

## Preparation of Cerium Hydrides

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**Abstract**—The conditions of the reaction between  $\text{CeCl}_3$  and  $\text{LiH}$  are optimized so as to obtain  $\text{CeH}_{2.73}$  or a mixture of  $\beta$ - and  $\gamma$ - $\text{CeH}_2$ .

In recent years, there has been intense interest in cerium intermetallics, which have been proposed for use as metal-hydride electrodes for high-capacity rechargeable batteries with good cyclability [1]. The magnetic properties of cerium intermetallics are of both theoretical and practical interest [2]. Cerium hydrides can be used as model compounds in the fabrication of metal-hydride electrodes and also in the preparation of fine-particle cerium for the synthesis of intermetallics.

$\text{CeH}_2$  and  $\text{CeH}_3$  are commonly prepared using Sieverts vacuum apparatuses. After thoroughly removing surface oxides, crushed cerium (1- to 3-g pieces) is loaded into the reactor, which is then pumped down to  $10^{-1}$ – $10^{-2}$  Pa and filled with pure hydrogen. The reaction temperature is 700–800°C for the synthesis of  $\text{CeH}_2$  [3, 4] and 150–200°C for  $\text{CeH}_3$  [5].

$\text{CeH}_2$  can also be prepared by heat-treating  $\text{CeH}_3$  at 400°C for 0.5 h, while continuously pumping out the hydrogen being released [6].

$\text{CeH}_3$  and  $\text{CeH}_2$  differ drastically in thermal stability: the former decomposes starting at 200°C, while the latter is stable up to 800–900°C. Rapid decomposition of  $\text{CeH}_2$  occurs only above its melting point (1080°C), but it retains some hydrogen even at 1200°C [7].

Direct reaction between cerium and hydrogen yields two fcc phases,  $\beta$  and  $\gamma$ , both of composition  $\text{CeH}_2$ , which differ in lattice parameter:  $a = 5.581$  and  $5.645 \pm 0.003$  Å, respectively. These phases also differ in the position of hydrogen, which occupies all the tetrahedral interstices in the  $\beta$  phase and octahedral interstices in the  $\gamma$  phase [8, 9].

Samples of composition  $\text{CeH}_{2.73}$  are single-phase and have an fcc structure with a lattice parameter  $a = 5.53$  Å. As the composition  $\text{CeH}_3$  is approached, the powder x-ray diffraction (XRD) peaks from cerium hydride become ever broader, which impedes accurate determination of its lattice parameter [10, 11].

Previously [12], we described a process for the preparation of  $\text{TbH}_{2.1}$  through the reaction between terbium chloride and lithium hydride. The purpose of

this work was to prepare different cerium hydrides by this process.

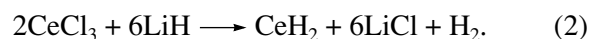
In our preparations, we used analytical-grade  $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$  (technical specifications TU 6-09-04-126-84),  $\text{OSCh}$  4-5  $\text{NH}_4\text{Cl}$  (RF Standard GOST 3773-72), LGK-1  $\text{LiH}$  (TU 95-760-84), and B-grade helium (TU 51-940-80).

To purify the helium and determine cerium and hydrogen, we used the same techniques as described previously [12].

XRD studies were carried out on a DRON-3 powder diffractometer (Ni-filtered  $\text{CuK}_\alpha$  radiation).

Anhydrous  $\text{CeCl}_3$  was prepared by reacting  $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl}$  during heating. To this end, a mixture of  $\text{Ce}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$  (30.0 g) and  $\text{NH}_4\text{Cl}$  (88.0 g) (2.5-fold excess of  $\text{NH}_4\text{Cl}$  with respect to the stoichiometric value) placed in a quartz tube was gradually heated to 830°C under flowing helium in an inclined tubular quartz reactor until the cessation of water and ammonia release and  $\text{NH}_4\text{Cl}$  deposition on the cold walls of the reactor (12 h). The yield of anhydrous  $\text{CeCl}_3$ , obtained in the form of a porous, colorless mass, was 96.4% (25.9 g). The cerium content of the reaction product (56.80 wt %) was close to the nominal value of 56.85 wt %.

Cerium hydrides were prepared by reacting  $\text{CeCl}_3$  with  $\text{LiH}$  added in an excess with respect to reactions (1) and (2) [13]:



**Cerium hydride  $\text{CeH}_{2.73}$ .** A mixture of anhydrous  $\text{CeCl}_3$  (3.50 g, 0.014 g/mol) and  $\text{LiH}$  (0.51 g, 0.064 g/mol) was loaded into a stainless steel (1Kh18N9T) crucible. The crucible was mounted in a quartz reactor, which was then introduced into a furnace. The mixture was heated to 740°C over a period of 1.5 h in an inert-gas flow and held at temperature for 50 min. After cooling, the reaction products were placed in ice water. Cerium hydride was filtered off and

dehydrated in ethanol, which was then displaced by hexane. The hexane was removed by flowing helium. The resultant black pyrophoric powder of cerium hydride (1.92 g) contained 94.8 wt % Ce and 1.6 wt % H. Using XRD analysis, this phase was identified as  $\text{CeH}_{2.73}$ . In addition, the powder contained  $\text{CeO}_2$  impurity.

The contents of  $\text{CeH}_{2.73}$  and  $\text{CeO}_2$  were estimated at 79 and 21%, respectively. Their lattice parameters were determined to be 5.525 and 5.403 Å, in agreement with earlier data:  $a = 5.53$  Å for  $\text{CeH}_{2.73}$  [10] and 5.4110 Å for  $\text{CeO}_2$  [14].

**Cerium hydride  $\text{CeH}_2$  ( $\beta$  and  $\gamma$  phases).** A mixture of anhydrous  $\text{CeCl}_3$  (4.00 g, 0.016 g/mol) and LiH (1.00 g, 0.126 g/mol) was reacted in the same way as above. The temperature was raised to 720°C over a period of 40 min, fixed for 75 min, and then raised to 1000°C over a period of 30 min. Next, the furnace was shut off. In this way, we obtained black powder containing 98.3 wt % Ce and 1.4 wt % H. As found by XRD, the powder consisted of  $\beta$ - $\text{CeH}_2$  (68%,  $a = 5.584$  Å) and  $\gamma$ - $\text{CeH}_2$  (32%,  $a = 5.637$  Å). The lattice parameters of  $\beta$ - and  $\gamma$ - $\text{CeH}_2$  reported in [8] are 5.581 and 5.645 Å, respectively. No cerium oxides were detected in our sample.

Thus, the process described previously [12] can be used to prepare cerium hydrides. The major steps of this process are heat treatment of a mixture of  $\text{CeCl}_3$  with an excess of LiH, water leaching, and drying of the hydride phase. Heat treatment at 700–740°C leads to the formation of  $\text{CeH}_{2.73}$ , while that at 1000°C yields a mixture of  $\beta$ - and  $\gamma$ - $\text{CeH}_2$ . The impurity phase  $\text{CeO}_2$  is likely to result from the hydrolysis and oxidation of the unstable, reactive hydride  $\text{CeH}_{2.73}$ .

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