Research Article

Electrical Properties of Gd- and Mn-Doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ Thick Films for Ethanol Gas Sensors

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Abstract.
Herein, electrical properties of ethanol gas sensing based on Gd- and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ thick films were investigated. The Gd- and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ were synthesized by coprecipitation method and formed to thick films using screen-printing techniques with sintering temperature at 900 $^\circ$C. X-ray diffraction and scanning electron microscopy were conducted to determine the crystal and morphological structures. The results showed that the synthesized materials have three phases i.e., tetragonal, cubic, and hexagonal, respectively for Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$. Also, the average particle size is of about 0.51 µm. Among all those circumstances, synthesized materials indicate good performances as ethanol gas sensing that showed in the electrical properties’ measurement. It tested A differently in ethanol containing i.e., 0 ppm, 100 ppm, 200 ppm, and 300 ppm. The highest response to ethanol gases reached at 300 ppm, it is 332 with optimum temperature at 289 $^\circ$C. We hope our findings could be beneficial and helpful in the perfect fabrication of ethanol gas sensors in future.

Keywords: electrical properties, thick films, doped, ethanol, sensors

1. INTRODUCTION

Nowadays, the pollution in the form of liquids, solids, or gasses which are produced from the industrial field have become an alarming situation around the world. The several pollutants are toxic gasses such as nitrogen dioxide, acetone, methanol, ammonia, and ethanol. From all of them, ethanol is the important concern because it is considered to have an adverse effect on human beings and has a long-term exposure that leads to several diseases including cardiovascular and respiratory infection [1]. It is due to the ethanol characteristic that is easy to volatilize into air [2]. To solve the problem,
the researchers has been developed gas sensors to detect the ethanol in the air and minimize the negative impact that might occurred. Some of the researchers established the ethanol gas sensor using metal oxide semiconductor (MOS) due to their higher response. MOS that are widely used as ethanol gas sensors are ZnO, Co$_2$O$_4$, SnO$_2$, MoO$_3$, LaFeO$_3$, and so on [3–7]. It becomes interesting to choose a good type of MOS for ethanol gas sensor applications.

Recently, LaFeO$_3$ has attracted much attention to applied as ethanol gas sensors due to their electrical properties. LaFeO$_3$ belongs to ABO$_3$ perovskite-structured oxide materials that have many advantages, especially has an excellent response and stability [8]. Therefore, some of method has been developed to produced LaFeO$_3$ in-between sol-gel, solvothermal, and coprecipitation [9–11]. However, the researchers were convinced that coprecipitation is the most suitable method to produce LaFeO$_3$ for ethanol gas sensors due to their superiority. The coprecipitation method can produce materials in a small grain sizes or nanoparticle [12]. For gas sensors applications, a small grain sizes exhibited the higher response and giving a good performance to detect the targets [13]. Also, Suhendi et al claimed that to produce a small grain size can be obtained with added doping. Their work proven that SrO doping on LaFeO$_3$ decreased the grain sizes of about 0.42 μm to 0.26 μm [14]. The other researchers also applied doping for gas sensors application. An example, Gd-doping ZnO that was conducted by Colak and Karakose (2022). Their work claimed that 3 mol% of Gd-doping ZnO increased the performance in detecting the target gasses [15]. Furthermore, Suhendi et al (2020) also added 0.17 wt% Mn-doping to LaFeO$_3$ and found that the response of gas sensors was increased of about 6.98 to 23.89 in 300 ppm ethanol gasses containing [16]. Based on the previously report, this work was attempt to combine the doping i.e. Gd and Mn to LaFeO$_3$. It was conducted with the aim to produce a good performance of ethanol gas sensors.

Here in, the Gd and Mn doping to LaFeO$_3$ was made into thick film ceramics using screen-printing techniques caused by several reasons such as low-cost, easy in preparation, and can improve the surface area which can be a benefit for gas sensing application[17]. Also, in this work we used the La$_2$O$_3$ precursor and Fe$_2$O$_3$ from the yarosite minerals extraction to utilize the natural resources of Indonesia, so that the final material that we used to detect the ethanol gasses is Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ thick film ceramics. Then, some characterization including crystal structure, morphological structure, and electrical properties were conducted to verify their performance. Hoping all the findings of this work can be a useful thing for the development of ethanol gas sensors.
2. RESEARCH METHOD

This research was conducted by several steps including the synthesized of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3-\text{LaFeO}_3-\text{La}_2\text{O}_3 \) powders, screen-printing techniques to form these powders into thick films, and characterization to reveal their performance as ethanol gas sensors. The synthesized of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3-\text{LaFeO}_3-\text{La}_2\text{O}_3 \) powders was prepared by coprecipitation method in accordance with the experiment that has been done by Suhendi et al in 2021 [18]. Firstly, the precursor that consist of 46 mol% Lanthanum Oxide (La2O3), 46 mol% Ferric Oxide (Fe2O3) from yarosite extraction, 5 mol% Manganese Oxide (Mn2O3), and 3 mol% Gadolinium Oxide (Gd2O3) were prepared. All the precursors respectively dissolved in Hydrochloric Acid (HCl) 10 M using a magnetic stirrer for about 5 hours. Each solution that was produced was mixed until it became a homogeneous solution. Then, the Ammonia Hydroxide (NH4OH) was added until the solution produced the precipitate. The precipitate dried at 100 \(^\circ\)C for about 6 hours and calcined at 600 \(^\circ\)C for about 3 hours. Lastly, the products were grinded to become powders.

The powders that were produced were formed into thick films using screen printing techniques as illustrated in Figure 1. This approach required several materials such as alumina substrate, silver (Ag) paste, and organic vehicles that consist of ethyl cellulose and alpha-terpineol in the ratio 1:9. Firstly, the material paste was prepared by mixing the Gd-and Mn-doped \( \text{Fe}_2\text{O}_3-\text{LaFeO}_3-\text{La}_2\text{O}_3 \) powder and organic vehicle in the composition ratio of 7:3. These mixtures are stirred for about 2 hour or until homogeneous. Then, alumina substrate is also prepared in the size of 1 cm x 0.5 cm as illustrated in Figure 1a. After that, the silver (Ag) paste was coated over the alumina substrate and fired at 600 \(^\circ\)C for about 10 minutes as illustrated in Figure 1b. The silver (Ag) paste is used as an electrode in the ethanol gas detection processes. The last step is to print the material paste over the alumina substrate that has been coated with silver (Ag) paste previously as illustrated in Figure 1c and fired at 900 \(^\circ\)C for about 2 hours.

Hereafter, the thick films based on Gd-and Mn-doped Fe2O3-LaFeO3-La2O3 were characterized using x-ray diffraction (XRD) and scanning electron microscopy (SEM) to determine their crystal and morphological structures. The XRD characterization were conducted using PANanalytical X’Pert PRO seri PW3040/X0 and informed the crystal structure that obtained from the XRD graphical pattern that formed from the intensity and the angle of bragg diffraction which matched to the literatures. Then, the crystallite size is also informed which is obtained from the calculation using Debye-Scherrer equation as shown in Equation 1 [19–22].
To use this “Old Style Equation” as a “template,” highlight the entire line, then use cut and paste to the new location. Note that the equation number will automatically update (increment).

\[ D = \frac{0.89\lambda}{B \cos \theta} \] (1)

Where \( \lambda \) is a wavelength of the x-ray sources (this characterization was use Cu \( K\alpha = 1.5404 \times 10^{-10} \text{ m} \)), \( B \) is the intensity of peak of full width at half-maximum (FWHM), and \( \theta \) is the angle of Bragg diffraction that use in the characterization. Meanwhile, SEM characterization was conducted using JEOL JSM 6360 LA and informed the image with a certain magnification. This characterization confirmed the particle size of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3\text{-LaFeO}_3\text{-La}_2\text{O}_3 \). Then, the third characterization is electrical properties investigation that is conducted to ensure the Gd-and Mn-doped \( \text{Fe}_2\text{O}_3\text{-LaFeO}_3\text{-La}_2\text{O}_3 \) based thick film performances on the detection of ethanol gases. The electrical properties were characterized using a static gas chamber in three variations of ethanol gas concentration i.e. 0 ppm, 100 ppm, 200 ppm, and 300 ppm. This characterization informed the performance of gas sensors including response and operating temperature. The response was known from the resistance value at various temperatures shown in the R-T graphic which is processed with the calculation using Equation 2 [23–27].

\[ \text{Respon} = \frac{R_t}{R_s} \times 100\% \] (2)
where \( R_g \) is the resistance value of gas sensors in the ethanol gas containing and \( R_a \) is the resistance value at ambient condition (without ethanol gas).

3. RESULTS AND DISCUSSION

In this work, we conducted the characterization of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3\)-LaFeO\(_3\)-La\(_2\)O\(_3\) thick film ceramics as the proponent data for their electrical properties as ethanol gas sensors. These characterizations respectively are XRD and SEM. XRD were used to determine the crystal characteristics including crystal structure, lattice parameter, and crystallite size of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3\)-LaFeO\(_3\)-La\(_2\)O\(_3\). These characteristics were known with the analysis that conducted to the XRD pattern shown in Figure 2. The analysis were carried out using Match3! and confirmed that the materials has three phase i.e. \( \text{Fe}_2\text{O}_3\), LaFeO\(_3\), and La\(_2\)O\(_3\). It is respectively fitted with the Inorganic Crystal Structure Database (ICSD) No. 00-033-0664, 98-003-2636, and 96-006-9890. Each phase has a different crystal structure, there are tetragonal for \( \text{Fe}_2\text{O}_3\), cubic for LaFeO\(_3\), and hexagonal for La\(_2\)O\(_3\).

![XRD Pattern of Gd-and Mn-doped Fe\(_2\)O\(_3\)-LaFeO\(_3\)-La\(_2\)O\(_3\)](image)

**Figure 2:** XRD pattern of Gd-and Mn-doped \( \text{Fe}_2\text{O}_3\)-LaFeO\(_3\)-La\(_2\)O\(_3\).
The analysis also informed the lattice parameter and crystallite size for each phase that respectively shown in Table 1. The lattice parameters were known from the analysis using match 3!, meanwhile the crystallite size was known from the calculation using Debye-Scherrer formula that shown in Equation 1. The crystallite size has an influence on the materials performance as gas sensors. A small crystallite size provides a better response of the sensors to detect the targets, including on the detecting or recognizing the ethanol as the targets [28].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameters (Å)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>a: 8.481 b: 8.481 c: 25.677</td>
<td>21.8</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>a: 3.926 b: 3.926 c: 3.926</td>
<td>10.2</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>a: 3.631 b: 3.631 c: 5.865</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Then, from the XRD pattern also formed the other peaks outside of the ICSD fitted. These peaks might be formed from the impurities that brought from the Fe₂O₃ precursor. In this work, the Fe₂O₃ precursor that used were from the yarosite mineral extraction. These impurities were consist of several compound that shown in Table 2 as reported by Ariyani et al at 2017 [29].

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe₂O₃</td>
<td>91.30</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃</td>
<td>3.30</td>
</tr>
<tr>
<td>3</td>
<td>SiO₂</td>
<td>2.05</td>
</tr>
<tr>
<td>4</td>
<td>TiO₂</td>
<td>3.02</td>
</tr>
<tr>
<td>5</td>
<td>CaO</td>
<td>0.16</td>
</tr>
<tr>
<td>6</td>
<td>MnO</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Hereinafter, the SEM characterization was conducted to determine the average particle size of Gd-and Mn-doped Fe₂O₃-LaFeO₃-La₂O₃. The result of SEM characterization is an image with a certain magnification as shown in Figure 3. From the analysis, it is known that the average particle size of Gd-and Mn-doped Fe₂O₃-LaFeO₃-La₂O₃ is about 0.51 µm. These sizes make an impact on their performance as ethanol gas sensors, it seems like the results obtained from the electrical properties measurements.

The electrical properties measurements were conducted to ensure the performance of Gd-and Mn-doped Fe₂O₃- LaFeO₃-La₂O₃ on detecting the ethanol gas as target. The electrical properties were conducted with resistance measurement using an
ohmmeter in every 3 °C increment of temperature until obtained the R-T graphic as shown in Figure 4a. The measurements informed that the resistance decreased as the temperature increased. Also, the resistance at the same temperature increased as the ethanol gas concentration increased. It occurred when the thick film surfaces were exposed to the ethanol gasses, the absorbed oxygen reacted with the ethanol by releasing the trapped electrons to the Gd-and Mn-doped Fe_2O_3-LaFeO_3-La_2O_3. These interaction were explained in the Equation 3 \[30\]. The ethanol concentrations that were used in the measurement are 0 ppm, 100 ppm, 200 ppm, and 300 ppm.

\[
\text{C}_2\text{H}_5\text{OH (gas) + 6O}^- \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \quad (3)
\]

Then, Srinivasan et al (2019) revealed if the resistance of the materials semiconductor were higher in the ethanol gas contain than in the without ethanol gas (ambient condition), the materials accordingly to the p-type semiconductor \[31\]. It confirmed that the Gd-and Mn-doped Fe_2O_3-LaFeO_3-La_2O_3 that produced in this work are p-type semiconductors.

Figure 3: SEM characterization image of Gd-and Mn-doped Fe_2O_3-LaFeO_3-La_2O_3.

Figure 4: (a) The resistance and (b) The response of Gd-and Mn-doped Fe2O3-LaFeO3-La2O3.
The resistance that produced the measurement was calculated using Equation 2. These calculations informed the response value of Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ on detecting the ethanol gas as shown in Figure 4b. An optimum response was reached in the 300 ppm, it is about 332 with the optimum temperature of about 289 °C. The value of response is included to a good performance of Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$. It is possible from doping that it provides a strong effect. Hu et al. (2017) claimed that a good performance was obtained from a different characteristic of the doping, also the doping can help the main materials to bind the oxygen atoms that contain in the ethanol gasses. These processes can increase the responses [32].

These processes are also explained by the sensing mechanism of Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ on detecting the ethanol gasses. The sensing mechanisms were adsorption and desorption of gas molecules on the thick film surface. It shown by the reaction in Equation 4 to 6 [33].

\[
\begin{align*}
\text{O}_2 \text{(gas)} & \leftrightarrow \text{O}_2 \text{(ads)} \quad (4) \\
\text{O}_2 \text{(ads)} + \text{e}^- \text{(CB)} & \leftrightarrow \text{O}^- \text{(ads)} \quad (5) \\
\text{O}^- \text{(ads)} + \text{e}^- \text{(CB)} & \leftrightarrow 2\text{O}^- \text{(ads)} \quad (6)
\end{align*}
\]

4. CONCLUSION

An electrical properties of Gd-and Mn-doped Fe2O3-LaFeO3-La2O3 thick films has been successfully investigated. In the first, we have to prepare the powders of Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ by coprecipitation method and formed to thick films using screen-printing techniques. Then, the characterizations were conducted using XRD and SEM to espouse the materials performance as ethanol gas sensors. These characterization were obtained the three phase of crystal structure i.e. tetragonal, cubic, and hexagonal. Also, informed the average of particle size of about 0.51 µm. Lastly, the analysis of the electrical properties of Gd-and Mn-doped Fe$_2$O$_3$-LaFeO$_3$-La$_2$O$_3$ -based thick films revealed a good performance as ethanol gas sensors with the highest response 332 (300 ppm) and operating temperature at 289 °C.

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