

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

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**Abstract.** Fabrication of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  thick film ceramics using  $\text{Fe}_2\text{O}_3$  powder extracted from yarosite mineral as ethanol gas sensor has been successfully performed.  $\text{Fe}_2\text{O}_3$  powder extracted from yarosite mineral as the basic material in this research can increase the added value yarosite mineral.  $\text{Fe}_2\text{O}_3$  powder and 10% mol of CaO dissolved in HCl were mixed with  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  powder dissolved in aquades. The solution of  $\text{Fe}_2\text{O}_3$ ,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  and CaO mixed and then precipitate using  $\text{NH}_4\text{OH}$ . The  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  precipitate was calcined at temperature  $800^\circ\text{C}$  for 2 hours to produce  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  powder.  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  powder was crushed and mixed with Organic Vehicle to produce a  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  paste. Using the screen printing technique, the  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  paste is coated on the alumina substrate and then fired at  $600^\circ\text{C}$  for 2 hours to produce the thick film ceramic  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ . Based on XRD and SEM characterization data, the thick film ceramics  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  were made even though some of  $\text{Fe}_2\text{O}_3$  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  $290^\circ\text{C}$  -  $295^\circ\text{C}$ .

## 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  $\text{LaFeO}_3$ . The thick film ceramics of  $\text{LaFeO}_3$  has good response to the presence of ethanol gas [2, 5-6].

In this research, the thick film ceramic of  $\text{LaFeO}_3$  was added with 10% mole  $\text{Ca}^{2+}$  to make a thick film ceramic of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  and the  $\text{Fe}_2\text{O}_3$  used was that extracted from yarosite mineral. The addition of  $\text{Ca}^{2+}$  ions in  $\text{LaFeO}_3$  can increase the conductivity value as well as the sensitivity of the gas sensor



[7]. Purity of the  $\text{Fe}_2\text{O}_3$  is 91,30% [3]. Yarosite mineral contains materials such as  $\text{SiO}_2$  and  $\text{TiO}_2$  other than  $\text{Fe}_2\text{O}_3$  [8, 9].

## 2. Material and method

Thick film ceramic of  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  was synthesized from  $\text{Fe}_2\text{O}_3$  powder extracted from yarosite mineral,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  powder and  $\text{CaO}$  powder using co-precipitation method. The compounds contained in the  $\text{Fe}_2\text{O}_3$  powder extracted from yarosite minerals are shown in table 1 [3]. The amount of  $\text{Fe}_2\text{O}_3$ ,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{CaO}$  powder used in the fabrication of  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  is 0.8244 gram, 2.3963 gram, and 0.0967 gram respectively.  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  powder were dissolved in 10 M HCl solvent, and  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  powder dissolved in aquades solvent. The solutions of  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  were mixed, then added a  $\text{NH}_4\text{OH}$  to produce the  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  precipitate. The  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  precipitated was dried at  $100^\circ\text{C}$  and then calcined at  $800^\circ\text{C}$  for 2 hours to produce  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  powder. The  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  powder was crushed to produce a nanoparticle-sized powder. The crushed  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  powder mixed with Organic Vehicle (OV) with a ratio between  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  and Organic Vehicle (OV) powder is 70%: 30% to yield the  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  paste. Paste  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  coated on alumina substrate ( $\text{Al}_2\text{O}_3$ ) using screen printing technique, then fired at  $600^\circ\text{C}$  for 2 hours to produce the thick film ceramic  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$ .

**Table 1.** Content of compounds in yarosite mineral.

No	Compound	% Weight
1	$\text{Fe}_2\text{O}_3$	91.30
2	$\text{Al}_2\text{O}_3$	3.30
3	$\text{SiO}_2$	2.05
4	$\text{TiO}_2$	3.02
5	$\text{CaO}$	0.16
6	$\text{MnO}$	0.17

The crystal structure and morphology of the thick film ceramic  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  can be seen from the analysis result of XRD (X-Ray Diffraction, X-ray XRP PRO series,  $\lambda = 1,540598 \text{ \AA}$ , PAN) and SEM characterization (Scanning Electron Microscope, JEOL JSM – 6360 LA). The electrical resistance of the thick film ceramics of  $\text{La}_{0,9}\text{Ca}_{0,1}\text{FeO}_3$  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):

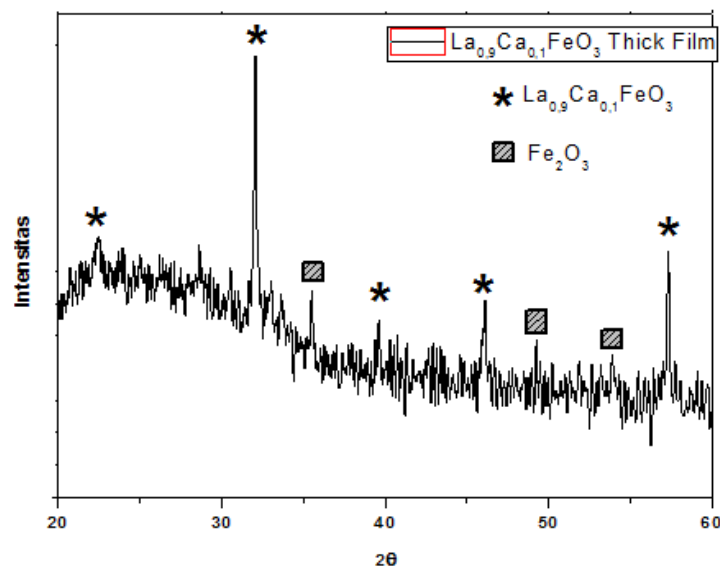
$$S = \frac{R_g - R_o}{R_o} \quad (1)$$

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 $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$

Pattern result XRD characterization thick film ceramic of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  is shown in figure1. The resulting pattern XRD thick film ceramics of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  has been made, matched with the  $\text{LaFeO}_3$  database (JCPDS No. 37 - 1493) and  $\text{CaO}$  (JCPDS No. 37 - 1497).

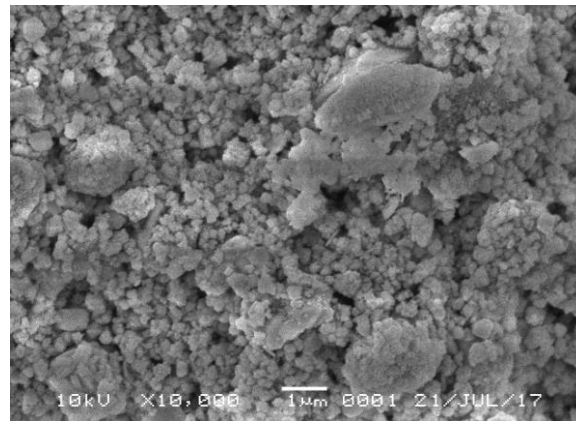


**Figure 1.** Pattern result XRD characterization of ceramic thick film  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ .

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

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

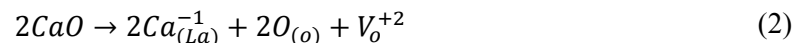
Characterization SEM of thick film ceramics  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  is shown in figure 2. From the figure it can be seen that the micro structure of the thick film ceramics of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  has almost uniform grain size, and contains many pores.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



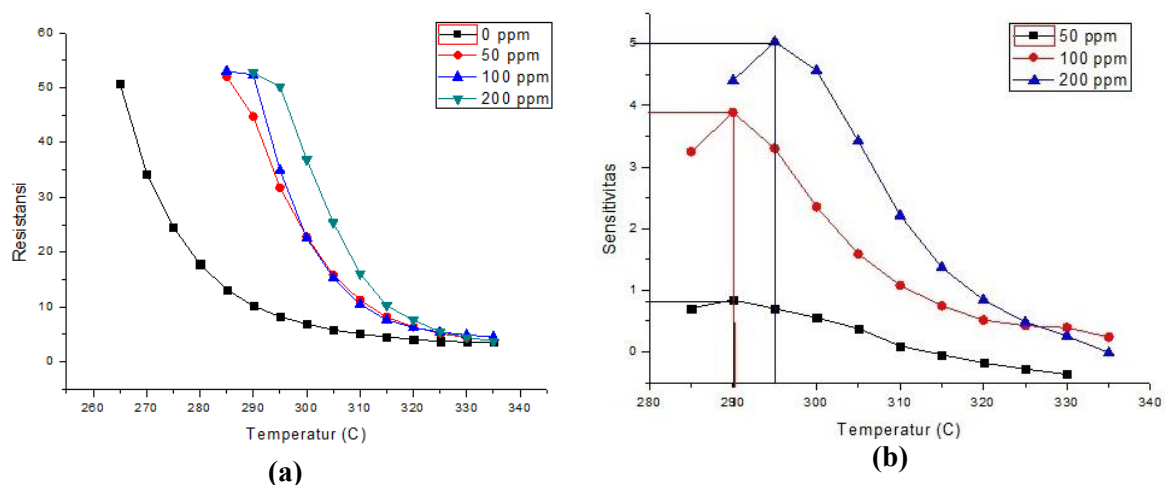
**Figure 2.** Morphology of thick film ceramics  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ .

### 3.3. Electrical characterization of thick film ceramic $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$

Electrical characterization was shown by profile resistance function temperature of the thick film ceramics of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ . 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  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  with varying ethanol content. The graph showed that the much ethanol content, the value of resistance at the same temperature is increased. Substitution of  $\text{Ca}^{2+}$  in  $\text{La}^{3+}$  ion has produce oxygen vacancy, this mechanism based on the Kröger Vink equation (2).



The substitution of  $\text{Ca}^{2+}$  in  $\text{La}^{3+}$  ion may inhibited grain growth.  $\text{LaFeO}_3$  added  $\text{Ca}^{2+}$  ion has smaller grain size compared to  $\text{LaFeO}_3$  without  $\text{Ca}^{2+}$  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  $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$  based gas sensor has a lower working temperature compared to  $\text{LaFeO}_3$  based gas sensor. Figure 3 (b) showed the sensitivity function temperature graph of thick film ceramics of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  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  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ .

#### 4. Conclusions

The powder of  $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  from yarosite minerals,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  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  $\mu\text{m}$ . 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  $290^\circ - 295^\circ\text{C}$ .

#### References

- [1] Yadav A K, Singh R K and Singh P 2016 Fabrication of Lanthanum Ferrite Based Liquefied Petroleum Gas Sensor *Sensor and Actuators B* **229** p. 25-30.
- [2] Haron W, Wisitsoraat A and Wongnawa S 2017 Nanostructured Perovskite Oxide- $\text{LaMeO}_3$  (M = Al, Co, Fe) Prepared by Co-Precipitation Method and Their Ethanol-Sensing Characteristics *Ceramics International* Another reference.
- [3] Suhendi E, Novia H, Syarif D G and Prajitno D H 2010 Studi Awal Pembuatan Keramik Film Tebal (Thick Film) Berbasis  $\text{Fe}_2\text{O}_3$  dari Bahan Dasar Lokal untuk Sensor Gas Alkohol *Prosiding Seminar Nasional Penelitian, Pendidikan dan Penerapan MIPA, Fakultas MIPA, Universitas Negeri Yogyakarta*.
- [4] Xiao H, Xue C, Song P, Li J and Wang Q 2015 Preparation of Porous  $\text{LaFeO}_3$  Microspheres and Their Gas-Sensing Property *Applied Surface Science* – 29743.
- [5] Suhendi E, Witra, Hasanah L and Syarif D G 2017 Characteristics of a Thick Film Ethanol Gas Sensor Made of Mechanically Treated  $\text{LaFeO}_3$  Powder *AIP Conference Proceedings* **1848**, 050008.
- [6] Fan H T, dkk. 2011 Preparation of  $\text{LaFeO}_3$  Nanofibers by Electrospinning for Gas Sensors with Fast Response and Recovery *Nanotechnology* 22(11).
- [7] Kong L B and Shen Y S 1996 Gas Sensing Property and Mechanism of  $\text{Ca}_x\text{La}_{1-x}\text{FeO}_3$  Ceramics *Sensor and Actuators B* **30** p. 217-221.
- [8] Suhendi E, Novia H and Syarif D G 2013 Karakteristik Listrik Keramik Film  $\text{Fe}_2\text{O}_3$  dengan Variasi Ketebalan yang dibuat dari Mineral Lokal di Atmosfir udara dan Atmosfir Alkohol **7** (1) ISSN : 1979 – 8911.
- [9] Syarif D G, Guntur D S and Yamin M 2005 Pembuatan Keramik Termistor NTC Berbahan Dasar Yarosit dan Evaluasi Karakteristiknya *Prosiding Seminar Nasional Sains dan Teknik Nuklir, P3TkN-Batan, Bandung*.