Anharmonicity in LiBH$_4$−LiI induced by anion exchange and temperature

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The feasibility of spatially resolved Raman spectroscopy probing diffusion multiples as a high-throughput method to study phase transformations in Li-ion conductors is demonstrated. The method is applied to the pseudobinary LiBH$_4$−LiI system, which shows high Li-ion conductivity in the HT-phase of LiBH$_4$. The vibrational properties measured as a function of composition and temperature corroborate the formation of a solid solution of Li(BH$_4$)$_{1-c}$I$_c$ over nearly the entire phase diagram ($0 < c \leq 0.8 \pm 0.2$). The results shed light on anharmonic effects responsible for the structural phase transformation in this system. © *2010 American Institute of Physics.*
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The development of advanced materials is usually conducted via the characterization and subsequent selection of materials, which are prepared in a slightly different manner than that used for a known material. The proper deviation from the original preparation method may be based on theoretical considerations (computational design of materials),[1] physical[2] or chemical[3] concepts, intuition, or simply luck. The second step of the materials development is the optimization of the materials within the predefined parameter space. Here, high-throughput experiments are of great importance because the number of required experiments grows exponentially with the number of parameters.[4–7] In this letter, we present a high-throughput method based on spatially resolved Raman spectroscopy on diffusion multiples. The method is applied to the LiBH$_4$−LiI system,[8,9] which shows high Li-ion conductivity. The search for and development of lithium-ion conductors is significantly important because of their possible application as solid electrolytes to improve safety and energy-density related issues of conventional lithium ion batteries. Recently, it was found that LiBH$_4$ exhibits a fast lithium-ion conduction (more than 1 $\times 10^{-3}$ S/cm above 390 K).[10] The ion conductivity of LiBH$_4$ falls by three orders of magnitude at approximately 390 K due to its structural transition from the high temperature (HT-) phase to the low temperature (LT-) phase. However, Matsuo *et al.*[11] and Maekawa *et al.*[8] demonstrated that the HT-phase of LiBH$_4$ is stabilized below 390 K by ballmilling with lithium halides, resulting in enhanced conductivity at room temperature. In this letter, we apply a high-throughput method on the LiBH$_4$−LiI system to investigate the vibrational properties within a wide concentration range. The particular strength of an optical detection method is the spatial resolution.[6,7] This allows one to map the whole phase diagram and to study phase transformation at constant temperature using a single sample.

A diffusion couple made from LiBH$_4$−LiI is locally probed by measuring spatially resolved Raman spectra along a line perpendicular to the interface (see Fig. 1). Raman scattering is based on the inelastic scattering of photons by phonons, i.e., quantized lattice vibrations. The corresponding selections rules make Raman spectroscopy very sensitive to the symmetry of the crystal structure. If the crystal structure does not change, the relative intensity change in the transitions may be attributed to the relative amount of different phases in a sample (see, e.g., Refs. 12–15). The frequency and width of the transitions bear information on coupling of the vibrating species to their environment.[16]

LiBH$_4$ and LiI were purchased from Sigma–Aldrich Fine Chemicals, (95%). The powder was pressed into pellets of 10
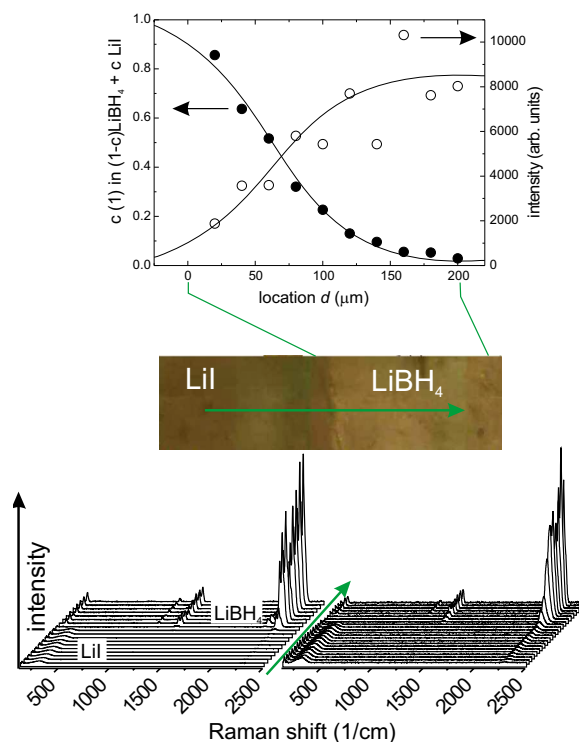

FIG. 1. (Color online) Middle panel: Micrograph of the LiBH$_4$/LiI interface in a composite pellet for diffusion experiments, which was probed by Raman spectroscopy. The corresponding spectra measured prior to (left) and after (right) annealing are shown in the bottom panels. The top graph shows the diffusion profile as obtained from the intensity of the BH$_4$ stretching vibrations and from an evaluation of the concentration c as calculated from peak positions.
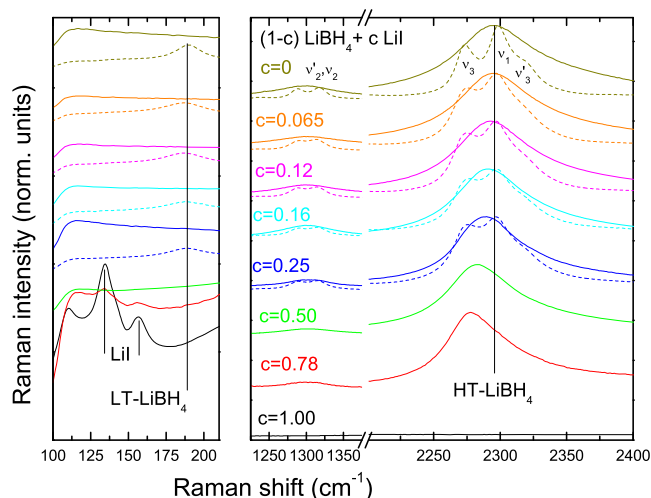
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FIG. 2. (Color online) Raman spectra of ball milled $(1-c)$LiBH$_4$+c LiI, where $c=0$, 0.065, 0.12, 0.16, 0.25, 0.5, and 0.78 measured in the LT- (dashed lines) and HT- (full lines) phases.

FIG. 3. (Color online) Normalized, spatially resolved Raman spectra of a $(1-c)$LiBH$_4$+c LiI diffusion multiple as a function of location d (corresponding to Fig. 1) and temperature. The curves are shifted by an increasing offset except in the left panel to highlight the disappearance of peaks at the phase boundary (red spectrum: $d=20$ μm corresponding to $c=0.8$). Blue dashed and green dashed-dotted lines are reference spectra of LiI and LiBH$_4$, respectively. The peak positions of the stretching vibrations are plotted in Fig. 4.

mm diameter, which were cut into halves. Two halves, one of each different pellet, were then pressed into one single pellet giving a relatively sharp interface (see Fig. 1). For annealing, the composite pellet was enclosed between a CF-35 window and blind flange in Ar gas. In addition, powder mixtures with nominal compositions of $(1-c)$LiBH$_4$+c LiI where $c=0$, 0.065, 0.12, 0.16, 0.25, 0.50, and 0.78 were mechanically milled for 5 h under Ar atmosphere. All sample handling took place in purified Ar atmosphere. X-ray spectra of the samples up to $c=0.5$ are published in Ref. 9, the spectrum of $c=0.78$ shows the coexistence of HT-LiBH$_4$ and LiI (Ref. 22). Spatially resolved Raman spectra were obtained with a Bruker Senterra instrument of 3 cm^{-1} spectral resolution (spatial resolution $\simeq 5$ μm) using a 532 nm laser and a home built heating stage.

The phase transition of LiBH$_4$ has been thoroughly studied,[17,18] in particular, by Raman spectroscopy.[19,20] The structural phase transition from the ordered orthorhombic (*Pnma*) LT-phase to the disordered hexagonal HT-phase (P6$_3$ cm) takes place around 380 K. The structural changes become apparent by three main changes in Raman spectra. The external modes change, in particular the strong peak around 195 cm^{-1} vanishes. The stretching modes broaden, and virtually merge into one. The splitting of the bending mode ν_2 is abolished. The changes of external modes are explained by the change in symmetry of the crystal structure including the deviation of the BH$_4$ tetrahedrons (internal modes: bending and stretching vibrations). For a transition from the *Pnma* structure to hexagonal P6$_3$*mc*, one would also expect the site group of BH$_4^-$ to evolve from C_s symmetry toward trigonal symmetry; indeed the site group splitting of several modes vanishes, and the splitting is zero.[19] Such a change is already observed for the bending mode ν_2 in LiBH$_4$ already below the phase transition temperature. The splitting is continuously reduced from ~ 47 cm^{-1} at 10 K to ~ 20 cm^{-1} at just below the phase transition temperature.

Instead of by increasing temperature, we are able to induce the phase transition by adding LiI. Figure 2 shows the Raman spectra of ball milled $(1-c)$LiBH$_4$+c LiI samples. The changes are very small, and since each sample is individually prepared and measured, the data shows appreciable scatter. Changes within the LT-phase are thus discussed later
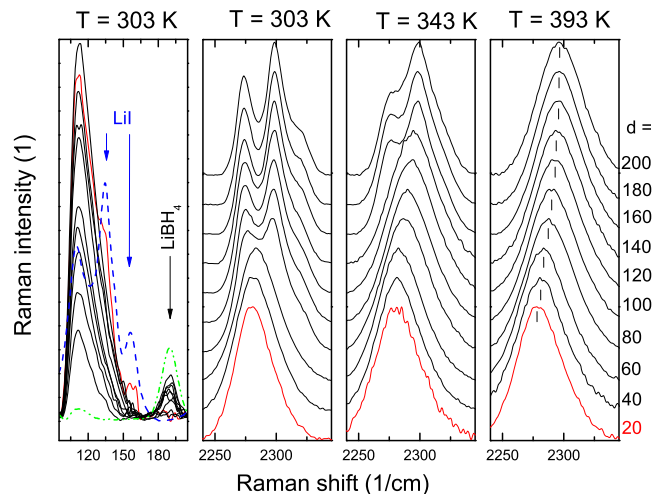
when using gradient samples. The spectra of the HT-phase of ball milled $(1-c)$LiBH$_4$+c LiI samples are essentially similar to that reported for HT-LiBH$_4$, but show a distinguishable effect. The maxima of the stretching vibrations shift continuously from 2297 cm^{-1} ($c=0$) to 2277 cm^{-1} ($c=0.8$). This is evidence for a change in the environment of the BH$_4^-$ tetrahedrons due to substitution of neighboring BH$_4^-$ ions by I$^-$ ions and a change in the lattice parameter.[9] The effect is clear enough to be used as a fingerprint for the determination of the iodide concentration in gradient samples.

Figure 1 shows spatially resolved Raman spectra of a LiBH$_4$−LiI diffusion multiple as a function of location d prior to and after annealing. Taking the intensity I of the BH$_4$ stretching vibrations as a rough estimate of the concentration, the interface broadens after annealing at 480 K for $\tau=119$ h. Alternatively, the concentration may also be determined by the spectral information from the Raman measurement (described later). Both data sets give a similar concentration distribution (broadening $\Delta d=70$ μm), after a fit to the function $c=1/2$ erfc$[(d-d_0)/\Delta d]$ using the concentration derived from the spectral information, respectively, $I \propto$ erfc$[-(d-d_0)/\Delta d]$ using the intensity information. This allows for an estimate of the diffusion parameter $D =\Delta d^2/(4\tau) \simeq 2 \times 10^{-15}$ m^2/s.[21] This value is similar to that for diffusion of BH$_4^-$ anions in LiBH$_4$ (Ref. 14) and thus indicates of an exchange of BH$_4^-$ and I$^-$ ions forming a solid solution of Li(BH$_4$)$_{1-c}$I$_c$.

To determine the concentration c in the gradient sample, we use the relation of the peak position to the stretching vibration in the HT-phase to the concentration as measured for individual ball-milled samples as a calibration. Selected temperature dependent spectra at various locations in the diffusion multiple are shown in Fig. 3. In agreement with the previous data set, only small changes upon LiI substitution are observed at room temperature, while the stretching mode of HT-LiBH$_4$ shifts by approximately 20 cm^{-1}. This shift is used to determine the amount c in diffusion samples by utilizing the correlation of frequency shift and concentration c
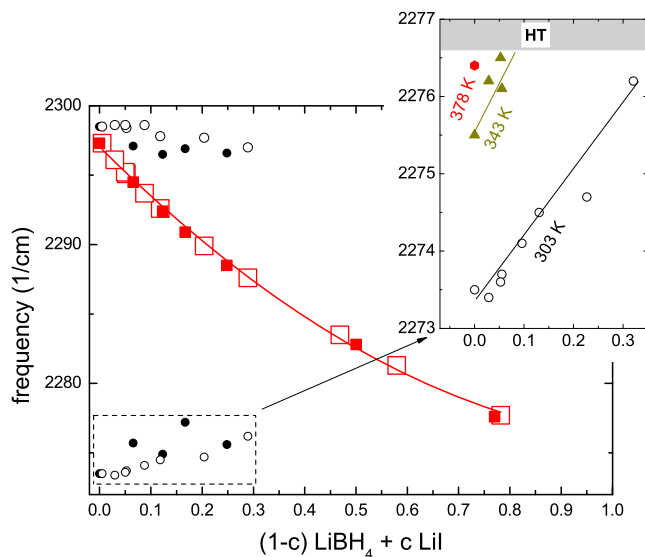
FIG. 4. (Color online) Raman frequencies of the main stretching vibrations in $(1-c)$LiBH$_4$+c LiI as a function of the iodide concentration, c, measured at room temperature (LT-phase) and above the phase transition temperature (HT-phase). Filled symbols refer to ball-milled samples and open symbols to the gradient sample. Circles correspond to measurements of the LT-phase ($\nu_3 \simeq 2275$ cm^{-1}, $\nu_1 \simeq 2298$ cm^{-1}), and squares to measurements of the HT-phase. The line is a parabolic fit through the data points of the ball-milled samples, from which the concentrations of the measurement points on the gradient sample are derived. The inset is an enlargement of the dashed rectangle showing the dependence of the Raman shift in the LT-phase on concentration and temperature.

of ball-milled samples (see Fig. 4). Furthermore, the maximum shift defines the solubility range of $0 < c < 0.8 \pm 0.2$ for the solid solution Li(BH$_4$)$_{1-c}$I$_c$. The concentration at the phase boundary is confirmed using the appearance of the Raman excitations attributed to LiI. They appear at $d < 20$ μm corresponding to $c \simeq 0.8$ (red spectrum in Fig. 3) and indicating a two phase region of LiI and Li(BH$_4$)$_{0.2}$I$_{0.8}$. X-ray diffraction on ball-milled samples up to $x=0.8$ (see Ref. 22) and in the paper of Oguchi *et al.*,[9] as well as the continuing shift in the lattice parameters provide a second confirmation.

Having determined the concentration, we have a well-defined data set yielding the vibrational properties of nearly the whole LiBH$_4$–LiI pseudobinary phase diagram, which is summarized in Fig. 4. As discussed above, the changes in the LT-phase upon iodide substitution are relatively small. In particular, no new peaks are found. The inset of Fig. 4 gives the peak positions of the ν_1 mode in the LT-phase, measured at room temperature, 343, and 383 K (just before the phase transition of pure LiBH$_4$). Interestingly, the dynamic properties change in the same way irrespective of whether induced by temperature or by substituting BH$_4^-$ by I$^-$. This is strong evidence that these changes are due to the peculiar dynamics of LT-LiBH$_4$, and a pretransition toward the HT-phase. Hagemann *et al.*[19] modeled the changes by two terms: a volume driven effect and an amplitude driven (anharmonic) effect. The substitution of BH$_4^-$ by I$^-$ has a significantly stronger impact on the volume change in the unit cell than changing temperature.[9,17] Therefore, the similarity of substitution and temperature effect corroborates the hypothesis that anharmonic effects are the driving force of the change in dynamics and the phase transition. The potential in which each atom

moves, and which is the origin of anharmonic effects, depends strongly on the next neighbors of the atom and is changed by the substitution of next BH$_4^-$ neighbors by I$^-$. Ordered structures (e.g., the LT-phase) are less sensitive to local perturbation because its effect is averaged over several units cells (as used in the virtual-crystal model by Nordheim[23]). In disordered structures (e.g., the HT-phase), the local next neighbor interaction is most important, explaining the striking difference of the impact of iodide substitution on the vibrational properties in the LT- and HT-phases, respectively.

In conclusion, we have demonstrated the use of diffusion multiples probed by spatially resolved Raman spectroscopy. We applied the method on the LiBH$_4$–LiI system to investigate its vibrational properties as a function of composition and temperature. The results substantiate the importance of anharmonic effects in the structural phase transformation in this system.

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