Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 2(3), 2012, 172-178
ISSN 2277-2669

H_2S GAS SENSING BEHAVIOR OF MODIFIED $LaCoO_3$ THICK FILM

A. V. KADU[*] and S. V. JAGTAP[a]

Department of Chemistry, Prof Ram Meghe College of Engineering and Management, Badnera, AMRAVATI – 444701 (M.S.) INDIA
[a]Department of Physics, Bar. R.D.I.K.N.K.D., Badnera, AMRAVATI – 444701 (M.S.) INDIA

(*Received : 28.02.2012; Revised : 15.03.2012; Accepted : 24.03.2012*)

ABSTRACT

Thick films of pure and various concentrations of $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.1, 0.2, 0.3 & 0.4) were prepared by sol-gel technique. Morphological and structural properties of the samples were obtained using the scanning electron microscopy (SEM) and X-ray diffraction techniques respectively. The H_2S gas sensing properties of these thick films were investigated at different operating temperatures and H_2S gas concentrations. The surface resistance of thick films decreases when exposed to H_2S gas. The $La_{1-x}Sr_xCoO_3$ based sensor with x = 0.3 shows better sensitivity towards H_2S gas at an operating temperature 210^oC. The effect of Sr doping on sensitivity, response time and recovery time of the sensor in the presence of H_2S and other reducing gases were studied and discussed.

Key words: H_2S gas sensor, $La_{1-x}Sr_xCoO_3$, Sensitivity & Selectivity.

INTRODUCTION

Sensors play an important role in the areas of emissions control, environment protection, public safety, and human health. Much more public concern today than ever before over erious environmental issues is further promoting the development of sensors with both high sensitivity and rapid response[1,2]. In addition to in-depth exploration of gas sensing mechanisms. The use of sensors is basically for measurements of physical quantities and for controlling some systems. Today our environment is polluted by number of gases exhausts from auto and chemical industry. In order to detect measure and control the gases one should know the amount and type of gases present in the ambient. Therefore the need to monitor and control these gases has led to the research and development of very large variety of sensors using different materials and technologies.

H_2S is a colourless, toxic, flammable and malodorous gas as sources from gasoline, natural gases, city sewage, volcanic gases and hot springs with smells like rotten eggs. It can also be produced from bacterial breakdown of organic matter or wastes produced by human and animal. Other sources are craft paper mills, tanneries and petroleum refineries. H_2S gas is badly harmful to human body and the environment. Meanwhile the type of oil and natural gas is correlative with the concentration of H_2S. The oil and natural gases mines can be found depending on the concentration of H_2S. Therefore, the detection and monitoring of H_2S are of high importance for both resource exploitation and human health. In the recent

Available online at www.sadgurupublications.com
[*]Author for correspondence; E-mail: ashishkadu26@rediffmail.com

researchers, a number of semiconductor sensors have been found to be sensitive to H_2S including WO_3, In_2O_3, ZnO and a few pervoskite type materials[3-7].

The pervoskite oxides (ABO_3) were used as gas sensor materials for their stability in thermal and chemical atmospheres. Modifications in microstructure, processing parameters and also concentration of acceptor/donor dopant can vary the temperature coefficient of the resistance and conductivity of ABO_3 oxides. Sensors based on ABO_3–type complex oxide material, of rare earth elements have an outstanding merit of its high sensitive and selective characteristics. These characteristics can be controlled by selecting suitable A and B atoms or chemically doping A′ and B′ elements equivalent respectively to A and B into ABO_3 to obtain $A_xA'_{1-x}B_yB'_{1-y}O_3$ compound[8,9].

In the recent years, a number of semiconductor sensors have been found to be suitable for H_2S gas e.g. SnO_2, WO_3, In_2O_3, ZnO_2 and a few perovskite-type materials like $NdFeO_3$ and $NiFeO_4$[10-13]. $LaCrO_3$ based compounds are usually synthesized by the traditional solid state reaction method, urea combustion method[14,15]. Sol–gel approach, as a classical method, has a lot of inherent merits with better homogeneity, higher purity, and lower temperature of preparation. The aim of present work is to prepare nanocrystalline $La_{1-x}Sr_xCoO_3$ thick films by sol-gel route and to investigate their sensing properties for H_2S gas.

EXPERIMENTAL

Material synthesis

The $La_{1-x}Sr_xCoO_3$ (x = 0.0, 0.1, 0.2, 0.3 & 0.4) were synthesized by sol-gel method using ethylene glycol as a solvent. All reagents were of analytical grade were used. Firstly, the analytically pure grade La $(NO_3)_3{\cdot}6H_2O$, Sr $(NO_3)_2.6H_2O$, Co $(NO_3)_3{\cdot}9H_2O$ and citrate acid were weighed and dissolved in ion-free water at 80°C for 3 h. Then ethylene glycol was added under constant stirring to obtain a homogeneous and stable sol. The solution was further heated in pressure vessel at about 130°C for 12 h. The material was then heated in a furnace at 350°C for 3 h. The powder was then calcined at 800°C for 6 h in order to improve the crystallinity of materials.

Characterization of samples

The synthesized samples were characterized by powder XRD using a Siemens D 5000 diffractometer. The XRD data were recorded by using Cu Kα radiation (1.5406 Å). The intensity data were collected over a 2 θ range of 10-70°. The average crystallite size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of all prominent lines. The microstructure of the materials was evaluated by scanning electron microscopy (SEM).

Fabrication and analysis of gas sensors

The prepared powders were mixed with PVA (polyvinyl alcohol) to form paste, and then the paste was coated onto an Al_2O_3 tube on which two platinum wires had been installed at each end. A small Ni–Cr alloy coil was placed through the tube as a heater, which provided operating temperature at 50-350°C. The temperature was controlled by adjusting the heating power. Gas response is defined as the ratio of change in resistance of the sample on exposure to a test gas to the resistance in the presence of air.

$$Sensitivity(S) = \left|\frac{R_a - R_g}{R_a}\right| = \frac{\Delta R}{R_a}, \qquad \ldots(1)$$

where Ra is the resistance in air, Rg the resistance in a sample gas and ΔR the change in resistance. The response of the sensor for H_2S was tested in the presence of other gases so that the selectivity can be determined.

RESULTS AND DISCUSSION

X-ray diffraction study

The XRD patterns of the compositions $LaCoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ prepared by sol-gel method calcined at 800°C are presented in Fig. 1. Fig. 1(a), shows the XRD pattern, which is in good agreement with XRD results previously reported in the literature for $LaCoO_3$[16]. The diffraction data is good agreement with JCPD card of $LaCoO_3$ (JCPDS No. 24-1016). All the diffraction peaks of the phases are indexed as perovskite-type with tetragonal structure. Fig. 1(b), shows the XRD pattern of $La_{0.7}Sr_{0.3}CoO_3$ nanomaterial. Extremely broad reflections are observed indicating nanosized particle nature of the material obtained. The mean crystallite sizes (D) of $La_{0.7}Sr_{0.3}CoO_3$ powder was deduced from half height width of XRD peaks based on the Scherer's equation, $D = 0.9\lambda/\beta cos\theta$, where D is the average size of the particles, λ is wavelength of X-ray radiation, β the full width at half maximum of the diffracted peak and θ is the angle of diffraction[17]. The average particle size of the nanocrystalline $La_{0.7}Sr_{0.3}CoO_3$ according to the scherrer formula was in the range of 30–35 nm.

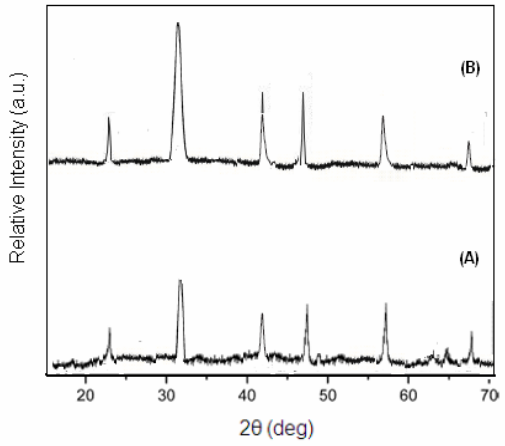

Fig. 1: XRD spectra of (A) $LaCoO_3$ (B) $La_{0.7}Sr_{0.3}CoO_3$ calcined at 800°C

Sem analysis

Fig. 2(a), undoped $LaCoO_3$ sample shows randomly distributed grains with smaller size and large agglomeration of particles are observed. Fig. 2(b), shows the microstructure of a most sensitive sample $La_{0.7}Sr_{0.3}CoO_3$ consisting of giant grains of Sr-species associated with smaller grains of $LaCoO_3$. This shows more porosity, giving largest effective surface area. It gives clear evidence for a porous structure, which together with the small particle size points at the films being excellent for gas sensing applications.

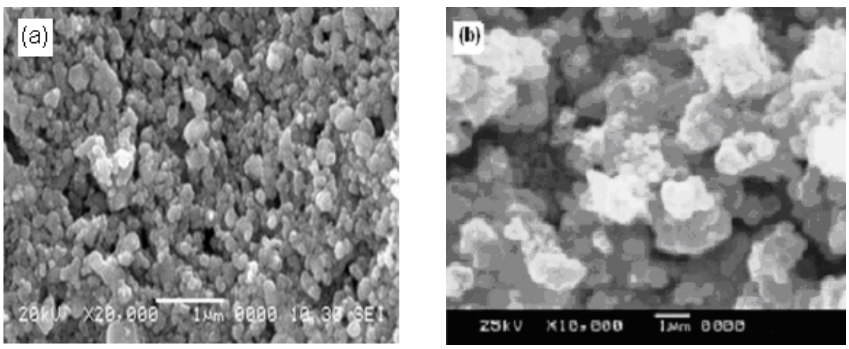

Fig. 2: SEM micrograph of samples (a) $LaCoO_3$ and (b) $La_{0.7}Sr_{0.3}CoO_3$

Gas sensing characteristics

Electrical characterization of samples $La_{1-x}Sr_xCoO_3$ (x = 0.1, 0.2, 0.3 & 0.4) synthesized by sol-gel method and calcinied at 800°C has been carried out in a gas test chamber. The resistance of the films decreased upon exposure to H_2S gas. Fig. 3 shows gas sensing response of H_2S gas, at different operating temperatures (50-400°C) for thick films of pure $LaCoO_3$. The enhanced sensitivity with increasing the temperature can be attributed to two facts. On one hand, the thermal energy obtained is high enough to overcome the activation energy barrier of the surface reaction; on the other hand, the adsorbed oxygen species convert from O_2^- to O^- at elevated temperatures, and thus an increase in electron concentration results from the sensing reaction of a test gas and O^-[18].

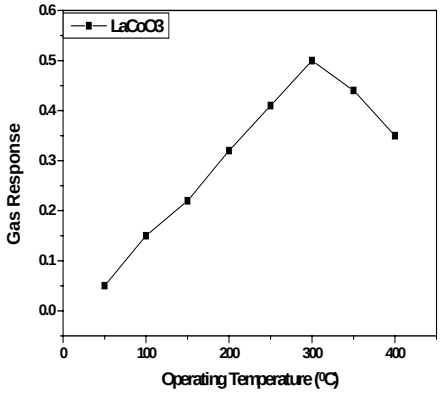

Fig. 3: H_2S gas response vs operating temperatures for $LaCoO_3$ calcined at 800°C

Thus, the pure $LaCoO_3$ shows response towards H_2S gas at high operating temperature 300°C, which is rather high and practically inconvenient in view of commercial standards. Therefore, efforts were made to modify the $LaCoO_3$ based sensors by doping with Sr, so as to be operated at lower operating temperatures with high sensitivity and selectivity. Fig. 4 shows gas sensing response of H_2S gas, for thick films of pure $LaCoO_3$ doped with different concentrations of Sr. From the figure it is clear that the response values of every doped sample apparently increased with increasing the operating temperature.

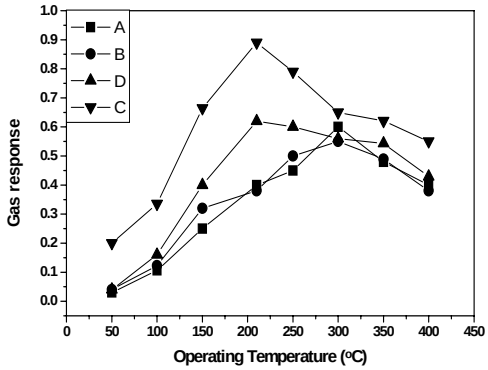

Fig. 4: H_2S gas response Vs operating temperatures for (A) $La_{0.9}Sr_{0.1}CoO_3$, (B) $La_{0.8}Sr_{0.2}CoO_3$, (C) $La_{0.7}Sr_{0.3}CoO_3$ & (D) $La_{0.6}Sr_{0.4}CoO_3$ calcined at 800°C

In this figure, it is observed that the $La_{0.7}Sr_{0.3}CoO_3$ thick film had the largest sensing response at an operating temperature 210°C. It is indicating that Sr doping can greatly improve the sensitivity of $LaCoO_3$

based sensor towards H_2S gas. We know that the semiconductor oxide gas sensors can detect different gases by changing the conductivity of their surface due to the reaction of the reducing gases with adsorbed oxygen. Sr doping in $LaCoO_3$ promotes the deviation from stoichiometry and enhances the surface defect. A large surface defect concentration creates more active surface states for adsorbed oxygen[19,20].

Selectivity is the ability that a gas sensor to distinguishes between different kinds of gases. Fig. 5 shows the cross sensitivity of $La_{0.7}Sr_{0.3}CoO_3$ for NH_3, LPG and H_2 gases as a function of operating temperature. It is evident from the figure that the $La_{0.7}Sr_{0.3}CoO_3$ sensor was highly selectivity to H_2S gas against NH_3, LPG and H_2 gases. The sensor shows high degree of selectivity towards H_2S gas than other reducing gases.

Fig. 6 depicts the variation of sensitivity of $La_{0.7}Sr_{0.3}CoO_3$ sample with H_2S gas concentrations at 210°C temperature. It is clear from the figure that the gas response goes on increasing linearly with gas concentration up to 200 ppm and saturated beyond it. The rate of increase in gas response was relatively larger up to 200 ppm. Thus, the maximum sensitivity was obtained at higher concentration of H_2S gas, i.e., 200 ppm.

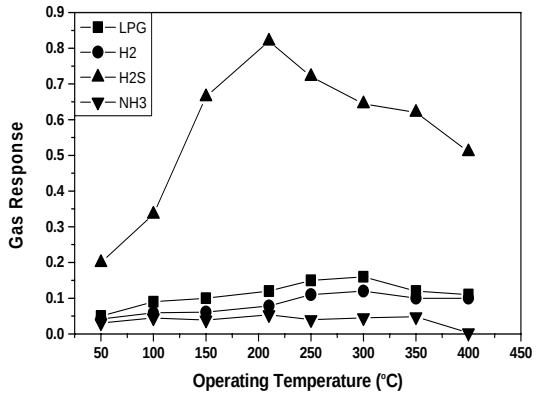

Fig. 5: Cross sensitivity vs operating temperatures for different reducing gases for $La_{0.7}Sr_{0.3}CoO_3$

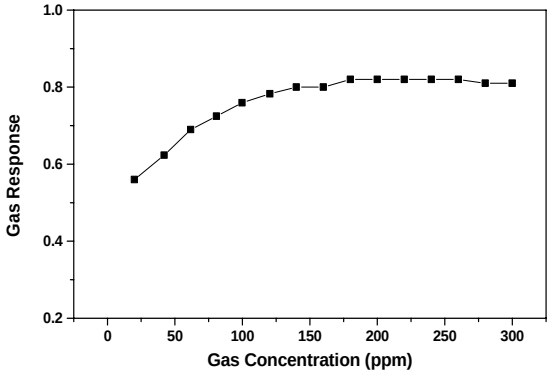

Fig. 6: Gas Response of $La_{0.7}Sr_{0.3}CoO_3$ to H_2S gas of different concentration at an operating temperature 10°C

The response and recovery times of $La_{0.7}Sr_{0.3}CoO_3$ sample is represented in Fig. 7. The response was quick (~ 40 s) to 200 ppm of H_2S while the recovery was moderate (~ 80 s). The quick response may be due to faster oxidation of gas.

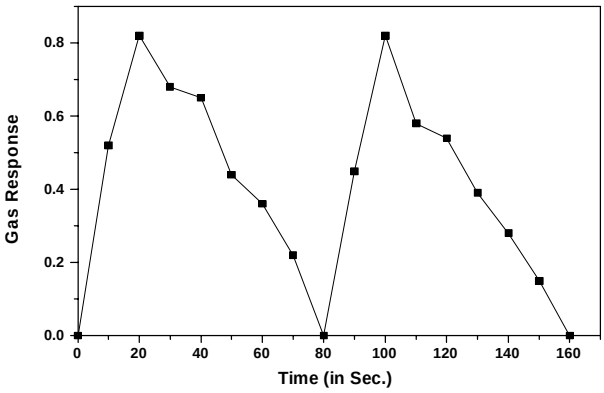

Fig. 7: The response and recovery characteristics to 200 ppm H_2S gas of $La_{0.7}Sr_{0.3}CoO_3$

CONCLUSION

Nanocrystalline $La_{0.7}Sr_{0.3}CoO_3$has been synthesized by a convenient sol–gel route. The XRD pattern of $La_{0.7}Sr_{0.3}CoO_3$ shows perovskite-type with tetragonal structure. The results revealed that the particle size is in the range of 30–35 nm for $La_{0.7}Sr_{0.3}CoO_3$ with good crystallinity. From the results obtained, pure $LaCoO_3$ showed low response to H_2S gas. Sr doped $LaCoO_3$ thick films were found to be high sensitive for H_2S gas. Among all other synthesized samples $La_{0.7}Sr_{0.3}CrO_3$ thick film was found to be optimum and showed highest response to H_2S gas at 210^oC. The sensor is very promising for H_2S detection in the range 200 ppm with a response time in second range.

ACKNOWLEDGEMENT

The authors are also indebted to Principal, Dr. M.S Ali, Principal, Prof Ram Meghe College of Engineering & Management, Badnera- Amravati, India for his kind cooperation during this research work.

REFERENCES

1. D. E. Williams, Semiconducting Oxides as Gas-Sensitive Resistors, Sensors and Actuators B, **57**, 1-16 (1999).
2. N. Barsan, M. Schweizer-Berberich, W. Göpel, Fundamental & Practical Aspects in the Design of Nanoscaled SnO2 Gas Sensors, Fresnius J. Anal. Chem., **365**, 287-304 (1999).
3. G. Sberveglieri, S. Groppelli, P. Nelli, C. Perego, G. Valdre and A. Camanzi, Detection of Sub-ppm H2S Concentrations by SnO_2 (Pt) Thin Films Grown by the RGTO Technique, Sens. Actuators B, **55**, 86-89 (1998).
4. D. J. Smith, J. F. Velelina, R. S. Falconer and E. L. Wittman, Stability Sensitivity and Selectivity of Tungsten Trioxide Films for Sensing Applications, Sens. Actuators B, **13**, 264-268 (1993).
5. W. H. Tao, C. H. Tsai, H_2S Sensing Properties of Noble Metal Doped WO3 Thin Film Sensor Fabricated by Micromachining, Sens. Actuat. B, **81**, 237-247 (2002).
6. J. Q. Xu, X. H. Wang and J. N. Shen, Hydrothermal Synthesis of $In2O_3$ for Detecting H2S, Sens. Actuators B, **115**, 642 -646 (2006).
7. Y. L. Liu, H. Wang, Y. Yang, Z. M. Liu, H. F. Yang, G. L. Shen and R. Q. Yu, Hydrogen Sulphide Sensing Properties of $NiFeO_4$ Nanopowder Doped with Noble Metal, Sens. Actuators B, **102**, 148-154 (2004).

8. W. Yan, L. Sun, M. Lui and W. Li, Study of Sensing Characteristics of Rare Earth Pervoskites for Alcohol, Acta Scientiarium Naturalium Universitaties Jilinesis, **2**, 52-56 (1991).

9. L. Kong and Y. Shen, Gas Sensing Property of and Mechanism of CaxLa1-XFeO_3 Ceramics, Sensors and Actuators B, **30**, 217-221 (1996).

10. W. H. Tao and C. H. Tasi, H_2S Sensing Properties of Noble Metal Doped WO_3 Thin Film Sensor Fabricated by Micromachining, Sensors and Actuators B, **81**, 237-247 (2002).

11. J. Q. Xu, X. H. Wang and J. N. Shen, Hydrothermal Synthesis of In2O3 for Detecting H2S, Sensors and Actuators B, **115**, 642-646 (2006).

12. C. H. Wang, X. F. Chu and M. M. Wu, Detection of H_2S Down to ppb Levels at Room Temperature using Sensors Based on ZnO Nanorods, Sensors and Actuators B, **113**, 320-323 (2006).

13. Y. L. Liu, H. Wang, Y. Yang, Z. M. Liu, H. F. Yang, G. L. Shen and R. Q. Yu, Hydrogen Sulfide Sensing Properties of $NiFeO_4$ Nanopowder Doped with Noble Metal, Sensors and Actuators B, **102**, 155-161 (2004).

14. Xiufang Zhu, Qin Zhong, Xuejun Zhao and Han Yan, Synthesis and Performance of Y-Doped La0.7Sr0.3CrO_3 as a Potential Anode Material for Solid Oxygen Fuel Cells Applied Surface Science **257**, 1967–1971 (2011).

15. Martinelli, M. Ferretti and M. R. Cimberle, The Crystal & Magnetic Structure of Ti-Substituted LaCrO3 Materials Research Bulletin, **46**, 190–193 (2011).

16. X. Ding, Y. Liu, L. Gao and L. Guo, Synthesis and Characterization of Doped LaCrO3 Perovskite Prepared by Edta-Citrate Complexing Method, J. Alloys Compd., **458**, 346–350 (2008).

17. B. D. Cullity, In Elements of X-ray Diffraction, 2nd Edition, Addison Wesley, 155-165 (1978).

18. T. G. Nenov and S. P. Yordanov, Ceramic Sensors, Technology and Applications, Technomic Publishers, Lanscaster, 138-144 (1996).

19. V. E. Henrich and P. A. Cox, The Surface Science of Metal Oxides, Cambridge University Press, Cambridge, 257-264 (1994).

20. X. Liu, B. Cheng, J. F. Hu, H. W. Qin and M. H. Jiang, Sens. Actu. B, **133**, 340–344 (2008).