Preparation and humidity sensing behavior of cadmium – zinc ferrite nanocomposite

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Abstract. Cadmium Zinc ferrite (Cd₀.₈Zn₀.₂Fe₂O₄) nano-composites (NC) were prepared by auto-combustion method, and annealed at 650°C. The humidity sensing behavior of this composite has been studied. The ability of a ferrite to sense the ambient water molecules depends on their interaction with ferrite material’s porous surface. The Cd₀.₈Zn₀.₂Fe₂O₄ NC samples exhibit a high value of sensitivity to humidity, equal to 1.483 MΩ%/RH; this high sensitivity is due to two reasons. The first reason for this is the porous morphology of the prepared NC samples, confirmed from the SEM images. The second reason is the low value of crystallite size as more active sites for adsorption and desorption of water molecules become possible when the crystallite size is reduced. The humidity sensing behavior of the prepared composite films, based on electrical impedance measurements, exhibit an excellent reproducibility of 98%, as well as good response and recovery times of 86 seconds and 44 seconds, respectively. Therefore, it is a good candidate for humidity sensing applications.

1. Introduction

The preparation of a good humidity sensor is vital in many areas of use, like manufacturing processes, different industries, environment, human health monitoring as well as in the maintenance of humidity in the surroundings of different characterization instruments. High relative humidity (RH) can adversely affect materials, pharmaceuticals, food products as well as human comfort; therefore, there is a need to control the same. In this direction, it is necessary to use a highly sensitive humidity sensor having good response and recovery time as well as repeatability. Nano-structured metal oxides, ceramics (including mixed ferrite materials) and polymeric materials based humidity sensors are based on monitoring one of the humidity sensitive electrical properties of the material, like for example, its electrical resistivity, capacitance or impedance [1, 2]. Ceramic material based humidity sensors can be used at room temperature. Nano-ceramics can be used as humidity sensors due to the porous nature of this material, the pores being created during the combustion process. The ability of a ferrite to sense the ambient water molecules depends on their interaction with ferrite material’s porous surface. In other words, it depends on the reactivity of the surface (of the ferrite material). In fact, this reactivity varies with the changes in composition as well as morphological structure of the ferrite material. This depends on the method of its preparation. The different methods of preparing ferrites are chemical co-precipitation methods, which include sol-gel method, milling and auto-combustion methods, sono-
chemical technique, reverse micelle method and thermal (including hydro-thermal) preparation technique. The study of metal ferrite materials for sensor applications is of contemporary research interest [3]. In fact the synthesis of cadmium zinc ferrites by various methods like solid state reaction method [4] and soft chemical synthesis method [5] and the characterization of the prepared material using various techniques like x-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Mossbauer Spectroscopy [6] and Coincidence Doppler Broadening Spectroscopy (CDBS) technique of Positron Annihilation Spectroscopy [7] among many others has been performed by researchers. The studies revealed that the Cd–Zn ferrite samples prepared by solid state reaction method have a cubic spinel ferrite structure and that the prepared ferrite has a paramagnetic nature. In this direction, the application of Cd–Zn ferrites as a photo-catalyst has been explored [5]. It was found that cadmium substituted zinc ferrites exhibits the highest levels of photo-catalytic activity when exposed to solar radiation, when compared to zinc ferrites and cadmium ferrites. The electrical conductivity of Cd–Zn ferrites has been investigated by Ghatak et al [8]. In this paper, the zinc cadmium ferrite of a particular optimized composition has been prepared by auto-combustion method, and its application as a humidity sensor has been comprehensively investigated by performing suitable experiments.

2. Materials and methods

In this section, the auto-combustion method which has been followed to prepare the Zn-Cd ferrites will be described. This will be followed by a discussion on the technique used to study the humidity sensing behaviour of the prepared samples.

2.1. Sample preparation

The preparation of cadmium zinc (Cd$_x$Zn$_{1-x}$Fe$_2$O$_4$, with $x=0.8$) NC ferrite was by following an auto-combustion method, with citric acid as the fuel. Cadmium nitrate, ferric nitrate and zinc ferrite, in proper stoichiometric ratio, were separately dissolved in double distilled water. A suitable weight of citric acid (fuel) was also dissolved separately in distilled water; then, all three solutions were mixed thoroughly to form a homogeneous solution. Later, ammonium hydroxide was added to obtain pH of seven (neutral solution of the mixture). The mixture was then continuously stirred on a heating mantle maintained at 90°C till combustion takes place. After the combustion is completed, the resultant (residue) was powdered using mortar and pestle. The powder was carefully stored in a properly labeled container and sealed. Later, the powder was annealed in a vacuum furnace maintained at 650°C in order to obtain the final product (cadmium zinc nano-composite ferrite material). Agglomeration of nano-particles can be reduced at higher sintering temperatures. The prepared nano-composite was characterized by using different techniques.
Figure 1a. Graph of impedance versus percentage relative humidity. The repeatability or reproducibility of the measurement was approximately 98%.

2.2. Experimental apparatus

The set-up to measure humidity based on the value of an electrical parameter (impedance) has been described in detail elsewhere [9-12]. It consists of a chamber made of glass (wherein the humidity is controlled); in this glass chamber, the actual sensor (sensing element) was fixed by using electrodes made of silver and the sample was connected to an impedance analyzer (Wayne Kerr Precision Component Analyzer, 6440B); the impedance measurements were performed at a frequency of 300 Hz [9]. The processes of humidification and dehumidification were achieved by using saturated aqueous solutions of potassium sulfate and potassium hydroxide, respectively. The percentage Relative Humidity (%RH) inside the chamber was measured using a standard hygrometer (HTC-1 hygrometer). The humidity sensing characteristics of the sample for the range of humidity varying from 10 up to 95 %RH have been investigated.

3. Results and discussion

The change in the electrical impedance of the sample (sensor) with increase in %RH has been measured using an impedance analyzer as described earlier in the experimental section of this paper. The data obtained are graphically displayed in Fig. 1(a–c). From these plots, it can be seen that the electrical impedance of the film decreases with an increase in %RH in the chamber (as sensed by the sensing element).
The plot of impedance versus time is given in this figure. From this data, the response time was determined to be 86 seconds and the recovery time is 44 seconds.

The fig 1 (a-c) shows three distinct sections for the variation of electrical impedance with %RH, namely, a low humidity region which varies from 10 up to 35 %RH, a mid-humid section in the %RH range between 35 and 60 %RH and finally, a high humidity section in the region from 60 up to 90 %RH [9-11]. A good humidity sensor is expected to have a high sensitivity and reproducibility (or repeatability), as well as low response and recovery times. The change in electrical impedance of the prepared ferrite material with respect to a corresponding change in %RH is defined as the sensitivity of the prepared material for humidity sensing applications. The sensitivity is determined from the plot of electrical impedance of the sample versus the %RH (the sensing response curve), from the slope of the straight line fit, as shown in Fig.1 (c) [9-11]. The average value of sensitivity is calculated by taking the mean of all the measured values of sensitivity in the three regions mentioned earlier, and covering the entire range of %RH, starting from 10 up to 90 %RH. The Cd$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ NC samples exhibit a high value of average sensitivity to humidity, equal to 1.483 MΩ/%RH; this high sensitivity is due to two reasons. One of the main reasons for this high sensitivity is the porous nature of the surface morphology (see Fig. 2 (a-c) and Fig 3 (a-c)). Another important factor is the low crystallite size of the sample material; this is because of the fact that the surface to volume ratio increases as the crystallite size decreases, and therefore more active sites for adsorption and desorption of water molecules are possible [9-12]. It can also be noted from Fig 1 (c) that the sensor is most sensitive in the lower ranges of %RH, whereas it is least sensitive in the higher range of %RH. Some other parameters of the sensor, namely, repeatability (reproducibility) and response as well as recovery time of the sensor have also been investigated and shown in Fig. 1(a–b). The material gave ~98% reproducible results, as can be seen from Fig 1 (a), by variation of RH% in both increasing and decreasing order, that is, from the adsorption and desorption profiles, respectively.
Figure 1c. The plot of impedance versus %RH is shown in the figure. Sensitivity was measured to be 1.483 MΩ/%RH.

The humidity sensing mechanism for the nature of plots shown in Fig 1 (a-c) can be explained with the help of a chain reaction process (which occurs on the surface of a porous film), called the Grotthuss chain reaction. Note that, at the beginning (just before the sensor material was exposed to moisture), the composite material was dried and has vacant pores on its surface. So, with exposure to moisture in the glass chamber, the hydroxyl ions (OH\(^-\)) of the water molecules will be attracted to the positively charged metal ions (M\(^+\)) on the surface of the sample. This electrostatic force results in a linkage between the OH\(^-\) and M\(^+\), and thus forms a chemisorbed layer [10-12]. During this chemisorption process, hydronium ion (H\(^+\)) is released, which is responsible for the decrease in the electrical impedance of this composite sample. Therefore, a sharp decrease in impedance and consequently, a high sensitivity is observed in the less humid (low %RH) region. As the humidity inside the chamber increases, the water molecules form the next layer on the sample surface, but because of the larger distance in this case, when compared to the first layer, obviously lesser magnitude of electrical force acts between OH\(^-\) and M\(^+\). Hence, the physically adsorbed water molecules in the second layer form a physisorbed layer which is attracted by the weak Vander Waals’ forces. So, relatively less number of H\(^+\) ions is produced in this case, and this is manifested experimentally as a relatively less drop in impedance. Therefore, less sensitivity to humidity is observed in middle range of %RH. The situation aggravates in the high humidity region, wherein multiple physisorbed layers of water molecules are formed on the surface of the sample. In addition, capillary condensation too takes place in this high humid region. Hence, because of the least production of H\(^+\) ions, there is the lowest change or decrease in the experimentally measured impedance with respect to %RH in the high humidity region and therefore, the sample shows the least sensitivity to humidity in this region.
Figure 2 (a-c). SEM images of the Cd$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ nano-composite (before annealing) showing a porous structure.

Figure 3 (a-c). SEM images of the Cd$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ nano-composite (after annealing at 650°C) showing the nano-structural and porous features of the Zn-Cd nano-ferrite material used for humidity sensing applications.

Fig. 2 (a-c) shows the SEM images of the nano-composite, as prepared, revealing a porous morphology, whereas the SEM images in Fig. 3 (a-c) show the nano-features of the prepared ferrite as well as its porous nature, after annealing it in a vacuum furnace at 650°C. These images confirm the porous and nano-structural features of the prepared composite material (by auto-combustion method), before and after annealing.

4. Conclusions
An auto-combustion chemical approach with citric acid as fuel was used to prepare Cadmium Zinc ferrite (Cd$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$) nano-composite material from its chemical precursors. After suitable characterization, the humidity sensing behavior of this composite has been studied. The average value of sensitivity of this material is found to be equal to 1.483 MΩ/%RH. The response time is 86 s and the recovery time is 44 s. Sensor measurements were made with a reproducibility of 98%.

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