Infrared Spectroscopic and Computational Studies on Li₄FeH₆ with High Gravimetric Hydrogen Density

Takahiro Ogata¹,*,1, Toyoto Sato¹,*,2, Shigeyuki Takagi¹, Hiroyuki Saitoh², Yuki Iijima¹, Biswajit Paik³ and Shin-ichi Orimo¹,5

1Institute for Materials Research, Tohoku University, Sendai 980–8577, Japan
2Quantum Beam Science Research Directorate, National Institute for Quantum and Radiological Science and Technology, Hyogo 679–5148, Japan
3WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980–8577, Japan

We report the vibrational properties of Li₄FeH₆ with the highest gravimetric hydrogen density in Fe-based complex hydrides. The Fourier transform infrared (FTIR) spectrum shows a broad and weak peak at 600–1000 cm⁻¹ and an intense one at 1400–1800 cm⁻¹, which are assigned with the aid of first-principles calculations to be the H–Fe–H bending modes, and the antisymmetric Fe–H stretching modes, respectively. From the obtained peak frequency of asymmetric stretching modes of Li₄FeH₆, the Fe–H bond length is estimated to be 1.6 Å, which is in good agreement with the one predicted by first-principles calculations.

Keywords: hydrogen storage, complex hydride, infrared spectroscopies, first-principles calculations

1. Introduction

Iron(Fe)-based complex hydrides, which contain Fe-hydrido complex anion [FeH₆]⁴⁺, have been the subject of extensive investigation because of practical interest as potential hydrogen storage materials.¹⁻³ In the complex hydrides, [FeH₆]⁴⁺ is generally counterbalanced by alkaline-earth metals (e.g. Mg₂FeH₆) or mixed alkali/transition metals (e.g. Li₂FeH₆).³⁵⁻⁶ The gravimetric hydrogen densities reach 5.5 mass% when Mg is adopted as a countercation. Very recently, we have successfully synthesized a novel complex hydride, Li₄FeH₆, using a high pressure cubic-anvil-type apparatus based on a prediction by first-principles calculations.⁶,⁷ This is the first complex hydride of which [FeH₆]⁴⁺ is counterbalanced by alkali metal elements, and has the highest gravimetric hydrogen density of 6.7 mass% in the Fe-based complex hydrides.

The crystal structure of Li₄FeH₆ was theoretically elucidated to have a trigonal K₃CdCl₆-type with a = 7.97 Å and c = 9.76 Å in the space group R-3c (No. 167) and Z = 6 (Fig. 1), which is the same structure type as that of the isomorphic Li₃RuH₆ and Li₃OsH₆.⁹ In the complex hydride, Fe is octahedrally coordinated by six hydrogen atoms with Fe–H bond length of 1.61 Å.¹⁰ The [FeH₆]⁴⁺ is surrounded with eight cations (Li atoms) which form corner-sharing cube as shown in Fig. 1. This is similar to the edge-sharing cube in the related compounds M₂ZH₆ (M² = divalent metal cation), in spite of having different crystal structures (note that M₂ZH₆ adopts a face-centered cubic K₃PtCl₆-type structure).¹⁰ Although the experimental confirmation of the crystal structure, especially the hydrogen positions, has been strongly desired, it is technically difficult to synthesize a large volume of samples enough for the structure analyses, using the high pressure cubic-anvil-type apparatus.

In this regard, we have recently reported a unique way to estimate the bond length between the center atom and the hydrogen in the related Ru-hydrido complex anion using the vibrational properties. The idea is based on a linear relationship between the frequencies of antisymmetric Ru–H stretching modes and the Ru–H bond length in [RuH₆]⁴⁻.¹¹ This method would allow for the estimation of the bond length even in the case of a tiny amount of sample obtained.

In this study, we first investigated the vibrational properties of Li₄FeH₆ in detail (especially, the hydrogen atomic motions), using Fourier transform infrared (FTIR) spectroscopy combined with first-principles calculations. Based on the results, the Fe–H bond length was estimated.

2. Experimental Procedure

2.1 Synthesis

The starting materials, LiH (95% Sigma-Aldrich) and Fe (99.9% Sigma-Aldrich) powders were mixed in a molar ratio of 6:1 and the mixture was pressed into a pellet with a diameter of 1.0 mm and a thickness of 1.0 mm in the same manner as in Ref. 7. The pellet, encapsulated in a pyrolytic boron nitride reaction capsule, was loaded together with a hydrogen...
source AlH$_3$\textsuperscript{12,13}) into a NaCl capsule with a diameter of 1.5 mm and a height of 3.5 mm. The pellet reacted with hydrogen fluid, which was supplied from the hydrogen source, to synthesize Li$_4$FeH$_6$ at 5.5 GPa and 700°C for 24 hours by using a cubic-anvil-type apparatus. The synthetic conditions were determined based on in-situ synchrotron x-ray diffraction data measured at BL14B1 of SPring-8. The details of the high-temperature and high-pressure synthesis techniques are described in Refs. 7, 14–16).

All samples were handled in an Ar-gas-filled glove box with a dew point below 183 K and with less than 1 ppm of O$_2$ to avoid hydro-oxidation.

2.2 Characterizations

All samples were characterized by X-ray powder diffraction (PANalytical XPERT PRO diffractometer) using Cu K$_\alpha$ radiation (λ = 1.5406 Å for K$_\alpha$1 and 1.5444 Å for K$_\alpha$2).

The vibrational spectra of Li$_4$FeH$_6$ were measured using FTIR (Thermo Scientific Nicolet iN10) spectroscope. For the FTIR spectroscopic studies, a thin sample, approximately a few μm thick, was prepared in an Ar-gas-filled diamond anvil cell, and transmission spectra were measured with a microscope FTIR spectrometer.

2.3 First-principles calculations

The lattice dynamics of 22-atom primitive unit cell of Li$_4$FeH$_6$ were studied using first-principles calculations based on density-functional theory (DFT). We used plane-wave basis sets and the projector augmented-wave method\textsuperscript{17,18}) with-in the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof,\textsuperscript{19}) as implemented in the Vienna Ab-Initio Simulation Package (VASP).\textsuperscript{20,21}) Well-converged plane-wave basis sets with cutoff energy of 800 eV were employed. The Brillouin-zone sampling was performed using the special k-points method\textsuperscript{22}) with an 8×8×8 mesh. The structural parameters were taken from Ref. 6). The zone-center phonon frequencies were obtained using first-principles perturbation theory (DFPT).

3. Results and Discussions

3.1 Synthesis

Figure 2 shows the X-ray diffraction patterns of the as-milled and the hydrogenated 6LiH + Fe with a simulated X-ray diffraction pattern of Li$_4$FeH$_6$. Only the peaks from the Fe metal are observed in the pattern of the as-milled sample because of low X-ray scattering from LiH composed of light elements. After the hydrogenation, new peaks are observed and indexed by a trigonal unit cell with $a = 7.989(6)$ Å and $c = 9.651(9)$ Å using indexing programs.\textsuperscript{23,24}) This is in good agreement with previously reported unit cell parameters of Li$_4$FeH$_6$.\textsuperscript{6,7}) Thus, Li$_4$FeH$_6$ was successfully synthesized. Although we attempted to optimize synthesis conditions for a higher quality sample with less amount of Fe by adjusting the starting material ratios, ball-milling times, as well as the synthesis temperature and duration, it was found that the present condition (5.5 GPa and 700°C for 24 hours on the ball milled 6LiH and Fe) yielded the highest purity of Li$_4$FeH$_6$ in our experiments. Saitoh et al., reported that high temperature at around 900°C was necessary to obtain a high purity Li$_4$FeH$_6$ in order to accelerate the reaction kinetics.\textsuperscript{7}) Hydrogen pressure higher than 6 GPa pressure was required to avoid subsequent decomposition of Li$_4$FeH$_6$ during synthesis. Although the sample is not a single phase, the quality was good enough for the FTIR to access the hydrogen atomic motion in Li$_4$FeH$_6$.

3.2 Vibrational properties

Figure 3 shows the FTIR spectrum of Li$_4$FeH$_6$. The spectrum has broad and weak peaks at 600–1000 and an intense peak at 1400–1800 cm$^{-1}$. We performed first-principles phonon calculations to assign the experimentally observed frequencies to the vibrational modes. The calculated zone-center phonon frequencies are shown by tick marks.
a total of 63 optical phonon modes. The calculated frequencies between 1470 and 1710 cm$^{-1}$ originate from the Fe–H stretching modes, whereas those ranging from 710 to 950 cm$^{-1}$ are related to the H–Fe–H bending modes. The remaining frequencies are associated with the Li translational or FeH$_6$ librational modes. Among these frequencies, there are a total of 28 IR active modes, which are shown by tick marks in Fig. 3. From a comparison of the observed and calculated frequencies, the broad and weak peaks at 600–800 cm$^{-1}$ in the experimental FTIR spectrum can be understood to originate, respectively, from the H–Fe–H bending modes, and the antisymmetric Fe–H stretching modes.

The observed FTIR frequencies related to the Fe–H stretching modes of Li$_2$FeH$_6$ are very close to those reported for Ca$_2$FeH$_6$.\textsuperscript{25} Supposing that the frequencies of the anti-symmetric Fe–H stretching modes are linear with Fe–H bond length as reported for the Ru-based complex hydrides,\textsuperscript{11} the Fe–H bond length in Li$_2$FeH$_6$ should be comparable to that in Ca$_2$FeH$_6$, and is estimated to be 1.6 Å. This is in good agreement with that predicted by first-principles calculations.\textsuperscript{60}

4. Conclusion

We successfully synthesized Li$_2$FeH$_6$ at 5.5 GPa and 700°C for 24 hours and investigated the vibrational properties. From the FTIR spectroscopic studies, the antisymmetric Fe–H stretching modes were observed at around 1560 cm$^{-1}$. Based on a relationship between the frequencies of the anti-symmetric modes and Fe–H bond distances in [FeH$_6$]$^{2-}$, the Fe–H bond distances was estimated to be 1.6 Å, which was consistent with the previously predicted value by first-principles calculations.

Acknowledgements

The authors would like to thank Ms. H. Ohmiya and Ms. N. Wariwine for technical supports, and the use of SR16000 supercomputing resources at the Center for Computational Materials Science of the Institute for Materials Research, Tohoku University. This research was supported by the JSPS KAKENHI Grant Numbers 16K06766, 16H06119, and 25220911 from MEXT, Japan and Collaborative Research Center on Energy Materials in IMR (E-IMR), Tohoku University. The synchrotron radiation experiments were performed at BL14B1 of SPring-8 with the approval of Japan Atomic Energy Agency (JAEA) (Proposal Nos. 2013B3602 and 2013B3614).

References