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On the Structure of the Complex Hydride $BaReH_9$

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Our interest in materials for hydrogen storage applications has prompted us to investigate the structure of complex metal hydrides.[1] The ideal storage material would have a very high hydrogen density. Of the known complex metal hydrides, dipotassium nonahydridorhenate, K_2ReH_9[2] has a hydrogen density of 103 g of H/L, approximately 1.5 times that of liquid hydrogen. It also has a 3:1 hydrogen to metal atom ratio, one of the highest known. The $[ReH_9]^{2-}$ anion has tricapped trigonal prismatic symmetry (D_{3h}).[3] In the revised synthesis of this hydride,[4] the disodium salt is first synthesized and then converted to the dipotassium salt by way of the barium salt. This intermediate, $BaReH_9$, has no reported characterizations, however the hydrogen-to-metal ratio is 4.5:1, making it the metal hydride with the highest known hydrogen to metal ratio. With the higher hydrogen-to-metal ratio, the hydrogen density might also be expected to be increased. For this reason, we have undertaken an investigation of this compound.

Barium nonahydridorhenate was prepared according to the published procedure from the disodium salt.[4] The conversion gave average yields of approximately 95%; overall yields of approximately 40% were obtained based on the initial perrhenate. The dried white powder slowly turned gray and eventually black when exposed to air for periods of several weeks. X-ray powder diffraction and IR measurements of the colored powder after prolonged exposures showed the presence of the hydride with an additional strong peak at 1450 cm^{-1} but no perrhenate absorptions. The frequency of the new absorption corresponds to the frequency normally attributed to carbonate impurities.[2] The decomposition of this salt therefore appears to proceed via a pathway different from that of the alkali metal salts.[4b]

An IR spectrum of the dried white powder, in KBr pellets, was measured on a Perkin-Elmer 883 spectrophotometer. An NMR spectrum of a $Ba(OD)_2/D_2O/CD_3OD$ solution of the product was measured with a Bruker AMX-400 spectrophotometer. The IR spectrum showed a strong, broad absorption at 1870 cm^{-1} with shoulders at ~2000 and 1830 cm^{-1} and a second strong absorption at 690 cm^{-1} with shoulders at ~740 and 640 cm^{-1}. The spectrum corresponds well with the reported spectra for the dipotassium and disodium salts[4] where the absorptions were assigned to the a''_2 stretching and the a''_2 and e' bending modes of the tricapped trigonal prism (D_{3h} point symmetry).[5] The NMR showed a single proton resonance at −9.1 ppm, as was reported for Na_2ReH_9.[4b]

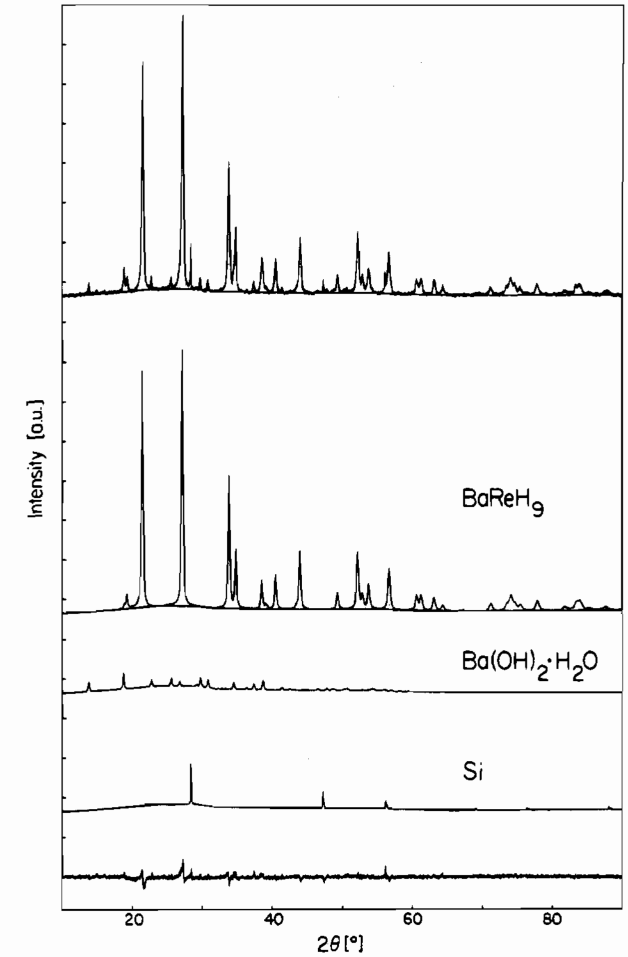

Figure 1. Observed (top), calculated and difference (bottom) X-ray powder diffraction patterns. (Cu Kα radiation).

The dried white powder was measured under argon by X-ray powder diffraction with a Philips PW1820 diffractometer (Cu Kα radiation, Bragg−Brentano geometry, Si added as internal standard). The pattern was initially indexed to an orthorhombic *C* cell;[6] space group *Cmcm* (No. 63). Two metal atoms, sites 4*a* and 4*c*, were found to be occupied by direct methods.[7] The atomic arrangement was recognized as the NiAs structure-type[8] and the cell was therefore transformed to hexagonal $P6_3/mmc$ (No. 194) [$a = 5.2905(1)$ Å, $c = 9.3327(1)$ Å], with Ba at site 2*a* and Re at site 2*c*. The remaining low intensity, unindexed peaks were identified as $BaOH)_2 \cdot H_2O$.[9] A three-phase ($BaReH_9$, $Ba(OH)_2 \cdot H_2O$, Si) Rietveld refinement (program DBWS-9006)[10] was performed on the data. In all, 22 parameters (one zero, one displacement, one transparency, three scale, six half-width, one asymmetry, two mixing, five lattice, and two thermal displacement) were refined giving $R_p = 2.59\%$, $R_{wp} = 3.61\%$, and $S = 1.79$. An R_{Bragg} of 3.96% was obtained for the hydride phase. Figure 1 shows the observed, calculated and difference

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Table 1. Single Crystal X-ray Diffraction Data for $BaReH_9$

formula	$BaReH_9$	T (°C)	293
fw	332.63	radiation	Mo $K\alpha_1$
a (Å)	5.287(1)	λ (Å)	0.7107
c (Å)	9.323(2)	abs (μ (mm^{-1}))	35.2
vol (Å^3)	225.7(1)	R^a	3.1
space group	$P6_3/mmc$	$R_w{}^b$	2.2
Z	2	S	2.94

^{a} $R = \sum_i||F_o - |F_c||/\sum_i|F_o|$. ^{b} $w = 1/\sigma(|F_{rel}|)$.

Table 2. Atomic Coordinates and Thermal Parameters for $BaReH_9$

	site	x	y	z	U_{iso} (Å^2)
Ba	2a	0	0	0	0.0197(3)
Re	2c	$^1/_3$	$^2/_3$	$^1/_4$	0.0166(2)
H1^a	6h	0.15	2x	$^1/_4$	
H2^a	12k	0.45	2x	0.11	

^{a} Proposed positions; not refined.

patterns. The difference pattern shows small discrepancies in the profile shape of the main hydride peaks due to deficiencies in the Rietveld asymmetry parameter in DBWS-9006.

Transparent, hexagonal single crystals of the $BaReH_9$ were obtained by slowly diffusing ethanol into an alkaline H_2O/methanol solution of the hydride. A data set of the complete reflection sphere was collected on a nearly spherical crystal (radius: 0.052(5) mm) with a STOE STADI4 four-circle diffractometer for an hexagonal P cell to a maximum of 60° 2θ. The cell parameters were refined with the lattice constant refinement routine included with the STOE STADI4 software using $\omega/-\omega$ measurements for a reflection list containing six reflections (9.8–25.2° in 2θ) and their equivalent reflections (72 reflections total). The data were refined with the Xtal3.2 program package.[11] The refinement was consistent with the powder data refinement. Crystallographic data and atomic coordinates can be found in Tables 1 and 2. No electron density peaks could be observed for the hydrogen atoms.

The refined structure corresponds with what would be expected for the metal atom structure of $BaReH_9$. Each Re is surrounded by six Ba (6 × 3.841(1) Å) in a trigonal prismatic configuration. The distances approximate those observed for K–Re in the dipotassium salt (K–Re1: 6 × 3.701(8) Å; K–Re2: 6 × 4.003(7) Å).[2] The closest Ba–Ba and Re–Re distances are 4.661(1) and 5.287(1) Å respectively. A tricapped trigonal prism of hydrogen around the Re, with H–Re distances of 1.68–1.69 Å, could be formed by placing hydrogen on sites 12k and 6h (see Table 2). The H–Ba distances would be 2.71 (H1) and 2.87 Å (H2); the H1–H2, H1–H1, and H2–H2 distances would be 1.97, 2.38, and 1.85 Å respectively. All of the distances for the two proposed sites are in agreement with those reported for the single crystal neutron diffraction study of K_2ReH_9.[3] Figure 2 shows the structure of $BaReH_9$ with hydrogens at the proposed positions. The hydrogen density of this salt is 134 g of H/L, approximately twice that of liquid hydrogen.

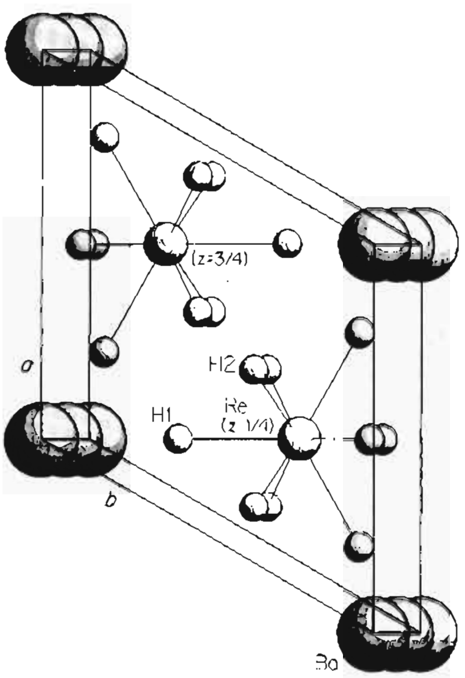

Figure 2. Structure of $BaReH_9$ with proposed hydrogen positions shown: Ba, large spheres; Re, medium spheres; H, small spheres.

A neutron powder diffraction pattern of a hydride sample of the Ba salt was measured on the DMC diffractometer at the Paul Scherrer Institute. All of the main coherent scattering peaks observed in the pattern could be assigned to either the $BaReH_9$ model (with proposed H positions) or to $Ba(OH)_2 \cdot xH_2O$ impurities. Refinement of the hydrogen positions was not possible due to the low coherent-peak-intensity-to-background ratio and uncertainity in the $Ba(OH)_2 \cdot xH_2O$ structures. The high background intensity was due to the incoherent neutron scattering by hydrogen. The extreme high cost of preparing a large volume sample from deuterated ethanol excluded the use of $BaReD_9$ in the study; single crystals of sufficient size for neutron diffraction have not been obtained.

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Supplementary Material Available: Full tables of single crystal and powder collection and refinement parameters and powder *hkl*, *d* and *I* data (3 pages). Ordering information is given on any current masthead page.

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