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Fabrication of Co-modified $SmFeO_3$ thick film for detection of H_2S gas

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ABSTRACT

In present work, Co-modified SmFeO3 thick films are fabricated to investigate its gas response towards hydrogen sulphide (H2S) gas. Pure SmFeO3 powder is prepared by sol-gel method and thick films of SmFeO3 are prepared by screen printing technique. Co-modified SmFeO3 thick films are prepared by dipping pure SmFeO3 thick films in 0.1 M cobalt chloride solution for 5 min followed by firing at 500^{0}C. Morphology and elemental composition of both pure and Co-modified SmFeO3 thick films are studied by Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray Analysis (EDAX) techniques respectively. Gas response of Co-modified SmFeO3 thick film towards 50 ppm H2S gas is measured at different operating temperatures from room temperature to 400^{0}C. Co-modified SmFeO3 thick film exhibited maximum gas response (3.24) at 200^{0}C. Gas sensing mechanism and temperature dependence of H2S gas response are discussed in details.

Keywords: - Co-modified SmFeO3 thick film, Dipping technique, Gas response, Optimal operating temperature, Adsorption.

1. INTRODUCTION

The growing need for environmental monitoring has stimulated considerable research on solid-state gas sensors based on semiconductor metal oxides. Materials such as ZnO, TiO_2, SnO_2, and their composites are well known for their application in solid-state gas sensors [1–3]. Perovskite-type oxides with the general formula ABO_3 have also been extensively investigated for solid state gas sensor due to their highly tunable physical and chemical properties [4–6]. Rare-earth orthoferrite such as $LaFeO_3$ and $SmFeO_3$ have been reported to exhibit excellent sensing performance toward both oxidizing and reducing gases [7–10]. $SmFeO_3$ is a promising p-type rare-earth orthoferrite that has been widely studied for the detection of oxidizing gases [9-10]. Its key advantages include p-type electrical conductivity, high oxygen-ion mobility, and strong catalytic activity toward oxidizing gases. The properties of $SmFeO_3$ can be effectively tailored by doping at either the A-site or B-site of the perovskite structure. Such modifications introduce structural defects and oxygen vacancies, which significantly influence its gas-sensing behavior. One effective approach to generate additional oxygen vacancies is the incorporation of oxidizing or reducing elements into $SmFeO_3$, which can be achieved through doping or surface modification (dipping) methods. Dopants such as Co, Ce, and Ni have been explored for the modification of $SmFeO_3$ [11-13]. Cobalt, being a reducible element, can induce a higher concentration of oxygen vacancies when introduced into pure $SmFeO_3$. In cobalt-doped $SmFeO_3$, each Co^{2+} ion contributes one electron, and the resulting cobalt misfit effectively acts as an oxygen vacancy [11]. However, since the Co–O bond is weaker than the Fe–O bond, chemical stability issues may arise under reducing gas environments. Therefore, the controlled addition of cobalt to pristine $SmFeO_3$ is essential to balance enhanced conductivity with structural stability. R. C. Michel reported the synthesis and characterization of $SmCoO_3$ for enhanced gas-sensing applications [14]. Enhanced ethanol sensing performance of $SmFe_{0.7}Co_{0.3}O_3$ was also reported by Ma Zhao *et al.* [11]. In our previous work, ammonia gas sensing properties of pure and Co- modified $SmFeO_3$ thick films (dipping time 1 min, 3 min and 5 min) were reported [15]. It was observed that, Co-modified $SmFeO_3$ thick film (dipping time 3 min) exhibited excellent ammonia gas sensing properties as compared to other samples. In present work, gas response of Co-modified $SmFeO_3$ thick film (dipping time 5 min) towards H_2S gas is investigated.

2. EXPERIMENTAL

2.1 Preparation of thick films

Pure nanocrystalline $SmFeO_3$ powder was prepared by sol-gel method. $SmFeO_3$ thick films were then

formed onto the glass substrate by screen printing technique. Details of sol-gel method and screen printing techniques were described in previous publications [12]. For surface modification, 0.1 M aqueous cobalt chloride solution was prepared and $SmFeO_3$ thick film was dipped into this solution for 5 min and then fired for 30 min at 500^0C.

2.2 Characterization techniques

X-Ray Diffraction pattern of pure $SmFeO_3$ powder was obtained from PW 3071 powder diffractometer. The morphology of thick film was studied by Field Effect Scanning Electron Microscope (JSM- 7610F, JEOL Japan) operated at 15 kV. The elemental analysis of the films was carried out by the Energy Dispersive X-ray Analysis (EDAX) integrated to FE-SEM.

2.3 Gas sensing measurements

The gas response of Co surface modified $SmFeO_3$ thick film was studied in static gas sensing set-up. The operating temperature was varied from room temperature to 400^0C and resistance of thick film was measured first in air and then in presence of fixed concentration (50 ppm) of target gas like liquid petroleum gas (LPG), carbon dioxide (CO_2), hydrogen (H_2), chlorine (Cl_2) and hydrogen sulfide (H_2S). For p-type SMO, gas response is expressed as (R_g/R_a) where R_g and R_a represents resistance of semiconducting material in target gas and in air respectively [12-13].

3. RESULT AND DISCUSSION

3.1 XRD study

XRD pattern of $SmFeO_3$ powder prepared by sol-gel method is presented and explained in our earlier publications [15]. Obtained XRD pattern confirmed that as prepared $SmFeO_3$ powder has perovskite phase with orthorhombic symmetry and Pnma space group [10-11]. Narrow and sharp peaks indicated crystalline nature of powder. The average crystallite size calculated using Scherrer's formula is 50.08 nm.

3.2 FE-SEM study

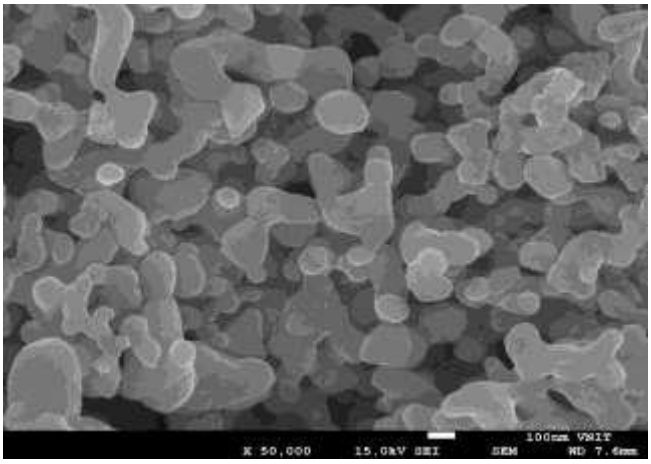

Fig- 1: FE-SEM micrograph of Co-modified $SmFeO_3$ thick film [16].

FE-SEM micrograph of Co-modified $SmFeO_3$ thick film is shown in Fig. 1. Large numbers of $SmFeO_3$ grains are present indicating the porous nature of the film. Particles are irregular in shape and some particles are agglomerated. Co particles are dispersed on basic $SmFeO_3$ structure and can be confirmed in the EDAX micrograph. Therefore this film favors the adsorption and desorption processes in gas sensing mechanism.

3.3 EDAX study

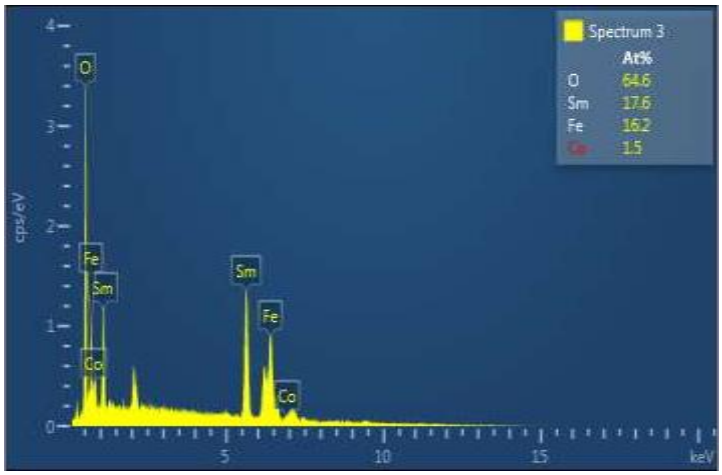

Fig- 2: EDAX image of Co-modified $SmFeO_3$ thick film [16].

Fig. 2 is the EDAX spectrum of Co-modified $SmFeO_3$ thick film. It reveals the presence of Co on the film along with Sm, Fe and O. Further, no other element is observed in EDAX spectrum which means purity of sample.

3.3 H_2S gas sensing study

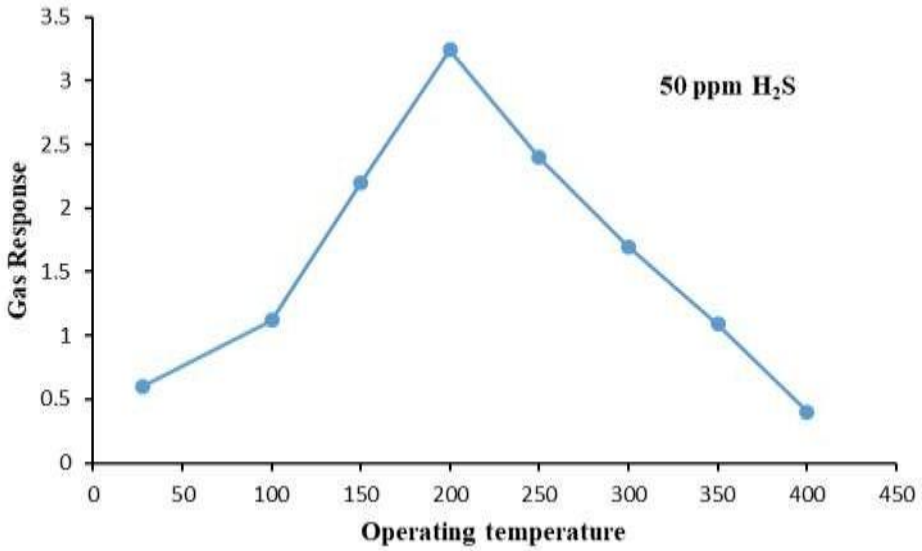

Fig- 3: Temperature dependence of gas response for Co-modified $SmFeO_3$ thick film towards 50 ppm H_2S.

Gas response of Co-modified $SmFeO_3$ thick film towards 50 ppm H_2S gas is measured at different operating temperatures from room temperature to 400^0C. The temperature dependence of H_2S gas response of Co- modified $SmFeO_3$ thick film is shown in Fig. 3.

Fig. 3 shows that initially, response towards 50 ppm H_2S increases with increase in operating temperature. At 200^0C, maximum response (3.24) is obtained. But later on response decreases with further increase in temperature. Thus, Co-modified $SmFeO_3$ thick film has optimal operating temperature 200^0C at which its response towards 50 ppm H_2S gas becomes 3.24. This type of temperature dependence of gas response and gas sensing mechanism can be explained as follows.

The gas response is related to the adsorption of oxygen species in air and surface reactions of target gas

molecules with adsorbed oxygen. In ambient air, oxygen species from air are adsorbed on oxygen deficient surface of $SmFeO_3$ sensor. These adsorbed oxygen species extract electrons from bulk $SmFeO_3$ due to their strong electron affinity and highly reactive atomic or molecular species O_2^-, $2O^-$ and O^{2-} depending on temperature are
obtained [15]. Therefore, hole-accumulation layer is formed near the surface and sensor resistance decreases. When H_2S gas is introduced in chamber, surface reactions occur between H_2S gas molecules and the active oxygen species resulting in the decomposition of H_2S gas molecules along with emission of electrons. In Co-modified $SmFeO_3$ based sensor, Co^{2+} ion can also extract electron during electron transfer. Therefore, Co misfits also act as oxygen deficiency to adsorb oxygen from air.
At lower operating temperature, rate of surface reaction is low because H_2S gas molecules do not have sufficient thermal energy to react with oxygen species and hence sensor response is low. At 200^0C, the rate of surface reaction is high so that maximum number of H_2S gas molecules interact with maximum oxygen species and hence sensor response becomes maximum. But if temperature is further increased, gas diffusion near the surface decreases and sensor response decreases. The surface reaction of H_2S gas with adsorbed oxygen species can be expressed as [17]

$$H_2S_{(g)} + 2O^-_{(ads)} \rightarrow H_{2(g)} + SO_{2(g)} + 2e^- \quad (1)$$

4. CONCLUSIONS

Pure $SmFeO_3$ thick films are modified by dipping technique and characterized by FE-SEM and EDAX techniques. As fabricated Co-modified $SmFeO_3$ thick films showed maximum response (3.24) towards 50 ppm H_2S gas at 200^0C. Thus Co-modified $SmFeO_3$ thick film can be a potential candidate for H_2S gas sensor. It would be interesting to investigate selectivity, stability and response-recovery time of Co-modified $SmFeO_3$ thick film.

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6. REFERENCES

[1]. X. Han, Y. Sun, Z. Feng, G. Zang, Z. Chen, J. Zhan, Au-deposited porous single –crystalline ZnO nanoplates for gas sensing detection of total volatile organic compounds, RSC Adv. 6 (2016) 37750–37756.
[2]. R. B. Pedhekar, F. C. Raghuwanshi, V. D. Kapse, Low Temperature H_2S Gas Sensor Based on Fe_2O_3 Modified ZnO-TiO_2 Thick Film, International Journal of material Science and Engineering, 3 (2015) 219-230.
[3]. T. Li, W. Zeng, Z. Wang, Quasi-one-dimensional metal-oxide-based heterostructural gas-sensing materials: A review, Sensors and Actuators B: Chemical, 221 (2015) 1570–1585.
[4]. P. Hao, G. Qu, P. Song , Z. Yang, and Q Wang, Synthesis of Ba-doped porous $LaFeO_3$ microspheres with perovskite structure for rapid detection of ethanol gas, Rare Materials, 40 (2021) 1651–1661.
[5]. L Wu, X Shi, H Du, Ce-doped $LaCoO_3$ film as a promising gas sensor for ethanol, AIP Advances, 11 (2021) 055305.
[6]. J Xiang, X Chen, X. Zhang, L Gong, Y Zhang, K Zhang, Preparation and characterization of Ba-doped LaFeO3 nanofibers by electrospinning and their ethanol sensing properties, Material Chemistry Physics, 213 (2018) 122–129.
[7]. Y. Zhang, H. Zou, J. Peng, Z. Duan, M. Ma, X. Xin, X. Zheng, Enhanced humidity sensing properties of $SmFeO_3$-modified MoS_2 nanocomposites based on the synergistic effect, Sensors and Actuators B: Chemical, 272 (2018) 459-467.
[8]. Hao-Tian and Huang, NO_2 sensing properties of $SmFeO_3$ porous hollow microspheres, Sensors and Actuators B: Chemical, 265 (2018) 443-451.
[9]. M. Mori, A. Noguchi and Y. Itagaki, VOC Detection by p-Type Semiconducting Sensors Using Nano-Sized $SmFeO_3$ particles, Sensors, 22 (2022) 5616.
[10]. Y. Itagaki, M. Mori, Y. Hosoya, O3 and No3 sensing properties of $SmFe_{1-x}Co_xO_3$ perovskite oxides, Sensors and Actuators B: Chemical, 122 (2007) 315-320.
[11]. M. Zhao, H. Peng, J. Hu, Z. Han, Effect of cobalt doping on the microstructure, electrical and ethanol-sensing properties of $SmFe_{1-x}Co_xO_3$, Sensors and Actuators B: Chemical, 129 (2008) 953–957.
[12]. R. B. Mankar, V. D. Kapse, Fabrication and characterization of Ce modified $SmFeO_3$ thick film,

Aayushi International Interdisciplinary Research Journal, 109 (2022) 367-369.
[13]. S. M. Bukhari, J. B. Giorgi, Ni doped $Sm_{0.95}Ce_{0.05}FeO_3$ perovskite based sensors for hydrogen detection, Sensors and Actuators B 181 (2013) 153-158.
[14]. C. R. Michel, E. Delgado, G. Santilan, A.H. Martinez, A Chavez, An alternative gas sensor material : Synthesis and electrical characterization of $SmCoO_3$, Material Research Bulletin, 42 (2007) 84-93.
[15]. R. B. Mankar, V. D. Kapse, D. R. Patil, Gas sensing properties of pure and Co-modified nanocrystalline $SmFeO_3$ thick film, Asian Journal Of Chemistry, 35 (2023) 1485-1490.
[16]. R. B. Mankar, V. D. Kapse, Gas sensing properties of Co surface modified thick film Conference Proceeding, National Conference on Recent Advancement in Science and Technology 2 (2024) 172-175.
[17]. P. S. Shewale, V. B. Patil, H_2S gas sensing properties of nanocrystalline Cu-doped ZnO thin films prepared by advanced spray pyrolysis, Sensors and Actuators B: Chemical, 186 (2013)226-234.