

Structures of Perovskite Oxyhydrides Synthesized by a High-Pressure Flux Method

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Perovskite oxyhydrides containing oxide (O^{2-}) and hydride (H^-) anions have attracted attention as catalysts and hydride ion conductors for energy storage. These multi-component compounds are typically difficult to synthesize since hydride is easily volatile at high temperatures and is a strong reducing species to reduce the transition metal cations to the metal. Chemists overcame these difficulties by using low-temperature topochemical reactions. For example, the layered perovskite $LaSrCoO_3H_{0.7}$ was synthesized by topochemical reduction from $LaSrCoO_4$ by using CaH_2 . The series of $Sr_{n+1}V_nO_{2n+1}H_n$ ($n = 1, 2, \infty$) with an anion-ordered (layered) perovskite structure can be also synthesized from a topochemical reduction of the oxide precursor $Sr_{n+1}V_nO_{3n+1}$ by using CaH_2 [1]. These compounds are Mott-insulators, while $SrVO_2H$ ($n = \infty$) exhibits unusual pressure-induced insulator-to-metal transition due to the π -blocking nature of H^- [2]. Sr_2VO_3H ($n = 1$) can also be synthesized by high-pressure and high-temperature reaction, where oxyhydrides directly form from a reaction of oxide and hydride precursors [3]. The advantage of high-pressure and high-temperature reaction is that the hydride content x in $Sr_2VO_{4-x}H_x$ can be tuned by the preparation composition of the precursors, while the topochemical reduction can only be accessible to the $x = 1$ phase (Sr_2VO_3H). Therefore, by using the high-pressure and high-temperature reaction, the electronic and magnetic properties of $Sr_2VO_{4-x}H_x$ can be controlled by x . However, in contrast to $Sr_2VO_{4-x}H_x$ ($n = 1$), the perovskite $SrVO_{3-x}H_x$ ($n = \infty$) has not been able to be synthesized without a significant amount of impurity through high-pressure and high-temperature reaction [4].

We overcome this problem by adding $SrCl_2$ as a flux and successfully synthesize single-phase $SrV(O,H)_3$ and $Sr_3V_2(O,H)_7$.

In order to estimate the hydride contents of the samples, we carried out neutron powder diffraction (NPD) measurements of $SrV(O,H)_3$ and $Sr_3V_2(O,H)_7$ on HERMES of the Institute for Material Research, Tohoku University, installed at the T1-3 port in the guide hall of JRR-3 reactor in Japan Atomic Energy Agency (JAEA), Tokai. The incident neutron was monochromated to 2.19647 Å by the 331 reflection of Ge Crystals. Figure 1 shows the NPD patterns of $SrV(O,H)_3$ and $Sr_3V_2(O,H)_7$ synthesized by the high-pressure flux method. We observed high backgrounds from incoherent scattering suggesting the samples are oxyhydride phases. Although the backgrounds are high and the intensity is insufficient to reveal the structure's details, we will carry out the Rietveld refinements of the data.

- [1] F. D. Romero *et al.* *Angew. Chem. Int. Ed.* **53**, 7556 (2014).
- [2] T. Yamamoto *et al.* *Nat. Commun.* **8**, 1217 (2017).
- [3] J. Bang *et al.* *J. Am. Chem. Soc.* **136**, 7221 (2014).
- [4] K. Miyazaki *et al.* *Inorg. Chem.* **60**, 15751 (2021).

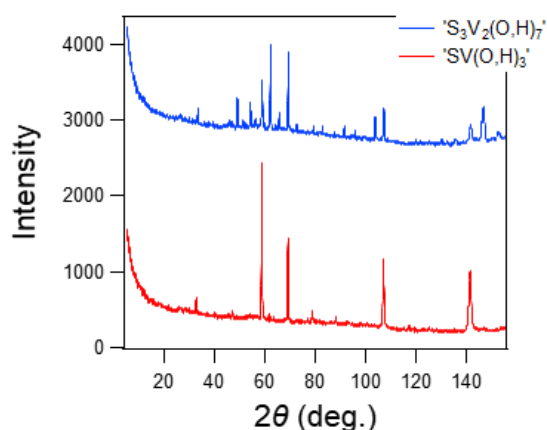


Fig. 1. NPD patterns of $SrV(O,H)_3$ and $Sr_3V_2(O,H)_7$.