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研究課題名(和文) Synthesis and Modification of Novel Oxyhydrides Perovskites

研究課題名(英文) Synthesis and Modification of Novel Oxyhydrides Perovskites

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研究成果の概要(和文)：本テーマでは、高圧合成法を用いて、新しいペロブスカイト型酸水素化物の合成を試みた。その結果、高圧合成法を使えば、通常の方法では得られない新しい遷移金属化合物が合成できることが証明できた。その一つとして、O<sub>2</sub>-/H-がランダムに固溶しているSrCrO<sub>2</sub>Hがある。SrCrO<sub>2</sub>Hは八面体間の歪みがない立方晶系であるため、他のクロム酸化物と比べ、極めて高いNeel点を有している。このように、高圧合成法は、新しい酸水素化物や興味深い物性を持つ新物質の合成に極めて有効である。

研究成果の概要(英文)：In this project, we have studied the possibility of synthesizing novel oxyhydride perovskites materials via the use of high pressure synthesis. We have shown that high pressure allows yielding novel structures containing transition metals that cannot be formed via ambient pressure techniques. Among the structures discovered is a stoichiometric disordered SrCrO<sub>2</sub>H. Interestingly, this cubic framework presents the highest Neel temperature observed in chromium oxides in reason of the lack of structural distortions. High pressure synthesis is therefore an interesting path towards forming novel oxyhydrides and possibly reach exotic properties.

研究分野：High-Pressure Synthesis

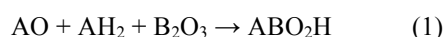
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### 1. 研究開始当初の背景

The development of perovskite oxides  $ABO_3$  has allowed tremendous achievements in numerous technological fields (catalysis, dielectrics, superconductivity, etc...). Although, a lot of work has been performed on substituting the anionic site with nitrogen  $N^{3-}$  or fluorine  $F^-$  towards the elaboration of photocatalysts and dielectrics, few investigations exist on the synthesis of perovskite oxyhydride  $ABO_2H$ . Nitride and fluoride substitutions of the oxide anion allow tuning the electronic and magnetic properties of the oxide structures owing to their different properties such as electronegativity, ionic polarizability and size. The hydride anion  $H^-$ , however, unlike the oxide, nitride and fluoride anions, only possesses a  $1s$  orbital (vs.  $2s$ ,  $2p$ ) and its combination with  $O^{2-}$  in an extended framework could grant the access to novel exotic properties.

#### 研究の目的

Most reported perovskite oxyhydride ( $BaTiO_{2.4}H_{0.6}$ ,  $LaSrCoO_3H_{0.7}$ ) are prepared by reacting perovskite oxide precursors ( $BaTiO_3$ ,  $LaSrCoO_4$ ) with hydrides ( $CaH_2$ ,  $NaH$ ,  $LiH$ ) as reducing agents.[1-3] This technique allows the incorporation of the hydride anion topochemically during the reduction process. The use of this pathway however does not always yield oxyhydrides and many topochemically-reduced materials do not exhibit the presence of the hydride anion. Here in this project, we investigated the synthesis of novel oxyhydride perovskites  $ABO_2H$  by using a “direct” technique under high-pressure and high-temperature via the reaction of binary oxides and hydrides:



, where A is an alkali earth metal and B a transition metal. The use of high pressure allows the stabilization of the binary hydride that would decompose under ambient pressure and high temperature conditions. The formation of such structures could allow the expansion of the relatively new oxyhydride family and allow a better understanding of the hydride anion properties, its interaction with transition metals as well as its structural impact in extended frameworks.

The second part of the project consisted in the modification of the novel oxyhydrides towards a conversion into conductors; however, the challenging synthesis conditions (small sample amount), the air and thermal instability of the

samples as well as the presence of impurities prevented us from further studies. We therefore focused our interest to the expansion of part one and the synthesis of perovskites and layered oxyhydride structures using high-pressure synthesis.

### 3. 研究の方法

In order to predict the feasibility of each candidate materials we used the Goldschmidt tolerance factor:

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (2)$$

where  $r_A$ ,  $r_B$  and  $r_X$  are the radii of the A, B and  $O^{2-}/H^-$  sites, respectively. Several candidate compositions ( $ABO_2H$  and  $ABOH_2$ ) were determined with a tolerance factor between 0.8 and 1.0 and three new oxyhydride materials were prepared successfully.

The samples were typically prepared in a  $N_2$ -filled glovebox and inserted in NaCl cells. These assemblies were placed in graphite sleeves (heater) and then in cubic pyrophyllites (pressure-transmitting medium) (Fig. 1). All the reactions were performed in a cubic anvil type high-pressure apparatus. Reactions were carried out at pressures and temperatures between 1 to 7 GPa and 700-1200 °C. Presence of hydrogen in the obtained samples was confirmed by mass spectrometry. Their crystal structure as well as the presence of the hydride anion were determined by Rietveld analyses of synchrotron X-ray and neutron powder diffraction.

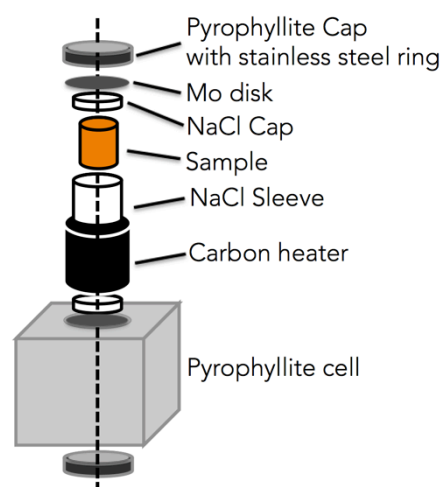


Figure 1. Structure of a typical high-pressure cell for the synthesis of oxyhydrides.

### 4. 研究成果

(1) This project has allowed the discovery of novel oxyhydride structures with different transition metals (Cr, Mn and Sc). Among them,

SrCrO<sub>2</sub>H (Fig. 2) was successfully prepared and showed a high Néel temperature ( $T_N \approx 380$  K) (*Angewandte Chemie International Edition*, 2014). Most Cr<sup>3+</sup> containing oxide perovskites (A<sup>3+</sup>CrO<sub>3</sub>) are distorted owing to the small sizes of trivalent cations. The use of hydride permitted the large Sr<sup>2+</sup> ion at the A site and the stabilization of the cubic symmetry. The lack of distortions in SrCrO<sub>2</sub>H contributes to the high temperature antiferromagnetic ordering.

(2) This work showed that the use of high pressure allows the stabilization of phases that could not be obtained under ambient pressure techniques or topochemical techniques. As shown in Figure 3, SrCrO<sub>2</sub>H was best prepared around 5 GPa. We note that the use of topochemical hydride reduction on SrCrO<sub>3</sub> does not yield an oxyhydride phase.[4]

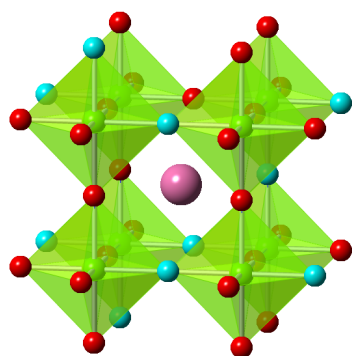


Figure 2. Schematic crystal structure of SrCrO<sub>2</sub>H. The blue, red, pink and green balls represent hydrogen, oxygen, strontium and chromium, respectively.

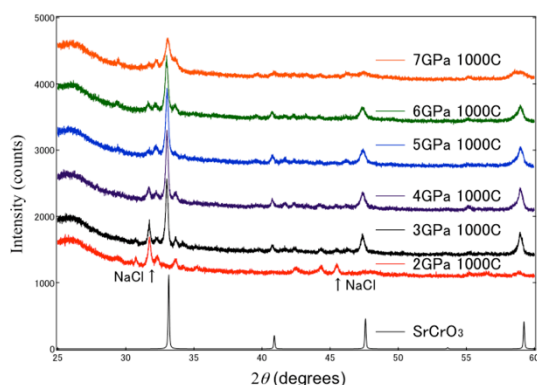


Figure 3. Evolution of the X-ray diffraction pattern of SrCrO<sub>2</sub>H as a function of the synthesis conditions and comparison of the Bragg peaks of SrCrO<sub>2</sub>H ( $a = 3.84$  Å) with that of simulated SrCrO<sub>3</sub> ( $a = 3.82$  Å).

(3) Attempts to synthesize structures containing later transition metals under high pressure (example: Cu, Co) did not yield oxyhydride structures. This may be explained by the instability of these elements in highly reducing

atmospheres. Investigation of the synthesis of 4d and 5d row materials were also attempted using Zr, Nb and Ta at the B site and alkali ions at the A site. Many difficulties were encountered given the high-pressure cell design, as most alkali metal reacted with the NaCl sleeve.

## Conclusion

This project has allowed the synthesis of novel oxyhydride structures under high pressure (Mn, Cr, Sc), notably SrCrO<sub>2</sub>H. These results are promising towards a further expansion of the oxyhydride family and a better understanding of the impact of hydride-substitution in oxide materials.

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## 5. 主な発表論文等

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[雑誌論文] (計 1 件)

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## 6. 研究組織

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