Synthesis, characterization and sensitivity tests of perovskite-type LaFeO$_3$ nanoparticles in CO and propane atmospheres

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**Abstract**

Nanoparticles of perovskite-type LaFeO$_3$ were synthesized by a simple process using stoichiometric lanthanum and iron nitrates, ethylenediamine, and distilled water as a solvent. Microwave radiation, with a power of $\sim$350 W, was applied for solvent evaporation. The obtained precursor powders were calcined at 200, 400, 500, 600 and 700 °C in static air, and analyzed by X-ray diffraction and cyclic voltammetry. The samples showed catalytic activity and high physical and chemical stability. The calcined powders at 700 °C were analyzed through scanning and transmission electron microscopy; agglomerated nanoparticles, forming a porous structure, were observed with an average size of 28 nm. Their magnetic properties correspond to magnetization up to 0.83 emu/g and coercivity of 182 Oe. Pellets from these powders were prepared to measure the sensitivity to CO and propane gases, obtaining high performance at different gas concentrations and operation temperatures.

**1. Introduction**

Advances in the preparation of new transition metal oxides have allowed the development of complex materials such as the perovskite-type oxides. These compounds are grouped among the advanced materials due to their special physical and chemical properties [1–10]. Materials with a perovskite-type structure take the general form of $ABO_3$ [11,12], where $A$ stands generally for a lanthanide or an alkaline earth element, such as La, Pr, Nd, Gd, Sm and Sr; $B$ represents a transition metal, mainly Co, Fe and Ni [13]. Several combinations that can be accomplished through $A$ and $B$ yield a great variety of compounds with highly relevant chemical and physical properties for technological applications [14], e.g. gas sensors, electrodes for solid oxide fuel cells (SOFC), catalysts, magnetic devices, among others [15–20]. Since past decades, several investigation groups have used different synthesis methods to obtain perovskite-type materials, being the ceramic method the most commonly employed [14]. Nevertheless, other chemical routes have been explored [21], such as the synthesis of Sm$_{1-x}$Ba$_x$CoO$_3$ through an aqueous solution method [22], LaFeO$_3$ through sol-gel route [23], BaTiO$_3$ by means of a sol-precipitation process [24] and LaCoO$_3$ through a glycine nitrate (G/N) plus EDTA route [25]. These synthesis routes allowed obtaining nanomaterials with high porosity and specific morphologies of a great relevance due to its potential applications.

Recently, the research on perovskite-type oxides as possible gas sensors has been extensive, due to the high thermal stability, catalytic activity and semiconductor behavior of the oxides [26,27]. For example, Ca$_{x}$Pb$_{1-x}$TiO$_3$ has been studied as a possible humidity sensor [28], SmFeO$_3$ is considered for the detection of NO$_2$ and CO [29], and SrFeO$_3$ is a strong candidate as an ethanol vapors sensor [17]. The lanthanum ferrite, LaFeO$_3$, is being nowadays heavily investigated because it shows an excellent electric response in different gases. Different authors [30–33] report the successful use of this perovskite-type oxide, with different morphologies (ranging from thin films to hollow fibers) for detecting triethylamine, CO, NO and NO$_2$. A pending issue is, notwithstanding the foregoing, to determine the best microstructure
2. Experimental

2.1. Synthesis of LaFeO₃

An aqueous synthesis route containing ethylenediamine was used to obtain the oxide. The synthesis was as follows: three solutions were prepared using 0.004 mol of La(NO₃)₃, 6H₂O (Alfa Aesar, 99%), 0.004 mol of Fe(NO₃)₃·9H₂O (Monterrey, 98%) and 2 mL of ethylenediamine (Sigma, ≥ 99%) using 5 mL of distilled water as a solvent. Each solution was stirred at 375 rpm for 15 min; thereafter, the ethylenediamine and ferric nitrate solutions were mixed (yielding a fine brownish precipitate) and the lanthanum nitrate was slowly added to such mixture. The resulting colloidal suspension was continuously stirred at room temperature during 24 h. The solvent was then evaporated by means of a typical microwave oven (General Electric, model JES769WK) in cycles of 60–90 s at ~350 W (the suspension’s temperature was of 90 °C during each cycle). After the solvent’s evaporation, a brownish paste was obtained, which was then heated at 200 °C during 8 h. The resulting precursor powder was divided in 4 portions, which were calcined at 400, 500, 600, and 700 °C, respectively. The calcination was as follows: starting at room temperature, the powders were heated at a rate of 100 °C/h; thereafter, the powders were kept at the given calcination temperature for 5 h.

2.2. LaFeO₃ powders characterization

All the calcined powders were analyzed by means of XRD (RIGAKU SmartLab diffractometer, CuKα radiation, 2θ scanning angle of 20–70°, at 0.02° steps with a duration of 1 s). The microstructures were observed using SEM (JEOL JSM-6390LV, high vacuum, secondary electron emission). In order to observe the oxide nanoparticles by means of TEM (JEOL JEM-2010, accelerating voltage of 200 kV), the powders were dispersed in isopropyl alcohol for 5 min and were placed on a formvar carbon copper grid, 400 mesh. The magnetic characterization was made using a magnetometer (VSM-VersaLab CryoFree), applying a cyclic magnetic field in the range ~30 a +30 kOe, at room temperature.

2.3. Voltamperometric analysis using carbon paste electrodes (CPE)

2.3.1. CPEs preparation

Unmodified CPEs were prepared as reported elsewhere [34]: a mixing 0.2 g of graphite powder (Alfa-Aesar, particle size: 2–15 μm, 99.9995% purity) and 100 μL of paraffin oil (Golden Bell, ρ = 0.85 g cm⁻³) in an agate mortar. The resulting paste was packed inside a polyethylene tube (inner diameter: 3 mm, length: 7 cm) with a plug for pressing the paste or for getting rid of it when its reaction finished. The electric contact of the paste was made using a platinum wire welded to a copper wire. By exuding 0.1 mm of paste from the tube and polishing the new surface over a paper sheet, the electrode’s surface was regenerated before each experiment. After preparation, the electrodes were immersed in deionized water for 24 h. The modified CPEs were prepared mixing 0.16 g of graphite powder, 0.04 g of the synthesized powders, 100 μL of paraffin oil (this ratio graphite/sample/oil turned out to be the optimum) and using the procedure before mentioned.

2.3.2. Solutions

The working solution was a Briton-Robinson buffer of pH 2 with 0.15 mol L⁻¹ of potassium chloride as electrolyte. The buffer was prepared mixing equal volumes (0.04 mol L⁻¹) of boric, acetic and phosphoric acids.

2.3.3. Instrumentation

The voltamperometric tests were performed using a potentiostat (PAR, model VersaStat 3) and software (VersaStudio v2.20.4631). A three-electrodes cell was used: the MCPEs as working electrodes (surface area: 7.06 ± 0.01 mm²), a graphite rod (Alfa Aesar, Johnson Matthey 99.9995%, surface area: 0.85 ± 0.01 cm²) as a counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The results are reported as potential vs. SCE potential.

2.4. Sensitivity tests

The gas sensitivity tests of the LaFeO₃ were performed in two atmospheres: carbon monoxide (CO) and propane (C₃H₈). For the tests, the electrical resistance of LaFeO₃ pellets (diameter: 12 mm, thickness: 500 μm) was recorded at different temperatures and gas concentrations. The pellets were prepared with 0.5 g of LaFeO₃ powders pressed at a rate of 0.5 t / mm² for 90 min with a manual pressure machine (Simplex Ital Equip-25 t). Two ohmic contacts were attached to the pellets’ surface by means of colloidal silver (Alfa Aesar, > 99%). The pellets were placed inside a measurement chamber in a vacuum of 10⁻³ Torr. The partial pressure inside the chamber, as a reference for the gas concentration, was continuously monitored by means of a simple detector (Leybold, model TM20). The electrical resistance was recorded using a digital multimeter (Keithley 2001). The gas detection system was set up as reported elsewhere [35]. The gas sensitivity (S) was calculated by means of the relative difference of electrical conductances: S=(Gₓ–G₀)/G₀ where Gₓ and G₀ are the electrical conductances in the sampled gas (CO or C₃H₈) and air, respectively.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the X-ray diffraction patterns of the calcined powders at 200, 400, 500, 600 and 700 °C. The main diffraction peaks corresponding to a perovskite-type LaFeO₃ are present since...
the sample calcined at 200 °C. Such peaks are located on the 2θ positions (in °): 22.6, 32.3, 38.1, 39.7, 41.4, 46.2, 47.8, 52.1, 53.6, 57.4 and 67.4, which can be indexed, according to the file PDF 01-088-0641, to the diffraction planes as follow: (001), (121), (112), (220), (131), (202), (212), (103), (311), (123) and (242), respectively. This corresponds to an orthorhombic crystal structure with space group Pnma and cell parameters: a = 5.56 Å, b = 7.85 Å and c = 5.55 Å. The unit cell of LaFeO3 consists of 4 perovskite-type distorted units [36]. It is also shown in Fig. 1 that the peak intensity rises with the calcination temperature, which suggests that the samples’ crystallinity improves with temperature. The peak width is an indication of the presence of nanocrystalline materials.

An important aspect of our work is the fact that the synthesis temperatures of the LaFeO3 were relatively lower than those reported in the literature. For example, using solid state reaction methods, and lanthanum and iron oxides as precursor mixtures, reported temperatures have been over 1300 °C [37]. And by means of “soft chemistry methods”, temperatures between 500 and 950 °C have been reached [38]. Therefore, according to all consulted reports, the microwave-assisted aqueous solution method, used here, can be regarded as an economical and practical route for synthesizing the LaFeO3, because diffraction peaks, though of low intensity, can be found even from ~200 °C.

3.2. Electrochemical analysis by means of cyclic voltamperometry

Solid-state gas sensors are based on resistance changes caused by exposure of the sensor surface to a target species. Gas sensors should exhibit a stable and reproducible response for a period of time. Therefore, used gas-sensing materials should be characterized by high chemical stability. In this work, the physical and chemical stability of LaFeO3 was analyzed by electrochemical tests. This property provides an opportunity to work in different mediums [39]. Two cyclic voltamperograms with only CPE are shown in Fig. 2. The potential scanning began in the positive direction in the CV forward and in the negative direction in the CV reverse, starting both with an open circuit potential (OCP) of 0.5 V in a range of 2 to −2 V at a scan rate of 100 mV s⁻¹. In the CV forward, 5 peaks are mainly seen, and were denoted as A, B, C, D and E, respectively, while in the CV reverse, only two peaks, A and E, are observed. The reduction peak E at −2 V is due to the H₂ gas formation by electrolysis (in both cases). Peak A, which starts at 1.3 V, is due to the addition of the species oxidation of the electrolyte and the buffer, and the O₂ gas formation by the electrolysis. The reduction currents B (at 0.5 V), C (at −1 V) and D (at −1.6 V) appear only when the oxidation peak A is generated. Peak B only forms when the electrolyte is KCl, hence the peak is linked to the electrolyte’s reduction. Peaks C and D only appear when the electrolyte combines with the B-R buffer, hence they are related to the buffer’s reduction.

Voltamperograms obtained with the perovskite-MCPE are depicted in Fig. 3. In all cases, the potential scanning began in the positive direction with an OCP of 0.5 V in a range of 2 to −2 V at 100 mV s⁻¹. The same current peaks were obtained as the CPE, which shows that the powders calcined at, and above, 400 °C were not chemically nor physically modified, even with the used acidic pH (~2). In addition, because of a no redox peak was observed, no other compound was formed during the reaction. Comparing the peaks linked to the electrolyte’s reduction (peak B) for both types of electrodes (CPE and perovskite-MCPEs), a difference in the potentials is evident: 0.5 V and −0.2 V, respectively. This displacement to lower potentials means that the electrolyte’s reduction is being promoted by the use of the perovskite-type oxide [40], i.e. the reduction reaction is being catalyzed [41]. The voltamperogram of the calcined sample at 200 °C shows a difference with those of the other perovskites. The reduction and oxidation peaks F and F′, respectively, depend on the oxidation peak A, because they will not appear if the latter is not generated. Such peaks are an indication that other species, different to the perovskite, are present and chemically active. Gorbunov et al. [42], report that the ethylenediamine and the transition-metal nitrates generate complexes which decompose at temperatures above 200 °C, which suggests that peaks F and F′ are due to redox reactions of metallic complexes still in the sample. The diffractogram corresponding to the mentioned sample (see Fig. 1), which shows lower crystallinity, indicates the existence of other species formed during the synthesis process.

This results demonstrate the high physical and chemical stability of LaFeO₃ samples synthesized at, and above, 400 °C.

3.3. SEM analysis

Fig. 4 shows two typical SEM micrographs of LaFeO₃ powders after calcination at 700 °C. These micrographs present two magnifications: a) 200X and b) 5000X. A sponge-like morphology can be seen in Fig. 4(a). This morphology is the result of the agglomeration of very small particles, which have a lot of macro pores (size: 2–15 μm) distributed along their surface. At a greater magnification (5000X, Fig. 4b), smaller pores (~0.3 μm) also can be observed. This porosity can be attributed to particle coalescence due to the chelating effect of the ethylenediamine and the released gases during the thermal decomposition of the organic material in the sample [43].
3.4. TEM analysis

Fig. 5 shows two TEM images of the oxide’s surface from sample obtained at 700 °C. It is evident an agglomeration of LaFeO₃ nanoparticles with almost the same particle size in the range of 9.1–54 nm with an average sized estimated of 27.7 nm, with a standard deviation of 9.5 nm (Fig. 6). More details of the surface features can be found at higher magnifications (Fig. 5b), where irregularities in the shape and some pores of size ~5 nm can be identified. The high porosity of the LaFeO₃ surface is fully evident. Inset in Fig. 5(b) shows also a selected area electron diffraction pattern (SAED) to confirm the oxide’s polycrystalline nature. The effect of ethylenediamine in the formation of very small structures of materials, like nanorods, nanowires, and nanoparticles, has been discussed in previous studies. The microstructure is influenced by the presence of ethylenediamine [43,44] because it acts as a template, which at a first step is incorporated to the inorganic grid and afterwards escapes leaving nanocrystals of certain morphology [45]. These morphologies follow the crystallization principles of LaMer and Dinegar [43,44,46].

3.5. Magnetic properties

The results shown in what follows correspond to the LaFeO₃ powders synthesized at 700 °C. Fig. 7 shows a hysteresis loop of the LaFeO₃ measured at room temperature and a maximum applied field (H_max) of 30 kOe, yielding a maximum magnetization (M_max) of 0.83 emu/g, which indicates that the LaFeO₃ exhibits a weak ferromagnetic behavior. The coercivity (H_C) was 182 Oe. These results are in agreement with those reported by Tang et al [47], with saturation magnetization M of 0.514 emu/g for nanoparticles with sizes ranging 80–100 nm of the same oxide, synthesized by burning the precursor solutions using microwave radiation (at 850 W). The magnetization can be changed according the particle size, shape and its distribution, the remanence energy is reduced as a function of particle size. This is dissipated by the nanoparticles as the particle size is diminished [48].
3.6. Gas sensitivity

Figs. 8 and 9 show the sensitivities of the LaFeO₃ nanoparticles (synthesized at 700 °C) as a function of the gas concentrations. Carbon monoxide sensitivity tests were performed at the following gas concentrations: 0, 5, 50, 100 and 200 ppm and at temperatures: 23, 150, 250 and 350 °C. The sensitivity, as a function of the CO concentration, is shown in Fig. 8(a); a zoom of the temperatures 23, 150 and 250 °C is depicted in Fig. 8(b). At 23 and 150 °C, the LaFeO₃ did not show variation of the sensitivity to any CO concentration. However, when the CO was injected to the measurement chamber at 250 and 350 °C, variations of the oxide's electrical resistance were detected. At 250 °C, the calculated sensitivities were 0, 0.03, 0.04, 0.06 and 0.09 for CO concentrations of 0, 5, 50, 100 and 200 ppm, respectively, while at 350 °C the sensitivities increased to 0, 0.08, 0.18, 0.31 and 0.47 for the same CO concentrations range. It is evident that LaFeO₃ is clearly sensitive to concentration change of CO, and that sensitivity is affected by the temperature.

The sensitivity tests in propane, with the same temperatures as the CO, are shown in Fig. 9. Again, below 150 °C no significant variations on the electrical resistance were detected. At 350 °C, the calculated sensitivities were 0, 0.47, 1.21, 1.57, 2.05 and 3.04 for propane concentrations of 0, 5, 50, 100, 200, and 300 ppm, respectively, while at 350 °C the sensitivity increases to 0, 0.83, 2.06, 4.11 and 3.14 for the same propane concentrations range.

The observed sensitivity trend has been widely reported in the literature for different oxides [43,49,50]. The gas sensing mechanism of materials like the LaFeO₃ involves the chemisorption of the oxygen and its subsequent reaction with the sampled gas. In fact, the ionization state of the chemisorbed oxygen depends on the working temperature: below 150 °C, molecular O₂− species are mainly found; above 150 °C, more reactive O− and O²− atomic species dominate [51,52]. The formation of atomic oxygen species at high temperatures increases the solid-gas interactions, hence the sensitivity of the gases is improved. In addition, the sensitivity rises with the gas concentration, no matter what gas it is, since the more gas concentration the more desorption reactions. At low temperatures (< 150 °C) there is no enough thermal energy to promote desorption, no matter the gas concentration. In addition, the sensitivity decreased when the test gases were removed from the chamber, indicating that LaFeO₃ nanoparticles had a high performance for the different gas concentrations and temperatures.

The gas sensitivity results were compared with similar previous works finding that we have succeeded obtaining a...
better sensitivity. For example, ZnSnO3 showed maximum sensitivities of ~7 (CO) and ~1.5 (propane) at a temperature of 250 °C and a gas concentration of 300 ppm [53]; for CoSn2O4, the maximum sensitivities were ~7 (CO) and ~5 (propane) at 350 °C and a gas concentration of 300 ppm [49], while ZnO showed a maximum sensitivity of ~6 at 300 °C and a propane concentration of 300 ppm [35]. A sensitivity of ~10 (CO) and ~40 (propane) was reached for perovskite-type LaCoO3 nanoparticles (average size of 70 nm) at 350 °C and a gas concentration of 300 ppm [33]. A sensitivity of ~6 at 300 °C and a propane concentration of 200 and 300 ppm, respectively, [43]. Part of this success is due to the fact that the gas response of materials depends on the microstructure. The gas sensitivity of the sensor material is enhanced with decreasing particle size down to the nanometer scale. In addition, perovskite oxides can provide microstructural and morphological stability to improve the sensor performance [54].

4. Conclusions

Porous LaFeO3 nanoparticles were synthesized by means of a microwave-assisted aqueous solution method. This is an interesting alternative route for the synthesis of such perovskite-type oxides because it can be successfully accomplished at lower temperatures than those employed with other methods. The LaFeO3 powders prepared at and above 400 °C exhibited great physical and chemical stability, apart from the catalytic activity they showed during the electrochemical tests. The magnetic behavior of the oxide was relatively weak, with a maximum magnetization of 0.83 emu/g and a coercivity of 182 Oe. The LaFeO3 nanoparticles were very sensitive to CO and propane at different gas concentrations and working temperatures. Maximum values of the sensitivity were approximately 17 and 31 for CO and propane respectively, at the maximum gas concentration and the highest temperature. Our results greatly encourage the use of this oxide, especially prepared by our method, as a gas sensor.

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