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INFLUENCE OF RARE EARTH IONS (LA^{3+}) ON GAS SENSING PROPERTY CADMIUM FERRITES

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Abstract:

The nanocrystallite powders of La^{3+} added Cd ferrites were synthesized by oxalate co-precipitation method. The structural analysis was done by XRD, SEM and FT-IR techniques. The X-ray diffraction study confirms cubic spinel structure material. The crystallite size and grain size lies in the range of 28.87 to 30.40 nm and 0.67 to 1.2 μm respectively. The grain size of La^{3+} added cadmium ferrite is smaller than Cadmium ferrite. FT-IR show two absorption band in high and low frequency region. The La-cd ferrite is sensitivity to ethanol gas as compared to LPG and Cl_2. The sensitivity of La-Cd sensor is higher than Cd sensor. The response and recovery time of La-Cd sensor shorter than Cd sensor.

Keywords: Synthesis; crystallite size; Gas Sensor; Response time.

Introduction:

The sensors are the devices which convert physical or chemical quantity into electrical signals convenient to use [1]. The gas sensors to detect reducing and oxidizing gases need to be developed. The wide range of sensor materials based on metal oxide semiconductors has been developed [2].

Many studies have been reported on preparation of ferrite gas sensing materials [3-7]. Chen *et al.* [4] prepared Cu, Zn, Cd and Mg ferrite are by co-precipitation method and tested for the sensing properties of reducing gases of 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. The zinc ferrite was used as hydrogen sensor by Mukherjee *et al.* [5]. They showed that the hydrogen adsorption and water adsorption control the response and recovery kinetics of gas sensing. The gas sensing was investigated by Iftimie *et al.* [6] at operating temperature between 300 to 500 °C for ethyl alcohol, methane, liquefied petroleum gas, formaldehyde and ammonia. They found that the gas sensitivity depends largely on microstructure, such as grain size, surface area and pores. Liu *et al.* [7] reported magnesium ferrite and response was tested for CH_4, H_2S, LPG and C_2H_5OH. The magnesium ferrite sensor exhibited highest response to LPG. The sensitivity depends on the pore size, porosity and specific area.

In present communication, we report investigations of gas sensing properties of nanocrystallite Cd-La ferrites for liquid petroleum gas (LPG) chlorine (Cl_2) and ethanol (C_2H_5OH), prepared by oxalate co-precipitation method.

Materials and method:

Synthesis and Characterization

La^{3+} added $CdFe_2O_4$ were synthesized by the oxalate co-precipitation method [8]. The high purity analytical reagents (AR), $3CdSO_48H_2O$ (purity 99.99%, Sd fine), $La_2(SO_4)_38H_2O$ (purity 99.9%, Alafa Aesar) and $FeSO_47H_2O$ (purity 99.5%, Thomas Baker) were used as starting materials. The co-precipitate obtained was dried and presintered at 700°C for 6 h in air. The presintered powder was milled in an agate mortar with AR grade acetone and sintered at 1050°C for 5 h. The sintered powder was mixed with binder (2% polyvinyl alcohol by weight) 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.

The X-ray diffraction (XRD) patterns were obtained at room temperature on Philips PW-3710 X-ray powder diffractometer in the range of 20-80° using CuK_α radiation (λ= 1.5424 A°). The micrographs of fractured surfaces of the pellets were taken on a scanning electron microscope (JEOL – JSM 6360 model, Japan). The IR absorption spectra of powdered samples were recorded in the range of 350 cm^{-1} to 800 cm^{-1} on Perkin-Elmer FT-IR spectrum one spectrometer using KBr pellet technique.

The gas sensitivity of the sensor elements was tested for C_2H_5OH, LPG, and Cl_2. The sensitivity (S) was calculated by using equation **[9],**

$$S\,(\%) = \frac{\Delta R}{Ra} X\,100 = \frac{|Ra - Rg|}{Ra} X\,100 \quad (1)$$

Results and discussion:

Characterization

The XRD pattern, SEM micrograph and IR absorption spectra of Cd-La ferrite samples under investigations are already reported [8]. The typical XRD pattern of $CdFe_2O_4$ is presented in Fig. 1. All the samples show single phase cubic spinel structure. The average crystallite size lies in the range 28.87 to 30.40 nm. SEM micrograph of La added $CdFe_2O_4$ is presented in Fig. 2. The average grain size in the samples lies in the range of 0.67 µm to 1.2 µm. Typical IR absorption spectra of La added $CdFe_2O_4$ is presented in Fig.3. It shows two absorption bands in the frequency range of 350–800cm^{-1}. this shows well formation of ferrites. The high and low frequency absorption bands (υ_1 and υ_2) are observed in frequency range of 555 to 556 cm^{-1} and 468 to 469 cm^{-1} respectively [8].

Gas 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 [6]. The metal ions on the surface of Cd-La ferrite sensors adsorb atmospheric oxygen by transferring electrons from conduction band to adsorbed oxygen atom, resulting in the formation of ionic species such as O^- or O^{-2}. With increasing operating temperature the state of oxygen adsorbed on the surface of Cd-La ferrite sensors under goes the following reaction [10],

$$O2gas \Leftrightarrow O2ad \quad (2)$$

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

$$O^-_{ad} + e- \Leftrightarrow O^{2-}_{ad} \quad (4)$$

The oxygen species capture electrons from the conduction band of Cd-La ferrite sensors leading to decreased electron concentration resulting in increased resistance of the Cd-La ferrite sensors. When the reducing gases (R) are introduced, they are adsorbed on the surface of the Cd-La ferrite sensors as [10],

$$R \Leftrightarrow Rad \quad (5)$$

They react with O^- releasing the trapped electrons to the conduction band of the sensors subsequently lowering the resistance. The reaction between the adsorbed gas and the adsorbed oxygen is for example, O^-_{ad} and O^{2-}_{ad} will then be [10],

$$Rad + O^-_{ad} \Leftrightarrow ROad + e^- \quad (6)$$

$$Rad + O^{2-}_{ad} \Leftrightarrow ROad + 2e^- \quad (7)$$

Finally desorption of the resulting product will take place as [10],

$$ROad \Leftrightarrow ROgas \quad (8)$$

This explanation holds good for reducing gases under test. The possible reaction of these gases on the Cd-La sensor can be explained as [11],

$$C_4H_{10} + 13O^{2-} \xrightarrow{218^oC} 5H_2O + 4CO_2 + 26e^- \quad (9)$$

$$Cl_2 + 4O^{2-} \xrightarrow{218^oC} 2Cl^- + 2O_2 + 6e^- \quad (10)$$

$$C_2H_5OH + 6O^- \xrightarrow{350^oC} 3H_2O + 2CO_2 + 6e^- \quad (11)$$

There are four adsorption behavior of chlorine on the oxide surface [12-14]

$$Cl_2 + O^{2-}_{2(ad)} \rightarrow 2Cl_{(ad)} + O_2 + 2e^- \quad (12)$$

$$Cl_2 + 2O^x_o \rightarrow 2Cl^-_o + O_2 + 2e^- \quad (13)$$

$$Cl_2 + 2e \rightarrow 2Cl^-_{(ad)} \quad (14)$$

$$Cl_2 + 2V_o + 2e^- \rightarrow 2Cl^-_o \quad (15)$$

Here subscript 'ad' and 'o' are the spaces absorbed on the sensor surfaces and species occupying the lattice oxygen site respectively and Vo is the oxygen vacancy. These reaction shows n-type conduction mechanism of sensor. Thus, on the oxidation of single molecule of gas liberate plurality of electrons in the conduction band, resulting an increase in conductivity of the sensors.

Sensitivity

The variation of gas sensitivity with operating temperature of Cd-La and Cd ferrite sensors for LPG, Cl_2 and C_2H_5OH is presented in Fig. 4(a,b) respectively. From this figure, it is observed that the sensitivity of all the samples under investigations, for each test gas, increases with increase in temperature, reaches maximum corresponding to optimum operating temperature and decreases thereafter. The response of the sensor (change in resistance) to presence of test gases depends on activation processes viz. speed of chemical reaction on surface of the grain and speed of the diffusion of the gas molecules to the surface. The activation energy of chemical reaction is higher. At low temperature response is restricted by speed of chemical reaction and at high temperature it is restricted by speed of diffusion of gas molecules. At intermediate temperature speed of two processes becomes equal. At this temperature the sensitivity is highest [14]. Thus in present investigation, for every gas there is specific temperature at which sensor sensitivity attains its peak value. The temperature corresponding to peak value is function of gas, chemical composition and additives [15].

From Fig. 4 it can be noticed that at operating temperature of 350°C, Cd ferrite sensor and 310°C, for Cd-La ferrite exhibits highest sensitivity to ethanol than that for LPG and Cl_2. The requirement of higher operating temperature is probably because of smaller specific area and lower surface activity of this senor, resulting in weaker interaction between test gases and sensor surface. Similar results are reported by Chen *et al.* [4] for Zn ferrite. For mixed ferrite sensors the sensitivity depends on operating temperature and compositon. Fig 4. further shows that the addition of La^{3+} in Cd ferrite sensors has increased the sensitivity and selectively to ethanol while by decreasing the sensitivity to other reducing gases LPG and Cl_2.

Response-Recovery time

The typical response and recovery characteristics of $CdFe_2O_4$ and La^{3+} added $CdFe_2O_4$ are presented in Fig. 5(a,b). From this figure it can be noticed that the response time of $CdFe_2O_4$ at operating temperature of 350°C to LPG, Cl_2 and ethanol is same (250s). The response time of Cd-La ferrite sensor, is 120s for LPG, Cl_2 and 150s for ethanol. This response of La^{3+} added Cd ferrite sensor is lower as compared Cd ferrite. The shorter response of Cd ferrite sensor to these gases is probably due to its highest porosity [16]. The poor recovery time is observed for all the samples due to bulk nature of sensing material. When Mg-Cd sensor is exposed to test gas it goes deeper inside the sensor and comes out slowely which gives longer recovery time.

Table: 1. Parameters of 5 wt% rare earth element (La^{3+}) added $CdFe_2O_4$

Rare earth ion	Crystallite Size D (nm)	Lattice Constant a (A°)	Grain Size (µm)	X-ray Density ρ_x (gm/cc)	Physical Density ρ_p (gm/cc)	Porosity P (%)	Gas Sensitivity (MΩ/%RH)
Cd	30.40	8.71	1.2	5.78	4.74	17.99	85
La^{3+}	29.87	8.69	0.67	6.12	4.95	19.07	90

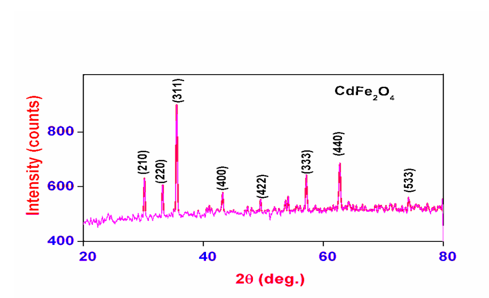

Fig. 1: Typical X-ray diffraction patterns of $CdFe_2O_4$

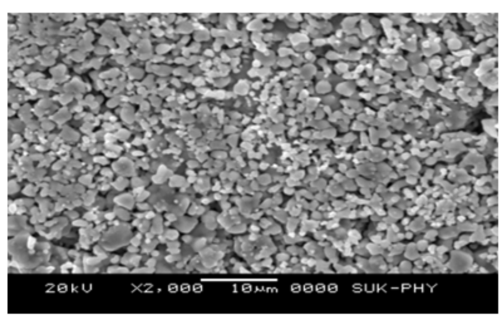

Fig. 2: SEM micrograph of 5wt% La^{3+} ions added $CdFe_2O_4$

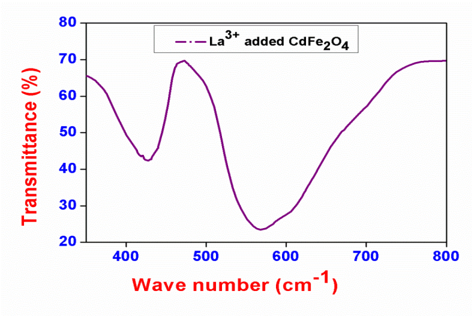

Fig. 3: Typical FT-IR spectra of 5wt% La^{3+} ions added $CdFe_2O_4$

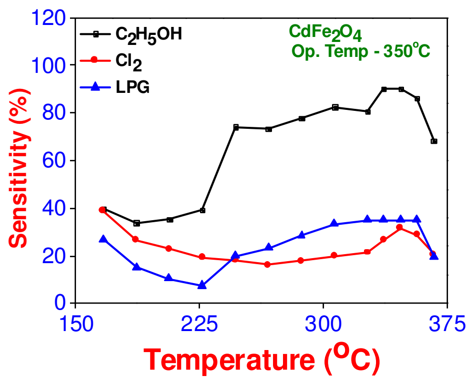

Fig. 4a Variation of sensitivity with temperature of $CdFe_2O_4$

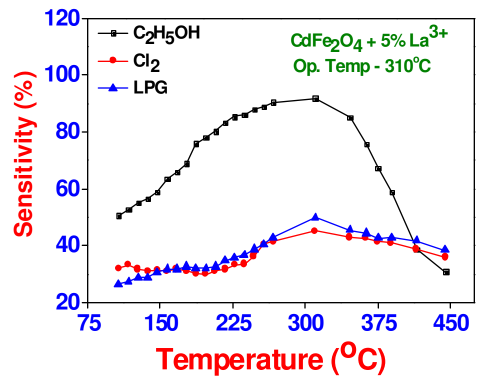

Fig. 4b Variation of sensitivity with temperature of $CdFe_2O_4$+ 5 wt% La^{3+}

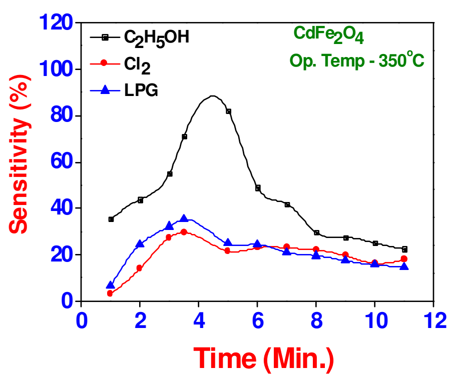

Fig. 5a Response /recovery of $CdFe_2O_4$

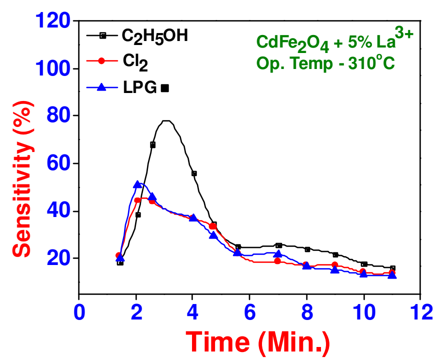

Fig. 5b Response /recovery of $CdFe_2O_4$+ 5 wt% La^{3+}

Conclusion:

Cd-La ferrites under investigation have single phase cubic spinel structure. Their average crystallite size lies in the range of 29.87 to 30.40 nm. Cd-La ferrite sensor exhibits high sensitivity to ethanol and low LPG and Cl_2 at 310°C as compared to Cd ferrite which is attributed to smaller grain size. The shorter response and recovery time is observed for Cd-La ferrite sensor compared to Cd ferrite. The response and recovery times depend on type of gas and composition. The sensitivity and response /recovery time shows that Cd-La ferrite be suitable material for the fabrication of C_2H_5OH (LPG and Cl_2) and sensors respectively.

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