High pressure synthesis of novel Li-TM hydrides (TM = Nb, Ta)

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Abstract

High-pressure synthesis has been widely used for exploration of novel materials. In this study, new Li-based hydrides in Li-Nb and Li-Ta systems have been successfully synthesized under GPa-order by using a cubic-anvil-type apparatus. And crystal structures, thermal stabilities of novel hydrides were investigated.

For Li-Nb-H system, novel hydride with primitive hexagonal structure was synthesized at 973 K under 5 GPa. Its lattice parameter was $a = 0.56250(5)$ nm, $c = 0.57416(4)$ nm. A structural model of the hydride was CaCu$_5$-type structure ($P6/mmm$, No. 191). For Li-Ta system, novel hydride with C-face centered monoclinic structure was obtained at 973 K under 5 GPa. Its lattice parameter was $a = 0.7918(5)$ nm, $b = 0.8012(4)$ nm, $c = 1.030(7)$ nm, $\beta = 111.27(6)$. These novel hydrides in Li-Nb and Li-Ta systems were decomposed at 510 K and 573 K, respectively, and these values were about 400 K lower than that of LiH (>953 K).

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1. Introduction

Li and Li-based hydrides are good candidates for hydrogen storage materials because of high gravimetric hydrogen density. For example, complex hydrides, such as LiAlH$_4$ and LiBH$_4$, have high hydrogen content.

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However, since the Li-based hydrogen storage materials usually have relatively high working temperatures (more than 573 K for LiBH₄) and lower kinetic with hydrogen, further improvement in performance is required for hydrogen storage media applications. One of approaches to solve these problems is thermodynamically destabilization using combined system. For example, LiBH₄ combined with MgH₂ was thermodynamic destabilized, and the dehydrogenation temperature was lower than that of LiBH₄ [1]. Another approach is exploring novel hydride with high hydrogen content. High-pressure synthesis is used to explore new compounds. Up to now, more than 20 hydrides in Mg-X systems (X = TM or RE ; TM = transition metal, RE = rare earth), such as Mg₂LiH₄ [2], Mg₂TiH₄ [3], Mg₃MnH₆ [4], Mg₃REH₉ (RE = La, Ce, Pr) [5] and so on, were reported. The author group has also reported novel hydrides, such as a Mg₆.₇TaH₁₄ and the Mg-Ta hydride having FCC structures, by using high pressure synthesis [6].

As is well known, alkaline metals such as Li posses high compressibility of atomic radii [7]. This means that atomic ratio between lithium and components would change under the pressure of GPa-order. As a result, novel compounds might be synthesized. Moreover, melting point of lithium hydride is theoretically estimated to increase about 200 K under 5 GPa [8]. This allows solid-state reaction at higher temperature under the pressure of GPa order than that of ambient pressure.

In this study, novel Li-TM (TM = Nb, Ta) hydrides were investigated. In Li-TM system, no hydride has been reported. Exploration of new Li-TM hydrides by using high-pressure method has never been conducted up to now. It seems to be possible to obtain new Li-TM hydrides by high-pressure method due to the merits as mentioned above. Nb and Ta form hydrides and stabilities of their hydrides are lower than that of lithium hydride. Therefore, novel Li-TM hydrides are expected to have lower stabilities than that of lithium hydride.

The purpose of this study is to explore new hydride of the Li-TM (TM= Nb, Ta) systems by using the anvil-type apparatus and to investigate the crystal structure, thermal stability and hydrogen content of the newly found hydrides.

2. Experimental procedures

LiH (95 wt%, the major impurity was metallic Li), NbH (hydrogenated metal Nb of 99.9 wt% purity) and TaH (hydrogenate metal Nb of 99.9 wt% purity) powders were used as precursor materials. Powder mixtures with a nominal composition were pressed into pellets and placed into boron nitride (BN) or copper (Cu) containers. On the other hand, a NaCl container was used for synthesis using a hydrogen source. High pressure hydrogen was generated by thermal decomposition of an internal hydrogen source (NaBH₄ + Ca (OH)₂). The NaCl container was expected to work as a gas-sealer and electrical insulator. Samples were heated with or without hydrogen source at 973 – 1073 K for 2 - 8 h under high pressure in the order of gigapascals and then quenched. Phase identification was carried out by powder X-ray diffraction (XRD) using Cu-Kα radiation. Then, lattice parameters were refined by CELL program [9]. Thermal stability was investigated using a differential scanning calorimeter (DSC) under Ar-gas flow.

3. Results

3.1. Li-Nb system

Figure 1 shows XRD patterns of LiH-ₓ mol%NbH (ₓ = 12.5 - 50) prepared at 1073 K for 2 h under 5 GPa. An unidentified phase and precursor NbH phase appeared in all samples. Relative intensity of the unidentified phase increased with increasing the amount of LiH in starting mixtures. It was found that
novel hydride was synthesized, because the unidentified phase was obtained in Li-Nb-H ternary system, and not in binary systems.

Figure 2 shows XRD patterns of LiH-20 mol%NbH synthesized with hydrogen source at 973 K for 2 or 8 h under 5 GPa. For the sample prepared for 8 h, relative intensity of the novel hydride phase is stronger than that of the sample prepared for 2 h. But it is difficult to identify the Li-rich phase by XRD since lithium has low X-ray scattering factor. Therefore chemical composition of the hydride was not determined in this study.

Crystal structure of the novel hydride obtained in Li-Nb system was investigated. By using the indexing program TREOR [10], a primitive hexagonal structure was suggested from the line positions of the new compound and its lattice constant was refined to be $a = 0.56250(5)$ nm, $c = 0.57416(4)$ nm. Moreover, this novel hydride was found to be CaCu$_5$-type structure ($P6/mmm$, No. 191), where Nb is located on Ca site and Li on Cu site by using FOX [11]. Figure 3 shows XRD patterns of $x = 20$ and that of simulated primitive hexagonal structure ($P6/mmm$, No.191). The simulated pattern has good agreement with the observation. The metal atomic positions of novel Li-Nb hydride were shown on the inset table in Fig. 3. Figure 4 shows the crystal structure of the novel Li-Nb hydride.

Figure 5 shows a DSC curve of LiH-20 mol%NbH prepared at 973 K for 2 h under 5 GPa in order to investigate thermal stability of the novel hydride. Three endothermic peaks were observed at 405 K, 510 K and 581 K, respectively. Figure 6 shows XRD patterns of the samples before and after heat treatment up to 453 K, 573 K and 723 K. For the sample after heat treatment up to 453 K, relative intensities of appeared phases were almost the same as those of the sample after DSC. NbH is reported to transform from an orthorhombic structure to a cubic structure at about 400 K by J. M. Welter et al. [12]. Therefore, the endothermic peak observed at 405 K was due to phase transformation of residual NbH in the sample. Diffraction pattern of the novel hydride phase was disappeared after heat treatment up to 573 K, and NbH phase and Nb phase were observed. Thus, new hydride is found to decompose at 510 K with an endothermic reaction. A Li-rich phase couldn’t be identified from the sample after DSC up to 573 K due to the low atomic scattering factor of lithium. The endothermic peak observed at 581 K was attributed to the dehydrogenation of NbH.
3.2. Li-Ta system

Figure 7 shows XRD patterns of LiH-20 mol%TaH prepared with hydrogen source at 973 K for 2 or 8 h under 5 GPa. For each sample, an unidentified phase and a precursor TaH phase was observed. Relative intensity of the unidentified phase of the sample synthesized for 8 h was stronger than that of the sample synthesized for 2 h. It was found that novel hydride was synthesized, because the unidentified phase was obtained in Li-Ta-H ternary system, not binary systems. However, chemical composition of the novel
hydride was not investigated any more in this study, since it is difficult to index Li-rich phase due to the low X-ray scattering factor of lithium. Further investigation is required to determine the chemical formula of the hydride.

Crystal structure of the novel hydride in Li-Ta-H system was investigated. All unidentified diffraction lines were regarded as belonging to one single phase. Using the indexing program program TREOR, a C-face centered monoclinic unit cell was suggested from the line positions of the new hydride and its lattice constants were refined to be \( a = 0.7918(5) \text{ nm}, \ b = 0.8012 \ (4) \text{ nm}, \ c = 1.030(7) \text{ nm}, \ \beta = 111.27(6) \)°. Miller index as C-faced centered monoclinic were shown in Figure 8 Two potentially applicable space groups, such as \( C1c1 \) (No. 9) and \( C12/c1 \) (No. 15) were suggested from the result of miller indexing. A structural model of the novel hydride was not determined in this study. Further investigation is required.

Figure 9 shows DSC curve of LiH-20 mol%TaH prepared with hydrogen source at 973 K for 8 h under 5 GPa and DSC curves of TaH, which is raw material, and appeared in the samples. An Endothermic peak was observed at 573 K. Figure 10 shows XRD patterns of the samples before and after DSC measurement. For the sample after DSC, diffraction peaks of novel hydride phase have disappeared and Ta phase was observed as a main phase and Ta2H phase was also detected. Consequently, novel Li-Ta hydride phase was found to decompose to Ta or Ta hydride phase and some Li-rich compounds at the 573 K with endothermic reaction. As is the case with Li-Nb system, decomposition temperature of the new hydride lowered about 400 K compared with that of LiH (> 953 K). Accordingly, Nb and Ta were found to be effective elements to destabilize LiH. Novel hydrides in Li-V system were not investigated in this study. But if novel Li-V hydrides exist with the same structures as those of the hydrides obtained in this study, they could have higher hydrogen contents and lower stabilities.

4. Conclusion

Novel hydrides in Li-Nb, Li-Ta systems were synthesized by using high-pressure up to 5 GPa. For the Li-Nb system, a novel hydride was synthesized under the pressure of 5 GPa at 973 K for 8 h, and
structurally characterized by X-ray powder diffractions as primitive hexagonal structure (space group $P6/mmm$, No. 191) with $a = 0.56250(5)$ nm, $c = 0.57416(4)$ nm. For the Li-Ta system, the novel hydride was obtained under 5 GPa at 973 K for 8 h. the hydride has a C-face centered monoclinic structure with $a = 0.7918(5)$ nm, $b = 0.8012(4)$ nm, $c = 1.030(7)$ nm, $\beta = 111.27(6)^{\circ}$. These novel hydrides obtained in Li-Nb and Li-Ta systems were thermally stable up to 510 K and 573 K, respectively.

Fig.9 DSC curves of LiH-20 mol%TaH prepared at 973 K for 2 and 8 h under 5 GPa with hydrogen source and precursor TaH measured under Ar flow.

Fig.10 XRD patterns of LiH-20 mol%TaH prepared at 973 K for 8 h under 5 GPa with the hydrogen source before and after DSC measurement.

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