Experimental report

05/11/2021

Proposal: CRG-2812 **Council:** 10/2020

Title: Study of the D-Hf phase diagram using in-situ neutron diffraction

Research area: Physics

This proposal is a new proposal

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Samples: Hf
HfD

Instrument	Requested days	Allocated days	From	To
D1B	2	2	16/02/2021	18/02/2021

Abstract:

Study of the D–Hf phase diagram using *in situ* neutron diffraction

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Context

H-Hf phase diagram knowledge is a key to understand and solve technical issues. In the next fast reactors, hafnium hydride can be used as control rods[1] and very recently, the use of hafnium with palladium has shown its usefulness for optical hydrogen sensors[2].

This phase diagram contains four different phases: the hexagonal phase α–Hf(*hP*2, Mg, $P6_3/mmc$), the distorted cubic phase δ'–HfH_{2-x} (unknown structure), the cubic phase δ–HfH_{2-x} (*cF*12, CaF_2, $Fm\bar{3}m$) and the tetragonal phase ε–HfH_2 (*tI*6, ThH_2, $I4/mmm$) which are shown in Figure 1. However, the phase diagram is only partially known, assumptions have been made to draw this diagram and thus, the phase transitions are still not well established.

Additionally, the existence of the tetragonal phase γ–HfH ($P4_2/mmc$) was recently predicted[3] by *ab-initio* calculations. In our laboratory, we have shown the existence of the γ–HfH and γ–HfD experimentally for the first time by doing hydrogen experiments using Sieverts' modified apparatus, see the red dashed line in Figure 1.

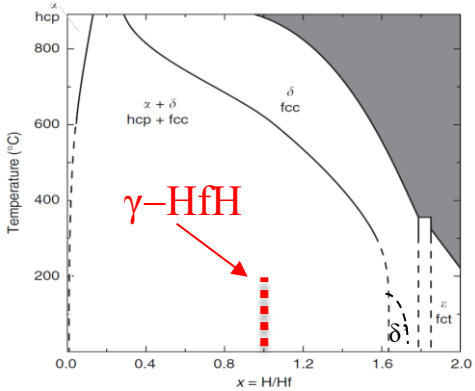

Figure 1. Phase diagram of H-Hf system taken from Boelsma et al[2] with red annotations.

The present work is dedicated to the study of the D–Hf system using *in situ* neutron diffraction at the ILL on D1B instrument[4]. Therefore, this work lies in the *in situ* study of both composition and temperature of this phase diagram.

Materials and Methods

One synthesized sample of deuteride $HfD_{0,994}$ has been provided and was studied *in situ* as a function of temperature, up to 850 °C (experiment 3 on the Figure 2), in a silica tube.

High purity hafnium has been provided and 2 experiments were carried out (experiment 1 and 2 on the Figure 2). The first experiment was to investigate the phase diagram at low deuterium content, $HfD_{0,217}$, up to 920 °C. This sample was desorbed and a pressure-composition isotherm at 700 °C was performed. The second experiment was to investigate pressure-composition at low temperature, *i.e.* 250 °C, up to $HfD_{1,96}$. Then this sample was heated up to 500 °C.

Each dot of the Figure 2 corresponds to a specific composition and temperature where an acquisition has been performed.

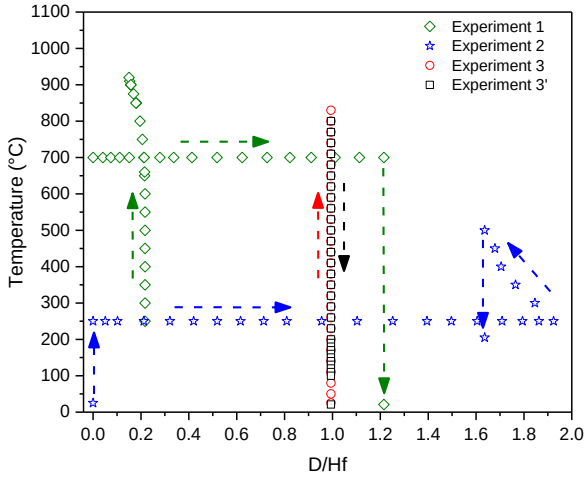

Figure 2. List of the different experiments performed at ILL.

The bound coherent scattering length is 7.7 for hafnium and 6.67 for deuterium. Relatively high absorption cross section of Hf (104 barn) has been taken care of during this experiment. Thus, the wavelength 1.28 Å available at D1B with a high flux has been used.

We used ICMPE hydrogen bench, deuterium bottle S11 ($2m^3$, 200 bars) and ICMPE stainless steel (up to 500 °C) and silica sample holder (provided by ILL and above 500 °C).

Results and Discussion

The 48 hours experiments help us to get lot of insights on this D–Hf phase diagram.

First, during the heating and the cooling of the third experiment, the monodeuteride γ–HfD was found to be reversibly stable up to 170 °C. We have fully determined the structure (PtS, *tP*4, $P4_2/mmc$), site occupancies and the composition of this deuteride for the first time experimentally.

We confirmed that the transition between the δ–HfD_{2-x} phase and ε–HfD_2 phase is a first order transformation, Figure 3.

The structure, site occupancies and composition of the δ'–HfD_{2-x} phase was fully identified for the first time, Figure 4. It was found that this structure is a superstructure of the δ–HfD_{2-x} phase and that the space group is *Ibam* with hafnium located in the 8*j* site and deuterium in the 8*g*, 4*b* and 4*a* sites. This structure for a binary system is not reported in the literature.

The two pressure-composition isotherms at 250 °C and 700 °C allowed us to determine the phases in equilibrium at low and high temperature.

Finally, this study led to an update of this phase diagram.

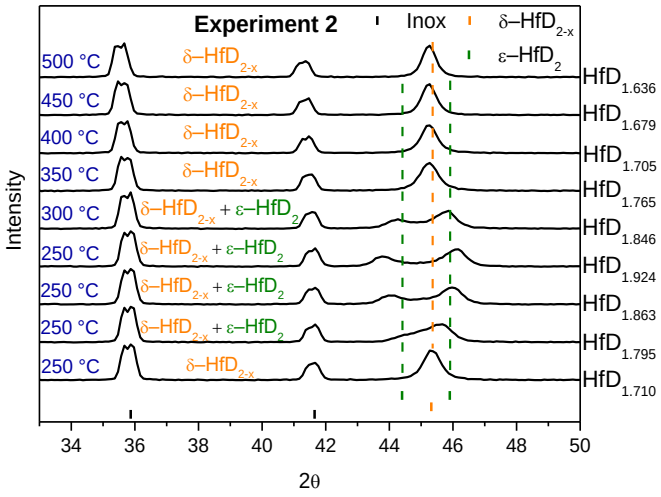

Figure 3. Evolution of the stability of δ–HfD_{2-x} and ε–HfD_2 phases as a function of composition and temperature.

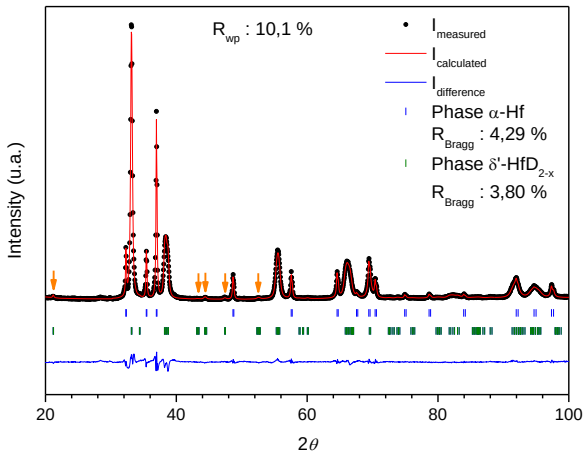

Figure 4. Diffractogram of $HfD_{0.99}$ where some peaks of the δ'–HfD_{2-x} phase are identified with an orange arrow.

Acknowledgments

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References

1. Kurosaki, K. *et al.* The δ′/δ phase transition in hafnium hydride and deuteride. *Journal of Nuclear Science and Technology* **52**, 541–545 (2015).
2. Boelsma, C. *et al.* Hafnium—an optical hydrogen sensor spanning six orders in pressure. *Nature Communications* **8**, 15718 (2017).
3. Bourgeois, N., Crivello, J.-C., Cenedese, P. & Joubert, J.-M. Systematic First-Principles Study of Binary Metal Hydrides. *ACS Comb. Sci.* **19**, 513–523 (2017).
4. Dottor, M.; Couturas, F.; Crivello, J.-C.; Joubert, J.-M.; Laversenne, L.; Nassif, V.; Puente Orench, I. *Study of the D-Hf Phase Diagram Using in-Situ Neutron Diffraction* (2021). https://doi.org/10.5291/ILL-DATA.CRG-2812.