



Article Particle Size Effect on Optical and Gas-Sensing Properties of $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Mn³⁺, and Cr³⁺) Compounds

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Abstract: In the present work, the morphological, optical, and gas-sensing properties of $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti, Cr, and Mn) nano-powders prepared via the auto-combustion route, were investigated. TEM images prove the nanoscale particle size of all the samples. Optical studies confirm the semiconductor behavior of the studied materials. The response of the prepared nano-powders towards the presence of two gas-reducing agents (ethanol and acetone) was investigated. From the resistance ratio under air and gas, it was possible to determine the response to different gases and deduce that $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ presents the highest responses to ethanol and acetone. Likewise, we deduced that the prepared materials were able to detect low concentrations of ethanol and acetone gases.

Keywords: optical properties; gas sensor; nanostructures; response time; recovery time

1. Introduction

The huge increase in released pollutants and toxic gases, especially from industries and automobiles, has adverse effects on the environment as well as on human health. This explains the increase in the research interest in developing new reliable gas sensor devices to be used in a wide application area [1,2]. It is also known that the principle of detection defines the gas sensor type, such as electrochemical [3], catalytic [4], metal oxide [5], or infrared [6]. Moreover, calorimetric, spectroscopic, and chromatography methods have been used for gas sensor manufacturing, which are highly expensive, and their uses are restricted due to their miniaturization difficulties for portable uses [7–9].

On the other hand, acetone (C_3H_6O) is known as a volatile, colorless, flammable liquid with a pungent aroma. It is majorly used as a solvent but is also used in laboratories, the medical and cosmetics industries, etc. It evaporates quickly in the air; therefore, acetone vapor can destroy the mucous membrane of the eyes, causing irritation when exposed. The inhalation of vapors can cause headaches, drowsiness, or dizziness. Importantly, acetone has been recently used as a potential breath marker for clinical diagnosis of abnormal blood sugar levels [10,11]. On the other side, ethanol (C_2H_5OH) is a flammable gas with an explosion range of 3.3–19%, which is used in various fields, especially for breath analysis



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and traffic safety (the alcohol breath concentration of car drivers) [12–14]. Therefore, controlling the concentration of ethanol and acetone in an exhaled gas environment is of significant importance.

Accordingly, the development of efficient and inexpensive gas sensors is of paramount importance. Semiconductor nanomaterials (such as CuO, Fe₂O₃, Co₃O₄, NiO, etc.) were considered the best solutions for gas-sensing applications due to their outstanding merits of low cost, a wide detection range and easy fabrication and integration [15–20]. Recently, some new and efficient semiconductor oxide material-based sensors were commercially used to detect numerous dangerous gases [21–23].

As an effect of this strong demand, in the last decade, many efforts have been made to identify new and more efficient sensitive materials suitable for monitoring acetone and ethanol gases at lower optimum working temperatures. H. Xu et al. [24] confirmed that Sr-doped BiFeO₃ reduced the optimum working temperature to 208 °C for acetone and ethanol gas detection, compared to the undoped iron bismuth material. Also, the optimum working temperatures for acetone and ethanol gas detection found by S. R. Jamnani et al. [25] are higher than 208 °C. Moreover, SnO₂-ZnO nanomaterials exhibit an optimum working temperature equal to 250 °C and 300 °C to detect ethanol and acetone gases, respectively [26].

Importantly, among p-type semiconductor materials, Lanthanum ferrites (LaFeO₃) attract continuous attention for their gas-sensing properties, while the synthesis methods, the substitution on one or both sites, plays a crucial role in enhancing these properties [27–32].

In the literature, it was confirmed that partial substitution of Lanthanum ions by divalent ones (such as Pb^{2+} , Ca^{2+} , Ba^{2+} ...) enhances the response and selectivity to different gases [33–35]. This is also the case when substituting Fe^{3+} ions with Mg^{2+} , Co^{2+} , or Mn^{3+} ones [31,36–38]. Accordingly, in this paper, we synthesized the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti^{4+} , Cr^{3+} , and Mn^{3+}) compounds via the autocombustion method and described a comprehensive study for the 3% Ti^{4+} , Mn^{3+} , and Cr^{3+} ion insertion effects on particle size and gas-sensing properties.

2. Materials and Methods

Nanosized La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O₃ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) were prepared using the auto-combustion method. In our previous work, the details are presented [39]. Stoichiometric amounts of Lanthanum nitrate La(NO₃)_{3.6}H₂O, iron nitrate Fe(NO₃)_{3.9}H₂O, barium nitrate Ba(NO₃)₂, calcium nitrate Ca(NO₃)₂ and titanium/manganese/chromium nitrates were the precursors, and glycine (C₂H₅NO₂) the fuel agent.

The prepared compounds were characterized via powder X-ray diffraction using a *Bruker D8 Advance* (Karlsruhe, Germany) diffractometer with Cu-K_{α} radiation (λ = 1.5406 Å). XRD data were recorded over a range of 2 θ = 10° to 100°. Transmission electron microscopy (*Hitachi H-800*- Tokyo, Japan) was used to study the morphology of the powders.

To prepare the gas sensors, the powder was drop-casted on a gold-patterned alumina substrate crossed by Ni-Cr heating wires. This method was previously reported in the literature [29,30] (Figure 1). To improve its performance (stability and repeatability), the sensors were kept at 300 °C for 2 days. The measurements were performed on a *WS-30A* system (China). Several steps were followed in order to measure the sensors at identical temperatures, as reported previously [40,41].

The relation $S = R_g/R_a$, where R_g and R_a represent the resistance of the sensor in the gas and in the air, respectively, was used to calculate the gas response.

The solid-state absorption spectra (UV-Vis) of the powders were recorded by collecting the total reflectance using a *Cary 5000 UV-Vis-NIR* NIR (Agilent Technologies, Santa Clara, CA, USA) spectrophotometer equipped with an integrating sphere (200–2500 nm range). Background correction was performed by collecting the baseline with 100% and 0% reflectance (using a Polytetrafluoroethylene, PTFE, reference sample, and the blocked beam, respectively) prior to the determination of the spectra of the solid samples. Conversion to absorption was performed assuming the Kubelka–Munk function, F(R) [42].



Figure 1. Schematic diagram of the gas-sensing measurement system.

3. Results and Discussion

3.1. Morphological Study

The particle size and shape of the prepared $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds were investigated using transmission electron microscopy (TEM). The TEM images are presented in Figure 2a–c, from which we deduce that all compounds present grains with different spherical, cubic, and polygonal shapes. It is shown that the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound shows more regularity in the particle shapes. The Image-J 1.52a software was used to calculate the particle size of the studied compounds by adjusting the particle size distribution with the Lorentzian formalism, as shown in Figure 2. The adjustment results confirm that the insertion of the Ti⁴⁺ ions in the M-site of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound decreases the particle size values. It is important to mention that the particle size has a crucial effect on the gas-sensing properties. Accordingly, we expected a higher gas response for the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound.



Figure 2. Cont.



Figure 2. (**a**–**c**) TEM micrographs and the corresponding histogram plots with the Lorentzian fitting of the particle size distribution of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Mn³⁺, and Cr³⁺) compounds, respectively.

3.2. Raman Scattering Studies

To further the structural study, Raman spectroscopy was used since it is more sensitive than XRD because its excitation energy is less penetrating than an X-ray [43].

The Raman spectra of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds are shown in Figure 3 for structural comparison. We previously studied the Raman vibrational modes of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound [44], which showed only 11 active vibrational modes. Furthermore, as previously confirmed in the literature, almost-doped LaFeO₃ ceramics crystalize in an orthorhombic structure that presents twenty-four active Raman modes, as described by the following equation [45]:

$$\Gamma = 7 A_g + 7 B_{1g} + 5 B_{2g} + 5 B_{3g}$$
(1)

According to the literature, below 200 cm⁻¹, the Raman-active modes of doped LaFeO₃ compounds are essentially a result of the A-site ion vibrations and known as (A) modes. Between 200 and 300 cm⁻¹, modes are associated with the oxygen octahedral tilt known as (T) modes, while modes present between 400 cm⁻¹ and 450 cm⁻¹ are attributed to the oxygen octahedral bending vibrations (B). Finally, the modes above 500 cm⁻¹ are identified by the oxygen stretching vibrations (S) [46].

At a very first look, the room temperature Raman spectra of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds appear completely in agreement with that of the parent LaFeO₃ perovskite [46,47], which confirms that all the studied compounds were crystalized in the orthorhombic structure and that there was no structural phase transition when partially substituting iron ions with Ti⁴⁺, Cr³⁺, and Mn³⁺ ones.



Figure 3. Raman spectra of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds.

Meanwhile, the introduction of these three ions induces a change in the intensity and width of some vibrational peaks. To better understand the insertion of Cr^{3+} , Ti^{4+} , and Mn^{3+} ions, we performed the Lorentzian deconvolution of the Raman spectra of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Cr^{3+} , and Mn^{3+}) compounds, as presented in Figure 4. According to the figures, one can clearly see the change in intensities and widths of Raman modes at the frequency range between 450 cm⁻¹ and 750 cm⁻¹, evidence of oxygen octahedral bending and vibrations. This confirms that the substitution affects the magnetic interactions, which induce the deformation of the octahedron FeO₆.



Figure 4. Cont.



Figure 4. Lorentzian fitting curves of the Raman signal of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Cr^{3+} , and Mn^{3+}) compounds.

3.3. Optical Properties

The optical reflectance spectra for all samples, as shown in Figure 5a, were obtained using diffuse reflectance spectroscopy (DRS) (Figure 5). To estimate the energy band gap, E_g , the Tauc plot, $(\alpha h\nu)^2$ as a function of $h\nu$, was plotted in the inset of Figure 5a. The linear extrapolation of the energy plot allowed the determination of the E_g values, which were found to be equal to 2.57, 2.50, and 1.22 eV for Cr, Ti, and Mn-doped samples, respectively. Consequently, these materials are candidates for photovoltaic devices and single junction solar cell [48].



Figure 5. (a) Diffuse reflectance spectroscopy measurements; the inset presents a Tauc plot for $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) samples; (b) the reflectance spectra of the studied samples.

The decrease in the band gap energy value observed for the Mn-doped compound can be explained by the difference in the ionic radii, which decreases the octahedral rotation, leading to a reduction in the band gap.

Moreover, this decrease can also be attributed to existing oxygen defects in the structure. As known, the energy level of the oxygen vacancy and the Fe- e_g and Fe- t_{2g} states are between the Mn- e_g and O-2p states and are the main contribution to the conduction bands and those of the valence of perovskite studied separately [49]. Impurity and defect levels behave as transitive steps to excite electrons. Thus, they could reduce the band gap. It is known that, in the optical linear field, the complex optical refractive index is given as follows:

$$\hat{n} = n(\lambda) + ik(\lambda) \tag{2}$$

Here, n is the real part, and k is the imaginary part. These parameters are the linear refractive index and the extinction coefficient, respectively, which can be calculated using the following relations [50–52].

1

$$c = \frac{\alpha_A}{4\pi} \tag{3}$$

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} + k^2}$$
(4)

The variation in the $n(\lambda)$ refractive index for different samples as a function of the wavelength is shown in Figure 6. The value of $n(\lambda)$ shows a significant decrease with an increasing wavelength. Above 900 nm, the refractive index remains almost constant.



Figure 6. The variation in refractive index as a function of wavelength for $La_{0.67}Ca_{0.2}Ba_{0.13}$ Fe_{0.97}M_{0.03}O₃ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) samples.

Using the refractive index $n(\lambda)$ and extinction coefficient k, we calculated the real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the dielectric constant using the following equations [53].

$$\varepsilon_1(\lambda) = n^2 - k^2 \tag{5}$$

$$\varepsilon_2(k) = 2nk \tag{6}$$

Figure 7a,b present the variation in $\varepsilon_1(\lambda)$ and $\varepsilon_2(\lambda)$ as a function of wavelength. For both $\varepsilon_1(\lambda)$ and $\varepsilon_2(\lambda)$, we notice the presence of two pics related to the high light absorption. The first is localized near 400 nm and related to the strong light absorption in the visible range, while the second large pic is related to the absorption in the IR region.



Figure 7. Variation of (**a**) reel and (**b**) imaginary parts of dielectric constants as a function of wavelength for $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) samples.

Figure 8 shows the variation in optical and electrical conductivity (δ_{opt} and δ_{el}) estimated using the following relations:

$$\delta_{opt} = \frac{\alpha nc}{4\pi} \tag{7}$$

$$\delta_{el} = \frac{\lambda nc}{2\pi} \tag{8}$$

Figure 8. Variation in (a) optical and (b) electrical conductivity as a function of wavelength for $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) samples.

Electrical and optical conductivities are two types of contributions that can be used to express conductivity. The first is concerned with the mobility of charge carriers in the material, whereas the second is concerned with the mechanism of electron–photon interactions. The conductivity of a semiconductor is proportional to the temperature and the band gap energy, E_g . As noticed in Figure 8a, the increment in optical conductivity is related to higher absorbance at a lower wavelength range due to the excited electrons that cross the forbidden band gap due to higher photon energy. It is known that optical conductivity is mainly associated with the free charges that absorb the photon energy, and therefore, a significant increase in optical conductivity occurs [53]. Moreover, we remark that Ti-doped materials present a higher optical conductivity in the UV region, which is related principally to the higher optical absorption of this material in this region. On the other hand, Mn-doped material, which presents the agglomeration of higher particles observed using TEM, is characterized by a lower optical absorption.

The electrical conductivity results (Figure 8b) show that the values are in the range of 102 S/m, which supports the semiconducting nature of the studied material [53]. In addition, we note that the electrical conductivity is much lower than the optical conductivity ($\sigma_{el} \ll \sigma_{op}$), which can be interpreted by the fact that the free charge carriers do not have sufficient energy to jump the potential barrier level [54].

3.4. Gas-Sensing Measurements

Ethanol and acetone gas-sensing measurements have been tested for $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds. To further understand the metal ion insertion effect on gas-sensing properties, we highlight the following three important parameters: the response, the operating temperature, and response/recovery times. It is important to mention that the optimum working temperature should be studied first, then other parameters could be tested at this temperature. For this, we performed a series of experiments in a temperature range from 160 °C to 260 °C under 100 ppm of ethanol and acetone gases, as shown in Figures 9a and 10a, respectively. For both gases, the response of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds increase to reach a maximum value at 200 °C and then decrease for further temperature increases. Accordingly, 200 °C is considered the optimum operating temperature for all compounds at which the response of different concentrations, selectivity, and response-recovery time properties are measured for both ethanol and acetone gases. It is worth noting that this temperature is lower than those reported for pure and doped Lanthanum ferrite materials [55–57], which confirms the utility of this work. As presented in Table 1, the obtained optimum temperature is also lower than those reported for other semiconductor sensors.

Furthermore, one can see from Figures 9a and 10a that at 200 °C, the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ (M = Ti⁴⁺) compound showed the highest response values towards 100 ppm of ethanol and acetone gases. Its response value to ethanol gas is almost equal to that of acetone gas, confirming the high utility of this compound for ethanol and acetone gas detection. The high response results of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound may be related to its lowest particle size, as deduced from the morphological study.

Sensor	S	C _g (ppm)	T _{opr} (°C)	Reference	
WO ₃ –SnO ₂ composite	1.73	300 (ethanol)	250	[58]	
Core-shell WO ₃ -SnO ₂ nanofibers	5.09	10 (ethanol)	280	[59]	
NiO nanosheets	4.09	500 (ethanol)	200	[60]	
LaFeO ₃ (Sol-gel)	0.55	500 (acetone)	275	[61]	
La _{0.7} Sr _{0.3} FeO ₃ (Sol-gel)	0.7				
La _{0.68} Pb _{0.32} FeO ₃ (Sol-gel)	50	7	240	[62]	
La _{0.67} Ca _{0.2} Ba _{0.13} Fe _{0.97} Ti _{0.03} O ₃ —	3.91	5 (ethanol)	200	— This work	
	3.82	5 (acetone)	250		

Table 1. The response towards ethanol and acetone gases in the studied materials (this work) compared with the literature results.

C_g: gas concentration; S: response; T_{opr}: optimum operating temperature.

Figure 9. (a) Response vs. temperature; (b) transient response of $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}B_{0.03}O_3$ (B = Ti⁴⁺, Mn³⁺, and Cr³⁺)-based sensors exposed to different ethanol gas concentrations at an operating temperature of 200 °C; (c) response vs. concentrations towards ethanol gas; and (d) the response and recovery time of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}B_{0.03}O_3$ (B = Ti⁴⁺, Mn³⁺, and Cr³⁺) gas sensors to 100 ppm.

For all La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O₃ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds, at 200 °C, the response tests under different ethanol and acetone concentrations were realized as presented, respectively, in Figures 9b and 10b. These response curves were deduced from the gas-sensing resistance curves (Response = R_g/R_a). One can see that when compounds are exposed to ethanol and acetone gases, the response (the resistance) of all compounds increases, confirming the p-type semiconductor behavior of all La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O₃ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) compounds. Furthermore, the response increases with increasing the ethanol and acetone gas concentration, showing an almost linear behavior. This is due to the presence of high gas-adsorbing vacancies on the surface of sensors [57]. It was reported that when the gas concentration increases, the quantity of adsorbed gas molecules on the surface increases unceasingly, leading to an increase in resistance. The increase in the sensor resistance is due to an increase in the electrons acquired by the p-type semiconductor sensor [63]. Once again, from these figures, we can deduce that the La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O₃ compound presents the highest response values towards

ethanol and acetone gases, which confirms the utility of the Titanium ion insertion for gas-sensing applications. On the other side, we plotted in Figures 9c and 10c the response vs. gas concentration curves. The response values of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound to 5 ppm of ethanol and acetone gases are equal to 3.94 and 3.68, respectively. It indicates that this compound is suitable for detecting very low ethanol and acetone concentrations, which have practical applications.

Figure 10. (a) Response vs. temperature; (b) transient response of $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}B_{0.03}O_3$ (B = Ti⁴⁺, Mn³⁺, and Cr³⁺)-based sensors exposed to different acetone gas concentrations at an operating temperature of 200 °C; (c) response vs. concentrations towards acetone gas; and (d) the response and recovery time of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}B_{0.03}O_3$ (B = Ti⁴⁺, Mn³⁺, and Cr³⁺) gas sensors to 100 ppm.

The response and recovery times are key vectors for a sensor and can be defined as the time required to reach a 90% response (recovery) when gas is in (out) [64]. For gassensing applications, quick response and recovery is very important. For all compounds, the response and recovery times were calculated for 10 ppm of both gases, and the resulting values are presented in Figures 9d and 10d (see Table 2). For the La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O₃ compound, the response and recovery times were less than 56 s. The short response and

recovery times and high response to very low ethanol and acetone gas concentrations allow this compound to be a potential candidate for gas-sensing applications.

Table 2. Recovery and response times of all $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Mn³⁺, and Cr³⁺) compounds when exposed to ethanol and acetone gases.

Gas	Time	$M = Ti^{4+}$	$\mathbf{M} = \mathbf{M}\mathbf{n}^{3+}$	$\mathbf{M} = \mathbf{C}\mathbf{r}^{3+}$
Ethanol	Response time	40.74	37.39	28.84
	Recovery time	43.67	26.35	48.03
Acetone	Response time	50.39	57.387	45.549
	Recovery time	56.32	49.347	59.739

The detection mechanism of the synthesized p-type semiconductor sensor is based on resistance behavior when exposed to gases [65–67]. In the air, oxygen species may be adsorbed on the nanoparticle's surface and O_2^- , O^{2-} , and O^- ions are consequently formed using the electrons captured from the conduction band of our sensor. A hole-accumulation layer is formed on the sensor's surface, leading to a decrease in resistance. The adsorption and desorption of oxygen can be explained by the following mechanism [68]:

$$O_{2(gaz)} \leftrightarrow O_{2(ads)}$$
 (9)

$$O_{2(gaz)} + \bar{e} \leftrightarrow O_{2(ads)}^{-} \tag{10}$$

$$O_{2(ads)}^{-} + \bar{e} \leftrightarrow 2O_{(ads)}^{-} \tag{11}$$

$$O^{-}_{(ads)} + \bar{e} \leftrightarrow O^{2-}_{(ads)} \tag{12}$$

Here, "gas" and "ads" refer to the state of gas and adsorption, respectively. These reactions show an increase in the concentrations of holes, leading to a lower resistance. When the gas sensor is in contact with the detected gas, the adsorbed oxygen reacts on the surface of the sensor as follows [69]:

$$R + O_{(ads)}^{n-} \leftrightarrow RO + n\bar{e} \tag{13}$$

Accordingly, when ethanol or acetone gas is introduced, the following reaction may occur, respectively, [20,61]:

$$C_2 H_6 O_{(gas)} + 6 O_{(ads)}^- \rightarrow 2 C O_2 + 3 H_2 O + 6 \overline{e}$$
 (14)

$$CH_3COCH_3 + 8O^-_{(ads)} \rightarrow 3CO_2 + 3H_2O + 8\bar{e} \tag{15}$$

During these reactions, the electrons are released back into the conduction band of the sensor. Their interaction with the holes implies a decrease in the charge carrier concentration on the surface of the sensor and, consequently, an increase in resistance [70].

4. Conclusions

In summary, this paper presents an in-depth study of the morphological, optical, and gas-sensing properties of the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}M_{0.03}O_3$ (M = Ti⁴⁺, Cr³⁺, and Mn³⁺) nanoparticle oxides which were prepared using the auto-combustion method. The analysis of TEM images shows the nanoscale of all samples with particle sizes equal to 36, 31, and 41 nm for Mn, Ti, and Cr-doped compounds, respectively. The optical study shows semiconductor behavior for all studied compounds. Based on Tauc plots, the band gap values were found to be equal to 2.57, 2.50, and 1.22 eV for Cr, Ti, and Mn-doped samples, respectively. Moreover, all compounds exhibit an optimum operating temperature equal to 200 °C for ethanol and acetone gas detection, which is lower than values in the literature for p-type MOX sensors. Compared to other studied compounds, the

 $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Ti_{0.03}O_3$ compound presents the highest response values to low concentrations of ethanol and acetone gases at 200 °C, confirming its utility for p-type MOX sensor manufacturing. Also, the $La_{0.67}Ca_{0.2}Ba_{0.13}Fe_{0.97}Mn_{0.03}O_3$ compound presents the lowest response and recovery time values (<37 s).

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