

A Mixed Oxide-Hydride Perovskite

Kenneth Poeppelmeier

The discovery of useful new materials is greatly facilitated by a detailed understanding of, and control over, the coupling of a material's properties to its atomic structure (1, 2). A wide range of techniques is now available to help researchers to achieve this goal. On page 1882 of this issue, Hayward *et al.* (3) report the synthesis and in-depth characterization of an unusual mixed-metal material that contains both oxide and hydride ions. Its unprecedented two-dimensional structure is related to the ubiquitous perovskites. Cobalt-hydride-cobalt bonding provides a new pathway for electronic and magnetic interactions.

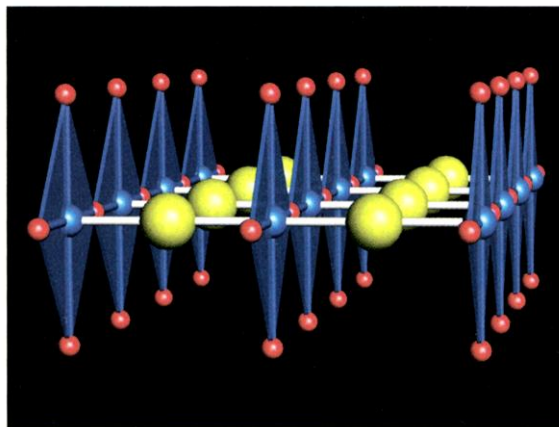
Interest in hydrides mainly stems from their strong reducing properties. Molecular hydrogen, H_2 , is not an effective reducing agent, compared with alkaline or alkaline earth metals. The hydride ion, H^- , is much better: At about -2.2 V, the standard potential for H^-/H_2 is comparable to the -2.4 V for Mg/Mg^{2+} . The hydride ion is thus one of the best reducing agents in the chemist's arsenal (4).

Few well-characterized compounds contain both hydride and oxide ions. Lanthanum hydride-oxide, $LaHO$, is extremely hygroscopic and will liberate hydrogen in contact with water (5). Two more recent examples, $Ba_3(AlO_4)H$ and $Ba_{21}Ge_5O_{52}H_{24}$ (6, 7), can be synthesized under extremely reducing conditions.

Hayward *et al.* now report the synthesis of a new member of this group. The authors use soft chemistry ("chimie douce"), which is carried out under moderate conditions (typically less than $500^\circ C$) and preserves the structural elements of the solid state reactants but changes their compositions. The group previously showed that solid NaH is an effective source of hydride ions at temperatures as low as $190^\circ C$ (NaH decomposes at $210^\circ C$). They now report that reaction of the perovskite-related $LaSrCoO_4$ and the thermally robust CaH_2 (which decomposes at $885^\circ C$) leads to the formation of the solid phases $LaSrCoO_3H_{0.7}$ and CaO . The work reveals how tolerant perovskite structures can be to changes in stoichiometry

and illustrates the novel materials that can be made through anion substitution.

The structure of $LaSrCoO_3H_{0.7}$ is related to the first ($n = 1$) member of the $A_{n+1}B_nO_{3n+1}$ family, which can be described as an intergrowth of one rock-salt AO block and n perovskite ABO_3 units. Chains of CoO_4 squares share two oppo-



An unusual arrangement. Chains of CoO_4 squares are linked by hydride anions (yellow spheres) in Hayward *et al.*'s new material.

site corners along one crystal direction. They are linked by the hydride anions (see the figure) and replace the CoO_2 sheets of the starting phase. A related, oxygen-deficient product, $LaSrCoO_{3.5-x}$, was expected on the basis of previous low-temperature reductions with ethylene, propylene, ammonia, or hydrogen (8–10), but it did not form.

It is particularly striking that during the reaction, transition metal reduction and hydride ion insertion both occur. Presumably molecular hydrogen (not water) is produced when hydride anions (rather than oxide anion vacancies) dominate solid state reactions. In other words, the oxygen removed from the $LaSrCoO_4$ is found in CaO , and the molecular hydrogen and the low-valent $Co(I)$ in the hypothetical " $LaSrCoO_3$ " undergo an oxidative addition reaction.

This low-temperature synthetic route shows that ternary transition metal oxides can form oxide-hydrides, despite the expectation that in a high-temperature solid state synthesis with a hydride source, the transition metal cation would be reduced to the metal. The synthesis also shows that

reduction by hydride ions can yield unexpected products. There is an ongoing discussion in the solid state community as to which cations and their oxidation states can exist with the hydride ion in mixed metal oxide/hydride perovskites at higher temperatures and low oxygen partial pressures (11, 12). The discovery of a mixed hydride-oxide phase such as $LaSrCoO_3H_{0.7}$ greatly increases our overall understanding and should lead to the discovery of related phases.

The wide range of characterization techniques brought to bear on the problem reflects how far solid state chemistry has advanced in recent years. The study demonstrates how a series of linked techniques,

from powder diffraction for indexing purposes, to neutron and synchrotron x-ray diffraction, electron microscopy, and muon spin resonance, can be combined to carry out a complete characterization. The muon spin resonance experiment in particular was vital for establishing that extra diffraction peaks in the neutron diffraction pattern were due to magnetic ordering.

The magnetic and electronic properties of oxides are controlled via the exchange pathway from the metal (cobalt) through oxygen back to the metal. With oxygen linking two metal centers, the interaction can be through σ (along the bond axis) or π (perpendicular to the bond axis) bonds. Hydrides allow only σ pathways and the strengths of the interactions are different. This new material and future family members can thus be expected to have interesting new magnetic and electronic properties.

References

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The author is in the Department of Chemistry, Northwestern University, Evanston, IL 60208, USA. E-mail: krp@northwestern.edu