Research Article

# Fabrication of Gadolinium Oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ Thick Films by Screen Printing Technique and Their Electrical Properties for Ethanol Gas Sensors

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**Published:** 27 March 2024

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**Abstract.**
Recently, there have been many researchers who discussed screen printing techniques (SPT) as a good approach to fabricate the thick films for gas sensor applications. In this work, the SPTs were conducted to fabricate the thick films based on gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ that were applied as ethanol gas sensors. The crystal and morphological structures were investigated using x-ray diffraction and scanning electron microscopy, respectively. It shows that there are three phases of the crystal structure of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ i.e., rhombohedral, orthorhombic, and hexagonal. The morphological structure shows an average particle size of about 0.61 μm. Furthermore, the electrical properties measurements were explored to ensure the performance of thick films in detecting the ethanol gases. Th measurements were conducted in the range of temperature of about 310 ˚C to 325 ˚C and in the various ethanol gas containing, it is 0 ppm, 100 ppm, 200 ppm, and 300 ppm. This result showed that the highest response of thick films in the existence of ethanol gases (300 ppm) is 427 with an optimum temperature of 319 ˚C. It is also confirmed that SPT has an excellent approach in thick film fabrication to produce gas sensor devices with good performance.

**Keywords:** fabrication, gadolinium oxide, doped, thick films, screen printing, electrical properties, ethanol, sensors

# 1. INTRODUCTION

Screen Printing Technique (SPT) is one of the suitable method for thick film fabrication that has been many used for several application, especially as sensing device [1]. Nowadays, some of researchers has been developed the sensing device which focused on ethanol gasses detecting due to their disadvantages in daily life such as caused the respiratory disease [2]. Both of them were reconcilable to the recent study that attracted attention by some researchers, that is fabrication of the ethanol gas sensors in the form of thick films. The sensor device in the form of thick films were afford to produce a good performance [3]. Moreover, the ethanol gas sensors study also focused on choosing a good materials that can detect the ethanol with a good response.

Metal oxide semiconductor (MOS) is considered to be one of the candidate materials that has been many used for gas sensors due to their properties such as low cost, easy to fabricate, and giving a high response on binding the targets [4]. For ethanol gas sensors, several kind of MOS has been used are $SnO_2$, ZnO, $Fe_2O_3$, $Gd_2O_3$, $LaFeO_3$, etc [5–9]. The characteristics of MOS that are suitable for gas sensor application are their advantages on excellent response, large specific surface area, also stability in thermal and chemical, and it can be found in $LaFeO_3$ [10]. Hence, this work developed $LaFeO_3$ with some treatment such as using natural resources of yarosite minerals as $Fe_2O_3$ precursor and added $Gd_2O_3$ doping. The utilization of yarosite minerals as $Fe_2O_3$ precursor for ethanol gas sensors caused by the higher contains of $Fe_2O_3$ that reach up to 91.30% and 8.70% others were impurities as shown in Table 1 [11]. This utilization has been conducted by Suhendi *et al* in 2021. Their experiment claimed that yarosite mineral indicate a good response to ethanol and can be utilized as material sensing, it also can be used as a solution to fabricate the ethanol gas sensor with saving a cost [12].

Table 1: The impurities component contained in yarosite mineral extraction.

| No. | Compound | Wt % |
|---|---|---|
| 1 | $Fe_2O_3$ | 91.30 |
| 2 | $Al_2O_3$ | 3.30 |
| 3 | $SiO_2$ | 2.05 |
| 4 | $TiO_2$ | 3.02 |
| 5 | CaO | 0.16 |
| 6 | MnO | 0.17 |

Then, to obtain a good performance of ethanol gas sensors also can be conducted by adding the doping to the MOS materials. The doping was convinced to increase the response of materials on binding the target detection, in this case was ethanol gasses. It caused by the decreased grain size of the materials that exhibited a higher response. It reveal by the previous study which claimed that the doping can decreased the grain size of the materials. It found that the addition of MnO doping on $LaFeO_3$ decreased the grain size from 0.61 μm to 0.36 μm [13]. Also, Rao *et al* in 2022 claimed that the Gd doping was increase the electrical properties performance of $Bi_2Fe_4O_9$ [13]. These findings become an important erudition to obtained the ethanol gas sensors device with the higher response.

Based on the previously explained, this work developed the thick film technology that is fabricated using SPT and applied as ethanol gas sensors. The selected material was $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ that used yarosite mineral extraction as $Fe_2O_3$ precursor to save the cost, and added the Gd doping to increase their performance on detecting the ethanol gasses. Several characterizations were conducted to ensure their performance including crystal characteristics, morphological structure, and electrical properties. This proposed ethanol gas sensor was expected to bring up the benefits for the development of gas sensor study, especially for ethanol gas sensors.

## 2. RESEARCH METHOD

### 2.1. Preparation of Gadolinium Oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ Powders And Thick Film Fabrication

The gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ powders were obtained by a coprecipitation method accordingly to the experiment that has been done by Suhendi *et al* in 2022 [14]. The preparation were processes by synthesis procedure that conducted using three materials precursor, consist of 50 mol% Lanthanum Oxide ($La_2O_3$), 47 mol% Ferric Oxide ($Fe_2O_3$) from yarosite mineral extraction, and 3 mol% Gadolinium Oxide ($Gd_2O_3$), it briefly shown in Figure 1a. The first step, all the precursors that has been mention above were respectively dissolve in Hydrochloric Acid (HCl) 5 M using magnetic stirrer for about 3 hours. Then, the solutions were mixed and stirred for about an hour or until the solution became homogeneous. Afterwards, Ammonia Hydroxide ($NH_4OH$) 25% was added and left it for about a night to produce the precipitate. The precipitate were dried at 100 ˚C for 6 hours and calcined at 600 ˚C for 3 hours. This step were produce the rough powders of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$. And the last step, the rough powders were grinded and filtered to obtained the uniform grain size.

Furthermore, the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ powders were fabricated into thick film. These processes were conducted by the screen-printing techniques (SPT). In this step, the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ powders were modified to be paste. It is conducted by mixing the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ powders and organic vehicles in ratio 7:3 for about 2 hours. The organic vehicle is the chemical compound that consists of ethyl cellulose and alpha-terpineol in a ratio of 1:9. Then, for the SPT procedure to fabricate the thick film were illustrated in Figure 1b. The alumina substrate with the size of 1 cm x 0.5 cm was prepared as illustrated in Figure 1b(1). Then, the silver (Ag) paste were used as electrode. The Ag silver were coat above of alumina substrate with the pattern that illustrated in Figure 1b(2) and fired at 600 °C for 10 minutes. Afterwards, the paste form of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ that has been prepared in the previously also coat above of Ag silver as illustrated in Figure 1b(3). The last, it fired at 800 °C for 2 hours.

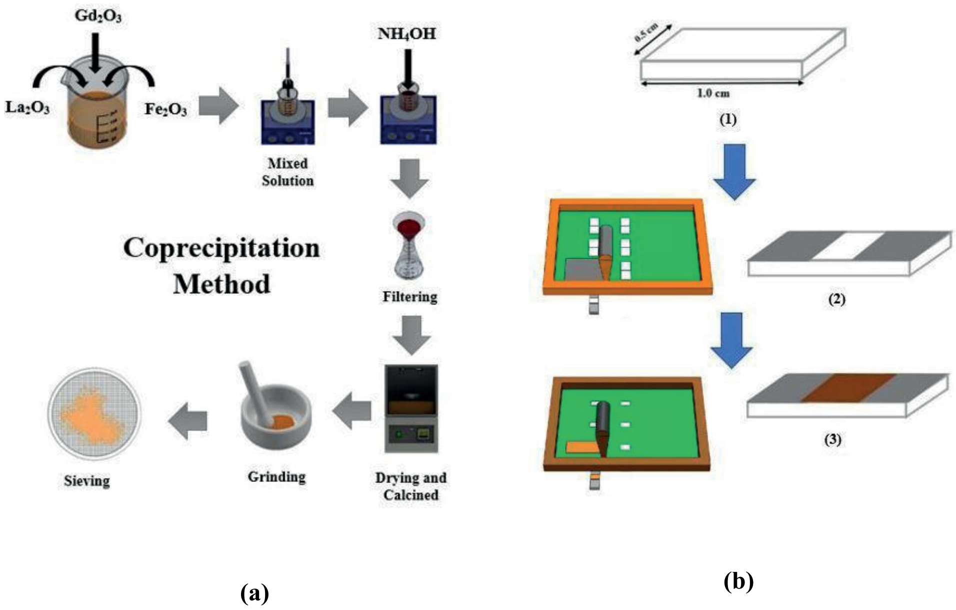


**Figure** 1: (a) A coprecipitation method to produce the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ (b) Thick film fabrication procedure.

## 2.2. Characterizations

To ensure the performance of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ thick films, some characterization were conducted i.e. x-ray diffraction (XRD) to analyzed the crystal characteristics, scanning electron microscopy (SEM) to analyzed the morphological structures, and electrical properties to obtained the response of thick films based on gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ on detecting the ethanol gasses.

### 2.3. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

The XRD characterization was used to analyze the crystal characteristics including the crystal structures, lattice parameters, and crystallite size. These characteristics were obtained from the analysis of the graphical pattern of intensity and the angle of Bragg diffraction. The analysis was conducted by comparing the pattern with the Join Committee of powder Diffraction Standard( JCPDS). Then, for the crystallite size were obtained from the calculation using Debye-Scherrer equation that shown in Equation 1 below [15, 16].

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

where λ is a wavelength of the x-ray (Cu $K_\alpha$ = 1.5404 x $10^{-10}$m), B is the full width at half-maximum (FWHM), and θ is the angle of Bragg diffraction.

Then, SEM characterization obtain the image that has a certain magnification. From the image, the analysis was conducted to confirm the grain size of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$.

**Electrical Properties Characterizations**

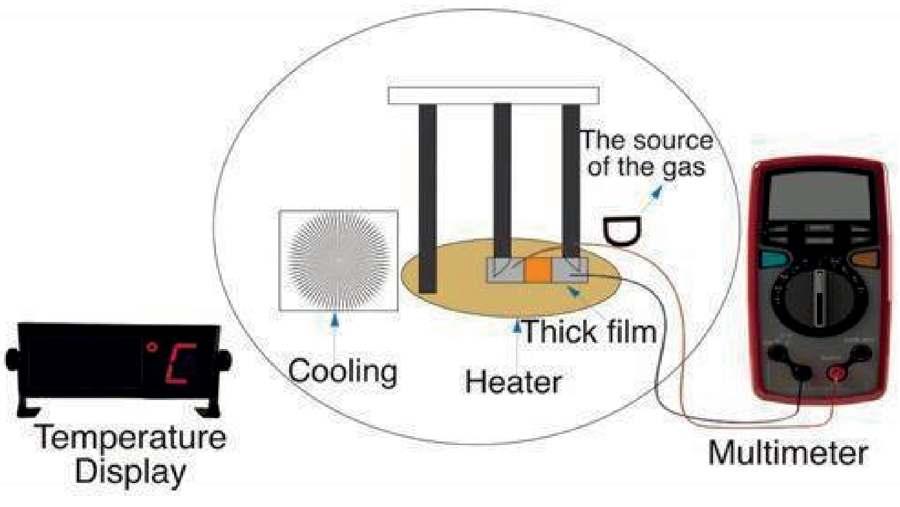


**Figure** 2: The illustration of a gas chamber for electrical properties measurements.

This characterization was considered to investigate the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ performance as ethanol gas sensors. In this work, the various ethanol concentration were used (0 ppm, 100 ppm, 200 ppm, and 300 ppm). This characterization were produce the resistance value of of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ thick film in various temperature (from room temperature up to 325 °C, starts to appear at 310 °C and recorded every 3 °C increase). These resistance measurement were illustrated in Figure 3. Then, these resistance were calculate using Equation 2 to confirmed the response of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ thick film on detecting the ethanol gasses [17, 18].

$$Response = \frac{R_g}{R_a} \, x \; 100\% (2)$$

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

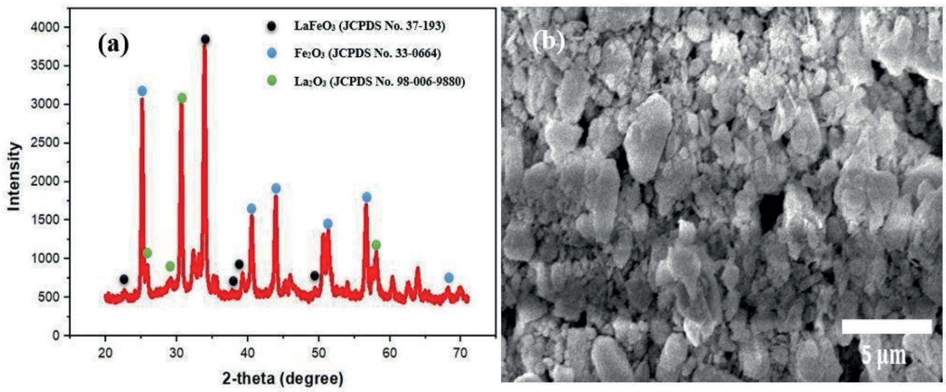


**Figure** 3: (a) XRD pattern and (b) SEM image of Gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$.

XRD dan SEM characterization were conducted to ensure the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ characteristics that consist of crystal and morphological structures. Firstly, the XRD characterization that conducted to confirm the crystal structures and the characterization results were shown in Figure 4a. The analysis confirms that the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ has three phases that consist of $Fe_2O_3$, $LaFeO_3$, and $La_2O_3$. They are respectively fitted with rhombohedral, orthorhombic, and hexagonal crystal structures. It is known from the analysis using match 3! and comparing with JCPDS No. 37-193, No. 33-0664, and No. 98-006-9880. The other characteristics were known as shown in Table 2, it is lattice parameters and crystallite size that obtained using Debye-Scherrer Equation as shown in Equation 1.

DOI 10.18502/kls.v8i1.15393

Table 2: Crystal characteristics of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$.

| Phase | Lattice Parameters (Å) | | | Crystallite Size (nm) |
|---|---|---|---|---|
| | a | b | c | |
| $Fe_2O_3$ | 5.087 | 5.087 | 13.806 | 22.9 |
| $LaFeO_3$ | 5.507 | 7.145 | 5.479 | 17.8 |
| $La_2O_3$ | 4.916 | 4.916 | 8.077 | 21.4 |

Then, the XRD pattern that illustrated in Figure 4a also showed the other peaks. These peaks were formed from the impurities contained in yarosite minerals.

The other characteristic that holds an important role in gas sensor performance is grain size. The materials that have a small grain size were disposed a high response on detecting the targets [19]. This characteristic was known by SEM characterization. This work confirms that gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ has a grain size of about 0.61 μm.

Furthermore, the electrical properties were analyzed to confirm the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ performance on detecting the ethanol gasses. The electrical properties characterization were conducted by the resistance measurement every temperature increase with the result that illustrated in Figure ??a. It shown that the gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ belong to p-type semiconductors because the resistance that produce in ambient condition were lower that the resistance in ethanol gas containing [20].

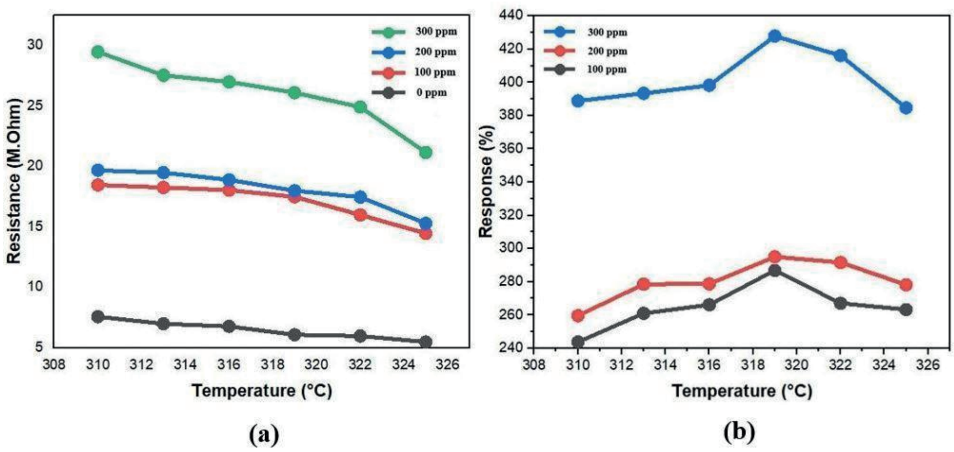


**Figure** 4: (a) Resistance and (b) Response of Gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$.

Then, the resistance that obtained in Figure 4a was processes with the calculation using Equation 2. This calculation were revealed the response of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ on detect the ethanol gasses. These calculation were shown as the graphic relation between response and temperature. It confirm that the highest response of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ was reach in 300 ppm, it is 427% with the operating temperature 319 °C.

The gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ response on detecting the ethanol gasses were explained by sensing mechanism. The response appears caused by the interaction between the ethanol gasses molecule and the thick film surface, these interaction were shown as the reaction in Equation 3 below [21]:

$C_2H_5OH$ (gas) + $6O^-$ $\leftrightarrow$ $2CO_2$ + $3H_2O$ + $6e^-$ (3)

In addition, the sensing mechanism also explained by the adsorption and desorption of ethanol gasses molecules on the surface of thick films. This work claimed that the operating temperature more than 300 °C, it involved the reaction occur were explained as the reaction in Equation 4 to 7 below [22]:

$O_2$ (gas) $\leftrightarrow$ $O_2$ (ads) (4)

$O_2$ (ads) + $e^-$ (surface) $\leftrightarrow$ $O_2^-$ (ads) (< 100 °C) (5)

$O_2^-$ (ads) + $e^-$ (surface) $\leftrightarrow$ $2O^-$ (ads) (100 – 300 °C) (6)

$O^-$ (ads) + $e^-$ (surface) $\leftrightarrow$ $O^{2-}$ (ads) (> 300 °C) (7)

The last, this work also comparing our result with the previously reported. It is conducted to known the performance of the ethanol gas sensors that fabricated in this work. The comparison were shown in Table 3 and confirmed that the operating temperature of this work was higher. However it revealed the higher response than the previously reported.

Table 3: The response comparison to the other works of $LaFeO_3$ based with doping.

| Materials | Doping | Response (%) | Operating Temperature (°C) | Ref. |
|---|---|---|---|---|
| $LaFeO_3$ | Sr | 305 | 300 | (24) |
| $LaFeO_3$/ $Fe_2O_3$ | Mn | 309 | 180 | (15) |
| $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ | Gd | 427 | 319 | This work |

## 4. CONCLUSION

SPT was successfully utilized in fabrication of thick film ceramics based on gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$ that applied as ethanol gas sensors application. The gas sensor shows a good performance in detecting the ethanol gasses, it is known from the response value in ethanol containing about 300 ppm reaching 427 with optimum temperature 319 °C. These performances were supported with the XRD and SEM characterization results. The XRD characterization shown the three phase of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$, these phase consist of $Fe_2O_3$, $LaFeO_3$, and $La_2O_3$ with the crystal structure respectively rhombohedral, orthorhombic, and hexagonal. Meanwhile, the SEM characterization informs that the average grain size of gadolinium oxide-doped $Fe_2O_3$-$LaFeO_3$-$La_2O_3$is about 0.61 μm. These results indicated a good performance of gas sensors. Hoping all the findings bringing up the contribution on development of the ethanol gas sensors in the future.

## Acknowledgments

This work was financially supported by “Hibah Penelitian Terapan Unggulan Perguruan Tinggi” Kementerian Riset, Teknologi dan Pendidikan Tinggi Republik Indonesia Research Grants in the fiscal year 2022.

## References

[1] Shen A, Kim SB, Bailey C, Ma AW, Dardona S. Direct write fabrication of platinum-based thick-film resistive temperature detectors. IEEE Sens J. 2018;18(22):9105–11.

[2] Qin Y, Wang X, Zang J. Room-temperature ethanol sensor based on ZIF-67 modified silicon nanowires with expanded detection range and enhanced moisture resistance. Chem Phys Lett. 2021;765:138302.

[3] Vishwakarma AK, Yadava L. Structural and sensing properties of ethanol gas using Pd-doped $SnO_2$ thick film gas sensor. Environ Sci Pollut Res Int. 2021 Jan;28(4):3920–7.

[4] Nikolic MV, Milovanovic V, Vasiljevic ZZ, Stamenkovic Z. Semiconductor gas sensors: Materials, technology, design, and application. Sensors (Basel). 2020 Nov;20(22):6694.

[5] Zeng Q, Cui Y, Zhu L, Yao Y. Increasing oxygen vacancies at room temperature in $SnO_2$ for enhancing ethanol gas sensing. Mater Sci Semicond Process. 2020;111:104962.

[6] Zhao S, Shen Y, Yan X, Zhou P, Yin Y, Lu R, et al. Complex-surfactant-assisted hydrothermal synthesis of one-dimensional ZnO nanorods for high-performance ethanol gas sensor. Sens Actuators B Chem. 2019;286:501–11.

[7] Mao JN, Hong B, Chen HD, Gao MH, Xu JC, Han YB, et al. Highly improved ethanol gas response of n-type α-$Fe_2O_3$ bunched nanowires sensor with high-valence donor-doping. J Alloys Compd. 2020;827:154248.

[8] Du L, Liu L, Tang X, Li Y, Xu S, Gong Y, et al. Ultrahigh sensitivity acetone sensor based on $Gd_2O_3/Fe_2O_3$ loose microspheres at low temperature. J Mater Sci Mater Electron. 2019;30(5):5008–13.

[9] Hao P, Qu GM, Song P, Yang ZX, Wang Q. Synthesis of Ba-doped porous $LaFeO_3$ microspheres with perovskite structure for rapid detection of ethanol gas. Rare Met. 2021;40(6):1651–61.

[10] Li F, Lv Q, Gao L, Zhong X, Zhou J, Gao X. Ultra-sensitive Ag-LaFeO3 for selective detection of ethanol. J Mater Sci. 2021;56(27):15061–8.

[11] Ariyani NI, Syarif DG, Suhendi E. "Fabrication and characterization of thick film ceramics La0, 9Ca0, $1FeO_3$ for ethanol gas sensor using extraction of $Fe_2O_3$ from Yarosite Mineral.," *IOP Conference Series: Materials Science and Engineering*. pp. 12037. *IOP Publishing* (2018).

[12] Suhendi E, Amanda ZL, Ulhakim MT, Setiawan A, And DG. Syarif, "The enhancement of ethanol gas sensors response based on calcium and zinc co-doped $LaFeO_3/Fe_2O_3$ thick film ceramics utilizing yarosite minerals extraction as $Fe_2O_3$ precursor.," *Journal of Metals*. Materials and Minerals. 2021;31(2):71–7.

[13] E. Suhendi, M.T.U. Latifah, A. Setiawan, and D.G. Syarif, "Studies on the effect of MnO doping on $LaFeO_3$ ceramics in comparison to yarosite mineral properties for ethanol gas sensors performance.," *International Journal of Nanoelectronics & Materials*. vol. 14, no. 4, p. 2021.

[14] Suhendi E, Putri AE, Ulhakim MT, Setiawan A, Syarif DG. "Investigation of ZnO doping on $LaFeO_3/Fe_2O_3$ prepared from yarosite mineral extraction for ethanol gas sensor applications.," *AIMS Materials Science*. vol. 9, no. 1, p. 2022.

[15] Niavol SS, Moghaddam HM. $SnO_2$ nanoparticles/reduced graphene oxide nanocomposite for fast ethanol vapor sensing at a low operating temperature with an excellent long-term stability. J Mater Sci Mater Electron. 2021 Mar;32(5):6550–69.

[16] Duan H, Wang Y, Li S, Li H, Liu L, Du L, et al. Controllable synthesis of Ho-doped in $2O_3$ porous nanotubes by electrospinning and their application as an ethanol gas sensor. J Mater Sci. 2018;53(5):3267–79.

[17] Umar A, Ibrahim AA, Algadi H, Nakate UT, Choudhury SP, Alsuwian T, et al. Selective ethanol gas sensing performance of flower-shaped CuO composed of thin nanoplates. J Mater Sci Mater Electron. 2021;32(14):18565–79.

[18] Wang Z, Li F, Wang H, Wang A, Wu S. An enhanced ultra-fast responding ethanol gas sensor based on Ag functionalized CuO nanoribbons at room-temperature. J Mater Sci Mater Electron. 2018;29(19):16654–9.

[19] Kang Y, Yu F, Zhang L, Wang W, Chen L, Li Y. Review of ZnO-based nanomaterials in gas sensors. Solid State Ion. 2021;360:115544.

[20] Srinivasan P, Ezhilan M, Kulandaisamy AJ, Babu KJ, Rayappan JB. Room temperature chemiresistive gas sensors: challenges and strategies—a mini review. J Mater Sci Mater Electron. 2019;30(17):15825–47.

[21] Liu C, Navale ST, Yang ZB, Galluzzi M, Patil VB, Cao PJ, et al. Ethanol gas sensing properties of hydrothermally grown α-$MnO_2$ nanorods. J Alloys Compd. 2017;727:362–9.

[22] A. Mirzaei, J.-H. Lee, S.M. Majhi, et al., “Resistive gas sensors based on metal-oxide nanowires.,” *Journal of Applied Physics*. vol. 126, no. 24, p.2019. https://doi.org/10.1063/1.5118805.