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# Impact of Microstructure on Humidity Influence on Complex Impedance of Iron Manganite

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**Abstract:** *This work deals with our continued research of oxide materials for potential application in gas/humidity sensing. We have made thick film samples using iron manganite powder synthesized by a sol-gel combustion method with a net-like structure, by screen printing on alumina substrate with PdAg interdigitated electrodes. The thick film samples were fired at two temperatures 600 and 800 °C. The powder morphology was retained and only the organic compounds in the paste were burnt-out at 600 °C, while at 800 °C the thick film surface morphology was different where grain growth and individual particles can be observed. We measured complex impedance in a temperature and humidity chamber at room temperature (25 °C) in the relative humidity range 30–90% and frequency 100 Hz – 1 MHz. The thick film surface morphology has a significant influence on the effect of humidity on complex impedance. The complex impedance of thick films fired at 600 °C was high and did not decrease noticeably with increase in relative humidity (RH), except for RH 80 and 90%, while thick film samples fired at 800 °C had an overall lower impedance that reduced more noticeably with increase in RH 40–70% and even more for RH 80 and 90%.*

## 1. INTRODUCTION

The operating principle of resistive-type oxide gas sensors is based on the change of resistance or conductance due to interactions between the oxide material and target gaseous compound [1, 2]. Thus the morphology and microstructure of oxide materials play a very important role in the gas sensing performance. The basic characteristic of nano-structured materials is a larger surface exposed to gas adsorption. Many synthesis techniques have been used to obtain oxide gas sensing materials resulting in different morphologies that have an influence on the gas sensing properties.

Iron manganite ( $\text{FeMnO}_3$ ) is an oxide with a cubic structure, known as bixbyite. Investigation of this material as bulk ceramics has shown that it can be a potential humidity sensing material [3]. We have previously investigated iron manganite powder obtained by solid state synthesis [4] in the form of screen-printed thick films [5] and confirmed that this oxide has potential in humidity sensing. We showed

that a porous structure was obtained with a relatively uniform particle distribution and average size of 495 nm. In this work we have analyzed how the thick film microstructure reflects on the change of complex impedance with relative humidity. We used iron manganite powder obtained by a sol-gel combustion method with a different morphology [6] in thick film samples fired at two temperatures and compared these two thick film morphologies with the thick film morphology analyzed in [5], to see whether we could obtain enhanced humidity sensing properties by changing the powder synthesis method.

## 2. MATERIALS

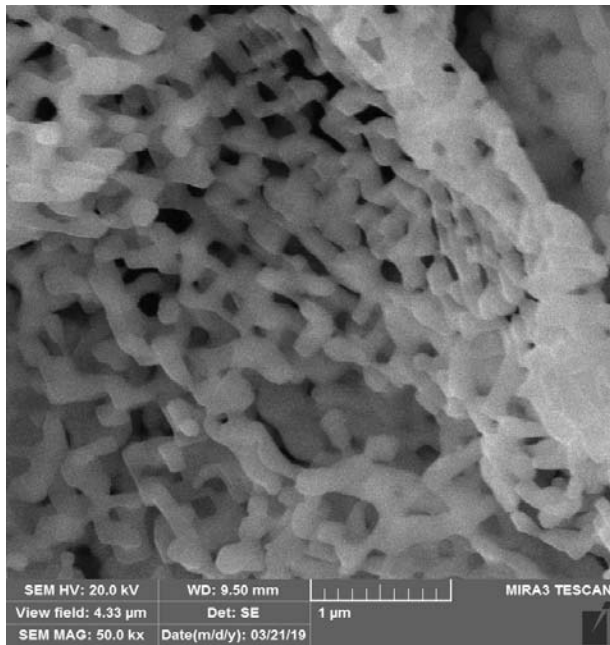
### 2.1 Powder synthesis and characterization

Nanocrystalline iron manganite powder was obtained by sol-gel combustion synthesis applying the method described in detail in [6]. X-ray diffraction (XRD) analysis of the synthesized powder confirmed the formation of iron manganite with a bixbyite cubic structure ( $Ia\bar{3}$ ) as described in detail in [6]. The

nanocrystalline powder morphology was observed by FESEM (TESCAN MIRA3 XM FESEM device) showing that the  $\text{FeMnO}_3$  powder had a net-like structure composed of plate-like particles. An example is shown in Fig. 1. The powder had a small specific surface area determined by the Brunauer-Emmet-Teller (BET) method from measured nitrogen isotherms, and a macroporous structure as described in detail in [6].

## 2.2 Thick film characterization

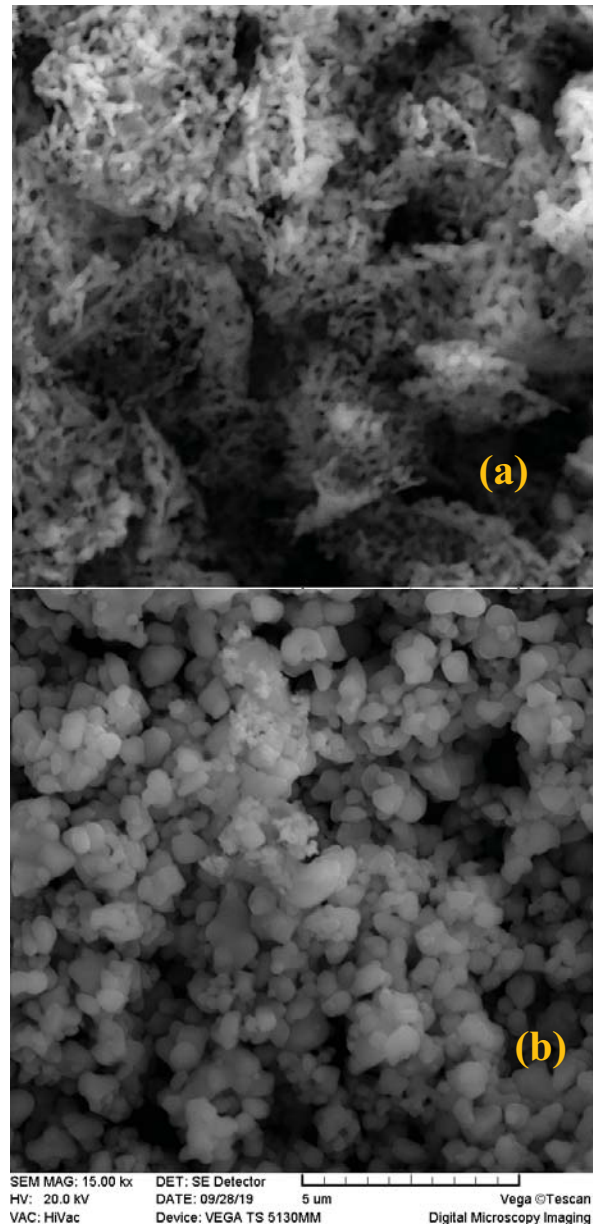
Thick film paste was made by adding organic vehicles to the obtained powder using the procedure described in detail in [7, 8]. Two layers (estimated average layer thickness 12–15  $\mu\text{m}$ , resulting in a 24–30  $\mu\text{m}$  thick film) were screen printed on alumina substrate with previously prepared test interdigitated PdAg electrodes (the same as in [5]), using the method described in detail in [8]. The thick film samples were fired at 600 and 800  $^\circ\text{C}$  for 3 h. Samples for Hall measurement and film thickness estimation were prepared in the same way, but two layers of thick film paste were screen printed on plain alumina substrate and fired at 800  $^\circ\text{C}$  for 3 h.



**Fig. 1.** FESEM image of synthesized iron manganite ( $\text{FeMnO}_3$ ) powder

Analysis of the surface of thick film samples fired at 600 and 800  $^\circ\text{C}$  by SEM (TESCAN Electron Microscope VEGA TS 5130MM) showed that the powder structure was retained at the lower firing temperature and still resembled a “net-like” structure

of connected particles and macro pores between them. The higher firing temperature resulted in grain growth, and formation of a structure consisting of individual particles with some neck formation between them, agglomerated particles and also clusters of small particles, indicating advancement of the sintering process (Fig. 2). For both firing temperatures (600 and 800  $^\circ\text{C}$ ), no closed pores within the particles could be observed on the thick film surface.



**Fig. 2.** SEM images of iron manganite thick film sensor sample surface fired at 600  $^\circ\text{C}$  (a) and 800  $^\circ\text{C}$  (b)

The pores between particles are most probably macropores or interparticle voids, as this was observed

in textural characterization of the synthesized powder from nitrogen adsorption/desorption isotherms and mercury (Hg) porosimetry measurements [6]. The powder morphology obtained at the higher firing temperature (800 °C) is more similar to the one we previously obtained for thick film samples of iron manganite powder obtained by solid state synthesis also fired at 800 °C [5].

The average film thickness (of the two screen printed thick film layers) was measured on an Optical Profilometer (HRM-300 Huvitz Upright Microscope with Panasis software). It was estimated to be 27 μm, and is shown in Fig. 3. This film thickness estimation was in accordance with previous estimations from FESEM images of the thick film cross-section (average layer thickness 12–15 μm) [9].

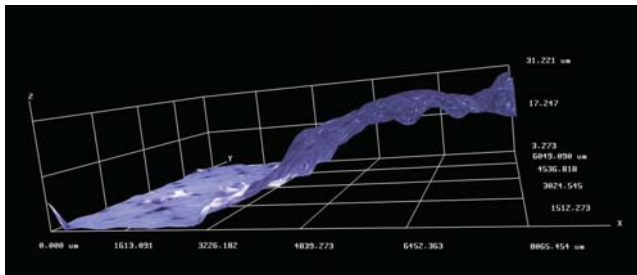


Fig. 3. Optical profilometer image of thick film sample, estimated film thickness 27 μm

Hall measurements at room temperature (Ecopia HMS-Hall effect measurement system) with an applied field of 0.37 T and current of 1 nA enabled determination of the carrier mobility  $\mu$  as 47.92 cm<sup>2</sup>/Vs, bulk concentration 9.609·10<sup>9</sup>/cm<sup>3</sup>, resistivity 1.356·10<sup>7</sup> Ωcm and average Hall coefficient 6.496·10<sup>8</sup> cm<sup>3</sup>/C.

### 3. INFLUENCE OF CHANGE IN RELATIVE HUMIDITY ON COMPLEX IMPEDANCE

Complex impedance of iron manganite thick film samples was measured in a temperature and humidity climatic chamber (JEIO TECH TH-KE-025) in the frequency range 100 Hz–1 MHz. We varied the applied voltage in the range 1–5 V at working temperatures of 25 °C (Relative Humidity - RH 30–90%), for samples fired at 600 and 800 °C. There is a significant difference in the measured complex impedance for the two applied firing temperatures. The firing temperature of 600 °C enabled burning-out of the organics present in the thick film paste, but the

morphology of the synthesized powder was retained (as shown in Fig. 2). The measured complex impedance was high, and almost did not change with increase in RH, except in the case of high RH of 80 and 90%, as shown in the example given in Fig. 4.

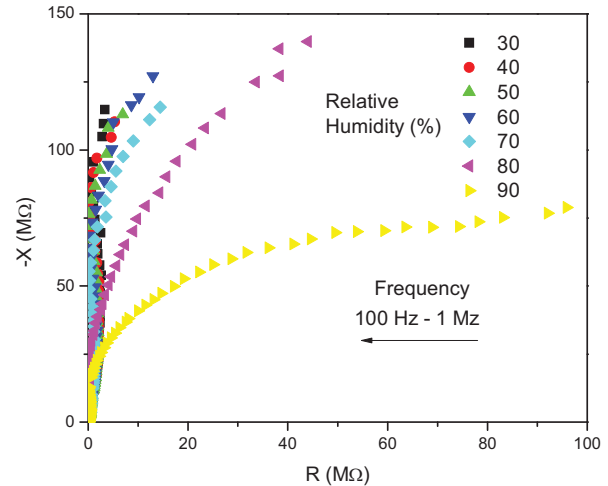


Fig. 4. Complex impedance of iron manganite thick film sample fired at 600 °C at 25 °C for RH 30–90%, applied voltage 1 V.

When the firing temperature was higher (800 °C), partial sintering of particles and grain growth occurred. The complex impedance was overall lower, and reduced more noticeably with increase in RH, though less for RH 40–70%, and much more noticeably for RH 70–90%, especially for RH 80–90%, where there is a very rapid decrease, as shown in the example in Fig. 5. So in both cases very high RH (80 and 90%) noticeably reduces the impedance.

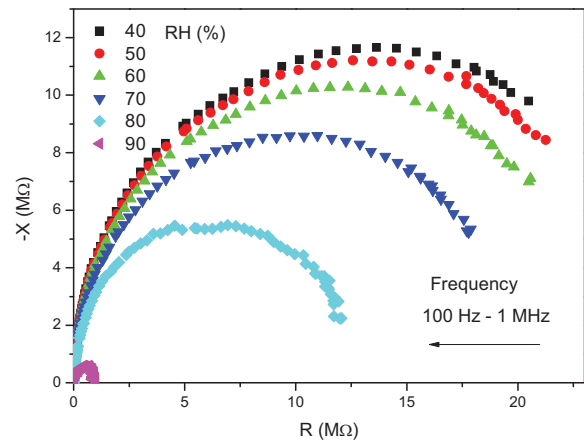
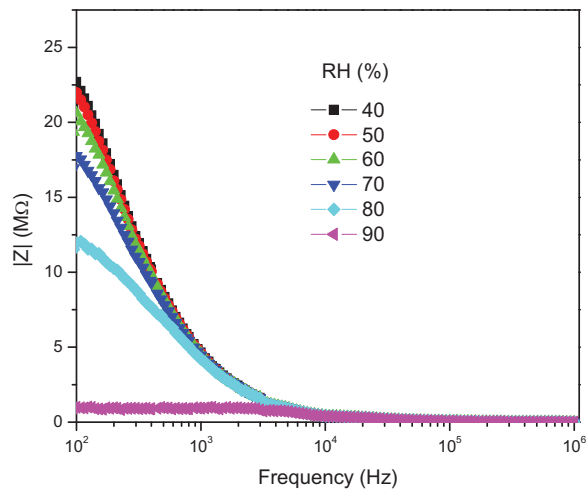


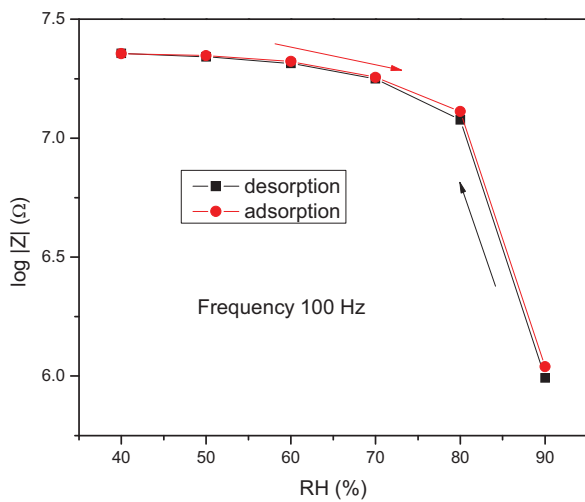
Fig. 5. Complex impedance of iron manganite thick film sample fired at 800 °C at 25 °C for RH 40–90%, applied voltage 5 V.

Fig. 6 shows impedance reduction with frequency as previously observed for iron manganite [5], higher in the lower frequency range, also as observed before. The difference is the much more noticeable reduction for higher relative humidity values of 80 and especially 90%, compared to the change in impedance noted for iron manganite obtained by solid state synthesis where the thick film surface reacted to smaller relative humidity [5].



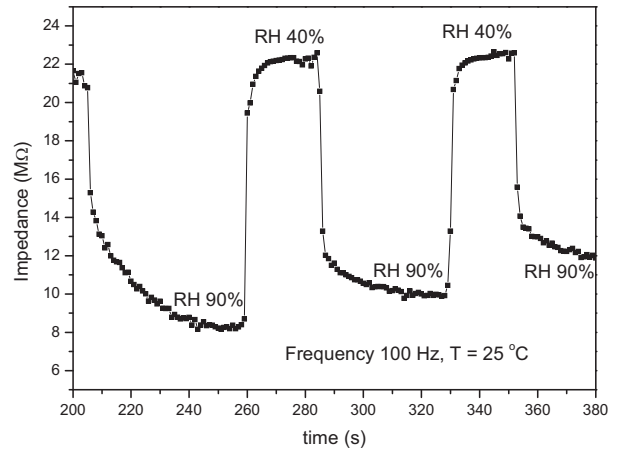
**Fig. 6.** Change of impedance with frequency in the RH range 40–90% for an iron manganite thick film sample fired at 800 °C, applied voltage 5 V

Adsorption/desorption curves measured at 100 Hz are given in Fig. 7, showing that the hysteresis value was low, below 2%.



**Fig. 7.** Absorption/desorption (hysteresis) curves measured at 100 Hz and 25 °C for an iron manganite thick film sample fired at 800 °C

Response/recovery measured at 100 Hz for change in relative humidity 40–90% is shown in Fig. 8. Though the response and recovery are relatively fast (under 10 s) what is noticeable is a baseline resistance drift that has been a well-known issue for metal oxide sensor devices [2]. This was not noted for iron manganite thick film samples made from the powder obtained by solid state synthesis [5].



**Fig. 8.** Response and recovery curves measured at 100 Hz and 25 °C for an iron manganite thick film sample fired at 800 °C, applied voltage 5 V

The noticeable difference in the thick film samples analyzed in this work made from iron manganite powder obtained by combustion synthesis compared to iron manganite thick film samples made using the powder obtained by solid state synthesis [5], is that the combustion synthesis method produced smaller particles, but a powder and thick film morphology that reacted notably with humidity only for high RH values. This is closely related to the gas/humidity sensing mechanism of oxide materials, where the material surface interacts with gas/water molecules [3, 9]. At lower RH chemisorption takes place, followed by physisorption, as RH increases. The thick film morphology obtained at 800 °C with noticeable macroporosity and larger particles responds with a decrease in impedance to increase in RH in the range 40–70%, while the net-like morphology of the thick film obtained at 600 °C does not. For high RH this process results in the formation of a liquid-like network of multilayers of physisorbed water in which protons move freely. This is accompanied by an increase in ionic conductivity and this is very noticeable for the thick film morphology analyzed in this work. This confirms that the oxide material

microstructure morphology has a significant influence on how it reacts to humidity and possibly other gaseous compounds.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] A. Mirzaei, B. Hashemi, K. Janghorban, “ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> based nanomaterials as gas sensors”, *J. Mater. Sci.: Mater. Electron.* Vol. 27, 2016, pp. 3109-3144
- [2] D. Zappa, V. Galstyan, N. Kaur, H. M. M. Munasinghe Arachchige, O. Sisman, E. Comini, “Metal oxide-based heterostructures for gas sensors – A review”, *Anal. Chim. Acta*, Vol. 1039, 2018, pp. 1-23
- [3] L. Leontie, C. Doroftei, A. Carlescu, “Nanocrystalline iron manganite prepared by sol-gel self-combustion method for sensor application”, *Appl. Phys. A*, Vol. 124, 2018, pp. 7501-8
- [4] M. V. Nikolic, M. D. Lukovic, N. Labus, “Influence of humidity on complex impedance and dielectric properties of iron-manganite (FeMnO<sub>3</sub>)”, *J. Mater. Sci.: Mater. Electron.*, Vol. 30, 2019, pp. 12399-12405
- [5] M. V. Nikolic, M. D. Lukovic, M. P. Dojcinovic, Z. Z. Vasiljevic, N. Labus, “Application of iron manganite thick films for humidity sensing”, Proceedings of the International Spring Seminar on Electronics Technology, 2019-May 8810291
- [6] Z. Z. Vasiljevic, M. P. Dojcinovic, J. B. Krstic, V. Ribic, N. B. Tadic, M. Ognjanovic, S. Auger, J. Vidic, M. V. Nikolic, “Synthesis and antibacterial activity of iron manganite (FeMnO<sub>3</sub>) particles against the environmental bacterium *Bacillus subtilis*”, *RSC Advances*, Vol. 10, 2020, pp. 13879-13888
- [7] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, M. Graetzel, “Fabrication of screen-printing pastes from TiO<sub>2</sub> powders for dye-sensitized solar cells”, *Prog. Photovolt. Res. Appl.*, Vol. 15, 2007, pp. 603-612
- [8] M. V. Nikolic, Z. Z. Vasiljevic, M. D. Lukovic, V. P. Pavlovic, J. B. Krstic, J. Vujanecvic, N. Tadic, B. Vlahovic, V. B. Pavlovic, “Investigation of ZnFe<sub>2</sub>O<sub>4</sub> spinel ferrite nanocrystalline screen-printed thick films for application in humidity sensing”, *Int. J. Appl. Ceram. Technol.* Vol. 16, 2019, pp. 981-993
- [9] M. V. Nikolic, Z. Z. Vasiljevic, M. D. Lukovic, V. P. Pavlovic, J. Vujanecvic, M. Radovanovic, J. B. Krstic, B. Vlahovic, V. B. Pavlovic, “Humidity sensing properties of nanocrystalline pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>) based thick films”, *Sens. Actuator. B.: Chem.* Vol. 277, 2018, 654-664