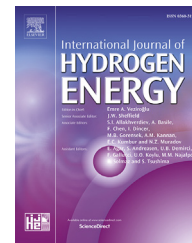




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Phase stability of some rare earth trihydrides under high pressure

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ABSTRACT

Phase stability of lanthanum, gadolinium and erbium trihydrides have been studied at high pressure in diamond anvil cell. Raman high pressure studies up to 40 GPa of lanthanum trihydride and deuteride have shown more complex spectra than one can expect from the factor group analysis for stoichiometric LaH₃. Our studies have shown that the stoichiometric lanthanum trihydride and deuteride undergo pressure induced phase transformation presumably of hydrogen ordering origin.

Investigations of the phase stability of erbium and gadolinium trihydrides have been performed using argon as pressure transmitting medium in Raman scattering method. The same medium has been used for X-ray diffraction analysis under pressure for erbium trihydride. Significant difference in the transition pressure as compared to earlier results obtained in quasi hydrostatic conditions has been noticed both in X-ray and Raman scattering measurements. Deviatoric stresses present in earlier nonhydrostatic measurements can be blamed for its discrepancy.

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Introduction

Hydrogen-rich materials have attracted a lot of attention in the last decades mainly as potential hydrogen storage materials. As an important class of such compounds, metal hydrides have been considered. Beyond being regarded for hydrogen storage, metal hydrides offer the attractive physical properties to be potentially used in the electronics and other applications.

In this respect the family of rare earth hydrides seems to be very promising, especially that the physical properties of these hydrides can be tuned by hydrogen concentration from the metallic to semiconductors behavior. Reaction of hydrogen saturation is reversible, so the switching for metal

to isolator and vice versa can be realized by changing hydrogen pressure over the metals. This phenomenon has been presented by Griessen et al. in their famous Nature paper [1].

Another stimulus for the study of these systems was the discovery of pressure induced phase transformation in a row of rare earth trihydrides [2], which attracted a lot of attention from both experimentalists and theoreticians as well [3–10]. It is commonly accepted that the pressure induced structural transformation in this trihydrides is result of the hydrogen-hydrogen interaction in metal lattice in accordance with Switendick criteria [11]. Mechanism of this transformation has been described in details by Machida et al. [9] as a result of long-period stacking structures that consist of cubic and hexagonal planes. Rare earth hydrides quite recently became

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the object of investigations as a components of complex hydrides for hydrogen storage [12,13].

Lanthanum trihydride has been selected for the measurements because to our knowledge Raman scattering under pressure has not been performed so far on this stoichiometric compound. Lanthanum trihydride has cubic, sometimes referred to as BiF₃ structure according to [14]. Therefore, according to group factor analysis only one Raman active mode should be present. Our preliminary measurements have shown quite rich Raman spectrum coming from LaH₃ sample. It should be mentioned that the X-ray diffraction study by Boroch et al. [15] performed on stoichiometric lanthanum trihydride has shown additional to the peaks indexed as fcc structure quite intense peaks of unknown origin.

Our preliminary study of high pressure Raman scattering study on lanthanum trihydride have shown interesting phase transition unknown up to now. We suggest that this transition could be similar to that observed in the heat capacity measurements at low temperature [16]. The superstructure lines in the neutron diffraction pattern and X-ray measurements of stoichiometric LaD₃ has been reported also by Udovic et al. [17,18] for stoichiometric lanthanum trideuteride at temperature about 260 K. These results suggest the appearance of a low temperature phase transformation presumably of the second type of order which was interpreted as due to an ordering of the D atoms on off-centre positions in the octahedral interstices of the metal atom network. It was also postulating that a long-range-ordered pattern of displacements of the La metal atoms from the ideal fcc symmetry was occurring in addition to long-range-ordered displacements within the D sublattices.

As it is commonly known that the value of transition pressures depend on the hydrostaticity within diamond anvil cell, we decided to check how the transmitting media influence the determination of transition pressures of erbium and gadolinium trihydrides by using gaseous argon loaded at high pressure together with the corresponding specimens.

Materials and methods

Samples of trihydrides and lanthanum deuteride, gadolinium and erbium trihydrides were obtained from nominally 99.9% pure metals by direct absorption under the gaseous hydrogen and deuterium pressure of 15.0 MPa and 300 °C during 4 h in a high pressure Sieverts apparatus as described earlier [19]. The purity and predicted structure of the samples used for high pressure studies have been confirmed by powder X-ray diffraction and elemental analysis before loading in diamond anvil cell (DAC).

Initial sample has been analyzed using X-ray diffraction method while composition has been determined by weighting sample of about 1.5 g before and after charging it with hydrogen. Value of 3.00 ± 0.03 in atomic ratio H/La has been obtained. X-ray diffractogram of lanthanum trihydride is shown in Fig. 1. Similar pattern was obtained for lanthanum deuteride. According to Klavins et al. [20] lattice parameter determined in our measurements as equal 5.619 Å corresponds to stoichiometric trihydride of lanthanum.

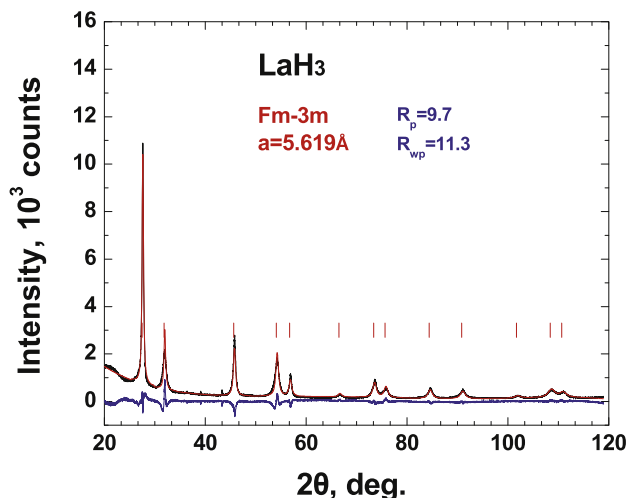


Fig. 1 – XRD pattern of the initial LaH₃ sample (black), its Rietveld fit (red) and fit residue (blue). Ambient conditions, CuK α radiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

X-ray diffraction pattern of initial sample of erbium trihydrides taken outside of diamond anvil cell is shown in Fig. 2.

Lattice parameter shown in Fig. 2 is exactly the same as reported for stoichiometric erbium trihydrides by Ref. [21] and no contamination of the sample has been noticed.

The high pressure X-ray diffraction studies were conducted at custom made facilities that operates in energy dispersive X-ray diffraction mode.

Samples were loaded into 200 μ m hole in the rhenium gasket preindented to a thickness of \sim 50 μ m, along with a

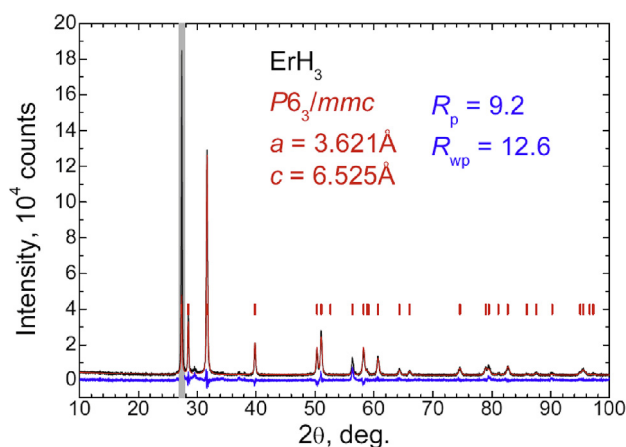


Fig. 2 – XRD pattern of the initial ErH₃ sample (black), its Rietveld fit (red) and fit residue (blue). Ambient conditions, CuK α radiation. Due to a strong texture the (002) peak was excluded from the refinement, as shown by the gray shadowed area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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