

Structural Transitions in Ternary Borohydrides: Possible Hydrogen Storage Candidates

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Introduction

There is an ongoing search for suitable hydrogen storage materials. In the quest for a suitable material, much more needs to be known about the way hydrogen interacts with other atoms in a variety of materials. To better guide both experimental and theoretical researchers in this quest, the variation of physical properties when changing pressure can be a very powerful tool. One class of possible hydrogen storage materials are the metal hydrides which absorb large amounts of hydrogen. Significant progress has been made in this field by studying adsorption characteristics of the binary and ternary hydrides. The ternary hydrides such as MXH_4 ($M = \text{Li, Na, X} = \text{Al, B}$) show a sequence of phase changes with large volume collapses under pressure [1]. We have successfully performed high pressure measurements on the Na-based compounds.

Methods and Materials

The hydride samples were obtained from Sigma Aldrich (97% purity). For in situ X-ray diffraction studies, the powdered sample was compressed in a Mao-Bell-type diamond anvil cell (DAC). A drilled hole in a stainless steel gasket was filled with the sample, ruby chips for pressure determination and silicone fluid as pressure transmitting fluid. All X-ray diffraction patterns were collected at the 16-IDB beamline at the High Pressure Collaborative Access Team, Sector 16 of the Advanced Photon Source of Argonne National Laboratory, using a monochromatic beam. Raman measurements were performed at UNLV using a Raman experiments with a resolution of 1 cm^{-1} were performed using an Ar-ion laser with an excitation wavelength of 514.5 nm operating at 100 mW.

Results

We have previously shown that NaBH_4 indeed undergoes a structural transition from cubic to orthorhombic through an intermediate tetragonal phase [2] which has been confirmed by recent high pressure neutron diffraction studies [3]. By replacing B with Al, one alters the bonding, and hence the hydrogen storage properties. The results of high pressure Raman studies on NaAlH_4 are shown in Fig. 1. As can be seen in Fig. 1, there are two pressure induced structural transitions in NaAlH_4 labeled HP I and HP II.

Discussion

At ambient pressure, NaBH_4 and NaAlH_4 crystallize in cubic and tetragonal structures respectively. As mentioned previously, NaBH_4 transforms to an orthorhombic ($Pnma$) state at around 9 GPa through an intermediate tetragonal ($P42_1c$) phase. The low pressure Raman data in Fig. 1 agree well with previous ambient pressure results [4]. Namely, the lower wavenumber (less than 600 cm^{-1}) peaks corresponding to various librational and torsional modes and the higher wavenumber peaks corresponding to various bending modes occur at the same

wavenumbers. Theoretically, it was predicted that NaAlH_4 should display a phase transition from tetragonal to orthorhombic at about 6-7 GPa [5]. This is in reasonable agreement with our experimental findings shown in Fig. 1. Unlike the calculations that find the orthorhombic (presumably the HP I labeled phase) should be stable up to 20 GPa, our Raman data is consistent with a further pressure induced phase transition (labeled HP II) above 10 GPa. Diffraction studies are planned to determine the structure of the HP II phase.

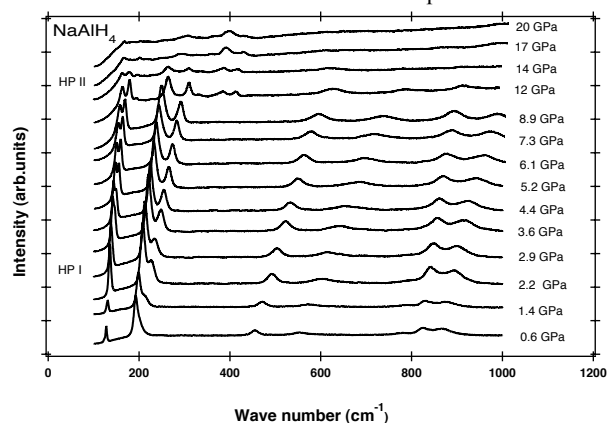


Fig. 1. High-pressure room temperature Raman data for NaAlH_4

In conclusion, we have found that the Na ternary hydrides undergo structural transitions at high pressure. These results give a power test to theoretical studies that intend to predict the bonding properties of ternary hydrides.

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