Materials Research. 2022; 25:e20210554
DOI: https://doi.org/10.1590/1980-5373-MR-2021-0554

An Analysis of Electronic Properties of $LaFeO_3$ using Density Functional Theory with Generalized Gradient Approximation-Perdew-Burke-Ernzerhof Method for Ethanol Gas Sensors

Hendi Haryadi[a], Edi Suprayoga[b], Endi Suhendi[a]*

[a]*Department of Physics, Universitas Pendidikan Indonesia, Indonesia.*
[b]*National Research and Innovation Agency (BRIN), Research Center for Quantum Physics, Indonesia.*

Received: October 25, 2021; Revised: February 15, 2022; Accepted: April 10, 2022

$LaFeO_3$ is one of the multiferroic perovskite that is widely used for gas sensor applications. In this study, an analysis of the electronic properties of the band gap energy data was conducted using density functional theory with Generalized Gradient Approximation-Perdew-Burke-Ernzerhof (GGA-PBE) method on $LaFeO_3$ for ethanol gas sensor. Changes in the value of the band gap energy resulting from the adsorption-oxidation-desorption mechanism, were discussed in this paper. The results showed that the band gap energy for $LaFeO_3$ before, during and after being exposed to ethanol gas molecules were ±1.4 eV, ±0.4 eV, and ±0.9 eV, respectively. Changes in the value of the band gap energy indicate that there has been an adsorption-oxidation-desorption mechanism in the system, which is the basic mechanism for a gas sensor to work. Therefore, this mechanism is used as an indication for gas sensors. Hence, $LaFeO_3$ can be a candidate for gas sensor applications, especially ethanol gas.

Keywords: *$LaFeO_3$, Density Functional Theory, Sensor, Ethanol, GGA-PBE.*

1. Introduction

$LaFeO_3$ is a multiferroic perovskite material commonly applied as an electrode material for fuel cells and chemical sensors, especially gas sensors[1]. $LaFeO_3$, as a gas sensor constituent material, is widely used to detect the presence of gases that have oxygen in their molecules due to oxygen deficiency in the perovskite material[2]. $LaFeO_3$ exhibits p-type semiconductor properties in air. The adsorption of gas molecules, such as oxygen, affects the conductivity of this material due to an increase in the concentration of holes, which is the main charge carriers in p-type semiconductors. The resistance of this material also increases after being exposed to a reducing gas such as ethanol. The interaction between the reducing gas and the adsorbed oxygen causes a change in conductance, which is used as a gas sensor signal[3]. This material responds to 100 ppm of ethanol gas molecules over 80% in a temperature range of 140 to 240°C. In addition, it is also found that sensors with the same material have the best response and selectivity to ethanol gas; 500 ppm at 128 at 220°C or the highest response to 500 ppm ethanol gas reaches 57.8 at 260°C[3].

Simulations of the adsorption mechanism of the $LaFeO_3$ gas sensor are still far from satisfactory, especially on how the gas sensor signal is viewed from the electronic properties of the material when there is an adsorption mechanism with gas molecules. Therefore, a simulation of the $LaFeO_3$ adsorption mechanism with ethanol gas molecules was carried out in this study. Ethanol gas was chosen because the sensor has many benefits, such as monitoring drivers whether or not they are drunk, controlling the fermentation process, and testing food packaging. Because the chemical formula of ethanol is C_2H_5OH, its oxygen element is expected to affect the conductivity of the $LaFeO_3$ material as a gas sensor constituent material[4].

One of the methods for detecting gas using a material on the sensor is based on the changes in the material's electronic properties after interacting with gas molecules. The electrical conductivity of a material changes dramatically as the density of the charge carriers of the holes changes when exposed to gas molecules. This happens because the gas molecules themselves have a charge for each atom, which will affect how the charge carriers are mobilized in the materials. This change will affect the density of states and band structure of the material which can be analyzed from the magnitude of the band gap energy[5]. This band gap energy is obtained from the calculation of the distance between the valence band and the conduction band from the band structure. A gas molecule will disrupt the band structure of the sensor material because it has a charge. In that way, there will be a shift or a change in the band structure which will cause the movement of electrons or holes from the valence band and conduction band of the sensor material to change. This change will be used as a signal for the gas sensor[6].

The signal from the gas sensor itself comes from calculating the band gap energy data from $LaFeO_3$ before, during, and after simulating the adsorption mechanism with ethanol gas molecules. This calculation will be carried out using the PHASE program with a Density Functional Theory mathematical approach with the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) method. This calculation will calculate the band structure and culminate in the band gap energy after the band structure

*e-mail: endis@upi.edu

is obtained. This study is expected to determine the value of the band gap energy and analyze the electronic properties of $LaFeO_3$ when simulating the adsorption mechanism with ethanol gas.

2. Simulation

$LaFeO_3$ elaborated in this study is $LaFeO_3$ (001) with 1 cell layer thickness in the orthorhombic cell with the structure parameter of the $LaFeO_3$ in angstrom: a = 5.600805, b = 5.661924, and c = 7.94467. This structure contains 4 La atoms, 4 Fe atoms, and 12 oxygen atoms. The $LaFeO_3$ is not in the form of a supercell since this paper only focuses on band structure study. Hence, there is also no vacuum layer.

Simulations were carried out to determine the electronic properties of $LaFeO_3$ from the band gap energy data employed by the PHASE program. PHASE is a program that focuses on calculating electronic structures based on Density Functional Theory and pseudopotential schemes[7]. This program applies Density Functional Theory (DFT) with Generalized Gradient Approximation from Perdew-Burke-Ernzerhof (GGA-PBE) for the exchange-correlation function. Knowing this program uses Density Functional Theory (DFT) with Generalized Gradient Approximation from Perdew-Burke-Ernzerhof (GGA-PBE), based on previous studies, it is shown that this exchange-correlation function ignores the correct value for the band gap energy's value[8]. Therefore, Hubbard's correction was added to the calculations in this study so that the energy band gap values do not deviate too much. The correction value used in this study is 4 eV given to the d orbital of the Fe atom[9].

The atomic coordinates of $LaFeO_3$ were obtained from the material project database[10] and ethanol gas molecules from the Crystallography Open Database[11]. In this simulation, ultrasoft pseudopotentials were implemented for every atom involved, including the ethanol gas molecules. Ultrasoft pseudopotential is a potential that is used to overcome the effects of the movement of electron nuclei of an atom with an effective potential to get the cut-off energy as low as possible[12].

The value of k-points, cut-off energy, and distance between the gas molecules and $LaFeO_3$ is determined from the convergence results with the total energy of the system. Based on the convergence results, the determined k-points are the value of 4×4×4, a cut-off energy value as much as 60 Ry, and a gas molecule distance to $LaFeO_3$ is 1 Å as shown in Figure 1.

In this study, ferromagnetism was used so that the circumstances given by the spin-up and spin-down would be distinct. In addition, the high point of symmetry in the Brillouin zone in this structure uses the orthorhombic crystal type shown in Figure 2. Both of these would affect the plot of the band structure.

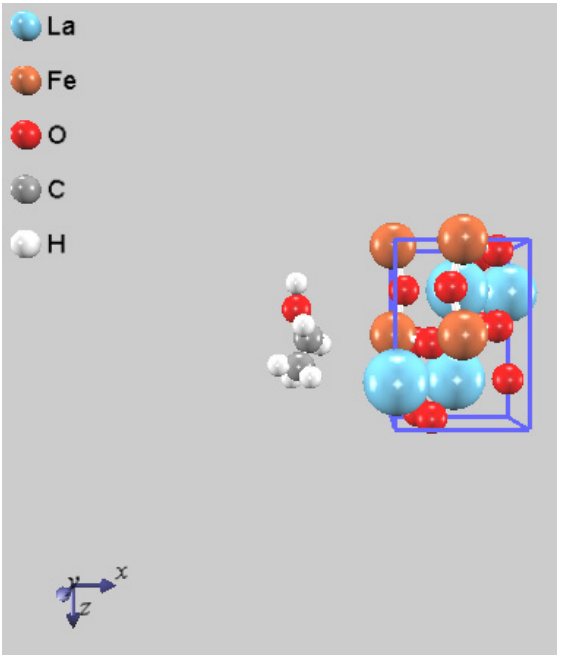

Figure 1. Initial configuration condition of $LaFeO_3$ with a distance of 1 Å.

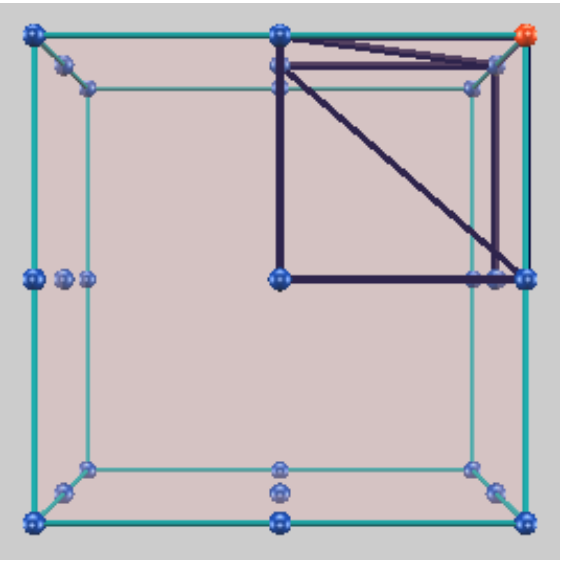

Figure 2. High point of symmetry for the orthorhombic crystal type in this system.

3. Results and Discussions

3.1. Band structure

The band structure plot is obtained from the density of states (DOS) calculation results. However, the analysis of the DOS will not be explored further in this study.

Calculation of the DOS was carried out on the three structures before, during, and after exposure to ethanol gas molecules. Before getting exposed to ethanol gas molecules, the pseudopotential used was based on the atoms present in the $LaFeO_3$ material. When getting exposed, a pseudopotential was used based on the atoms present in the material $LaFeO_3$ and ethanol, whose chemical formula is C_2H_5OH. After being exposed to the ethanol gas molecule, the calculated results when being exposed were used as the input. The pseudopotential was removed for the ethanol gas

molecule. This was done as an analogy that the ethanol gas molecules were rapidly vacuumed.

After calculating the DOS in three conditions, the results from the calculation were used as the initial conditions for the calculation of band structure. The results of the band structure calculation consisted of high symmetry points in the Brillouin zone of orthorhombic crystals owned by $LaFeO_3$ and the energy eigenvalues of each high symmetry point. Figures 3(a), 3(b), and 3(c) are the results of the band structure plot of the three states.

If it is examined as a whole, each state shows a tendency of adsorption-oxidation-desorption on the band structure. The ethanol gas molecules interfere with the $LaFeO_3$ from the charge carrier side and the chemical reactions. Thus, there is a shift or change in the band structure. It is confirmed in previous studies that the phenomenon of adsorption-oxidation-desorption is the basic mechanism for gas sensors to operate. Changes in the material properties of the material itself would be used as a signal for the gas sensor[6].

3.2. The band gap energy

The band gap energy is obtained from a distance between 2 bands, usually the valence and conduction bands. The distance between these two bands arises from the calculation of the band structure, which is affected by the calculation of the density of states. The calculation of the density of states is needed as an input for the calculation of the band structure. The density of states is the charge density in the ground state with a certain point *k*. In the band structure, the states are labeled by *k* and the band index *n*. For example, the energy when the band is very flat at *k* finite, the density of states will be large. This is because there are many different values of the *k* state for the same energy. Therefore, the initial conditions for plotting the band structure result from the density of states calculation.

For the band gap energy, it is found that ± 1.4 eV is the band gap energy value for $LaFeO_3$ before getting exposed to ethanol gas molecules, ±0.4 eV for $LaFeO_3$ when exposed to ethanol gas molecules, and ±0.9 eV for $LaFeO_3$ after being exposed to gas molecules. The aforementioned values are the results of measurements of the gap distance formed in Figures 3(a), 3(b), and 3(c).

Based on the calculation of the band gap energy, it is found that the band gap energy value for $LaFeO_3$ before being exposed to ethanol gas molecules is ± 1.4 eV. When compared with the project reference materials, this value is almost similar, with a value of ± 1.436 eV[10]. On the other hand, some references show different band gap energy values, such as those showing that the measured band gap energy has a value of 2.34 eV[13] or 2.1 eV[14]. This difference in value is caused by different correlation exchange functions. In this study, GGA-PBE was used, while for reference[13], PBEsol was employed. In addition, the ground state used in this study is ferromagnetic, while in the reference, it is antiferromagnetic. This is the situation given by the spin-up and spin-down, which for antiferromagnets are the same, while for ferromagnets it is different[15].

When $LaFeO_3$ is exposed to ethanol gas molecules, a change in the band gap energy value can be observed and measured for as much as ± 0.4 eV. This can be explained

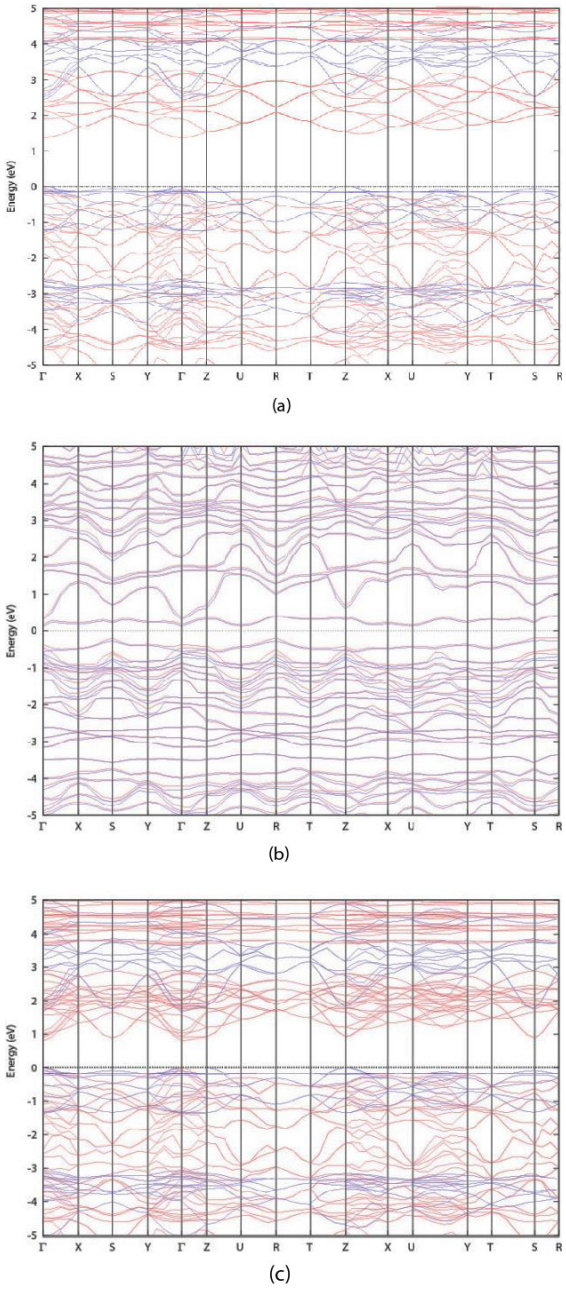

Figure 3. (a) The $LaFeO_3$ band structure before being exposed to the ethanol gas molecules; **(b)** The $LaFeO_3$ band structure when being exposed to the ethanol gas molecules; **(c)** The $LaFeO_3$ band structure after getting exposed to the ethanol gas molecules. The red ribbon shows the spin up calculation result, while the blue one represents the spin down calculation result.

by the surface of $LaFeO_3$ that has lost oxygen ligands in the FeO_3 group and its exterior cations. The decrease in ionicity at the surface is associated with surface covalence. This effect is important in forming the covalent bonds with unfamiliar molecules to be adsorbed. In general, $LaFeO_3$ is antiferromagnetic, in which holes are produced by the presence of missing oxygen ligands and cation breakdown. This is used by reducing gas, which in this case is ethanol, to change the

conductance of $LaFeO_3$, and this affects the system's density of states. This is because the number of charge carriers per unit volume, in this context, are holes, changes[16]. Hence, the band structure also changes since it is linked to the results of the density of states.

As mentioned in the previous section, $LaFeO_3$, is a p-type semiconductor material in which the charge carriers are holes. The resistance of this material is highly dependent on the oxygen content. At room temperature, $LaFeO_3$ adsorbs oxygen molecules on the surface. The gas sensing mechanism of this material involves an adsorption-oxidation-desorption process, in which the process, which involves oxygen, plays an important role[17].

Holes were transferred from a portion of the crystal to chemically absorb the oxygen. This process would form a hole depletion, providing high resistance to the sensor. When the sensor is exposed to a reducing gas, such as ethanol, the molecules of this gas become oxidized by the ionized oxygen and are adsorbed (O_2^-, O^-, O^{2-}) through the catalytic interactions. This oxidation produces a number of holes and increases the conductivity of the gas sensor[17].

The reaction that occurs is written as follows:

$$O_2(gas) + e^- \leftrightarrow O_2^-(ads) \quad (1)$$

$$O_2^-(ads) + e^- \leftrightarrow 2O^-(ads) \quad (2)$$

$$2O^-(ads) + e^- \leftrightarrow O^{2-}(ads) \quad (3)$$

With this method, O_2 plays a role of a charge-accepting molecule and attracts holes from the surface of the metal oxide. This reduces the potential barrier for the holes to move and the $LaFeO_3$ become exposed to the gas molecules. At moderate temperatures, the gas molecules react with the absorbed oxygen, and the holes are released back into the valence band with increasing resistance. In the presence of reducing gas, the adsorbed oxygen on the sensor surface reacts with the reducing gas as follow[16]:

$$R + O_{ads}^{n-} \rightarrow RO + ne^- \quad (4)$$

For better understanding, Figure 4 illustrates the oxygen adsorption mechanism in the gas sensor.

Therefore, in the band structure, it is shown that the band gap energy becomes small. This indicates that it is easier for the holes to move to other energy states, representing the number of holes. This resulted from the reaction between the oxygen and the $LaFeO_3$ surface as the sensor surface.

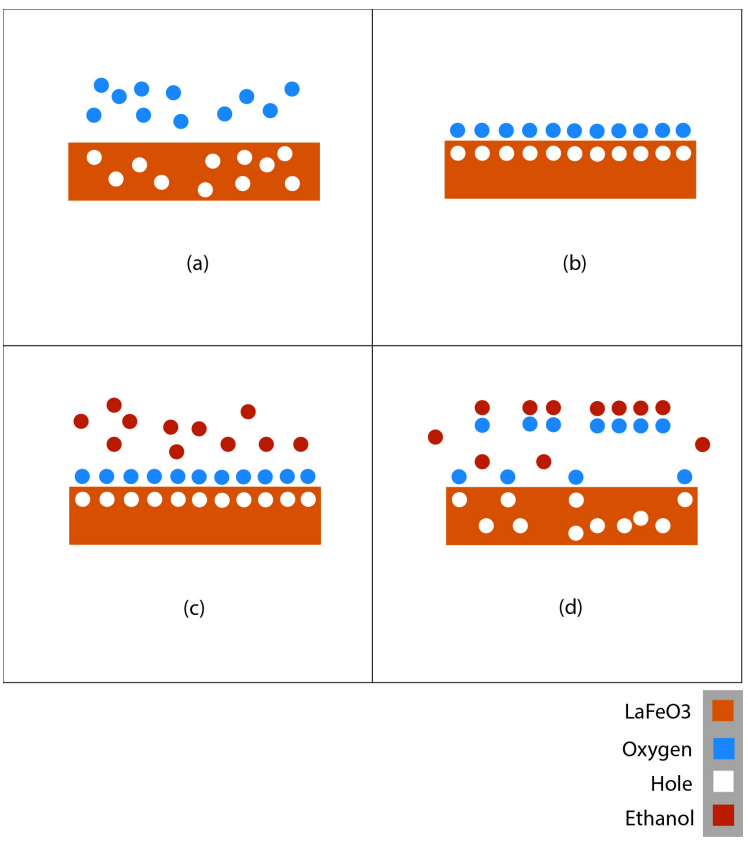

Figure 4. The illustration of oxygen adsorption in a gas sensor (a) $LaFeO_3$'s holes are not adsorbing the oxygen yet, (b) $LaFeO_3$'s holes are adsorbing the oxygen molecules on the surface, (c) $LaFeO_3$ is exposed to the ethanol gas, and (d) The molecules of ethanol gas are oxidized by ionized oxygen and are adsorbed. This oxidation produced a number of holes and increases the conductivity of the gas sensor.

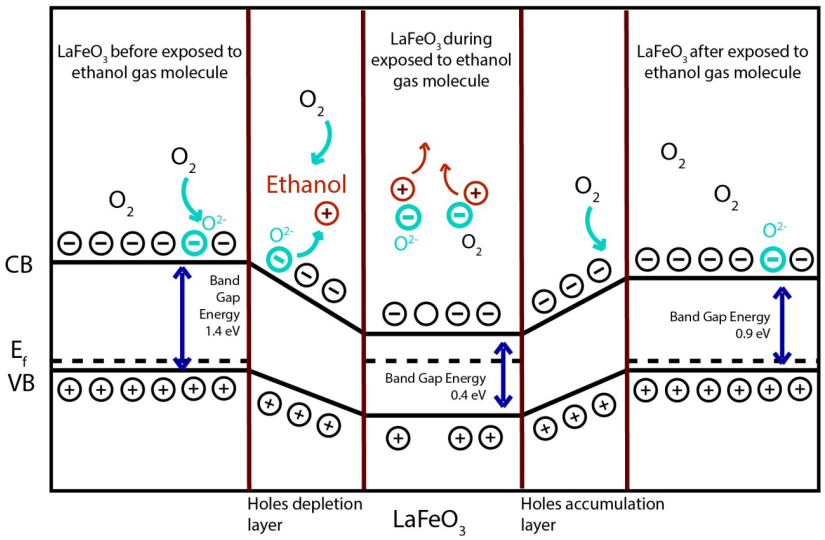

Figure 5. Band gap energy in the band structure represented by band bending diagram.

Figure 5 shows how band gap energy in the band structure can be represented by a band bending diagram.

Although there is a distance between the gas molecule and the $LaFeO_3$, the change in DOS that affects the band structure and the value of the band gap energy is measurable. This is because the valence hole charge of the gas molecule has an electric potential as a function of distance represented by the use of pseudopotential input. Thus, the changes can still be measured by the distance.

After the ethanol gas molecules are vacuumed from $LaFeO_3$, the band structure of the material is expected to return to its original state. However, considering the calculation results, the band structure of $LaFeO_3$ slightly shifted from the original point when the material had not been exposed to ethanol gas molecules, that was from ± 1.4 eV to ± 0.9 eV. The assumption that might be able to answer this is knowing that technically being vacuumed in this program is to remove ethanol gas molecules only, so that the existing input for this state is not the same as the input for the state before being exposed to the ethanol gas molecules. On the other hand, this shows that $LaFeO_3$ can be considered to be reversible, even though the values were different.

4. Conclusion

An analysis of the electronic properties of the band gap energy has been conducted using density functional theory with Generalized Gradient Approximation-Perdew-Burke-Ernzerhof (GGA-PBE) as its exchange-correlation function on $LaFeO_3$ (001) for ethanol gas sensor by PHASE program. This study also employed the Hubbard correction of 4 eV in the d orbital of the Fe atom for better results in the band gap energy value. The band gap energy was calculated in 3 states: before, during, and after exposure to ethanol gas molecules. $LaFeO_3$ showed a band gap energy value as much as ± 1.4 eV, before being exposed to the ethanol gas molecule. However, the band gap energy value changed to ± 0.4 eV when exposed to the ethanol gas molecule at a distance of 1 Å. After being vacuumed, the $LaFeO_3$ gave a band gap energy value of ± 0.9 eV. The shrinking value of band gap energy is caused when the sensor was exposed to a reducing gas, such as ethanol. The molecules of this gas were oxidized using ionized oxygen and were adsorbed through catalytic interactions. With this method, O_2 played a role as a charge-accepting molecule and attracted holes from the metal oxide's surface. This reducesd the potential barrier for the holes to move, and the $LaFeO_3$ became exposed to the gas molecules. However, the band structure of $LaFeO_3$ slightly shifted from the original point from ± 1.4 eV to ± 0.9 eV since the material had not been exposed to ethanol gas molecules. This is because the system is being vacuumed to remove ethanol gas molecules only so that the existing input for this state is no longer similar to the input for the state before being exposed to the ethanol gas molecules.

Based on its band structure for every specific condition, it is shown that in $LaFeO_3$, an adsorption-oxidation-desorption mechanism based on the band gap energies from them, the band structures occur. This is the mechanism found in gas sensors to make them work. This mechanism is used as a signal for gas sensors, so $LaFeO_3$ can be a candidate for gas sensor applications, especially for ethanol gas.

5. Acknowledgment

The author would like to thank Yusuf Putra Nugraha and Ahmad Thariq for providing tech support for this research.

6. References

1. Laysandra H, Triyono D. Effect of Fe_3O_4 addition on dielectric properties of $LaFeO_3$ nano-crystalline materials synthesized by sol-gel method. IOP Conf Ser Mater Sci Eng. 2017;188:012039.
2. Sharma N, Kushwaha HS, Sharma SK, Sachdev K. Fabrication of $LaFeO_3$ and rGO-$LaFeO_3$ microspheres based gas sensors for

detection of NO_2 and CO. RSC Advances. 2020;10(3):1297-308. http://dx.doi.org/10.1039/C9RA09460A.
3. Thuy NT, Le Minh D, Giang HT, Toan NN. Structural, electrical, and ethanol-sensing properties of $La_{1-x}Nd_xFeO_3$ nanoparticles. Adv Mater Sci Eng. 2014;685715.
4. Tharsika T, Thanihaichelvan M. Highly sensitive and selective ethanol sensor based on ZnO nanorod on SnO_2 thin film fabricated by spray pyrolysis. Front Mater. 2019;6:122.
5. Mao S, Lu G, Chen J. Nanocarbon-based gas sensors: progress and challenges. J Mater Chem A Mater Energy Sustain. 2014;2(16):5573-9.
6. Ji H, Zeng W, Li Y. Gas sensing mechanisms of metal oxide semiconductors: a focus review. Nanoscale. 2019;11:22664-84.
7. Kato C, Kato S, Oshima M, Yoshikawa N, Sato F, Hatada T, et al. A package of simulation software [Internet]. 2014 [cited 2021 Oct 25]. Available from: http://www.ciss.iis.u-tokyo.ac.jp
8. Bagayoko D. Understanding Density Functional Theory (DFT) and completing it in practice. AIP Adv. 2014;4:127104.
9. Liu X, Cheng B, Hu J, Qin H. Theoretical calculation of ethanol molecule adsorption on $LaFeO_3$ (0 1 0) surface. Comput Mater Sci. 2013;68:90-4.
10. Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, et al. The materials project: a materials genome approach to accelerating materials innovation. APL Mater. 2013;1(1):011002.
11. Vaitkus A, Merkys A, Gražulis S. Validation of the crystallography open database using the crystallographic information framework. J Appl Cryst. 2021;54(Pt 2):661-72.
12. Vanderbilt D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys Rev. 1990;41:7892-5.
13. Scafetta MD, Cordi AM, Rondinelli JM, May SJ. Band structure and optical transitions in $LaFeO_3$: theory and experiment. J Phys Condens Matter. 2014;26:505502.
14. Hao P, Qiu G, Song P, Yang Z, Wang Q. Construction of porous $LaFeO_3$ microspheres decorated with NiO nanosheets for high response ethanol gas sensors. Appl Surf Sci. 2020;515:146025.
15. Jia T, Zeng Z, Lin HQ, Duan Y, Ohodnicki P. First-principles study on the electronic, optical and thermodynamic properties of ABO3 (A = La,Sr, B = Fe,Co) perovskites. RSC Adv. 2017;7:38798-804.
16. Toan NN, Saukko S, Lantto V. Gas sensing with semiconducting perovskite oxide $LaFeO_3$. Physica B. 2003;327(2-4):279-82.
17. Benali A, Azizi S. Structural, electrical and ethanol sensing properties of double-doping $LaFeO_3$ perovskite oxides. Ceram Int. 2014;40(9):14367-73.