

An Experimental Study of Metal Ferrite Nanoparticles with Special Reference to Nickel Ferrite, Zinc Ferrite, and Cobalt Ferrite

Thinzar Wut Yee^{*}, Htee Mu Wah^{**}, Aung Thu Hein^{***}, Aye Aye Hnin^{****}

Abstract

Using the conventional ceramic technique, humidity sensitivity of metal ferrite nanoparticles [MFe₂O₄, M (II) = Ni, Zn, and Co] was examined. The spinel structure and infrared spectral analysis of the compounds prepared by this method were confirmed by XRD and FTIR studies. Furthermore, the surface morphology was observed by scanning electron microscopy. All the samples were also subjected to dc electrical conductivity studies at room temperature. For the applications of humidity sensing materials, the resistance of the samples was observed in the relative humidity range of 40 RH% – 98 RH% and the sensitivity factors ($S_f = RH_{40\%}/RH_{98\%}$) were calculated. Among the metal ferrites, Zinc ferrite possessed the highest humidity sensitivity factor whereas Nickel ferrite and Cobalt ferrite possessed low sensitivity factors.

Keywords: humidity sensor, metal ferrite nanoparticles, conventional ceramic technique, electrical conductivity, electron microscopy

1. Introduction

According to the cutting edge technology, ferrites are employed in a truly wide range of applications because of their effectiveness as magnetic materials, semiconductors, pigments, catalysts refractories and have been contributed materially to the advances in electronics. In the area of new materials, ferrites with permeability up to 30,000 and power ferrites for frequencies up to 10 MHz have been made available commercially [Li, (2010)]. Moreover, improvements and innovations continue to take place; many new theories, applications, and preparation technologies are currently development under the field of ferrites [Maria1, (2013)]. The majority of metal oxides, mixed metal oxides and ferrites have revealed better sensitivity to certain gas and humidity. Furthermore, Cobalt ferrite (CoFe₂O₄), copper ferrite (CuFe₂O₄) and nickel ferrite (NiFe₂O₄) are inverse spinels. However, ZnFe₂O₄ has a normal spinel structure with Zn²⁺ in tetrahedral sites and Fe³⁺ occupying octahedral sites. Nickel ferrite, as a p-type semiconducting oxide, is a good sensor for detecting oxidizing gases like chlorine. Cobalt and copper ferrites are p-type semiconductors, whereas zinc and magnesium ferrites are n-type semiconductors. For various gas-sensing applications, NiFe₂O₄, CdFe₂O₄ and ZnFe₂O₄ spinel ferrites have been extensively studied. [Satyanarayana, L, Reddy, K M and Sunkara, V M. (2003)].

Due to the recognized importance of water vapor concentration the measurement of humidity has received great attention in many areas where meteorology, medicine, industry and agriculture. The desirable characteristics of humidity sensors are high sensitivity, good chemical and thermal stability. The relative humidity (RH), which is the ratio of actual vapour pressure to the saturated vapour pressure at a given temperature, is the most frequently used parameter to specify humidity. [Xiao, S H, Xu, H J, Hu, J, Jiang, W F and Li, X J. (2008)]

In this work, the samples were prepared by conventional ceramic technique which is appropriate, environmentally-friendly, economical and efficient. The synthesized metal ferrite nanoparticles were explored for their humidity-sensing property.

* Dr., Demonstrator, Department of Physics, Bago University

** Assistant Lecturer, Department of Physics, Bago University

*** Assistant Lecturer, Department of Physics, Bago University

**** Dr., Associate Professor, Department of Physics, Bago University

2. Experimental procedure

2.1. Preparation of MFe_2O_4 [M (II) = Ni, Zn, Co]

In this work, metal ferrites were prepared by the conventional ceramic method.

Firstly, the raw materials of Analytical Reagent (AR) grade: Nickel Oxide (NiO) and Iron Oxide (Fe_2O_3); Zinc oxide (ZnO) and Iron Oxide (Fe_2O_3); Cobalt oxide (CoO) and Iron Oxide (Fe_2O_3) were weighed according to their desired stoichiometric compositions and mixed. Secondly, the mixture of each sample was ground by ball-milling for 3 h using a laboratory-made ball-milling machine to be very fine powder and to prepare precursor solid solution. Finally, the precursor solid solutions were calcined at 1080°C for 3 h in vacuum chamber.

2.2. Fabrication of humidity sensor

The calcined ferrites were ground again with acetone for about 3 h in an agate mortar, then the as-prepared ferrites were made circular shape pellets by using hydraulic pellet-maker with the pressure 5 ton (~ 70 MPa). Then the pellets were polished by using filtered-paper to get the smoothing surface. Dimensions of the samples were measured by using digital Vernier-Caliper (Taiwan). Thicknesses of the samples are listed in Table 1. Area of the each of the sample was used as $1.14 \times 10^{-4} \text{ m}^2$. These sample powders and pellets were sintered at 1200°C for 4 h in an air atmosphere to complete the inter-diffusion of the component metal ions into the desired crystal lattice. The samples were heated and cooled at the room temperature.

2.3. Method of characterization

The structural studies were carried out using X-ray diffractometer for 2θ values ranging from 10° to 70° using Cu-K α radiation at $\lambda = 1.5418 \text{ \AA}$. The crystallite size D was calculated using the Debye–Scherrer formula $D = \frac{0.89\lambda}{\beta \cos\theta}$, where λ is the wavelength of the incident X-ray, and β is the full width at half maximum in radians of the maximum intensity peak and θ is the angle at which the maximum peak occurs. The values of the lattice parameter ‘ a ’ for the samples were calculated by using the formula $a = d\sqrt{h^2 + k^2 + l^2}$, where h , k and l are the miller indices of the crystal plane and ‘ d ’ is the interplanar spacing obtained by the XRD pattern. Moreover, the surface morphology of the sintered metal ferrite samples compacts was studied by SEM at the desired magnification.

2.4. Humidity and Electrical conductance measurements

In this measurement, to measure the changes in surface conductivity, the dc electrical resistance of the samples in different humidity levels in the form of pellets was determined by a two-probe method as a function of the applied field. The silver paste was used as a conductor to ensure ohmic contacts. The samples were electrically connected to a dc power supply and XSW TDK 0302 Humidity Meter in series. Humidity sensitive electrical resistances and voltages of the samples were observed in the relative humidity range of 40 RH% – 98 RH% by using FLUKE 189 digital multimeter. The refrigerator was used as the humidity generator. The sensitivity factor, S_f , was calculated by the ratio of resistances, $R_{40\%}/R_{98\%}$, where $R_{40\%}$ and $R_{98\%}$ are the dc resistances at 40% and 98% RH, respectively.

To determine the activation energy of the samples, the temperature-dependent electrical conductance experiments were carried out using the linearized form of the expression

$I = I_0 \exp \frac{E_a}{kT}$, where I is current, E_a the activation energy, k the Boltzmann constant and T the temperature ($^{\circ}\text{C}$). To get this goal, the samples were kept inside a cylindrical furnace, which was connected to a microprocessor-controlled temperature programmer. In the temperature range, $120\text{--}300^{\circ}\text{C}$ under ambient conditions, the activation energy of the composites was determined from the temperature-dependent electrical conductance experiments.

3. Results and discussion

3.1. FTIR studies

As a common feature of all spinel ferrites, figure (1.a-c) showed two absorption bands below 600 cm^{-1} . The high-frequency band (tetrahedral site is assumed as ν_1 -mode) lies in the $580\text{--}600\text{ cm}^{-1}$ range and the low-frequency band (octahedral site molecule is assigned as ν_2 -mode) in the $400\text{--}420\text{ cm}^{-1}$ range. This difference in the band position is attributed to the vibration of tetrahedral and octahedral components in the spinel ferrites. Generally, the results indicate the phase formation of the samples (with molecular vibration).

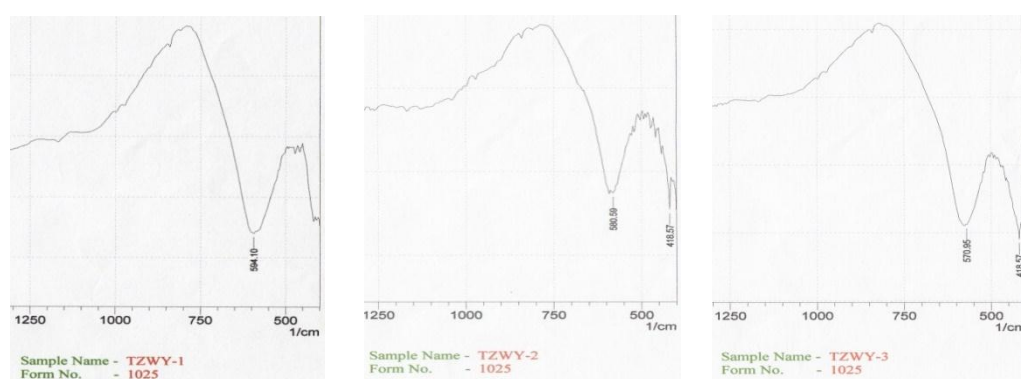


Figure1. FTIR spectra of (a) NiFe_2O_4 , (b) ZnFe_2O_4 and (c) CoFe_2O_4

3.2. X-ray diffraction studies

The powder XRD figure (2.a-c) showed peaks corresponding to NiFe_2O_4 , ZnFe_2O_4 and CoFe_2O_4 . All the peaks correspond to the metal ferrites. On comparison with the standard JCPDS profiles and the experimental results, the phases NiFe_2O_4 (JCPDS: 89-4927, Cubic), ZnFe_2O_4 (JCPDS: 89-1012, Cubic) and CoFe_2O_4 (JCPDS: 22-1086, Cubic) are identified. The average crystallite size of all the metal ferrite samples calculated by Debye–Scherrer's formula is found to be $44\text{--}64\text{ nm}$, which confirms that the prepared sample powders have nanocrystalline nature. The values of crystallite sizes and the lattice parameter are calculated from the most prominent peak in the XRD are shown in Table 1.

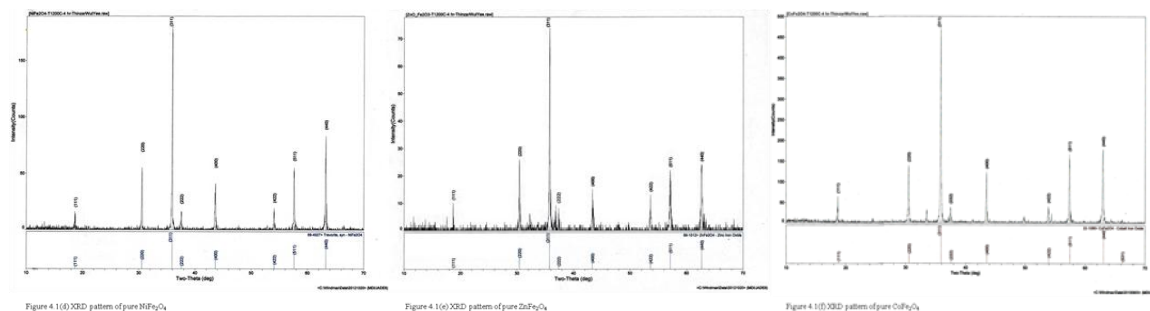


Figure 2. X-ray diffraction spectra of (a) NiFe_2O_4 , (b) ZnFe_2O_4 , and (c) CoFe_2O_4 .

3.3. Scanning electron microscopy

To understand the relationship between the parameters as well as the behaviour when used in practical applications and examine the microstructure and morphology as an important role in determining the magnetic and electrical properties of the samples, scanning electron microscope (SEM) was used. Figure (3.a-c) depicts the structure of the sample materials where were exposed the grain shape was irregular distribution of grains like that spherical in nature. And then the samples are composed of round aggregates of small grains. Among them, some pores have poor grain boundary in which ZnFe_2O_4 was the clear grain boundary. The grain sizes of the samples are listed in Table 1.

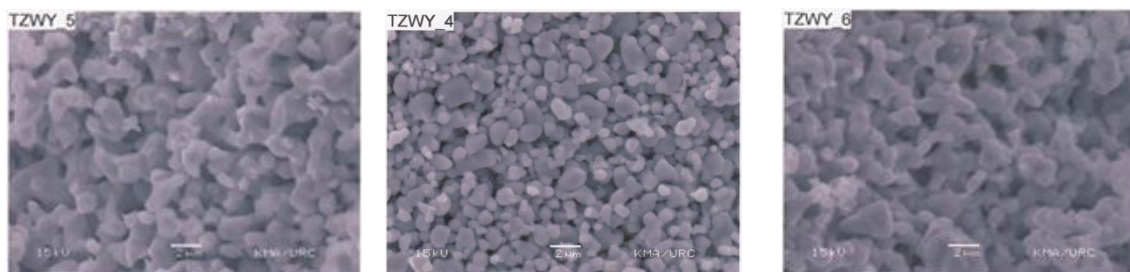


Figure 3. SEM micrograph of (a) NiFe_2O_4 , (b) ZnFe_2O_4 , and (c) CoFe_2O_4 .

3.4. Electrical Conductance Study

In this paper, to indicate the ohmic contact of the electrodes, electrical conductance measurement of all the samples suggested that the current increased linearly with the applied voltage. When applying voltage was 10 V, the temperature dependence of electrical conductance carried out in the 120–300°C range. In polycrystalline materials, the activation energy for electrical conduction includes the energy required to raise the carriers from the dominant levels to their corresponding transport bands. And it also required creating the carriers in the dominant levels. The activation energies calculated from the temperature dependence of conductance data are listed in Table 1.

3.5. Humidity Sensitive Electrical Properties Study

Humidity sensitive electrical resistances R_H versus relative humidity RH% of the investigated NiFe_2O_4 , ZnFe_2O_4 and CoFe_2O_4 are shown in figure (4.a-c). As shown in these graphs, the electrical resistance of NiFe_2O_4 , ZnFe_2O_4 and CoFe_2O_4 decreased with increase in relative humidity. For NiFe_2O_4 , it showed a resistance of 72.959M Ω at 40% RH and 9.6670M Ω at 98% RH, respectively. Similarly, the RH% of ZnFe_2O_4 showed a resistance of 65.129M Ω and 2.325M Ω at 40% and 98% respectively. The RH% of CoFe_2O_4 showed a resistance of 96.746M Ω and 9.966M Ω at 40% and 98% respectively. The obtained sensitivity factors (S_f) of the samples are tabulated in Table 1. As a presented result, the sensitivity factor of the pure ZnFe_2O_4 was the largest one. It can be suggested that microstructure (porosity, grain size, and structural defects) has a great role in the electrical resistivity. Smaller grains imply an increase of the grain boundary surface which normally account for high resistivity of a polycrystalline material. The larger the specific surface area and porosity of the specimens, the more water vapours can be physically adsorbed, resulting in a larger decrease of the resistivity.

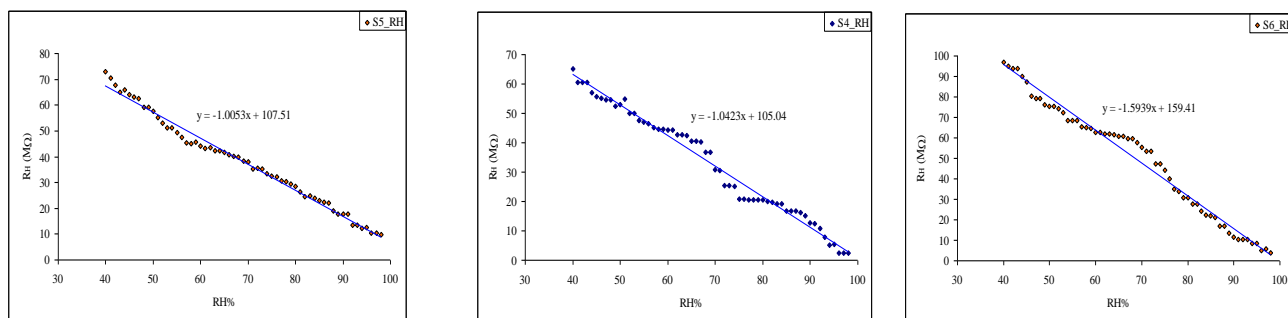


Figure 4. Plot of the variation of electrical resistance R_H with relative humidity RH% of (a) NiFe_2O_4 , (b) ZnFe_2O_4 , and (c) CoFe_2O_4 .

Compound	Thickness (mm)	Lattice constants (\AA)	crystallite size (nm)	Grain size (μm)	Activation energy (eV)	Sensitivity factor (S_f)
NiFe_2O_4	2.62	8.2697	46.83	0.40 – 1.60	0.104	7.5472
ZnFe_2O_4	2.57	8.3219	63.30	0.40 – 1.40	0.093	28.0124
CoFe_2O_4	2.52	8.2939	54.02	0.80 – 2.20	0.103	9.7076

Table 1. Structural, physical characteristics, activation energy and humidity response of the ferrite compound

Conclusion

Metal ferrite nanoparticles have been successfully experimented by the conventional ceramic technique. The samples were heated at 1200°C for 4 h and studied for humidity sensing behavior by XRD, FTIR and SEM methods. The XRD demonstrates that the samples are single-phase crystalline materials and cubic structures. The FTIR spectra show that the phase formation of the samples is valid. The SEM studies revealed that the samples were Nano grain size. All the studies exhibited that Zinc ferrite is a good material for humidity sensor due to the higher sensitivity factor of 28.0124. Furthermore, according to the higher surface area and higher porosity formed in the surface of the samples, Zinc ferrite has a rich humidity sensing factor. The low activation energy of the samples is a huge improvement for a good humidity sensor. Nevertheless, the poor-sensitivity factors of Nickel ferrite and Cobalt ferrite are suitable for the electrical devices.

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