

Gas Sensing Properties of Pure and Co Surface Modified Nanocrystalline SmFeO₃ Thick Films

RAJENDRA B. MANKAR^{1,*}, VIVEK D. KAPSE² and D.R. PATIL³

¹Department of Physics, Smt. Radhabai Sarda Arts, Commerce and Science College, Anjangaon Surji-444705, India

²Department of Physics, Arts, Science and Commerce College, Chikhaldara-444807, India

³Bulk and Nanomaterials Research Laboratory, Department of Physics, R.L. College, Parola-425111, India

*Corresponding author: E-mail: rbmankar@gmail.com

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In present work, nanocrystalline SmFeO₃ perovskite oxide powder was prepared by sol-gel method. Thick films of SmFeO₃ were fabricated onto a glass substrate by screen printing technique and heated at 500 °C for 30 min. As-prepared pure nanocrystalline SmFeO₃ thick films were dipped into 0.1 M aqueous solution of cobalt chloride for different intervals of time. Microstructure and surface morphology of both pure and Co surface modified SmFeO₃ thick films were investigated by energy dispersive X-ray analysis (EDAX) and field effect scanning electron microscopy (FE-SEM) techniques. The FE-SEM micrograph reveals the porous nature of thick films. EDAX analysis showed that both pure and Co modified thick films are oxygen deficient. Gas sensing performance of these films was tested for different gases. The highest response and selectivity was recorded to 50 ppm NH₃ gas at 200 °C for SmFeO₃ thick film dipped into cobalt chloride solution for 3 min. The effect of cobalt doping and its dipping time on microstructure, surface morphology and gas sensing properties of pure SmFeO₃ thick film was discussed.

Keywords: SmFeO₃, Surface modification, Perovskite, Gas sensor.

INTRODUCTION

Recently, perovskites of type ABO₃ (A: rare earth, B: transition metal) have attracted a great deal of attention due to their variable chemical and physical properties. They have wide range of applications including solid oxide fuel cell [1], catalysis [2], photoluminescence [3] and gas sensors [4-7]. Their properties such as ionic and electronic conductivity, chemical stability can be tuned for particular application by partial substitution at A-site and/or the B-site. SmFeO₃ is one of the rare earth orthoferrite extensively studied as chemical gas sensor material. Its conductivity increases with exposure to oxidizing gases and decreases with the exposure to reducing gases. Due to p-type semiconductivity, SmFeO₃ have been typically studied for detection of oxidizing gases such as ozone, oxygen and NO₂ [8-11]. But under reducing conditions, SmFeO₃ was reported to be chemically unstable due to phase separation of Sm₂O₃ and Fe₂O₃ [12]. Further, at low temperature very poor response was recorded for these sensors under both oxidizing and reducing conditions due to their very low electrical conductivity.

Ammonia is colourless gas and easily reacts with water to form ammonium hydroxide which is highly irritating. Common sources of ammonia are refrigerant gas, pesticides, explosives, dyes, *etc.* Hence most of the people are exposed to ammonia. From breathing, swallowing or skin contact, ammonia enters into human body and reacts with water to form ammonium hydroxide which is very corrosive and damage body cells [13]. Therefore detection of ammonia is essential. In present work, a pure SmFeO₃ based gas sensor is fabricated to test its performance for the detection of ammonia. The sensor responds to ammonia gas but showed poor sensitivity at small temperature due to low electrical conductivity. Therefore, it is evident that to use SmFeO₃ based gas sensor for the detection of reducing gases like ammonia, there is a need to improve its electrical conductivity.

Generally conductivity is related to the oxygen vacancies presents on the surface. Formation of oxygen vacancies increases by increasing temperature and by incorporating additives [14]. But high working temperature has adverse effect on the stability of a sensor. Therefore, incorporating additives to base material

can be effective and also practical way. Incorporation of additives to base material can be achieved either by doping or dipping method. Cobalt, being reducible element, is expected to induce more oxygen vacancies in SmFeO_3 . Co doped SmFeO_3 has been reported for its improved electrical conductivity especially to ozone and NO_2 [15]. However, for reducing gases, issue of chemical stability may arise because Co-O bond is weaker than Fe-O bond. Furthermore, high specific surface area and small crystallite size are essential requirements since they directly affect the gas sensing properties. Number of techniques like co-precipitation method, sol-gel method and hydrothermal method have been adopted to increase the specific surface area and to decrease crystallite size [16,17]. Among these methods, sol-gel method is simple, low cost synthesis route that requires lower calcination temperature to obtain single phase perovskite.

In this work, Co surface modification of as-prepared pure SmFeO_3 thick films was achieved by dipping technique. The Co surface modified SmFeO_3 based sensors were examined as ammonia sensor.

EXPERIMENTAL

Powder preparation: In present study, as-synthesized SmFeO_3 powder was prepared by sol-gel method. Stoichiometric high purity powders of samarium nitrate [$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$], iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and citric acid monohydrate were mixed in the ratio 1:1:1. The mixture was grounded in agate mortar for 30 min. The mixture was then dissolved in ethylene glycol solution under constant stirring at 75 °C for 2 h. This yields a sole which was then dried into a gel. The gel was dried in oven at 110 °C for 12 h and finally calcined at 800 °C for 4 h to form SmFeO_3 powder.

Thick film preparation: SmFeO_3 powder was screen printed on a glass substrate in the desired pattern using the procedure reported elsewhere [18,19]. The fine powder of SmFeO_3 is thoroughly mixed with a solution of ethyl cellulose (temporary binder) in a mixture of organic solvents such as α -terpineol, 2-butoxy ethanol and 2-butoxyethyl acetate. The ratio of inorganic to organic part was kept at 75:25. To obtain thick coherent paste with proper viscosity, the mixture was continuously grinded in the mortar and pestle. The as-prepared thixotropic paste was then screen printed on glass substrate in desire pattern manually by using squeegee. These thick films were allowed to dry in air and then fired at 500 °C for 30 min in muffle furnace to remove binder and other temporary ingredients.

Surface modification of thick films: As-prepared thick films were dipped into 0.1 M aqueous solution of cobalt chloride for 1, 3 and 5 min. After drying, these films were heating at 550 °C for 30 min. These surface modified films were termed as Co-modified films.

Characterization: To determine crystal structure, crystallite size and lattice parameters, X-ray diffraction analysis was carried out by PW 3050 diffractometer using $\text{CuK}\alpha$ radiation of wavelength of 1.54 Å. The scans were recorded in the range $2\theta = 10^\circ$ to 99° at a scan rate of 0.02 °/s. Crystalline phase was determined by using powder diffraction file database (JCPDS card no. 39-1490). To study the surface morphology and elemental analysis of samples, FE-SEM images and EDS spectra of samples

were recorded by JSM-7610F, JEOL Japan, operated at 15 kV unit.

Gas sensing measurements: Gas sensing tests were carried out using static gas sensing set up. As-prepared SmFeO_3 thick films with ohmic contacts are the sensor elements. Sensing element was directly kept on a heater in gas chamber and exposed to different gases. By using sensitive digital multimeter, electrical resistance of sensor element was measured before and after its exposure to test gas at different operating temperatures and different concentrations of test gas.

RESULTS AND DISCUSSION

Structural properties: The X-ray diffraction pattern of as-prepared SmFeO_3 powder sample is shown in Fig. 1. Crystal structure of as-synthesized nanocrystalline SmFeO_3 powder has been discussed in our earlier publication [20]. The observed peaks in XRD pattern were consistent with the standard JCPDS card no. 39-1490 indicating the perovskite phase with orthorhombic symmetry and $Pnma$ space group for prepared powder (62). Sharp peaks in XRD pattern suggested crystallinity of the sample. Absence of any impurity peak confirmed the purity of sample. Lattice constants a, b and c were found to be 5.604, 7.704 and 5.397 Å, respectively. The Debye-Scherrer's formula, $D = 0.89\lambda/\beta\cos\theta$; where λ is wavelength X-ray, θ is diffraction angle and β is true half-peak width, was applied to calculate the average crystallite size and estimated as 50.08 nm.

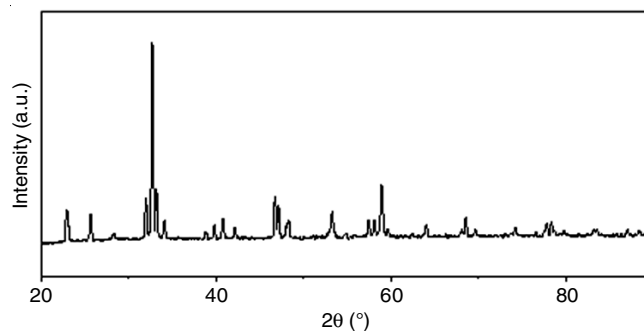


Fig. 1. X-ray diffraction pattern of pure powder SmFeO_3

Morphological study: To investigate surface morphology of fabricated thick films, the FE-SEM technique was employed. Fig. 2 depicts the FE-SEM micrographs of pure and Co-modified nanocrystalline SmFeO_3 thick films prepared at 500 °C for 30 min. The micrograph for pure SmFeO_3 consists of large numbers of grains indicating that film is porous. The grain size was found in the range of 50-70 nm. Particles are irregular in shape with some particles agglomerated containing very fine particles indicating the high porosity. The smaller particles distributed around the larger grains were observed in all three micrographs for Co-modified SmFeO_3 thick films. The smaller particles may be attributed as CoO_2 grains and the modified thick film appears to be comparatively highly porous that favours the adsorption and desorption mechanism.

EDX studies: The quantitative analysis of both pure and Co-modified thick films was carried out using energy dispersive spectrometer and can be seen in Fig. 3. The wt.% of Sm, O, Fe and Co is presented in Table-1. All the samples were observed

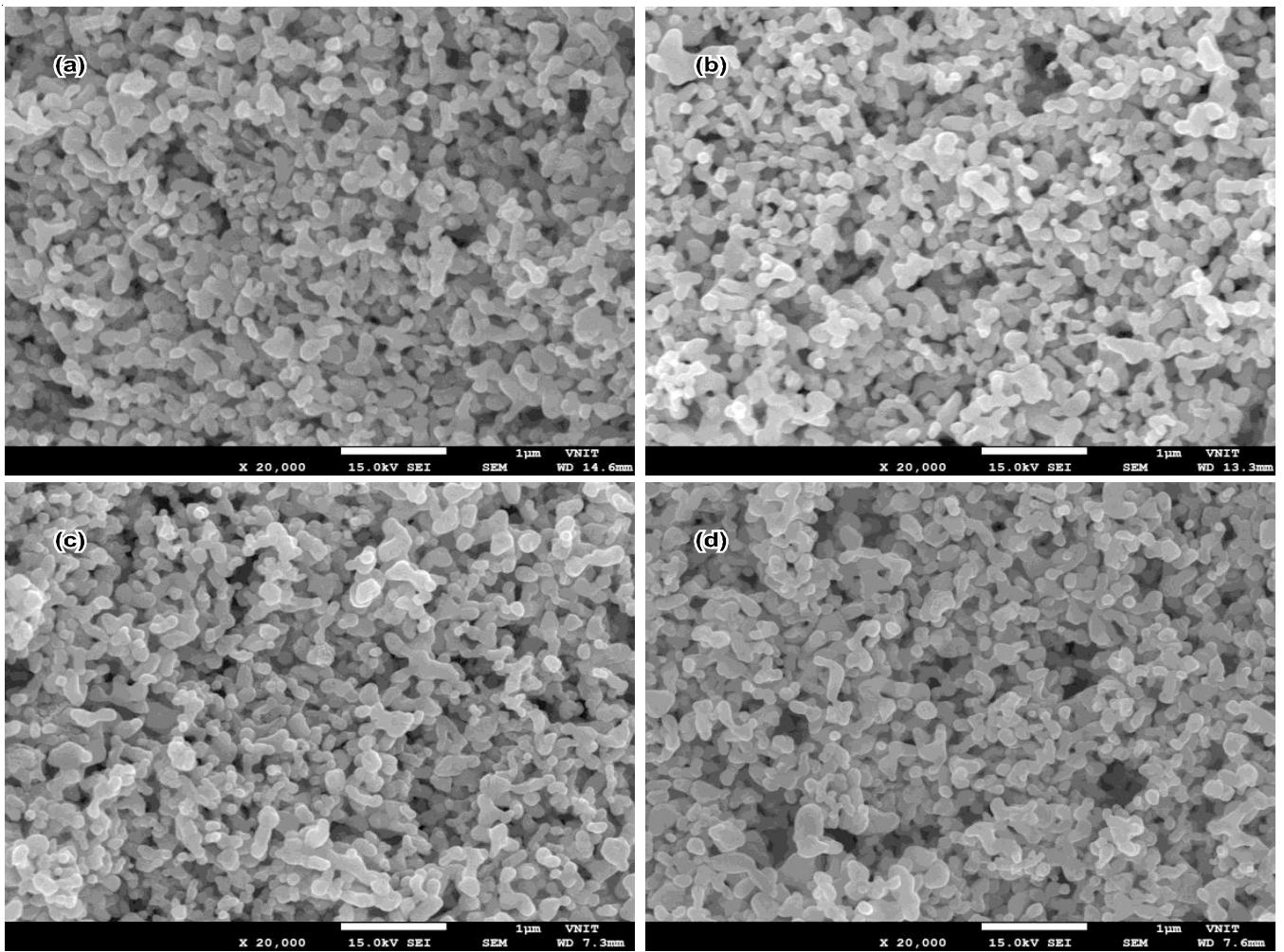


Fig. 2. FE-SEM images of (a) pure SmFeO₃, (b) Co-modified SmFeO₃ (dipped for 1 min), (c) Co-modified SmFeO₃ (dipped for 3 min) and (d) Co-modified SmFeO₃ (dipped for 5 min)

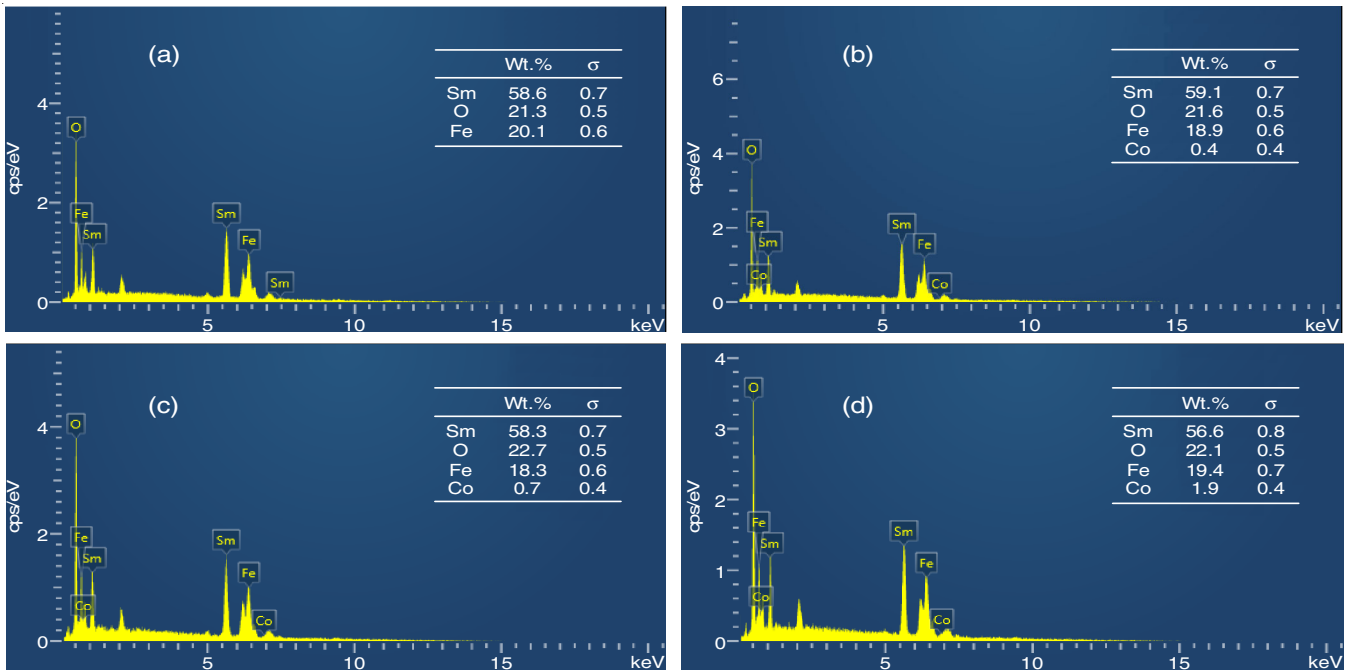


Fig. 3. EDAX images of (a) pure SmFeO₃, (b) Co-modified SmFeO₃ (dipped for 1 min), (c) Co-modified SmFeO₃ (dipped for 3 min) and (d) Co-modified SmFeO₃ (dipped for 5 min)

Material (wt.%)	Dipping time (min)			
	0	1	3	5
Sm	58.6	59.1	58.3	56.6
O	21.3	21.6	22.7	22.1
Fe	20.1	18.9	18.3	19.4
Co	0	0.4	0.7	1.9

to be oxygen deficient, however, the weight percentage of Co increases with dipping time.

Gas sensing properties: Sensitivity is defined as the ratio of change in conductance of the sample on exposure to gas to the original conductance in air [21]. The conductivities of sensor were measured before and after exposure to target gas and sensitivity is determined directly using eqn. 1:

$$S = \frac{G_g - G_a}{G_a} \quad (1)$$

where G_a is conductance in air and G_g is conductance in target gas.

Gas response and operating temperature: Firstly, the sensitivity of pure SmFeO_3 thick film to liquid petroleum gas (LPG), carbon dioxide, ammonia, ethanol, hydrogen, chlorine and hydrogen sulfide was measured at various operating temperatures ranging from 28 to 400 °C. Maximum sensitivity ($S = 2.07$) was recorded to 50 ppm NH_3 gas at 200 °C. Variation of sensitivity to 50 ppm NH_3 gas with the operating temperatures is illustrated in Fig. 4. Sensitivity increases with increasing operating temperature, attains its maximum at 200 °C and then decreases with further increase in operating temperature. Thus, the optimum operating temperature for pure SmFeO_3 sensor to 50 ppm ammonia gas is 200 °C.

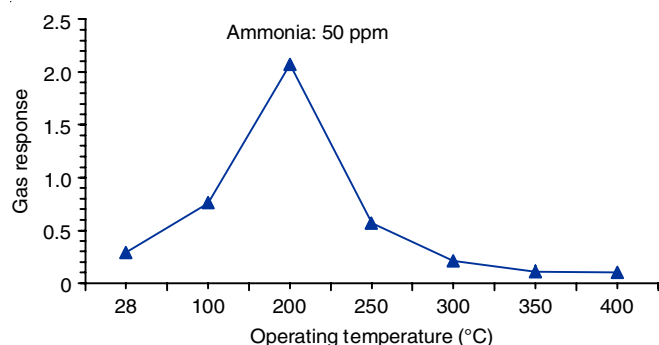


Fig. 4. Variation of sensitivity to 50 ppm ammonia with operating temperature for pure SmFeO_3

Fig. 5 depicts the variation in sensitivity with operating temperature of pure SmFeO_3 thick film and Co-modified SmFeO_3 films (dipping times 1, 3 and 5 min) to 50 ppm NH_3 gas. It has been observed for all samples that sensitivity increases with increasing operating temperature, attains its maximum at 200 °C and then decreases with further increase in operating temperature. It is clear from Fig. 5 that the optimum operating temperature to NH_3 gas is almost same (200 °C) for pure as well as all Co-modified SmFeO_3 films. But pure sample showed weak response ($S = 2.07$) while Co-modified sample (dipping time

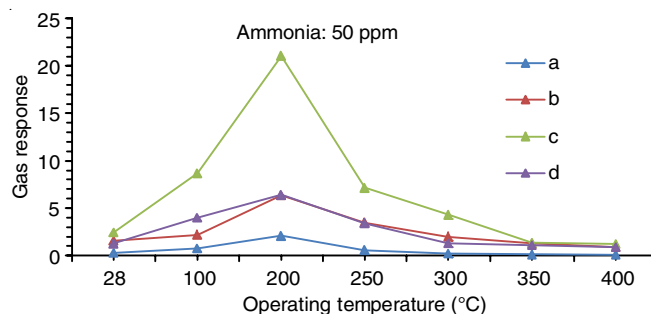


Fig. 5. Variation of sensitivity to 50 ppm ammonia with operating temperature for (a) pure SmFeO_3 , (b) Co-modified SmFeO_3 (dipped for 1 min), (c) Co-modified SmFeO_3 (dipped for 3 min) and (d) Co-modified SmFeO_3 (dipped for 5 min)

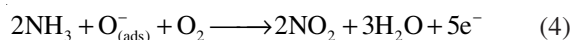
3 min) showed maximum response ($S = 21.07$) to 50 ppm NH_3 gas at 200 °C. Thus, the Co surface modified SmFeO_3 thick film (dipping time 3 min) was observed to be more sensitive than pure SmFeO_3 thick film towards NH_3 .

The sensitivity is related to change in resistance of sensor when exposed to air and target gas. When is exposed to air, oxygen species are adsorbed on the surface by extracting electrons from conduction band due to its strong affinity to oxygen. The possible electron transfer processes are given in eqns. 2 and 3 [22]:



This results in the formation of hole accumulation layer on the surface and resistance of film decreases (base line resistance). Chemisorbed oxygen may exist in molecular form (O_2^-) below 150 °C and in atomic form (O^- or O^{2-}) above 150 °C. After exposure to reducing gas, gas molecules interact with active sites on film surface and trapped electrons are released back to material. As a result, hole accumulation layer becomes thin due to decrease in hole concentration and resistance of sensor increases.

The chemical reaction involved in pure SmFeO_3 thick film sensor to sense NH_3 gas is depicted in eqn. 4 [23]:



NH_3 molecule has lone pair of electron and donates the unpaired electron to metal ion of base material which has unfilled orbit. The coordinated NH_3 molecule then react with adsorbed oxygen and return back the trapped electron to base material thereby increasing sensor resistance.

Oxygen deficiency and defect density that leads to increase chemisorptions are generally responsible for the sensitivity of SmFeO_3 thick film sensor to NH_3 . In the Co-modified samples, cobalt ions exists in mixed-valance state Co^{2+} and Co^{3+} where Co^{2+} deliver one electron during electron transfer [17]. Thus, Co misfits act as oxygen deficiency to improve chemisorptions. This not only decreased base line resistance in air but also increases sensor resistance when exposed to NH_3 .

Gas response and gas concentration: For Co-modified SmFeO_3 thick film (dipping time 3 min), variation of sensitivity with NH_3 gas concentration at optimum temperature of 200 °C can be seen in Fig. 6. Sensor is insensitive to NH_3 gas up to 20

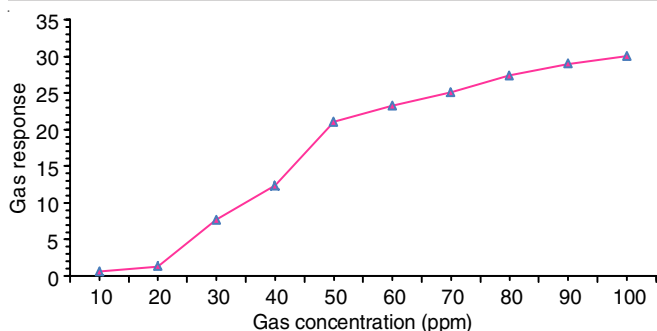


Fig. 6. Variation of ammonia gas response with concentration for Co-modified SmFeO₃ thick film (dipping 3 min)

ppm concentration. This low concentration region between 0 ppm to 20 ppm on characteristics curve is called cut off region. After 20 ppm, nearly linear increase in gas response with concentration was observed up to 50 ppm. This region of characteristics curve is active region of sensor where rate of increase of response is large. Beyond 50 ppm, rise of response is almost steady.

The reason for sensor being insensitive in cut off region is too low gas molecules exposed on the surface so that very low electrons are returned back to the material when exposed to NH₃ gas. But in active region, optimum number of gas molecules exposed on the sensor surface forming a monolayer on the film surface. They may react with maximum number of chemisorbed oxygen species on the film surface thereby enhancing gas response. If gas concentration is increased beyond active region, excess gas molecules will not be able to reach active sites of film and hence response remains saturated.

Gas response and dipping time: Fig. 7 depicts variation of gas response to NH₃ gas for Co-modified SmFeO₃ thick film dipped for different time intervals. The response to NH₃ gas goes on increasing with increasing dipping time and decreases further. The maximum response was recorded for film dipped for 3 min. indicating that the amount of Co (0.7 wt.%) introduced on SmFeO₃ surface would be optimum to improve adsorption mechanism. The highest response may be due to more cobalt misfits available for oxygen to be adsorbed while the decrease in response may be the result of insufficient number of misfits available on the surface [15]. In case of film dipped for 3 min, cobalt misfits would be optimum and would disperse uniformly throughout the complete film surface. This amount would be sufficient to promote the catalytic reaction effectively. As a result initial resistance of film is very small in air. Moreover, final resistance after exposure to ammonia becomes very large. This leads to largest sensitivity to ammonia. On the other hand, for dipping time smaller than optimum, cobalt misfits would be minimum and their dispersion would be poor. Due to this, initial resistance would be comparatively larger and hence response would be smaller. For dipping time larger than optimum, the number of cobalt misfits would be larger. This would mask and prevent gas to reach base material. This amount might not promote the reaction more effectively resulting in comparatively low response.

Selectivity of Co-modified SmFeO₃ thick film: Selectivity of sensor is its ability to respond to a certain gas in the presence of other gases. Fig. 8 shows the bar diagram representing the

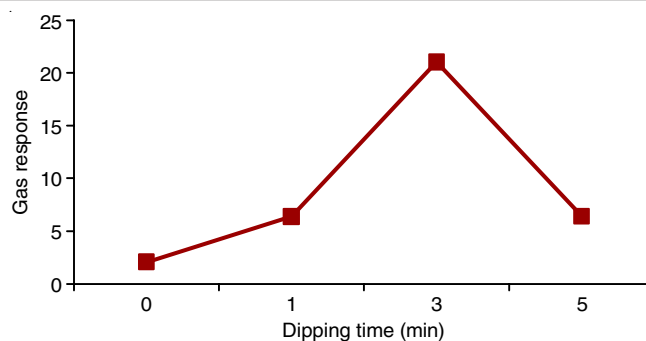


Fig. 7. Variation of gas response with dipping time of film

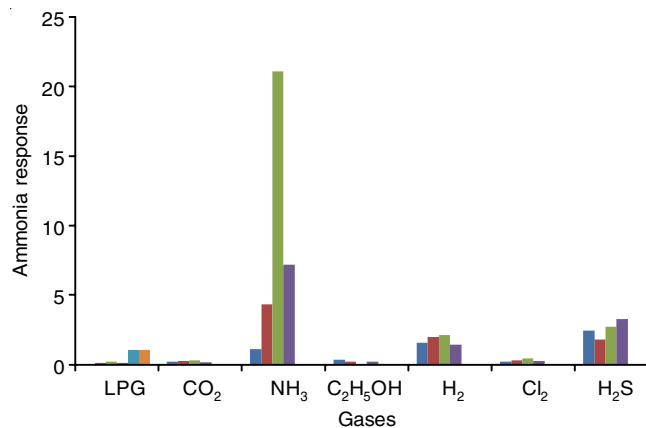


Fig. 8. Selectivity of Co-modified SmFeO₃ sensor (dipping time 3 min) operated at 200 °C

selectivity of Co modified SmFeO₃ sensor (dipping time 3 min) operated at 200 °C to LPG, NH₃, CO₂, C₂H₅OH, H₂, Cl₂ and H₂S gases.

The response to NH₃ gas at 200 °C is 21.07, which is much higher than those to LPG, CO₂, C₂H₅OH, H₂, Cl₂ and H₂S gases which are 0.21, 0.33, 0.03, 2.11, 0.46 and 2.69, respectively. The selectivity β is equal to S_1/S_2 where S_1 and S_2 represent response to NH₃ and other gases, respectively. For present sensor, β is higher than 5, which are generally required. The high selectivity to NH₃ may be attributed to surface modification (cobaltation) of SmFeO₃ films.

Response and recovery time of sensor: Response time is the time required for sensor to attain 80 % of maximum change in resistance on exposure to the target gas. Recovery time is defined as time taken by sensor to get back 80 % of original resistance in air. Fig. 9 depicts the response and recovery profiles of the most sensitive Co-modified thick film dipped for 3 min to 50 ppm NH₃ gas at 200 °C. When NH₃ gas was introduced, resistance of sensor increased and the response time was 15 s. After NH₃ gas was removed, resistance decreased rapidly and the recovery time was 30 s. Thus, Co-modified thick film dipped for 3 min exhibits a good response and recovery property.

Stability of sensor: In order to study the stability of Co-modified thick film dipped for 3 min, its resistance at 200 °C was continuously measured for 90 days. The results are graphically illustrated in Fig. 10. It is concluded that the resistance of sensor was almost stable, henceforth, developed sensor has good stability and durability.

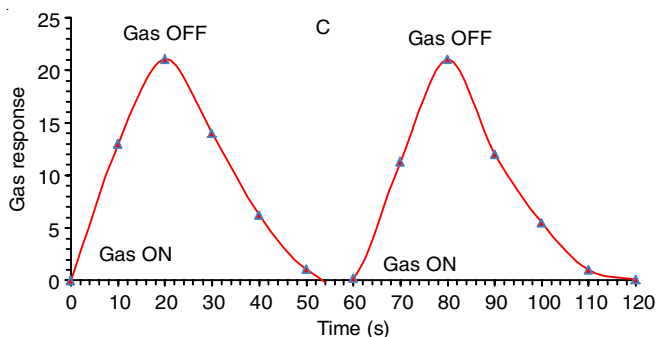


Fig. 9. Response and recovery profiles of Co-modified SmFeO₃ thick film dipped for 3 min

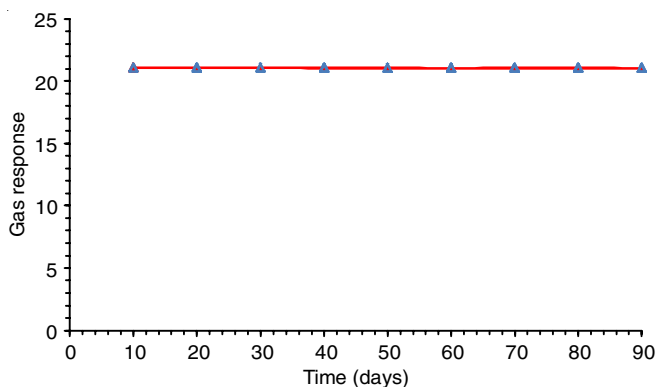


Fig. 10. Stability of Co-modified SmFeO₃ sensor dipped for 3 min

Conclusion

Pure SmFeO₃ thick film showed poor response to NH₃ gas at 200 °C. In order to improve its ammonia gas response, SmFeO₃ thick films were surface modified by dipping them into 0.1 M aqueous solution of cobalt chloride for 1, 3 and 5 min. All the Co-modified SmFeO₃ thick films showed better response to ammonia gas at 200 °C. Among them, Co-modified SmFeO₃ thick film dipped for 3 min has highest sensitivity to NH₃ gas at 200 °C and sensitivity increases with concentration in active region 20 to 50 ppm. Moreover, it was selective to ammonia suppressing the response to LPG, CO₂, C₂H₅OH, H₂, Cl₂ and H₂S gases. Thus surface modification of SmFeO₃ thick film with Co by dipping technique seems to be effective in improving sensing performance to ammonia gas.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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