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LaFeO₃ ceramics as selective oxygen sensors at mild temperature

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Abstract

In this study, an investigation about the oxygen sensing properties of lanthanum orthoferrite (LaFeO₃) ceramics is reported. LaFeO₃ nanoparticles were synthesized by using tartaric sol-gel route and annealed in air at different temperatures (500, 700 and 900 °C). The samples have been characterized by using thermal analysis (TA), BET surface area and porosity, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Results of sensing tests indicate that LaFeO₃ nanoparticles exhibit good response to oxygen at mild temperatures (300-450 °C). The effect of annealing temperature on gas sensing performance was investigated, demonstrating that LaFeO₃ ceramics obtained after annealing at 500 °C display better characteristics with respect to others. The oxygen sensor developed shows also high stability in humid environment and excellent selectivity to oxygen over other interfering gases such as CO, NO₂, CO₂, H₂ and ethanol.

Keywords: Gas sensor; LaFeO₃; perovskite; oxygen; sol-gel.

1. Introduction

Perovskite-type oxides with general formula ABO_3 (where A is a rare-earth element and B is a 3d transition metal) are ceramic materials with multiple and useful functional properties, showing great interest in several applications, e.g. in catalysis, advanced technologies, solid state chemistry and physics [1]. The properties of perovskite oxide materials are originated from the wide choice of cations to be loaded into the structure (chemical composition), from the possible cationic and/or anionic substitutions in the oxide structure (vacancies) and, finally, by structural defects creation caused by either cations or oxygen deficiency [2].

Among the different possible combinations between A and B sites in the perovskite structure, lanthanum orthoferrite ($LaFeO_3$) ceramic materials gain more and more importance due to their multiple and unique properties allowing their application in many fields such as catalysis, oxygen permeable membranes and fuel cells. $LaFeO_3$ is a p-type semiconductor and in the orthorhombic structure is an attractive electroceramics due to chemical stability at high temperature and mixed ionic/electronic conductivity [3]. $LaFeO_3$ -based ceramics were also reported to have good sensing properties towards many gases such as acetone, formaldehyde ethanol, SO_2 , NO_2 , CO, CH_4 , CO_2 and O_2 [4-13].

Here, the interest has been devoted to $LaFeO_3$ ceramics with aim to develop oxygen sensors operating at mild temperature. Oxygen sensors are applied in many fields [14]. However, for use in practical applications, they must satisfy a number of requirements including high sensitivity, selectivity, stability, low humidity effect, low detection limit and rapid response/recovery times. Many nanocrystalline metal oxides, as single or mixed phases and composites, have been investigated as sensitive materials for O_2 sensors. Many of these devices operate at high temperature (650-1000 °C), like Ga_2O_3 [15], $BaSnO_3$ [16], $SrTi_{1-x}Fe_xO_{3-\alpha}$ [17] and $La_2CuO_4-LaFeO_3$ [12], which is a limiting factor for application requesting low power consumption. On the other hand, O_2 sensors operating at near ambient temperature, including CeO_2 [18], $Pt-In_2O_3$ [19] and $SrTiO_3$ [20], suffer of long recovery times. Metal oxides-based sensors which operate at low-mild temperature (200-500 °C) have been proposed to overcome the above limitations [21, 22]. These

sensors display good sensitivity to oxygen but are generally not selective. Therefore, an improvement of the sensing characteristics is mandatory to fabricate oxygen sensors for practical applications.

In the present study, the oxygen sensing properties of LaFeO_3 ceramic materials prepared by using tartaric sol-gel route and annealed in air at 500, 700 and 900 °C were evaluated. Many studies reported the preparation of LaFeO_3 via sol gel route using different carboxylic acids as complexing agent [9, 23-25]. This method is a facile dominant tool for the synthesis of homogenous, crystalline metal oxides at nanoscale, which were extensively used for gas sensor applications, as demonstrated by the large literature body produced. However, only a limited number of papers focused their attention on the investigation of LaFeO_3 ceramic materials to detect oxygen. Therefore, with this paper, we are aiming to fill this void, reporting a detailed study on the oxygen sensing properties of LaFeO_3 ceramic and proposing correlations with the morphological and microstructural characteristics of these materials.

2. Experimental

2.1. Material preparation

LaFeO_3 ceramics were prepared by the sol-gel method which could be described as follows: an equimolar amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were firstly dissolved in distilled water and mixed into a homogeneous solution. Subsequently, in a separate beaker an appropriate aqueous solution of tartaric acid (TA) was prepared. The molar ratio of complexing agent to total metal ions ($\text{TA}/\text{Fe}^{3+} + \text{La}^{3+}$) was 1:2. Then, TA was added dropwise into nitrates solution under continuous stirring at room temperature for 15 min then at 70 °C on a hot plate, until solvent evaporation and a gel was formed. No precipitation was observed as water evaporated. The resulting gel was dried at 110 °C in an oven for 24 h to obtain a xerogel followed by calcinations at 500 °C (1 °C/min) for 3 h then the temperature was further raised to 700 °C (3 °C/min) and 900 °C (3 °C/min) for 3h, giving ceramic powders. The obtained samples are labeled as follow: LFO 500, LFO 700 and LFO 900.

2.2. Material characterization

The morphology of the synthesized samples was investigated by scanning electron microscopy (SEM) using a Zeiss Crossbeam 540 instrument operating at 20 kV. Microstructure and crystalline phases were individuated by XRD data, collected by a Bruker D8 Advance Diffractometer using the CuK α 1 wavelength of 1.5405 Å. The average crystallite size, d , was calculated using the Scherrer's formula:

$$\frac{0.9 \lambda}{B \cos \theta_B} \quad (\text{Eq. 1})$$

Where λ is the X-ray wavelength, θ_B is the maximum of the Bragg diffraction peak and B is the full width at half maximum (FWHM) of the XRD peak.

The textural properties were studied by N₂ adsorption-desorption measurements at liquid nitrogen temperature by means of a Micromeritics ASAP 2010 equipment. Before analysis, the samples were degassed for 2 h at 150 °C in vacuum. The Barrett-Joyner-Halenda (BJH) method was used for determining the pore size distributions, and in every case the desorption isotherm was used. BET surface area and porosity of the samples were evaluated by nitrogen sorption measurements carried out at 77 K. The theoretical surface area of the samples has been evaluated using Sauter formula [26]:

$$(\text{SSA}) = \frac{K}{D \rho} \quad (\text{Eq. 2})$$

Where: K is a shape factor dependent on the particle shape (6 for spherical particle), D is the average particle size estimated using Scherrer formula and ρ is the bulk density of LaFeO₃ ($\rho = 6.6 \text{ g cm}^{-3}$) [27].

TA analysis was carried out in a TA Q500 thermobalance, heating the as-synthesized sample, at a rate of 10 °C min⁻¹, up to 1200 °C in air flow (100 cm³ min⁻¹).

Micro-Raman studies were carried out by means of an apparatus Olympus BX 40 microscope equipped with a 100 X objective with an exciting wavelength of 532 nm from a 10 mW diode laser focused onto the sample surface.

DRIFTS studies were performed on a Thermo Nicolet Nexus IR spectrometer equipped with a standard IR source ($9600\text{--}50\text{ cm}^{-1}$) Ge KBr beam splitter ($7400\text{--}350\text{ cm}^{-1}$) and MCT detector cooled in liquid nitrogen. Spectra of the pure samples were collected at room temperature by cladding 64 scans at 4 cm^{-1} resolution in absorbance mode. The spectrum of an aluminum mirror was used as a background.

2.3. Sensors preparation and sensing tests

Devices for the sensing tests were fabricated by printing films (10–30 μm thick) of the LaFeO_3 dispersed in water on alumina substrates ($6 \times 3\text{ mm}$) and provided with Pt interdigitated electrodes. A Pt heater was located on the backside of the electrodes. Electrical and sensing tests were performed by introducing the sensor in a stainless steel test chamber, controlling the gas flow rate by mass flow meters, and using a data acquisition unit Agilent 34970A for resistance measurement, while a dual channel power supplier instrument Agilent E3632A was employed to bias the Pt heater. The concentration of O_2 in the sensor chamber was varied from 0 to 100 % (v/v). The gas response, S , is defined as $[(R-R_x)/R_x] \times 100$ where R_x is the baseline resistance in synthetic air 20% O_2 in nitrogen (R_{20}) or pure nitrogen (R_0), and R is the electrical resistance of the sensor at different O_2 concentrations.

3. Results and discussion

3.1. LaFeO_3 ceramic samples characterization

LaFeO_3 ceramic samples were prepared by annealing the as-prepared xerogel precursor at different temperatures (500, 700 and 900 $^\circ\text{C}$, respectively) in air. The behavior of the precursor material during the annealing process has been investigated by analyzing TG and DTG curves shown in Fig. 1. There are three regions of weight loss: the first weight loss started slowly at about 30 $^\circ\text{C}$ until 200 $^\circ\text{C}$ (with a maximum in the DTG curve

about 145 °C) could be attributed to the evaporation of residual water. The second weight loss increased drastically between 200 °C and 500 °C (with a maximum at about 319 °C). It could be ascribed to the decomposition/oxidation of organic compounds accompanied by gases release such as NO_x, CO₂. The third weight loss occurs between 500 °C and 650 °C (with maximum about 602 °C in the DTG curve) could be assigned to the decomposition of residual amorphous material [28, 29], or the formation of crystalline LaFeO₃ [30]. No further weight loss was observed after 650 °C. This indicates the complete decomposition of the precursor and confirms the formation of LaFeO₃ perovskite.

Fig. 2 shows IR spectra registered from xerogel precursor and LaFeO₃ powders annealed at different temperatures. The xerogel precursor spectrum exhibits a broad absorption band centered at 3530 cm⁻¹ associated with the stretching mode of the hydroxyl group (O-H) of intermolecular hydrogen bonds or molecular water. The absorption bands in the range 1250-1750 cm⁻¹ are attributed to C=O and C-O-C stretching vibrations [31]. IR spectra registered from annealed samples highlight that the intensity of bands related to adsorbed water and carbonate decreases with the increases of annealing temperature, due to the transformation of xerogel into LaFeO₃ phase. The presence of residual carbonates on the surface of LaFeO₃ perovskite prepared using different starting materials, can be associated to the reactions between surface oxygen and ambient CO₂ occurring during the storage of the samples in ambient air [32, 33].

Micro-Raman patterns of samples annealed at different temperatures confirm the formation of the LaFeO₃ orthorhombic structure with space group Pnma (Fig. 3). The main characteristic Pnma-point modes A, T, B, and S are clearly visible in the pattern of all samples [34]. Very strong second-order phonons contributes are also observed above 900 cm⁻¹, which involve predominantly oxygen vibrations. It is noteworthy that, increasing the annealing temperature, the ratio between the intensity of second-order phonons contributes and Pnma-point modes, increases.

The morphology of the LaFeO₃ powders treated at various temperatures was investigated by SEM analysis (Fig. 4). All the samples show the presence of partially sintered particles. The particles are connected with each other and the connection type varies from neck to sharp with increasing calcination temperature from 500 to 900 °C.

Furthermore, the increase of particles size is clearly observed. Indeed, the particles size distributions show the maximum value at 30, 80 and 200 nm for LFO 500, LFO 700 and LFO 900 ceramic samples, respectively.

X-ray powder diffraction analysis was carried out to investigate the crystal structures of the lanthanum ferrite annealed at different temperatures (Fig.5). All the main diffraction peaks identified were assigned to orthorhombic phase and were indexed on the basis of JCPDS file No. 37-1493 (space group Pnma). This observation is in agreement with earlier reports of preparation of orthorhombic LaFeO_3 [5, 25, 35].

An increase of the intensity of characteristic peaks is noticed while increasing the temperature from 500 °C to 900 °C, likely due to enhanced cristallinity of the samples. No peaks coming from other phases or impurities were detected; hence the prepared LaFeO_3 samples were pure. Using the Scherrer formula (Eq. 1) the average crystallites sizes were also calculated. After the instrumental broadening correction, the values were 34.8, 74.5 and 179.8 nm for samples annealed at 500, 700 and 900°C, respectively, in fairly agreement with SEM data.

The theoretical surface area (SSA) of the samples has been calculated using Sauter formula (Eq. 2). Assuming nonporous spherical particles, the theoretical specific surface area of LaFeO_3 samples were found to be equal to 26.1, 12.2 and 5 m²/g for LFO 500, LFO 700 and LFO 900 respectively. The textural properties of the annealed LaFeO_3 ceramic powders were experimentally analyzed by N₂ adsorption desorption measurements. Table 1 summarizes the data obtained.

BET surface area of the LaFeO_3 ceramics, measured through the Brunauer–Emmett–Teller (BET) isotherm, decreases with increasing the annealing temperature. The results are in good agreement with the theoretical BET surface area. The pore volume, micropore area and volume also decrease with the annealing temperature. The pore size distribution, i.e. the pore volume vs. pore size, of the ceramic samples, is reported in Fig. 6; the curve for the LaFeO_3 prepared at lower temperature, along with the smaller particle size and larger surface area, indicate that it could have enhanced performance in O₂ sensing with respect to samples annealed at higher temperature.

3.2. Electrical properties

An electrical characterization was performed to measure the resistance of the ceramic samples as a function of temperature. Fig. 7 (a) shows the resistance–temperature trend of the different annealed LaFeO_3 samples, in the range from 150 to 400 °C. All the samples display the typical semiconducting behavior, i. e. their resistivity decreases with increasing temperature in the temperature range investigated. This could be due to the ionization of oxygen vacancies [36], or, as Devan and Chougule suggested [37], to the increase in drift mobility of the charge carriers. The activation energies were calculated from the slope of Arrhenius plots shown in Fig. 7 (b). For LaFeO_3 annealed at 500, 700 and 900 °C there are two activation energies, E_{a1} and E_{a2} , at low (150-250 °C) and mild (300-400°C) temperature range, respectively.

For all the samples the activation energies values are higher in the low temperature range compared with the mild temperature range. The observed results are in good agreement with previous reports of other authors [31]. On the other hand, a reverse trend was mentioned by Murade et al. [38] for pure LaFeO_3 and Sr-doped LaFeO_3 ceramics prepared via citric sol-gel method and annealed for 6 h at 800 °C. They attributed this behavior to change in conduction mechanism from electronic conduction at low temperatures, to ionic at higher temperature. These contradictory results indicate that the synthesis process and/or thermal treatments are crucial in determining the electrical properties of LaFeO_3 ceramic materials.

3.3. Oxygen sensing properties

The oxygen sensing properties of LaFeO_3 ceramics were then investigated. Preliminary experiments suggested that the optimal operating temperature of the sensor (evaluated in term of optimal balance between high sensitivity and faster response/recovery dynamics) is 400 °C. Therefore, the oxygen performances of sensors based on the different annealed LaFeO_3 samples were compared at this operating temperature (see Fig. 8). Calibration curves show clearly as the response to oxygen decreases with the increasing of

annealing temperature. The sensor response is very high at low concentrations of oxygen (0-15%) and gradually goes towards saturation at high concentrations.

The typical dynamic characteristics of the sensors are reported in Fig. 9 (a), showing the transient response and recovery of LFO 500 sensor when exposed to a pulse of 5% at 400 °C in the background of dry air. The resistance of the sensor sharply increased, with a response time of only 4 seconds. After returning in dry air, the resistance decreased and time necessary to recovery the baseline was about 3 seconds. Interestingly, LFO 500 sensor shows the best dynamic characteristics compared to other ones (Fig. 9 (b)) this could be related to the smaller particle size and/or to the higher porosity of the LaFeO_3 particles annealed at 500 °C, which favors gas flowing within the structure of the sensing material [39, 40]. A similar trend was reported by Sahner et al. [41] investigating the response kinetic of two different lanthanum ferrates. They found that in the case of a homogenous fine-grained microstructure, the surface reaction of oxygen with vacancies was the time-limiting step of sensing mechanism and it was faster in comparison to diffusion-controlled mechanism typical of coarse-grained sensing films.

In Fig. S1 are reported for comparison the dynamic responses of the fabricated sensors, tested at different O_2 concentrations. Note that synthetic air (20% v/v of oxygen) was used as reference carrier. All sensors show p-type behavior, i. e. the resistance increases for pulses of oxygen lower than 20%, and decreases for higher oxygen concentrations.

In Fig 10 (a,b) are reported separately the response of the LFO 500 sensor to low and high oxygen concentration, respectively. The reliability and stability are key properties of a successful chemical sensor. As shown in Fig. 11 (a), the resistance of the sensor has been monitored decreasing first the oxygen concentration to 2% and subsequently increasing it, returning to initial value of 20%. The minimal hysteresis registered (Fig. 11 (b)), demonstrates the good reversibility and the absence of memory effects. This behavior can suggest a weak interaction between oxygen and the sensing LaFeO_3 ceramic film [42].

For a practical use, the sensor should have stable and repeatable response under the applicative conditions. In this respect, the ambient humidity is a parameter which can give

many problems to semiconductor gas sensors. The reproducibility of the LFO 500 sensor response was first verified at the optimal operating temperature of 400 °C in dry conditions. As shown in Fig. 12 (a), the response to sequential pulse of 2% O₂ in a background of 20% O₂, shows the excellent repeatability of the sensor. Then, the influence of humidity on the response to oxygen has been also evaluated (see Fig. 12 (b)). Oxygen sensing tests were performed in a large range of humidity conditions (0 – 94 RH%) at different oxygen concentrations, demonstrating an excellent humidity-independent behavior. Therefore, it may be concluded that the active sites responsible for oxygen sensitivity do not involve water-related processes but only O₂ adsorption takes place.

Finally, the developed sensor should be not influenced by the presence of other gases, i.e. should demonstrate high selectivity. This has been confirmed by data shown in Fig. 13 where is compared the response of LFO 500 sensor toward different gases with concentrations higher than typically present in indoor/outdoor ambient, such as NO₂, CO, NH₃, ethanol, CH₄ and CO₂.

This study demonstrated that the oxygen sensing properties of LaFeO₃ ceramics are related to the microstructural and morphological characteristics of the ceramic sensing material. As regard the higher sensitivity of the LFO 500 sensor, it can be attributed to the smaller size of LaFeO₃ particles. Therefore, the surface activity is enhanced and more sites are exposed to gas due to the larger surface to volume ratio. It is well known that the electrical conductivity in ceramic-type materials is due to the deviation from stoichiometry and the formation of ionic and electronic charge carriers, generated during the synthesis and the subsequent thermal treatments [43, 44]. When a metal oxide semiconductor is exposed to an oxygen-containing atmosphere, oxygen molecules are adsorbed as ions onto the surface of the material, and then behave as electrons traps. Interaction of oxygen gas with the surface of p-type semiconductors removes hole traps and inversely increases the number of charge carriers, thus the decrease of resistance in excess of oxygen can be interpreted as a consequence of the depletion of electrons in the valence band of LaFeO₃ perovskite ceramics.

The suggested mechanism is in agreement with other reports on perovskite materials as gas sensors operating at mild temperature [45].

In this temperature range, the gas sensing mechanism of LaFeO₃ sensor is based on the resistance variation of sensing material caused by oxygen adsorption on surface oxygen vacancies, as follows:

where $V_0^{\bullet\bullet}$ denotes the oxygen vacancy, O_0 represents lattice oxygen atom and $h^{\bullet}$ the hole. By this process is possible to observe that more atmospheric oxygen (O_2) recombines with vacancies higher holes concentration is generated, making the sensor less resistive.

The fast dynamics of the sensor developed is related to the favorable textural characteristics, such as a high porosity, which favors gas flowing within the structure of the sensing material

4. Conclusions

In summary, LaFeO₃ ceramics have been successfully prepared by sol-gel method and used as sensitive material for oxygen gas sensing at mild temperature. Structural analysis and morphological studies have shown that LaFeO₃ ceramics are composed of partially sintered particles whose size increases with increasing annealing temperature from 500 to 900 °C.

Gas sensing results revealed that the LaFeO₃ ceramic annealed at 500 °C has significantly better sensing performance than ones annealed at higher temperature. This behavior has been explained with the high aspect ratio of the LaFeO₃ ceramics annealed at 500 °C, resulting in a larger quantity of adsorbed oxygen. A reversible and stable response toward oxygen gas in the full concentration range (0–100%), at mild temperature and with almost no humidity interference has been demonstrated. The ease device fabrication, the stability and reproducibility of the response as well as and the fast dynamics imply that the developed sensor could serve as a promising platform for developing low-cost oxygen sensor for many practical applications.

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Fig. 1. Thermal analysis of the LFO xerogel recorded in air at a heating rate of 10 $^{\circ}\text{C}/\text{min}$.

Fig. 2. IR spectra of xerogel complex and LFO powders annealed at different temperatures.

Fig. 3. Raman spectra of LFO powders annealed at different temperatures.

Fig. 4. SEM images (left) and particles size distributions (right) of LFO powder annealed at different temperatures.

Fig. 5. XRD patterns of LFO samples annealed at different temperatures.

Fig. 6. Pore size distribution curves of LFO samples annealed at different temperatures.

Fig . 7. Resistance versus temperature (a) and Arrhenius plots (b) of LFO based sensors annealed at different temperatures measured in dry air. Values of activation energies, E_{a1} and E_{a2} , are expressed in eV.

Fig. 8. Calibration curves of LFO based gas sensors at operating temperature of 400 °C.

Fig. 9. a) Transient response and recovery of LFO 500 sensor when exposed to a pulse of 5% O_2 at 400 °C in the background of dry air; b) Comparison of dynamic parameters of the different sensors at the above conditions.

Fig. 10. Response of LFO 500 sensor, in the background of dry air at 400 °C, to a) low and b) high oxygen concentration pulses.

Fig. 11. a) Resistance variation of the LFO 500 sensor during decreasing and increasing steps of oxygen concentration; (b) Hysteresis characteristic.

Fig. 12. Response of LFO 500 sensor to: a) sequential pulses of 2% O₂ at 400 °C; b) different oxygen concentration under various relative humidity conditions.

Fig. 13. Response of the LFO 500 sensor to different gases at 400 °C.

Table 1. Textural properties of the investigated samples.

	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Micropore area (m ² /g)	Micropores volume (cm ³ /g)
LFO 500	24.59	0.153	18.52	3.677	0.001528
LFO 700	10.75	0.1	35.68	1.8049	0.000747
LFO 900	3.45	0.018	26.52	0.8	0.000342