European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

WGs and MC Meeting at Cambridge, 18-20 December 2013

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Year 2: 1 July 2013 - 30 June 2014 (*Ongoing Action*)

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WG1: work plan objectives

1.Protocols for synthesis of gas sensitive nanomaterials.
2. Protocols for synthesis of functionalized nanostructures for enhanced gas detection at partper-billion (ppb) level, stability and selectivity.

WG1 – Deliverables

Overview of the current state-of the-art on gas sensor materials and advanced nanostructures.

IMNR contribution:

- IMNR manufactures by wet chemical synthesis in hydrothermal conditions (low temperature and high pressures with low cost production) complex perovskite nanostructured materials (Cu, La,Cr doped $BaSrTiO_3$)
- Based on our previous experience in national and EU projects, in IMNR - Nanostructured Materials Lab. graphite, carbon nanotubes or even graphene can be functionalised using hydrothermal procedure in one step.
- IMNR elaborated an overview of the current state of the art regarding doped $BaSrTiO_3$(BST) materials with potential in gas detection.

Overview of the current state of the art – doped BST materials

Current state of the art	IMNR contribution
Yan et al. *[1]* obtained composite nanofibers based on $Ba_{0.8}Sr_{0.2}TiO_3$/PVP (poli)vinil pirolidona. The composite was calcinated at 800 C for 2 h and presented excellent sensorial properties in humidity detection at room temperature.	Hydrothermal synthesis
$BaSrTiO_3$ with initial Ba composition of 75,80,85 mol % were prepared by a high temperature hydrothermal synthesis. The powders were pressed into pellets, sintered at 300 ^{0}C for 3 h. Dielectric constant increased with increasing Ba content. [2]	Low cost of production
Thick films of BST were prepared by screen-printing technique. The films were surface customized by dipping them into aqueous solutions of $CuCl_2$ and CrO_3 for various intervals of time. These surface modified BST films showed improved sensitivity to H_2S gas (100 ppm) than pure BST film.	Dopant is directly introduced in the BST structure

References:

1. Yan Xia, Teng Fei, Yuan He, Rui Wang, Fan Jiang, Tong Zhang , Preparation and humidity sensing properties of Ba0.8Sr0.2TiO3 nanofibers via electrospinning, Materials Letters 66 (2012) 19–21

2. K.A.Razak, A. Asadov, J. Yoo, E. Haemmerle, W.Gao, Structural and dielectric properties of barium strontium titanate produced by high temperature hydrothermal method, Journal of alloys and Compounds 449 (2008) 19-23.

3. G H JAIN and L A PATIL, Gas sensing properties of Cu and Cr activated BST thick films, Bull. Mater. Sci., Vol. 29, No. 4, August 2006, pp. 403–411.

Current research activities

Doped $Ba_xSr_{1-x}TiO_3$ nanostructured materials with potential for H_2S detection

Cu doped $BaSrTiO_3$ (BST) nanostructured materials were synthetized in one step, by a hydrothermal procedure at low temperature (< 200 ^{0}C) and high pressure (200 atm). The as obtained powders were characterized by chemical analysis to determine composition, XRD and TEM analysis to determine morphology and microstructure. The presence of Cu in the BST structures can be revealed by the difference of morphology that exists between pure BST and Cu doped BST. Cu doped BST is a nanostructured materials, TEM analysis revealed a mixture of two components, a rounded shape crystalline one (100-200nm) and a partial cristalline one (5-10nm) (figure 2).

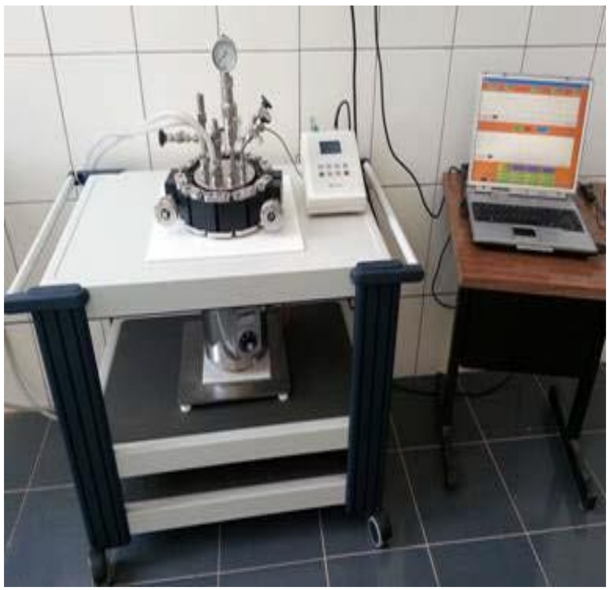


Figure 1. Berghoff autoclave 5 L

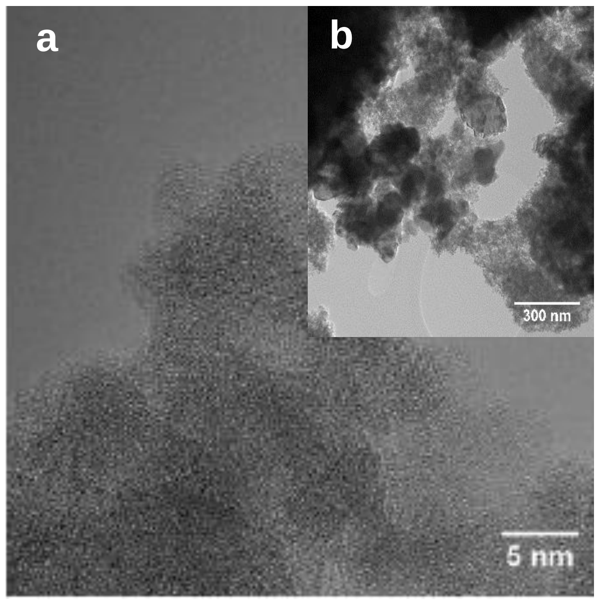


Figure 2. TEM analysis of a) BaSrTiO3 Cu1 and b) BaSrTiO3 Cu5

Figure 3. Gas sensor model obtained by lithography.

Current research activities

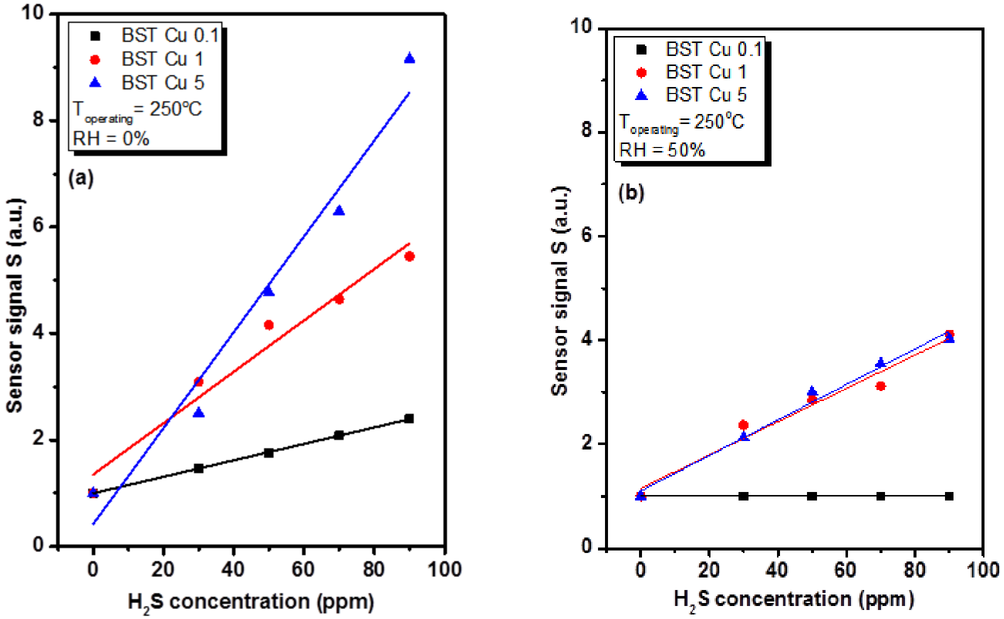


Fig. 4 Sensor signal as H_2S dependence (a)dry and (b)humid air

Gas-sensing properties were investigated through electrical resistance measurements.
The measurements were performed under dynamic flow regime, using a computer controlled Gas Mixing Station supplied with high purity 5.0 calibrated gases. The relative humidity (RH) of the synthetic air could be also controlled within 0 and 50% as average ambient surrounding.

The H_2S detection potential of BST nanostructured materials depend on Cu amount of doping and on RH as well. Figure 4a highlights both the linear dependence for all three samples and the relevance of Cu amount. Figure 4a and b proved the applicative potential of BST Cu doped at 250°C as operating temperature, especially in dry air.

Future works:

To obtain thin films of doped BST by RF sputtering on the sensorial structure.

Research Facilities

New Centre for Intensification of Metallurgical Processes at High Pressures & Temperatures –High PT Met
Project financed by Structural Funds for Research Infrastructures

High pressure Research Infrastructure

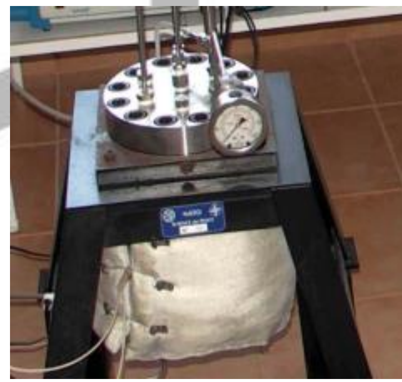
High pressure autoclave (4000 bar)

Spray-dry

High Temperature Research Infrastructure

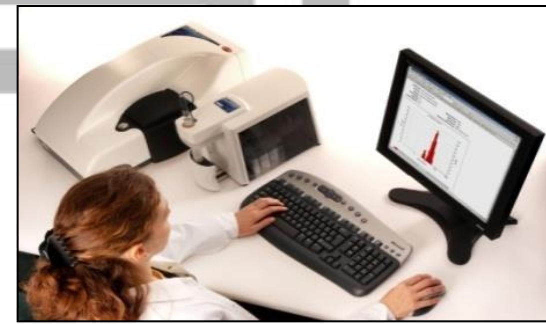
5-electron guns furnace, Torr SUA

Research Facilities

Hydrothermal system high capacity autoclave

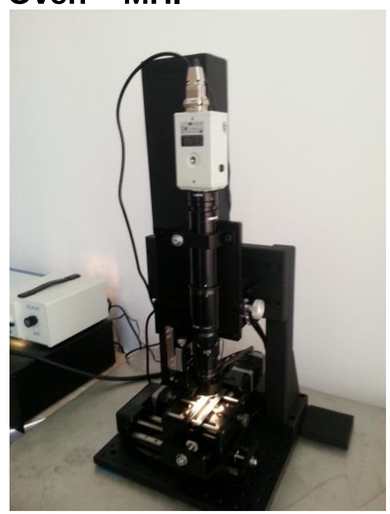
Controlled atmosphere
Oven – MHI



Zetaseizer Malvern

DSC Netzsch Maya F200

AAS ZEEnit 700
Analytik Jena



Scratch test Nanovea

D8 XRD Bruker diffractometer

In the field of sensing materials to detect hazardous gases the following research directions priorities in conection with TD 1105 aim are:

- **To establish nanostructured materials requirements together with WG1 members, for a large group of hazardous gases.**
- **Mechanism at the interface between perovskite sensor and gas should be more investigated and assessed. (thick films versus thin films - e.g. doped BST)**

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