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Liquid petrolium gas sensor based on nanocrystallite $Mg_{0.6}Cd_{0.4}Fe_2O_4$

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ABSTRACT

The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ ferrite powder was synthesized by oxalate co-precipitation method. The crystal structure and surface morphology were examined by XRD, SEM and FT-IR techniques. The nanocrystallite $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor was tested for LPG, Cl_2 and C_2H_5OH. The sensitivity was measured at various operating temperatures in the range of 100-400°C. The sensor shows highest sensitivity at operating temperature 225°C for LPG (~ 78%). It shows good sensitivity at operating temperature of 198°C for Cl_2 (~75%) and ethanol (~ 65%). The sensor exhibits a lower response and recovery time for LPG and Cl_2 as compared to C_2H_5OH. Copyright © 2013 VBRI press.

Keywords: Sensitivity; Selectivity; response/recovery time; grain size.

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Introduction

Recently semiconducting ferrites have used as gas sensors. Many studies have been reported on preparation of ferrite gas sensing materials [**1-6**]. Tianshu *et al.* [**2**] prepared cadmium ferrite by co-precipitation method and tested for C_2H_5OH, CO, H_2 and C_4H_{10}. The sensor shows high sensitivity and rapid response to C_2H_5OH gas at operating temperature of 380°C (90 at 200 ppm). Chen *et al.* [**4**] prepared MFe_2O_4 by co-precipitation method and tested for the sensing properties of reducing gases CO, H_2, LPG and C_2H_2. They reported that the sensitivity of samples depends on the kind of ferrite, grain size and specific surface area. Kadu *et al.* [**5**] observed high response to ethanol at operating temperature of 300°C for $Zn_{0.6}Mn_{0.4}Fe_2O_4$ nanomaterial. We [**6**] have reported magnesium ferrite as LPG, Cl_2 and C_2H_5OH sensor. The sensor shows high sensitivity to LPG. The sensitivity depends on the pore size, porosity and specific area. The control of these parameters is a problem in production of ceramic gas sensors. The large specific area results high sensitivity witin certain limits **[7]**.

Several methods are being used for synthesis of nano sized spinel ferrite such as sol-gel, combustion, solid state, citrate, hydrothermal synthesis and co-precipitation [**8**]. The solid state sintering route has disadvantages. The ferrites in present work have been synthesized by chemical solution method known as oxalate co- precipitation method. The advantage of this method is that, it results in very fine, high purity and homogenous powders.

In this communication, we report characterization (XRD, SEM and FTIR) and gas sensing properties of nanocrystallite $Mg_{0.6}Cd_{0.4}Fe_2O_4$ for liquid petroleum gas (LPG), chlorine (Cl_2) and ethanol (C_2H_5OH), prepared by oxalate co-precipitation method.

Experimental

Synthesis of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ ferrite powder

The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ ferrite powder was synthesized by the oxalate co-precipitation method. The high purity analytical reagents (AR), $MgSO_47H_2O$ (purity 99.99%, Sd fine), $3CdSO_48H_2O$ (purity 99.99%, Sd fine) and $FeSO_47H_2O$ (purity 99.5%, Thomas Baker) were used as starting materials. The detailed experimental procedure is explained elsewere [**8**]. The process of precipitation can be explained by following chemical reactions.

$$CdSO_4 + 2H_2O + C_2O_4^{-} \rightarrow CdC_2O_42H_2O + SO_4^{--}$$

$$MgSO_4 + 2H_2O + C_2O_4^{-} \rightarrow MgC_2O_42H_2O + SO_4^{--}$$

$$FeSO_4 + 2H_2O + C_2O_4^{-} \rightarrow FeC_2O_42H_2O + SO_4^{--}$$

The co-precipitate obtained was dried and presintered at 700°C for 6 h in air. The presintered powder was milled and sintered at 1050°C for 5 h. The sintered powder was mixed with binder and pressed into the pellets of 13 mm diameter by applying pressure of 7 tones/cm^2 under the hydraulic press. The pellets were finally sintered at 1050°C for 5 h.

Structural characterization

The X-ray diffraction (XRD) pattern was obtained at room temperature on Philips PW-3710 X-ray powder diffractometer in the range of 20-80° using CuK$_\alpha$ radiation (λ= 1.5424 A°). The crystallite size was calculated by Debye Scherrer's formula. The micrograph of fractured surface of the pellet was taken on a scanning electron microscope (JEOL – JSM 6360 model, Japan). The IR absorption spectrum of powdered sample was recorded in the range of 350 cm^{-1} to 800 cm^{-1} on Perkin-Elmer FT-IR spectrum one spectrometer using KBr pellet technique.

Gas sensing

The sensor assembly consists of test chamber, a dome vessel (glass chamber) made of thick glass (20 cm diameter and 8 ℓ volume). The test chamber was insulated properly to avoid heat losses. The sensor element (ferrite pellet) about 2 mm thickness and 13 mm in diameter was placed on the heater. An arrangement of two electrodes on the face of the sensor element with small strips of silver provided good ohmic contacts. DC voltage of 5 volts was applied across the sensor element with help constant potential voltage source. A well calibrated, cromel-alumel thermocouple was located in close contact with sensor element to measure operating temperature. The current flowing through sensor element was measured in dry air and in presence of gas with a picometer by two probe method in the range of 100 - 400°C. The gas sensitivity of the sensor element was tested for LPG, Cl_2 and C_2H_5OH. In order to get the thermodynamic stability and the initial structure, after each exposure to gas, the sensor element was heated to 50°C for 5 min. The sensitivity (S) was calculated by using equation [**9**],

$$S(\%) = \frac{\Delta R}{Ra} \times 100 = \frac{|Ra - Rg|}{Ra} \times 100 \qquad (1)$$

Results and discussion

Characterization by XRD, SEM and FT-IR

The X-ray diffraction pattern of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ is presented in **Fig. 1**. The X-ray analysis reveals the formation of single phase cubic spinel structure. The average crystallite size was determined by Debye Scherrer formula [**8**]. The average crystallite size 'D' is 27.79 nm (table 1). The average crystallite size is smaller than that prepared by ceramic method [**10**]. SEM microphotograph of fractured surface of pellet is shown in **Fig. 2**. The average grain size is 0.78 µm and smaller than those for ferrite prepared by ceramic method [**10**]. The grains are irregular in shape and some particles are found as agglomerated. The pores serve as adsorption sites and sensitivity depend on the size of the pores. Infrared absorption spectrum of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ system is presented in **Fig. 3** and shows two major absorption bands in the frequency range 350–800 cm^{-1}. The high and low frequency absorption band (υ_1, υ_2) are observed in frequency range 555 to 576 cm^{-1} and 431 to 472 cm^{-1} respectively. These bands are common characteristics of spinel ferrites [**11**]. The structural and gas sensing parameters are presented in **Table 1**.

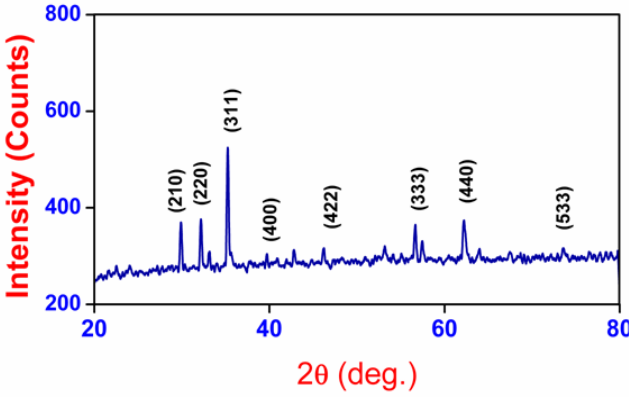

Fig. 1. X-ray diffraction pattern of $Mg_{0.6}Cd_{0.4}Fe_2O_4$.

Sensing mechanism

The gas sensing mechanism of ferrite sensor is surface controlled type where the change in resistance is controlled by species and amount of chemisorbed oxygen on the surface [**9**]. The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ based sensor is influenced by oxygen adsorbed on the surface of the material. The atmospheric oxygen molecules are physiosorbed on the surface site, get ionized by taking electrons from conduction band of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor and thus ionosorbed on the surface as to from O^- or O^{-2}.

This leads to increase in resistance of sensor material. The reaction kinematics may be explained by the following reactions [**12**],

$$O_{2gas} \Leftrightarrow O_{2ads} \quad (2)$$

$$O_{2ad} + e^- \Leftrightarrow 2O^-_{ads} \quad (3)$$

Fig. 2. SEM microphotograph of $Mg_{0.6}Cd_{0.4}Fe_2O_4$.

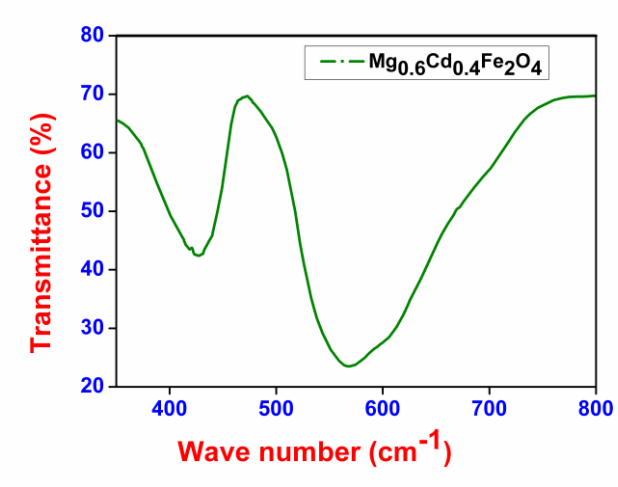

Fig. 3. FT-IR spectra of $Mg_{0.6}Cd_{0.4}Fe_2O_4$.

When the $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor is exposed to reducing gases (R = LPG, Cl_2 C_2H_5OH), they react with the chemisorbed oxygen, there by releasing the trapped electron back to the conduction band and decreases the resistance of sensor materials. The overall reaction of adsorbed gas with chemisorbed oxygen takes place as shown below,

$$R \Leftrightarrow Rad \quad (4)$$

$$R_{ad} + O^-_{ad} \Leftrightarrow RO_{ad} + e^- \quad (5)$$

Finally desorption of the resulting product will take place as [12],

$$RO_{ad} \Leftrightarrow RO_{gas} \quad (6)$$

The adsorption of the gas depends on type of the test gas and the sensor materials which further affect the sensitivity and response time. The gas sensing property of different gases is due to difference in the adsorption and reaction process [**13**].

The variation of gas sensitivity with operating temperature of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor for LPG, Cl_2 and C_2H_5OH is presented in **Fig. 4**. From this figure, it is observed that, the gas sensitivity reaches maximum at optimum temperature and decreases at higher temperature for all the test gases. We know that, at low temperature, the gas response is limited by the rate of chemical reaction, However at high temperature the rate of diffusion of gas molecules restricts the gas response. At the optimum temperature the rate of chemical reaction and diffusion of gas molecules becomes equal, attaining the equilibrium at that temperature; the sensor shows maximum response [**7**]. Thus in present investigation, for every gas there is specific temperature at which sensor sensitivity attains its peak value.

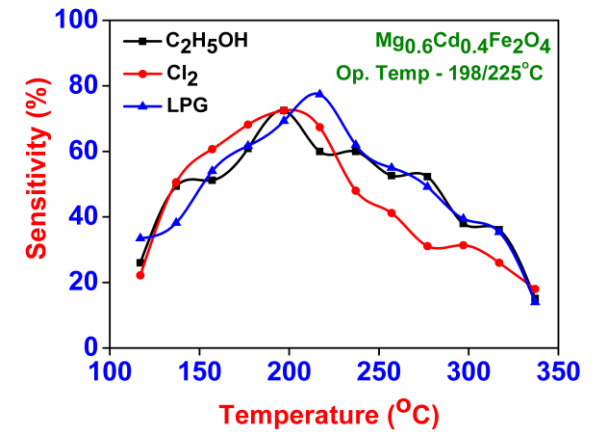

Fig. 4. Variation of sensitivity as a function of operating temperature of $Mg_{0.6}Cd_{0.4}Fe_2O_4$.

Table 1. Different parameters estimated from XRD, SEM, FT-IR and Gas sensing measurement of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ system

Lattice constant	Grain Size	Crystallite size	Operating temperature	Response and Recovery time (Sec)					
				LPG		Cl_2		C_2H_5OH	
a (A°)	(µm)	(nm)	T(°C)	Rise	Recovery	Rise	Recovery	Rise	Recovery
8.40	0.78	27.79	198	250	275	250	275	300	400

The desorption takes place at higher temperature known as optimal temperature At the optimal temperature , the activation energy may enough to complete the chemical reaction which results in the maximum adsorption of LPG. At higher temperature, the adsorbed oxygen ion would desorb from the surface of the sensor. Hence there would be less number of oxygen ions present on the surface of sensor to react with reducing gas and therefore the response fall at higher temperature. The increase and decrease of

sensitivity is observed in the graph shows adsorption and desorption phenomenon of the LPG. The reaction takes place as [**13**],

$$C_nH_{2n+2} + 2O^- \rightarrow C_nH_{2n} - O + e^- \quad (7)$$

Iftimie *et al*. [**9**] found that, the Mg-Mn ferrite show high sensitivity to LPG at operating temperature of 450 ^oC. The gas sensitivity depends largely on microstructure, such as grain size, surface area and pores. The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor is having lower operating temperature as compared to $MgFe_2O_4$ [**6**]. This is attributed to change in composition and higher porosity of this sensor. The n-type semiconducting nanoparticles of magnesium ferrite were prepared by solid state reaction by Liu *et al.* [**14**]. The magnesium ferrite sensor exhibited highest response to LPG. Rezlescu *et al* [**15**] reported higher sensitivity for Sn doped Mg ferrite than Mo substitution compared to pure magnesium ferrite. They attributed the faster response of Sn substituted Mg ferrite to high porosity and nanoprticles.

Respose and recovery time

The response and recovery time are the time taken by sensor element to reach 90% of maximum sensitivity and time to come back at original value when test gas is removed at operating temperature [**16**]. The typical response and recovery characteristics of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ are presented in **Fig.5**. From this figure it can be noticed that the response and recovery time of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor, at operating temperature of198^oC to LPG, Cl_2 and ethanol are (250, 275), (250,275) and (300,400) respectively. i.e response and recovery time for this sensor is same for LPG and Cl_2 while higher for ethanol. The shorter response of this sensor to these gases is probably due to its highest porosity [**6, 16**]. This sensor shows shorter response/recovery time than $MgFe_2O_4$ sensor.

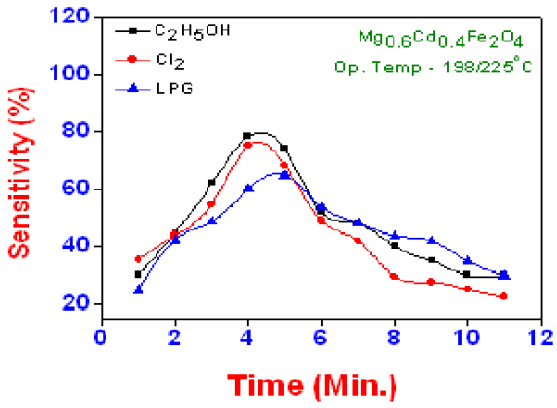

Fig. 5. Response and recovery characteristics of $Mg_{0.6}Cd_{0.4}Fe_2O_4$ in presence of LPG, chlorine and ethanol.

Conclusion

Nanocrystalline $Mg_{0.6}Cd_{0.4}Fe_2O_4$ ferrite has been prepared by oxalate co-precipitation method at a sintering temperature of 700 ^0C for 6 h. The XRD confirms single phase cubic spinel structure. The crystallite size, lattice constant and grain size are 27.79 nm, 8.40 A^o, and 0.78 µm respectively. Two absorption bands are found in frequency range of 575 cm^{-1} and 436 cm^{-1}. The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ sensor under investigation shows good response and selectivity to LPG and Cl_2 at an operating 198^oC and poor response to ethanol. The shorter response /recovery time is observed for LPG and Cl_2 gas. The $Mg_{0.6}Cd_{0.4}Fe_2O_4$ should be suitable material for the fabrication of LPG and Cl_2 gas sensors. The gas sensitivity depends largely on microstructure, working temperature and test gas.

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