



Fabrication of LiI-LiBH₄ solid solutions by cryomilling

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ABSTRACT

In this work, LiI-LiBH₄ systems were fabricated by ball-milling at room temperature and -60 °C. The formation of the solid solutions of LiI and LiBH₄ was confirmed for LiI-LiBH₄ and 2LiI-LiBH₄ whose crystal structure was wurtzite. Further increase of the LiI concentration resulted in the two phase mixture of wurtzite LiI-LiBH₄ and unreacted rock-salt LiI. On the other hand, the fraction of rock-salt LiI was significantly decreased when 3LiI-LiBH₄ was fabricated by ball-milling at -60 °C. 3LiI-LiBH₄ was confirmed to be a metastable phase; post annealing at 270 °C resulted in a segregation of rock-salt LiI. This report is the first example for the stabilized wurtzite LiI in a bulky form at room temperature.

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1. Introduction

It is well known that the crystal structures of most of the alkali halides are rock-salt type. For alkali borohydrides, rock-salt type structure is also stable at room temperature [1]. Alkali halides and borohydrides with the common cation form the rock-salt type solid solutions with wide compositional range [2]. Among the alkali borohydrides, only LiBH₄ is the exceptional. The crystal structure of LiBH₄ is orthorhombic at room temperature and above 115 °C its crystal structure changes to hexagonal [3]. High Li⁺ ion conduction appears at high temperature (HT) phase of LiBH₄ [4]. LiBH₄ also forms the solid solution with Li halides, however, the crystal structure is also different from those of other alkali borohydrides, which is wurtzite [5].

At the present stage, the maximum concentration of LiI in LiBH₄-LiI system is still under controversial. The solubility limit of LiBH₄-LiI system highly depends on the fabrication process. It has been reported that 25 mol% of LiI can be doped to LiBH₄ by sintering at 300 °C [5]. LiBH₄·LiI (50 mol% LiI) has been obtained by ball-milling at room temperature [6]. By the vapor deposition of LiI to the substrate at -250 °C, wurtzite LiI has been obtained, which is different from the crystal structure of LiI at room temperature (rock-salt type) [7]. LiBH₄-LiI systems with LiI concentration higher than 50 mol% can be considered as the stabilization of wurtzite LiI by doping BH₄⁻. However, LiI rich samples have not been obtained at room temperature in a bulky form and it can be speculated that the fabrication at lower temperature is favorable for

increasing the concentration of LiI. At low temperature, the reaction rate of the formation of solid solutions is generally less promoted because the mobility of ionic species are restricted. On the other hand, by using ball-milling, chemical reactions can proceed even under low temperature. For example, LiZn₂(BH₄)₅ has been fabricated by ball-milling of LiBH₄ and ZnCl₂ at liquid nitrogen temperature [8].

This work is the first report for the fabrication of LiBH₄-LiI solid solutions by cryomilling, which results in the stabilization of wurtzite LiI in a bulky form. The phase stability of the solid solution of LiI rich sample will be also investigated.

2. Materials and methods

LiBH₄ and LiI were purchased from Aldrich Co., Ltd. Mixed powder of LiI and LiBH₄ (ca. 0.6 ml) was sealed into an air-tight chrome steel pot (45 ml) with the 10 pieces of balls (10 mm in diameter) in Ar filled glove box. For cryomilling, milling pot was cooled at -60 °C for 1 h in cryovessel and subsequently ball-milling was performed for 5 min. After milling, milling pot was cooled at -60 °C for 1 h again. This cooling-milling cycle was repeated for 60 times, resulting in the total milling time of 5 h. Post annealing of the sample was conducted in Ar. Crystal structures of the samples were evaluated by XRD using MiniFlex (Rigaku Co.). Samples were sealed by Kapton[®] film during measurement. To investigate the local structure around Li⁺ in LiBH₄-LiI, ⁷Li MAS NMR was measured by ECA600 (JEOL Co). ZrO₂ tube with a diameter of 4 mm was sealed by greased spacers and rotated at 15 kHz.

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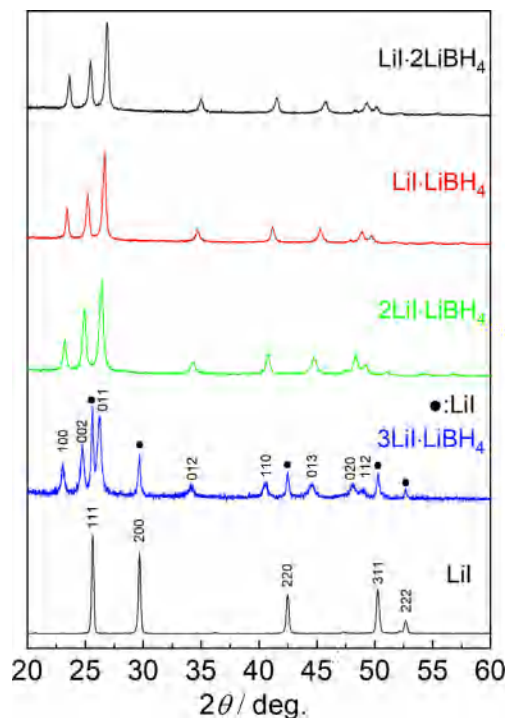


Fig. 1. (a): XRD patterns of $\text{LiBH}_4\text{-LiI}$ system fabricated by ball-milling at room temperature. The result for LiI (rock-salt structure) is also presented in the bottom.

3. Results and discussions

Fig. 1(a) shows XRD patterns of $\text{LiBH}_4\text{-LiI}$ systems ball-milled at room temperature. For the sample with LiI concentration below 67 mol%, the hexagonal phase of LiBH_4 is confirmed and other phases are not clearly observed. For $2\text{LiI}\cdot\text{LiBH}_4$ and $\text{LiI}\cdot\text{LiBH}_4$, these data are consistent with the already-known results, namely the stabilization of HT phase of LiBH_4 at room temperature by LiI dop-

ing [5]. However, the results for LiI-rich samples are rather different from the past reports. For example, Scripov et al., have been reported that $2\text{LiI}\cdot\text{LiBH}_4$ included a slight amount of rock-salt LiI while single phase of wurtzite was observed in this work [9]. This discrepancy would be due to the difference of the fabrication process; the sample was post-annealed at 280°C [9]. Hence, it can be interpreted that the high temperature sintering or post annealing of $\text{LiBH}_4\text{-LiI}$ systems would have a negative effect on the fabrication of the single phase especially for LiI-rich samples. This assumption is clearly supported by the results for further LiI-rich sample.

Rock-salt LiI are clearly observed for $3\text{LiI}\cdot\text{LiBH}_4$, which would be due to the excess of the solubility limit of LiI into hexagonal LiBH_4 (Fig. 1). Fig. 2 shows the XRD patterns for $3\text{LiI}\cdot\text{LiBH}_4$ fabricated by cryomilling at -60°C . Although slight peaks from rock-salt LiI were still detected, the relative intensity of wurtzite $\text{LiI}\cdot\text{LiBH}_4$ system was significantly increased. Lattice parameters for $\text{LiI}\cdot\text{LiBH}_4$ were plotted against LiI concentration in Fig. 2(b) and (c). Both a and c axis values are increased with increasing LiI concentration. These lattice expansions can be explained by the replacement of smaller BH_4^- with larger I^- in wurtzite matrix [5]. Fig. 3 shows NMR spectrum for $3\text{LiI}\cdot\text{LiBH}_4$ fabricated by cryomilling. The spectra for $2\text{LiI}\cdot\text{LiBH}_4$ and LiI are also presented as a comparison. One resonance peak was observed for $2\text{LiI}\cdot\text{LiBH}_4$, which was confirmed as a single phase of wurtzite LiI by XRD measurement. Therefore, this resonance peak would represent the 4-coordinated Li^+ in wurtzite LiI. The same peak is also observed for $3\text{LiI}\cdot\text{LiBH}_4$, which strongly indicates that wurtzite $\text{LiI}\cdot\text{LiBH}_4$ still exist as a main phase. On the other hand, a slight peak is detected approximately at -4.5 ppm. This side peak position is almost the same with that of rock-salt LiI. In conjunction with the result of XRD measurement, the resonance peak at -4.5 ppm can be attributed as a segregated rock-salt LiI.

The crystal structure of LiI was still kept a rock-salt structure after cryomilling (Fig. S1 in supplementary material). Furthermore, thin film of wurtzite LiI has been certainly obtained which was changed to rock-salt phase at 85°C [10]. On the other hand, wurtzite LiI cryomilled with LiBH_4 is stable up to 245°C (Fig. S2 of sup-

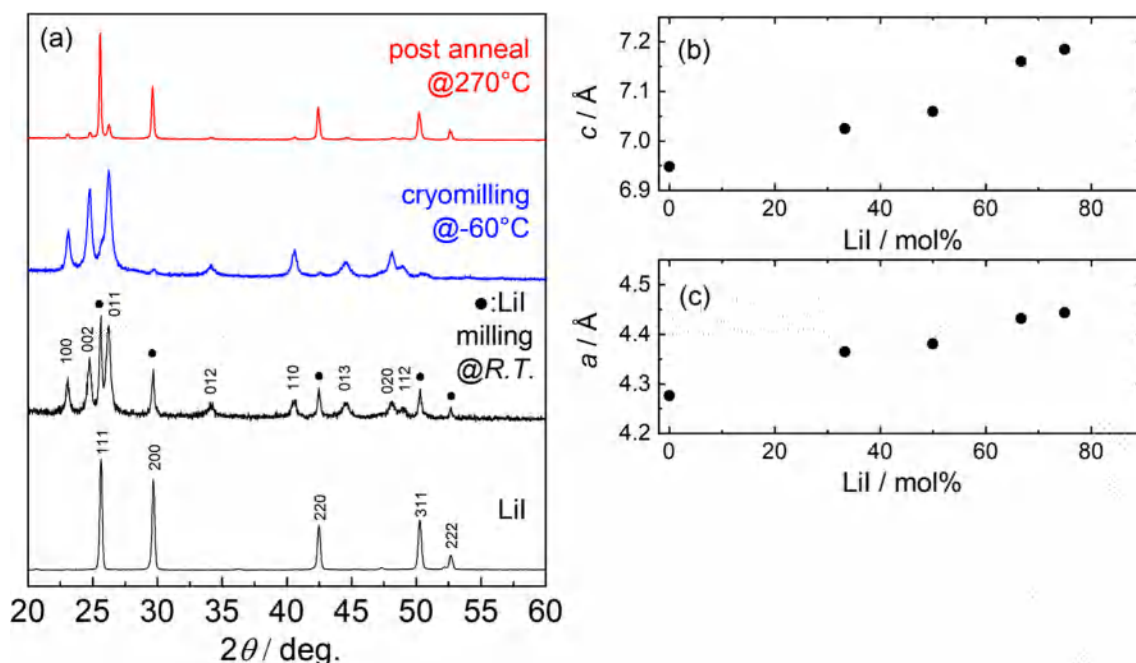


Fig. 2. (a): XRD patterns for $3\text{LiI}\cdot\text{LiBH}_4$ fabricated by ball-milling at room temperature (bottom) and by cryomilling at -60°C (middle). The result for the post annealed $3\text{LiI}\cdot\text{LiBH}_4$ is presented at the top of the figure. (b) and (c): Calculated lattice parameters of $\text{LiBH}_4\text{-LiI}$ with LiI concentration.

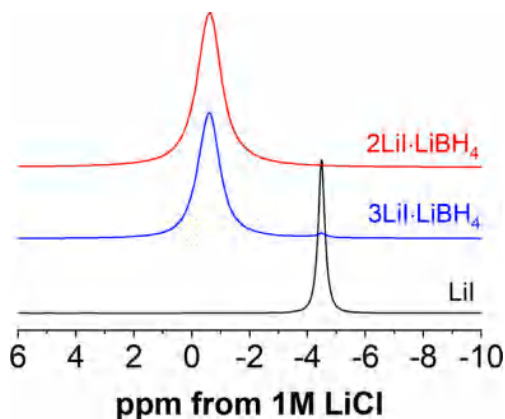


Fig. 3. ${}^7\text{Li}$ MAS NMR spectra for $2\text{LiI}\cdot\text{LiBH}_4$ (ball-milled at room temperature) and $3\text{LiI}\cdot\text{LiBH}_4$ (cryomilled at $-60\text{ }^\circ\text{C}$). As a comparison, the result of LiI (rock-salt) is presented in the bottom of the figure.

plementary material). The stability can be partially explained by the presence of BH_4 . The crystal structure of LiBH_4 has been reported to be hexagonal with 4-coordination [3]. Rock-salt structure is allowed only at high pressure [11]. Hence, perhaps the coexistence of Li^+ and BH_4^- in the rock-salt lattice (6 coordination) may not be energetically preferable at least under ambient pressure, which would be one of the explanation for the stabilization of wurtzite LiI by BH_4^- doping.

Cryomilling would be the key for the fabrication of $3\text{LiI}\cdot\text{LiBH}_4$. The mechanical energy can enhance the formation of LiI- LiBH_4 solid solution even at low temperature. $3\text{LiI}\cdot\text{LiBH}_4$ would not be obtained by sintering because the phase separation proceeds at high temperature as mentioned below. $3\text{LiI}\cdot\text{LiBH}_4$ was post-annealed at $270\text{ }^\circ\text{C}$ for 12 h. After post-annealing, XRD peaks for rock-salt LiI are significantly increased (Fig. 2). The lattice parameters of wurtzite LiI were decreased by post-annealing, which indicates that supersaturated LiI in $3\text{LiI}\cdot\text{LiBH}_4$ was segregated. Hence, it can be concluded that $3\text{LiI}\cdot\text{LiBH}_4$ obtained by cryomilling is a metastable. Although the temperature inside milling vessel was not monitored and controlled during milling, the effect of the cryomilling can be seen as the clear difference of the fraction of rock-salt LiI in $3\text{LiI}\cdot\text{LiBH}_4$. We emphasize that cryomilling is a powerful method for the fabrication of new phases which cannot be obtained by conventional ball-milling at room temperature.

4. Conclusions

In the present work, LiI- LiBH_4 system with LiI rich samples was fabricated by ball-milling. By ball-milling at room temperature, LiI- LiBH_4 and $2\text{LiI}\cdot\text{LiBH}_4$ can be obtained in a single phase of wurtzite structure. Further increase of LiI concentration resulted in a segregation of rock salt LiI. On the other hand, when $3\text{LiI}\cdot\text{LiBH}_4$ was fabricated by ball-milling at $-60\text{ }^\circ\text{C}$, the fraction of rock salt LiI was significantly decreased. Because LiI concentration is larger than LiBH_4 , obtained LiI- LiBH_4 systems can be considered as a stabilization of a wurtzite LiI by doping of LiBH_4 . Post annealing of cryomilled $3\text{LiI}\cdot\text{LiBH}_4$ resulted in a segregation of rock-salt LiI, indicating that cryomilled $3\text{LiI}\cdot\text{LiBH}_4$ is a metastable phase. Authors

believe that cryomilling is a powerful fabrication method for new phases.

CRediT authorship contribution statement

Reona Miyazaki: Conceptualization, Methodology, Writing - original draft, Visualization. **Takehiko Hihara:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.127775>.

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