A sensitive thick film as a candidate for ethanol gas sensor from Jarosite-based minerals

H Aliah	extsuperscript{1,*}, D G Syarif	extsuperscript{2}, R N Iman	extsuperscript{1}, A Sawitri	extsuperscript{3} and A Setiawan	extsuperscript{4}

\textsuperscript{1}Department of Physics, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution 105, Bandung 40614, Indonesia
\textsuperscript{2}Center for Applied Nuclear Science and Technology, BATAN, Jl. Taman Sari 71 Bandung 40132, Indonesia
\textsuperscript{3}Department of Physics, Halim Sanusi University, Jl. Laswi 1 Bandung 40271, Indonesia
\textsuperscript{4}Department of Physics Education, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudhi 229 Bandung 40154, Indonesia

*hasniahaliah@uinsgd.ac.id

Abstract. We report this study that aims to know thick film sensitivity to ethanol gas. The thick film was fabricated from local mineral, is Jarosite as a source of iron oxide, and mixed with zinc oxide and Mangan oxide. The semiconductor mixture powder was synthesized by the sol-gel method, whereas the film was fabricated by a screen printing method. The film sensitivity was known with a gas sensing performance analyzer. An ethanol gas was adsorbed well by a thick film with different electrical resistance values. Due to the difference in the electrical resistance value, the thick film exhibited good sensitivity performance. The highest sensitivity was achieved approximately \(91.7\%\) of 4 gas concentration level of ethanol. Besides, the morphology of the thick film was examined by SEM that showed a pyramid-like form with a little impurity around them. The pyramid-like form looks like a spinel structure with a complex spinel-type where this structure is very well utilized for gas sensor device applications. Furthermore, these characteristics of the thick film indicated an opportunity that it can be a candidate for an ethanol gas sensor device.

1. Introduction

As known that metal oxide semiconductor (MOS) was utilized in various applications, especially in gas sensing application such as \(\text{ZnO/Fe}_2\text{O}_3\) for \(\text{H}_2\text{S}\) or ethanol gases \([1,2]\), \(\text{MnO}\) for \(p\)-nitrophenol \([3]\), \(\text{NiO}\) formaldehyde gas \([4]\), \(\text{TiO}_2\) for \(\text{SO}_2\) gas \([5]\), and \(\text{Bi}_2\text{O}_3\) for \(\text{CO}_2\) gas \([6]\) that was synthesized with a different method. From the literature mentioned above that every of the material has suitable for different gases sensing.

Using a kind of the semiconductor material and synthesis method is important because they affect the structure that will be formed. According to literature, a spinel structure is the most promising candidate \([7,8]\). Spinel structure has a formula of \(\text{AB}_2\text{O}_4\), where \(\text{A}\) and \(\text{B}\) are metal ions \([9]\). The advantages of the spinel structure became one of the topics which it had attracted the researchers, so the various synthesis of the material was conducted by using various materials and methods to obtain distinguished material characteristics for the application.
Many device gas sensors with spinel structure had been conducted by some researchers who obtained high sensitivity with high purity commercial material. But, they still had lack in operating temperature [10-15]. Operating temperature is one of the key on gas sensor parameter which has functioned as a sensor performance controller [16].

To decrease operating temperature and increase sensitivity of the sensor device, we conducted this research with different materials. As our previous research, we had conducted by using a metal oxide that came from local mineral as a source of metal oxide. On the other hand, this research was conducted to compare sensitivity from high purity and self-extracted materials. Our previous research is to study the effectivity of the jarosite and manganite minerals as a source Fe$_2$O$_3$ and Mn$_2$O$_3$ against ethanol gas sensing. It had low sensitivity but able to operate under low temperatures [17]. Therefore, to enhance the sensitivity of the sensor added ZnO that was good to enhance sensor sensitivity [18,19]. Enhancing sensitivity had succeeded in the research later, but it had a high temperature [20,21], where they had heterogeneous structures consisted of hematite and spinel structure or mentioned as a composite [22]. To improve this research, we had conducted to change the experimental method by using the sol-gel method and added citric acid as a chelating agent to prepare sensor materials. The sensor gas device was fabricated thick film-based by using screen printing. The device performance was examined by Gas Sensing Performance Analyzer against ethanol gas, and a morphology structure was examined by SEM.

2. Methods
The research was through as follow: extraction of the metal oxide from jarosite, material synthesis, fabrication of thick film and characterization. The main purpose of this research is to check the method and materials against sensing performance of the Fe$_2$O$_3$: ZnO: Mn$_2$O$_3$ thick film that was tested under ethanol atmosphere in various concentration (ppm).

![Figure 1. Set up the equipment of a gas sensing performance analyzer.](image)

2.1. Materials and synthesis method
The precursor Fe$_2$O$_3$ was the result of the extraction of jarosite that came from a local mineral of Indonesia, MnSO$_4$.H$_2$O and ZnO powder from Merck with the purity of 96.80%. In a typical procedure, Fe$_2$O$_3$ was extracted from jarosite minerals by precipitation method. The synthesis of sensor materials was conducted by sol-gel. The sol-gel method effectively succeeded to form spinel structure [23,24].

A mol percentage that was used consisted of Fe$_2$O$_3$ powder (0.5 mol), ZnO (0.25 mol), and MnO (0.25 mol). Fe$_2$O$_3$ and ZnO were dissolved with HCl, whereas MnSO$_4$.H$_2$O was dissolved with H$_2$O. All solutions of them were mixed at temperature of 120 °C for one hour. The citric acid solution was added into a mixture solution and stirred. Afterward, they were fired without stirring at 80 °C temperature until
forming a gel. The gel was fired until dry at 80 °C, and then it was calcined at the temperature of 600 °C for 3 hours. Finally, a sample was crushed to be obtained powder.

2.2. Fabrication of thick film
To fabricate the thick film, it had been conducted by a screen printing method. The powder was mixed with an organic vehicle as a solvent to form a paste. The silver electrode paste was coated on the substrate of alumina and fired at 600 °C for 10 minutes. Afterward, the paste of Fe₂O₃: ZnO: MnO was coated. The layer by layer had been obtained, and then it was fired at 600 °C for 2 hours. Finally, the thick film of Fe₂O₃: ZnO: Mn₂O₃ was obtained.

2.3. The Sensitivity and morphology structure measurement
The thick film sensitivity was examined by a gas sensing performance analyzer. The thick film was placed into a chamber. Afterward, it was tested under ambient (non-target gas) and then tested at ethanol atmosphere. The examination was conducted between the temperature of 30 °C to 360 °C in different levels of ethanol concentration. The data was taken every increasing of 5 °C temperature. Furthermore, the sensitivity and optimum working temperature of the Fe₂O₃: ZnO: Mn₂O₃ thick film was known. Setting up equipment of gas sensing performance analyzer as shown in Fig.1. The equipment consists of the heater, chamber, temperature controller, ethanol container, power supply, and a multimeter.

The morphology structure of the thick film of Fe₂O₃: ZnO: Mn₂O₃ was examined by Scanning Electron Microscopy (SEM) from JEOL-SEM at the Center for Research and Study of Marine Geology (PPPGL) Indonesia. This examination was conducted to know what the structure had been formed with the synthesized method conducted.

3. Results and discussion
Examining characteristics was conducted in the chamber at two different conditions. The first condition was in ambient condition, and the second condition was in the environment that contained ethanol gas. Dependence of electrical resistance on temperature as shown in Fig.2, either in ambient or ethanol gas environment. The figure seems that electrical resistance had an inverted relation to temperature, whereas increasing temperature than its resistance as decreasing, which indicated characteristic of the semiconductor materials.

The thick film was operating in a range of 125-160 °C (see Fig.2). Operating temperature is one of the key on gas sensor parameter which has functioned as a sensor performance controller [16]. Generally, the normal working/operating temperature was at an interval of 200–500 °C [25]. But in this research, the sample had worked under a general operating temperature of MOS-based. It is a good condition that the sample could operate at a lower temperature. So it does not need consuming high energy. On the other hand, a difference of electrical resistance value in 0, 100, 200, and 300 ppm ethanol at the same temperature, the resistance had a significant gap. The result showed that the sample able to differ containing different ethanol concentration levels.

\[
\% \text{response} = \frac{R_a - R_e}{R_a} \times 100\%
\]

The difference of electrical resistance in every ethanol concentration level can be plotted becoming a percentage of the response function versus temperature, as shown in Fig.3. The percentage of responses was calculated by Eq.1, where \(R_a\) is electrical resistance in ambient, \(R_e\) is electrical resistance in target gas condition [5].
Figure 2. Characteristics of Fe$_2$O$_3$: ZnO: Mn$_2$O$_3$ thick film on the function of electrical resistance versus temperature.

The sensitivity of the sample was different in each of the operating temperatures between 125-160 °C (see Fig.3). The maximum sensitivity was at 130 °C temperature for ethanol ppm 100 and 200, whereas for ethanol ppm 300 at 125 °C. Sample sensitivity was over than 130 °C as decreasing known. This state happened because of as operating temperature increased, target gas mass that had adsorbed activated to react with oxygen on the layer surface. In order for a molecule of the target gas able to react with oxygen, so it has to pass the energy barrier. When the operating temperature had achieved maximum point, the adsorption of target gas and oxygen molecule was difficult conducted by sensing layer surface. It caused the happening loss of target gas molecules that affected the decreasing of sensitivity [26]. Thick film sensitivity in each concentration levels of ethanol ppm 100, 200, and 300 approximately 53.56%, 73.39%, and 91.70%, respectively. The high sensitivity of thick film against ethanol gas sensing and low optimum operating temperature is one of the signs of the effective material synthesis method and adding CA that had been used. Where the difference of synthesis method yields different structures even though the material is the same [27,28].

Figure 3. The sensitivity characteristics of Fe$_2$O$_3$: ZnO: Mn$_2$O$_3$ thick film.

Figure 4. SEM image of Fe$_2$O$_3$: ZnO: MnO complex spinel of a pyramid-like structure.

The thick film had formed a heterogeneous pyramid-like structure (see Fig.4). On top, the surface was still impurity that was assumed coming from raw materials of Fe$_2$O$_3$ (jarosite minerals). The structure looks like a spinel structure with a complex spinel-type [29]. Furthermore, the firing temperature (600 °C) was used effectively to form this structure and play an important role in the sensitivity against
ethanol gas [30]. Had successfully obtained a spinel structure came from jarosite mineral as a source of iron oxide, was an enough promising new candidate for sensing application. Even though there still has impurity, but it can be solved by increasing a high purity within an extraction process.

The sample structure was affected by adding CA. CA is a chelating agent having a function as a medium to help binding metal ions. So, the probability of the bond of metal ions will be higher, and the structure that is expected easy to be formed. As a comparison with previous research that did not add CA that adding CA improved thick film characteristics, either in developing the structure or sensitivity increasing [20,21].

On the other hand, the difference in using a source of oxide Mangan affected semiconductor material type. Semiconductor material that was yielded in this research having N-type, it was shown (see Fig.2) by electrical resistance value in ethanol condition less than ambient [31]. Dissimilar with our previous research that had used Mn$_2$O$_3$ yielded P-type semiconductor materials [21,22]. In the ethanol gas sensor of MOS-based, a sensor of N-type semiconductor will be more advantageous because the electrical resistance value is less and not need to consume high energy. Therefore, Fe$_2$O$_3$: ZnO: MnO thick film that has complex spinel looks pyramid-like structure capable for being a new candidate for an ethanol gas sensor device.

4. Conclusion
In this research, a Fe$_2$O$_3$: ZnO: MnO complex spinel looks pyramid-like structure in a CA medium by sol-gel method, and gas sensing properties had been examined. It had an operating temperature between 125-160 °C in each ethanol concentration which was injected. With increasing operating temperature, a sensor sensitivity decreasing and had maximum sensitivity at 130 °C with a percentage of 91.70%. The firing temperature was used effectively to form the spinel structure and play an important role in the performance of ethanol gas sensing. The structure is a complex spinel-type because of each other ions to complete. This research proves that the jarosite mineral capable for giving excellent characteristics and can be a promising new candidate for gas sensor applications.

Acknowledgments
This work was supported by Ministry of Religion of the Republic of Indonesia and Lembaga Penelitian dan Pengabdian kepada Masyarakat (LP2M) at Universitas Islam Negeri Sunan Gunung Djati Bandung.

References
[1] Zhang B, Fu X, Meng X, Ruan A, Su P and Yang H 2017 Ceram. Int. 43 5934-5940
[2] Fan K, Guo J, Cha L, Chen Q and Ma A J 2017 J. All. Comp. 698 336-340
[3] Kumar V, Singh K, Panwar S and Mehta S K 2017 Inter. Nano. Lett. 7 123-131
[4] Lahem D, Lontio F R, Delcorle A, Bilteryst L and Debliquy M 2016 IOP Conf. Series: Mater. Sci. Eng. 108 012002
[5] Syuhada N, Yulianto B and Nugraha N 2020 Adv. in Soc. Sci. Edu. Hum. Research 408 138-141
[6] Ahila M, Dhanalakshmi J, Selvakumari J C and Padiyan D P 2016 Matt. Res. Exp. 3 1-14
[7] Belle C J, Bonamin A, Simon U, Salazar J S, Pauly M, Colimb S B and Pourroy 2011 Sens. Act. B. 160 942-950
[8] Cornu L, Gaudon M and Jubera V 2013 J. Mater. Chem. C. 1 5419-5428
[9] Bragg W H 1915 Nature 95 561
[10] Lou X, Liu S, Shi D and Chu W 2007 Mat. Chem. Phys. 105 67-70
[11] Song H, Sun Y and Jia X 2015 Ceram. Intern.
[12] Kadu A V, Jagtap S V and Chaudari G N 2009 Curr. Appl. Phys. 9 1246-1251
[13] Cao Y L, Qin H Y, Niu X J and Jia D Z 2016 Ceram. Intern. 42 10697-10703
[14] Saeedabad S H, Baratto C, Rigoni F, Rozatti S M, Sbervelieri G, Vojisavljevic K and Malic B 2017 Mat. Sci. Semic. Procc. 71 461-469
[15] Nemufulwi M I, Swart H C, Mdllalose W B and Mhlongo G H 2019 Appl. Surf. Sci.
[16] Zhou T, Cao S, Zhang R, Tu J, Fei T and Zhang T 2019 ACS Appl. Mater. Interf.
[17] Aliiah H, Syarif D G, Iman R N, Sawitri A, Sanjaya M, Subkhi M N and Pitriana P 2018 IOP Conf. Ser. Mater. Sci. Eng 367 (2018) 012041 doi:10.1088/1757-899X/367/1/012041
[18] Darvishnejad M H, Firooz A A, Beheshtian J and Khodadadi A A 2016 RSC Adv.
[19] Li X W, Wang C, Guo H, Sun P, Liu F M, Liang X S and Lu G Y 2015 ACS Appl. Mater. Interf. 7 17811-17818
[20] Aliiah H, Syarif D G, Iman R N, Darmalaksana W, Setiawan A, Sawitri A, Malik A 2018 IOP Conf. Ser.: Mater. Sci. Eng. 434 (2018) 012027 doi:10.1088/1757-899X/434/1/012027
[21] Aliiah H, Iman R N, Sawitri A, Syarif D G, Setiawan A, Darmalaksana W and Malik A 2019 Mater. Res. Exp. 6 1-7
[22] Aliiah H, Syarif D G, Iman R N, Sawitri A, Darmalaksana W, Setiawan A, Malik A and Gumarang P 2019 Mat. Tod.: Procee. 13 36-40
[23] Li L 2011 J. Sol-gel Sci. Tech. 58 677-681
[24] Gore S K, Mane R S, Naushed M, Jadhav S S, Zate M K, Alothmanc Z A and Hui B K N 2015 Dalt. Trans. 44 6384-6390
[25] Dimitrov D T, 2019 J. Russ. Univ. Radioelect. 22(5) 93-106
[26] Zhao S K, Shen Y B, Yan X X, Zhou P F, Yin Y Y, Lu R, Han C, Cui B Y and Wei D Z 2019 Sens. Act B. 286 501-511
[27] Teh P F, Pramana S S, Sharma Y, Ko Y W and Madhavi S 2013 ACS Appl. Mater. Interf.
[28] Shi Z Z, Li Z L, Bai W S, Tuoliken A, Yu J and Liu X F 2019 Mater. Des. 162 235-245
[29] Zhao Q, Yan Z, Chen C and Chen A J 2017 Chem. Review 117 10121-10211
[30] Shinde S D, Patil G E, Kajule D D, Wagh V G, Gaikwad V B and Jain G H 2012 Int. J. Smart Sens. Intell. Syst. 5 277-294
[31] Fine G F, Cavanagh L E M, Afonja A and Binions R 2010 Sensors 10 5469-5502