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Research Article

CADMIUM DOPED COPPER FERRITE THICK FILM SPINEL BASED SENSORS FOR AMMONIA DETECTION

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ABSTRACT
Nanocrystalline $Cu_{1-x}Cd_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.6 and 0.8) mixed oxides, were successfully prepared by the ethylene glycol mediated citrate sol-gel method. The structure and crystal phase of the powders were characterized by X-ray diffraction (XRD) and microstructure by Scanning electron microscopy (SEM). X-ray diffraction pattern confirm the existence of single phase of cubic spinel crystal structure. The mean particle size of the nano-powders when calcined at 550^0 C is the range of 30-35 nm calculated by Scherrer's equation. The gas sensing properties were studied towards reducing gases like H_2, LPG, Ethanol, NH_3 and H_2S. The sensor response largely depends on the composition, temperature and the test gas species. It is observed that Cu–Cd ferrite shows high response to ammonia gas at relatively lower operating temperature. The $Cu_{0.6}Cd_{0.4}Fe_2O_4$ nanomaterial shows better sensitivity towards NH_3 gas at an operating temperature 230^0C. Incorporation of Cd improved the sensitivity, selectivity, response time and reduced the operating temperature for NH_3 sensor.

Keywords: *NH_3 Sensor, Cu–Cd Ferrite, Sensitivity, Selectivity*

INTRODUCTION
Toxic and harmful gases cause atmospheric pollution. The sensors are required basically for monitoring of trace gases in environment. In order to detect measure and control these gases; one should know the amount and type of gases present in the environment. Thus, the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies. Ammonia is utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, etc. A leak in the system can result the health hazards. Ammonia is harmful and toxic (Narasimhan *et al.,* 2001; de la Hoz *et al.,* 1996; Leung and Foo, 1992) in nature. The exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Therefore, all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations. It is therefore, necessary to monitor ammonia gas and to develop the ammonia gas sensor.

Semiconductor metal oxides as gas sensing materials have been investigated widely for practical applications, such as gas leak detection and environmental monitoring. One of the most promising approaches to the next generation of high performance gas sensors is the development of nanostructured sensing materials (Tan *et al.,* 2004). With the growing attention to environmental problems and the increase of the standard of living, there are imperative needs for solid-state gas sensors with high sensitivity and excellent selectivity in air quality monitoring and automotive application, especially for monitoring ammonia gas.

Few semiconducting oxide materials being used as gas sensors are ZnO, SnO_2, WO_3, Fe_2O_3, Ga_2O_3, Sb_2O_3, In_2O_3, $BaTiO_3$, $NiFe_2O_4$, $MgFe_2O_4$ (Wagh *et al.,* 2006; Patil and Patil, 2006; Jain *et al.,* 2006; Barrett *et al.,* 1990; Liu *et al.,* 1998; Seiyama and Era, 1971; Morrison, 1982; Cantalini *et al.,* 2000; Jain and Patil, 2006; Gopal Reddy *et al.,* 1999) etc. At present, the search for new gas sensing materials and developing the properties of conventional gas sensing materials has become an active research field. Spinel of the type $M_1^{2+}M_2^{3+}O_4$ attracts the research interest because of their versatile practical applications (Sugimoto, 1999; Raj *et al.,* 1995; McMichael *et al.,* 1992)15-17). $CuFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, $MgFe_2O_4$, $CdIn_2O4$ (Gopal Reddy *et al.,* 1999; Liu *et al.,* 2005; Szklarski *et al.,* 1989; Xiangfeng, 2003; Dong *et al.,* 2000; Xiangfeng *et al.,* 1999) etc. being used in gas sensing applications.

MATERIALS AND METHODS

In the present investigations, $Cu_{1-x}Cd_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.6 & 0.8) was prepared by ethylene glycol mediated citrate sol-gel method in order to obtain nano-particle size range. In particular, X-ray diffraction, Scanning electron microscopy observations, have been considered in order to determine both the micro-structure. The testing of these sensors towards different test gases like H_2, LPG, Ethanol, NH_3 and H_2S was carried at 100 ppm gas concentration. The gas sensing reaction mechanism on the sensors were proposed and discussed.

Experimental Technique

Material Preparation

All the reagents used for the synthesis of $Cu_{1-x}Cd_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.6 & 0.8) nanoparticles were analytical grade and used as received without further purification. The stoichiometric amounts of Copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], Cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$] and ferric nitrate ($Fe(NO_3)_3.9H_2O$) were dissolved in deionized water under magnetic stirring. Then, citric acid ($C_6H_8O_7.H_2O$) was mixed in the metal nitrate solution to chalet with metal ions in the solution. The molar ratio of citric acid to total moles of nitrates was maintained at 1:3.

A small amount of ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citrate solution. The neutralities solution was evaporated to dryness by heating at 90^0C on a hot plate with continuous stirring until it becomes viscous and finally formed a very viscous gel. The temperature is further raised up to 120^0C so that the ignition of the gel starts. The dried gel burnt completely in a self propagating combustion manner to form a lose powder. Finally, the as burnt powders were annealed at temperature 550^0C for 5 hrs with a heating rate of 50^0C per minute to obtain the spinal phase.

Structural & Gas Sensing Characterization

The crystal phases of calcined samples were analyzed using X ray diffraction (XRD) using a Siemens D 5000 diffractometer. The average grain size has been calculated from the XRD peaks using Debye–Scherrer formula.

The lattice parameters of the prepared powder samples were calculated from the XRD peaks by indexing corresponding peaks in a cubic space group *Fd*3*m*, using least square refinement. The fine powder was observed under a JEOL, JSM – 5600 N scanning electron microscope (SEM) by dispersion it on a carbon paste to determine the morphology.

Gas-Sensing Properties

The calcined $Cu_{1-x}Cd_xFe_2O_4$ powders were mixed with PVC as a binder to form pastes. The paste was coated onto an alumina tube on which two gold leads had been installed at each end. For this, the alumina tube was dipped several times in the prepared paste. The alumina tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter. A small Ni–Cr alloy coil was placed through the tube as a heater.

The heater provides operating temperatures from 200 - 400 ^{0}C. The temperature was controlled by adjusting the heating power. In order to improve their stability and repeatability, the gas-sensing elements were heated at 500^0C for 5 days in air. The gas sensitivity (*S*) is defined as the ratio of the change of resistance in presence of gas (R_g) to that in air (R_a),

$S = (R_a - R_g)/R_a = \Delta R/R_a$ -------- (1)

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RESULTS AND DISCUSSION

X-Ray Diffraction Study

Figure 1 shows the X-ray pattern of $Cu_{1-x}Cd_xFe_2O_4$ (a) x= 0 and (b) x = 0.4 shows the single-phase spinel structure without any ambiguous reflection. The calcined powder samples show XRD peaks and they are in good agreement with the standard XRD pattern, JCPDS (34-0425) of $CuFe_2O_4$. The lattice parameters are in the expected range with the lattice constant of $CuFe_2O_4$ (Choni *et al.,* 1980) and $CdFe_2O_4$ (Islam *et al.*, 2002) at either end. Lattice parameter increases linearly with the increase of cadmium content.

This could be attributed, as expected, to the large ionic radius of Cd^{2+} (0.78 A°) which when substituted in the lattice resides on the tetrahedral site and replaces the smaller Cu^{2+} (0.57 A°) or Fe^{3+} (0.49 A°) ions from the tetrahedral to the octahedral site (Ladgaokar and Vaingankar, 1998; Si *et al.*, 2005). No other phase was observed in the XRD pattern indicating that no chemical transformation took place during the heat treatment. The XRD graph indicated that the synthesized powders contain nano sized crystallites and complete phase formation with grain size of about 30-35 nm.

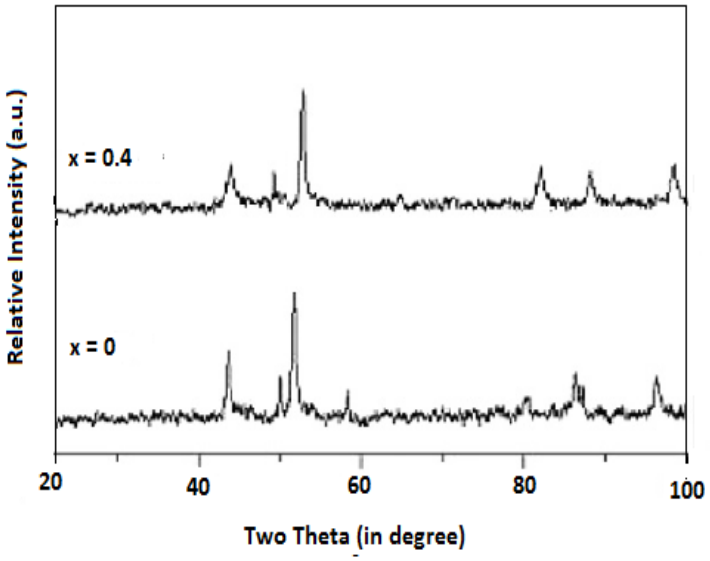

Figure 1: XRD Pattern of $Cu_{1-x}Cd_xFe_2O_4$ (a) x = 0 (b) x = 0.4 Calcined at 550 ^{0}C

Morphology Study

The SEM technique was employed for finding morphology of $Cu_{0.6}Cd_{0.4}Fe_2O_4$ as synthesized powder, calcined at 550^0 C. One can notice the presence of macro-agglomerations of very fine particles. The particle shapes are not well defined. Many large and small pores are present in the whole material. We assumed that the pores are mainly inter-granular because intra-granular pores are not seen on the SEM photograph.

Figure 2: SEM Image $Cu_{0.6}Cd_{0.4}Fe_2O_4$ as Synthesized Powder, Calcined at 550^0 C

Gas-Sensing Characteristics

The gas-sensing responses of $CuFe_2O_4$ to different reducing gases like ammonia (NH_3), hydrogen sulfide (H_2S), Ethanol (C_2H_5OH), Hydrogen (H_2) and liquefied petroleum gas (LPG) as a function of operating

temperature were studied. The $CuFe_2O_4$ nanocrystalline powder calcined at 550 ^{0}C for 6h exhibits good response to NH_3 at 300^{0}C. The response of $CuFe_2O_4$ towards NH_3, H_2S, Ethanol, H_2 and LPG is depicted in Figure 3. It was found that the sensor element based on $CuFe_2O_4$ could detect NH_3 at 300^{0}C with poor selectivity.

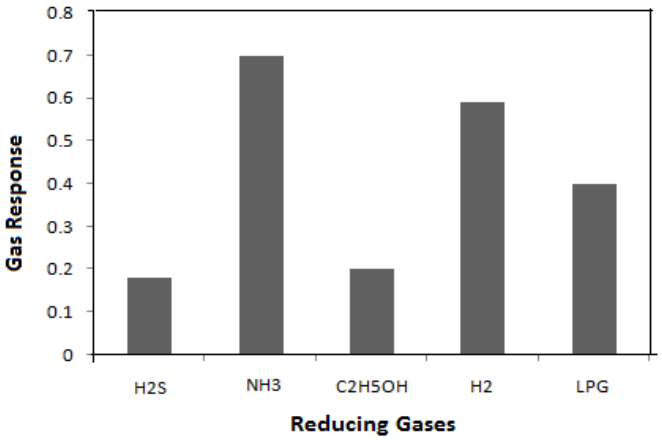

Figure 3: Response of $CuFe_2O_4$ towards Reducing Gases NH_3, H_2S, Ethanol, H_2 & LPG at 300^0 C

The reducing gas R acting on the $CuFe_2O_4$ surface can be described as

R (gas) ↔ R (ads)

O_2^- (ads) + e^-↔ $2O^-$ (ads)

R (ads) + O^- (ads) ↔ RO(ads) + e^-

In the absence of R, electrons are removed from $CuFe_2O_4$ conduction band by the reduction of O_2, resulting in the formation of O^- species and consequently the resistance of $CuFe_2O_4$ sensor increases. When R is introduced, it reacts with O^- (ads) to form RO, and electrons enter the conduction band of $CuFe_2O_4$ leading to decrease of resistance. In case of $CuFe_2O_4$, the carriers are believed to be due to excess metal ions at the interstitial positions, due to oxygen vacancies, act as electron donors. Reducing gas like NH_3 reacts with adsorbed oxygen ions. The possible reaction is,

$2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e^-$

Figure 4 illustrates the response of $Cu_{1-x}Cd_xFe_2O_4$ (x=0.0, 0.2, 0.4, 0.6 & 0.8) as a function of the operating temperature towards 100 ppm NH_3 gas. From the plots it is clearly evident that the $Cu_{0.6}Cd_{0.4}Fe_2O_4$, there was notable enhancement in the response to 100 ppm NH_3 gas with reduction in the optimal operating temperature. The operating temperature for maximum response towards 100 ppm NH_3 gas was observed at lower operating temperature 230 ^{0}C.

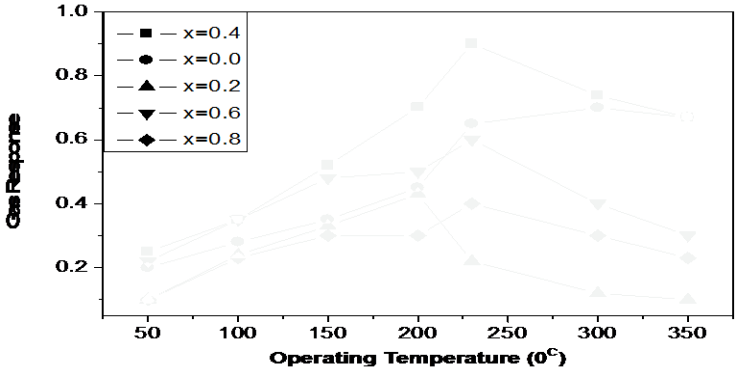

Figure 4: Response of $Cu_{1-x}Cd_xFe_2O_4$ (x =0.0, 0.2, 0.4, 0.6 and 0.8) towards100 ppm NH_3 Gas

Selectivity or specificity can be de fined as the ability of a sensor to respond to a certain gas in the presence of other gases. To know about the selective behavior of $Cu_{0.6}Cd_{0.4}Fe_2O_4$ towards NH_3 gas at

optimal operating temperature, its response to H_2S, Ethanol, H_2 and LPG was also studied. The results are shown in Figure 5. Furthermore, the response of $Cu_{0.6}Cd_{0.4}Fe_2O_4$ to H_2S gas was also measured at 230^0C in the presence of other tested interfering gases. For this, 100 ppm NH_3 gas was injected in the testing chamber, and then, in its presence, LPG, H_2S, H_2 and Ethanol were also injected. Thereafter, the change in the response of sensor element to 100 ppm of NH_3 gas was measured.

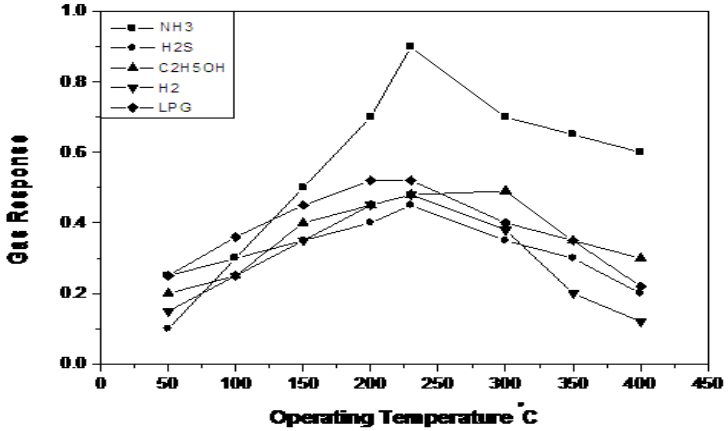

Figure 5: Selectivity of $Cu_{0.6}Cd_{0.4}Fe_2O_4$for Different Reducing Gases like NH_3, H_2S, Ethanol, H_2 and LPG

It can be seen that the response of sensor elements to NH_3 gas remains high after the introduction of interfering gases like LPG, H_2S and Ethanol besides NH_3 gas in the testing chamber. The influence of other reducing gases that are additionally present on the NH_3 gas characteristics was found to be nearly 0–14% at 230 ^{0}C. So, it can be seen that $Cu_{0.6}Cd_{0.4}Fe_2O_4$ increases the response along with enhancing the selectivity to NH_3 gas.

Response time is defined as the time needed for a sensor to attain 80% of maximum change in conductance upon exposure to a test gas, while recovery time as the time taken by a sensor to get back 80% of the origin al conductance in air. Recovery time of a sensor element is exponential in nature. The response-recovery characteristics of the $CuFe_2O_4$ and $Cu_{0.6}Cd_{0.4}Fe_2O_4$ sensor elements to 100ppm NH_3 gas at 230^0 C are shown in Figure 7. The response and recovery time of the $Cu_{0.6}Cd_{0.4}Fe_2O_4$ was found to reduce as compared with unmodified $CuFe_2O_4$. The result indicates that the $Cu_{0.6}Cd_{0.4}Fe_2O_4$ sensor can meet the practical application for NH_3 gas detection.

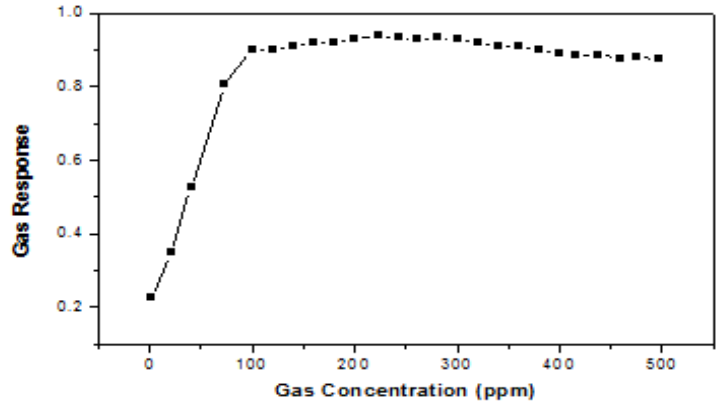

Figure 6: Variation of Gas Sensitivity of $Cu_{0.6}Cd_{0.4}Fe_2O_4$ with Gas Concentration

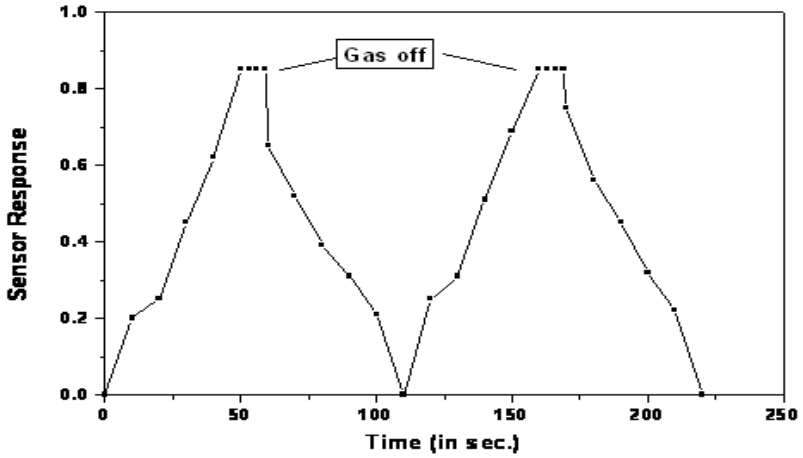

Figure 7: Response and Recovery Time of $Cu_{0.6}Cd_{0.4}Fe_2O_4$ for NH_3 Gas

Conclusion

In the present investigation we have presented the method of synthesis and a systematic improvement in the sensing properties of $Cu_{1-x}Cd_xFe_2O_4$ (x = 0, 0.2, 0.4, 0.6 & 0.8). The single cubic phase spinel structures of $Cu_{1-x}Cd_xFe_2O_4$ were identified through X ray diffraction and no impurity were detected. It is also show high degree of crystallinity and complete phase formation with grain size of about 30-35 nm. The results demonstrate the development of a new class of stable and very sensitive nanostructured materials for gas sensing. $Cu_{0.6}Cd_{0.4}Fe_2O_4$ is found to be sensitive for the detection of ammonia at 230^0C. The operating temperature was found to be reduced up to 230^0C by addition of Cd content. This sensor has good selectivity to NH_3 gas against LPG, H_2S, H_2 and Ethanol at 230 ^{0}C. Thus, the sensor is promising material for practical devices for the detection of a low concentration of NH_3.

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