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Experimental and computational studies on structural transitions in the LiBH$_4$−LiI pseudobinary system

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Structural transition properties of the LiBH$_4$+xLiI (x=0–1.00) pseudobinary system were examined by powder x-ray diffraction and differential scanning calorimetry combined with periodic density functional theory calculations. We experimentally and computationally confirmed the stabilization of the high-temperature [hexagonal, lithium super(fast-)ionic conduction] phase of LiBH$_4$ with x=0.33 and 1.00, and the results also imply the existence of intermediate phases with x=0.07–0.20. The studies are of importance for further development of LiBH$_4$ and the derived hydrides as solid-state electrolytes. © *2009 American Institute of Physics*.
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Lithium borohydride (LiBH$_4$) exhibits lithium super(fast-)ionic conductivity accompanied by a structural transition from low-temperature (LT, orthorhombic) to high-temperature (HT, hexagonal) phases by heating to approximately 390 K.[1] Since the structural transition is reversible, the HT phase with super(fast-)ionic conductivity transforms into the LT phase with lower conductivity by cooling to around 380 K. It would thus be highly desirable to stabilize the HT phase (or to prohibit the formation of the LT phase by cooling in) of LiBH$_4$ as a potential candidate of solid-state electrolytes at room temperature (RT).

It was recently suggested that the addition of lithium halides,[2–4] especially LiI,[3] stabilizes the HT phase of LiBH$_4$ below 380 K. For example, judging from the conductivity measurements, the hydride with a nominal composition of LiBH$_4$+0.33LiI showed no obvious structural transition from the HT to LT phases by cooling from 420 K down to RT.[3] Accordingly, the value of the conductivity at RT increases from the order of 10^{-8} S/cm for LiBH$_4$ to that of 10^{-5} S/cm for LiBH$_4$+0.33LiI. Systematic studies about the structural transition of LiBH$_4$ with and without LiI are highly required for further developments of LiBH$_4$ and the derived hydrides as solid-state electrolytes.

The purpose of the present study is, therefore, to experimentally and computationally examine the LiI-composition dependence of the structural and thermodynamical properties of the LiBH$_4$+xLiI (x=0–1.00) pseudobinary system.

The samples examined were synthesized from the powders of LiBH$_4$ and LiI (both from Aldrich Co. Ltd.). Approximately 500 mg of the powder mixture with nominal compositions of LiBH$_4$+xLiI (x=0, 0.07, 0.14, 0.20, 0.33, and 1.00) were mechanically milled for 5 h under Ar atmosphere. Then the samples were examined by powder x-ray diffraction (XRD, Cu Kα radiation, at RT) and differential scanning calorimetry (DSC, 5 K/min, under He atmosphere).

The samples were always handled in a glove box filled with purified Ar/He.

Periodic density functional theory (DFT) calculations were performed using the DACAPO planewave pseudopotential code[5] and the atomic simulation environment implementation[6] to investigate the relative ground state stabilities of the LT and HT phases in LiBH$_4$+xLiI. Ultrasoft pseudopotential are used to model the ionic cores and the exchange and correlation effects are described by the Perdew–Burke–Ernzerhof functional.[5] The Kohn–Sham wave functions are expanded in a plane wave basis with a cutoff energy of 350 eV, and the first Brillouin zone is sampled on a k-point grid with a spacing of approximately 0.05 Å^{-1} in all directions. Super cells containing 2–8 formula units (Li atoms) are used to describe the systems.

Figure 1 shows the powder XRD profiles of LiBH$_4$+xLiI. The diffraction peak intensities of the LT phase of LiBH$_4$ (x=0) drastically decrease with x=0.07. Only the peaks corresponding to the HT phase can be detected with x=0.33 and 1.00. The tendencies are consistent with the results on the conductivity[3] and the addition of LiI stabilizes the HT phase of LiBH$_4$ at RT. The LiBH$_4$+xLiI pseudobinary system probably forms Li(BH$_4$–I) solid solutions, similar to Li(Br–I) in the LiBr+xLiI system.[8] The lattice constants of the HT phase[9] (x=0, 0.33, and 1.00) summarized in Table I are found to increase with increasing x, as is well comparable with the previous estimation of the unit cell volumes.[3]

The thermodynamical properties of LiBH$_4$+xLiI were examined by DSC and the results of the second heating process are shown in Fig. 2. The endothermic peaks directly indicate the structural transition. (The single peak in each sample might prove its compositional homogeneity.) Both the peak temperatures (onset) and enthalpy changes (areas[11]) decrease by up to x=0.20, and the values are summarized in Table I. No endothermic peak was detected over x=0.33, indicating the HT phase is stabilized at RT. It should be

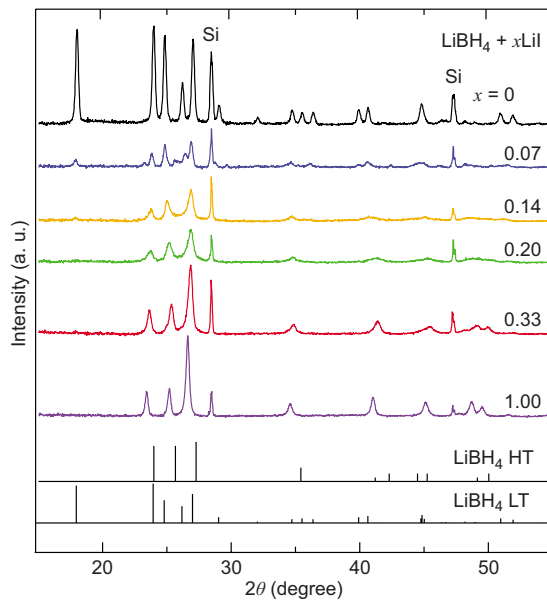$^{a)}$Electronic mail: orimo@imr.tohoku.ac.jp.

FIG. 1. (Color online) Powder XRD profiles of $LiBH_4 + xLiI$ ($x = 0 - 1.00$). The diffraction peaks are calibrated by Si internal standard. The standard diffraction peaks of the LT (orthorhombic) and HT (hexagonal) phases of $LiBH_4$ are shown for reference (Ref. 7).
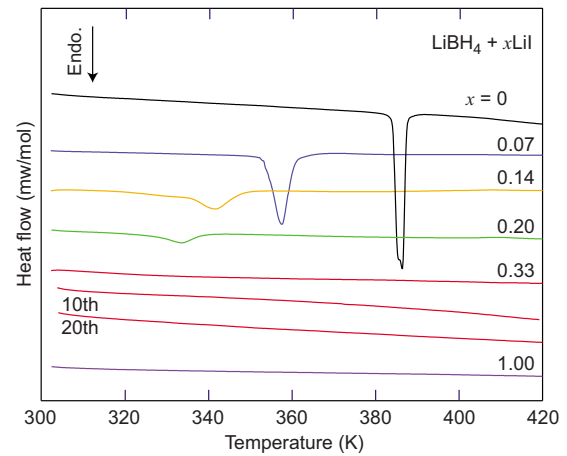

FIG. 2. (Color online) DSC profiles of $LiBH_4 + xLiI$. The intensities are normalized to show the heat flow per mole of the formula unit of $LiBH_4 + xLiI$. The area of the endothermic peak of each profile gives the experimental value of the enthalpy change ($\Delta H_{exp.}$), e.g., 4.18 kJ/mol with $x = 0$.

noted that no change was observed in the DSC profiles for $x = 0.33$ even after 10 and 20 heating/cooling cycles (heating up to 423 K and cooling down to RT), as shown in Fig. 2; the cyclic property is preferable for solid-state electrolytes.

The structural transition temperatures obtained from Fig. 2 and summarized in Table I were plotted as a function of x (top axis) and of "LiI mol%" (bottom axis), as shown in Fig. 3. We can confirm the stabilization feature of the HT phase in the $LiBH_4 + xLiI$ pseudobinary system. Near-linear decrease of the structural transition temperatures might be due to increased neighboring $[BH_4]^-$ distance[12] and to induced lattice anharmonicity[9,13,14] by I^- substitution [ionic radius of I^- (0.211 nm) $> [BH_4]^-$ (0.205 nm)].[15]

The enthalpy changes of the structural transition from the LT to HT phases were also determined by periodic DFT calculations and summarized in Table I. Tendencies of both the computational and experimental (from DSC) values show good agreement, that is, a monotonous decrease with increasing x. However, the decrease in the computational values up to $x = 0.33$ is not as pronounced as in the experiments.

So far, a number of the crystalline structures of $LiBH_4$ have been proposed and studied.[7,16–23] In the $LiBH_4 + xLiI$ pseudobinary system, possible intermediate (IM) phases are predicted to be stable at low x-values and a crystalline structure of the IM phase with $x = 0.14$ is shown in Fig. 4. The corresponding enthalpy change from the IM to HT phases, 2.3 kJ/mol, as in Table I, shows better agreement with the experiment. The powder XRD profiles were indexed (using indexing programs TREOR90[24] and PIRUM[25]) by orthorhombic unit cell for $x = 0$ and by hexagonal one for $x = 0.33$ and 1.00, but both unit cells lead to significant errors for $x = 0.07 - 0.20$.[26] The indexing results imply the existence of the IM phases, as was predicted by the DFT calculations. The details of the structural and thermodynamical properties of the IM phases are under investigation.

In summary, the powder XRD and DSC combined with the periodic DFT calculations revealed the structural and thermodynamical properties of the $LiBH_4 + xLiI$ ($x = 0 - 1.00$) pseudobinary system. The HT [hexagonal, lithium super(fast-)ionic conduction] phase of $LiBH_4$ can be stabilized with $x = 0.33$ and 1.00. Also, no significant change was observed in the DSC profiles for $x = 0.33$ even after 10 and 20 heating/cooling cycles. The experimental and computational results imply the existence of IM phases with $x = 0.07 - 0.20$.
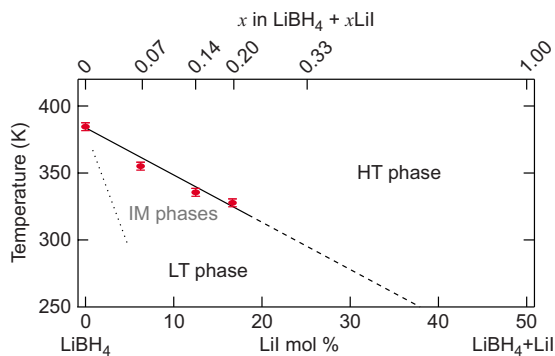
TABLE I. Lattice constants, a and c, of the HT [hexagonal, lithium super(fast-)ionic conduction] phase for $x = 0$, 0.33, and 1.00; structural transition temperature T_s; and experimental and computational values of enthalpy change, $\Delta H_{exp.}$ and $\Delta H_{theo.}$ (calculated for the transition from the LT to HT phases); for $LiBH_4 + xLiI$, value of $\Delta H_{theo.}$ in square bracket was calculated for the transition from the IM to HT phases using a possible IM phase of $LiBH_4 + 0.14LiI$ (shown in Fig. 4). Lattice constants for $x = 0.07$, 0.14, and 0.20 are left blank as none of them are indexed by orthorhombic and hexagonal unit cells. Lattice constants of (hexagonal-)LiI are also added for reference.

x in $LiBH_4 + xLiI$	a (Å)	c (Å)	T_s (K)	$\Delta H_{exp.}$ (kJ/mol)	$\Delta H_{theo.}$ (kJ/mol)
0	4.24 ± 0.02^a	6.87 ± 0.03^a	384 ± 3	4.18^b	7.7
0.07	⋯	⋯	354 ± 3	3.5 ± 0.3	⋯
0.14	⋯	⋯	334 ± 3	2.6 ± 0.1	6.3 [2.3]
0.20	⋯	⋯	326 ± 3	1.0 ± 0.3	⋯
0.33	4.354 ± 0.002	7.035 ± 0.005	⋯	⋯	6.2
1.00	4.389 ± 0.001	7.073 ± 0.003	⋯	⋯	0.0
LiI	4.514 ± 0.001^c	7.311 ± 0.002^c	⋯	⋯	⋯

[a]Reference 9.
[b]Reference 11.
[c]Reference 10.

FIG. 3. (Color online) Structural transition temperatures of LiBH$_4$+xLiI as a function of value x (top axis) and LiI mol% (bottom axis). The IM phases are predicted with $x=0.07-0.20$.
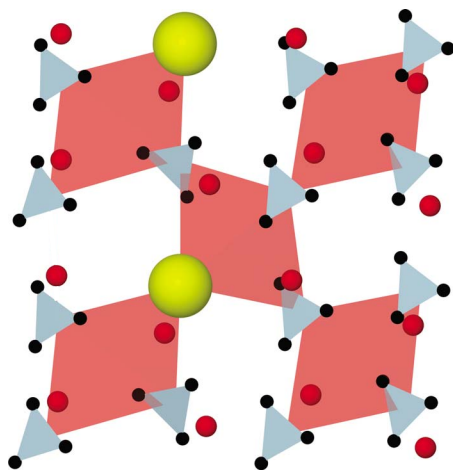
FIG. 4. (Color online) Crystalline structure of a possible IM phase of LiBH$_4$+0.14 LiI (in LiI space group $P4_2/mnm$). Red, yellow, and black circles correspond to Li, I, and H sites, respectively. B atoms are embedded in blue [BH$_4$]$^-$ tetrahedron.

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