Enhanced Gas Sensing Properties of Pd-incorporated Ce-$SmFeO_3$

R. B. Mankar*[1] and V. D. Kapse[2]

*[1]*Department of Physics, Smt. Radhabai Sarda Arts, Commerce and Science College, Anjangaon Surji 444705, Maharashtra State, India.*

[2]*Department of Physics, Arts, Science and Commerce College, Chikhaldara, 444807, Maharashtra State, India*

Abstract

This investigation deals with the incorporation of noble metal nanoparticles to Ce-$SmFeO_3$ sensing element for boosting its gas sensing performance. Series of Pd incorporated Ce-$SmFeO_3$ sensing elements Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 corresponding to dipping time 1 min, 2 min and 3 min, respectively, was prepared using simple dipping technique. Different dipping time interval ensures the incorporation of different concentrations of Pd on the surface of Ce-$SmFeO_3$. Porous microstructures of all the samples were observed in FE-SEM images. Incorporation of Pd and variation in the concentration of Pd were seen in elemental analysis. Ethanol gas response of Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 were measured. For 60 ppm ethanol gas, response of Pd-CeSF1 increased to 37.2 which was about 2.2 times more than the previously recorded response of 16.87 for CeSF. Additionally, shift in the corresponding optimal operating temperature from 100^0C to 80^0C was also observed. The contribution of palladium nanoparticles in increasing response of Pd-CeSF1towards ethanol gas and decaying its optimal operating temperature was elaborately discussed.

Keywords: Pd incorporated Ce-$SmFeO_3$, Noble metal, Ethanol sensor, Catalyst, Perovskite.[1]

---

*Corresponding Author

1. Introduction

Detection of target gas by semiconductor metal oxide based gas sensor is governed by the adsorption of gas molecules on the oxide surface of sensor [1]. The performance of chemiresistive gas sensor is influenced by the availability of adsorption sites. The availability of adsorption sites can be enhanced by increasing surface area. More adsorption sites are available if surface area is large. Preparation of SMOs with different morphologies is a general approach to increase the surface area [2]. Beside this, doping of base material has been frequently reported to increase the sensitivity of SMO [3-5]. Doping with noble metals seems to be more effective owing to their high catalytic activities [6-7]. Nobel metals can incorporate additional active surface sites thereby improving the adsorption of target gases.

P-type semiconducting $SmFeO_3$ is well known for its ability to detect ozone, NO_2 which are oxidizing gases [8-10]. Extremely low electrical conductivity and reducibility make $SmFeo_3$ unsuitable for monitoring VOCs and reducing gases [11]. But modified $SmFeO_3$, permitted due to its perovskite structure, has potential to sense even reducing gases like ethanol. Gas sensing properties of Co doped $SmFeO_3$ have been reported by some authors [12-14]. Ethanol, a well known volatile organic compound, has its present in foods, chemical industries etc [15]. Because of its toxicity, ethanol can cause liver damage, skin irritation etc. and therefore its monitoring has become essential. Doped semiconductor metal oxides and perovskite-type oxides based gas sensors have been fabricated by some researchers for monitoring of ethanol [16-18]. Although these sensors can detect ethanol, its gas response and optimal operating temperature has to be enhanced.

Previously, we have also prepared a series of Ce surface modified $SmFeO_3$ films by changing the dipping time intervals (1 min, 3 min and 5 min) and observed that all the films were selective to ethanol gas. The film having dipping time 5 min has maximum ethanol gas response (16.87) at optimal operating temperature 200^0C. With the literature review that noble metal incorporation boosted the gas sensing performance; in present work we incorporated Pd in various concentrations to this best Ce modified $SmFeO_3$ film and investigated the impact of Pd on its ethanol gas sensing characteristics.

2. Experimental

Our earlier publications demonstrated the fabrication of Ce modified $SmFeO_3$ sensor elements in the form of thick films [19]. In present work we used Ce modified $SmFeO_3$ film with dipping time of 5 min and marked it as CeSF. For incorporating Pd noble metal to CeSF, palladium (II) nitrate solution was taken. To this solution, CeSF films were dipped for different time intervals. Films with dipping timing 1 min, 2 min and 3 min were marked as Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 respectively. All the films were dried in air, fired in Muffle furnace and then treated for further investigations.

As prepared Pd-CeSF samples were investigated by FE-SEM and EDX methods. With FE-SEM, morphology of samples was visualized and with EDX, the concentration and dispersion of Pd was depicted. Gas sensing characteristics of samples were studied in static gas sensing set-up under 60 ppm ethanol gas. The resistance values of sensors were R_g and R_a respectively in presence of ethanol and air. Gas response is then calculated as (R_g/R_a) [20].

3. Results and Discussion

3.1. Characterization of Pd -CeSF

X-ray spectrum of $SmFeO_3$ powder was investigated in our earlier publication which confirmed the formation of single phase perovskite oxide with orthorhombic symmetry [14].

FE-SEM images of Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 were shown in Figure 1.

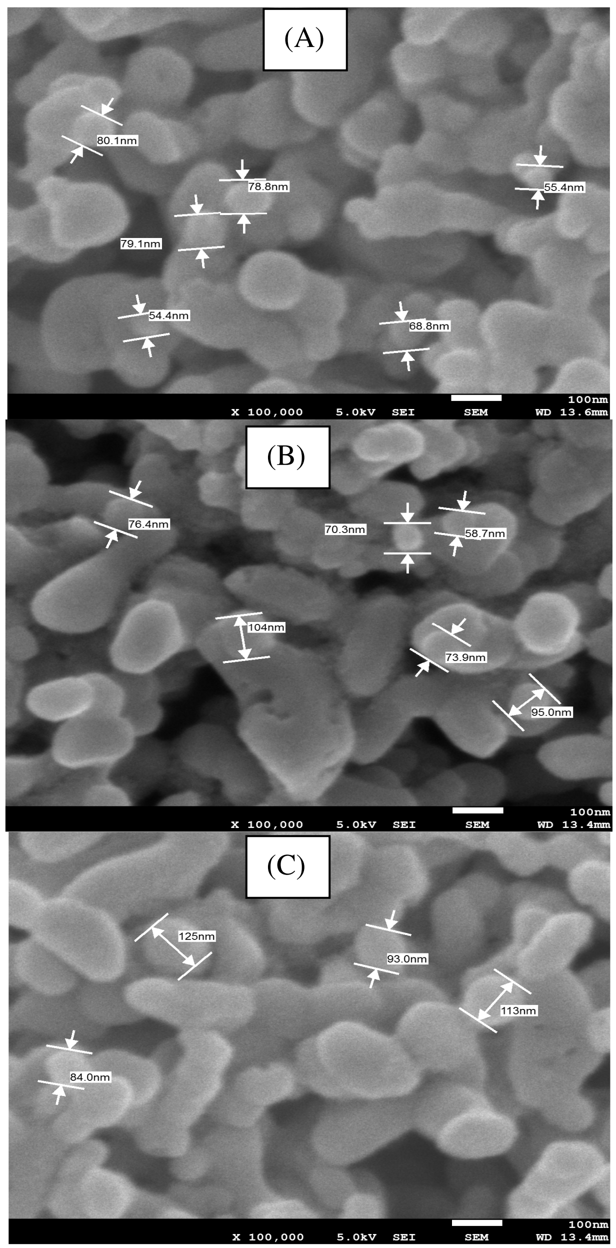

Figure 1. FE-SEM images of (A) Pd-CeSF1, (B) Pd-CeSF2 and (C) Pd-CeSF3

All the films seem to be consists of number of nanoparticles distributed non-uniformly and/or the cluster of nanoparticles at the surface. The average particle size ranges from 54 nm to 84 nm. The smallest average particle size (54.4 nm) was recorded in Figure 1(A) which is FE-SEM image of Pd-CeSF1 with dipping time 1 min. High porosity was observed on the surface of all the samples as compared to porosity of CeSF sample presented in earlier publication [19]. Pd-CeSF1film appears to have high porosity among Pd incorporated CeSF films.

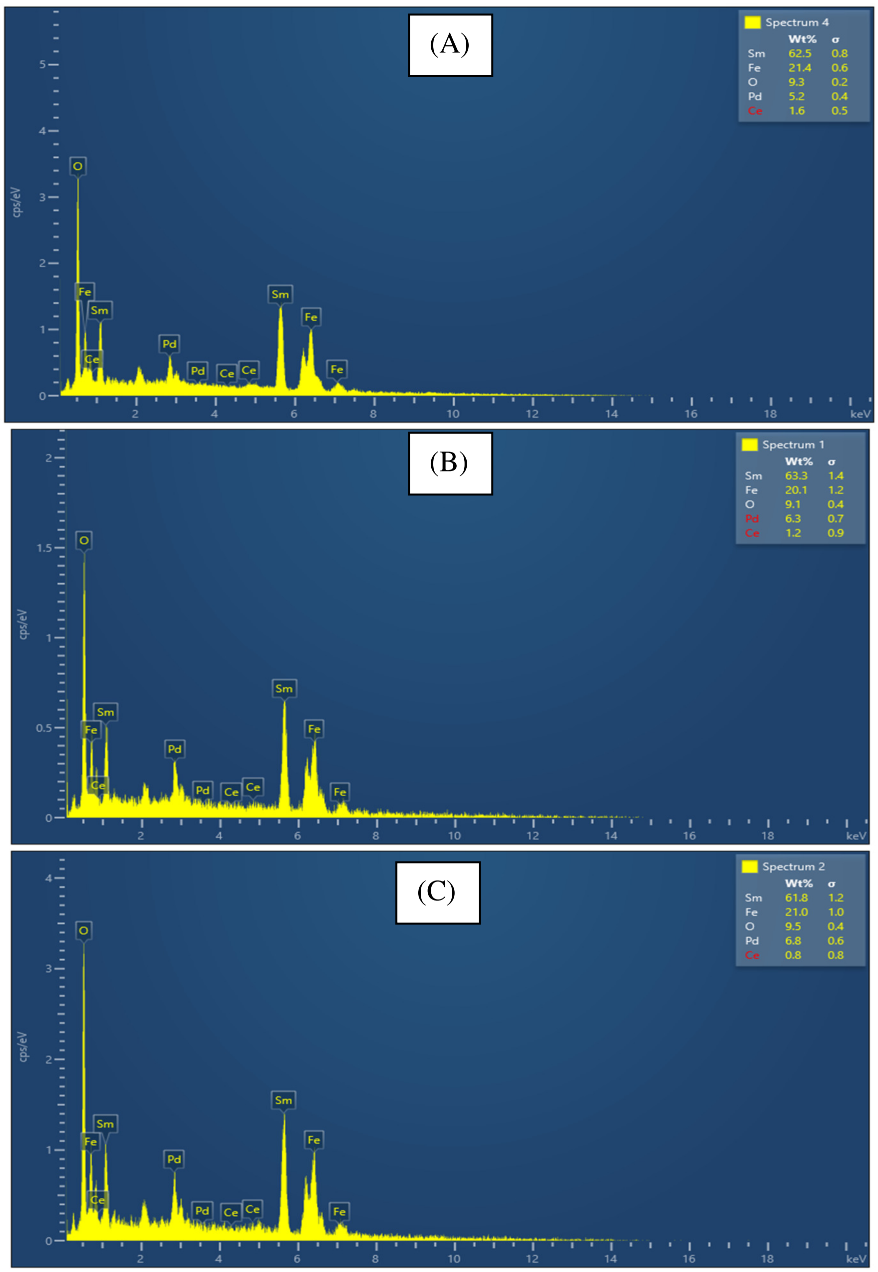

Figure 2. EDX spectra of (A) Pd-CeSF1, (B) Pd-CeSF2 and C) Pd-CeSF3

The EDX spectrum of Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 are shown in Figure 2. The results provide the confirmation of successful incorporation of Pd to CeSF film. Additionally concentration of incorporated Pd was found to be increased with the increase in dipping time.

3.2. Ethanol-sensing characteristics of Pd-CeSF

In order to determine optimal operating temperature, ethanol gas response of Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 based sensors were measured, by changing the operating temperature from 30 ^{0}C to 350 ^{0}C, towards 60 ppm ethanol gas concentration. The observations demonstrated that the optimal operating temperatures for Pd-CeSF1based sensor was 80 ^{0}C, and that for Pd-CeSF2 and Pd-CeSF3 based sensors was 100 ^{0}C. Figure 3 represents response of CeSF and Pd-CeSF films to 60 ppm ethanol in the operating temperature range 30^{0}C to 350^{0}C.

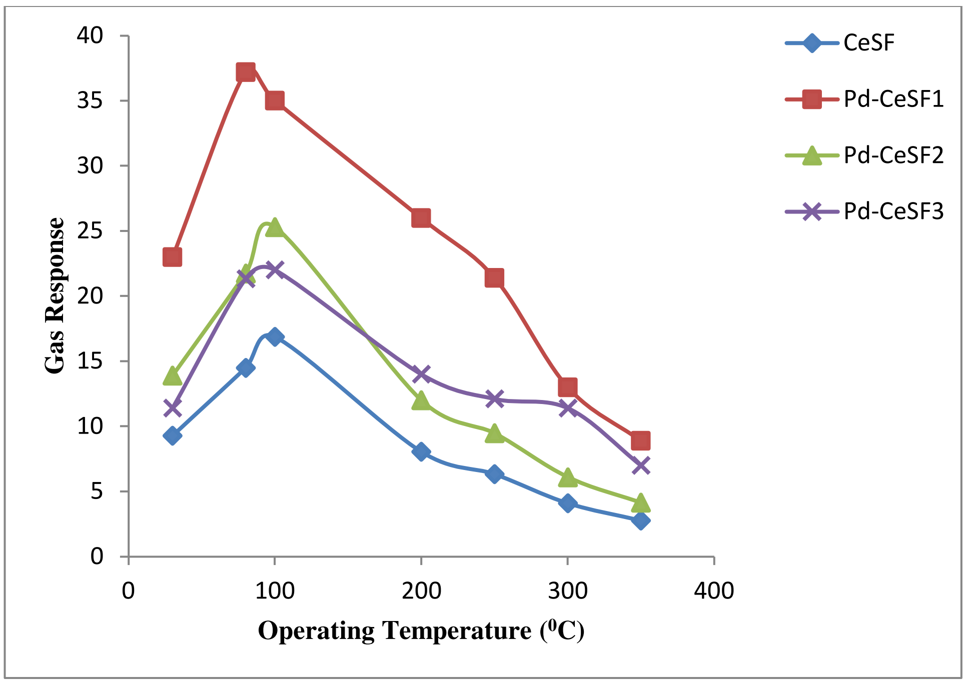

Figure 3. Response of CeSF and Pd-CeSF Films to 60 ppm Ethanol

The graph shows that all the three samples exhibited similar behavior in gas response and operating temperature. With the increase in operating temperature, growth in gas response was observed initially which then tended to decay in gas response with further increase in operating temperature. The carrier concentration and the activation energy of surface reactions strongly affect the values of gas response of sensor. The operating temperature of sensor has direct correlation with these two factors. The initial increase in gas response with operating temperature may be the result of activation of gas molecules and the trapping of conduction electrons [21]. The decay in gas response with further increase in operating temperature may be due to the fall in adsorption rate than desorption rate. For samples Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3, the maximum values of gas response were 37.2, 25.3 and 22 which were obtained at corresponding optimal operating temperatures 80^0C, 100^0C and 100^0C respectively. The results indicate that Pd doping improved the gas response and also decreased the optimal operating temperature.

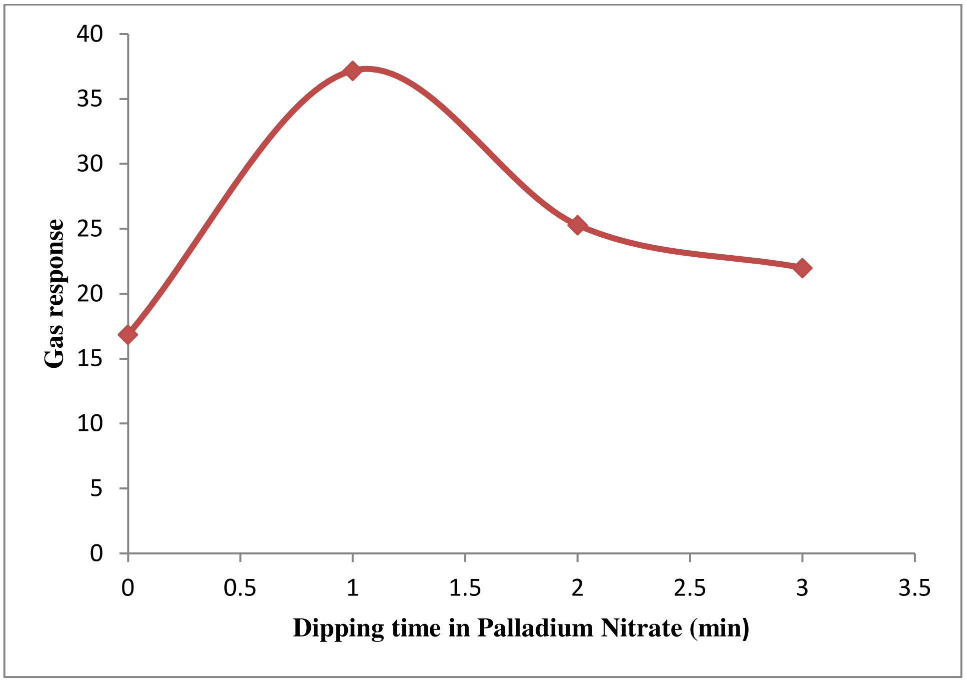

Figure 4. Ethanol Gas Response Variation with Dipping Time

Pd doping enhances the gas response but only optimum concentration of Pd can present maximum ethanol gas response. Increasing and then decreasing behavior of ethanol gas response with Pd concentration (or dipping time) was observed here as depicted in Figure 4.The surface defects increase with Pd concentration but not always. Concentration of Pd corresponding to dipping time 1 min was sufficient to produce maximum ethanol gas response. At this Pd concentration, best catalytic and sensitization effect of Pd could be observed. But at comparatively high Pd concentration (dipping time 2 min and 3 min), aggregation of Pd nanoparticles decreased the active sites and hence gas response was decreased.

To examine the stability of sensor, its response was noted regularly for 60 days. During this period, sensor showed almost constant gas response as shown in Figure 5.

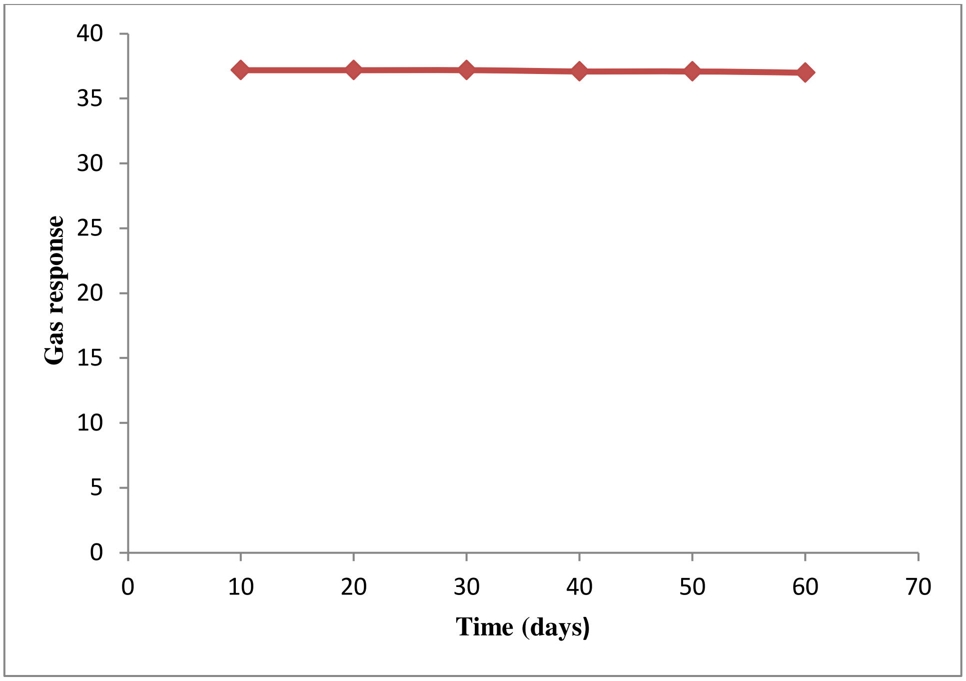

Figure 5. Stability of Pd-CeSF1-based Sensor

3.3. Ethanol-sensing mechanism of Pd-CeSF

According to ethanol gas sensing mechanism frequently reported by many authors, in ambient air, chemisorption of oxygen gas occurs on the surface of sensor [21]. This chemisorption includes i) adsorption of oxygen molecules from air and ii) absorption of electrons in the material by these adsorbed oxygen molecules to decomposed into molecular or ionic species depending on the temperature. The formation of electron hole accumulation layer near the surface is the final result of chemisorption of oxygen molecules which decreases the sensor resistance. When ethanol gas enters into the chamber, it is also adsorbed on the surface. The adsorbed ethanol gas reacts with chemisorbed oxygen ions to produce H_2O and CO_2 gases followed by reverting of captured electrons to the material. This so called desorption process reduces the width of hole accumulation layer resulting in the increase of sensor resistance.

When Pd is incorporated into CeSF sensor, the activation energy of surface reactions is decreased because of the reaction paths provided by Pd. Further, additional active surface sites are produced that boost the adsorption of ethanol gas. For palladium noble metal, chemical sensitization and electronic sensitization were reported to be impacting factors for boosting gas sensing performance [22-23]. Among them, chemical sensitization arises due to spill-over effect. The Pd nanoparticles now serve as active sites for adsorption and dissociation of oxygen molecules in ambient air. In ethanol gas environment, gas molecules are dissociated into corresponding atoms through catalytic activity of Pd. Then these dissociated atoms spill over from noble metal to the surface of metal oxide. Thus the rate of surface reactions is improved due to subsequent spillover. On the other hand, electronic sensitization originates due to the different fermi levels of SMO and Pd nano material. Pd nanoparticles also absorb electrons from SMO and the potential barrier is elevated [24].

4. Conclusion

Palladium nanoparticles were incorporated to Ce modified $SmFeO_3$ films (dipping time 5 min). As-prepared Pd-CeSF1, Pd-CeSF2 and Pd-CeSF3 films exhibited enhanced response to 60 ppm ethanol. In particular, Pd-CeSF1based sensor has maximum response (37.2) at lower operating temperature 80^0C. The enhanced ethanol gas sensing characteristics of Pd decorated Ce modified $SmFeO_3$ films were the results of sensitization mechanism of palladium.

Acknowledgment

Authors acknowledge VNIT, Nagpur, Maharashtra state, India for sample characterization.

REFERENCES

[1] A Mirzaei, S.G. Leonardi and G. Neri, "Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review", Ceram. Int., vol. 42, (**2016**), pp. 15119–15141.

[2] Ali Mirzaei, H. R. Ansari, M. Shahbaz, Jin-Y. Kim, H. W. Kim and S. S. Kim, "Metal Oxide Semiconductor Nanostructure Gas Sensors with Different Morphologies", Chemosensors, vol. 10, (**2022**), pp. 289.

[3] X. Yang, X. Hao, T. Liu, F. Liu, B. Wang, C. Ma and X. Liang, "CeO_2-based mixed potential type acetone sensor using $La_{1-x}Sr_xCoO_3$ sensing electrode", Sens. Actuators B Chem., vol 269 (**2018**), pp. 118-126.

[4] R. B. Pedhekar, F. C. Raghuwanshi and V. D. Kapse, "Low Temperature H_2S Gas Sensor Based on Fe_2O_3 Modified ZnO-TiO_2 Thick Film", Int. J. Mate. Sci. and Eng., vol. 3 (**2015**), pp. 219-230.

[5] X. Liu, L. Jiang, X. Jiang, X. Tian, X. Sun,Y. Wang, P. Hou, X. Deng and X. Xu, "Synthesis of Ce-doped In_2O_3 nanostructure for gas sensor applications", Appl. Surf. Sci., vol. 428 **(2018),** pp. 478–484.

[6] J. S. Jebakumar and A. V. Juliet, "Palladium doped tin oxide nanosensors for the detection of the air pollutant carbon monoxide gas", Sens., vol. 20, **(2020)**, pp. 5889.

[7] Y. Patil, R B Phedekar and F. C. Raghuwanshi, "Palladium doped zinc oxide nanomaterials for liquefied petroleum gas detection", International Journal of Engineering Science Invention (IJESI) vol. 9,**(2020),** pp. 32-42

[8] Hao-Tian and Huang, "NO_2 sensing properties of $SmFeO_3$ porous hollow microspheres", Sensors and Actuators B: Chemical, vol. 265, **(2018)**, pp. 443-451.

[9] Y. Itagaki, M. Mori, Y. Hosoya, H. Aono, and Y.Sadaoka, "O_3 and NO_2 sensing properties of $SmFe_{1-x}Co_xO_3$ perovskite oxides", Sens. Actuators B Chem., vol. 122, **(2007)**, pp. 315–320.

[10] M Mori, "Ozone detection in air using $SmFeO_3$ gas sensor for air quality classification", J. Ceram. Soc., vol. 119, **(2011)**, pp. 926-928.

[11] Masami Mori, "Influence of VOC structures on sensing property of $SmFeO_3$ semiconductive gas sensor", Sensors and Actuators B: Chemical, vol. 202, **(2014),** pp. 873-877.

[12] Kun Li, "High selectivity methanol sensor based on Co-Fe_2O_3/$SmFeO_3$ p-n heterojunction composite", Journal of Alloys and Compounds, vol. 765, **(2018)**, pp. 193-200.

[13] Jifan Hu, "Effect of Cobalt doping on the microstructure, electrical and ethanol-sensing properties of $SmFe_{1-x}Co_xO_3$ " Sensors and Actuators B, vol. 129, **(2008)**, pp. 953-957

[14] R. B. Mankar, V. D. Kapse and D. R. Patil, "Gas sensing properties of pure and Co modified nanocrystalline $SmFeO_3$ thick films", Asian J. Chem., vol. 35, **(2023),** pp. 1485-1490.

[15] L. Wu, X. Shi, H. Du, "Ce-doped $LaCoO_3$ film as a promising gas sensor for ethanol", AIP Advances, vol. 11, **(2021)**, pp. 055305.

[16] P. Hao, G.M. Qu, P. Song, Z.X. Yang and Q. Wang, "Synthesis of Ba-doped porous $LaFeO_3$ microspheres with perovskite structure for rapid detection of ethanol gas", Rare Met., vol. 40, **(2021)**, pp. 1651–1661.

[17] M. Tian, J. Miao, P. Cheng, H. Mu, J. Tu and J. Sun, "Layer-by-layer nanocomposites consisting of Co_3O_4 and reduced grapheme (rGO) nanosheets for high selectivity ethanol gas sensors", Appl. Surf. Sci., vol. 479, (**2019**), pp. 601–607.

[18] W. Tan, Q. Yu, X. Ruan and X. Huang, "Design of SnO_2-based highly sensitive ethanol gas sensor based on quasi molecular-cluster imprinting mechanism", Sens. Actuators B Chem., vol. 212, **(2015)**, pp. 47–54.

[19] R. B. Mankar and V. D. Kapse, “Fabrication and characterization of Ce modifiedSmFeO_3 thick film”, Aayushi International Interdisciplinary Research Journal, vol. 109, **(2022),** pp.367-369.
[20] Z. Li and J. Yi, “Enhanced ethanol sensing of Ni-doped SnO_2 hollowspheres synthesized by a one-pot hydrothermal method”, Sens. Actuators B Chem., vol. 243, **(2017)**, pp. 96–103.
[21] V. Inderan, M. M. Arafat, A.S. Haseeb, K. Sudesh and H. L. Lee, “A comparative study of structural and ethanol gas sensing properties of pure, nickel and palladium doped SnO_2 nano rods synthesized by the hydrothermal method”, J. Phys. Sci., vol. 30, (**2019)**, pp. 127–143.
[22] J. S. Jebakumar and A. V. Juliet, “Palladium doped tin oxide nanosensors for the detection of the air pollutant carbon monoxide gas”, Sens., vol. 20, **(2020),** pp. 5889.
[23] Y. Chen, H. Qin and J. Hu, “CO sensing properties and mechanism of Pd doped SnO_2 thick-films”, Appl. Surf. Sci., vol. 428 (**2018)**, pp. 207–217.
[24] M. Fisser, R. A, Badcock, P.D. Teal and A. Hunze, “Optimizing the sensitivity of palladium based hydrogen sensors”, Sens. Actuators B Chem., vol. 259, (**2018)**, pp. 10–19.