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Ammonia Gas Sensing Properties of Surface Modified $SmFeO_3$

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Abstract:

In this paper, thick films of nanocrystalline $SmFeO_3$ perovskite oxide are surface modified with cobalt. Surface modification involves dipping of $SmFeO_3$ thick films into 0.1 M aqueous solution of cobalt chloride for 1 min and firing in Muffle furnace at 5000C for 30 min. Dispersion of Co^{2+} ions on $SmFeO_3$ surface is confirmed from the EDS analysis. The FE-SEM analysis of the film revealed its porous nature and the formation of $SmFeO_3$ grains. Ammonia gas sensing properties of pure and Co surface modified $SmFeO_3$ thick film are investigated at 50 ppm concentration of ammonia gas. The investigations depict that Co surface modified SmFeO3 thick film has highest gas response of 6.35 at optimal operating temperature 200^0C. The ammonia gas response may be attributed to enhanced oxygen adsorption due to the cobalt contents dispersed on the surface of Co modified $SmFeO_3$ film. Response and recovery time recorded for the sensor towards 50 ppm ammonia at 200^0C are 16 s and 28 s respectively. Moreover, as-prepared Co surface modified $SmFeO_3$ sensor showed good stability and selectivity against LPG, CO_2, H_2, Cl_2, and H_2S. The ammonia gas sensing mechanism Co modified $SmFeO_3$ is discussed briefly.

Keywords: Surface modification, perovskite, dipping method, selectivity, $SmFeO_3$.

1. Introduction

In the last few decades, properties of perovskite-type oxides with general formula ABO_3 have been continuously investigated. They have shown excellent tunable physical and chemical properties. Therefore they have been employed in various fields including solid state gas sensors [1-2]. Some of the ABO_3 type rare earth orthoferrites such as $LaFeO_3$ and $SmFeO_3$ have been reported for their excellent gas sensing performance towards oxidizing and reducing gases [3-6]. $SmFeO_3$ is one of the potential p-type rare earth orthoferrite that has been extensively reviewed for the detection of oxidizing gases [7-9]. The advantageous of $SmFeO_3$ are p-type electrical conductivity, oxygen-ion mobility and high catalytic activity towards oxidizing gases. $SmFeO_3$ can be modified effectively by doping at A or B sites. This modification can produce structural defects in $SmFeO_3$ and therefore gas sensing properties are strongly affected. Modification of $SmFeO_3$ with Co, Ce, Ni and Mg has been reported by many researchers. S. M. Bukhari and others studied the effect of Ce, Ni doping on the gas sensing properties of $SmFeO_3$ and concluded that doped $SmFeO_3$ exhibited improved gas response [10-11]. H. Zhang and others prepared $SmFe_{0.9}Mg_{0.1}O_3$ by sol gel method and obtained excellent response towards 0.5 ppm acetone vapour [12]. Enhanced ethanol sensing properties of $SmFe_{0.7}Co_{0.3}O_3$ were also reported by Ma Zhao [13]. In our earlier paper, we have also presented the gas sensing properties of Co-doped $SmFeO_3$ perovskite oxide and observed that excessive Co doping may lead to decrease in stability of sensor in reducing environment [14]. Co is reducible dopants because Co-O bond is weaker than Fe-O bond. Therefore controlled addition of Co to pure $SmFeO_3$ is suggested for increasing electrical conductivity and gas response. Co can be added to either by doping or dipping techniques, although volume doping is frequently reported. Ammonia is toxic, corrosive and hence its detection at low ppm becomes essential. Many applications including medical diagnosis, animal housing, leak-detection in air conditioning systems requires monitoring of ammonia gas [15].

In this paper, ammonia gas sensing performance of screen printed Co surface modified $SmFeO_3$ thick film is studied.

2. Experimental

Preparation of nanocrystalline $SmFeO_3$ powder by sol-gel method and the formulation of its thixotropic paste follow the procedure described in our previous publications [14,16]. $SmFeO_3$ films are prepared by screen printing the paste on the glass substrate. For surface modification, $SmFeO_3$ films are dipped to 0.1 M aqueous cobalt chloride solution for 1 min and fired for 30 min at 550^0C before applying for further investigations. The films so prepared are named as “Co surface modified $SmFeO_3$ thick film”.

PW 3071 powder diffractometer was used to obtain X-Ray Diffraction pattern of pure $SmFeO_3$ powder. The morphological analysis of the films is carried out by Field Effect Scanning Electron Microscope (JSM- 7610F, JEOL Japan) operated at 15 kV. The elemental analysis of the films is carried out by the Energy Dispersive Spectrometer (EDS) integrated to FE-SEM.

The gas sensing properties of Co surface modified $SmFeO_3$ thick film are studied in static gas sensing set-up. The resistance of thick film is measured in air and then in presence of fixed concentration (50 ppm) of target gas by varying the operating temperature from room temperature to 4000C. The target gases used in the investigations are liquid petroleum gas (LPG), carbon dioxide (CO_2), ammonia (NH_3), hydrogen (H_2), chlorine (Cl_2) and hydrogen sulfide (H_2S) gas.

3. Results and Discussion

3.1 XRD study

XRD pattern of SmFeO3 powder is presented in our earlier publication confirming that SmFeO3 powder has perovskite phase with orthorhombic symmetry and Pnma space group [14]. The average crystallite size calculated using Scherrer’s formula is 50.08 nm.

3.2 FESEM study

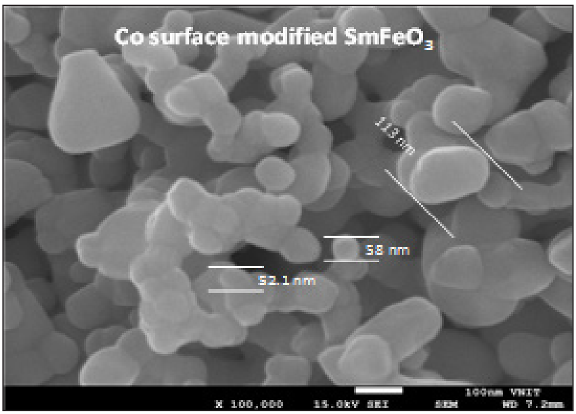

Fig. 1: FE-SEM image of Co surface modified $SmFeO_3$ thick film.

Fig. 1 is the FE-SEM image of Co surface modified $SmFeO_3$ thick film. Presence of large numbers of $SmFeO_3$ grains concludes 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 EDS micrograph. Therefore this film favors the adsorption and desorption processes in gas sensing mechanism.

3.3 EDS study

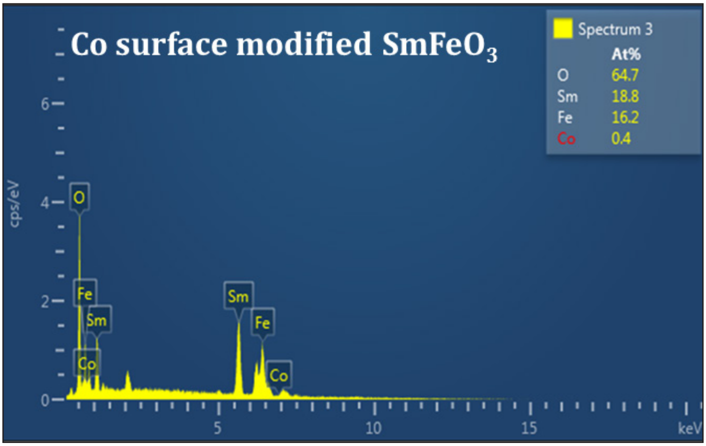

Fig. 2: EDS image of Co surface modified $SmFeO_3$ thick film.

Fig. 2 is the EDS image of Co surface modified $SmFeO_3$ thick film. It indicates the presence of Sm, Fe, O and Co on the film. Absence of any other element in the EDS image represents the purity of sample.

3.4 Gas sensing properties

Generally, gas response, optimal operating temperature, response-recovery time, selectivity and stability determine the performance of gas sensor. 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].

Gas response of Co surface modified $SmFeO_3$ thick film is measured towards 50 ppm NH_3 gas at different operating temperatures from room temperature to 400^0C. The temperature dependence of NH_3 gas response of Co surface modified $SmFeO_3$ thick film is depicted in Fig. 3.

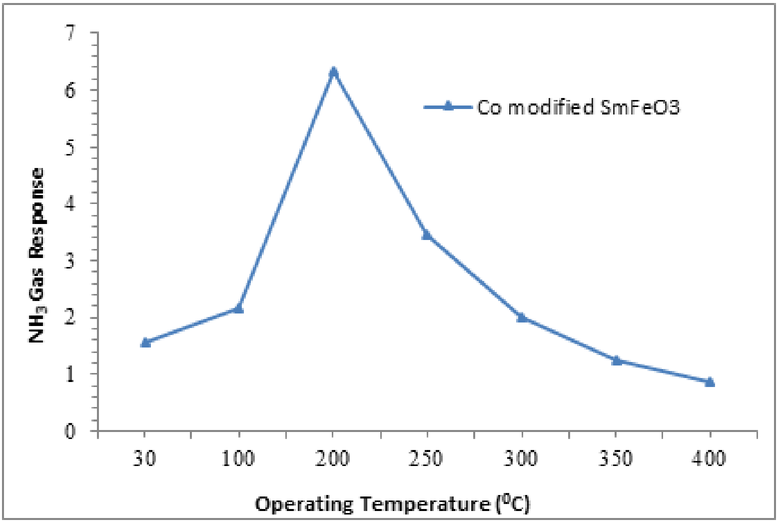

Fig. 3: Temperature dependence of gas response for Co surface modified $SmFeO_3$ thick film towards 50 ppm NH_3.

Fig. 3 shows that the highest response 6.35 for the sensor towards 50 ppm NH_3 is obtained at 200^0C. The gas response initially increases with the increasing operating temperature, becomes highest at 200^0C and finally decreases with the further increase in operating temperature. The gas response is related to the adsorption of oxygen species in air and surface reactions of NH_3 gas molecules with adsorbed oxygen. In Co surface modified $SmFeO_3$ thick film, Co misfits additionally provide active sites for the adsorption of oxygen and therefore gas response is higher as compared to $SmFeO_3$ thick film [13]. Adsorption rate increases with temperature and hence gas response increases. But above optimal operating temperature, although adsorption is more, amount of NH_3 gas molecules reacting with chemisorbed oxygen is less. Therefore decrease in gas response above optimal operating temperature is observed.

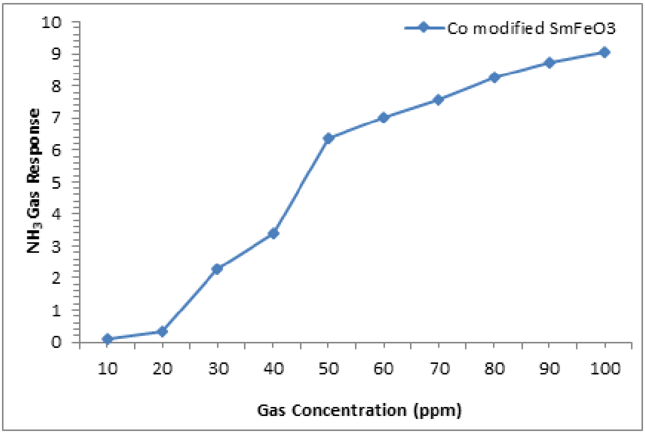

Fig. 4. Represents NH_3 gas response of Co surface modified $SmFeO_3$ thick film as a function of NH_3 gas concentration at 200^0C.

Fig. 4: Variation of NH_3 gas response for Co surface modified $SmFeO_3$ thick film with gas concentration at 200^0C.

The results showed that, below 20 ppm (cut off region), gas response of sensor is almost negligible due to extremely small change in resistance. Thereafter, linear increase in gas response was recorded. Up to 50 ppm, rate of increase in NH_3 gas response is high and then decreases. Here, the optimum NH_3 gas molecules are exposed on the sensor surface forming a monolayer on the film surface. They may react with maximum number active surface states on the film surface and hence gas response increases.

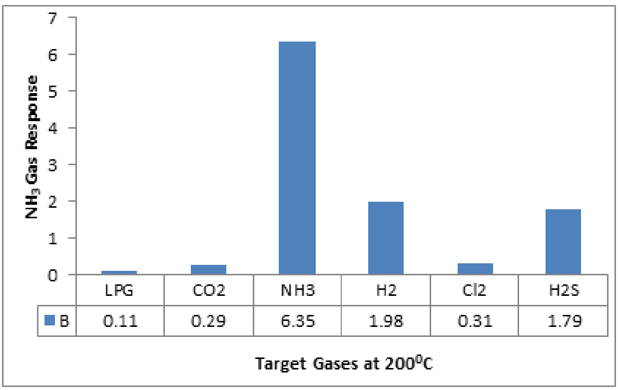

Fig. 5: Selectivity of Co surface modified $SmFeO_3$ thick film at 200^0C.

Selectivity of sensor is its ability to respond to a certain gas in the presence of other gases. Fig. 5 shows the bar diagram representing the gas response of Co surface modified $SmFeO_3$ sensor at 200^0C towards LPG, NH_3, CO_2, H_2, Cl_2 and H_2S gases. It is clear from Fig. 5 that, response to 50 ppm NH_3 gas at 200^0C is higher than those to LPG, CO_2, H_2, Cl_2 and H_2S gases even at higher gas concentrations (100 ppm). This indicates that Co surface modified $SmFeO_3$ sensor at 200^0C is selective to NH_3 gas.

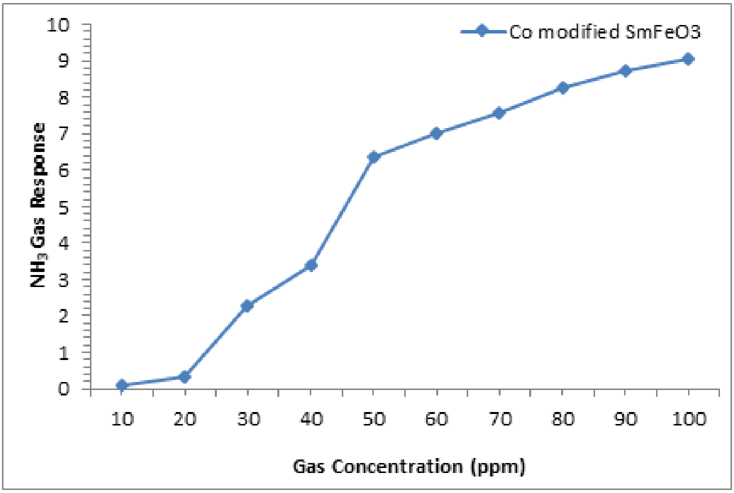

Fig. 6. depicts response-recovery profile of Co surface modified $SmFeO_3$ thick film towards 50 ppm NH_3 gas at 200^0C.

Response time and recovery time are 16 s and 28 s respectively. Fast response was ascribed to faster oxidation of NH_3 gas.

Fig. 6: Response-recovery profile of Co surface modified $SmFeO_3$ thick film towards 50 ppm NH_3 gas at 200^0C.

To study the stability of Co surface modified $SmFeO_3$ sensor, its response to 50 ppm ammonia at 200^0C is continuously measured for 60 days. The results graphically illustrated in Fig. 7, showed that Co surface modified $SmFeO_3$ sensor has good stability and durability.

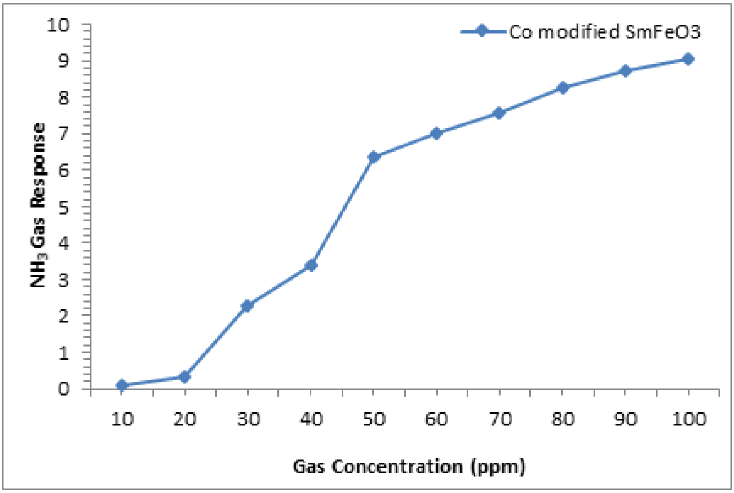

Fig. 7: Stability of Co surface modified $SmFeO_3$ thick film towards 50 ppm NH_3 gas at 200^0C

3.4 Ammonia gas sensing mechanism

Holes are the majority charge carriers in $SmFeO_3$. Oxygen species from air are adsorbed on the surface of $SmFeO_3$ sensor. These adsorbed oxygen species extract electrons from conduction band of $SmFeO_3$ as a result of which concentration of holes increases and sensor resistance decreases. During this adsorption, oxygen species becomes O_2^-,+ $2O^-$ and O^{2-} depending on the temperature.

$$0_{2(\text{air})} \xrightarrow{\text{upto } 150^0\text{C}} 0_2^- \xrightarrow{\text{upto } 450^0\text{C}} 20^- \xrightarrow{\text{above } 450^0\text{C}} 0^{2-} \quad (1)$$

When ammonia gas is introduced in chamber, the gas molecules interact with active species at the surface of sensor. During this desorption, ammonia gas molecules are decomposed to corresponding atoms and the extracted electrons are liberated [15].

$$2NH_3 + O^-_{(ads)} + O_2 \rightarrow 2NO_2 + 3H_2O \quad + \quad 5e^- \qquad (2)$$

As a result, concentration of holes decreases and sensor resistance increases. The difference between these two resistances produces gas response. In Co surface modified $SmFeO_3$, Co misfits also extract electron and become active species for adsorption of ammonia gas molecules. Therefore, Co surface modified $SmFeO_3$ exhibited enhanced gas sensing properties.

4. Conclusions

In summary, Co surface modified SmFeO3 thick films are prepared by simple dipping technique. The experimental investigations suggest the porosity of film and good dispersion of Co species. As prepared Co surface modified $SmFeO_3$ sensor is selective to NH_3 gas and exhibited highest gas response 6.35 at optimal operating temperature 200^0C. Moreover, sensor has good stability and response-recovery characteristics as compared to pure $SmFeO_3$ sensor.

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