Disproportionation reaction of LaH$_2$ at high pressure and low temperature

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Abstract. Structural change of LaH$_2$ has been investigated at high pressure and low temperature by synchrotron radiation X-ray diffraction. LaH$_2$ has an fcc metal lattice with interstitial hydrogen atoms located at tetrahedral sites. The fcc-LaH$_2$ decomposes into two phases, which have different hydrogen compositions such as hydrogen-poor LaH and hydrogen-rich LaH$_{2-\delta}$ phases, at 11 GPa at room temperature. In spite of largely suppressed diffusivity of the interstitial hydrogen atoms at low temperature, we have found the disproportionation reaction around 14 GPa at 200 K. Difference in the molar volume between each phases suggests monohydride LaH is formed as the disproportionation product even at low temperature. The volume fraction of the hydrogen-poor phase relative to the hydrogen-rich one at 200 K rapidly rises against pressure and reaches to ~0.45 at ~17 GPa.

1. Introduction

Rare-earth metals have a very high affinity for hydrogen and form various hydrogen-concentration states [1,2]. It is well known that the two stoichiometric hydrogen concentration states are realized, such as the dihydride RH$_2$ and trihydride RH$_3$ [1-7]. Ideally, RH$_2$ has a face-centered-cubic (fcc) metal lattice in which the tetrahedral (T) sites are filled with hydrogen atoms while the octahedral (O) sites remain empty. The hydrogenation reaction into RH$_2$ causes a large volume expansion. For example, molar volume of LaH$_2$ [3-7] is about 20% larger than that of lanthanum metal. Further absorbed hydrogen atoms come to occupy the O-sites, and RH$_3$ is formed eventually. RH$_3$ exhibits the fcc or hexagonal metal lattice [1,2]. The rare-earth metals with large ionic radius, such as lanthanum, cerium, and praseodymium, form the fcc-RH$_3$. When the fcc-RH$_3$ is formed, the molar volume of fcc-RH$_3$ is reduced by ~3% with excess hydrogen atoms in the O-sites [3-5]. This volume reduction is considered due to covalent-like bonding states between the O-site hydrogen and metal atoms.

Previous synchrotron radiation (SR) X-ray diffraction (XRD) measurements have revealed that fcc-LaH$_2$ decomposed into two different fcc phases at pressures above 11 GPa at room temperature [8]. The observed decomposition suggests that hydrogen-poor and hydrogen-rich phases are spontaneously formed by pressurization [8,9]. Recent neutron diffraction experiment of LaD$_2$ under high pressure confirmed that the deuterium-poor phase corresponds to the monodeuteride LaD [10] which never exists at ambient condition. The observed behaviour has been interpreted in terms of
disproportionation reaction. This reaction accompanies the transfer of hydrogen atoms from the T-sites to O-sites in the fcc metal lattice. The diffusivity of the hydrogen atoms should be largely suppressed at low temperature [11]. It is expected that the low temperature affects the disproportionation reaction, which is accompanied with the transfer of the hydrogen atoms between interstitial sites. We hence have investigated the pressure-induced disproportionation of fcc-LaH$_2$ at low temperature by SR-XRD measurements.

2. Experimental

2.1. Dihydride sample for high pressure experiments

Commercially available coarse powder with a nominal composition of LaH$_2$ was used. We picked out a small particle with a size of about 30 μm × 20 μm × 10 μm from the LaH$_2$ powder and loaded into the diamond anvil cell (DAC). The culet size of the diamond anvil is 450 μm. The powder sample and DAC were handled in a glove box charged with inert argon gas to prevent oxidation of the sample. To observe even the small structural changes we should pressurize a sample under quasi-hydrostatic condition. Hence we chose the helium fluids as the pressure medium because quasi-hydrostaticity is guaranteed over a wide pressure range [12].

2.2. X-ray diffraction measurements at high pressure and low temperature

SR-XRD patterns were measured using a diffractometer for DAC [13] installed in BL22XU at SPring-8. Monochromatized 30 keV X-rays (λ ~ 0.413 Å) were impinged into the sample and the XRD patterns were recorded on a large sized imaging plate. For low temperature measurements, the DAC was installed on the closed cycle helium refrigerator. In this study, we measured the XRD patterns on compression and decompression processes at 200 K. At first, the sample was pressurized up to ~4 GPa and successively cooling down to 200 K. XRD patterns measured up to ~19 GPa on compression and down to ~4 GPa on decompression at 200 K. The pressure of the sample was measured before and after each SR-XRD measurement using the ruby fluorescence method.

3. Results and discussion

3.1. Structural change of LaH$_2$ at high pressure and low temperatures

The XRD pattern at ambient pressure at room temperature indicates that the measured particle is a single phase without detectable impurities. The XRD profile is well indexed with an fcc lattice. The molar volume calculated from the XRD data at ambient condition is 27.3 cm$^3$/mol. This value is slightly larger than that of 27.1 cm$^3$/mol in previous experiment [8]. The difference in volume indicates that each sample particles exhibit different hydrogen concentrations in same LaH$_2$ sample powder. Molar volume of ideal fcc-RH$_2$ is larger than that of fcc-RH$_{2+δ}$ with excess hydrogen atoms in the O-sites. This implies that the small particle measured in the present experiment would have less excess O-site hydrogen atoms than previous measured one.

On compression at room temperature, the no structural transition is observed up to ~4 GPa. After cooling down to 200 K at 4 GPa, the metal lattice remains the fcc structure. Figure 1 shows the typical XRD patterns of LaH$_2$ sample recorded on the imaging plate at 200 K under high pressure. No structural change is observed below 13.5 GPa, while the cubic-tetragonal transition was observed around 5 GPa at room temperature by pressurization [8]. After holding a pressure for 1.75 hours at 13.5 GPa, additional Bragg reflections are appeared just outside of the original ones, indicating formation of a small fcc lattice. The intensities of the Bragg reflections of the small fcc phase increase and become almost constant around 17 GPa. At room temperature, similar structural change was observed above 11 GPa, and has been interpreted in terms of the disproportionation reaction into hydrogen-poor LaH and hydrogen-rich LaH$_{2+δ}$ phases [8]. We calculate the molar volume from the SR-XRD data. Molar volumes of small and original fcc phases at 14.9 GPa are 18.1 and 22.8 cm$^3$/mol, respectively, and difference between them is 4.7 cm$^3$/mol. This is comparable to that at room
temperature at 15.0 GPa of 4.6 cm$^3$/mol from the molar volumes of 18.2 and 22.8 cm$^3$/mol for LaH and LaH$_{2+\delta}$ phases obtained by previous experiment. Therefore we conclude that the observed structural change at low temperature is also the disproportionation reaction and the small fcc phase at 200 K corresponds to the LaH phase.

3.2. Pressure-induced disproportionation reaction at low temperature

Here, we estimate the volume fraction of each phase and hydrogen concentration from the SR-XRD data. The fraction is calculated from the reflection intensity ratio of 111 reflection of LaH and LaH$_{2+\delta}$ phases. We plot in figure 2(a) of the calculated fraction of the secondary LaH phase at 200 K as a function of pressure. The fraction of the LaH phase rapidly increases around 14 GPa and reaches to approximately 0.45 at ~17 GPa by pressurization. This trend is similar to previous experiment at room temperature. Some differences are found in the pressure variation of the volume fraction between the room temperature and 200 K. Remarkable one is sluggish change on decompression process.

The pressure variation of the hydrogen concentration of LaH$_{2+\delta}$ phase can be estimated using the pressure variation of volume fraction. We consider that the hydrogen concentration of the LaH phase is not change while the volume fraction of LaH increases in the progress of the disproportionation reaction. Figure 2(b) plots the estimated hydrogen concentration against the pressure. The hydrogen concentration of the LaH$_{2+\delta}$ phase increases from 2 at ~13.5 GPa and almost saturated around 3 at 17 GPa, indicating the formation of the fully occupied LaH$_3$ at high pressure as the disproportionation product.

The disproportionation reaction at low temperature seems to show the small time-dependence discussed below, while no detectable time-dependence is shown at room temperature. Hence the fraction and hydrogen concentration of LaH$_{2+\delta}$ phase should come to close in the equilibrium values at

Figure 1. Parts of X-ray diffraction patterns of LaH$_2$ recorded on the imaging plate. Diffraction patterns are measured at several pressures on compression at 200 K. Arrows indicate the Bragg reflections from the small-fcc (LaH) phase.

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Figure 1. Parts of X-ray diffraction patterns of LaH$_2$ recorded on the imaging plate. Diffraction patterns are measured at several pressures on compression at 200 K. Arrows indicate the Bragg reflections from the small-fcc (LaH) phase.
corresponding pressure after holding for infinite time. At 200 K, the secondary LaH phase is not observed just after reaching 13.5 GPa (see figure 1). After a hold for 1.75 hours the LaH phase appears and fraction of the LaH phase is estimated to be 0.07. However the pressure slightly increases into 13.8 GPa during this 1.75 hours. The increment of the fraction against pressure and time is 0.002 GPa/min. The fraction of the LaH increases from 0.12 at 14.1 GPa to 0.31 at 15.4 GPa by pressurization. The interval between these two measurements is about 30 min then the increment of the fraction is estimate to be 0.007 GPa/min. Furthermore, the increment of the fraction is 0.003 GPa/min when the pressure is held at ~15.4 GPa for about 70 min. The time-dependence would be caused by the temperature effect. It is difficult to distinguish between the pressure and temperature effects from this experiment. However, the variations of the fraction as well as hydrogen concentration suggest that the disproportionation reaction is sensitive to the pressure rather than the temperature.

3.3. Lattice distortion on disproportionation reaction at low temperature

We observe the change of the shape of the Bragg reflections after decomposition. When the secondary LaH phase is formed, the Bragg reflections of the hydrogen-rich LaH$_{2+\delta}$ phase are slightly broadened (see figure 1, 13.8 GPa). In particular, the Bragg reflections of LaH$_{2+\delta}$ phase show the significant broadening above ~15 GPa. Such large broadening of Bragg reflections was not observed in the measurements at room temperature. Generally, the intensity distribution of the Bragg reflection along the azimuth angle is related to the crystalline or grain sizes. Figure 3 shows the intensity distribution in the 111 reflections of LaH$_{2+\delta}$ phase along azimuth angle on compression and decompression processes. Before decomposition into LaH and LaH$_{2+\delta}$ phases, some sharp peaks are found in the Bragg spots. After decomposition, these sharp peak structures disappear and intensity distribution becomes smooth. Bragg spots recorded on the imaging plate also show the significant broadening. However the peak structures appear again on decompression and Bragg spots are almost recovered at 0.2 GPa at room temperature. Hence, the observed broadening would not be due to the grain collapses induced by the lattice mismatch with the formation of the LaH. In other words, the pulverization can not occur despite of the large volume change. Probably it is due to the lattice distortions or defects which are induced by formation of the LaH phase. At room temperature, there is no significant change in the intensity distribution across the decomposition. Low temperature and high pressure condition may prevent

![Figure 2](image-url)
relaxation of the original fcc lattice after formation of the secondary LaH phase. This large stress should cause the sluggish change on decompression process.

Figure 3. (left) X-ray diffraction pattern of LaH$_2$ sample at 13.8 GPa recorded on the imaging plate. (right) Intensity distribution in the 111 reflections of LaH$_{2+8}$ phase along azimuth angle.

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