

# Scientific Report on the EXAFS proposal: Effects of Zirconium on the hydrogenation and sensing properties of Yttrium thin films (code no. 26-01-1008)

## Background and aim of the Proposal

We recently developed a low-cost eye-readable, and color tunable hydrogen detector (figure 1A). The sensing mechanism is based on reversible change in the optical properties of yttrium-palladium (Y-Pd) thin films upon exposure to hydrogen<sup>[1]</sup>. Surprisingly the addition of different concentrations of zirconium (Zr) to the Y sensing layer resulted in a continuous increase in the hydrogen pressure required for the detector to change from one color to the other (plateau pressure for the transition  $\text{YH}_{2.1} \rightarrow \text{YH}_3$ ), while the optical contrast remains largely uncompromised. This is a very interesting behaviour as it paves way for the development of low cost optical hydrogen sensors with large detection range (from 0.1 mbar to 10,000 mbar) at room temperatures. However the exact origin of these effects is still unknown. Results from x-ray diffraction (XRD) suggest that changes in the microstructure of Y induced by the presence of Zr (or  $\text{ZrH}_2$ ) could be responsible for these tremendous and interesting thermodynamic effects. The Zr component is XRD amorphous therefore it is not yet clear if it is Zr or  $\text{ZrH}_2$  that is entirely responsible for this effect, and how such a huge thermodynamic effect could be caused by the presence of these materials. A possible chemical or electronic modification of the Y sensing layer by Zr could also lead to such effects. Therefore in the proposal (code no. 26-01-1008) we used EXAFS experiments to investigate the change in structure and/or chemical environment of Y and Zr of the sensing layer upon hydrogenation and dehydrogenation.

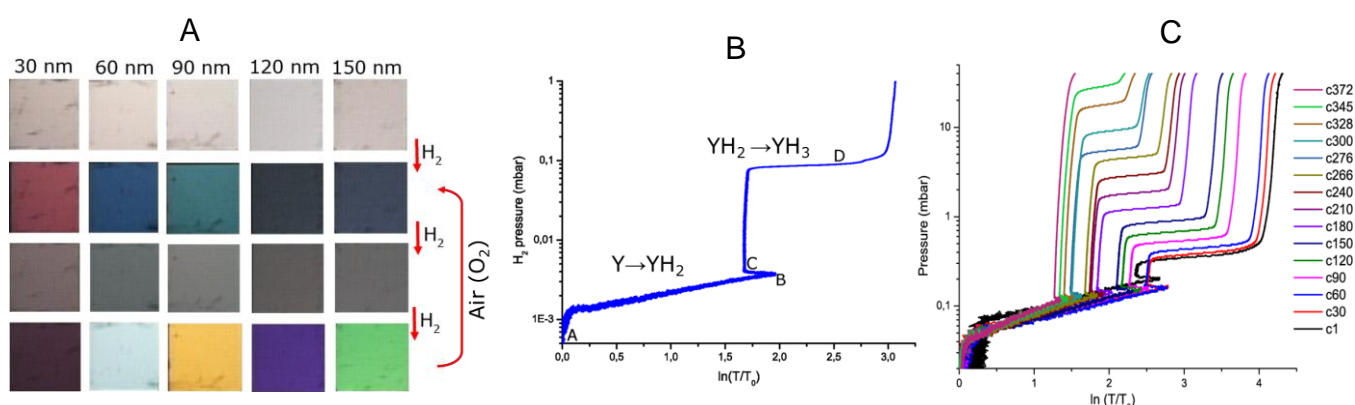


Figure 1: (A) Eye –readable and color tunable hydrogen indicator (B) Pressure transmission isotherm showing the hydrogen pressures corresponding to the four optical states seen in A, (C) PTI showing a continuous increase of the plateau pressure required for the transition  $\text{YH}_{2.1} \rightarrow \text{YH}_3$ , as a function of Zr concentration in the Y

## Experiments and Results

The Experiment was successfully conducted at DUBBLE beam line 26A from September 4-September 8, 2014 as scheduled. The measurements were carried out in fluorescence geometry at the Y (17.039 KeV) and Zr (17.998 KeV) K-edges. The beam-line is equipped with very excellent facilities that enabled both ex-situ and in-situ measurements to be conducted on the thin films, which resulted in obtaining high quality experimental data. The beam-line scientist Dr. Alessandro Long was also very helpful in making sure the equipment ran smoothly during the entire period. During this period, the Y and Zr K-edges of several samples were measured. The results (Figure 2) clearly indicate that Zr exists as highly dispersed clusters after preparation of Y-Zr metastable alloys. Upon hydrogenation,  $\text{ZrH}_x$  and  $\text{YH}_x$  are clearly seen which indicates that the Y and Zr do not remain as an alloy upon hydrogenation. An interesting observation is that upon full hydrogenation, the Zr-Zr coordination number increased significantly in the Y-Zr thin film sample alloy (figure 2) while the Zr-Zr distances is surprisingly lower than for the pure  $\text{ZrH}_2$  (figure 3). This suggests that formation of  $\text{YH}_3$  compresses the  $\text{ZrH}_2$  due to about 15% volume expansion in going from Y to  $\text{YH}_3$ . Although the detailed analysis of the experimental data is ongoing, the present results are a significant contribution to further understand the origin of the thermodynamic effects in the Y-Zr alloys, and which structural parameters can be used to improve it. However more experiments will be needed to completely understand especially the effect of higher Zr concentration on the structure and thermodynamics

of the Y-Zr systems. Extending the experiment to other Zr- rare-earth metal hydride systems (for example Gd-Zr and La-Zr systems) will also be beneficial in exploring how the chemical and structural properties of these materials influences the thermodynamic trend that do exist in these systems

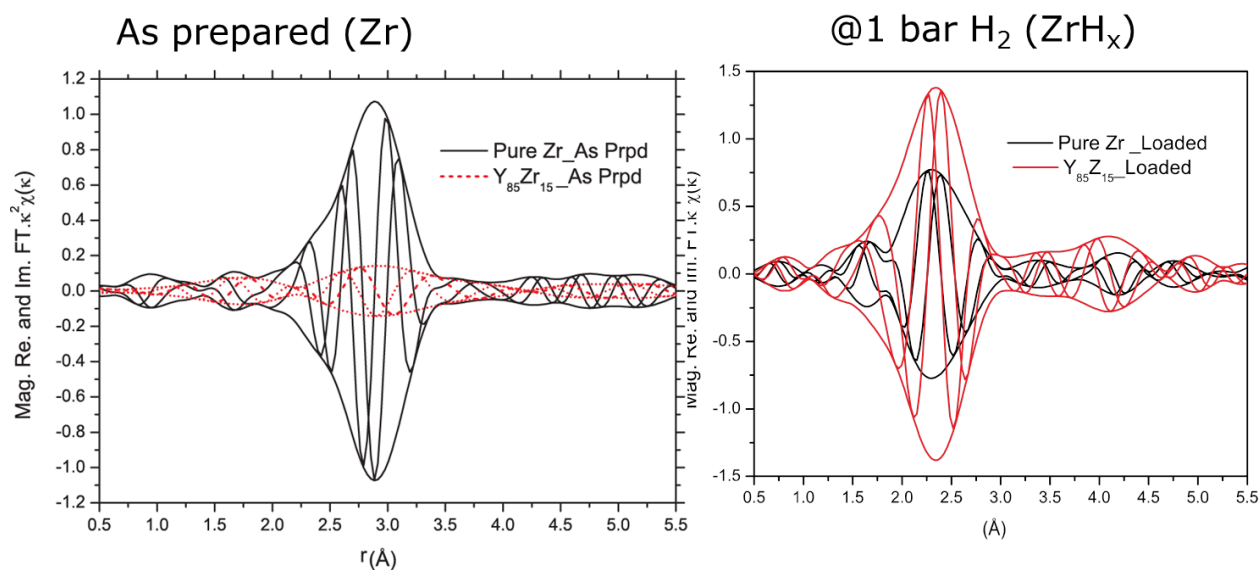


Figure 2. Magnitude and imaginary part of the phase-uncorrected Fourier transformed (FT)  $k^2\chi(k)$  for bulk Zr and  $Y_{85}Zr_{15}$  thin films in the as prepared state and after hydrogenation at 1 bar  $H_2$ .

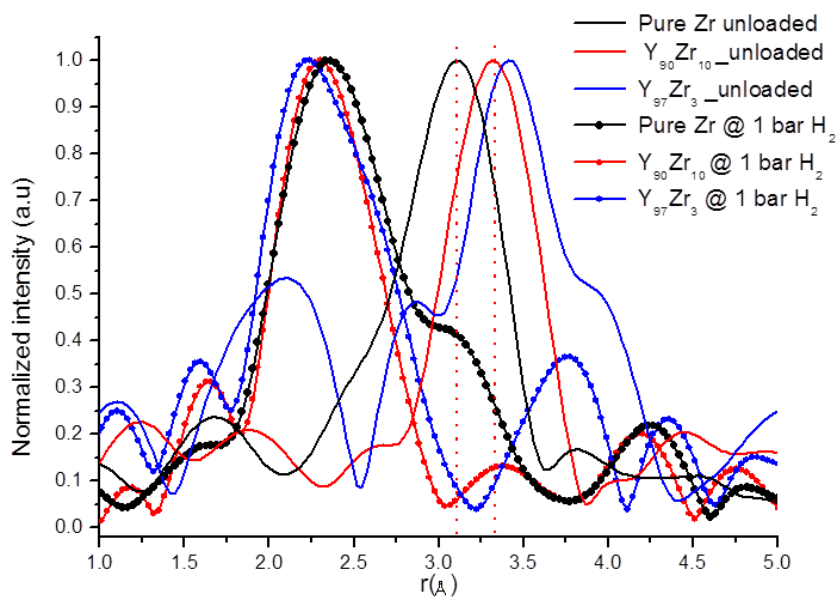


Figure 3. Results from Zr K-edge EXAFS showing the effect of zirconium concentration on the chemical environment of Zr upon hydrogenation (loaded) and dehydrogenation (unloaded) of  $Y_xZr_{1-x}$  thin films.

## References

- [1] P. Ngene, B. Dam, et al., *Adv. Funct. Mater.* 2014, 24, 2374