Infrared Spectroscopic and Computational Studies on Li_4FeH_6 with High Gravimetric Hydrogen Density

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We report the vibrational properties of Li_4FeH_6 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 Li_4FeH_6 , 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. [doi:10.2320/matertrans.M2016345]

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1. Introduction

Iron(Fe)-based complex hydrides, which contain Fe-hydrido complex anion $[\text{FeH}_6]^{4-}$, have been the subject of extensive investigation because of practical interest as potential hydrogen storage materials.^{1–8)} In the complex hydrides, $[\text{FeH}_6]^{4-}$ is generally counterbalanced by alkaline-earth metals (e.g. Mg_2FeH_6) or mixed alkali/transition metals (e.g. LiYFeH_6),^{3,9)} and the gravimetric hydrogen densities reach 5.5 mass% when Mg is adopted as a counteranion. Very recently, we have successfully synthesized a novel complex hydride, Li_4FeH_6 , 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 $[\text{FeH}_6]^{4-}$ 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 Li_4FeH_6 was theoretically elucidated to have a trigonal K_4CdCl_6 -type with $a = 7.97$ Å and $c = 9.76$ Å in the space group $R\bar{3}c$ (No. 167) and $Z = 6$ (Fig. 1), which is the same structure type as that of the isomorphous Li_4RuH_6 and Li_4OsH_6 .⁹⁾ In the complex hydride, Fe is octahedrally coordinated by six hydrogen atoms with Fe–H bond length of 1.61 Å.⁶⁾ The $[\text{FeH}_6]^{4-}$ 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 $M'_2\text{TH}_6$ (M' = divalent metal cation), in spite of having different crystal structures (note that $M'_2\text{TH}_6$ adopts a face-centered cubic K_2PtCl_6 -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.

Fig. 1 (left) Crystal structure and (right) local atomic arrangements around $[\text{FeH}_6]^{4-}$ complex anion of Li_4FeH_6 . Li, Fe, and H atoms are displayed as black, white, and small black circles, respectively.

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 $[\text{RuH}_6]^{4-}$.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 Li_4FeH_6 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

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source $\text{AlH}_3^{12,13}$) 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_4FeH_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 X'PERT PRO diffractometer) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$ for $\text{K}\alpha_1$ and $1.5444 \text{ \AA}$ for $\text{K}\alpha_2$).

The vibrational spectra of Li_4FeH_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_4FeH_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^{17,18)} within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof,¹⁹⁾ as implemented in the Vienna Ab-Initio Simulation Package (VASP).^{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 method²²⁾ with an $8 \times 8 \times 8$ 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 $6\text{LiH} + \text{Fe}$ with a simulated X-ray diffraction pattern of Li_4FeH_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 $a = 7.989(6) \text{ \AA}$ and $c = 9.651(9) \text{ \AA}$ using indexing programs.^{23,24)} This is in good agreement with previously reported unit cell parameters of Li_4FeH_6 .^{6,7)} Thus, Li_4FeH_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_4FeH_6 in our experiments. Saitoh *et al.*, reported that high temperature at around 900°C was necessary to obtain a high purity Li_4FeH_6

Fig. 2 X-ray diffraction patterns of (top) simulated Li_4FeH_6 , (middle) hydrogenated and (bottom) ball-milled $6\text{LiH} + \text{Fe}$ samples.

Fig. 3 Observed FTIR spectrum for Li_4FeH_6 . The calculated IR active zone-center phonon frequencies are shown by tick marks.

in order to accelerate the reaction kinetics.⁷⁾ Hydrogen pressure higher than 6 GPa pressure was required to avoid subsequent decomposition of Li_4FeH_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_4FeH_6 .

3.2 Vibrational properties

Figure 3 shows the FTIR spectrum of Li_4FeH_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 summarized in Table 1. Since the primitive unit cell of Li_4FeH_6 consists of 22 atoms, there are

Table 1 Zone-center optical phonon frequencies calculated for the 22 atom primitive cell of Li₄FeH₆. Infrared and Raman activities are shown in parentheses: IR = infrared active; R = Raman active.

Symmetry	Mode	Frequency (cm ⁻¹)					
A _{1g} (R)	FeH ₆ librational/ Li translational	156	510				
A _{2g}		238	416	474	533		
A _{1u}		223	308				
A _{2u} (IR)		232	370	533			
E _g	H–Fe–H bending	170	236	381	415	580	588
E _u (IR)		186	216	245	347	421	
A _{1g} (R)		944					
A _{2g}		924					
A _{1u}	Fe–H stretching	744	891				
A _{2u} (IR)		714	870				
E _g (R)		887	914				
E _u (IR)		765	777	846	855		
A _{1g} (R)	Fe–H stretching	1700					
A _{2g}		1681					
A _{1u}		1535					
A _{2u} (IR)		1474					
E _g (R)		1688	1709				
E _u (IR)		1480	1535				

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 FeH₆ 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 600–1000 cm⁻¹ and the intense peak at 1400–1800 cm⁻¹ in the experimental FTIR spectrum can be understood to originate, respectively, from the H–Fe–H bending modes, and the anti-symmetric Fe–H stretching modes.

The observed FTIR frequencies related to the Fe–H stretching modes of Li₄FeH₆ are very close to those reported for Ca₂FeH₆.²⁵⁾ 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,¹¹⁾ the Fe–H bond length in Li₄FeH₆ should be comparable to that in Ca₂FeH₆, and is estimated to be 1.6 Å. This is in good agreement with that predicted by first-principles calculations⁶⁾.

4. Conclusion

We successfully synthesized Li₄FeH₆ 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 [FeH₆]⁴⁻, the Fe–H bond distances was estimated to be 1.6 Å, which was consistent with the previously predicted value by first-principles

calculations.

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