The enhancement of ethanol gas sensors response based on calcium and zinc co-doped \LaFeO_3/\FeO_3 thick film ceramics utilizing yarosite minerals extraction as \FeO_3 precursor

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Abstract
A gas sensor is a renewed interest of research which has been developed to make a device that can be detected the harmful gases and applied in the several fields of industries. In this paper, we report the modified of gas sensor based thick film ceramic \LaFeO_3/\FeO_3 by added calcium and zinc co-doping prepared by screen-printed technique. In this work, yarosite mineral was utilized as \FeO_3 precursor. It aims to take the advantages of abundance natural resources in Indonesia to save a cost in gas sensor fabrication. Then, x-ray diffraction (XRD), scanning electron microscopy (SEM) and electrical properties characterization were applied to the calcium and zinc co-doped \LaFeO_3/\FeO_3-based thick film ceramics. It is obtained that the crystal structures were cubic with crystallite size at about 51.19 nm and 48.17 nm. SEM images informed that calcium and zinc co-doped caused the larger pores of \LaFeO_3/\FeO_3. It indicates that the gas sensors shows a response to the ethanol gases. Lastly, calcium and zinc co-doped can be a potential candidate to enhance the highly performance of gas sensors. Moreover, yarosite mineral also can be used to develop the future perspectives of ethanol gas sensors.

Keywords:
Co-doped \LaFeO_3/\FeO_3; \LaFeO_3/\FeO_3 thick film ceramics; Yarosite mineral; Ethanol gas sensing

1. Introduction

In recent decades, gas sensors have become an interesting topic in the research community. It is focused on modified materials as though added doping which aims to develop the gas sensors with good performances. Currently, gas sensors based on metal-oxide semiconductor (MOS) also have been attracting attention to study, especially to monitor the health and safety processes due to their advantages such as low-cost, easy in implementation and high compatibility [1]. MOS that were widely used as gas sensors were \ZnO [2], \SnO [3], \FeO [4], \InO [5], \WO [6], and \LaFeO [7]. Up to now, MOS-based gas sensors were classified into two groups i.e. n-type and p-type [8]. These types of MOS gas sensors were known based on the resistance changes on the gas exposed. The n-type of MOS gas sensors shows the reducing resistance while gases were exposed and its contrarily for p-type of MOS gas sensors [9]. N-type of MOS gas sensors have limitations in performance and p-type of MOS gas sensors appear as alternative materials to be applied as gas sensors [10]. MOS gas sensors have the advantages of being able to detect the harmful gases with a highly response [11], such as on detecting methanol [12], acetone [13], formaldehyde [14], toluene [15], acetylene [16], benzene [17], and ethanol [18].

Ethanol has the promising potential and can be used in several fields such as pharmaceutical, traffic safety on transportations and food industry [19]. It is important to utilize the gas sensor to detect ethanol gases for the safety and untoward incident in the industrial processes. Furthermore, the ethanol gas sensors are highly needed and very important in many conditions such as avoiding the driver who drunk in the driving condition and so on [20]. Therefore, the development of MOS gas sensor to detect the ethanol gases was necessary. One of the materials that were widely used as ethanol gas sensors is \LaFeO [21-24]. It due to a good response from \LaFeO in the field of gas sensors [25]. \LaFeO were synthesized from \LaCl, \H_2O and \FeO [26]. \FeO can be obtained from the raw material as though of yarosite minerals. In the recent years, studied about raw materials especially in utilization of yarosite minerals as \FeO precursor has been doing by Aliah et al. [27]. Moreover, the utilization of yarosite minerals as \FeO precursor also as the alternative solution to saving a cost. Yarosite minerals have the higher contains of \FeO up to 91.30% and the 8.7% others were impurities as shown in Table 1 [26].

Aliah et al. [27] claimed that yarosite minerals have a good potential to applied in many sectors, either gas sensors [27]. In the gas sensor application, response is the most important parameter that needs to be considered. Many researchers modified the materials with added doping to enhance the response of the gas sensor as doing by Liu et al. [28]. Kou et al. [29] and Singh et al. [30]. Thereout, some researchers have been developed a gas sensors with added doping especially for \LaFeO. It has been done by Ariyani et al. [26] and Suhendi et al. [31]. Ariyani (2018) developed \LaFeO with added CaO as a doping while Suhendi (2019) added AlO as a doping. Their research also utilized...
the yarosite minerals for FeO precursor. The response of the ethanol gas sensor that occurs in their experiment also indicates that yarosite mineral can be used as material sensing. Then, the added a doping to the main materials were aim to prevent the growth of crystallite size. It caused the reduce of crystallite size and become smaller \[23,25\]. The smaller crystallite size of materials shows a better response as gas sensors \[32\].

Based on the explained above, we report the ethanol gas sensor fabrication based on calcium and zinc co-doping LaFeO/FeO. FeO precursor originated from the yarosite mineral which is abundant in Indonesia. The utilization of yarosite minerals will save a cost in gas sensors fabricated. Moreover, the co-doping was added to find out the influence of co-doping to the morphological and response of gas sensors to the ethanol gases.

### 2. Experimental

#### 2.1 Chemicals

In this works, the main chemicals that prepared were lanthanum(III) chloride heptahydrate (LaCl\(_3\).7H\(2\)O), yarosite minerals extraction as FeO precursor, calcium oxide (CaO), zinc oxide (ZnO) and ammonium hydroxide (NH\(_3\)OH) 25 M. Then, the chemicals that used as solvent were hydrochloric acid (HCl) 2 M and aquadest. Furthermore, all solutions were hydrochloric acid (HCl) 2 M and aquadest. Furthermore, the other chemicals were prepared to fabricate the thick films i.e. silver (Ag) paste as electrodes, ethyl cellulose and alpha-terpineol.

#### 2.2 Synthesis of calcium and zinc co-doped LaFeO/FeO powder

Calcium and zinc co-doped LaFeO/FeO powder were prepared by coprecipitation method in accordance with the experiment that has been done by Suhendi et al. \[33\] in 2019. To prepare calcium and zinc co-doped LaFeO/FeO powder, 0.5 mol LaCl\(_3\).7H\(2\)O was initially dissolved in 20 mL aquadest. Then, 0.44 mol FeO from yarosite minerals extraction, 0.05 mol CaO and 0.01 mol ZnO were dissolved in 20 mL HCl 5 M, respectively. Furthermore, all solutions were mixed under vigorous stirring using a magnetic stirrer until homogeneous. The homogeneous solution was subsequently added by NH\(_3\)OH 25 M in slowly until the pH of the solution was about 7 and leave it in overnight. Then, the resulting precipitate was filtered, dried at 100°C for 8 h and calcined at 800°C for 2 h. Similar synthesis procedures were used to produce LaFeO/FeO powder as comparison using 0.5 mol LaCl\(_3\).7H\(2\)O and 0.5 mol FeO.

### 2.3 Thick film fabrication and characterization

The experimental steps to produce a thick film were divided into three steps. The initial step was preparing the material paste based calcium and zinc co-doped LaFeO/FeO. To prepare the material paste, organic vehicles were made from ethyl cellulose and alphetapen in ratio 1:9. The organic vehicles were mixed with calcium and zinc co-doped LaFeO/FeO powder and stirrer until homogeneous. The second step was preparing the substrate, the alumina substrate which has the thickness of 0.5 mm and the size of 1 cm \(\times\) 0.5 cm was coated with silver (Ag) electrode and its preparation using screen-printing technique as shown in Figure 1. Then, the substrate was fired at 600°C for 10 min. The last step, material paste based calcium and zinc co-doped LaFeO/FeO was coated over the silver (Ag) electrode using screen-printing technique as shown in Figure 2 and fired at 600°C for 2 h.

Calcium and zinc co-doped LaFeO/FeO-based thick film ceramics which have been made were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM) to observe the crystal and morphological structures, respectively. XRD characterization also informed the lattice parameters and crystallite size which were calculated using the Debye-Scherrer formula as shown in Equation (1) \[34-37\]. SEM characterization was conducted by taking up the images of the calcium and zinc LaFeO/FeO surface to analyze the morphological structures.

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{1}
\]

where \(D\) is the crystallite size (nm), \(K\) is the Scherrer constant which has the value in the range of 0.9 to 1.0 \[38\], this works were used \(K = 0.9\) according to Moshi et al. \[2012\] statement that normally scherrer constant was taken is 0.9 \[39\], \(\lambda\) is the x-ray wavelength (1,5406 Å), \(\beta\) is the full width at half maximum (FWHM) and \(\theta\) is the angle of the Bragg diffraction.
Furthermore, the electrical properties characterization was conducted using gas chamber tools to observe the performance of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ on detect the ethanol gases. The electrical properties informed the resistance function of temperature (R-T) which recorded every 5°C increase. These measurement processes were shown in Figure 3. These R-T functions were analyzed to determine the response of the samples on detecting the ethanol gases which were calculated using Equation (2) [40-42]. In this work, the various concentrations of ethanol gases were treated to the samples i.e. 100, 200, and 300 ppm.

$$\text{Response} = \frac{R_g-R_a}{R_a}$$  \hspace{1cm} (2)

where $R_g$ is the resistance of the samples in the gas chamber tools with ethanol gases containing and $R_a$ is the resistance of the samples in the ambient conditions (without ethanol gases).

3. Results and discussion

To examine the characteristics of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$-based thick film ceramics, the LaFeO$_3$/Fe$_2$O$_3$ were made as comparison. The characteristics were characterized using XRD and obtained the results as shown in Figure 4. The patterns exhibit well reflections at $2\theta = 22.55^\circ$, $32.17^\circ$, $39.68^\circ$, $46.11^\circ$, $57.46^\circ$, $67.43^\circ$ and $76.74^\circ$ corresponding to JCPDS No. 96-154-2033 which shows cubic structures. The reflections were matched with (100), (110), (111), (200), (211), and (220), and (301) of LaFeO$_3$. Then, the average of crystallite size was calculated using the Deybe-Scherrer equation as mentioned in Equation (1). The calculation found that calcium and zinc decreased the crystallite size, 51.19 nm to 48.17 nm. It occurs because the substituting calcium and zinc as co-doping on LaFeO$_3$/Fe$_2$O$_3$ prevent the growth of crystallite size. It is caused by Ca$^{2+}$ (0.134 nm) that has a smaller ionic radius than La$^{3+}$ (0.136 nm) [43]. It is also obtained on Zn$^{2+}$ (0.064 nm) to Fe$^{3+}$ (0.074 nm) [44]. The XRD characterization also reports that calcium and zinc co-doped caused the lattice parameter of LaFeO$_3$/Fe$_2$O$_3$ to sustain an expansion of about 3.8977 Å to 3.9516 Å. The expansion was obtained due to elastic deformation in the material which caused the strain when the dopant were added [45].

Other characterization was also explored to examine the characteristics of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$. SEM characterization was conducted to investigate the characteristics of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$. The SEM images were shown in Figure 5. It is found that calcium and zinc co-doping caused the pores of LaFeO$_3$/Fe$_2$O$_3$ became larger. It gives a better response of gas sensors [46]. It is indicated that calcium and zinc co-doping increased the response of LaFeO$_3$/Fe$_2$O$_3$ based gas sensor to the ethanol gases.

The response of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ to ethanol gases was informed by resistance function of temperature that obtained from resistance measurement in the electrical properties characterization as shown in Figure 6. The resistances were reduced as increasing temperature at any concentration of ethanol gases. The lowered resistance indicated that the conductivity of the gas sensors were increasing. This phenomenon is due to the electron transfer which increases the hole of the material to equate the Fermi level [47].

Figure 7 shows the response of calcium and zinc co-doping LaFeO$_3$/Fe$_2$O$_3$ and their comparison (LaFeO$_3$/Fe$_2$O$_3$) to the ethanol gases. The responses were derived from R-T graphical, then processed using Equation (2). The result informed that the calcium and zinc co-doping increased the response of LaFeO$_3$/Fe$_2$O$_3$ as shown in Table 2. The optimal response was subject to 300 ppm of ethanol gas exposed based on calcium and zinc co-doping LaFeO$_3$/Fe$_2$O$_3$. Moreover, these co-doping also reduce the operating temperature, namely 205°C to 190°C.

This experiment was utilized the yarosite mineral as Fe$_2$O$_3$ precursor. Table 1 indicates that yarosite mineral can be utilized as ethanol gas sensor material in the future. This experiment gives a better response than previously studies which utilized yarosite mineral as doing by Suhendi et al. [33] and Aliah et al. [48]. It is obtained by the co-doping which play an important role in the gas sensor performance.
Figure 5. SEM images of thick film ceramics based (a) LaFeO$_3$/Fe$_2$O$_3$ (b) calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$.

Figure 6. Resistance changes at different temperature in the ambient condition (0 ppm) and ethanol exposed (100 ppm, 200 ppm, 300 ppm) of thick film ceramics based on (a) LaFeO$_3$/Fe$_2$O$_3$ (b) calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$.

Figure 7. Response of thick film ceramics based on (a) LaFeO$_3$/Fe$_2$O$_3$ (b) calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ to ethanol gases.

Table 2. The response of calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ with their comparison (LaFeO$_3$/Fe$_2$O$_3$).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Response of ethanol gas sensor in various concentration</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 ppm</td>
<td>200 ppm</td>
</tr>
<tr>
<td>LaFeO$_3$/Fe$_2$O$_3$</td>
<td>1.724</td>
<td>2.237</td>
</tr>
<tr>
<td>Calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$</td>
<td>2.563</td>
<td>3.292</td>
</tr>
<tr>
<td>LaFeO$_3$ doping SrO</td>
<td>1.900</td>
<td>2.860</td>
</tr>
<tr>
<td>ZnFe$_2$O$_4$/Mn$_2$O$_3$</td>
<td>~0.59</td>
<td>~0.63</td>
</tr>
</tbody>
</table>
The responses occur by explaining the sensing mechanism. The mechanism of MOS sensor were explained by chemical reaction as shown in Equation (3) and (4) below [22]:

\[
\begin{align*}
C_2H_5OH + 6O_{(\text{ads})}^{-} & \rightarrow 2CO_2 + 3H_2O + 6ne^- \quad (3) \\
C_2H_5OH + 6O_{(\text{native})}^{-} & \rightarrow 2CO_2 + 3H_2O + 6ne^- \quad (4)
\end{align*}
\]

These equations informed that the surface of the material, in this work based on calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ will produce more holes with increasing temperature and concentration of ethanol gas. It is due to the electron on the material becoming more energetic to jump from the valence band to the conduction band. This phenomenon obtained the increase of hole production and it occurs until the sensor element is heated to a certain temperature. Afterward, the hole production will be decreased caused by the hole which combines with O$^-$ and O$_2$ ions and reform O$_2^-$ [49]. A certain temperature becomes an operating temperature of the gas sensing that was fabricated.

4. Conclusions

In summary, calcium and zinc co-doped LaFeO$_3$/Fe$_2$O$_3$ were made using coprecipitation method, then prepared by screen-printed technique to be a thick film ceramic that applied as ethanol gas sensors. These materials were characterized by XRD, SEM and electrical properties. These materials have a large pore and it causes a response to ethanol gases. The experiment confirmed that the crystal structure of LaFeO$_3$/Fe$_2$O$_3$ were cubic. Calcium and zinc co-doping decreased the LaFeO$_3$/Fe$_2$O$_3$ crystallite size of about 51.19 nm to 48.17 nm. Calcium and zinc co-doped also decreased the operating temperature of gas sensor based LaFeO$_3$/Fe$_2$O$_3$, it was 205°C to 190°C. The response also increased as the concentration of ethanol gases increased. Lastly, this work informed that calcium and zinc can be a good material doping to enhanced the gas sensor response, especially to ethanol gases. Moreover, in the future perspective, the utilized yarosite mineral also can be used to save a cost in the gas sensor fabrication.

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