Fabrication and Characterization of Thick Film Ceramics La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ for Ethanol Gas Sensor using Extraction of Fe$_2$O$_3$ from Yarosite Mineral

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Abstract. Fabrication of La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ thick film ceramics using Fe$_2$O$_3$ powder extracted from yarosite mineral as ethanol gas sensor has been successfully performed. Fe$_2$O$_3$ powder extracted from yarosite mineral as the basic material in this research can increase the added value yarosite mineral. Fe$_2$O$_3$ powder and 10% mol of CaO dissolved in HCl were mixed with LaCl$_3$,H$_2$O powder dissolved in aquades. The solution of Fe$_2$O$_3$, LaCl$_3$,H$_2$O and CaO mixed and then precipitate using NH$_4$OH. The La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ precipitate was calcined at temperature 800$^\circ$C for 2 hours to produce La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ powder. La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ powder was crushed and mixed with Organic Vehicle to produce a La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ paste. Using the screen printing technique, the La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ paste is coated on the alumina substrate and then fired at 600$^\circ$C for 2 hours to produce the thick film ceramic La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$. Based on XRD and SEM characterization data, the thick film ceramics La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ were made even though some of Fe$_2$O$_3$ did not react and the grain size is almost uniform, and there are many pores. Measurement of electrical characteristics shows a good response to the presence of ethanol gas, has high electrical sensitivity value and low optimum working temperature that is in the range 290$^\circ$C - 295$^\circ$C.

1. Introduction

A gas sensor is an electronic device that can generate electrical signals a response to chemical interactions with gases [1]. The ethanol gas sensor plays a role in detecting the presence of ethanol gas in food safety testing [2], testing of ethanol in room, in food and the human body via an alcohol test at the mouth (for drivers) [2-3]. Metal Oxide Semiconductor (MOS) is a capable material used to make gas sensors because it has many advantages, such as cheaper price, fast response time and can detect various types of gas [4]. Currently, many researchers employed p-type semiconductors as gas sensors, one is thick film ceramics of LaFeO$_3$. The thick film ceramics of LaFeO$_3$ has good response to the presence of ethanol gas [2, 5-6].

In this research, the thick film ceramic of LaFeO$_3$ was added with 10% mole Ca$^{2+}$ to make a thick film ceramic of La$_{0.9}$Ca$_{0.1}$Fe$_3$O$_5$ and the Fe$_2$O$_3$ used was that extracted from yarosite mineral. The addition of Ca$^{2+}$ ions in LaFeO$_3$ can increase the conductivity value as well as the sensitivity of the gas sensor.
[7]. Purity of the Fe₂O₃ is 91.30% [3]. Yarosite mineral contains materials such as SiO₂ and TiO₂ other than Fe₂O₃ [8, 9].

2. Material and method
Thick film ceramic of La₀.₉Ca₀.₁FeO₃ was synthesized from Fe₂O₃ powder extracted from yarosite mineral, LaCl₃·7H₂O powder and CaO powder using co-precipitation method. The compounds contained in the Fe₂O₃ powder extracted from yarosite minerals are shown in Table 1 [3]. The amount of Fe₂O₃, LaCl₃·7H₂O and CaO powder used in the fabrication of La₀.₉Ca₀.₁FeO₃ is 0.8244 gram, 2.3963 gram, and 0.0967 gram respectively. Fe₂O₃ and CaO powder were dissolved in 10 M HCl solvent, and LaCl₃·7H₂O powder dissolved an aquades solvent. The solutions of Fe₂O₃, CaO and LaCl₃·7H₂O were mixed, then added a NH₄OH to produce the La₀.₉Ca₀.₁FeO₃ precipitate. The La₀.₉Ca₀.₁FeO₃ precipitate was dried at 100°C and then calcined at 800°C for 2 hours to produce La₀.₉Ca₀.₁FeO₃ powder. The La₀.₉Ca₀.₁FeO₃ powder was crushed to produce a nanoparticle-sized powder. The crushed La₀.₉Ca₀.₁FeO₃ powder mixed with Organic Vehicle (OV) with a ratio between La₀.₉Ca₀.₁FeO₃ and Organic Vehicle (OV) powder is 70%: 30% to yield the La₀.₉Ca₀.₁FeO₃ paste. Paste La₀.₉Ca₀.₁FeO₃ coated on alumina substrate (Al₂O₃) using screen printing technique, then fired at 600°C for 2 hours to produce the thick film ceramic La₀.₉Ca₀.₁FeO₃.

Table 1. Content of compounds in yarosite mineral.

| No | Compound | % Weight |
|----|----------|----------|
| 1  | Fe₂O₃    | 91.30    |
| 2  | Al₂O₃    | 3.30     |
| 3  | SiO₂     | 2.05     |
| 4  | TiO₂     | 3.02     |
| 5  | CaO      | 0.16     |
| 6  | MnO      | 0.17     |

The crystal structure and morphology of the thick film ceramic La₀.₉Ca₀.₁FeO₃ can be seen from the analysis result of XRD (X-Ray Diffraction, X-ray XRP PRO series, λ = 1.540598 Å, PAN) and SEM characterization (Scanning Electron Microscope, JEOL JSM – 6360 LA). The electrical resistance of the thick film ceramics of La₀.₉Ca₀.₁FeO₃ was measured in a chamber without and with ethanol gas of 50 ppm, 100 ppm, and 200 ppm. The Measurement was conducted at Material Laboratory of PSTNT – BATAN, Bandung. The sensitivity value is calculated using the equation (1):

\[ S = \frac{R_g - R_o}{R_o} \]  

with, S is the sensitivity, \( R_g \) and \( R_o \) are respectively the resistance with ethanol gas and without ethanol gas.
3. Result and discussion

3.1. Characterization results X-Ray Diffraction (XRD) ceramic thick film La$_{0.9}$Ca$_{0.1}$FeO$_3$

Pattern result XRD characterization thick film ceramic of La$_{0.9}$Ca$_{0.1}$FeO$_3$ is shown in figure 1. The resulting pattern XRD thick film ceramics of La$_{0.9}$Ca$_{0.1}$FeO$_3$ has been made, matched with the LaFeO$_3$ database (JCPDS No. 37 - 1493) and CaO (JCPDS No. 37 - 1497).

![Figure 1. Pattern result XRD characterization of ceramic thick film La$_{0.9}$Ca$_{0.1}$FeO$_3$.](attachment:image1.png)

The results show that the maximum peak data matches with LaFeO$_3$ database (JCPDS No. 37 - 1493) and unmatched to the CaO database (JCPDS No. 37 - 1497). It shows that CaO dissolved to form La$_{0.9}$Ca$_{0.1}$FeO$_3$. The presence of Fe$_2$O$_3$ peaks indicated that Fe$_2$O$_3$ did not react well to form LaFeO$_3$. This situation occurs because the fired time is short and is due to the effect of Ca$^{2+}$ addition in LaFeO$_3$. Figure 1 shows several peaks that undefined or not fit with the LaFeO$_3$ database (JCPDS No. 37 - 1493) and CaO (JCPDS No. 37 - 1497) i.e peak with 20 in the range 270°C - 280°C. These peak may be from reacted material of on purity (table 1). The raw material contains not only the Fe$_2$O$_3$ compound but also other compounds such as SiO$_2$, Al$_2$O$_3$, K$_2$O, and Na$_2$O which may affect grain growth. Thick film ceramics of La$_{0.9}$Ca$_{0.1}$FeO$_3$ that has been made has an orthorhombic crystal structure. Calculation of crystallite size using Debye Scherrer equation shows that the average crystallite size of thick film ceramic La$_{0.9}$Ca$_{0.1}$FeO$_3$ was fabricated is 38,7625 nm.

3.2. Characterization Scanning Electron Microscope (SEM) of thick film ceramics La$_{0.9}$Ca$_{0.1}$FeO$_3$

Characterization SEM of thick film ceramics La$_{0.9}$Ca$_{0.1}$FeO$_3$ is shown in figure 2. From the figure it can be seen that the micro structure of the thick film ceramics of La$_{0.9}$Ca$_{0.1}$FeO$_3$ has almost uniform grain size, and contains many pores. The grain size of the thick film ceramics La$_{0.9}$Ca$_{0.1}$FeO$_3$ from SEM characterization data obtained by calculating some sample grain size, it is found that the average grain size of the thick film ceramic La$_{0.9}$Ca$_{0.1}$FeO$_3$ is 0.1785 μm (178,5 nm).
3.3. Electrical characterization of thick film ceramic La_{0.9}Ca_{0.1}FeO_3

Electrical characterization was showed by profile resistance function temperature of the thick film ceramics of La_{0.9}Ca_{0.1}FeO_3. Response gas sensor indicated by the sensitivity value and the optimum working temperature. Figure 3 (a) showed the graph resistance function temperature of the thick film ceramics of La_{0.9}Ca_{0.1}FeO_3 with varying ethanol content. The graph showed that the much ethanol content, the value of resistance at the same temperature is increased. Substitution of Ca^{2+} in La^{3+} ion has produce oxygen vacancy, this mechanism based on the Kröger Vink equation (2).

\[ 2CaO \rightarrow 2Ca(La)^{1-} + 2O_2 + V_6^{+2} \]  

(2)

The substitution of Ca^{2+} in La^{3+} ion may inhibited grain growth. LaFeO_3 added Ca^{2+} ion has smaller grain size compared to LaFeO_3 without Ca^{2+} ion added. Smaller grain size can decrease electrical resistance and reduced interconnection between the grains. This situation has result the electron conduction path becomes smaller. So, the thick film ceramics of La_{1-x}Ca_xFeO_3 based gas sensor has a lower working temperature compared to LaFeO_3 based gas sensor. Figure 3 (b) showed the sensitivity function temperature graph of thick film ceramics of La_{0.9}Ca_{0.1}FeO_3 based gas sensor. The effect of ethanol content as shown in figure 3 (b) may increase the sensitivity value.

Figure 3. (a) The graph resistance function temperature and (b) The graph sensitivity function temperature of thick film ceramics La_{0.9}Ca_{0.1}FeO_3.
4. Conclusions

The powder of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ from yarosite minerals, $\text{LaCl}_3\cdot7\text{H}_2\text{O}$ and $\text{CaO}$ has been successfully synthesized using a co-precipitation method. Thick film ceramics of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ for ethanol gas sensor has been successfully made by screen printing techniques. The $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ thick films have orthorhombic crystal structure, with average crystallite size calculated using the Debye Scherrer equation of 38.7625 nm. The thick film ceramic of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ has average grain size of 0.1785 $\mu$m. The thick film ceramics of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ contain many pores. The ethanol gas sensor made from $\text{Fe}_2\text{O}_3$ extracted from yarosite mineral has working temperature in range 290$^0$ - 295$^0$C.

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