J. Myanmar Acad. Arts Sci. 2018 **Vol. XVI. No.2**

STUDY ON ELECTRICAL PROPERTIES OF NICKEL-ZINC-COBALT FERRITES HUMIDITY SENSORS

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Abstract

Nickel-Zinc-Cobalt ferrites with the formula $Ni_{0.97-x}Zn_x Co_{0.03} Fe_2O_4$(where x = 0.25, 0.50 and 0.75) and pure $NiFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$havebeen prepared by conventional ceramic technique. Starting materials of Analytical Reagent (AR) grade Nickel Oxide (NiO), Zinc Oxide (ZnO), Cobalt Oxide (Co_3O_4), and Iron Oxide (Fe_2O_3) with the desired stoichiometric compositions were used to synthesis the samples. Theas-prepared samples were made into circular shape pellets and their electrical properties were investigated in the relative humidity range of 40 RH% – 98RH%.The electrical resistance decreased with increase in relative humidity and the dc voltage and capacitance increased with increase in relative humidity. Sensitivity and sensitivity factor of the samples were examined for the application of humidity sensor.

Keywords: Nickel-Zinc-Cobalt ferrites, $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$, conventional ceramic technique, relative humidity, Sensitivity and sensitivity factor

Introduction

A humidity sensor is a device which can covert the ambient moisture variation into an electrical signal variation. The humidity sensors can be classified as resistive-type and capacitive-type. The sensitive materials will gradually change due to a very slow irreversible reaction with water vapor in atmosphere. The investigation for the problem is focused on improving water-resistive properties of the material. Humidity sensors based on semiconducting oxides have certain advantages compared to other types of humidity sensors(Ahmad, 2012; Harris, 2009; IIslam, 1998).

Spinel ferrites, with common formula of MFe_2O_4 (where M is a divalent metal ion), have wide technological applications, e.g., in multilayer chip inductor (MLCI), high-speed digital tape or recording disks, rod antenna, and humidity sensor. Ferrite nanocrystals are also of interest in various

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applications, such as inter-body drug delivery, bioseparation, and magnetic refrigeration systems, in particular due to their specific properties, such as superparamagnetism. In addition, among ferrospinels Zinc ferrites are used in gas sensing, catalytic application, and absorbent materials. (Iyer, 2009; Maria1, 2013)

Chemical and structural properties of spinel ferrite nanocrystals are affected by their compositions and synthesis methods, and corresponding electric and magnetic properties depends on cation substitutions. Doping ferrite nanocrystals with various metals, such as Chromium, Copper, Manganese, Cobalt, and Zinc are usually used to improve some of their electric or magnetic properties (Li, 2010). For example, Ni-Zn ferrites have applications as soft magnetic materials with high frequency (due to high electrical resistivity) (Thang, 2005).

This paper is devoted to study the humidity sensitive electrical properties of Ni-Zn-Co ferritesand pure Ni ferrite, Co ferrite and Zn ferrite in the relative humidity range of 40 RH% – 98 RH%.

Materials and Method

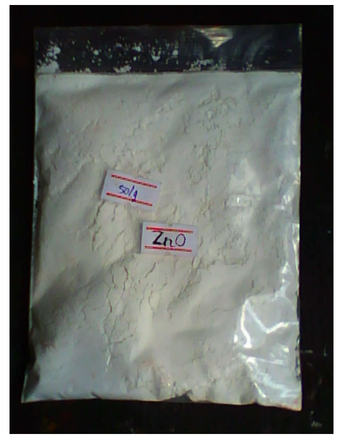
Preparation of Nickel-Zinc-Cobalt Ferrites

Experimental procedures for the preparation of Nickel-Zinc-Cobalt ferrites, $Ni_{0.97-x}Zn_{x}Co_{0.03}Fe_{2}O_{4}$ (where x = 0.25, 0.50 and 0.75) using conventional ceramic technique were as follows:

First, the raw materials of Analar (AR) grade Nickel Oxide (NiO), Zinc Oxide (ZnO), Cobalt Oxide (Co_3O_4), and Iron Oxide (Fe_2O_3)were weighed according to their desired stoichiometric compositions and mixed together. The mixture of each sample was ground by ball-milling for 3 h using laboratory-made ball-milling machine to a very fine powder and to prepare precursor solution. Then the precursor solid solutions were calcined at 1080°C for 4 h in vacuum chamber. The calcined solid solution was crushed again at room temperature. The crushed powders were pressed into pellets by using laboratory made pellet-maker. The pellets were finally sintered at 1200°C for 4 h to form ferrites. In the sample preparation, DELTA A Series Temperature

Controller DTA4896 and K-type thermocouple (1300°C) were used as the temperature controller and temperature sensor.

Furthermore, pure Nickel ferrite, Cobalt ferrite and Zinc ferrite were prepared by conventional ceramic technique using the above procedure. Photographs of the starting materials, DELTA A Series Temperature Controller DTA4896, laboratory-made ball-milling machine, pellet-maker, and experimental setup of sample preparation system are shown in Fig 1(a - i) respectively.



(e) ball-milling machine

(f) plastic coated stainless-steel ball

(g) temperature controller

(h) temperature controller

(i) experimental setup of sample preparation system

Figure 1. Photographs of the (a – d) starting materials, (e) laboratory-made ball-milling machine, (f)plastic coated stainless-steel ball, (g -h) DELTA A SERIES temperature controller at 1080°C and 1200°C and (i) complete experimental setup of sample preparation system

Humidity Sensitive Electrical Property Measurement

Humidity sensitive electrical properties of the Nickel-Zinc-Cobalt ferrites, $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(where x = 0.25, 0.50 and 0.75) were investigated in the relative humidity range of 40 RH% - 98 RH%. Firstly, the as-prepared ferrites were made circular shape pellets by using SPECAC hydraulic press with the pressure 5 ton (~70 MPa) as shown in Fig 2. Then the pellet was 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 1.14×10^{-4} m^2. The sample was then fixed on glass plate and silver contacts were made over the sample to ensure good electrical contact.

In this measurement, XSW TDK 0302 Humidity Meter was used as the humidity sensing element. Humidity sensitive electrical resistance and voltage of the sample were observed by two probe method by using FLUKE 189 digital multimeter. The refrigerator (TOSHIBA) was used as the humidity generator. Photographs of the experimental setup of humidity sensitive electrical property measurement are shown in Fig 3(a - b). Also, the as-prepared samples pure Nickel ferrite, Cobalt ferrite and Zinc ferrite were made into pellets and their humidity sensitive electrical properties were observed in the above same condition. Thicknesses of the pure Nickel ferrite, Cobalt ferrite and Zinc ferrite pellets are also listed in Table 1.

Figure 2. Photograph of SPECAC hydraulic pellet maker

Table 1. Thickness of the $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(where x = 0.25, 0.50 and 0.75)and pure Nickel ferrite, Cobalt ferrite and Zinc ferrite pellets

Sr No	Contents x of Zn in $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$and Pure Ni, Co, Zn Ferrite	Thickness (mm)
1	0.25	2.54
2	0.50	2.51
3	0.75	2.55
4	$NiFe_2O_4$	2.62
5	$CoFe_2O_4$	2.57
6	$ZnFe_2O_4$	2.52

Figure 3. Photographs of the (a) sample and sensor in the same condition, (b) and (c) experimental setup of humidity sensitive electrical property measurement

Results and Discussion

Humidity sensitive electrical resistances R_H versus relative humidity RH%, dc voltage V_H and capacitance C_H versus relative humidity RH% of the investigated Nickel-Zinc-Cobalt ferrites,$Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(where x = 0.25, 0.50 and 0.75) and pure Nickel ferrite, Cobalt ferrite and Zinc ferriteare shown in Fig 4(a – f) andFig 5(a – f) respectively.

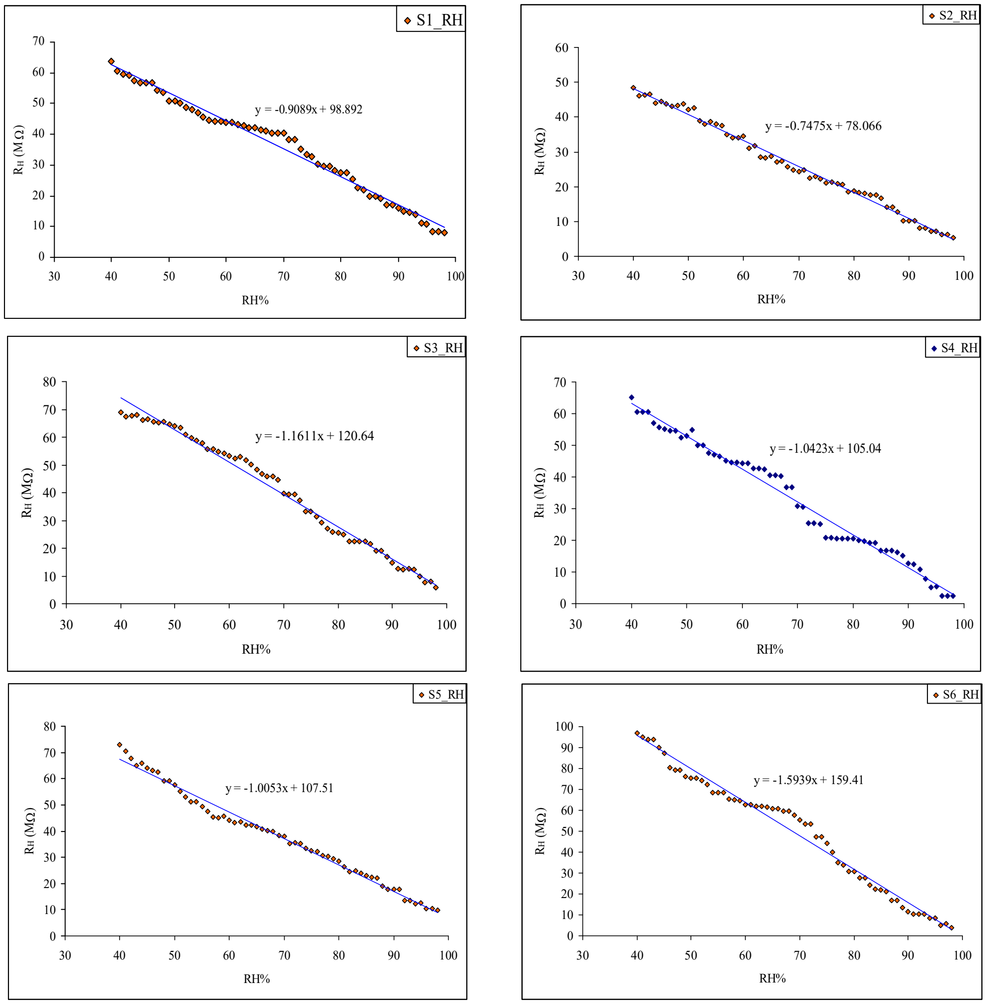


Figure 4. Plots of the variation ofelectrical resistance R_H with relative humidity RH% of $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$where (a)x = 0.25, (b) x = 0.50, (c) x = 0.75 and (d) pure $NiFe_2O_4$, (e) $CoFe_2O_4$ and (f) $ZnFe_2O_4$

(b)

As shown in RH versus RH% graphs, the electrical resistance of the $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(where x = 0.25, 0.50 and 0.75) and pure Nickel ferrite, Cobalt ferrite and Zinc ferrite decreased with increase in relative humidity and the obtained R_H versus RH% curves were fitted with linear type to examine the sensitivity of the sample. The slope of the R_H versus RH% graph can be taken as the sensitivity of the sample. In this work, the obtained sensitivities of the samples are tabulated in Table 2. The sensitivity of the pure $ZnFe_2O_4$ and the largest concentration of Zn in $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4orNi_{0.97-x}Zn_x Co_{0.03}Fe_2O_4$(where x = 0.75)sample are the most sensitive materials among the investigated samples. The resistance changes in porous spinel type ferrites with increasing of humidity level occur because of adsorption and capillary condensation of water. The sensitivity factor "S_f" of the sample can be evaluated by using the following relation,

$$S_f = R_{40\%}/R_{98\%}$$

where $R_{40\%}$ and $R_{98\%}$ are the electrical resistances of the $Ni_{0.97-x}Zn_x Co_{0.03}Fe_2O_4$(where x = 0.25, 0.50 and 0.75) and pure Nickel ferrite, Cobalt ferrite and Zinc ferrite at the relative humidity 40 RH% (start point) and 98 RH% (end point) respectively. According to above relation, the sensitivity factors were calculated and obtained as follows.

For $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(x = 0.25),

$S_{f\_S1} = R_{40\%}/R_{98\%} = 8.0075$

For $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(x = 0.50),

$S_{f\_S2} = R_{40\%}/R_{98\%} = 9.2205$

For $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$(x = 0.75),

$S_{f\_S3} = R_{40\%}/R_{98\%} = 11.9960$

For pure $NiFe_2O_4$,

$S_{f\_S4} = R_{40\%}/R_{98\%} = 24.3939$

For pure $CoFe_2O_4$,

$S_{f\_S5} = R_{40\%}/R_{98\%} = 7.5472$

For pure $ZnFe_2O_4$,

$S_{f\_S6} = R_{40\%}/R_{98\%} = 28.0125$

The obtained sensitivity factors are also presented in Table 2. As presented in Table 2, the sensitivity factor of the pure $ZnFe_2O_4$was the largest one. It can be suggested that microstructure (porosity, grain size, structural defects) has a great role on 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 vapors can be physically adsorbed, resulting in a larger decrease of the resistivity. One can see that the sensitivity of the pure $ZnFe_2O_4$ and the largest concentration of Zn in $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$or $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$ (where x = 0.75)sample are the most sensitive materials to humidity change.

Table 2. Sensitivity and sensitivity factor of the $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$ (where x = 0.25, 0.50 and 0.75) and pure Nickel ferrite, Cobalt ferrite and Zinc ferrite

Sr No	Contents x of Zn in $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$and Pure Ni, Co, Zn Ferrite	Sensitivity (MΩ/RH%)	Sensitivity factor
1	0.25	0.9089	8.0075
2	0.50	0.7475	9.2205
3	0.75	1.1611	11.9960
4	$NiFe_2O_4$	1.0423	28.0125
5	$CoFe_2O_4$	1.0053	7.5472
6	$ZnFe_2O_4$	1.5939	24.3939

As shown in Fig 5(a – f), dc voltage and capacitance increase with increasing humidity due to the water adsorption on sample surface is likely the dominant factor for electrical conduction. Thus, the surface area would provide more sites for water adsorption and produce more charge carriers for electrical conduction.

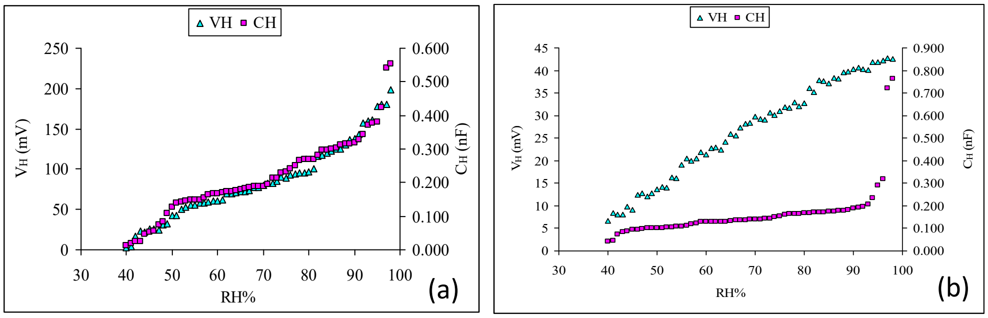


Figure 5. Plots of the variation of dc voltageV_H and capacitance C_H with relative humidity RH% of $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$where (a) x = 0.25 and (b) x = 0.50

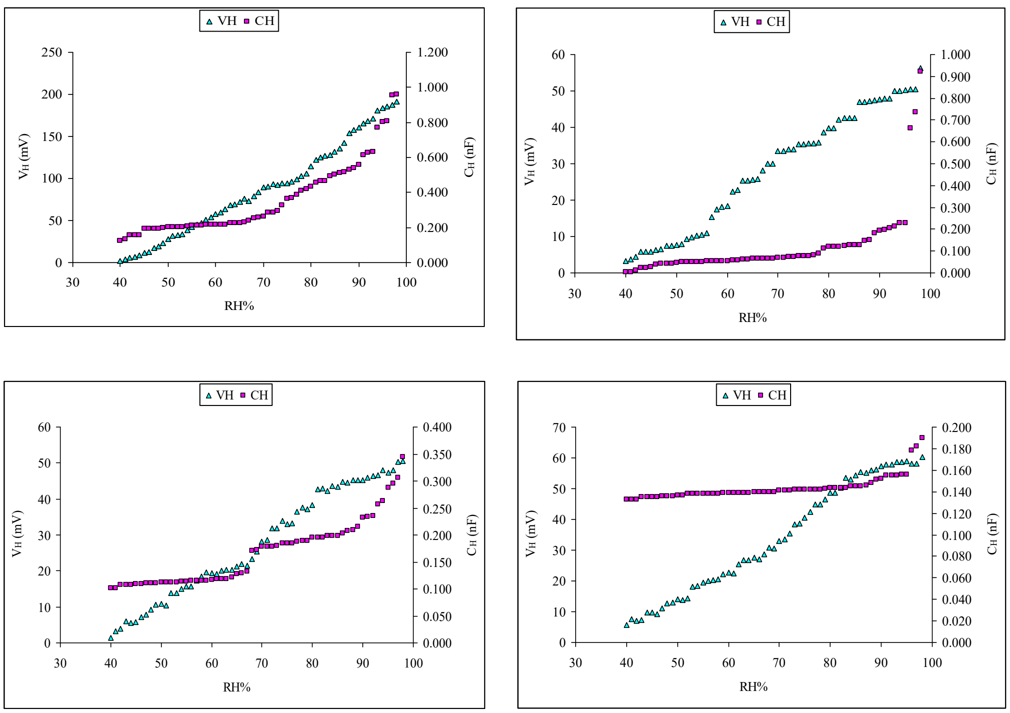


Figure 5. Plots of the variation of dc voltage V_H and capacitance C_H with relative humidity RH% of (c) $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$where x = 0.75 and (d) pure $NiFe_2O_4$, (e) $CoFe_2O_4$ and (f) $ZnFe_2$

(d)

Conclusion

Nickel-Zinc-Cobalt ferrites, $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$ (where x = 0.25, 0.50 and 0.75)and pure $NiFe_2O_4$, $CoFe_2O_4$and $ZnFe_2O_4$were prepared by conventional ceramic technique. Variation of the electrical resistances, dc voltages and capacitances of the as-prepared disc shapes pellets were investigated in the relative humidity range of 40 RH% – 98RH%.From this study, according to experimental results, the pure $ZnFe_2O_4$ and the largest concentration of Zn in $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$or $Ni_{0.97-x}Zn_xCo_{0.03}Fe_2O_4$ (where x = 0.75)sample are the most humidity sensitive materials among the investigated samples. It can be suggested that these samples can be suitable for the application of humidity sensors.

Acknowledgements

The authors feel indebted to Professor Dr. Zeya Oo, Visiting Professor ,Department of Engineering Physics, Yangon Technology University, Yangon, Myanmar, for his valuable suggestions and comments for this work.

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