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DTA/TG Studies on Some Lanthanide Hydrides and Nitrides

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Introduction

Functional materials are the basis of advances in many kinds of industrial products. Especially chemical compounds based on lanthanides become more and more important, due to their versatile chemistry and electronic configuration. As a consequence, they found a broad field of potential applications. There is no doubt that oxidic lanthanide materials form the most important pool of applicable compounds, at the moment, but lanthanide hydrides and nitrides have come into focus for specialized functional materials. The most prominent features of some lanthanide hydrides are superconductivity and the ability to switch between metal and insulator states and optical switching,[1-2] respectively, depending on the hydrogen content. But applications reach even further, e.g. as models for theoretical studies, catalysts, educts in syntheses, neutron absorbers in reactor components or even as hydrogen storage media. Lanthanide nitrides are more renown for their application in electronics, catalysis, and as precursors in solid-state chemistry for LED phosphors. Although, large amounts of the two aforementioned classes of materials are needed and several syntheses yielding nano- or micrometer-sized materials are known,[3-4] it is almost impossible to find exact data on synthesis conditions, suited for large-scale precursor production. That was the reason for this study, to determine and compare the reaction parameters of different lanthanides, large, intermediate, and small. We aimed for optimal synthesis conditions of metal hydride/nitride precursors. Therefore, we conducted detailed DTA/TG measurements on several lanthanide metals and their respective hydrides. We were thereby able to derive optimal temperature programs for the hydration and nitridation of the plain metals/hydrides.

DTA/TG Measurements of Several Lanthanides (Metals and Hydrides)

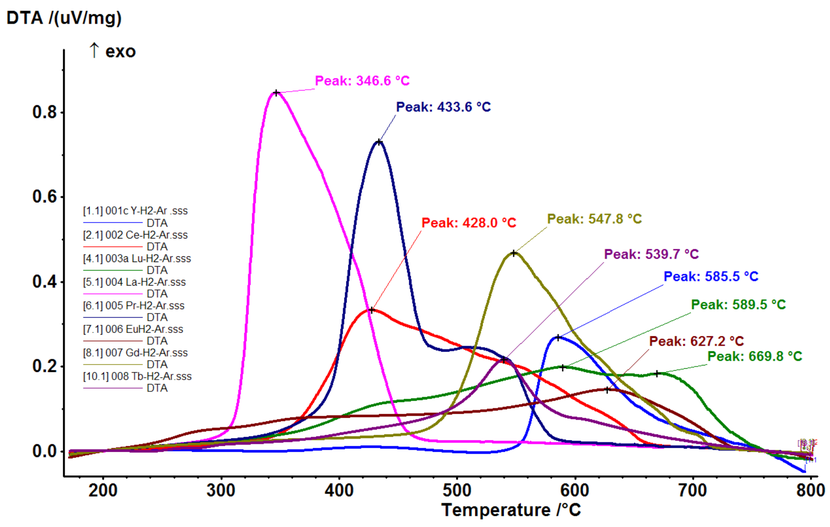

Figure 1: Comparison of DTA measurements of Y, La, Ce, Pr, Eu, Gd, Tb, and Lu in Ar/H_2 (35%)

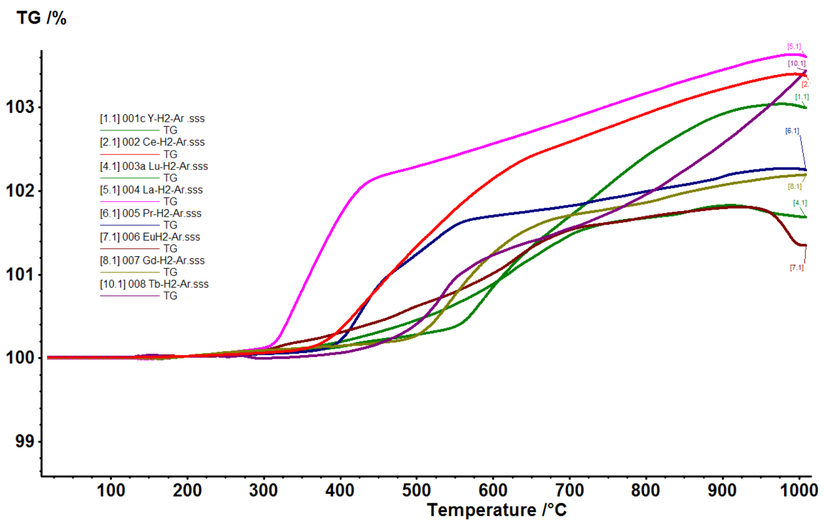

Figure 2: Comparison of TG measurements of Y, La, Ce, Pr, Eu, Gd, Tb, and Lu in Ar/H_2 (35%)

Table 1: Theoretical weight gain of lanthanide hydrides and nitrides with respect to the plain metals and the corresponding hydrides

Element	Hydride [%]	Nitride [%]
Y	3.4	11.9
La	2.2	7.7
Ce	2.2	7.7
Pr	2.1	7.6
Eu	1.3	7.8
Gd	1.9	6.9
Tb	1.9	6.8
Lu	1.7	6.2

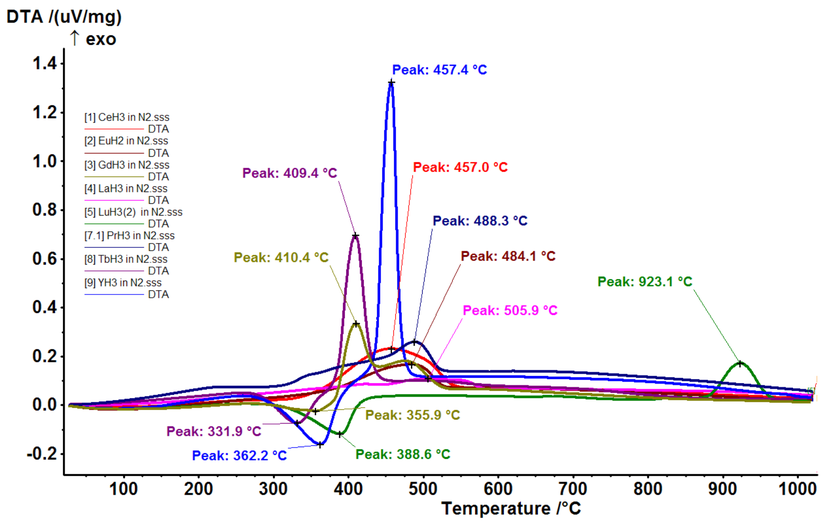

Figure 3: Comparison of DTA measurements of YH_3, LaH_3, CeH_3, PrH_3, EuH_2, GdH_3, TbH_3, and LuH_3 in N_2 (5.0) atmosphere

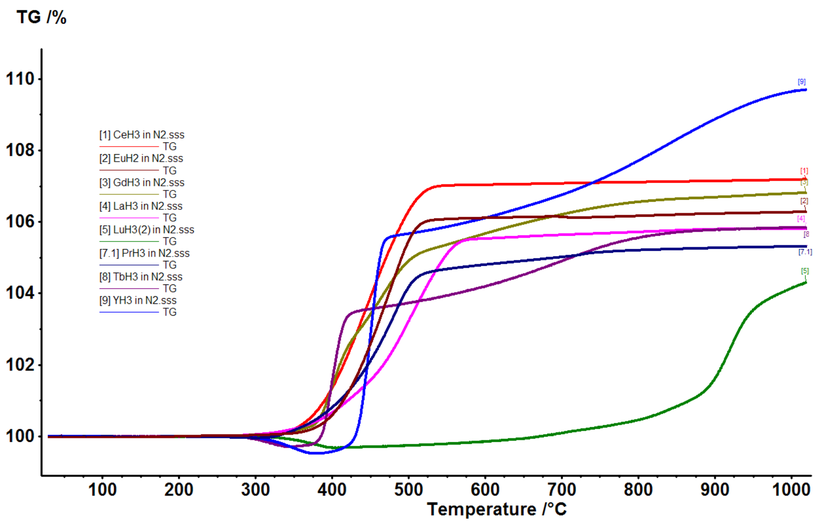

Figure 4: Comparison of TG measurements of YH_3, LaH_3, CeH_3, PrH_3, EuH_2, GdH_3, TbH_3, and LuH_3 in N_2 (5.0) atmosphere

The hydration of the lanthanide metals appears to be rather complicated. Some metals exhibit the expected exothermic reaction peak at low temperatures and subsequent linear increase of mass (Y, La, Gd). Others, such as Ce, Pr, Eu, Tb and Lu show slightly deviant characteristics. This is probably due to surface and "size" effects that affect the reactivity of the metals and lead to broad and/or multiple peaks visible in DTA graphs.

The results of the nitridation show in most cases more distinct DTA reaction peaks for the hydrides and confirm the expected trend that smaller Ln are less reactive than bigger ones.

Y and La Hydride

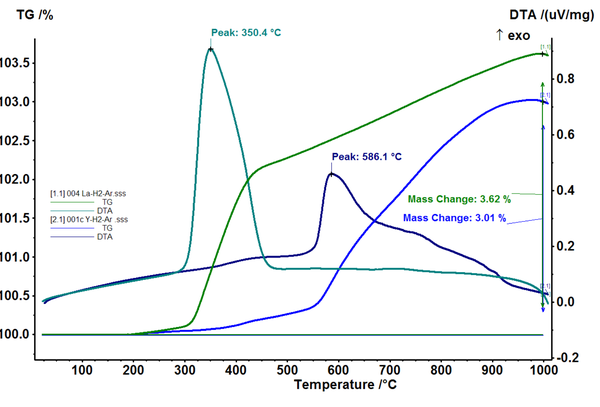

Figure 5: DTA/TG data of plain Y and La metals in Ar/H_2 (35%)

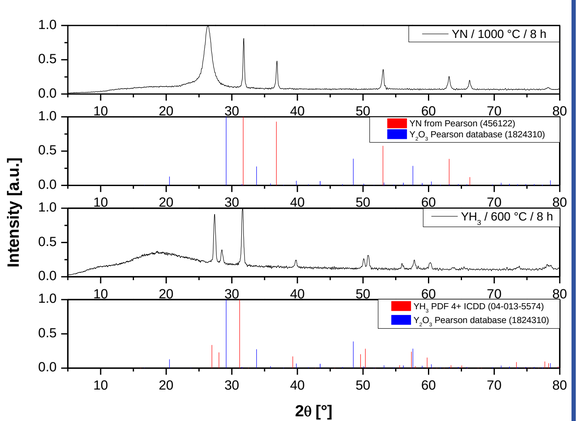

Figure 6: XRD patterns of as synthesized YH_3 and LaH_3 compared to theoretical patterns

The DTA data shows two distinct exothermic reaction peaks for the hydration of Y and La. As expected, La reacts at lower temperatures than the "smaller" Y. Both metals show linear increase of mass once the reaction was initialized. Phase formation and purity was confirmed by XRD measurements. The broad peaks between 12-25° and 22-28° 2θ are due to protective foils that shield the materials from moisture and air during measurements.

Y and La Nitride

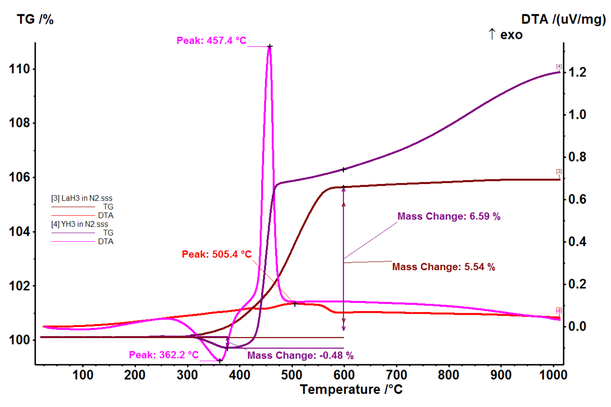

Figure 7: DTA/TG data of YH_3 and LaH_3 in N_2 (5.0)

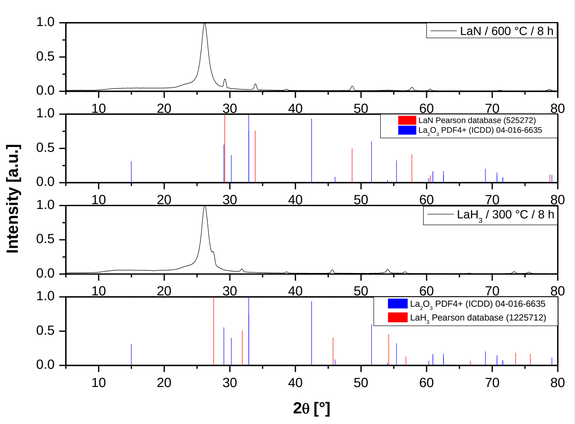

Figure 8: XRD patterns of as synthesized YN and LaN compared to theoretical patterns

YH_3 in contrast to LaH_3 appears to cleave some water or H_2 before the nitridation starts. But the reaction proceeds more pronounced than for LaH_3. Judging from TG data the nitridation of LaH_3 starts slightly earlier as has been found for the hydration, as well. Again, phase formation and purity was confirmed by XRD data. The broad peaks from 22-28° 2θ are due to protective foil that shield the materials from moisture and air.

[1] B. Kong et al., J. Phys. Chem. Sol. 74 **(2013)**, 1322-1328
[2] J. N. Huiberts et al., Nature (London) 380 **(1996)**, 231
[3] H. Imamura et al., Catal. Lett. 88, 1-2 **(2003)**, 69-72
[4] H. Imamura et al., J. Alloys Compd. 451 **(2008)**, 636-639