

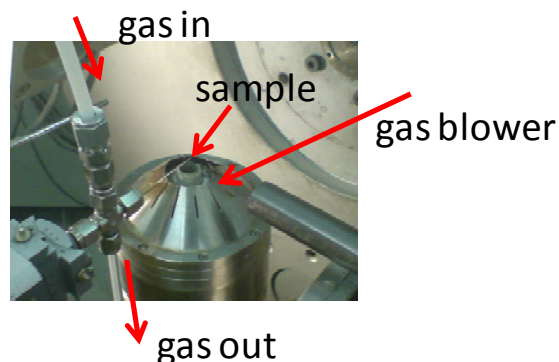


	<b>Experiment title:</b> <b>Phase transitions in WO<sub>3</sub> nanowires studied in situ by time resolved high resolution powder diffraction</b>	<b>Experiment number:</b> <b>HS-3892</b>
<b>Beamline:</b> ID 31	<b>Date of experiment:</b> from: <b>24 Juli 2009</b> to: <b>29 Juli 2009</b>	<b>Date of report:</b> 28 February 2010
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr	<i>Received at ESRF:</i>
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## Report:

The aims of our experiment were

- to investigate the phase transitions as well as the stability of individual phases in WO<sub>3</sub> under conditions close to operating conditions of sensors;
- to prove the occurrence of charge induced phase transitions in WO<sub>3</sub> under conditions close to operating conditions of sensors;
- to verify the reversibility of phase transition in 1D WO<sub>3</sub> (nanowires) under conditions close to operating conditions of sensors.



Accordingly, the following experiments have been performed: In situ time-resolved high resolution powder diffraction at temperatures from rt. to ~ 550°C in cyclical oxidising (oxygen) and reducing (4 vol. H<sub>2</sub> in He) conditions; repeated several times to see reproducibility/ reversibility of the transformations. Samples: WO<sub>3</sub> powders synthesized by different methods and having different crystal shape (nanowires, nanoparticles) and size (~ 3 nm to 300 nm) loaded in capillaries and heated with a gas blower.

Figure. Schematic of the set-up.

The question about the functional differences of different WO<sub>3</sub> phases is relatively vague. Despite numerous studies of the gas sensing properties of WO<sub>3</sub> samples (nanopowders, powders, 1D structures), there have been no common opinion /understanding of the influence of phase composition on the gas sensing properties. This is due mainly to three reasons. Firstly, in the majority of works the phase composition was not studied and the structural characterisation was not performed. Secondly, because of the polymorphism and accordingly of the variety of possible phase transitions, which in turn depend on the particle size (see above) WO<sub>3</sub> is difficult candidate to study. Thirdly, the possible phase transitions in WO<sub>3</sub> during the operating of the sensors (at operating temperatures of sensors) were not considered. The latter lead to the fact that one compares the properties of different WO<sub>3</sub> phases even studying the same samples. Although the theoretical understanding of the structural influence on the WO<sub>3</sub> properties is not yet achieved, one can expect that different WO<sub>3</sub> phases (surface structures) will possess different reactivity and consequently different functional properties. For example, one usually assumes that the sensing properties (surface reactivity) of the WO<sub>3</sub> is mainly determined by the (sub-) surface oxygen vacancies <sup>[1]</sup> or (sub-)surface W<sup>5+</sup> atoms <sup>[2]</sup> and the conduction and sensing mechanism is related to the formation and mobility of different polarons and charge transitions. For example, according to DFT studies <sup>[3]</sup>, the band gap in WO<sub>3</sub> phases increases with increasing distortion of the octahedral structure. However, for all phases studied (simple cubic, monoclinic P2<sub>1</sub>/m and P2<sub>1</sub>/c, and tetragonal P4-nmm and P4-ncc) the formation energies of oxygen vacancies are very similar; all of them induce states resonant with the conduction band (which is of predominantly W 5d character) <sup>[4]</sup>. The relationship between the structural composition (crystal symmetry), oxygen vacancy formation energy and gas sensing properties is not yet understood. Oxygen vacancy is a simply way to describe the WO<sub>3</sub> semiconducting properties (herein they act as donor levels) as well as to induce electron excess in WO<sub>3</sub>. The additional electron can be localised (small polaron), delocalised on a few ions (large polaron), or infinitively delocalised (conduction electron) <sup>[5]</sup>. Depending on the concentration of additional electrons (number of W<sup>5+</sup> centres), the additional electrons can be localised (small polarons), delocalised on few (large polarons) or infinite (conductive electrons) number of tungsten ions. Consequently, the relationship between the gas sensing properties (conductivity response to gaseous ambient) and oxygen deficiency has to be expected. Is there any relationship between catalytic properties (which mainly due to the W=O bonds) and gas sensing (oxygen deficiency)? How important is for WO<sub>3</sub> its ability to incorporate oxygen deficiency and to stabilise W<sup>4+</sup>/W<sup>6+</sup> or W<sup>5+</sup>/W<sup>6+</sup>, or W<sup>5+</sup>/W<sup>5+</sup> redox pairs? How does this ability influence its gas sensing properties?

The results of our experiments have not yet been completely evaluated. The main preliminary conclusions are as follows:

- a. WO<sub>3</sub> is a difficult material to study. It possesses a variety of crystalline phases; in many cases there are a mixture of two or more different phases in the samples studied (for example, coexistence of triclinic and monoclinic phases in WO<sub>3</sub> spacemens; two monoclinic phases – P2<sub>1</sub>/n and Pc in commercial (Aldrich 55,008-6) nanopowders; herein after the annealing at 600°C the P2<sub>1</sub>/n phase dominates; triclinic and monoclinic in WO<sub>3</sub> nanocrystals prepared from the tungstic acid (tungstite, WO<sub>3</sub>×H<sub>2</sub>O));
- b. phase transitions occur at operating temperatures of sensors (between r.t. and 500°C) independent of gas atmospheres studied;
- c. in 1D WO<sub>3</sub> nanostructures, a transformation from single-crystalline to polycrystalline structures (due to Rayleigh instability) occurs during the heating (between 400-500°C); this lead to the destruction of the 1D structures;
- d. a transformation from tetragonal (P-42<sub>1</sub>m) to orthorhombic (Pcnb) phase at ≈ 375°C, and then to tetragonal (P4/ncc) has been observed on polycrystalline pearl-necklace 1D samples.

The manuscript is currently under preparation and will be submitted for publication in 2010.

## References

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