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Magnetic, dielectric and sensing properties of manganese substituted copper ferrite nanoparticles

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ABSTRACT

Manganese substituted copper ferrite nanoparticles were synthesized by an auto-combustion technique using metal nitrates and urea for gas sensor application. The products were characterized by XRD, SEM, EDX, TEM and VSM techniques. The effect of annealing temperature on the particle size, magnetic and dielectric properties of Mn–Cu ferrite nanoparticles was analyzed. The size of the particles are in the range of ~9–45 nm. The effect of annealing on the magnetic properties is discussed with the help of variation in saturation magnetization (*Ms*) and coercivity (*Hc*) by vibrating sample magnetometer (VSM). The dielectric loss and dielectric constant have been measured in the frequency range of 100 kHz–5 MHz. Furthermore, Conductance response of Mn–Cu ferrite nanomaterial was measured by exposing the material to reducing gas like liquefied petroleum gas (LPG).

1. Introduction

A great attention is focused nowadays on sensors in the field of nano research. At the same time the behavior of sensing materials is induced due to the change in property of materials at nano scale. These certain behaviors change is clearly identified in the ferrite nanoparticles, which are favorably exhibiting the sensor properties. Nanosized manganese substituted copper ferrites are found to exhibit interesting structural and magnetic properties. The possible different applications of the ferrite nanoparticles are magnetic storage, as precursors for ferrofluids, magnetic guided drug-delivery agents and gas sensors [1,2]. Recent years have seen increased interests in studying the gas sensing properties of ferrites [3–6]. Y-L. Liu et al. reported the sensing response of magnesium ferrite ($MgFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) for methane (CH_4), hydrogen sulfide (H_2S), liquefied petroleum gas (LPG) and ethanol gas (C_2H_5OH) [2,4]. The gas sensing response of copper ferrite ($CuFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) for hydrogen sulfide (H_2S) and that of nickel ferrite ($NiFe_2O_4$) for chlorine gas (Cl_2) was reported by Gopal Reddy et al. [3]. The novelty of copper in the ferrites has identified extensively for use in sensor application. The magnetic behavior of $CuFe_2O_4$ has been reported by J.Z. Jiang et al. and P.B. Pandya et al. [7,8]. We gathered only very limited information about the gas sensing properties of nanocrystalline ferrites to reducing gases. Consequently, it is interesting to investigate the gas-sensing properties of ferrites. Also it reveals that the magnetic properties and gas-sensing efficiency of the material depend on its micro-structure properties. There are several methods for synthesizing nanosized magnetic spinel ferrite particles, such as co-precipitation [9–12], sol–gel [13], standard double-sintering method [14], microwave-induced combustion [15], microwave sintering method [16], sol–gel auto-combustion method [17], reverse micelle reaction process [18], and evaporation method [19]. The present attempt is made on manganese substituted copper ferrite nanoparticles by an auto-combustion method using urea as a fuel. The study mainly focuses on the effect of manganese substitution and preparation method on the magnetic and gas-sensing properties of $CuFe_2O_4$ nanoparticles. The results indicate that the process is convenient, inexpensive, environment friendly and efficient for preparation of Mn substituted $CuFe_2O_4$ nanoparticles with the grain size of about ~9–45 nm and also the sensor responding appreciably to different gases like methanol, ethanol, LPG, NH_3, H_2 and CO.

2. Experimental technique

2.1. Synthesis process

Nanocrystalline manganese doped cupper ferrite has been prepared with the chemical formula $Mn_{0.4}Cu_{0.6}Fe_2O_4$ by an auto-combustion technique. The analytical grade manganese nitrate [$Mn(NO_3)_2 \cdot 6H_2O$], copper nitrate [$Cu(NO_3)_2 \cdot 6H_2O$], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], and urea [$CO(NH_2)_2$] were used as raw materials. Subsequently, 5.02 g of manganese nitrate, 8.37 g of cupper nitrate, 40.4 g of ferric nitrate and urea were dissolved in

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deionized water to form mixed solution, using a magnetic stirrer. Then the mixture was heated at 160 °C to dehydrate until self-ignition takes place. Being ignited in air at room temperature, the dried gel burnt in a self propagating combustion, giving rise to the evolution of large amount of gases and producing a dry and loose ferrite powder. Throughout the process no pH adjustment was made. The influence of heat treatment on particle size and dielectric properties were studied, a portion of the as-burnt ferrite powders was sintered at 600 °C and 900 °C for 5 h.

2.2. Equipment used for characterization

The Mn–Cu ferrite powders were subjected to XRD analysis with Rigaku X-ray diffraction unit (Model ULTIMA III) to explore the structural properties. The Scanning electron microscope (SEM with EDX) was used to examine the particle morphology, using a JEOL 5600LV microscope at an accelerating voltage of 10 kV. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were recorded on a Technai G20-stwin using an accelerating voltage of 200 kV. The magnetic properties of the samples were investigated using vibrating sample magnetometer (Lakeshore VSM 7410). The dielectric properties of as-burnt and sintered samples were measured by Digital LCR meter (Model TH2816A) in the frequency range from 100 kHz to 5 MHz.

2.3. Gas sensor process

For chemical sensor application, the sensor materials were mixed and ground with deionized water in an agate mortar to form a paste, then the resulting paste was coated on an alumina tube substrate having a pair of silver electrodes on either side followed by drying and calcination at 400 °C for 2 h. Finally, a Ni–Cr heating wire was inserted into the tube to heat the sensor. Measurements were carried out at different temperatures, different concentrations of gas etc. The sensor response (S), defined as the ratio ($S = (Ra\text{-}Rg)/Ra$), where Ra and Rg are the sensor resistance in air and in test gas, respectively. The response time is defined as the time required for the variation in conductance to reach 90% of the equilibrium value after which a test gas is injected. The recovery time as the time necessary for the sensor returned to its original conductance in air.

3. Results and discussion

3.1. Structural analysis

Fig. 1 depicts the XRD pattern to determine the phase compositions of the as-burnt and annealed samples of Mn–Cu ferrite nanoparticles under different fuel ratios. The reflection peaks correspond to the characteristic interplanar spacing between (220), (311), (222), (400), (422), (511) and (440) planes of the spinel ferrite with a cubic symmetry, demonstrating the formation of Mn–Cu ferrites as per JCPDS data (74-2072). XRD pattern of the as-burnt powder contains no secondary peaks, which suggests that the sample has pure spinel structure. From the results, the Mn–Cu ferrite phase formed contained some impurity peaks, which are due to decomposition of the ferrites to α-Fe_2O_3 phase, above the annealing temperature of 500 °C [20–22]. These secondary peaks slowly dissolved at 900 °C, it may be fully dissolved above 1200 °C [23,24]. The diffraction peaks become narrower and sharper suggesting that there is an increase in particle size upon annealing. The average particle size of prepared powder has been calculated using Debye-Scherer formula [25].

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

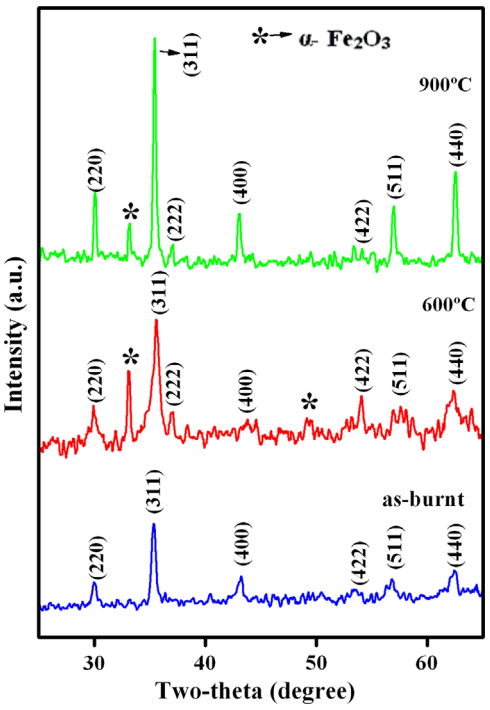

Fig. 1. Indexed XRD pattern of manganese substituted $CuFe_2O_4$ nanoparticles.

Table 1
Crystal parameters of Mn–Cu ferrite nanoparticles (A—as burnt, B—annealed at 600 °C and C—annealed at 900 °C).

Parameters	Mn–Cu ferrite nanoparticles		
	Sample (A)	Sample (B)	Sample (C)
Particle size (t) nm	9	16	47
Lattice constant(a) Å	8.41	8.42	8.42
Saturation magnetization (Ms) emu/g	63.9	19.9	29.3
Coercivity (Hc) G	118.9	237.3	150.4
Dielectric constant (ε)	854.3	501.2	398.7
Dielectric loss (D)	4.96	4.46	3.08

The lattice parameter (a) has been calculated from X-ray diffraction data using the formula.

$$\frac{1}{d^2} = \frac{1}{a^2}(h^2 + k^2 + l^2) \quad (2)$$

The crystalline size (t) and lattice parameter (a) for all the samples are listed in Table 1. From the table, it is clear that lattice parameter and crystalline size were increased with annealing temperature. The crystalline sizes of the samples are in the range ~9–45 nm.

3.2. SEM and EDX analysis

The external morphology of the nanocrystalline Mn–Cu ferrite nanoparticles annealed at 900 °C has been visualized by scanning electron micrograph (SEM). From Fig. 2a, the SEM photographs of Mn–Cu ferrite nanoparticles clearly show the agglomeration of primary nanoparticles to give large and irregular crystals, which may be the effect of preparation method, defects and also the effect of annealing. The compositional analysis of the nanocrystalline