



Ozone detection based on nanostructured $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ thin films

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S. Smiy, M. Bejar, E. Dhahri, T. Fiorido, Marc Bendahan, et al.. Ozone detection based on nanostructured $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ thin films. *Journal of Alloys and Compounds*, 2020, 829, pp.154596. 10.1016/j.jallcom.2020.154596 . hal-02867068

HAL Id: hal-02867068

<https://amu.hal.science/hal-02867068>

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Manuscript Number:

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

Article Type: Full Length Article

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

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Fiorido; Marc Bendahan; Khalifa Aguir

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}O₃ 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

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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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 **$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$** compound toward the Ozone oxidizing gas.

Thank you for your consideration,

Yours Sincerely;

Pr. Moez BEJAR

Prime Novelty Statement

The $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sample has been prepared using the drop coating method. The structural and Ozone gas-sensing properties were reported. The gas sensing properties of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ thin films

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ABSTRACT

The present paper describes the synthesis of gas sensors based on thin films perovskite-type $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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.

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), destined 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 gas-sensing in the detection of many gases, including HCHO , CH_4O and CH_3COCH_3 [5-9]. Also, derivatives 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 $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$ to alcohol [11]. In another study, H.

Saoudi et al. [12] have reported that introducing Cobalt (Co) in B-site in $\text{La}_{0.8}\text{Ca}_{0.1}\text{Pb}_{0.1}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ perovskite materials will increase the response because the sample with $x=0.05$ shows the higher sensitivity of NH_3 -gas compared to $\text{La}_{0.8}\text{Ca}_{0.1}\text{Pb}_{0.1}\text{FeO}_3$ 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 ($0 - 50 \text{ ppb}$), good ($50 - 100 \text{ ppb}$), poor ($100 - 200 \text{ ppb}$) and very poor ($> 200 \text{ ppb}$) [3]. For all the above reasons, the monitoring of the Ozone concentration in our atmosphere is becoming a serious issue.

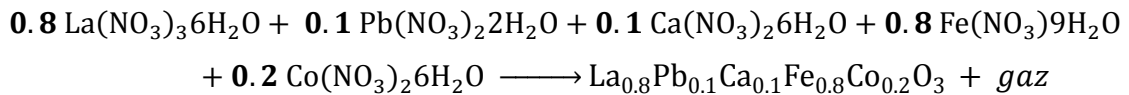
In our previous published work related to this framework, we have demonstrated the high sensing properties of $\text{La}_{0.885}\text{Pb}_{0.005}\text{Ca}_{0.11}\text{FeO}_{2.95}$ towards the NH_3 -gas [1].

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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ has been prepared by mixing different nitrates: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursors according to the proportion indicated in the equation below:



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 ($4 \text{ mm} \times 4 \text{ mm}$) 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 °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 °C after each drop to remove the solvent. The thin film properties were optimized at 8 drops which makes a total of 20 μ l. Finally, after the deposit of 8 drops a heating for one hour at 550 °C will take place(**Fig. 1**).

II-3) Ozone sensing measurement:

To investigate the ozone sensing properties of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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.

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

Where β is the width at half height, ε is the coefficient due to structural defects, k represents the grain form factor ($k = 0.9$), λ is the radiation wavelength ($\lambda = 1.5406 \text{ \AA}$) and θ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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°C and 280°C. Fig. 5 shows the resistance variation versus time at 170, 190, 260 and 280 °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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor. The maximum of the sensitivity (R_a/R_g) has been reached at 170 °C when our sensor was exposed to 100 ppb for 1min, 170 °C is considered as the operating temperature (T_{Op}) of the sensor.

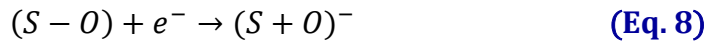
The sensor performances have also been evaluated with different ozone concentrations and the results are presented in Fig. 6(a). The results exhibit the sensing ability of the thin-film in all the studied ozone concentrations. In the same way, Fig. 6(b) shows that the response intensities increase together 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 (τ_{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 (τ_{resp}), recorded and gathered in Table 3, have revealed that τ_{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, $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor has low response time values compared to other perovskite materials, such as SmFeO_3 [3].

The $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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_2 model [24]. In fact, our thin film presents an increase in hole concentration because when oxygen species are adsorbed in $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor [1].



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



IV- CONCLUSION

In this research paper, the $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ 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 $170\text{ }^{\circ}\text{C}$. 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 $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor.

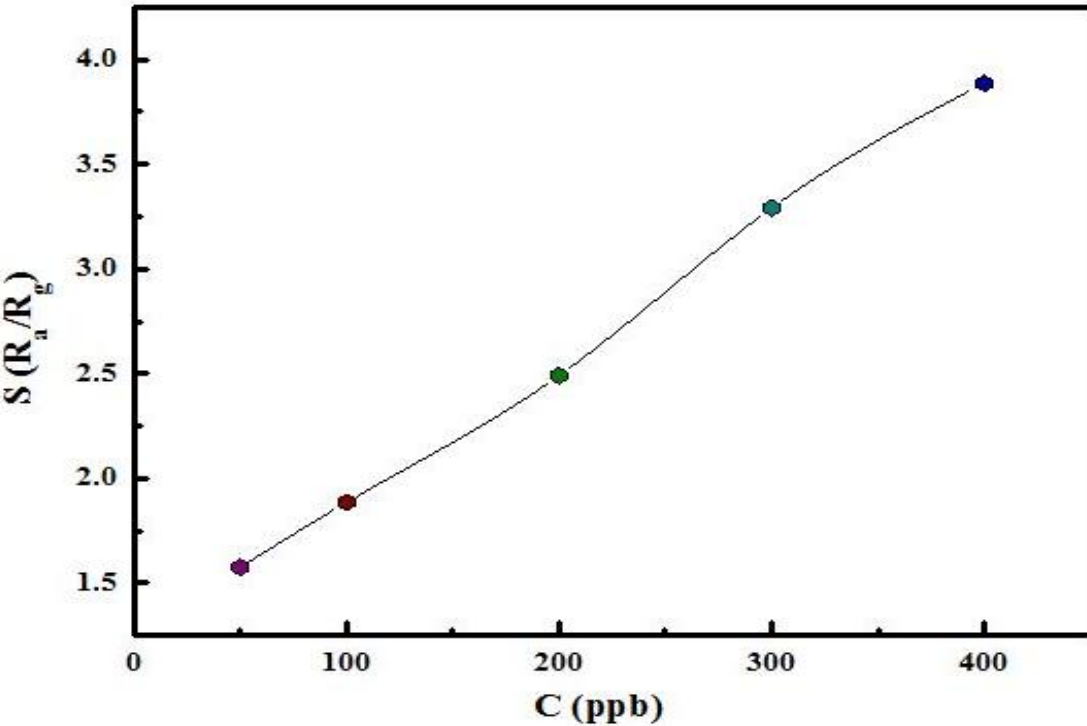
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Graphical abstract



Research Highlights

- $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sample crystallizes in the orthorhombic structure with Pnma space group.
- Our compound presents a nano-metric size.
- $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ shows a *p*-type semiconductor behavior.
- $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor can detect the Ozone-gas even with low concentration equal to 50 ppb.
- $T=170^\circ\text{C}$ is the operating temperature of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor.

Table 1: The relationship between response ($S = R_a/R_g$) and temperature (T) of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ based sensors to Ozone gas.

T (°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		

Table 2: Response values ($S = R_a/R_g$) of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor (our study) compared to others materials considered for Ozone sensing application.

<i>Sensors</i>	T (°C)	C (ppb)	S	References
WO_3 (EG : 50 μm)	250	200	1.7	[19]
WO_3 (EG : 50 μm)	250	400	2.3	[19]
WO_3 (EG : 50 μm)	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]
$\text{SrTi}_{0.925}\text{Fe}_{0.075}\text{O}_3$	250	75	3	[21]
$\text{SmFe}_{0.8}\text{Co}_{0.2}\text{O}_3$	200	400	3	[22]
$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	170	50	1.6	Our study
$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	170	100	1.9	Our study
$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	170	200	2.5	Our study
$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	170	300	3.3	Our study
$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$	170	400	3.9	Our study

Table 3: Response times (τ_{resp}) of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor at different concentrations (C) at the operating temperature of 170 °C compared to the SmFeO_3 sensor.

<i>Sensors</i>	T (°C)	C (ppb)	τ_{resp} (min)	References
<i>$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$</i>	170	50	3.5	Our study
<i>$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$</i>	170	100	3.0	Our study
<i>$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$</i>	170	200	2.5	Our study
<i>$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$</i>	170	300	2.2	Our study
<i>$\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$</i>	170	400	2.1	Our study
<i>SmFeO_3</i>	200	50	8.4	[3]
<i>SmFeO_3</i>	200	300	5.2	[3]
<i>SmFeO_3</i>	200	500	4.0	[3]
<i>SmFeO_3</i>	200	3000	1.2	[3]

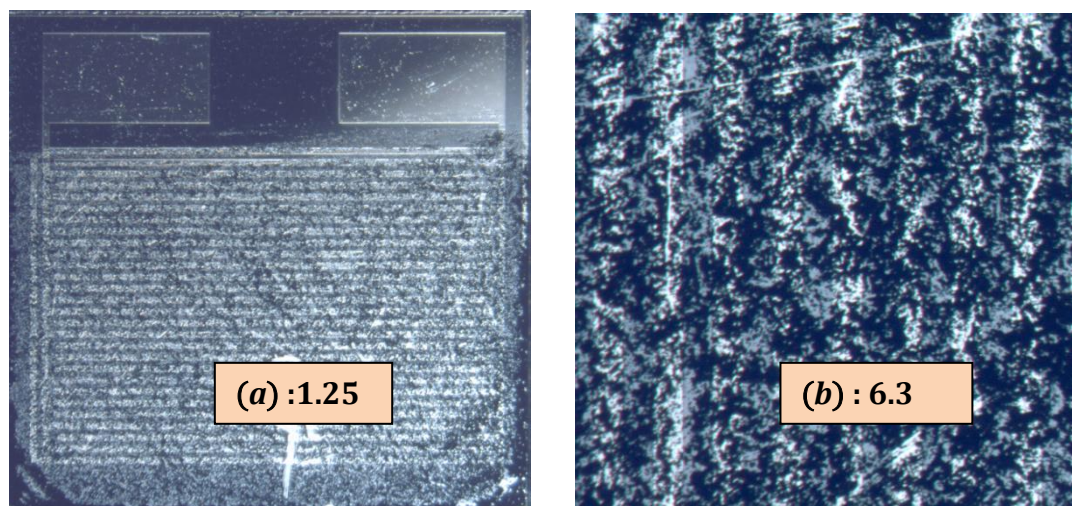


Figure 1: (a) Optical sensor view after drop coating of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor and (b) the zoom of the figure.

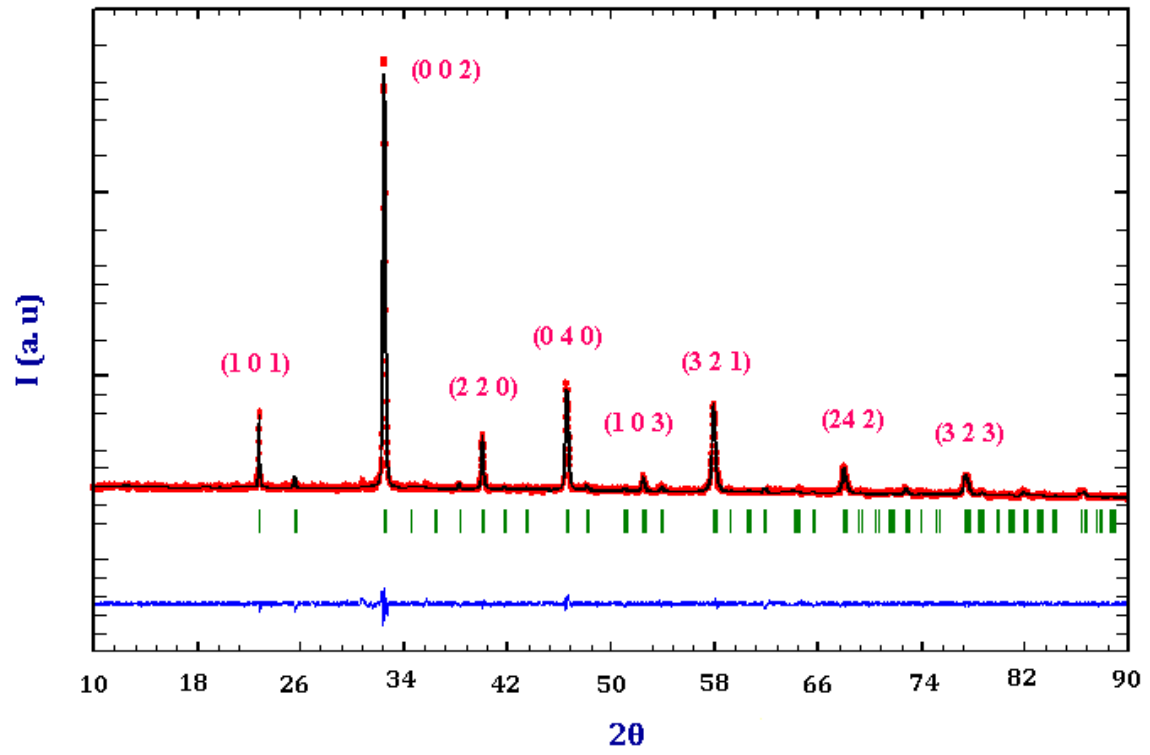


Figure 2: Observed (red), calculated (black solid line), their difference patterns (blue) and the Bragg positions (green) of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor and the secondary phase which is attributed to the Fe_3O_4 impurity.

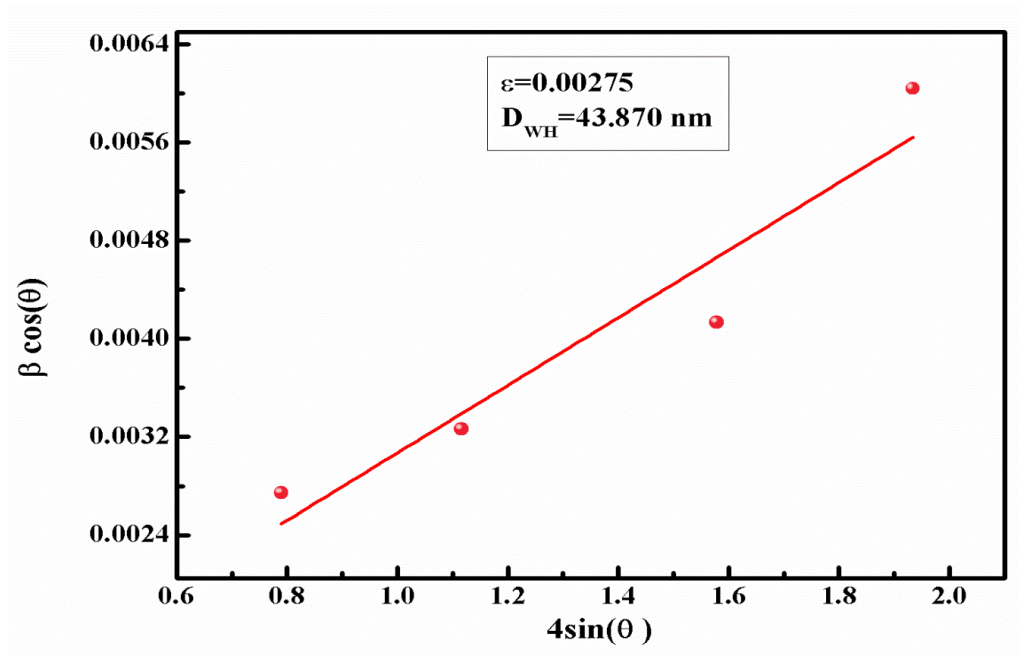


Figure 3: The Williamson–Hall analysis plots of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor.

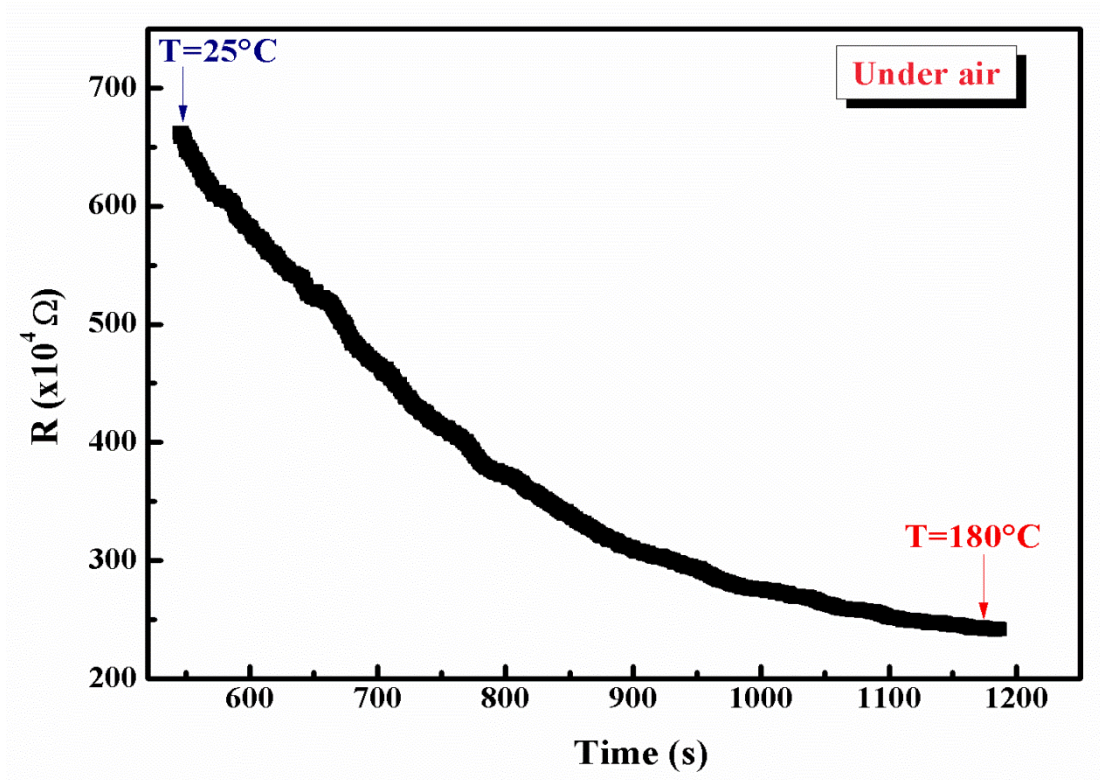
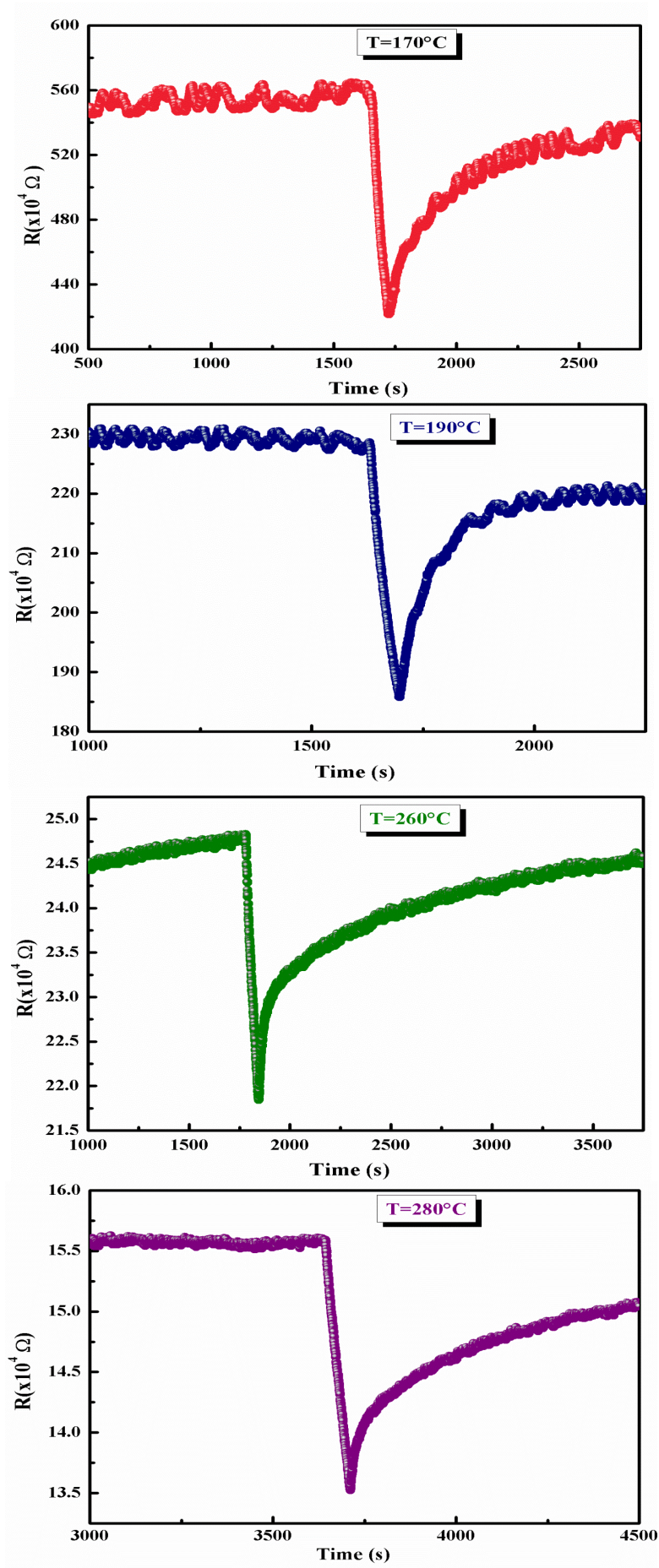
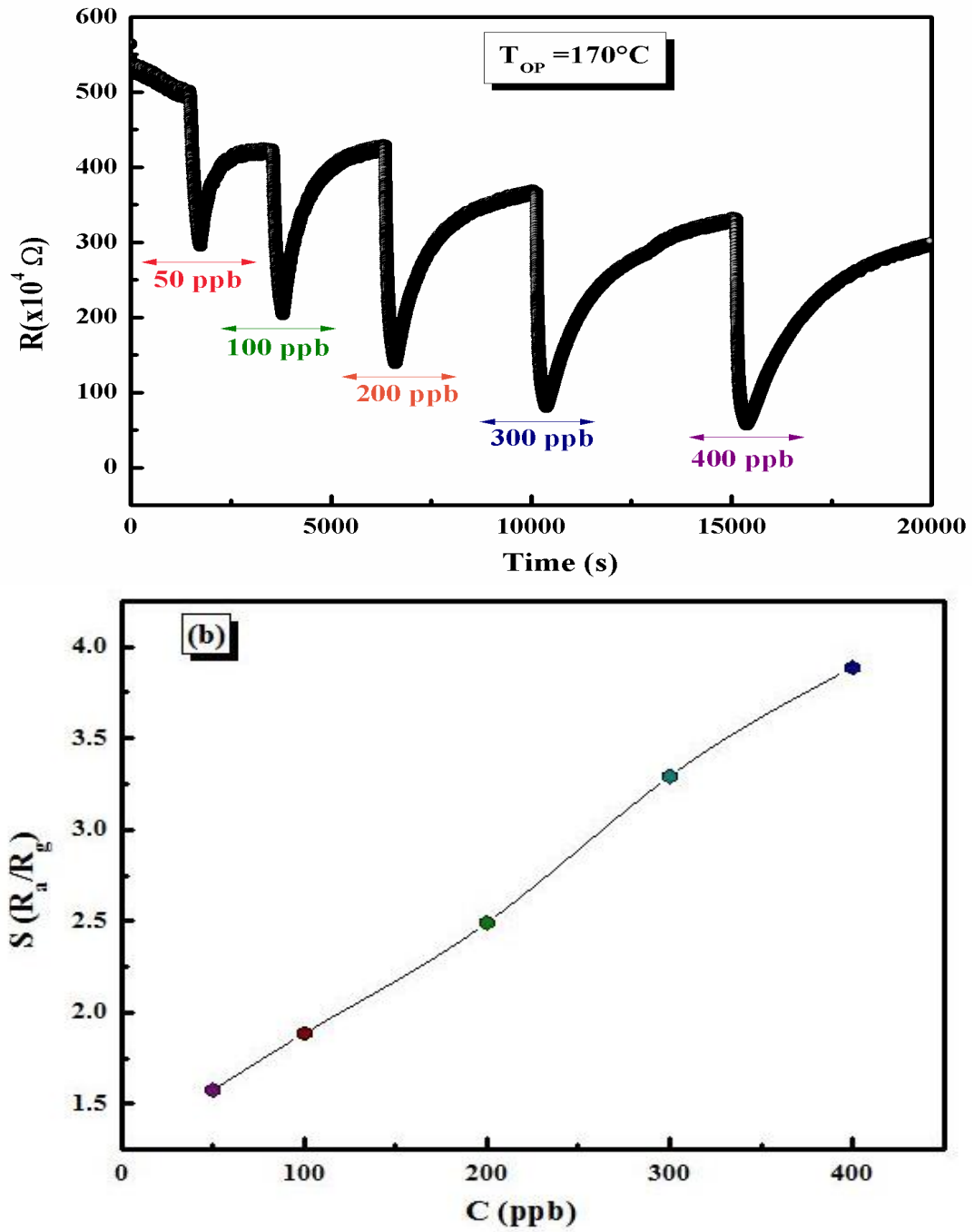


Figure 4: Resistance vs. time of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor.



Figures 5: Ozone gas response of $\text{La}_{0.8}\text{Pb}_{0.1}\text{Ca}_{0.1}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ sensor as a function of time at several temperatures (170, 190, 260 and 280 °C).



Figures 6: $La_{0.8}Pb_{0.1}Ca_{0.1}Fe_{0.8}Co_{0.2}O_3$ sensor response (S) to (a) oxidizing gas (O_3) and (b) sensor responses depending on the O_3 concentration.

Declaration of interests

☒ 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: