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Synthesis and Gas Sensing Properties of Manganese Ferrite Nanoparticles by Sol - Gel Method

N. N. Gedam[1], A. V. Kadu[2], S. V. Jagtap[3]

[1]Department of Chemistry, M. J. F. Commerce, Science and V. R. Art's College, Bhatkuli, Dist. Amravati.
[2]Department of Chemistry, Prof. Ram Meghe College of Engineering and Management, Badnera, Amravati.
[3]Department of Physics, Bar. R.D.I.K. & N.K.D., Badnera, Amravati.

Abstract:

The purpose of this study is to determine the effect of temperature on the microstructure of Manganese Ferrite **(**$MnFe_2O_4$) nanoparticles. The synthesis of $MnFe_2O_4$ (MFO) nanoparticles carried out by using sol - gel citrate method followed by calcinations. The nanocomposite was characterized by means of x-ray powder diffraction. Obtained XRD measurement data was crystalline in phase with a spinel structure. Additionally, sensor performance of undoped and surface modified by 1.5 wt % Pd over MFO were studied under different operating temperature and different reducing gases such as NH_3, H_2S, CO and ethanol. The result reveals that material exhibit excellent sensitivity and selectivity toward ammonia gas at 180^0C proving their applicability in gas sensors.

Keywords: - Spinel, XRD, Sensitivity, Selectivity.

1. Introduction:

The great release of hazardous pollutants into the environment is increasing with the industrialization progression. The continuous release of different gases such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2) hydrogen sulphide (H_2S), nitrogen dioxide (NO_2) and volatile compounds creates various issues including ozone depletion, acid rain, sick house syndrome and global warming. The toxic gases may cause asthma, skin burning, dizziness, drowsiness, vomiting, nausea, cancer, lung issues, weight loss etc. For safety of living beings including animals, plants and humans, there is a need to develop sensors to detect these toxic gases quickly. Therefore, many researchers are tried to develop gas sensors for the detection of such gases.

Ammonia (NH_3) is a toxic, colourless, and harmful gas, which needs to be detected in medical, industrial and living environments [1, 2]. It is an atmospherically, industrially and biologically key inorganic compound which can be extensively used in many industries including fertilizer, household cleaners, petroleum, fire power plants, rubber, organic compounds, food processing, medicines, automobile, etc. [3, 4]. However, in these applications, there is a high possibility of ammonia release into the atmosphere, causing severe air pollution. Smaller concentrations of ammonia can exert multiple effects on human health including irritation on eyes, skin and upper respiratory tract along with nausea, dizziness and fatigue [5]. On the other hand, higher concentrations of ammonia can cause serious concerns such as cardiac arrest and damage to the birthing system. In short, highly sensitive, instant, accurate and effective ammonia gas sensing at low temperature has become an important factor for health care, environmental monitoring and industrial safety.

Metal oxide based chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic vapors. The main advantages of chemical sensors are their low price, small size, high sensitivity, and low power consumPdion. Numerous materials have been reported to be usable as metal oxide sensors including both single (e.g., ZnO, In_2O_3, CeO_2, SnO_2 and Fe_2O_3) and multi-component oxides ($BiFeO_3$, $MgAl_2O_4$, $SrTiO_3$, and $Sr_{1-y}Ca_yFeO_{3-x}$) for both oxidizing and reducing gases. $MnFe_2O_4$ (MFO) is one of the most promising candidates in MOS based gas sensors. $MnFe_2O_4$ nanoparticles are of great interest for their remarkable inherent biocompatibility because of the presence of Mn^{2+} ions, tunable magnetic properties, higher transition temperature, and excellent chemical stability for room temperature applications. Moreover, nano magnetism of ferrite nanoparticles provides the opportunity for

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several biomedical applications because these possess higher magnetic suscePdibility than normal superparamagnetic materials and negligible coercivity (i.e., field needed to demagnetize) and retentivity (i.e., residual magnetism after field removal). Properties of ferrites depend on their composition and microstructure, which in turn depend on their synthesis processes. There are various chemical and physical methods [6–19] to synthesize ferrite nanoparticles, such as chemical co-precipitation, sol-gel method, reverse micelle, microwave hydrothermal, sonochemical, forced hydrolysis, one-step, high energy ball milling, solvothermal, and microemulsion method. Sol-gel has several advantages over others, such as (i) uniform and homogeneous nanoparticles of semi-spherical sizes (ii) control of particle size by varying the reaction parameters such as reaction temperature (iii) composition flexibility and (iv) large scale preparation technique.

The present work deals with the investigation of doped and undoped $MnFe_2O_4$ synthesized by sol-gel citrate method for high sensitivity towards ammonia gas. The results showed that there is an increase in gas response of MnFe2O4 doped with 1.5 wt% Pd when exposed to ammonia (NH3) than other gases like hydrogen sulphide (H2S), carbon monoxide (CO) and ethanol at an operating temperature 160^0C.

2. Experimental

2.1. Materials

Manganese(II) nitrate tetrahydrate ($Mn(NO_3)_2.4H_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), Citric acid (99.57%), poly vinyl alcohol (PVA) and ethanol were purchased from S.D. Fine chemicals. All the chemicals were of analytical grade, commercially available and used without further purification.

2.2. Materials Synthesis

The nanocrystalline $MnFe_2O_4$ specimen was prepared by using sol-gel citrate method. A stoichiometry mixture of mangenese nitrate and ferric nitrate were magnetically stirred with citric acid and ethanol at 80°C for 2 h to get homogeneous and transparent solution. The solution was further heated at about 130°C for 12 h in a pressure vessel to form the gel precursor. The prepared product was subjected to 3 h heat treatment at 350°C in a muffle furnace and then milled to a fine powder. The dried powder then calcined in the range of 450-750°C in order to improve the crystallinity of ceramic. Incorporation of noble metal such as palladium (Pd) in the $MnFe_2O_4$ was performed by the impregnation technique. Aqueous solution of $PdCl_2$ was impregnated followed by drying over night at 110°C in an oven followed by calcination at 600°C for 2 h.

2.3. Catalyst fabrication

The synthesized nanocompound was ground into a fine powder and mixed with 2 % polyvinyl alcohol (PVA) as a binder and 5 % ethanol as a solvent to obtain a paste. PVA plays many crucial roles in synthesizing nano ferrites including control of the nanoparticles growth, prevention of agglomeration and production of nanoparticles in uniform shapes [20]. The resulting paste was coated onto the alumina tube substrates provided with platinum wire electrodes for electrical contacts. After coating, the element was sintered at 600°C for 2 h in a vertical furnace.

2.4. Physical measurements

2.4.1. X-ray diffraction

The crystal structure of the film was determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with monochromatic CuKα radiation (1.5406 A°). The intensity data were collected over a 2θ range of 20–80^0 C. The average crystallite size of the samples was estimated for prominent peaks with the help of Debey-Scherrer equation

$$D_c = \frac{K\lambda}{\beta\cos\theta} \quad \text{----------- (1)}$$

Where β is the breadth of the observed diffraction line at its half-intensity maximum, k is the shape factor which usually takes a value of about 0.9 and λ is the wavelength of Cu K_α radiation.

2.4.2. Gas Sensing Characterization

The measuring principle of gas sensing properties is described elsewhere. The gas sensitivity (*S*) is defined as the ratio of the change of resistance in presence of gas (Rg) to that in air (Ra),

$$S = (Ra - Rg)/Ra = \Delta R/Ra \qquad \text{----------- (2)}$$

3. Results and Discussion

3.1. X-ray Diffraction

The synthesized samples were characterized by X-ray diffraction. Figure 1 shows the X-ray diffraction (XRD) for MFO prepared by sol-gel citrate method, calcined at 650°C for 6 h. The peaks belong to the spinel ferrite. The broadening of different peaks indicates that the particles are in nanometer scale. Their average crystallite size of the samples was estimated with the help of Debye-Scherrer formula and it was found to be 40 nm.

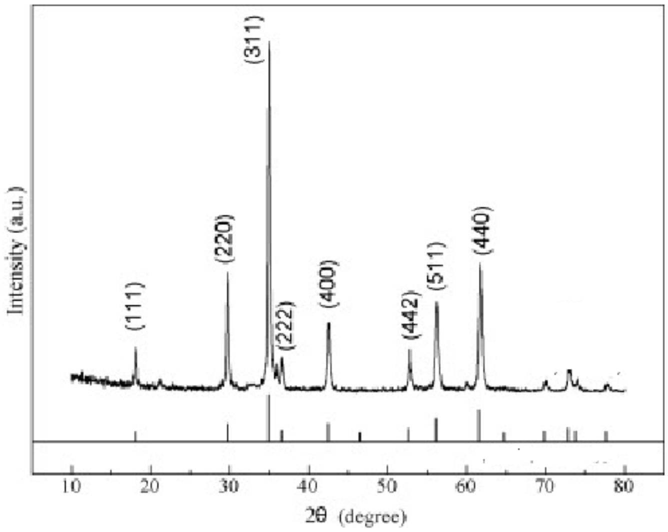

Fig. 1: - XRD pattern of $MnFe_2O_4$

3.2. Gas sensing characteristics

The gas response which is thermally activated depends on the operating temperature is presented in Figure 2, which shows the response of MFO sensor to H_2S, NH_3, CO and ethanol. The gas response was measured as a function of operating temperature. MFO senses all reducing gases but the response for NH_3 gas at 220^{0}C is much higher as compared to other reducing gases.

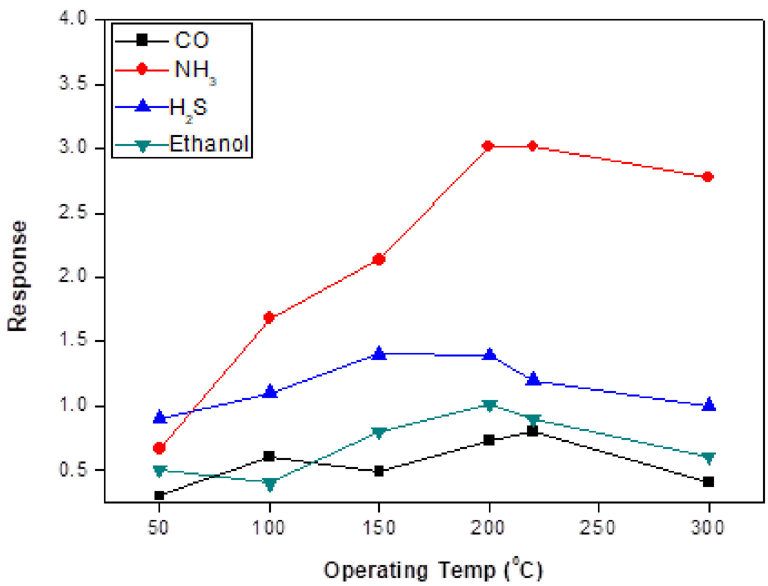

Fig. 2: Response of $MnFe_2O_4$ for various reducing gases as a function of operating temperature.

3.3. Effect of Pd as an additive

Figure 3 shows the sensor response versus operating temperature for the 1.5 wt.% Pd incorporated MFO nanoparticles towards NH_3. From the graph it is clearly evident that incorporation of Pd results in a drastic decrease in the operating temperature for maximum response by more than 50^0C. The operating temperature for the maximum response is observed around 160^0C. The Pd doped makes possible NH_3 adsorption at lower operating temperatures, and thus the sensitivity of the Pd doped sensor to NH_3 is quite large. Hence due to incorporation of noble metal Pd in synthesized samples, it not only increases the sensor response but also increases the selectivity of NH_3 gas against remaining reducing gases.

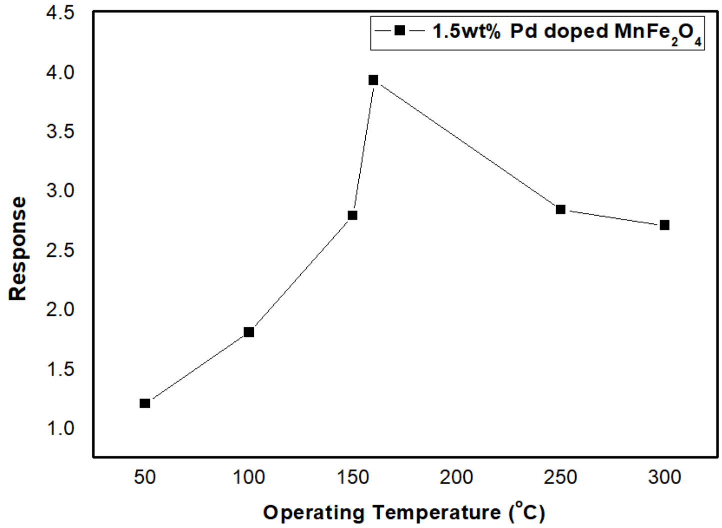

Fig 3: - Sensor response versus operating temperature for the 1.5 wt.% Pd doped MFO

4. Conclusion

In summary, (1) we synthesized nanocrystalline $MnFe_2O_4$ by a using sol-gel citrate method. (2) XRD pattern of $MnFe_2O_4$ shows nanocrystalline with average particles size 40 nm. (3) The material was found to be good sensitive towards NH_3 in comparison to other reducing gases. (5) Pd incorporation lowered the operating temperature by more than 50^0C and improves the sensing characteristics of NH_3.

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