

Metastable $\text{In}_4\text{Sn}_3\text{O}_{12}$ in Sensor Application

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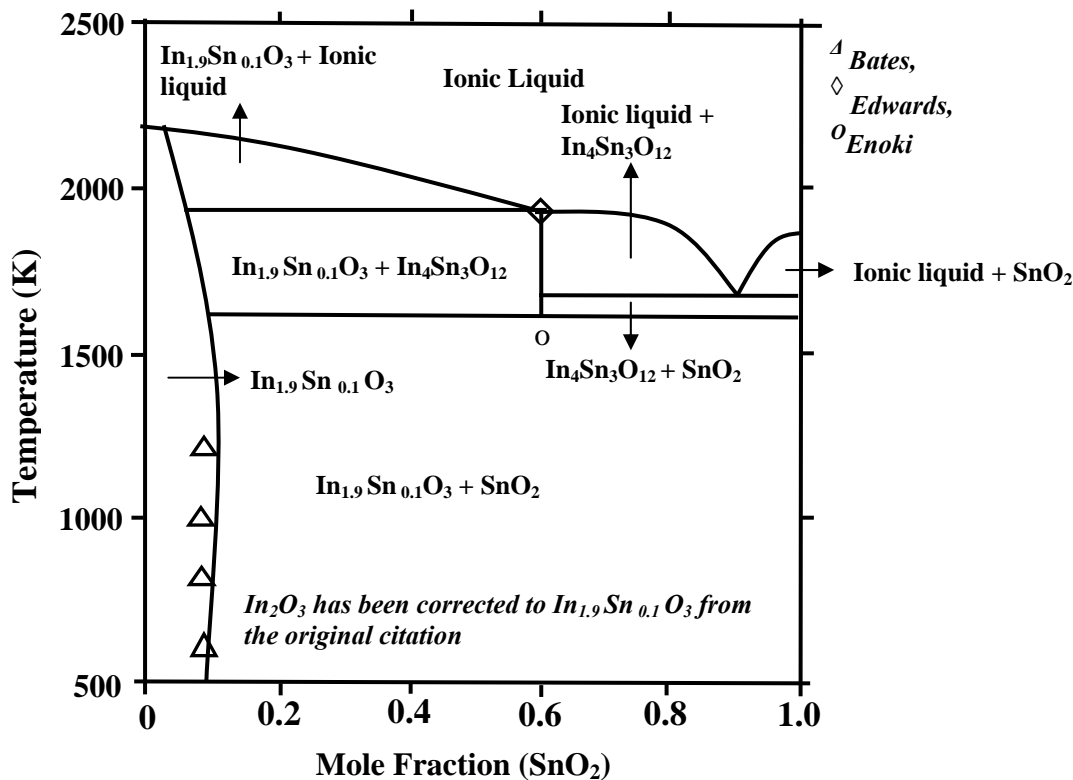
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Abstract

$\text{In}_4\text{Sn}_3\text{O}_{12}$ is considered as a high temperature phase of the binary In_2O_3 - SnO_2 mixture. As shown by Isomäki et al, this specific phase is stable in the temperature region of about 1.600 °C to, depending on the mole fraction, 1.950 °C.^[1] Furthermore, this phase can be found throughout almost the whole range of the mole fraction (0,1~1 SnO_2)(**Graph 1**). As a matter of fact, by applying Flame Spray Pyrolysis (FSP) to synthesize this ITO-like metal oxide, these temperatures are reached during combustion of the organometallic precursors. Rapid quenching of the nascent nanocrystalline particles results in the formation of a highly porous layer, solely containing particles of $\text{In}_4\text{Sn}_3\text{O}_{12}$, when combusting a solution containing 43 wt% Sn in In_2O_3 .

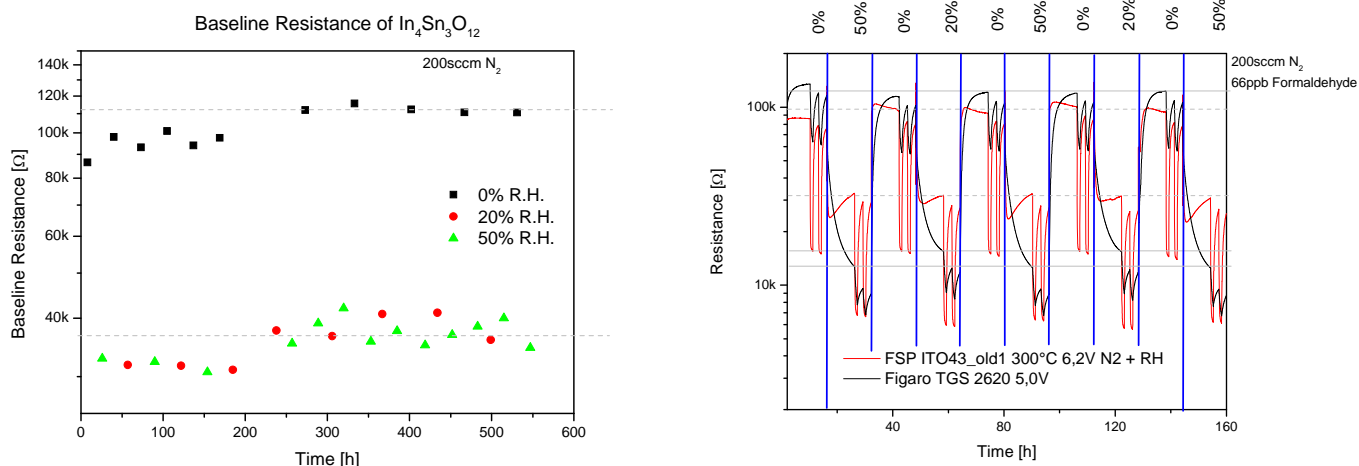
Applying this layer as a sensing layer for formaldehyde detection showed, that the reported phase is by far more stable at room temperature and operating conditions (200 - 350 °C) than expected. For the evaluation of the sensors stability, the baseline resistance as well as the evolution of the sensor signal over time is taken into account.



Graph 1 Binary phase diagram of In_2O_3 - SnO_2 as a function of temperature. $\text{In}_4\text{Sn}_3\text{O}_{12}$ is stable at high temperature.

1 Measurements with inert gas carrier

In an inert atmosphere of N_2 and alternating background of relative humidity up to 50%, the sensor works stable over a period of more than 300 hours as shown in **Graph 2**. The baseline resistance of the material in dry conditions is fluctuating as effect of minimal changes in the surrounding conditions (e.g. room temperature/relative humidity) but is stable around $110k\Omega$. Adding water vapor to the atmosphere leads to the formation of surface hydroxyl and an injection of electrons to the conduction band of the material.^[2] As a result there is a drop in the resistance observable. Interestingly this change in the resistance is not scalable, meaning there is almost no change when going from 20 to 50% r.h. Once the surface hydroxyl species are formed the surface seems to be occupied quickly. Having a look at the data observed on the reference sensor (Figaro TGS 2620, 5.0V; SnO_2 -based material) shows a clearly different behavior. Depending on the water concentration in the atmosphere, the resistance of the sensing device changes as shown in **Graph 2b**.

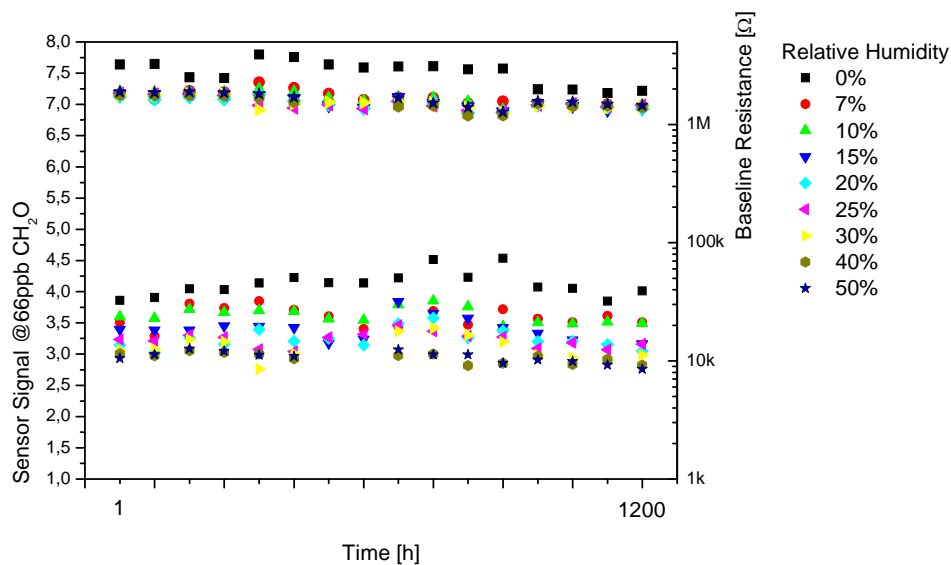


Graph 2 a) evolution of the baseline resistance at different backgrounds of relative humidity. b) evolution of the sensor response. black: Figaro TGS 2620 - reference; red: $In_4Sn_3O_{12}$.

2 Oxygen Background

Changing the atmosphere in terms of oxygen content, so switching to synthetic air, the sensors resistance increases as expected.^[2] Most properly the surface is getting covered with chemisorbed oxygen species (O^-) which results in a band bending and therefore a depletion layer. At dry conditions the sensor resistance therefore is around $1M\Omega$. Introducing humidity to the system, the resistance does not change much, which means that the ionosorbed oxygen is the major contributor here to the surface coverage under operation conditions.

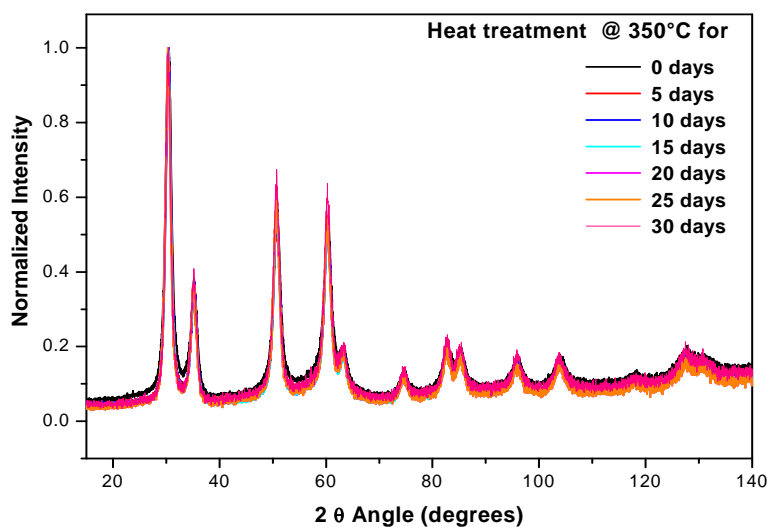
Testing the response to formaldehyde at different concentrations of water vapor in the background reveals that there is some kind of a competitive reaction of water and formaldehyde going on, since at wet conditions the response drops, as shown in **Graph 3**. The sensor signals are changing reproducibly in a very shallow window, but compared to standard SnO_2 sensors these changes are negligible. Looking at the stability of the baseline resistance and the sensor signal revealed that the sensor works reproducible for more than 1200h in the background of oxygen and water vapor.



Graph 3 Evolution of the baseline resistance (upper signals; right axis) and the sensor signal to 66 ppb formaldehyde (lower signals; left axis) and different .

3 Stability of the Powder

To validate these finding under operando conditions, XRD studies were performed on the powder material itself. The nascent In₄Sn₃O₁₂ nanoparticles were collected on a glass fiber filter, isolated and than stored at 350°C in air over a period of one month. To proof the stability, consecutive XRD measurements were made. As shown in Graph 4, the XRD analysis did not show any sign of decay of the material, the diffraction pattern did not change at all.



Graph 4 Evolution of the X-ray diffraction pattern of the FSP generated powder (In₄Sn₃O₁₂), stored at 350°C in air and consecutive control measurements.

Conclusion

In this research we show that it is possible, by utilizing FSP as method to synthesize, to quench a meta stable phase which responds quite well to an atmosphere containing formaldehyde. Furthermore the phase is stable under operation conditions, which makes it a possible candidate for further industrialization.

The here presented findings lead to the conclusion that $\text{In}_4\text{Sn}_3\text{O}_{12}$ is a metastable phase, stable at room- and elevated temperatures up to 350°C for prolonged time, making it suitable to be used in sensor applications. Looking at the different behavior in terms of interferant such as water and oxygen, compared to SnO_2 and WO_3 , leads to the assumption that the sensing mechanism related to $\text{In}_4\text{Sn}_3\text{O}_{12}$ may be quite different from the mechanisms established for the latter two prototype materials. So there is still much workload ahead to reveal the sensing mechanism concerning this specific binary oxide.

All in all, we can conclude that the material is stable, since all measurements presented herein were carried out on the same sensing element and are still going on.

Hopefully this research opens a new field of investigation on this specific and on other ternary phases in terms of selectivity and sensing mechanisms and therefore the gain of new, useful material for gas sensing applications.

Literature

- [1] I. Isomaki, M. Hamalainen, W. Gierlotka, B. Onderka, K. Fitzner, *J. Alloys and Compounds* **2006**, 422, 173.
- [2] D. Koziej, N. Barsan, U. Weimar, J. Szuber, K. Shimanoe, N. Yamazoe, *Chemical Physics Letters*, **2005**, 410, 321-323.