International Journal of Scientific Research in Science and Technology
Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)
© 2021 | IJSRST | Volume 8 - Issue 1

Nanocrystalline $Mg_{0.6}Cd_{0.4}Al_2O_4$ Thick Film Gas Sensor for the Detection of LPG, CH_4, CO_2

S.V. Agnihotri [1*], V.D. Kapse[2]

[1*]Department of Physics, Amolakchand Mahavidyalaya, Yavatmal, Maharashtra, India

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

ABSTRACT

This paper reports that $Mg_{0.6}Cd_{0.4}Al_2O_4$ nano-powders can be used as a gas-sensing material for detecting LPG, CH_4, CO_2, gas. Powder was prepared by the co precipitation method. The powder was characterized by X-ray diffraction (XRD) and XRD pattern showed that $Mg_{0.6}Cd_{0.4}Al_2O_4$ was still cubic spinel phase with orthorhombic structure and its crystallite size is about 9.7 nm. The thick film was prepared by screen printing technology. The gas sensitivity of $Mg_{0.6}Cd_{0.4}Al_2O_4$ based sensor was investigated. The sensor exhibited high sensitivity and good selectivity towards LPG gas.

Keywords: Nanomaterial, $MgAl_2O_4$, doped $MgAl_2O_4$, X- ray diffraction, FTIR, SEM- EDS, Co precipitation, Screen printing, gas sensor.

I. INTRODUCTION

The different types of gas sensor are catalytic gas sensors, infrared gas sensors, semiconductor gas sensors, etc. The gas sensor is used for the detection of the hazardous gases in the environs. Gas sensors based on metal-oxides that are playing an important role in the detection of toxic pollutants and the control of industrial processes. Chemiresistive metal oxides are useful materials for detection of LPG, CO_2 and CH_4 due to their established advantages such as low cost, compactness and ease of implementation with integrated-circuit technology. Systematic studies have been carried out under co precipitation method. Thick and thin films are the two techniques for the fabrication of gas sensor. Thick film gas sensors based on semiconductor oxides and prepared by screen-printing technique have certain advantages over other types of gas sensors, such as low cost, simple construction, small size, and good sensing properties [1, 2, 3]. The operation of gas sensor in actual situations does the demand of analysis of the response in the presence of interfering gases. In reality the interference of mention gases is a well-known disturbance in gas detection in domestic uses. The sensing principle of semiconductor gas sensor is based on the change in the resistance of a semiconductor oxide film when specific gases interact with its surface [4]. The surface to bulk ratio is much larger than that of coarse micro-grained materials, which yields a large interface between the metal oxide and the gaseous medium. The doping concentration is increase the sensitivity of the material. The sensitivity of semiconductor oxide materials has been enhanced by reducing the particle size, and better properties have been reported for sizes in 5–50 nm range [5-7]. There are many reports available on semiconducting metal oxide. Among these magnesium aluminate gas sensor is a potential candidates for the gas sensing device. Currently the $Mg_{0.6}Cd_{0.4}Al_2O_4$ has been prepared by coprecipitation [8], hydrothermal synthesis [9, 10], sol–gel method [11, 12]. In the present study, we report on the preparation of nanosized $Mg_{0.6}Cd_{0.4}Al_2O_4$ spinel via coprecipitation method. Characterization of the spinel was carried out by using powder X-ray diffraction, infrared spectra and scanning electron micrograph. The gas sensing properties of thick film based on the metal oxide are determined.

II. METHODS AND MATERIAL

The materials were prepared by a co precipitation method. The appropriate amounts of starting materials $Al(NO3)_2$(99.0%), $(Mg(NO_3)_2$ $6H_2O$, $Cd(NO_3)_2$ were dissolved in distilled water mixed well with each other at 80°C temperature under constant magnetic stirring, where the molar ratio of Al/Mg was 2:1. In this process, ammonia was used as precipitant. Then, the appropriate amount of aqueous ammonia solution (25 wt%) was added to the above solution and the mixture was stirred until complete precipitation occurred at a pH between 8 and 9. The precipitate was filtered, washed with distilled water and ethanol, and dried in oven at 110°C. The dry precipitate was calcinated at 800°C for 4h to obtain the $Mg_{0.6}Cd_{0.4}Al_2O_4$ nanoparticles. The $Mg_{0.6}Cd_{0.4}Al_2O_4$ sensitive layer has been prepared by screen printing technic on glass substrate. This structure underwent a subsequent annealing at 200°C for 1 hour in dry air. The sensor response was evaluated as the ratio Rair/Rgas for the n-type materials and as Rgas /Rair for the p-type. To study the sensitivity of the sensors in presence of different concentrations of LPG, CO_2, CH_4, flow of concentrated mixtures of the gases were mixed with air flow.

III. RESULTS AND DISCUSSION

3.1 Structural characterization

X-ray method are useful because they are non-destructive and do not require elaborate sample preparation. The nano-crystalline, Cd doped $MgAl_2O_4$ was characterized by XRD, at the annealed condition. Nanomaterial were amorphous became partially or fully crystalline after annealing. Peaks corresponding to the tetragonal form of $Mg_{0.6}Cd_{0.4}Al_2O_4$, the XRD patterns of the annealed catalysts with no preferred orientation or texture evident. Fig. 1 show the X-ray diffraction spectra of $Mg_{0.6}Cd_{0.4}Al_2O_4$ annealed at 800°C. It was clearly seen that the $Mg_{0.6}Cd_{0.4}Al_2O_4$ powder had cubic spinel structure. Average crystallite size was calculated using Debye Scherer formula. The average crystallite size of the prepared material is 9.7 nm. Fig.1 shows the formation of $MgAl_2O_4$ with the respective concentration of doping of Cd.

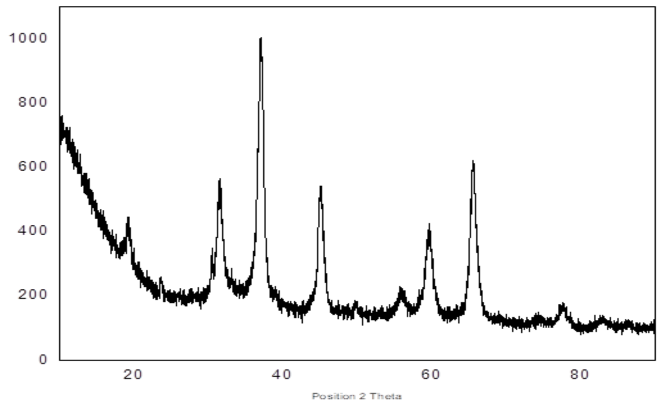

Fig.1. X-ray diffraction spectra of $Mg_{0.6}Cd_{0.4}Al_2O_4$ powder annealed at 800° c.

3.2 Fourier transforms infrared spectroscopy (FTIR)

Optical study of $Mg_{0.6}Cd_{0.4}Al_2O_4$ powder was carried out in the wavelength range 400-4000 at room temperature. Transmittance spectra recorded for the powder at 800^0c as a function of wavelength are shown in Figure (2). The large specific surface area of the powders enables the rapid adsorption of H_2O and CO_2 from the atmosphere, as evidenced by the FT-IR spectra of the samples. The broad at 34641.87cm^{-1} may be assigned to the stretching vibration of H_2O molecules, while the band from 1629.02cm^{-1} band is attributed to H_2O bending. The absorption band at 2923.91cm^{-1} is due to the stretching vibration of CO_2. The spiky bands, 696.26 and 510.44 cm^{-1} confirms the formation of normal spinel cubic structure.

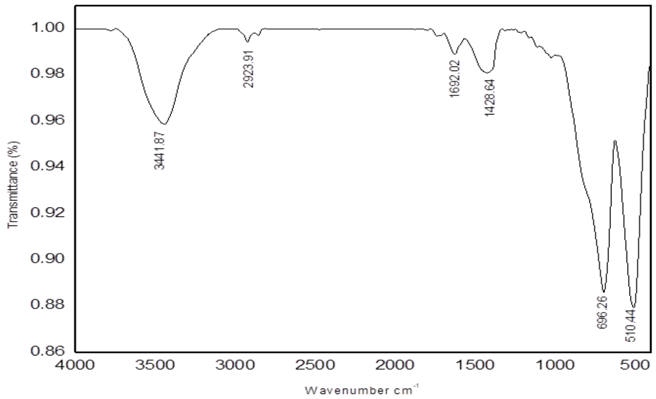

Fig. 2: FTIR Spectra of Mg0.6Cd0.4Al2O4.

3.3 Scanning Electron Microscopy with dispersive X-ray analysis (SEM-EDAX)

The SEM uses a focused beam of high-energy electrons, ranging from a few KeV to 50KeV, to generate a variety of signals at the surface of solid specimens. The SEM is also capable of performing analyses of selected point locations on the sample, this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions crystalline structure, and crystal orientations. The EDX analysis system works as an integrated feature of scanning electron microscope. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most x-rays had been received. Fig.3 shows the SEM image of the thick film gas sensor. The films exhibiting a porous structure have a large fraction of atoms residing at surfaces and interfaces between the pores, which suggests that the microstructure of the films is suitable for gas-sensing purposes. The EDS spectrum of 200^{0}C annealed pure thick film sensor obtained is shown in fig.4. Fig. 4 shows EDS spectrum contains wt percent of MgK 8.52%, AlK 34.38% and CdK 11.62%. Spectrum reveals presence of MgO and Cd elements only. $Mg_{0.6}C_{0.4}Al_2O_4$ thick film sensor. Spectrum gives clear evidence for the presence of cadmium doped in the sample.

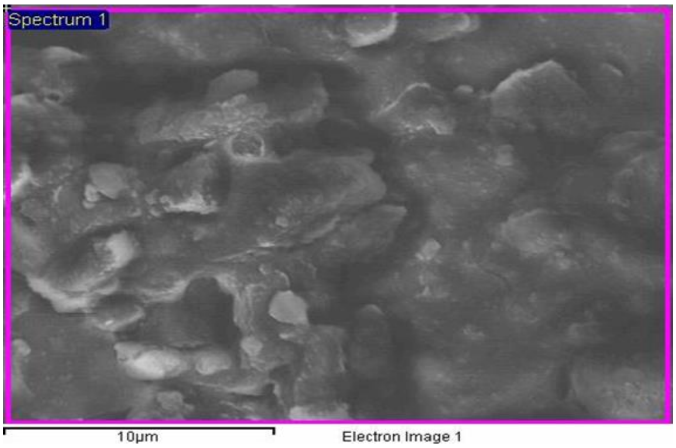

Fig. 3: SEM image of Mg0.6Cd0.4Al2O4 sensor.

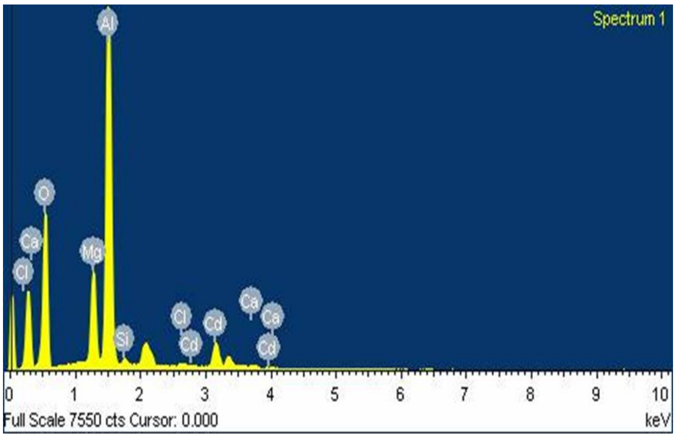

Fig. 4: EDS spectrum of $Mg_{0.6}Cd_{0.4}Al_2O_4$ thick film sensor.

3.4 Gas sensing characteristics

The morphology of the thick film catalysts were characterized by SEM. This reaction can be influenced by many factors, including internal and external causes, such as the natural properties of base materials, surface area, microstructure of sensing layers, surface additives, temperature, humidity, etc. Gas sensing characteristics of metal oxides are sensitivity, selectivity, selectivity, accuracy, speed of response, recovery time and stability.

The gas sensor performance towards LPG, CO_2, and CH_4 at operating temperature at 200°c was examined in this study. Fig.5. shows operating temperature response to 500 ppm of LPG gas sensor based on ($Mg_{0.6}Cd_{0.4}Al_2O_4$) sample annealed at 200°C. We can see that their sensitivity and corresponding optimal operating temperature are different. Fig.5 shows change in gas response (%) with temperature ($Mg_{0.6}Cd_{0.4}Al_2O_4$) film sensors for 500 ppm of LPG gas. The gas response initially remains very low at lower temperatures and increases with increase in temperature. With further increase in temperature, it goes on decreasing. The gas response shows a maximum which corresponds to operating temperature of the sensor film. For ($Mg_{0.6}Cd_{0.4}Al_2O_4$) thick film, the gas response is found to be 10 at an operating temperature 328K.

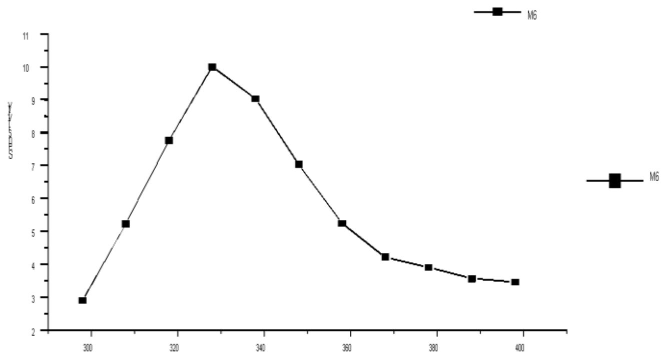

Fig.5: shows the relation between operating temperature and sensitivity.

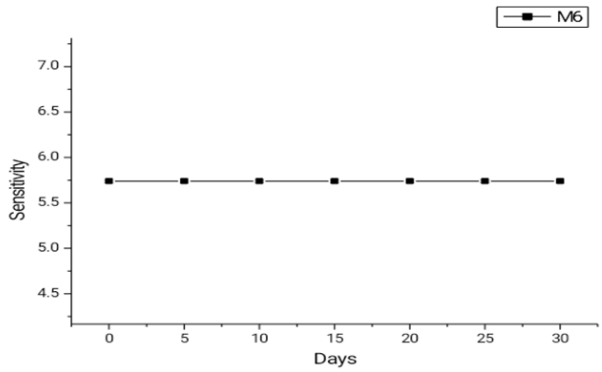

Fig.6: Long term stability curve of (Mg0.6Cd0.4Al2O4) based sensor.

Fig.7. shows the sensitivity of sensor at 303k temperature towards a concentration of 500 ppm. The response time is defined as the time taken by the sensor to reach 90% of maximum value and recovery time is taken as the time taken by the sensor to reach 10% of original value. The response of the sensor was measured by the R gas/ Rair. As the gas was turned-off, the response of the same film fell rapidly, indicating that the good recovery of the resistance was obtained.

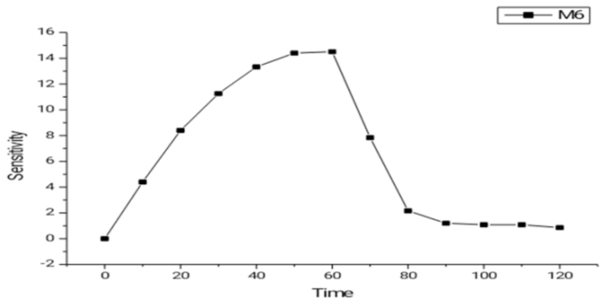

Fig.7: Response and recovery characteristics of sensor at 500 ppm LPG.

The responses of LPG, CO2, CH4 of 500 ppm at 296k is as shown in fig.8. The selectivity of the gas sensor is more than 5. The gas sensor has more response towards LPG gas.

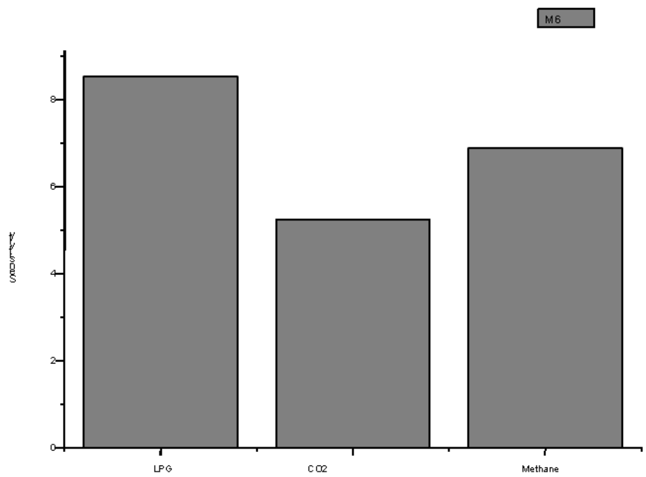

Fig.8: Gas responses to different gases at the concentration of 500 ppm.

The screen-printed sensors were tested for different gases. The choice of these sensors for LPG, CH_4 and CO_2 gas with optimum proportions. The results of the sensors when exposed to different gases at concentrations of 0, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppm are shown in Fig.9. It can be seen that the sensors display an almost linear response over this range.

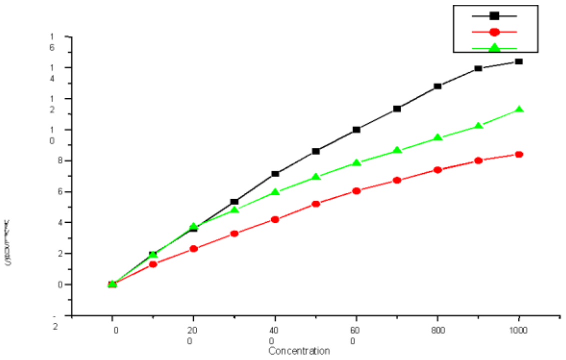

Fig.9: Curve of concentration verses sensitivity.

IV. CONCLUSION

The structural and morphological investigations have proven the nanocrystalline nature of the metal oxide powder synthesized by coprecipitation method. This method was very simple and low cost. Thick film was fabricated by screen printing technology. This can be used for the detection of the different gases in environment. LPG, CO_2, CH_4 are very important for disaster supervision purpose so that this study is quite significant. It was found that synthesized $Mg_{0.6}Cd_{0.4}Al_2O_4$ based thick film works as a sensor at room temperature. The value of sensitivity of sensor was 10 for LPG gas. The sensor was 90% reproducible. Thus the experimental results demonstrate that nanosized $Mg_{0.6}Cd_{0.4}Al_2O_4$ thick film is appropriate promising material for the LPG sensing.

V. ACKNOWLEDGEMENTS

The authors thank to Sophisticated Analytical Instrument Facility, Chandigarh, for providing XRD facility. A special thanks to S.A.I.F., Indian Institute of Technology, Bombay for carrying out FT-IR, SEM-EDAX.

VI. REFERENCES

[1]. W. Noh, Y. Shin, J. Kim, W. Lee, K. Hong, S.A. Akbar, J. Park, Solid State Ionics 152-153 (2002) 827–832.
[2]. M. C. Carotta, G. Martinelli, Y. Sadaoka, P. Nunziante, E. Traversa, Sens. Actuat., B Chem. 48 (1998) 270–276.
[3]. V. Guidi, M. A. Butturi, M. C. Carotta, B. Cavicchi, M. Ferroni, C. Malagu, G. Martinelli, D. Vincenzi, M. Sacerdoti, M. Zen, Sens. Actuat. B Chem. 84 (2002) 72–77.
[4]. M .J. Madou, S.R. Morrison, Academic Press, San Diego, (1999).
[5]. C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Sens. Actuat. B 3(1991) 147–155.
[6]. N. Yamazoe, Sens. Actuat. B 5 (1991) 7–19.
[7]. Y. Shimizu, M. Egashira, MRS Bulletin, June (1999), pp. 18–24.
[8]. G. Aguilar-Rios, M. Valenzuela, P. Salas, H. Armendariz, P. Bosch, G. Del Toro, R. Silva, V. Bertin, S. Castillo, A. Ramirez-Solis, I. Schifter, Appl. Catal. A Gen. 127 (1995) 65–75.
[9]. J. Wrzyszcz, M. Zawadzki, J. Trawczy'nski, H. Grabowska, W. Mi'sta, Appl. Catal. A Gen. 210 (2001) 263–269.
[10]. M. Zawadzki, J. Wrzyszcz, Mater. Res. Bull. 35 (2000) 109–114.
[11]. A. R. Phani, M. Passacantando, S. Santucci, Mater. Chem. Phys. 68 (2001) 66-71.
[12]. C.O. Arean, B.S. Sintes, G.T. Palomino, C.M. Carbonell, E.E. Platero, J.B. P. Soto, Microporous Mater. 8 (1997) 187.