Journal of Alloys and Compounds 404–406 (2005) 140–143

Journal of ALLOYS AND COMPOUNDS

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First-principles study on copper-substituted lithium borohydride, $(Li_{1-x}Cu_x)BH_4$

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Received 18 May 2004; received in revised form 31 August 2004; accepted 28 September 2004

Abstract

Our recent analysis using the first-principles calculations for $LiBH_4$ [K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, Phys. Rev. B 69 (2004) 245120], which is rather stable and desorbs hydrogen only at elevated temperatures, reveals that the charge compensation by Li^+ cations is a key feature for the stability of the internal bonding $[BH_4]^-$ anions. Considering this character, we have proposed the partial substitution of more electronegative elements for Li to lower the dehydriding temperature. The effect of the cation substitution is examined theoretically. We select copper as a substituent element, since the ionic radii of Cu^+ and Li^+ are almost the same but the electronegativity of Cu is larger than that of Li. Assuming the same crystal structure as orthorhombic $LiBH_4$, the calculations on $(Li_{1-x}Cu_x)BH_4$ are performed for $x = 0.25$, 0.5, 0.75, and 1. It is confirmed that the heat of formation increases with increasing the Cu content x. The optimum x is predicted to be around $x = 0.3$ for practical applications.

PACS: 71.20.Ps; 61.66.Fn; 77.22.-d; 63.20.Dj

Keywords: Hydrogen storage materials; Electronic states; Clusters

1. Introduction

Lithium borohydride, $LiBH_4$, is a potential hydrogen storage material [1] because of its extremely high hydrogen content of 18.5 mass%. The structure of $LiBH_4$ is orthorhombic at ambient conditions and the compound undergoes a phase transition to a hexagonal structure at high temperature (∼381 K) [2]. The dehydriding reaction is caused by the decomposition of $LiBH_4$ into LiH and B, where 13.5 mass% hydrogen is released. This material is, however, rather stable and desorbs hydrogen only at elevated temperatures, above the melting point of about 540 K. For practical applications, the destabilization of $LiBH_4$ to decrease the dehydriding temperature is an important research direction. To this end, the understanding of the basic material properties is of great interest. Recently, we have studied the fundamental properties including the structural, electronic, dielectric, and vibrational properties using the first-principle calculations [3]. From these analyses, it is expected that the charge compensation by Li^+ is a key feature for the stability of the internal bonding of $[BH_4]^-$ anions, and so the suppression of the charge transfer by the partial substitution of more electronegative elements for Li is effective to lower the dehydriding temperature.

In this study, the effect of the cation substitution has been examined for $LiBH_4$, theoretically. We select copper as a substituent element. The ionic radii of Li^+ and Cu^+ are 0.59 and 0.60 Å for four coordination and 0.76 and 0.77 Å for six coordination, respectively. Considering these

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0925-8388/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2004.09.090

similarities of the ionic radii, Cu is expected to be a good substituent element for Li. On the other hand, the Pauling's electronegativity of Cu is 1.9 which is larger than 1.0 of Li.

2. Method

The present calculations have been performed using the ultrasoft pseudopotential method [4] based on density functional theory [5]. The generalized gradient approximation [6] is used for the exchange-correlation energy. The computational details can be found in [3] and the references therein.

3. Results and discussion

The calculations on $(Li_{1-x}Cu_x)BH_4$ are performed for $x = 0.25$, 0.5, 0.75, and 1. Although a synthesis of $CuBH_4$ has been reported by Klingen [7], no structural information is available. Therefore, assuming the same crystal structure as orthorhombic $LiBH_4$ [8], Li atoms in the unit cell which contains four formula units are replaced by Cu atoms. For $x = 0.5$, two Li atoms to be replaced are chosen so as to make the Li–Cu interatomic distance shorter than the Li–Li and Cu–Cu distances. The lattice constants and atomic positions are fully relaxed.

The results of the structural optimization are summarized in Table 1. The experimental data of the lattice constants for $LiBH_4$ are $a = 7.179$ Å, $b = 4.437$ Å, and $c = 6.803$ Å [2]. The deviation of the calculated lattice constants from the experimental values is 2, −1, and −3%, respectively. The calculation predicts a nearly ideal tetrahedral shape for BH_4 complexes in $LiBH_4$, where the bond lengths are almost constant and the bond angles are close to the ideal value, $\theta_{\mathrm{H–B–H}} = 109.5^\circ$. This contradicts the experimental results [1,2] that BH_4 complexes are strongly distorted. Although more detailed investigation is required, we expect that the discrepancies may be caused by the experimental difficulties in identifying hydrogen positions due to their weak X-ray scattering power. For $(Li_{1-x}Cu_x)BH_4$, the shape of BH_4 complexes also retains a nearly ideal tetrahedral geometry. The changes in lattice constants from the theoretical values of $LiBH_4$ is typically ±2%; the largest one is −8% for a in $CuBH_4$.

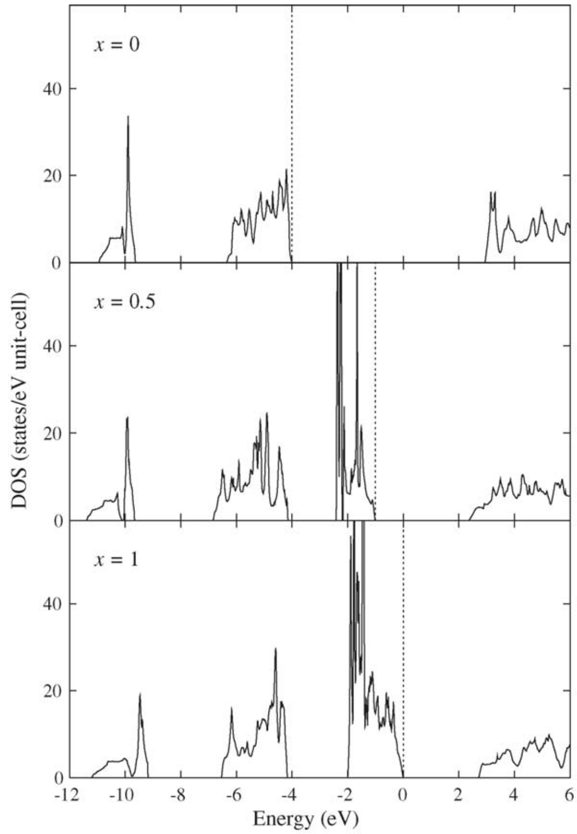

Fig. 1. Densities of states for $(Li_{1-x}Cu_x)BH_4$ ($x = 0$, 0.5, and 1). The vertical dashed lines indicate the top of valence states. For clear comparison, the origins of the energies are shifted by −4 and −1 eV for $x = 0$ and 0.5, respectively.

Fig. 1 shows the densities of state for $(Li_{1-x}Cu_x)BH_4$ ($x = 0$, 0.5, and 1). The electronic structures are non-metallic. The occupied states of $LiBH_4$ are composed of B-2s, B-2p, and H-1s orbitals [3]. A boron atom constructs sp^3 hybrids and forms covalent bonds with surrounding four H atoms. A deficient electron to form these bonds is compensated by a Li^+ cation. Similar characters are found for Cu-substituted $LiBH_4$ except for the existence of Cu-3d states, which appear in the middle of the energy gap of $LiBH_4$ and are located at the top of the valence states. The occupied states constructed from B-2s, B-2p, and H-1s orbitals are distributed over an energy interval of about 7 eV, which are almost the same as those of $LiBH_4$. The size of energy gaps decreases with increasing the Cu content x.

Table 1
The lattice constant, a, b, and c (Å), bond lengths $d_{\mathrm{B–H}}$ (Å), and bond angles $\theta_{\mathrm{H–B–H}}$ (°) for $(Li_{1-x}Cu_x)BH_4$

x	a	b	c	$d_{\mathrm{B–H}}$	$\theta_{\mathrm{H–B–H}}$
0	7.343	4.399	6.588	1.23–1.24	108–111
0.25	7.152	4.420	6.635	1.23–1.27	107–112
0.5	6.844	4.415	6.708	1.23–1.26	107–114
0.75	6.711	4.449	6.640	1.23–1.28	105–114
1	6.758	4.468	6.452	1.25–1.27	108–110

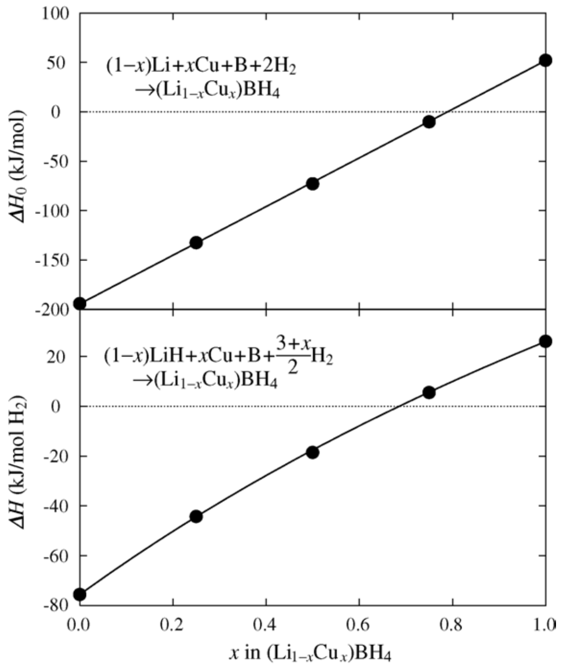

Fig. 2. Heat of formation of $(\mathrm{Li}_{1-x}\mathrm{Cu}_x)\mathrm{BH}_4$. The points represent the calculated values. The solid curve in the lower panel is obtained by assuming the linear relation between ΔH_0 and x.

The calculated heats of formation are shown in Fig. 2. The upper panel gives the heats of formation ΔH_0 when $(\mathrm{Li}_{1-x}\mathrm{Cu}_x)\mathrm{BH}_4$ is produced from the elements, Li, Cu, B, and H_2. As the Cu content x increases, ΔH_0 increases linearly and becomes positive at $x \simeq 0.8$. The heats of formation ΔH given in the lower panel is more closely related to hydriding/dehydriding reactions in which LiH is taken into account as a decomposed product. The variation of ΔH is also monotonous and the range is from -75 to 26 kJ/mol H_2. Considering $x = 0.3$, $\Delta H = -39$ kJ/mol H_2 ($\Delta H_0 = -121$ kJ/mol) and the effective hydrogen content is 8.6 mass%, which are encouraging for practical applications.

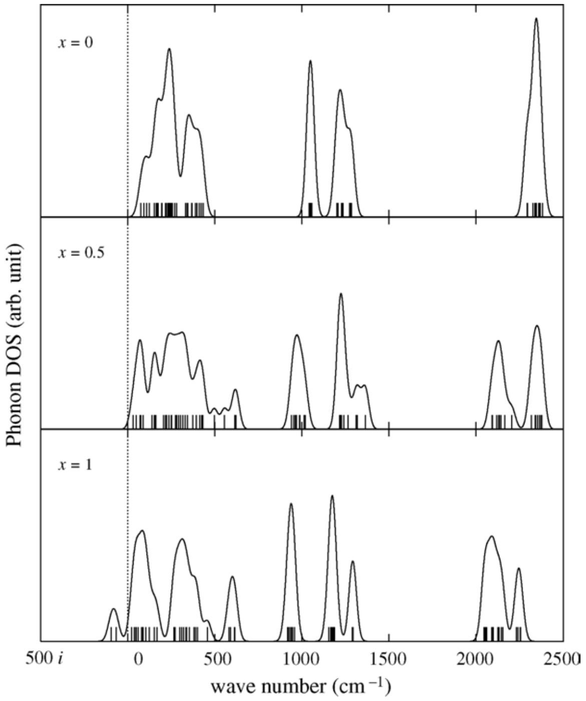

Fig. 3. Phonon densities of states for $(\mathrm{Li}_{1-x}\mathrm{Cu}_x)\mathrm{BH}_4$ ($x = 0$, 0.5, and 1). The contribution of the optical Γ-phonon modes is only taken into account. The straight lines indicate the calculated values and the solid curves denote the results of the Gaussian broadening with a width of 30 cm^{-1}.

The phonon frequencies for $x = 0$, 0.5, and 1 are given in Fig. 3. The eigenmodes located at the region higher than 2000 cm^{-1} correspond to the internal B–H stretching vibrations of BH_4 complexes [3]. The frequencies of these modes decrease with increasing the Cu content, indicating that the Cu substitution for Li destabilizes the internal bonding of BH_4 complexes. For $x = 1$, two weak soft modes of 97i and 65i cm^{-1} are found. The eigendisplacements of these soft modes correspond with nearly rigid rotations of BH_4 complexes. When the soft modes are frozen, ΔH is lowered by 5 kJ/mol H_2. The phonon calculation for $x = 0.5$ gives no soft modes, which suggests that the assumed orthorhombic structure is at least metastable for $x \leq 0.5$, not unstable. Note that the contributions of the zero-point energies are neglected for the results shown in Fig. 2, which raise ΔH by 19 and 18 kJ/mol H_2 for LiBH_4 and $(\mathrm{Li}_{0.5}\mathrm{Cu}_{0.5})\mathrm{BH}_4$, respectively. The amount of these contributions is insensitive to x, and so, ΔH–x curve for $x \leq 0.5$ most likely moves upward rigidly when the zero-point energies are taken into consideration.

4. Conclusions

From recent theoretical analyses for LiBH_4, we have proposed the partial substitution of more electronegative elements for Li to lower the dehydriding temperature. This idea is examined theoretically in the case of Cu as a substituent element. The optimum Cu content is predicted to be around $x = 0.3$. A similar idea has been successfully applied for LiNH_2 [9].

Acknowledgment

This study was partially supported by the New Energy and Industrial Technology Development Organization (NEDO), Basic Technology Development Project of Hydrogen Safety and Utilization (2003), #03003087-0.

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