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High-pressure synthesis of novel hydrides with high hydrogen densities – Li₃AlFeH₈ and LiAlFeH₆

Recent progress in synthesis techniques and theoretical calculations has enabled us to obtain novel hydrides with high hydrogen densities. Such hydrogen-rich materials are expected to be used as hydrogen storage materials. Some of them may show functionalities such as high-temperature superconductivity and fast ionic conductivity. We are synthesizing iron-containing complex hydrides because this class of materials consist of $[FeH_6]^{4-}$ complex anions and tend to have high hydrogen densities, and iron is one of the most common metals. As example of iron-containing complex hydrides, we have already synthesized YLiFeH₆ and Li₄FeH₆.

We are attempting to synthesize other ironcontaining complex hydrides with higher hydrogen densities by incorporating H⁻ anions into ironcontaining complex hydrides. Since the $[FeH_6]^{4-}$ complex anion is tetravalent and it is necessary to follow the 18-electron rule, possible combinations of countercations are limited to four types (Fig. 1(a)). When we try to synthesize a lightweight hydride, the combinations are severely limited. If we can incorporate H⁻ anions into an iron complex hydride, the number of combinations of countercations will markedly increase as shown in Fig. 1(b). The purpose of the present study [1] is to synthesize the theoretically predicted Li₃AlFeH₈[2] using a high-pressure technique, which is a powerful technique for synthesizing novel hydrides.

The starting material was a powder mixture of LiH, AlH₃, and pure iron with a molar ratio of 3:1:1. The starting material was compacted into a small disk and was placed in a sample capsule made of boron nitride. The sample was pressurized to a target pressure ranging from 4-7 GPa at room temperature and then heated 600-800°C. We changed the pressure and temperature to find the synthesis conditions with the aid of *in situ* measurements. Hydrogenation of the sample was achieved using a high-pressure cell developed by Fukai and Okuma [3]. A capsule made of NaCl was used as the hydrogensealing capsule. Hydrogen was evolved from a powder mixture of NaBH₄ and Ca(OH)₂ at around 400°C and confined in the hydrogen-sealing capsule. The sample was hydrogenated in a boron nitride capsule, in which hydrogen can permeate but other by-products from the internal hydrogen source cannot permeate.

We observed the structural changes of the sample during the hydrogenation reaction *in situ* by synchrotron radiation X-ray diffraction (SR-XRD) measurement at SPring-8 **BL14B1**. After the high-pressure treatment, the sample was quenched to room temperature and depressurized to ambient pressure. The recovered sample under ambient conditions was characterized by a conventional X-ray diffractometer.

We searched for hydrogenation conditions of the powder mixture by in situ SR-XRD measurement. Figure 2 shows a series of X-ray diffraction profiles of the sample hydrogenated at 5 GPa and 600°C. New Bragg peaks were observed approximately 50 min after the sample was heated to 600°C in hydrogen fluid. The Bragg peaks were indexed by the unit cell of the theoretically predicted Li₃AIFeH₈, indicating that the powder mixture was hydrogenated to form Li₃AIFeH₈. The inset of Fig. 2 shows the time evolution of the peak intensity of the 011 Bragg peak from Li₃AIFeH₈. The increase in the peak intensity finished at around 300 min. Unreacted iron was still observed at this stage, indicating that a single phase of Li₃AIFeH₈ cannot be obtained by a further hydrogenation reaction at 5 GPa and 600°C.

The hydrogenated sample was recovered under ambient conditions. Figure 3(a) shows the powder X-ray diffraction profile of the sample and the calculated profile for theoretically predicted Li₃AlFeH₈



Fig. 1. Schematics of charge neutrality in iron-containing complex hydrides (a) without H^- anion incorporation and (b) with H^- anion incorporation.

(crystal structures shown in this article were drawn using the VESTA program [4]). The calculated profile reproduces the experimentally obtained one; we confirmed that the theoretically predicted Li_3AIFeH_8 was synthesized.

We searched for synthetic conditions where the single phase of Li_3AIFeH_8 can be obtained. Unfortunately, we could not obtain a single phase of Li_3AIFeH_8 up to 9 GPa and 900°C.

Another novel hydride, LiAlFeH₆, was found while optimizing the synthesis conditions of Li₃AlFeH₈. Figure 3(b) shows an X-ray diffraction profile of the recovered sample hydrogenated at 9 GPa and 900°C. The observed Bragg peaks were indexed by a hexagonal lattice. The chemical composition of the novel hydride was predicted to be LiAlFeH₆ based on the relationship between the constituent ions and the crystal structure volume reported by Sato *et al.* [5]. The crystal structure obtained by the first-principles calculations is shown in the inset of Fig. 3(b). The experimentally obtained X-ray diffraction profile was reproduced by the calculated profile for the theoretically predicted crystal structure.

The theoretically predicted Li_3AIFeH_8 was synthesized at 5 GPa. We did not obtain single-phase Li_3AIFeH_8 ; however, another novel hydride, $LiAIFeH_6$, was also synthesized while optimizing the reaction pressure-temperature conditions for Li_3AIFeH_8 .



Fig. 2. (a) Series of synchrotron radiation powder X-ray diffraction profiles of the powder mixture hydrogenated at 5 GPa and 600°C. Bragg peaks with filled circles and Miller indices are from Li_3AIFeH_8 . (b) Time dependence of the integrated intensity of the 110 Bragg peak of Li_3AIFeH_8 .

We demonstrated that the combination of highpressure synthesis and *in situ* SR-XRD is a powerful approach for obtaining novel hydrogen-rich materials. We are currently investigating the properties of the obtained hydrides.



Fig. 3. Powder X-ray diffraction profiles of recovered samples hydrogenated at (a) 5 GPa and 650°C and (b) 9 GPa and 900°C. The insets show the schematics of the crystal structures of (a) $L_{13}AIFeH_8$ and (b) LiAIFeH8. Calculated profiles for the theoretically predicted crystal structures are shown in dashed lines. Bragg peaks with filled circles, filled squares, up-pointing triangles, and down-pointing triangles are from $L_{13}AIFeH_8$, pure iron, LiAIFeH6, and unknown phase, respectively.

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