

# Ozone detection based on nanostructured L a 0.8 P b 0.1 C a 0.1 F e 0.8 C o 0.2 O 3 thin films

S. Smiy, M. Bejar, E. Dhahri, T. Fiorido, Marc Bendahan, K. Aguir

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#### Manuscript Draft

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Title: Ozone detection based on nanostructured La(0.8)Pb(0.1)Ca(0.1)Fe(0.8)Co(0.2)O(3)thin films

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Abstract: The present paper describes the synthesis of gas sensors based on thin films perovskite-type La\_0.8 Pb\_0.1 Ca\_0.1 Fe\_0.8 Co\_0.2 O\_(3) over a [Sio] \_2/Si substrate with interdigitated Pt-electrodes using the drop coating method. The perovskite starting nanoparticles have been prepared by the sol-gel method and they have an orthorhombic structure with Pnma space group. The prepared thin film has been tested as a sensitive film for ozone detection and shows a promising response. The detection of low concentration of ozone (equal to 50 ppb) makes the prepared thin film a potential sensor for ozone detection.

**Cover Letter** 

#### **Cover letter**

#### Pr. Moez BEJAR

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22/12/2019

Dear Editors of the Journal of Alloys and compounds.

I am pleased to submit our manuscript entitled:

"Ozone detection based on nanostructured  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  thin films" for consideration for publication in the Journal of Alloys and compounds.

It has not been published elsewhere and that it has not been submitted simultaneously for publication elsewhere. In this manuscript, we investigated the response of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  compound toward the Ozone oxidizing gas.

Thank you for your consideration,

Yours Sincerely;

Pr. Moez BEJAR

### **Prime Novelty Statement**

The  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sample has been prepared using the drop coating method. The structural and Ozone gas-sensing properties were reported. The gas sensing properties of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  shows that ours sensor can detect low concentrations of Ozone-gas and we deduced that our sensor can be used as promising candidates to detect Ozone-gas added to that our captor is able to detect this dangerous gas at different concentration.

Ozone detection based on nanostructured

 $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  thin films

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**ABSTRACT** 

The present paper describes the synthesis of gas sensors based on thin films perovskitetype La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> over a SiO<sub>2</sub>/Si substrate with interdigitated Ptelectrodes using the drop coating method. The perovskite starting nanoparticles have been prepared by the sol-gel method and they have an orthorhombic structure with *Pnma* space group. The prepared thin film has been tested as a sensitive film for ozone detection and shows a promising response. The detection of low concentration of ozone (equal to 50 ppb) makes the prepared thin film a potential sensor for ozone detection.

*Keywords*: perovskite, drop-coating, thin films, semiconductor, gas sensor, ozone.

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**I-INTRODUCTION** 

Recently, the synthesis of advanced materials for many applications has been widely investigated in literature. In particular, the interest for the perovskite materials  $LnMO_3$ (Ln: lanthanide and M: trivalent cations), destinated for innovative technological applications, such as catalysis, magnetocaloric and gas sensing field, have grown steadily

**[1-4]**.

The  $LaFeO_3$  is a potential functional material which is used in many fields such as gassensing in the detection of many gases, including HCHO,  $CH_4O$  and  $CH_3COCH_3$  [5-9]. Also, derivates of  $LaFeO_3$  are very used in the detection of dangerous gases. Song et al. have proven that introducing Pb in the A-site to replace Lanthanum (La) increase the response of  $LaFeO_3$  material [10]. In addition, the introduction of Ca in  $LaFeO_3$  has caused the increase of sensitivity of  $La_{1-x}Ca_xFeO_3$  to alcohol [11]. In another study, H.

Saoudi et *al.* **[12]** have reported that introducing Cobalt (Co) in B-site in  $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$  perovskite materials will increase the response because the sample with x=0.05 shows the higher sensitivity of  $NH_3$ -gas compared to  $La_{0.8}Ca_{0.1}Pb_{0.1}FeO_3$  sample.

The ozone-gas has been emerged in many fields, *e.g.* textile, food, water treatment, pharmaceutical and chemical industries [3]. Consequently, ozone constitutes one part of the summer toxic smog. However, for a concentration above  $120 \, ppb$  in the atmosphere, Ozone could cause serious health problems (*e.g.* burning eyes, lung damage and respiratory irritation) [13, 14]. Moreover, the air quality is classified referring to the Ozone amount in the atmosphere: very good  $(0 - 50 \, ppb)$ , good  $(50 - 100 \, ppb)$ , poor  $(100 - 200 \, ppb)$  and very poor  $(> 200 \, ppb)$  [3]. For all the above reasons, the monitoring of the Ozone concentration in our atmosphere is becoming a serious issue. In our previous published work related to this framework, we have demonstrated the high sensing properties of La<sub>0.885</sub>Pb<sub>0.005</sub>Ca<sub>0.11</sub>FeO<sub>2.95</sub> towards the NH<sub>3</sub>-gas [1].

In line with our interest in the study of gas sensing, we report in the present research the synthesis of a thin film gas sensor based perovskite-type  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  over a  $SiO_2/Si$  substrate with interdigitated Pt-electrodes using a drop coating as a new method.

#### **II- EXPERIMENTAL DETAILS**

#### II-1) Preparation of perovskite nano-powder

Nano-powder of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  has been prepared by mixing different nitrates:  $La(NO_3)_36H_2O$ ,  $Pb(NO_3)_22H_2O$ ,  $Ca(NO_3)_26H_2O$ ,  $Fe(NO_3)_39H_2O$  and  $Co(NO_3)_2$  6H<sub>2</sub>O as precursors according to the proportion indicated in the equation below:

$$\textbf{0.8} \, \text{La}(\text{NO}_3)_3 6\text{H}_2\text{O} + \textbf{0.1} \, \text{Pb}(\text{NO}_3)_2 2\text{H}_2\text{O} + \textbf{0.1} \, \text{Ca}(\text{NO}_3)_2 6\text{H}_2\text{O} + \textbf{0.8} \, \text{Fe}(\text{NO}_3) 9\text{H}_2\text{O} \\ + \textbf{0.2} \, \text{Co}(\text{NO}_3)_2 6\text{H}_2\text{O} \longrightarrow \text{La}_{0.8} \text{Pb}_{0.1} \text{Ca}_{0.1} \text{Fe}_{0.8} \text{Co}_{0.2} \text{O}_3 + gaz$$

Then, the collected powder has been sintered at 300, 600 and 900 °C for 24h for each temperature.

#### II-2) Thin film preparation

The perovskite thin-film was deposited over the  $SiO_2/Si$  substrate (4 mm x 4 mm) with interdigitated Pt- electrodes by the drop coating method. Firstly, a slurry of 20 mg of

perovskite mixed with  $20 \, ml$  of 2-propanol has been prepared and ultrasonicated for  $10 \, min$  at  $40 \, ^{\circ}C$  to ensure a good homogenization for the mixture. Subsequently, the deposition of the thin film was assured by coating the substrate drop by drop using a micropipette. The process has been combined with heating at  $50 \, ^{\circ}C$  after each drop to remove the solvent. The thin film properties were optimized at 8 drops which makes a total of  $20 \, \mu l$ . Finally, after the deposit of 8 drops a heating for one hour at  $550 \, ^{\circ}C$  will take place(**Fig. 1**).

#### II-3) Ozone sensing measurement:

To investigate the ozone sensing properties of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  films, the sensors have been introduced in a test chamber allowing the control of the sensor temperature under variable gas concentrations. Dry air has been used as a reference gas. Ozone gas was generated by oxidizing oxygen using a pen-ray UV lamp (Stable Ozone Generator  $UVP/185 \, nm$ ). The intensity of the UV radiation was varied by shifting a shutter around the lamp. The different ozone concentrations are obtained in the range of  $30-800 \, ppb$  with a flow rate of dry air maintained at  $0.5 \, l/min$ .

The operating temperature of the sensor has been adjusted between 160 °C and 280 °C to determine the best sensor response. In this case, our sensor was exposed to *100 ppm* ozone-concentration for *1 min* in order to identify the best operating temperature.

The applied dc voltage for sensor measurement is 1V and the current is measured using a computerized sourcemeter type Keithley 4250. The sensor response is defined as  $S = R_a/R_g$ , where  $R_a$  and  $R_g$  are the resistance under air and the resistance when the sensor is exposed to ozone-gas, respectively.

#### **III- RESULTS AND DISCUSSION**

#### III-1) Scaling analysis

The Rietveld refinement of the X-ray diffractogram of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  nanopowder **(Fig. 2)** has revealed that our sample crystallizes in the orthorhombic structure with the *Pnma* space group. The lattice refined parameters a, b and c are 5.5493, 7.8489 and 5.5394 Å, respectively. The (hkl) Miller indices corresponding to the main reflexion planes of our sensor are  $(1\ 0\ 1)$ ,  $(0\ 0\ 2)$ ,  $(2\ 2\ 0)$ ,  $(0\ 4\ 0)$ ,  $(1\ 0\ 3)$ ,  $(3\ 2\ 1)$ ,  $(2\ 4\ 2)$  and  $(3\ 2\ 3)$ . Moreover, the analysis using "X0 Pert High Score Plus" program has shown the presence of  $Fe_3O_4$  as secondary phase.

The crystallite size  $(D_{W-H})$  of the powder has been evaluated using the Williamson-Hall method **[15]**  $(\beta \cos(\theta) = f(4\sin(\theta)))$  **(Fig. 3)**. The sensor has shown a nanometric crystallite size equal to 43.870 nm.

$$\beta \cos(\theta) = k\lambda/D_{WH} + 4\varepsilon \sin(\theta)$$
 (Eq. 2)

Where  $\beta$  is the width at half height,  $\varepsilon$  is the coefficient due to structural defects, k represents the grain form factor (k=0.9),  $\lambda$  is the radiation wavelength ( $\lambda=1.5406$  Å) and  $\theta$  is the angle corresponding to each peak.

#### III-2) Ozone sensing properties:

**Fig. 4** shows the variation of the electrical resistance as a function of time under dry air with a temperature increasing from 25 to 180 °C. The results show that the resistance decreases with increasing the temperature, which proves the semiconductor behavior of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor **[16]**.

In order to determine the operating temperature of our compound, the sensor responses in presence of  $100 \, ppb$  of ozone have been carried out at different temperatures between  $160^{\circ}$ C and  $280^{\circ}$ C. **Fig. 5** shows the resistance variation versus time at 170, 190, 260 and  $280^{\circ}$ C during ozone exposing time of  $1 \, min$ .

The results show that the sample displays reversibility and the curves present good stability of the baseline. Furthermore, the sample resistance has declined upon exposure to an oxidizing gas [17], indicating the p-type semiconductor behavior of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor [18]. In fact, with an oxidizing gas, such as Ozone, the conductivity increases due to the enhancement of the holes of concentration.

**Table.1** summaries the ozone  $(O_3)$ -responses values of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor. The maximum of the sensitivity  $(R_a/R_g)$  has been reached at  $170 \, ^{\circ}C$  when our sensor was exposed to  $100 \, ppb$  for 1min,  $170 \, ^{\circ}C$  is considered as the operating temperature  $(T_{op})$  of the sensor.

The sensor performances have also been evaluated with different ozone concentrations and the results are presented in **Fig.** 6(a). The results exhibit the sensing ability of the thin-film in all the studied ozone concentrations. In the same way, **Fig.** 6(b) shows that the response intensities increase together with the ozone concentration and reach a maximum of 3.6 for the concentration of 400 ppb. The recorded values are depicted in **Table 2**. These values are better compared with those reported earlier [19-22].

The response time  $(\tau_{resp})$  is another important parameter to evaluate the sensor, which is the time required to reach 90 % of the electrical resistance when the sensor is exposed to Ozone gas [1]. The response time values  $(\tau_{resp})$ , recorded and gathered in **Table 3**, have revealed that  $\tau_{resp}$  decreases when increasing the concentration at the operating temperature of 170 °C. The same trend was observed previously by Masami Mori and *al.* [3]. In contrast, La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> sensor has low response time values compared to other perovskite materials, such as SmFeO<sub>3</sub> [3].

The La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> response, signal and response time are influenced by the quantity and quality of oxygen adsorbed on the surface of our sensor [23]. On the surface, atmospheric oxygen can be adsorbed very easily and atoms or molecules become chemisorbed ions  $O^-$  or  $O_2^-$ . When the temperature increases the state of oxygen on the surface undergoes the following reactions (from Eq. 3 to Eq. 6) and this phenomenon is demonstrated theoretically by using the SnO<sub>2</sub> model [24]. In fact, our thin film presents an increase in hole concentration because when oxygen species are adsorbed in La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> the sensor surface will capture electrons from our sensor which is a p-type semiconductor and consequently a depletion region of electrons is thus formed [25]. Added to that, at the operating temperature ( $T_{Op}$ ) we have a maximum of oxygen adsorbed on the surface of La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> sensor [1].

$$O_{2(gas)} \leftrightarrow O_{2(ads)}$$
 (Eq. 3)

$$O_{2(ads)} + e^- \leftrightarrow O_{2(ads)}^- \tag{Eq. 4}$$

$$O_{2(ads)}^{-} + e^{-} \leftrightarrow 2O_{ads}^{-}$$
 (Eq. 5)

$$O_{(ads)}^- + e^- \leftrightarrow O_{(ads)}^{2-}$$
 (Eq. 6)

The chemical reactions process between free adsorption site S and the triatomic gases, as Ozone  $(O_3)$ , are [26]:

$$S + O_3 \rightarrow (S - O) + O_2$$
 (Eq. 7)

$$(S-O) + e^- \rightarrow (S+O)^-$$
 (Eq. 8)

#### **IV- CONCLUSION**

In this research paper, the  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor has been successfully prepared by the drop coating method and tested as an ozone sensor. The prepared thin-film showed sensitivity to ppb-levels of ozone gas. The resistance study as a function of

time at different working temperatures depicted the good sensitivity of our sensor especially at the operating temperature of  $170\,^{\circ}C$ . In addition, our sensor can be used in the distinction of the air quality for the ozone and sub-ppm levels detection becomes possible.

Our study shows the possibility of the use of our sensor in the field of the detection of ozone-gas. Another necessary part of our work is the study of the selectivity of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor.

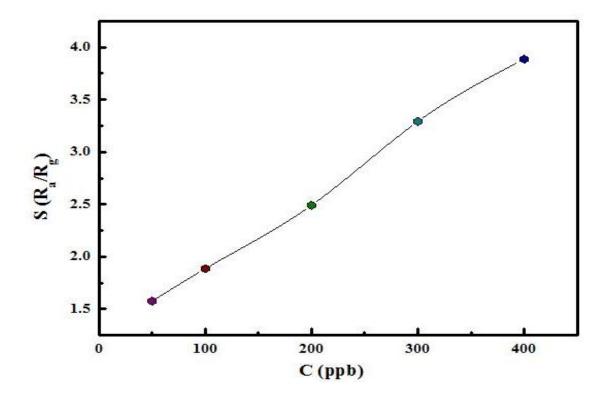
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# **Graphical abstract**



# **Research Highlights**

- $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sample crystallizes in the orthorhombic structure with Pnma space group.
- Our compound presents a nano-metric size.
- $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  shows a p-type semiconductor behavior.
- $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor can detect the Ozone-gas even with low concentration equal to 50 ppb.
- T=170°C is the operating temperature of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor.

**Table 1**: The relationship between response  $(S = R_a/R_g)$  and temperature (T) of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  based sensors to Ozone gas.

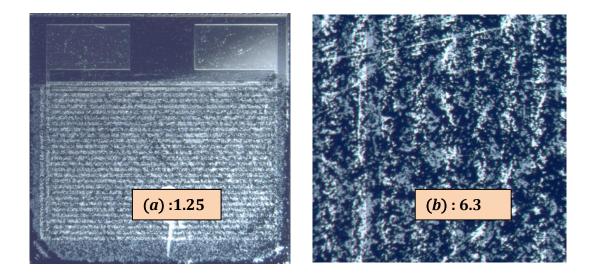
| <i>T</i> (°C) | S     | T (°C) | S     |
|---------------|-------|--------|-------|
| 160           | 1.282 | 230    | 1.146 |
| 170           | 1.286 | 240    | 1.129 |
| 180           | 1.139 | 250    | 1.131 |
| 190           | 1.206 | 260    | 1.118 |
| 200           | 1.187 | 270    | 1.106 |
| 210           | 1.152 | 280    | 1.132 |
| 220           | 1.186 |        |       |

<u>**Table 2**</u>: Response values  $(S = R_a/R_g)$  of La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> sensor (our study) compared to others materials considered for Ozone sensing application.

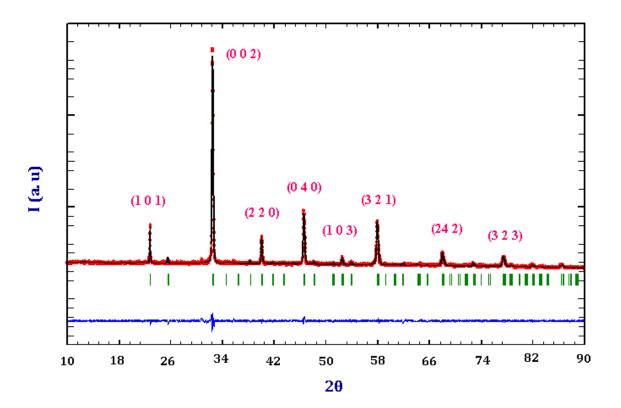
| Sensors                                       | T<br>(°C) | C<br>(ppb) | S    | References |
|---|-----------|------------|------|------------|
| <b>WO</b> <sub>3</sub> (EG : 50μm)            | 250       | 200        | 1.7  | [19]       |
| <b>WO</b> <sub>3</sub> (EG : 50μm)            | 250       | 400        | 2.3  | [19]       |
| <b>WO</b> <sub>3</sub> (EG : 50μm)            | 250       | 800        | 2.8  | [19]       |
| $WO_3$  | 300       | 50         | 1.25 | [20]       |
| $WO_3$  | 300       | 100        | 1.42 | [20]       |
| $WO_3$  | 300       | 150        | 1.78 | [20]       |
| $WO_3$  | 300       | 175        | 2.25 | [20]       |
| $SrTi_{0.925}Fe_{0.075}O_3$                   | 250       | 75         | 3    | [21]       |
| $SmFe_{0.8}Co_{0.2}O_3$                       | 200       | 400        | 3    | [22]       |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 50         | 1.6  | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 100        | 1.9  | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 200        | 2.5  | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 300        | 3.3  | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 400        | 3.9  | Our study  |

<u>Table 3</u>: Response times  $(\tau_{resp})$  of La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> sensor at different concentrations (*C*) at the operating temperature of 170 °C compared to the SmFeO<sub>3</sub> sensor.

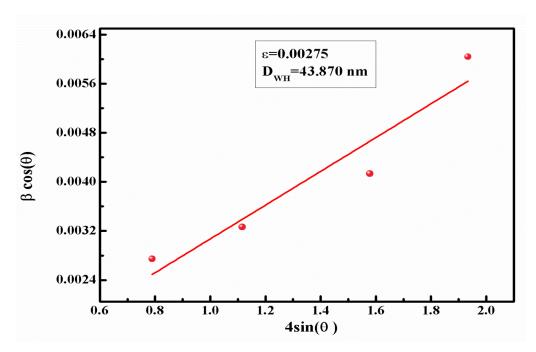
| Sensors                                       | Т<br>(°С) | C<br>(ppb) | $	au_{resp} \ (	extit{min})$ | References |
|---|-----------|------------|------------------------------|------------|
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 50         | 3.5                          | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 100        | 3.0                          | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 200        | 2.5                          | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 300        | 2.2                          | Our study  |
| $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ | 170       | 400        | 2.1                          | Our study  |
| SmFeO <sub>3</sub>                            | 200       | 50         | 8.4                          | [3]        |
| SmFeO <sub>3</sub>                            | 200       | 300        | 5.2                          | [3]        |
| SmFeO <sub>3</sub>                            | 200       | 500        | 4.0                          | [3]        |
| SmFeO <sub>3</sub>                            | 200       | 3000       | 1.2                          | [3]        |

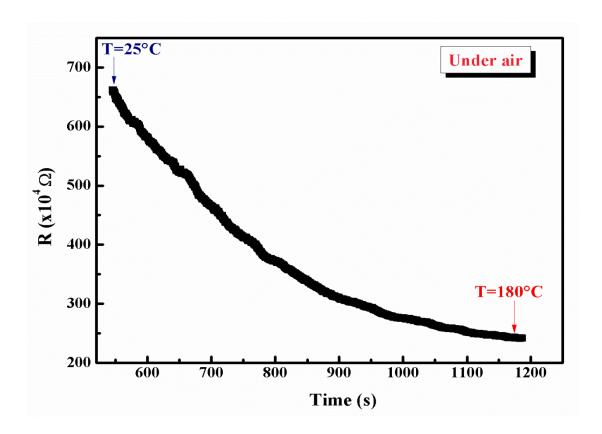


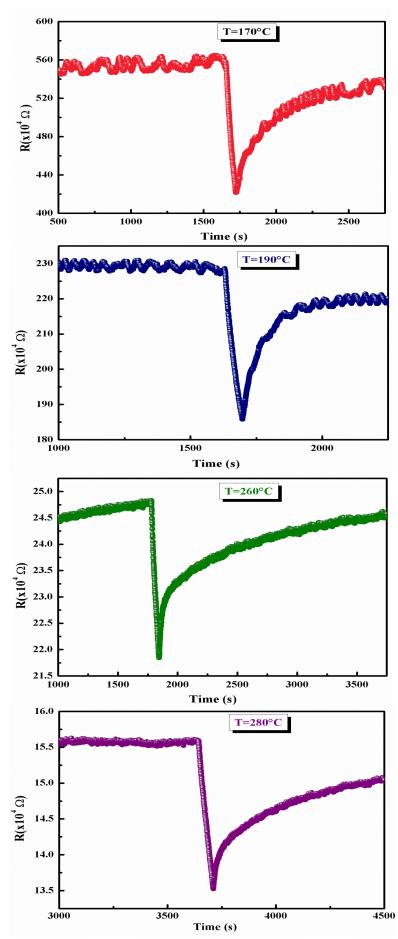
**Figure 1:** (*a*) Optical sensor view after drop coating of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor and (*b*) the zoom of the figure.



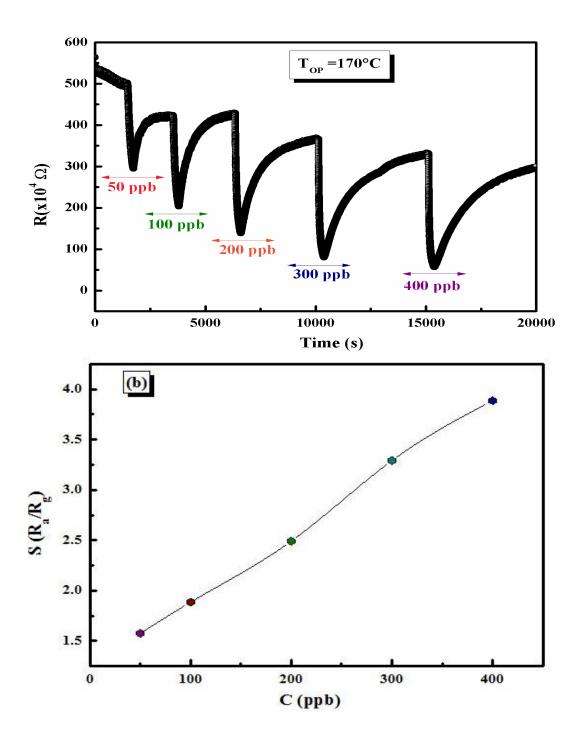
**Figure 2:** Observed (red), calculated (black solid line), their difference patterns (blue) and the Bragg positions (green) of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor and the secondary phase which is attributed to the  $Fe_3O_4$  impurity.







**Figures 5:** Ozone gas response of  $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$  sensor as a function of time at several temperatures (170, 190, 260 and 280 °C).



<u>Figures 6:</u> La<sub>0.8</sub>Pb<sub>0.1</sub>Ca<sub>0.1</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> sensor response (S) to (a) oxidizing gas ( $O_3$ ) and (b) sensor responses depending on the  $O_3$  concentration.

\*Declaration of Interest Statement

| Declaration of interests   |
|--|
| $\boxtimes$ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. |
| ☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:   |
|  |