

Research Paper

# Ionic Conductivities and Melting Transition Studies of $\text{NaBH}_4$ , $\text{KBH}_4$ , and Their Mixtures

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## ABSTRACT

As ionic conductivities are related to the intrinsic structural features of materials, they are useful for elucidating structural changes. Herein, the ionic conductivities of crystals of  $\text{NaBH}_4$ ,  $\text{KBH}_4$ , and their mixtures are determined for the first time. The melting and decomposition temperatures of various compositions are also measured. Thermal studies indicate that both the hydrides are well-mixed chemically, which is accomplished through a solid-state reaction using a simple ball milling process. The melting temperatures of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes show large negative departures from linearity likely due to the formation of a new structural phase such as rhombohedral  $\text{NaK}(\text{BH}_4)_2$ . However, the ionic conductivities of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes exhibit only small deviations from linearity with varying  $x$  values. The Na-rich samples of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  exhibit fast ion conduction behaviors and the ionic conductivity of  $3 \times 10^{-3} \text{ Scm}^{-1}$  is obtained at approximately  $50^\circ\text{C}$  below the melting point.

**Keywords:**  $\text{NaBH}_4$ ,  $\text{KBH}_4$ , Ionic conductivity, Melting transition, Decomposition

## I. Introduction

Metal borohydrides have high gravimetric and volumetric hydrogen capacities. The dehydrogenation and rehydrogenation characteristics of these hydrides have attracted significant interest, owing to their possible applicability in reversible hydrogen storage materials for on-board vehicular applications. Many studies on the hydrogen desorption properties of lithium borohydrides have been reported. However, the thermodynamics and kinetics of hydrogen exchange in lithium borohydrides are not favorable for reversible hydrogen storage [1,2].

Sodium and potassium borohydrides have not been extensively studied because of their high decomposition temperatures. The melting point of  $\text{NaBH}_4$  was reported as  $498$  or  $505^\circ\text{C}$  in the two different studies in the literature [3,4], and the decomposition in the molten state was reported to start at  $565$  or  $577^\circ\text{C}$ , respectively.  $\text{KBH}_4$  also exhibits an identical decomposition pathway, but the melting and decomposition temperatures are much higher, i.e., by approximately  $100^\circ\text{C}$ . The melting and decomposition temperatures in complex borohydrides are key parameters for the material design of potential hydrogen-storage materials. Therefore, recent studies on alkali metal borohydrides have focused on lowering or tuning the decomposition temperatures. Recently, the thermodynamic properties and phase diagrams of  $\text{NaBH}_4$ - $\text{KBH}_4$  and  $\text{LiBH}_4$ - $\text{NaBH}_4$ - $\text{KBH}_4$  systems have been reported [5,6].

In addition to hydrogen storage, a current challenge in the metal borohydride system involves the achievement of fast ion conduction before the occurrence of decomposition. Crystalline  $\text{LiBH}_4$  and related compounds are fast Li-ion conductors with promising applications such as electrolytes in all solid-state lithium batteries [7,8]. Ionic

conductivities are related to the intrinsic structural features and reflect the structural changes. However, the ionic conductivities of  $\text{NaBH}_4$  and  $\text{KBH}_4$  crystals have not been measured till date. The aim of the present work is to study the melting and decomposition characteristics as well as the ionic conductivities of a solid solution of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  with various compositions.

## II. Experimental

$\text{NaBH}_4$  and  $\text{KBH}_4$  with nominal purities of 99 and 97 %, respectively, were purchased from Sigma-Aldrich (St. Louis, Missouri, United States) and used directly without pretreatment. Powder mixtures with nominal compositions of  $(1-x)\text{NaBH}_4 + x\text{KBH}_4$  with  $x = 0, 0.25, 0.5, 0.75$ , and  $1$  were mechanically milled using Spex Sample Prep 8000 mixer/mills for 2 h under  $0.1 \text{ MPa}$  argon. The sample handling and loading were performed in an Ar-filled glove box.

For ionic conductivity measurements, compressed pellets (thickness of  $1.5 \text{ mm}$  and area of  $78 \text{ mm}^2$ ) were prepared with evaporated gold contacts. The electrical conductivity measurements were carried out in the temperature range of  $200$ – $600^\circ\text{C}$  with average intervals of  $0.5^\circ\text{C}$ . The impedances were determined using an HP model 4284A impedance analyzer (Hewlett-Packard, Palo Alto, California, United States) measuring a frequency range from  $100 \text{ Hz}$  to  $1 \text{ MHz}$ , which afforded the bulk conductivity measurements through a typical impedance analysis.

Thermal analysis was performed using differential scanning calorimetry (DSC; DSC-50, Shimadzu Corporation, Kyoto, Japan). The sample chamber was purged with purified nitrogen and measurements were carried out at a heating rate of  $5^\circ\text{min}^{-1}$  from  $30$  to  $700^\circ\text{C}$ .



### III. Results and discussion

$\text{NaBH}_4$  and  $\text{KBH}_4$  are tetragonal at low temperatures and transform into cubic phases at approximately  $-83$  and  $-203$  °C, respectively [9]. Recently, bialkali metal borohydrides,  $\text{LiK}(\text{BH}_4)_2$  and  $\text{NaK}(\text{BH}_4)_2$ , were synthesized and reported to exhibit new structural phases [10]. Unfortunately, these borohydrides were not found to be promising for hydrogen-storage applications as the former is very stable to allow hydrogen release and the crystal structure of the latter is metastable [6].

For  $\text{NaBH}_4$ , two DSC peaks are observed upon heating the sample. The first endothermic peak is due to melting and the second endothermic peak is due to the decomposition in the molten state. After melting,  $\text{NaBH}_4$  decomposes according to the following reaction.



This reaction is known to occur partially during melting and continue at high temperatures with hydrogen release at the decomposition temperature. Theoretically, a total of 10.4 wt(%) of  $\text{H}_2$  is released upon the completion of the decomposition reaction. The decomposition of  $\text{NaBH}_4$  can also be described by the reaction shown below [11], particularly for mixed compounds such as  $\text{NaBH}_4/\text{MgH}_2$  [12] and  $\text{NaBH}_4/\text{Al}$  [13], where  $\text{NaH}$  dissociates into  $\text{Na}$  and  $\text{H}_2$  at high temperatures.



To investigate the melting and decomposition characteristics of mixed  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes, the DSC data were collected (Fig. 1). The melting peak of  $\text{NaBH}_4$  is centered at  $502$  °C, which is in excellent agreement with the reported values [3,4]. The decomposition peak is observed at  $579$  °C, and is also in good agreement with the reported values of  $565$  or  $595$  °C [4,11]. The melting and decomposition behaviors of  $\text{KBH}_4$  are similar to those of  $\text{NaBH}_4$  except that these temperatures for  $\text{KBH}_4$  are much higher (by approximately  $100$  °C). The melting peak of  $\text{KBH}_4$  is centered at approximately  $610$  °C, which is consistent with reported values of  $607$  or  $625$  °C [3,4]. The decomposition peak of  $\text{KBH}_4$  is observed at  $664$  °C, which is slightly

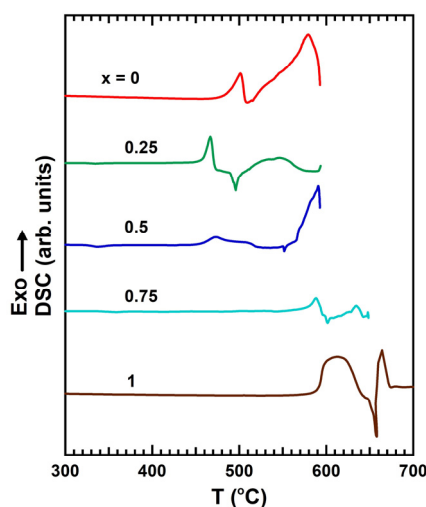


Figure 1. (Color online) DSC plots of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes.

lower than the reported value of  $686$  °C [4]. For all mixtures, identical melting and decomposition pathways are observed without the appearance of DSC peaks of pure  $\text{NaBH}_4$  and  $\text{KBH}_4$  crystals. This suggests that both hydrides are chemically well mixed via a solid-state reaction by simple ball milling. This is plausible because both  $\text{NaBH}_4$  and  $\text{KBH}_4$  have same cubic structures at high temperatures.  $\text{NaBH}_4$  has high structural stability under heavy deformation conditions imposed by milling [14].

As observed in the DSC data, the melting peaks are slightly broad and the melting starts from approximately  $10$  °C below the peak temperature. Therefore, to measure the starting point of this transition more precisely, the dielectric constants were measured for the pellet-type samples coated with gold electrodes. When the temperature increases, partial dehydrogenation first occurs on the surface of the pellet samples. Thus, the dielectric constants increase abruptly with electrode damage at the beginning of the melting transition as shown in Fig. 2. The melting transition of  $\text{NaBH}_4$  is sharper than that of  $\text{KBH}_4$ , as observed in both thermal and electrical data. This indicates that the hydrogen desorption kinetics of  $\text{NaBH}_4$  are faster than those of  $\text{KBH}_4$ . The peak temperatures observed in the DSC data are higher than those obtained from the dielectric constant measurements. However, the starting temperatures of DSC melting peaks are consistent with those observed in the dielectric constant analysis.

The melting temperatures of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes show large departures from linearity as shown in Fig. 3. This type of negative departure is well known in mixed alkali glasses and crystals in which the properties related to structural relaxations exhibit negative deviations with varying  $x$  concentrations [15,16]. However, the ionic conductivities of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes exhibit only small deviations from linearity with variation in  $x$ , which are discussed later. The bialkali borohydride with  $x = 0.5$  ( $\text{NaK}(\text{BH}_4)_2$ ), synthesized by mechanical milling, was reported to exhibit a new crystal structure with rhombohedral symmetry, most likely in the space group  $R\bar{3}$  [10]. Recently, another bialkali borohydride,  $\text{LiK}(\text{BH}_4)_2$ , was synthesized and was found to be highly stable up to  $380$  °C [17]. The new compound  $\text{LiK}(\text{BH}_4)_2$  has a structure that is closely related to that of the orthorhombic  $\text{LiBH}_4$ , and this new phase is present across the complete range of the reaction series of  $\text{LiBH}_4$  and  $\text{KBH}_4$ . Accordingly,  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  is not just assumed to be a simple mixture of cubic

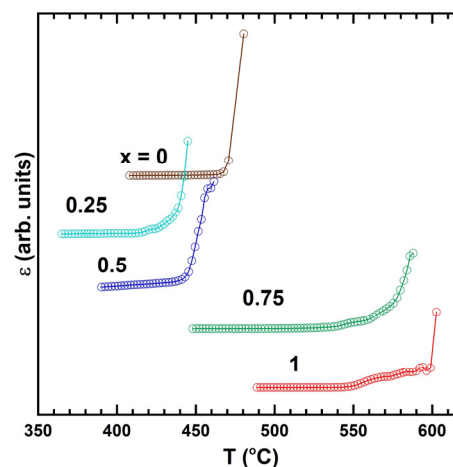


Figure 2. (Color online) Temperature dependences of the dielectric constants of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes.

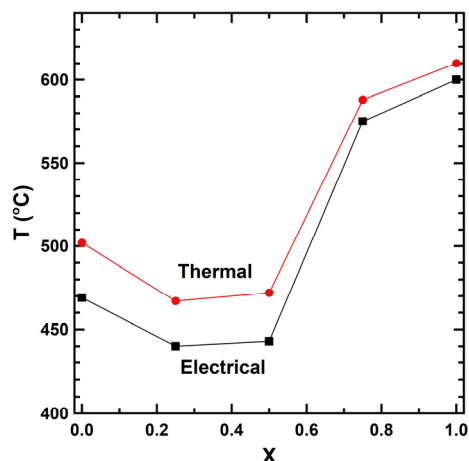


Figure 3. (Color online) Melting temperatures of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes.

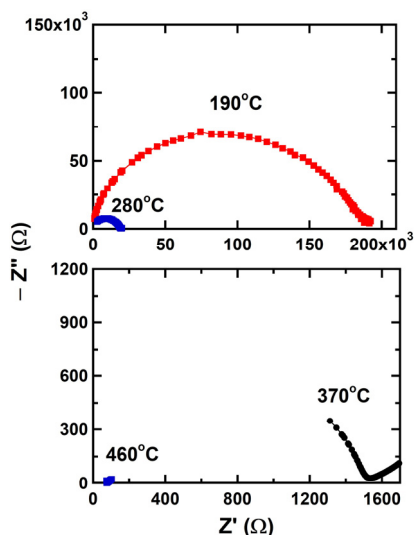


Figure 4. (Color online) Complex impedance plots of  $\text{NaBH}_4$ .

$\text{NaBH}_4$  and  $\text{KBH}_4$ , but also includes the new phase such as the rhombohedral  $\text{NaK}(\text{BH}_4)_2$ . The decreases in the melting temperatures of the complexes with  $x = 0.25$  and  $0.5$  are likely due to the formation of new crystalline phases.

The ionic conductivities of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  samples were measured in the cooling scan after the samples were annealed at temperatures of approximately  $50^\circ\text{C}$  below the melting points. Figure 4 shows the results of the frequency-dependent complex impedance measurements for  $\text{NaBH}_4$ . The complex plane spectrum consists of two parts, a high-frequency region owing to the electrical properties of the bulk and a low-frequency region characterized by a straight line because of the surface layer polarization. The high-frequency region can be approximated as a semicircle to determine the real part of the impedance  $Z'$ , which corresponds to the ionic conductivity of the material. As the temperature increases, the bulk semicircle shifts toward a low value of impedance and high frequency. Consequently, for the frequency range covered, the electrode impedance becomes more dominant with an increase in temperature.

Bulk conductivity values, extracted from the complex plane

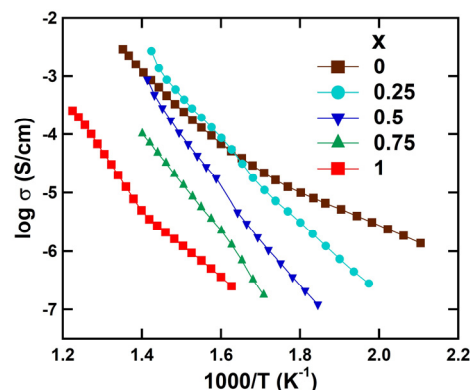


Figure 5. (Color online) Arrhenius plots of the ionic conductivities of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes.

plots, were analyzed using the Arrhenius equation:

$$\sigma = A \exp(-E/k_B T),$$

where  $A$  is the pre-exponential factor and  $E$  is the apparent activation energy for ion migration. The temperature dependences of the ionic conductivities of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  are shown in Fig. 5. In  $\text{LiBH}_4$ , the ionic conductivity of the high-temperature phase is due to the Li superionic conduction [18,19]. For both  $\text{NaBH}_4$  and  $\text{KBH}_4$ , the ionic conduction is also assumed to be caused by the cation motion. At high temperature, the highest ionic conductivity is obtained for  $x = 0.25$ . This type of increase in conductivity is also observed in mixed alkali-metal ionic conductors [20]. The Na-rich samples of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  exhibit fast ion conduction and the ionic conductivity values reach  $3 \times 10^{-3} \text{ Scm}^{-1}$  at approximately  $50^\circ\text{C}$  below the melting point.

For both  $\text{NaBH}_4$  and  $\text{KBH}_4$ , a curvature is observed in the conductivity plots, which increases with an increase in temperature, indicating the dominance of one transport mechanism at low temperature and another at high temperature. The upward bend can be caused by many different factors such as defect interactions, new defect mechanisms, or an intrinsic temperature dependence of the migration or formation parameters of the defects [21]. If the type of defect is assumed to be identical for all temperatures, the migration enthalpy is larger for the high-temperature transport mechanism than for the low-temperature transport. The temperatures at which the low-temperature regime changes to the high-temperature regime is approximately  $340^\circ\text{C}$  for  $\text{NaBH}_4$  and  $440^\circ\text{C}$  for  $\text{KBH}_4$ . The activation energies for  $\text{NaBH}_4$  are  $0.60 \text{ eV}$  in the low-temperature region and  $1.40 \text{ eV}$  in the high-temperature region. The activation energy in the low-temperature region is comparable to that of  $\text{LiBH}_4$  ( $0.53 \text{ eV}$ ), which is measured just above the structural transition temperature at  $117^\circ\text{C}$  [18]. However, the activation energies for  $\text{KBH}_4$ , i.e.,  $1.08 \text{ eV}$  in the low-temperature region and  $1.95 \text{ eV}$  in the high temperature region, are higher than those for  $\text{NaBH}_4$ .

For alkali borohydrides, when the low-temperature tetragonal phase transforms to a high-temperature cubic phase, the orientationally disordered  $\text{BH}_4$  groups are observed [9,22]. The upward bend in the ionic conductivities is attributed to the onset of the reorientational disorder of the tetrahedral groups at high temperatures [23,24]. The reorientation motions of the borohydride ions can serve as an additional degree of freedom to enhance the cationic mobility, affording an

increased conductivity at high temperatures. However, for the mixtures, no significant bend is observed in the Arrhenius plots and the activation energies are in the range of 1.40–1.80 eV, which belong to the high-temperature regime. This can be ascribed to the rotational disorder of the hydride ions at low temperature due to the highly disordered structure of the mixed system.

#### IV. Summary

For all  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  complexes, identical melting and decomposition paths are observed, indicating that both hydrides are chemically well-mixed through a solid-state reaction using a simple ball milling process. The decreases in the melting temperatures of complexes with  $x = 0.25$  and  $0.5$  are due to the formation of new crystalline phases. A curvature is observed in the conductivity plots, which increases with an increase in temperature. This indicates that one transport mechanism is dominant at low temperature and another is dominant at high temperature. For the mixtures, no noticeable bend in the Arrhenius plots is observed, indicating that these are present in the high-temperature regime. The Na-rich samples of  $\text{Na}_{1-x}\text{K}_x\text{BH}_4$  exhibit fast ion conduction and the ionic conductivities attain a value of  $3 \times 10^{-3} \text{ Scm}^{-1}$  at high temperatures. The anion mixing in complex hydrides may be a potential approach to achieve fast-ion conductivity, but we still need more studies how to lower the melting temperature and stabilize the fast-ion conducting structures in these compounds.

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