ ($x \approx 0.7$) with an $n=1$ RP perovskite (K_2NiF_4) structure (Figure 1 a). Its structure, stability, and physical properties are discussed and compared with CaH_2-reduced $LaAMnO_{4-\delta}$ phases (A = Sr, Ba).[12] We also argue H/O order–disorder in comparison with other mixed-anion compounds.

For the synthesis of $LaSrMnO_{4-x}H_x$, we varied temperature (900–1100 °C), pressure (< 5 GPa), and molar ratio of

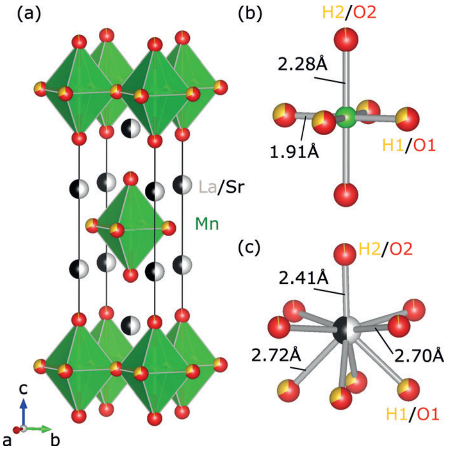

Figure 1. a) $LaSrMnO_{3.3}H_{0.7}$ structure; b), c) coordination geometry around Mn (b) and La/Sr (c).

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starting reagents. In appropriate conditions, we found a body-centered tetragonal phase ($a \approx 3.82$ Å, $c \approx 13.19$ Å) along with impurities. The impurity amount was minimized when reacted at 1000 °C and 5 GPa with La_2O_3:SrO:SrH_2:MnO:$Mn_2O_3 = 1:1:0.9:1.1:1.4:0.3$. As shown in Figure 2, the synchrotron X-ray diffraction (SXRD) and neutron diffraction (ND) patterns at RT was readily indexed with the K_2NiF_4 structure (*I*4/*mmm*) with cell parameters close to $LaSrMnO_4$.[13] The K_2NiF_4 structure was thus employed for Rietveld refinements with La/Sr at 4*e*, Mn at 2*a*, O1 at 4*c*, and O2 at 4*e*. We could not detect sizable amount of vacancy or hydrogen at the apical O2 site from ND/SXRD, while SXRD analysis on the equatorial O1 site occupancy showed the vacancies giving $LaSrMnO_{3.552(32)}$. However, ND analysis based on the anion vacancy model gave an incoherent composition $LaSrMnO_{2.90(3)}$ with an extremely low Mn valence of +0.80. As the quadrupole mass spectrometry (Supporting Information, Figure S1) showed a release of large amount of hydrogen above 150 °C, H was added at O1 where H/O atoms are randomly distributed at O1. This led to a consistent stoichiometry of $LaSrMnO_{3.3}H_{0.7}$. The sample prepared in a different condition (having larger amount of impurities) also gave the identical composition (Supporting Information, Figure S2 and Table S2).

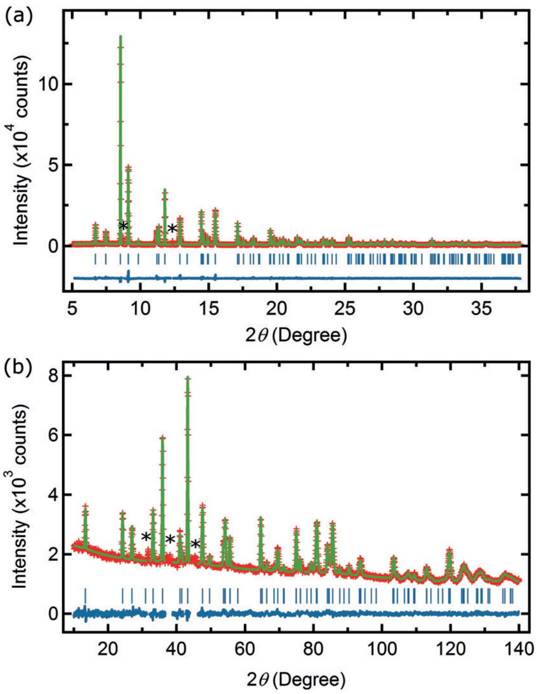

Figure 2. Rietveld refinement of a) SXRD and b) ND for $LaSrMnO_{3.3}H_{0.7}$. The red crosses and green and blue curves indicate the observed, calculated, and difference data. Green ticks are the calculated position of Bragg peaks. Asterisks indicate reflections from unknown impurity.

As shown in Figure 1 b, the $Mn(H,O)_4O_2$ octahedron is stretched with shorter equatorial Mn−O1/H1 bonds (1.9 Å) and longer apical Mn−O2 bonds (2.3 Å) along the *c* axis. The Mn−O2/Mn−O1 ratio of 1.2 is similar to those of $LaSrMn^{2.34+}O_{3.67}$, $LaSrMn^{2+}O_{3.5}$, and $LaSrMn^{3+}O_4$,[13] implying that the Jahn–Teller (JT) effect of Mn^{3+} is not a main origin of octahedral distortion. We also observed anisotropic peak broadening that may emerge from strains along *a* and *b* (see structural analysis in Supporting Information), possibly arising from randomly distributed short Mn−H and long Mn−O bonds.

It is noteworthy that low-temperature CaH_2 reactions of $LaSrMnO_4$ at 420 °C and 480 °C yield only oxygen-deficient phases, $LaSrMnO_{3.67}$ and $LaSrMnO_{3.5}$, respectively.[12] The manganese valence of +2.3 in $LaSrMnO_{3.3}H_{0.7}$ is close to $LaSrMnO_{3.67}$, but is higher than $LaSrMn^{2+}O_{3.5}$, implying superiority of CaH_2 reduction in terms of yielding compounds with a smaller valence. Even more remarkable is the fact that only HP condition gives an oxyhydride, instead of oxide. We consider HP reaction can avoid decomposition SrH_2 to Sr and H_2, while allowing incorporation of H^- in the structure. Possibly, the excess use of SrH_2 in the optimized reaction (10 %) generates a high H_2 gas pressure and helps in forming the oxyhydride.

A number of topochemical reactions using metal hydrides (CaH_2, NaH, LiH) have been reported.[14] In most cases, they lead to highly reduced oxides, rather than oxyhydrides. The present result indicates that reduced oxides accessible by topochemical hydride reactions are good candidates for a direct HP reaction to yield oxyhydrides. It is interesting to revisit, for example, $La_{1-x}Ca_xMnO_{2+\delta}$ and 4H-$BaMnO_{2+\delta}$,[15,16] with the HP method. A topochemical reaction of oxides with CaH_2 under high (H_2) pressure will be an alternative strategy. Interestingly, anion vacancies in $LaSrMnO_{3.67}$ and $LaSrMnO_{3.5}$ are present only within the MnO_2 layers, suggesting that if an oxyhydride is allowed to form, the H^- site is predictable from its oxygen-deficient phase.

The magnetic susceptibility of $LaSrMnO_{3.3}H_{0.7}$ (Figure 3) is fitted with the Curie–Weiss formula, $\chi = C/(T-\theta) + \chi_0$, where C, θ, and χ_0 denote the Curie constant, the Weiss temperature and a constant term, giving $C = 3.88(6)$ emu K mol^{-1}, $\theta = -149(3)$ K and $\chi_0 = 5.8(8) \times 10^{-4}$ emu mol^{-1}. The effective moment of $\mu_{\text{eff}} = 5.57\ \mu_B$ agrees well with the theoretical value (5.63 μ_B). The θ value indicates strong antiferromagnetic interactions. A deviation from the Curie–Weiss law below 80 K signifies development of short-range spin correlations. Despite the large $|\theta|$, the susceptibility keeps increasing with temperature, until it

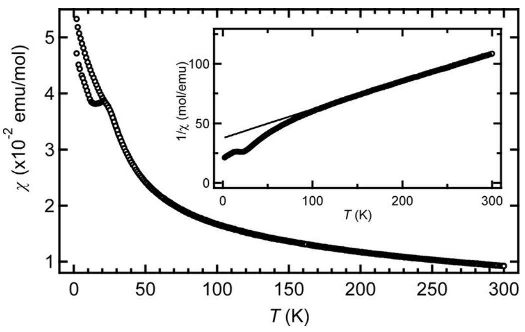

Figure 3. Magnetic susceptibility of $LaSrMnO_{3.3}H_{0.7}$. Inset: inverse susceptibility and the Curie–Weiss fit (black line).

exhibits a kink at 22 K (in ZFC process). However, ND data at 6 K (Supporting Information, Figure S3) lacks magnetic reflections, suggesting a spin glass state below $T_{SG}=22$ K. A deviation between ZFC and FC processes at T_{SG} is consistent with the spin glass nature. The AC susceptibility (Supporting Information, Figure S4) displays a frequency (ω) variation of transition temperature (T_f), with ω fitted by $\omega=\omega_0\propto(T_f/T_{SG}-1)^{zv}$.[17] The relaxation time $\tau_0(=2\pi/\omega_0)$ of $3.99(9)\times10^{-11}$ s and the dynamical critical exponent zv of 7.3(2) are typical for oxide spin glasses.[18]

The spin glass transition in our compound suggests strong spin frustration. The frustration index f, defined by $|\theta|/T_{SG}$, is as large as 6.0. In A_2MO_4 systems, predominant magnetic interactions are the nearest-neighbor and next-nearest-neighbor interactions, J_1 and J_2, in the MO_2 square lattice. The latter interaction is usually much weaker when M-O-M angle is close to 180° as in the present case. Thus, the competition between J_1 and J_2 is not the origin of spin frustration. We propose that the spin frustration originates from the mixed valence of Mn^{2+} (d^5) and Mn^{3+} (d^4). According to the Goodenough–Kanamori rule,[19] J_{1a} via Mn^{2+}–Mn^{2+} and J_{1b} via Mn^{3+}–Mn^{3+} are antiferromagnetic, while J_{1c} via Mn^{2+}–Mn^{3+} is ferromagnetic. The mixed interactions induce frustration within the MnX_2 layer and the resultant spin glass transition. Interestingly, an oxygen-deficient $LaSrMnO_{3.67}$ with a similar Mn valence of +2.34 has $\theta=-258$ K and $T_{SG}=60$–75 K, giving a smaller f of 4.3.[12] This implies enhanced frustration in our material with a greater ferromagnetic contribution. Inequivalent Mn-O-Mn and Mn-H-Mn bonds for each J_{1i} (i = a, b, c) may also account for the enhanced frustration. In fact, $Mn^{2+}TaO_2N$ has a larger f of 9.2[20] than the isostructural oxide $Mn^{2+}TiO_3$ with $f=6$,[21] resulting in different spin structures.

The utmost feature in $LaSrMnO_{3.3}H_{0.7}$ is the selected occupation of H^- ions in the perovskite layer. There are numerous studies on anion order/disorder in perovskite-based mixed-anion systems.[21] For instance, $SrTaO_2N$ has a preference of *cis*-TaO_4N_2 octahedra, leading to a novel anion order.[22] In $SrVO_2H$, the JT effect gives *trans*-VO_4H_2 octahedra and the infinite-layer structure results.[9] Unlike ABO_3, the pristine A_2BO_4 affords two distinct crystallographic oxygen sites: the axial O2 site surrounded by five A and one B atoms and the equatorial O1 site surrounded by four A and two B atoms. Since the A cation in A_2BO_3X is in general more electropositive, there is a tendency that a more/less electronegative anion occupies the O1/O2 site.[20,21] Such anion order is often encountered in oxyfluorides with F^- at the axial site (Sr_2CoO_3F, Sr_2NiO_3F),[24,25] in oxynitrides with N^{3-} at the equatorial site (Sr_2TaO_3N, Sr_2NbO_3N),[23,26] though few exceptions like Nd_2AlO_3N exist.[27] Given the electronegativity of H (2.2), H^- is likely to occupy the O1 site, which is what has been observed previously in Sr_2VO_3H,[9] $LaSrCoO_3H_{0.7}$,[4] and now in $LaSrMnO_{3.3}H_{0.7}$.

Using Pauling's electrostatic valence rule,[28] Fuertes et al. have demonstrated a predictability of the anion order from refined structural data on RP perovskite oxynitrides and oxyhalides (F, Cl, Br).[22c,23] Here, the valence of the anion site approximately matches the bond strength sum b at O1 ($4\times$ A−O and $2\times$ B−O) and O2 ($5\times$ A−O and $1\times$ B−O) defined as $b_{O1}=4z_A/v_A+2z_B/v_B$ and $b_{O2}=5z_A/v_A+z_B/v_B$ (z = formal valence, v = coordination number). Sr_2TaO_3N and Sr_2CoO_3F have $(b_{O1}, b_{O2})=(2.56, 1.94)$ and (1.89, 1.61), implying the occupation of N/F at the O1/O2 site.[27] Interestingly, this rule does not hold in oxyhydrides: Sr_2VO_3H (1.89, 1.61), $LaSrCoO_3H_{0.7}$ (1.68, 1.67), and $LaSrMnO_{3.3}H_{0.7}$ (1.88, 1.77). The electronegativity of H may be too small to apply the principle based on the electrostatic arguments. Finally, given with a order–disorder transition at $\delta=0.7$ in $Sr_2VO_{4-\delta}H_\delta$,[8] $LaSrMnO_{4-x}H_x$ with $x>0.7$ may induce in-plane anion order, which will be a future study and hopefully such efforts contribute to achieve a global understanding of anion order/disorder in oxyhydrides and more generally mixed-anion materials.

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