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PrNi and CeNi hydrides with extremely high H-density

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Abstract

The new hydrides, $PrNiH_x$ and $CeNiH_x$ were synthesized by two different techniques: at low hydrogen pressure (p_{H_2}) and elevated temperature, and at $p_{H_2} = 60$ bar and room temperature. The products of both techniques have similar crystal structure derived from the CrB-type. The volume expansion due to hydrogenation reaches 25% in $PrNiH_{4.3}$ and 29% in $CeNiH_{4.0}$. PrNi is an effective hydrogen getter.

Keywords: Crystal structure and symmetry; Intermetallics

1. Introduction

Physical properties of rare-earth (RE) compounds are closely related to the strength of the hybridization of the *4f-electronic* states with conduction electron states. Therefore, processes capable of changing the *4f-hybridization* can bring about totally new regime of their behavior. Hydrogen absorption takes a special place among such tools, since it can provide an increase of the unit cell volume by at least several percent. CeNi and PrNi were chosen as the objects for hydrogenation because in CeNi the lattice volume determines whether the ground state is magnetic or not [1–3], and Pr^{3+} typically has low-lying crystal field states, which makes it sensitive to changes of the local symmetry. Both effects, i.e. the volume expansion and the modification of the local symmetry, can be easily achieved by hydrogenation, although to our knowledge none of the materials has been studied as a hydride so far. CeNi as well as PrNi crystallize in CrB-type orthorhombic structure (space group *Cmcm*, $Z = 4$).

The present work reports on unusual sorption properties of both compounds, and describes crystal structure variations due to hydrogenation. Magnetic and specific heat studies of the hydrides will follow.

2. Experimental details and results

CeNi and PrNi intermetallics were synthesized by arc melting of the constituent metals (3N purity for RE components and 4N for Ni) under argon atmosphere. The ingots were subsequently sealed in evacuated silica tubes, annealed at 435 °C for 1 week and slowly cooled down to room temperature. The crystal structure was probed by powder X-rays diffraction (Cu or Co Kα radiation, Bragg–Brentano geometry), showing a good agreement with literature data [4,5]. The same diffraction apparatus was used for structural studies of hydrides.

Prior to hydrogenation, the samples were crushed into sub-millimeter particles and their surface was activated in dynamic vacuum of 10^{-6} mbar for 2 h at 250 °C. After the activation, the reaction chamber containing the sample was cooled down to room temperature at continuous pumping.

Hydrogenation was performed by two different methods. In the first method, the reaction chamber was filled with hydrogen gas at pressure $p_{H_2} < 1$ bar at room temperature. Neither PrNi nor CeNi absorbed hydrogen at this pressure

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even after several hours of exposure. In order to trigger the absorption, a sample had to be heated to 160 °C. At this temperature, the pressure of hydrogen in the reaction chamber started to decrease rapidly. The necessity to heat the samples in the hydrogen atmosphere is apparently connected to their surface activation because already after one heating cycle, the studied intermetallics were absorbing hydrogen even when cooled down to room temperature. The final composition of the hydrides was $PrNiH_{3.6 \pm 0.1}$ and $CeNi_{3.0 \pm 0.1}$. Hydrogen content was determined by the pressure drop in a calibrated volume.

This method of synthesis has revealed a getter-like behavior of PrNi. Namely, if the starting amount of hydrogen in the chamber was lower than the volume necessary to produce a saturated hydride, the final pressure p_{H_2} was always below 0.3 mbar, which corresponds to zero within the precision of our capacitance pressure gauge.

X-ray diffraction pattern for $PrNiH_{3.6}$ is shown in Fig. 1b, the data for $CeNiH_{3.0}$ look similar. In both patterns part of the diffraction peaks was due to impurities. In $PrNiH_{3.6}$, they originated from an unidentified phase observed already in the parent compound, and in $CeNiH_{3.0}$ additional diffraction peaks were coming from CeH_x (space group $Fm\bar{3}m$, $a = 5.580(16)$ Å). Binary Ce hydride was formed probably because of the longer, compared to PrNi, exposure of CeNi to high temperature in the hydrogen atmosphere, as well as due to a higher reactivity of Ce.

In order to improve the quality of the hydrides, hydrogenation was carried out at room temperature and $p_{H_2} = 60$ bar. At these conditions, the reaction dynamics was much slower compared to the first method. It took typically 1–2 days to reach the saturation. The materials obtained by the high-pressure technique contained more hydrogen: $PrNiH_{4.3 \pm 0.3}$ and $CeNiH_{4.0 \pm 0.3}$, but still their diffraction patterns were similar to those of $PrNiH_{3.6}$ and $CeNiH_{3.0}$ (compare Fig. 1a and b). The hydrogen content in $PrNiH_{4.3}$ and $CeNiH_{4.0}$ has larger error bars because it was determined from weight change due to the hydrogenation.

The lattice parameters of the hydrides obtained by both methods are the same within the precision of experiment. Yet the diffraction patterns for $PrNiH_{4.3}$ and $CeNiH_{4.0}$, which were synthesized at room temperature, have lower scatter and narrower peaks than those for $PrNiH_{3.6}$ and $CeNiH_{3.0}$ obtained at 160 °C. Additional error in the structural data for the last two compounds is introduced by the presence of an unidentified phase and CeH_x. The difference in the quality of the patterns leads to larger error for the lattice parameters for $PrNiH_{3.6}$ and $CeNiH_{3.0}$ (see Table 1).

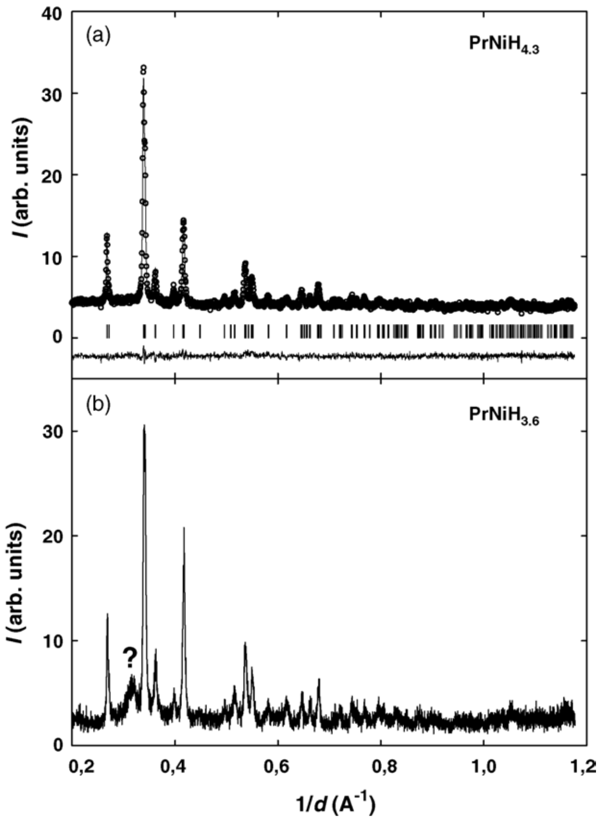

Fig. 1. X-ray diffraction patterns of the PrNi hydrides obtained at (a) $p_{H_2} = 60$ bar and room temperature and (b) $p_{H_2} < 1$ bar and 160 °C. The pattern for $PrNiH_{4.6}$ (a) was fitted using the Rietveld technique ($R_B = 9.4\%$). Fitting results as well as the calculated peak positions are shown in (a). The question mark in (b) denotes an impurity phase, which was present already in the parent PrNi.

Powder X-rays analysis has indicated that the hydrides crystallize in the same CrB-type orthorhombic structure (space group *Cmcm*) as the parent compounds, even though hydrogen absorption resulted in enormous volume increase of more than 20% (Table 1). Full refinement of the X-ray data was performed using the FullProf software suite by Rodriguez-Carvajal [6]. The crystal structure was normalized using the program Structure Tidy [7]. They revealed that hydrogenation resulted in a displacement of metal atoms

Table 1
Lattice parameters for PrNi–H and CeNi–H

	a (Å)	$\Delta a/a$ (%)	b (Å)	$\Delta b/b$ (%)	c (Å)	$\Delta c/c$ (%)	$\Delta V/V$ (%)
PrNi	3.831	–	10.543	–	4.369	–	–
$PrNiH_{3.6}$	3.885(4)	1.4	11.821(12)	12.1	4.825(6)	10.4	26
$PrNiH_{4.3}$	3.881(1)	1.3	11.821(3)	12.1	4.823(1)	10.4	25
CeNi	3.754	–	10.575	–	4.376	–	–
$CeNiH_{3.0}$	3.967(21)	5.7	11.91(5)	12.6	4.841(17)	10.6	32
$CeNiH_{4.0}$	3.925(4)	4.6	11.859(11)	12.1	4.838(4)	10.6	29

All compounds crystallize in the orthorhombic CrB-type structure, space group *Cmcm*. Lattice parameters for PrNi and CeNi are taken from Refs. [4,5], respectively.

within the unit cell. They occupy the same 4*c* crystallographic positions in $PrNiH_{4.3}$ and in PrNi but the *y* coordinates are changed: the atomic positions of Pr and Ni in $PrNiH_{4.3}$ are Pr (0, 0.1317(4), 1/4) and Ni (0, 0.4051(7), 1/4), and in PrNi–Pr (0, 0.13822(4), 1/4) and Ni (0, 0.4276(1), 1/4) [4]. The pronounced changes of the lattice parameters naturally lead to variations of the interatomic distances. The largest increase, reaching 23.6%, is found for the Ni–Ni spacing. The Pr–Pr and Pr–Ni distances increase by ≈8.1 and 12.8%, respectively. These data are suggestive of one of the possible hydrogen sites lying in the Pr_2Ni_4 octahedra with the center (E) in the crystallographic position 4*a* (1/2, 1/2, 0). In such case, the distances between nearest neighbours would be: E–E, 2.411(1) Å; E–Pr, 1.969(4) Å and E–Ni, 2.545(4) Å. On the other hand, the series of large empty trigonal prisms with centers at $y = 1/4$ and 3/4 can also play an important role in hydrogenation process.

Taking into account that one unit cell of the CrB-type structure contains four formula units, one can easily see that the hydrogen volume concentration in $PrNiH_{4.3}$ and $CeNiH_{4.0}$ is larger than about 10% higher than in $LaNi_5$, the standard hydrogen storage material. The specific volume in $PrNiH_{4.3}$ equals 12.9 $Å^3$/H atom, in $CeNiH_{4.0}$ equals 14.1 $Å^3$/H atom. If taking structure data for $LaNi_5H_{6.9}$ ($CaCu_5$ structure type, $a = 5.399$ Å and $c = 4.290$ Å) from Refs. [8–10], we obtain 15.7 $Å^3$/H atom for$LaNi_5H_{6.9}$.

Attempts to obtain lower ternary hydrides by decomposition of the saturated hydrides at elevated temperatures were unsuccessful. They resulted in the decomposition of $PrNiH_{4.3}$ and $CeNiH_{4.0}$ into corresponding binary hydrides REH_x and PrNi (CeNi), or, if the temperature exceeded 600 °C, into REH_x and Ni.

3. Conclusions

PrNi and CeNi hydrides were obtained for the first time, using two different synthesis techniques. The sample quality is higher for the high-pressure hydrogen absorption at room temperature, leading to 4 hydrogen atoms per formula unit, PrNi acts as effective hydrogen getter until it absorbs about 3 hydrogen atoms per formula unit.

The relative variation of the lattice parameter *a*, $\Delta a/a$ for the CeNi hydride is about four times larger than for the PrNi hydride (see Table 1), which may be related to a of Ce valence decrease upon hydrogenation.

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