5602 *Inorg. Chem.* **2009**, *48*, 5602–5604
DOI: 10.1021/ic9005423

Inorganic Chemistry
Communication

Structural and Dynamic Properties of BaInGeH: A Rare Solid-State Indium Hydride

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Received March 20, 2009

BaInGeH was synthesized by hydrogenating the intermetallic compound BaInGe. The crystal structure determination from the powder neutron diffraction data of BaInGeD [$P3m1$, $Z = 1$, $a = 4.5354(3)$ Å, $c = 5.2795(6)$ Å] reveals the presence of hydrogen in tetrahedral voids defined by three Ba atoms and one In atom.

The chemistry of molecular complexes containing Al–H and Ga–H bonds has been well developed in recent years.[1] Lewis base adducts of alane (AlH_3) and gallane (GaH_3) have been utilized in both organic and inorganic synthesis, as well as in materials chemistry, as volatile precursors in chemical vapor deposition.[2–4] However, indane (InH_3) and its derivatives have traditionally been scarce. Kinetic effects and a weaker In–H bond compared to Al–H and Ga–H lead to the thermal instability of such compounds.[5–9] Similarly, Al and Ga form crystalline salt-like ternary hydrides with alkali and alkali-earth metals, which have been studied extensively over the past years because of their potential use as hydrogen storage materials. Again, this chemistry is not paralleled for In, where compounds $AInH_4$ (A = Li–Cs)[10] have been reported but are only stable as ethereal solutions, and until today extended solid-state structures containing terminal In–H bonds have not been structurally characterized. Here, we report a rare example of a solid-state compound containing In–H bonds, BaInGeH, and compare its structural and dynamic properties with those of BaAlGeH and BaGaGeH.

The recently described polyanionic hydrides AeAlSiH (Ae = Ca, Sr, Ba), SrGaGeH, BaGaSiH, BaGaGeH, and BaGaSnH contain separated terminal Al–H and Ga–H entities, respectively.[11–13] Such compounds are obtained from the hydrogenation of ternary intermetallic precursors representing derivatives of the AlB_2 structure. Provided that an In-containing precursor can be found, expectations are raised that polyanionic hydrides may afford the elusive In–H bond within a solid-state system and, at the same time, allow a comparison with Al–H and Ga–H bonds in similar, or even the same, metal atom environments.

BaInGeH is obtained by hydrogenation of BaInGe.[14] This intermetallic compound has previously not been reported and may represent the only stable In compound among the otherwise ubiquitous nine-electron AlB_2-type AeTrTt (Ae = Ca, Sr, Ba; Tr = Al, Ga, In; Tt = Si, Ge, Sn) systems.[15] Powder X-ray diffraction patterns of arc-melted samples show the basic reflections of the hexagonal AlB_2 type [$a = 4.572(1)$ Å; $c = 5.101(2)$ Å], while electron diffraction clearly

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(14) All steps of the synthesis and sample preparation for diffraction experiments were carried out under dry argon. Ba (99.9%, Aldrich), In (99.9%, Aldrich), and Ge (99.999%, Alfa Aesar) were used as received. The starting material BaInGe was prepared by arc-melting (low current arc) stoichiometric amounts of the pure elements. For hydrogenation, a cold-pressed pellet of BaInGe was loaded into a corundum crucible and placed into a stainless steel autoclave. The reaction was carried out at 300 °C for 3 days and a hydrogen pressure of 80 bar. BaInGeD was prepared analogously but at 275 °C. BaInGe, BaInGeH, and BaInGeD were characterized by powder X-ray diffraction (Siemens D5000, Bragg–Brentano geometry; Cu Kα radiation; Si standard). BaInGe has a metallic luster, while the hydride and deuteride are dullish gray. All compounds react slowly with air/moisture, yielding a black, amorphous material.
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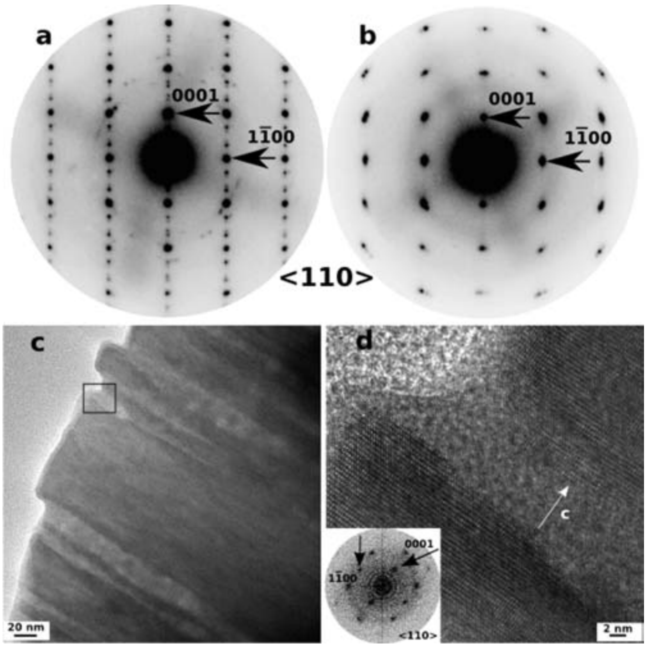

Figure 1. Selected area electron diffraction patterns of BaInGe (a) and BaInGeH (b) along the $\langle 110\rangle$ zone axis. BaInGeH shows the reciprocal lattice of the trigonal SrAlSiH structure type, while BaInGe crystals reveal satellite reflections with respect to the AlB$_2$-type basis structure corresponding to a wave vector $\mathbf{q} = [(1/3) - \delta][0001]^*$. (c) TEM image of a BaInGeH crystal oriented along $\langle 110\rangle$, showing alternating areas of crystalline and amorphous material. (d) High-resolution image of the region marked in part c. The interface between these two regions is perpendicular to the hexagonal axis of the SrAlSiH type, shown by the arrow.

reveals an incommensurate modulation along the c^* direction (Figure 1a). Modulations arising from slight corrugations of TrTt hexagon layers are well-known for systems AeTrTt.[16] The hydride retains the hexagonal unit cell of the precursor with only slightly changed lattice parameters [$a = 4.5354(3)$ Å; $c = 5.2795(6)$ Å], and electron diffraction does not indicate any superstructuring arising from the metal atom arrangement (Figure 1b). Despite the structural similarity between the intermetallic compound and the hydride, as is apparent from their similar diffraction patterns, the hydrogenation of BaInGe may actually be a complex process where H first degrades BaInGe to an amorphous material from which the hydride recrystallizes (Figure 1c,d).

At this stage, the results pointed to BaInGeH with the SrAlSiH structure, although with peculiarities not observed for Al and Ga representatives. The simple trigonal SrAlSiH structure (space group *P*3*m*1; Figure 2a), realized for AeAlSiH and AeGaTtH, displays slightly puckered hexagon layers in which Al (Ga) and Tt atoms are arranged strictly alternating. These layers are stacked on top of each other with the same orientation and sandwich Ae atoms. H is exclusively attached to Al or Ga and further coordinated by three Ae atoms (Figure 2b). Compounds with the SrAlSiH structure can be considered Zintl phases with a layered electron-precise polyanion built from three-bonded $[\text{Al}-\text{H}]^-$/$[\text{Ga}-\text{H}]^-$ and three-bonded, lone pair carrying Tt$^-$ entities. The charge of the polyanion is counterbalanced by Ae^{2+} cations. Accordingly, H is considered as a part of the polyanion and terminally bonded to the group 13 metal.[12,13]

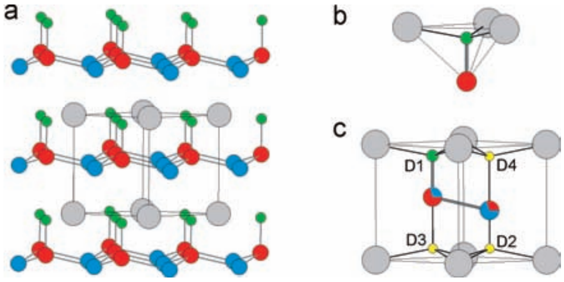

Figure 2. (a) Trigonal SrAlSiH structure type (M, gray; Tr, red; Tt, blue; H, green). (b) Tetrahedral environment H in the SrAlSiH structure. (c) Unit cell of BaInGeD showing the arrangement of metal atoms (note that In and Ge atoms are disordered on the corrugated hexagon layer) and possible locations for D atoms in tetrahedral voids (In/Ge)Ba$_3$ (main site D1, green; weakly occupied sites D2−D4, yellow).

The structure of BaInGeH was determined from the refinement of neutron powder diffraction data of a deuterated sample BaInGeD measured at 300 K.[17] The initial refinement of the SrAlSiH-type model yielded poor agreement between calculated and measured intensities, and a difference Fourier map indicated a residual nuclear density where a possible second D site would be (D2; Figure 2c). Refinement of a second model, with a second deuterium site and mixed occupied In/Ge sites gave a better fit ($\chi^2 = 2.416$ vs 2.571), with a D1/D2 ratio of 0.848(1)/0.152(1). In this model, occupancies were constrained so that the overall stoichiometry BaInGeD was maintained. Upon release of this constraint on D, the total amount of deuterium remained close to 1 (the occupancies of the D1 and D2 sites were refined to 0.77(3) and 0.23(1), respectively). This indicates that the empirical formula BaInGeD is accurate and the compound is electron-precise, consistent with AeAlSiH, SrGaGeH, and BaGaTtH. When the low-temperature data set was refined, a deuterium site ratio 0.95(3)/0.10(2) was obtained and, curiously, deuterium was no longer on the D2 site but changed to the D4 site. The presence of large-scale D disorder can also be seen in ^{2}H NMR (shown as Supporting Information), showing multiple D environments (at least three) that are clearly recognizable, although resonances are rather broad.

We now compare BaInGeD with BaAlGeD[18] and BaGaGeD,[13] which crystallize with a disorder-free SrAlSiH structure. Al−D and Ga−D distances are 1.73 and 1.71 Å, respectively. These values are considerably longer than terminal Al−H and Ga−H distances observed in molecular species TrH$_n$ or tetrahedral complexes TrH$_4^-$ occurring in salt-like alkali-metal compounds, which are in the range of 1.57−1.65 Å.[1,19,20] The In−D distance in BaInGeD is 1.76 Å, slightly longer than terminal In−H distances in molecular

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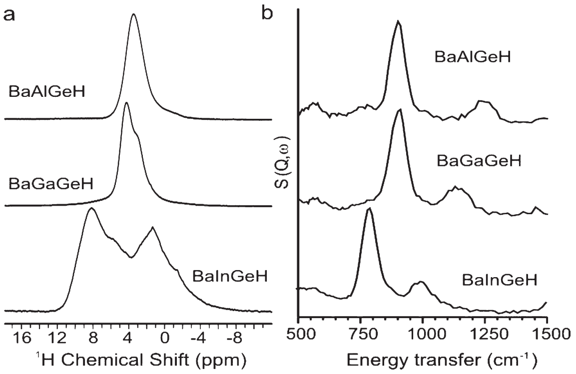

Figure 3. ^{1}H MAS NMR (a) and INS spectra (b) of BaInGeH, BaGaGeH, and BaAlGeH.

compounds (1.68−1.72 Å).[4,6−8] While the Ba−D distances in BaAlGeD and BaGaGeD are the same (ca. 2.59 Å), it is considerably larger in BaInGeD (2.65 Å). Interestingly, a computationally relaxed structure for BaInGeH based on the ideal, disorder-free SrAlSiH model yields a In−H distance of 1.97 Å, while the Ba−H distance corresponds closely to the value in the experimental structure.[21] The discrepancies between calculated and experimental In−H distances may be the result of the observed structural disorder.

The thermal stability of BaInGeH is lower than that of BaAlGeH and BaGaGeH. BaInGeH begins to lose hydrogen at around 250 °C, and decomposition is complete at 300 °C. According to powder X-ray diffraction, the product of desorption is BaInGe; however, diffraction peaks are very broad and indicate poor crystallinity. In contrast, desorption temperatures for both BaGaGeH are BaAlGeH are well above 400 °C.[13,18]

The magic angle spinning (MAS) ^{1}H NMR spectra for BaTrGeH are quite different from one another (Figure 3a).[22] The spectrum for BaAlGeH is characteristic of a single site, while that for BaGaGeH is characteristic of a single site with a shoulder. The spectrum for BaInGeH has a main, broad peak and a smaller peak upfield from the main peak, indicating multiple H sites. The main peak has a shoulder feature and resembles the profile of the peak in BaGaGeH but is much broader. The shoulder feature in BaGaGeH and BaInGeH is probably associated with amorphous inclusions in the samples (cf. Figure 1c,d). The shoulder feature is also observed in the ^{1}H NMR spectra of other AeGaTtH compounds and does not originate from disordered H atoms in the positions D2−D4.[13] The chemical shifts (of the main peak) travel downfield when moving down group 13: $\delta = 3.3$ ppm (BaAlGeH), $\delta = 4.2$ ppm (BaGaGeH), and $\delta = 8.1$ ppm (BaInGeH). The inelastic neutron scattering (INS) spectra of BaTrGeH (Figure 3b) are characterized by two narrow, high-intensity bands, which correspond to Tr−H bending and stretching modes at lower and higher energies, respectively.[23] The frequencies of the stretching modes decrease from around 1200 cm^{-1} for Al−H and Ga−H to around 1000 cm^{-1} for In−H. This mode is a direct measure of the Tr−H bond strength, which accordingly decreases from Al to In. Generally, bending mode frequencies are around 900 and 800 cm^{-1} for Al−H/Ga−H and In−H, respectively. This mode, where H displaces toward Ba atoms in the tetrahedral environment Ba$_3$Tr, reflects indirectly the strength of Ae−H interactions and shifts to higher frequencies for stronger Ae−H interactions. The trend in Tr−H bending frequencies is paralleled by Ba−H distances, which are larger for BaInGeH.

Although polyanionic hydrides afford the elusive In−H bond, the structural and spectroscopic investigation of the series BaTrGeH shows clearly that BaInGeH is distinguished from its lighter homologues. The inherently weak In−H bond well-known for molecular species casts also peculiarities for solid-state hydrides. In contrast to the Al and Ga compounds, BaInGeH is H-disordered and the difference between the Tr−H stretching and bending modes is small. This indicates the transition from a polyanionic hydride with covalent, directional Tr−H bonds to an interstitial hydride, where H occupies tetrahedral voids in a less preferred manner (cf. Figure 2c).

Acknowledgment. This research has been supported by National Science Foundation Grant DMR-0638826 and has made use of the ASU Magnetic Resonance Research Center and Manuel Lujan, Jr., Neutron Scattering Center at Los Alamos National Laboratory, which is funded by the Department of Energy's Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, under DOE Contract DE-AC52-06NA25396. G.P.H. acknowledges support from the DOE through Grant DE-FG02-05ER46235.

Supporting Information Available: Rietveld fit to the neutron powder diffraction pattern of BaInGeD, tables of atomic coordinates and selected interatomic distances, the ^{2}H NMR spectrum of BaInGeD, the computationally relaxed structural parameters and band structure of ordered BaInGeH, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Solid-state MAS ^{1}H NMR experiments were carried out at room temperature on a Varian VNMRS 400 MHz spectrometer equipped with a 2.5 mm triple resonance MAS probe operating at 399.7 MHz. Powders of BaAlGeH, BaGaGeH, and BaInGeH were filled in zirconia rotors in an argon-filled glovebox and spun at a frequency of 25 kHz. The ^{1}H NMR signal transients were recorded with a spin−echo pulse sequence where the $\pi/2$ and π pulses were 3 and 6 μs, respectively. The τ delay between pulses and the following second pulse was set to one rotor period and a recycle delay of 60 s was utilized. ^{1}H NMR chemical shifts were referenced indirectly by setting the ^{1}H NMR resonance of adamantane to 1.63 ppm.

(23) BaTrGeH samples for INS spectroscopy were loaded into sealed aluminum sample holders under a helium atmosphere. The spectra were measured at 10 K on the filter difference spectrometer instrument at the Lujan Center at Los Alamos National Laboratory. Data were treated by discrete, direct deconvolution of the instrument resolution function, which provides an energy resolution on the order of 4−5%.