

LaNi_xFe_{1-x}O₃ thin films: *p*-type ethanol sensors

C. Garzella, G. Sberveglieri
*I.N.F.M. and Dept. of Chemistry
and Physics for Materials -
University of Brescia, 25133
Brescia-Italy
garzella@tflab.ing.unibs.it*

E. Bontempi, L.E. Depero
*I.N.S.T.M. and Structural
Chemistry Laboratory,
University of Brescia, 25133
Brescia-Italy
depero@bsing.ing.unibs.it*

Abstract

*Sol-gel LaNi_{0.25}Fe_{0.75}O₃ thin films were deposited by means of spin-coating. After three depositions on allumina substrates, the films were annealed at 873 K. The films morphology was observed by AFM. The structural characterization was performed by means of Wide Angle X-ray diffraction (WAXRD), Glancing Incidence X-Ray diffraction (GIXRD), and microdiffraction. The gas sensing response for two alcohol were tested. The results show that LaNi_{0.25}Fe_{0.75}O₃ thin films have a *p*-type response and may be a good candidate to detect low ethanol concentrations.*

1. Introduction

LnTO₃ (Ln = rare earth and T = transition metal) phase generally have a distorted perovskite-type of structure. They are typically *p*-type semiconductor, in which substitution of low valence cations produces additional mobile anion vacancies [1]. They often exhibit highly non-stoichiometry compositions, that make these oxides particularly attractive for many technological application, as for example, for sensors devices. Indeed, different LnTO₃ phases were proposed for detection of humidity [2], alcohol [3], oxygen [4], CO [5], and NO [6].

For the preparation of LnTO₃ phases, several methods have been proposed, including sol-gel, hydrothermal treatments, pyrolysis or combustion, thermal decomposition of wet-chemically precipitation and sputtering [7-12].

The chemical route results very suitable for sensible films deposition. Until now, almost all studies about these compounds have been performed on single crystals and powders obtained by solid-state reactions [13]. This technique has several drawbacks, like poor phase homogeneity and scarce control of the particle size. On the contrary, sol-gel preparations present several advantages like low processing temperatures, and control of the stoichiometry, size and shape of the particles [14].

In a recent paper [15], we reported the characterisation of LaNiO₃, LaFeO₃ and their solid solution LaNi_{0.3}Fe_{0.7}O₃ powders, prepared by sol-gel. For treatments at temperatures lower than 1023 K, both LaFeO₃ and LaNi_{0.3}Fe_{0.7}O₃ phases were indexed by a cubic structure, while for high temperature treatments (1173 and 1273 K) reflections characteristic of the orthorhombic phase were detected.

In this study the structural and electrical properties of LaNi_{0.25}Fe_{0.75}O₃ thin films, prepared by sol-gel and deposited by spin-coating, are described. In particular it is shown that this material, differently from powders, is poorly crystallised after the treatment at 873 K. Indeed the crystallisation of the film is complete only after a thermal treatment at 1023 K. Moreover preliminary results on sensor activity are reported from which it appears that these films are potential candidate for use as ethanol sensor.

2. Preparation method

The preparation of LaNi_{0.25}Fe_{0.75}O₃ was carried out starting from three precursor solutions. Lanthanum(III)acetate hydrate 5.05 g, nickel(II)acetatetetrahydrate 0.095 g and iron(III)citrate 3.15 g were separately dissolved in water. A little amount of propionic acid was added to the first solution for favoring salt dissolution. The three solutions were then mixed together and appropriate amount of citric acid (1 equivalent of citric acid per equivalent of cation) was added. Ammonia was also added in order to have all the components in solution.

Film deposition by spin-coating were performed onto of 3×3 mm² (250 μm thick) and 10×10 mm² (500 μm thick) allumina substrates for electrical and structural characterisation, respectively. On the former substrates platinum interdigitated system and bonded gold contacts were deposited. After the deposition by SCS 8'' Desk-Top Precision Spin Coating System Model P-6708D, films were heated at 773 K for 4 hours in air. Film deposition and annealing treatment were repeated for three times. The last thermal treatment was at 873 K.

3. Structural characterization

3.1. Morphology

The morphological characterisation was obtained by the high resolution Autoprobe CP-Research model AP-2001 from Thermomicroscopes. All the analyses were performed in the contact mode.

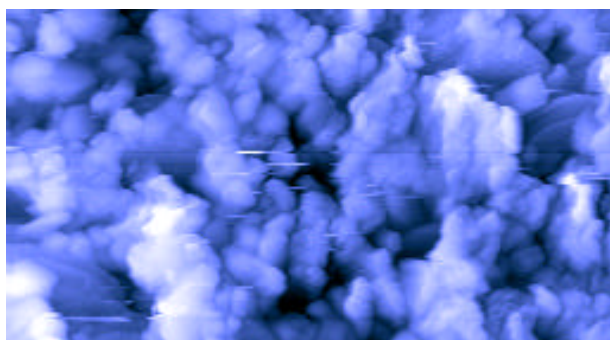


Figure 1. AFM image of a LaNi_{0.25}Fe_{0.75}O₃ thin film (y axis = 60 micron).

Figure 1 shows an AFM image of the LaNi_{0.25}Fe_{0.75}O₃ thin film (Y axis = 60 micron).

The layer appears homogeneous and porous. The particles sizes were estimated to be between 100 and 150 nm. Since the absorption is related to the films surface area, these morphological features make this material suitable for gas sensing applications.

3.2. Microstructure

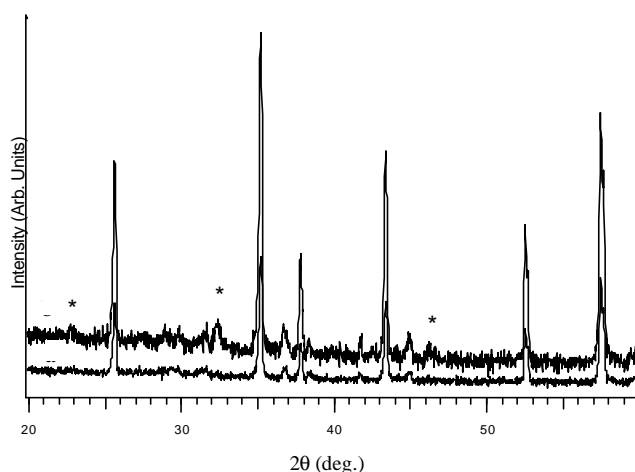


Figure 2. GIXRD spectra collected at 1° of incidence for the sample a) as deposited (see preparation method) and b) annealed at 1023 K for 15 hours. The stars indicate the LaFeO₃ perovskite phase peaks (JSPDS, card n° 742203) [16].

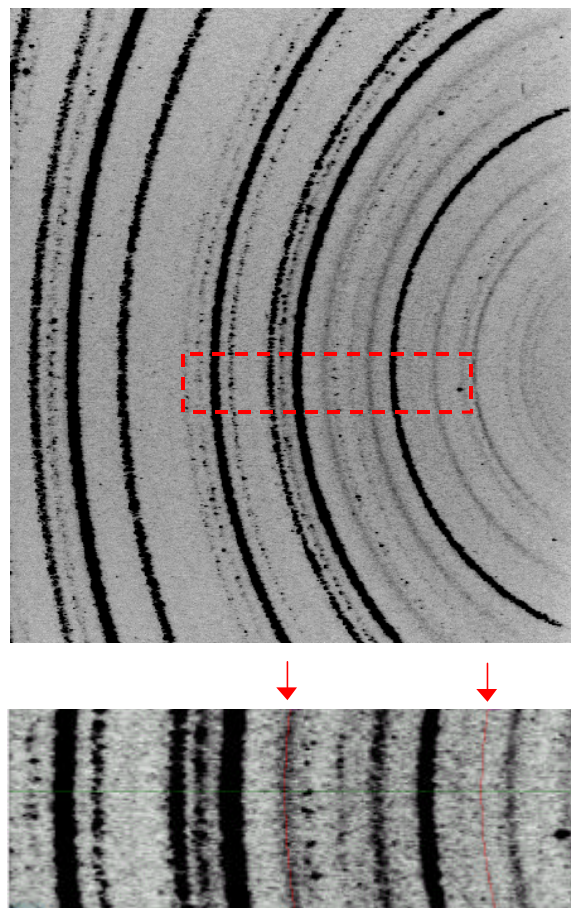


Figure 3. X-Ray microdiffraction 2D image, obtained on the LaNi_{0.25}Fe_{0.75}O₃ film, with an incidence angle of 1°. X-Ray Microdiffraction employs an x-ray beam focused in a spot of 300 µm and combined with a 2-dimensional image-plate detector. The bottom figure is a magnification of the selected area. It shows the main LaFeO₃ peaks (at 2θ = 32.1 and 46.2°).

Wide Angle X-ray diffraction (WAXRD) and Glancing Incidence X-ray diffraction (GIXRD) spectra were collected by a Bruker “D8 Advance” diffractometer equipped with a Göbel mirror. The angular accuracy was 0.001° and the angular resolution was better than 0.01°.

The X-Ray Microdiffraction spectra were collected by a D/max-RAPID Rigaku microdiffractometer, equipped with the cylindrical imaging plate (IP) detector. The collimator spot was 300 µm.

In WAXRD spectrum, not reported here, only the substrate peaks were detected.

Fig 2a show the GIXRD spectra collected at 1° of incidence for the LaNi_{0.25}Fe_{0.75}O₃ sample. Also on the GIXRD pattern only the Al₂O₃ substrate peaks were detected. To verify possible preferred orientation, X-Ray diffraction was performed by the microdiffractometer.

Fig. 3 shows the 2D patterns for a $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ sample, collected with the incidence angle of 1° . The magnification of Fig. 3 (bottom figure) shows the main LaFeO_3 peaks (at $2\theta = 32.1$ and 46.2°), indicating that a small amount of perovskite phase is crystalline. The image shows also that Debye rings have similar intensity in all directions. This amount was not detectable with GIXRD technique.

Sample homogeneity was verified by performing microdiffraction spectra in different points.

The pattern shown in Fig. 2b was collected on the $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ sample after the annealing at 1023 K for 15h: the LaFeO_3 perovskite phase was identified (JSPDS, card n° 742203) [16]. Thus the annealing process produces a well-crystallised film.

4. Electrical characterisation

We tested the gas sensing response of these materials towards two alcohol (methanol and ethanol) also in presence of interfering gases as nitrogen dioxide and carbon monoxide. Details on the experimental set-up, based on the flow-through technique, are reported elsewhere [17]. Constant flow of synthetic air of 0.3 l/min was used as gas carrier and the desired concentrations of pollutants were obtained mixing the certified gas with the synthetic air. All the measurements were made under controlled humidity (RH 30%) and the temperature of the chamber containing the sensors was set at 293 K.

The changes in the electrical properties due to variations of the atmosphere were measured by the Volt Amperometric technique. We applied a constant potential of 5 V to the sensing layer and the picoammeter detects the conductance variation as a function of time. Both the gas flow and the electrical parameters were controlled by a PC, which also registers the conductance change of the sensors.

Gas measurements were made at constant temperature and the gases concentrations were varied for ethanol and methanol in the range 30-100 ppm. The working temperature was varied in the range between 673 K and 773 K, since during preliminary measurements no appreciable response was registered below 623 K.

Figure 4 reports the dynamic response of the $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ thin films as increasing concentrations of ethanol were introduced in the test chamber at 773 K and 30% RH. In these tests, the relative change of the resistance was high (40% for 30 ppm EtOH, 60% for 50 ppm and 80% for 100 ppm). The current decreased when the gas was introduced, pointing out a *p-type* behaviour. The measurements highlighted that these films were stable and that the recovery of the signal was complete when the air flux was restored after the gas test.

The dynamic of these sensors was very fast as it can be noticed in Fig. 4. The response and recovery times

were defined as the times the conductance takes to reach 90% of $(R_f - R_0)$ when the gas was introduced and to recover 30% of $(R_f - R_0)$ when the flux of air was restored. The response and recovery times for ethanol were respectively about one minute and two minutes at 673 K and 773 K. Very fast response was observed at 723 K (response time for 100 ppm ethanol was 18 sec).

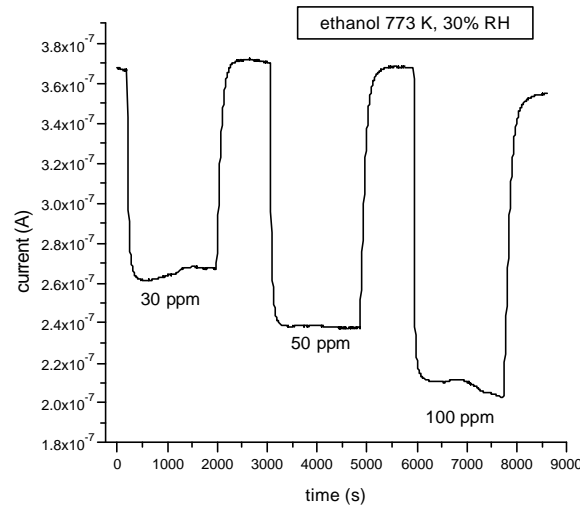


Figure 4. Dynamic response of the $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ thin films towards different concentrations of ethanol at 773 K, 30% RH.

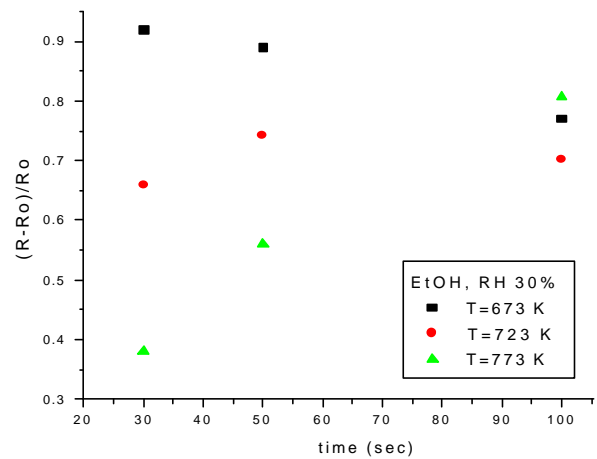


Figure 5. Trend of the $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ film response vs. ethanol concentration at three different temperatures.

The behavior of the response at different temperatures was also investigated. Figure 5 reports the response obtained at three different temperatures versus ethanol concentration.

As seen, the best sensing properties were obtained at 673 K. The response versus concentration is quite flat, but for the highest temperature.

No appreciable response was observed for the other gases tested. Thus, $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ thin film seems a selective sensor for ethanol.

5. Conclusions

Sol-gel $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ thin films were prepared by spin-coating. The deposited layers are nanostructured and porous.

Both WAXRD and GIXRD techniques were not able to detect the film phase, while the microdiffraction technique allowed to conclude that only a small amount of the as deposited film was crystalline.

After the annealing at 1023 K for 15 hours the film completely crystallized in the perovskite phase (JSPDS, card n° 742203 [16]).

The electrical characterization showed that $\text{LaNi}_{0.25}\text{Fe}_{0.75}\text{O}_3$ thin films are selective to ethanol detection. The response of these layers is *p-type*. This can be an interesting feature for applications in sensors arrays since the p-type response can be easily picked out from the more usual n-type sensors response (e.g. SnO_2 , TiO_2 etc.).

6. References

- [1] E.D. Wachsman, in *Progress in Ceramic Basic Science: Challenge Towards the 21st century*, The Chemical Society of Japan, Tokyo (1996) 131
- [2] J.P. Lukaszewicz, *Sensors and Actuators B*, 4 (1991) 227.
- [3] H. Obayashi, T. Kudo, *Nippon Kagaku Kaishi*, (1980) 1568.
- [4] T. Arakawa, H. Kurachi and T. Shiokawa, *J. Mater. Sci.*, 20 (1985) 1207.
- [5] Y. Takahashi, *J. Mater. Sci. Lett.*, 3 (1984) 251.
- [6] Y. Matsuura, S. Matsushima, M. Sakamoto, *J. of Mater. Chem.*, 3 (1993) 767.
- [7] Y. Sadaoka, H. aono, E. Traversa, M. Sakamoto, *J. of Alloys and Compounds* 278, (1998) 135.
- [8] M. Yoshima, S.T. Song, S. Somiya, *Yogyo Kyokaishi*, 90 (1982) 91.
- [9] M.H. Zang, Y. Teraoka, N. Yamazoe, *Chem. Lett.*, (1987) 665.
- [10] A. Furusaki, H. Konno, R. Furuichi, *Nippon Rigaku Kaishi*, (1992), 612.
- [11] C.D. Chandler, C. Roger, M.J. Hampden-smith, *Chem. Rev.* 93, (1993) 1205.
- [12] E. Traversa, S. Matsushima, G. okada, Y. Sadaoka, Y. Sakai, K. Watanabe, *Sensors and Actuators B* 24, (1995) 661.
- [13] M.F. Yan, H.C. Ling, H.M. O'Bryan, P.K. Gallagher, and W.W. Rhodes, *IEE Trans. Components, Hybrids, Manuf. Technol.*, 11 (4), (1998) 401
- [14] J. Mahia, C. Vazquez-Vazquez, M.I. Basadre-Pampin, J. Mira, J. Rivas, M.A. Lopez Quintela, and S.B. Oserdorff, *J. Am. Ceram. Soc.*, 79(2) (1996), 407.
- [15] E. Bontempi, C. Garzella, A. Piubelli, S. Rapagna, E. Tempesti, S. Valetti, P.L. Villa and L. E. Depero, submitted
- [16] JC-PDF database, International Centre for Diffraction Data, 1998
- [17] G. Sberveglieri, L.E. Depero, S. Groppelli and P. Nelli, *Sensors and Actuators B*, 26-27 (1995) 89-92.