SYNTHESIS AND CHARACTERIZATION OF NICKEL FERRITES PREPARED BY DIFFERENT METHODS FOR HUMIDITY SENSOR APPLICATION

Aung Ye Htun[1], Aye Aye Lwin[2] and Win Kyaw[3]

Abstract

Nickel ferrites, $NiFe_2O_4$, were prepared by three different preparation methods; solid state reaction (SSR) method, chemical co-precipitation (CCP) method and auto-combustion (AC) method. XRD technique was used to investigate the crystalline phase formation and to examine the lattice parameters of the samples. From XRD patterns, the samples analogous to cubic structure and the lattice parameters were found with small variation. The average crystallite sizes were obtained as 74.11 nm (solid state reaction method), 85.31 nm (chemical co-precipitation method) and 49.04 nm (auto-combustion method). Morphological features and porosities of the samples were examined by SEM. The samples were made into circular shaped pellets and their humidity sensitive electrical properties were investigated in the relative humidity range of 50 RH% - 99 RH% with the step of 1 RH% for humidity sensor application.

Keywords: $NiFe_2O_4$, solid state reaction, chemical co-precipitation, auto-combustion, XRD, SEM, humidity sensor application.

Introduction

The increased concern about environmental protection led to the development in sensors field [Patil, (2013)]. Apart from the technological importance ferrite materials have shown advantages in the field of sensors due to its mechanical strength, resistance to chemical attack and stability [Gadkari, (2013)]. Ferrites have spinel structure, which is mainly used in gas, stress and humidity sensors [Ahmad, (2012); Rezlescu, (2002)].

Humidity sensors are potentially in demand in industries like cloth driers, air coolers, broiler forming, cereal stocking and medical field. Humidity sensors based on the metal oxide materials have advantages such as low cost, simple construction and ease of placing the sensor in the operating environment [Attia, (2006)]. The ability of a metal oxide to sense the presence of water molecules depends on the interaction between water molecules and surface of the metal oxide i.e. the reactivity of its surface [Brito, (2010)]. The reactivity depends on the composition and morphological structure, which depends on the preparation procedure.

A large number of methods have been developed to prepare $NiFe_2O_4$ (NFO), such as the standard solid-state reaction method, co-precipitation method, auto-combustion method, solvothermal method and hydrothermal method [Fawzi, (2010); Vagolu, (2013)]. In this work, $NiFe_2O_4$ were prepared by the standard solid-state reaction (SSR) method, chemical co-precipitation (CCP) and auto-combustion (AC) method. The obtained Nickel ferrites were characterized by XRD and SEM to investigate the structural and microstructural characteristics of the samples. Furthermore, humidity sensitive electrical resistance was investigated in this work.

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Materials and Method

Preparation of Nickel Ferrites using Three Different Methods

Nickel ferrites, $NiFe_2O_4$, have been prepared by the standard solid state reaction method, co-precipitation method and auto-combustion method. The chemical reagents used were as follows:

(1) Nickel Oxide [NiO] and Ferric Oxide [Fe_2O_3] for standard solid-state reaction method,

(2) Nickel Sulphate Hexahydrate [$NiSO_4.6H_2O$], and Ferrous Sulphate Heptahydrate, [$FeSO_4.7H_2O$] in which Sodium Hydroxide [NaOH] as an agent for co-precipitation method and

(3) Nickel Nitrate Hexahydrate [$Ni(NO_3)_2.6H_2O$] and Ferric Nitrate Nonahydrate [$Fe(NO_3)_3.9H_2O$] in which Urea [$CO(NH_2)_2$] as a fuel for auto-Combustion method.

For solid state reaction method, Nickel Oxide (NiO) and Ferric Oxide (Fe_2O_3) were used. For co-precipitation method, Nickel Sulphate Hexahydrate [$NiSO_4.6H_2O$], and Ferrous Sulphate Heptahydrate, [$FeSO_4.7H_2O$] were used. For auto-combustion method, the stoichiometric ratio of metal nitrates and Urea were used. Flow diagrams of the experimental procedures of the sample processes of three different preparation methods are shown in Figure 1.

XRD and SEM Measurements

The X-ray diffraction measurement was carried out by using RIGAKU MULTIFLEX X-ray diffractometer [Universities' Research Centre (URC), University of Yangon]. Morphological features of the samples prepared by three different methods were investigated by JEOL JSM-5610LV Scanning Electron Microscope (SEM) [Universities' Research Centre (URC), University of Yangon] with the accelerating voltage of 15 kV, the beam current of 50 mA and 5500 times of photo-magnification.

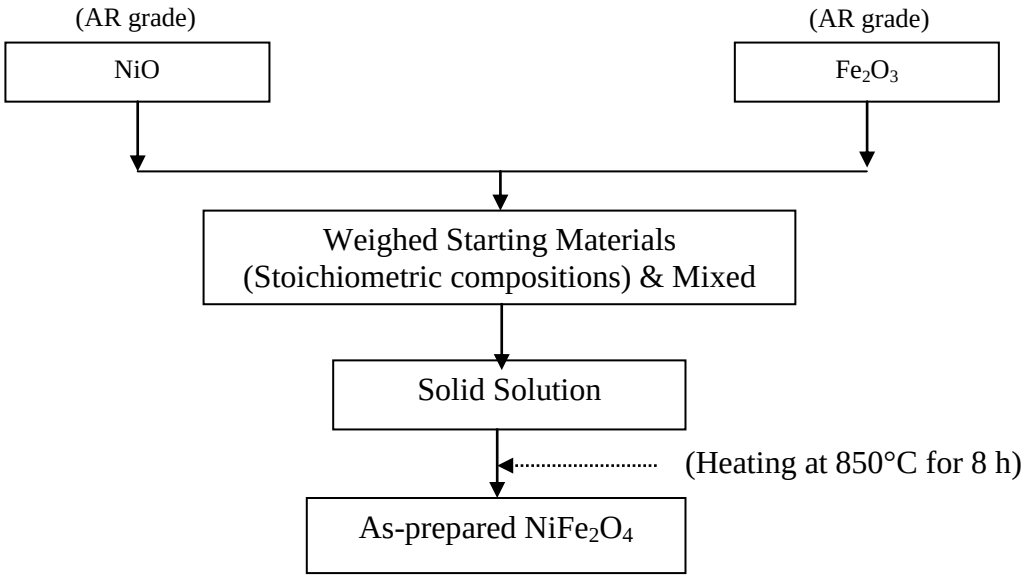

Figure 1(a) Preparation procedure of $NiFe_2O_4$ using solid state reaction method

Humidity Sensitive Electrical Resistance Measurement

Humidity sensitive electrical resistance of the $NiFe_2O_4$ pellets were investigated in the relative humidity range of 50 RH% - 99 RH%. Firstly, the samples were made into circular shape pellets by using SPECAC hydraulic press with the pressure 5 ton (~70 MPa). Thickness and area of the each of the sample were as 2.5 mm and 1.14×10^{-4} m^2 respectively. In this measurement, XSW TDK 0302 Humidity Meter was used as the humidity sensing element. Humidity sensitive electrical resistance was observed by two probe method by using FLUKE 189 digital multimeter. The refrigerator (Haier) was used as the humidity generator. Photographs of the experimental setup of humidity sensitive electrical resistance measurement are shown in Figure 2.

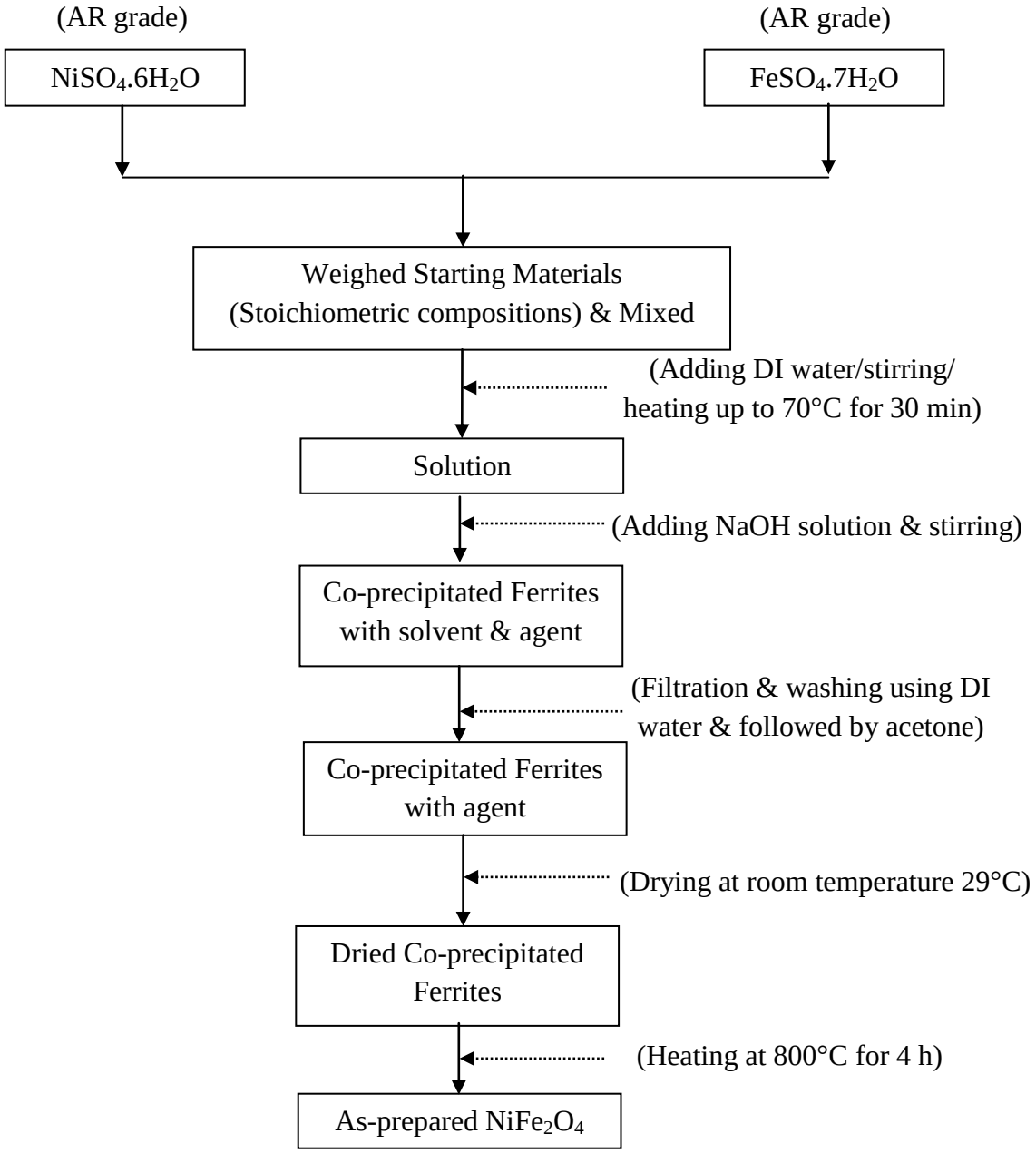

Figure 1(b) Preparation procedure of $NiFe_2O_4$ using co-precipitation method

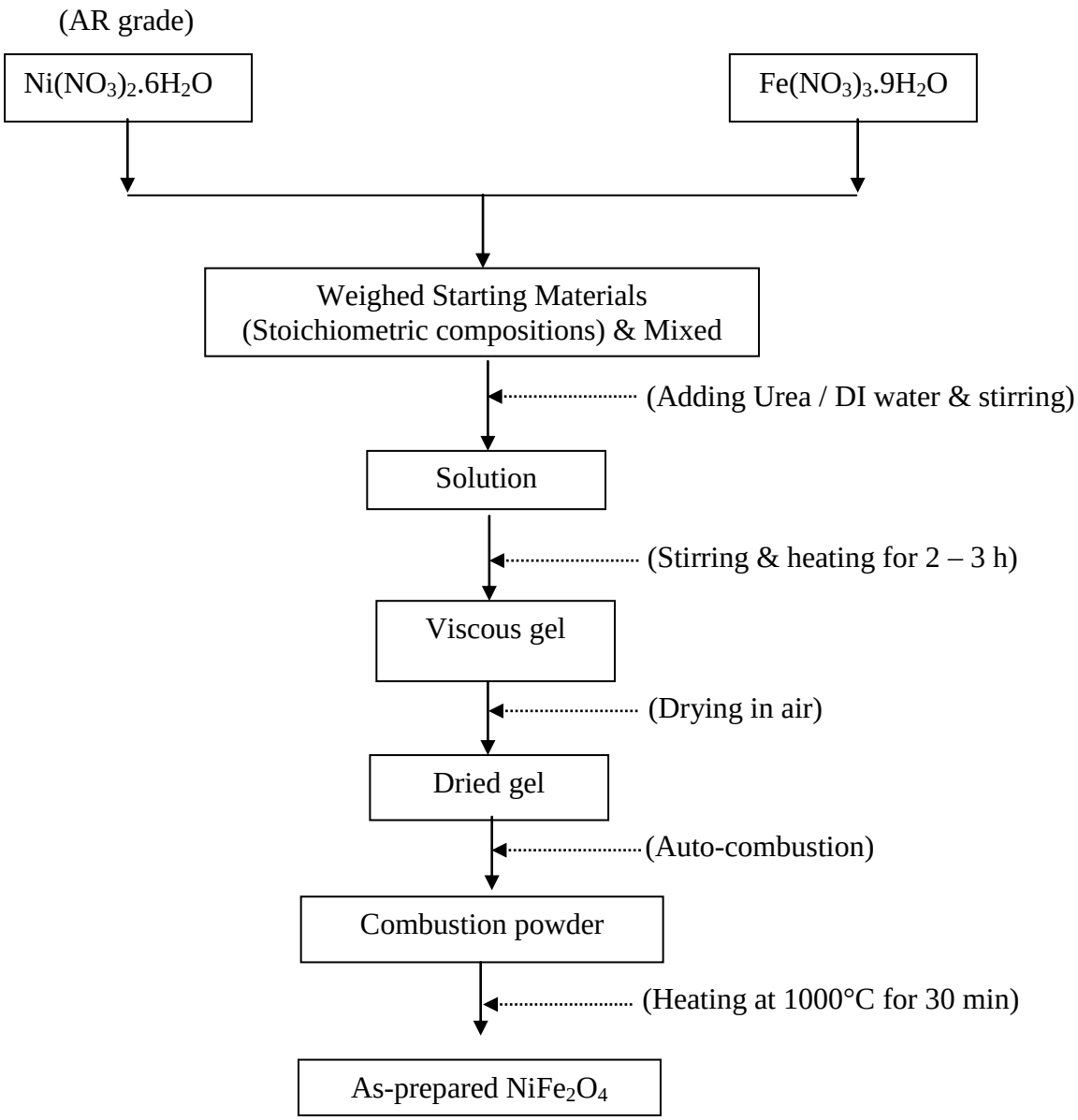

Figure 1(c) Preparation procedure of $NiFe_2O_4$ using auto-combustion method

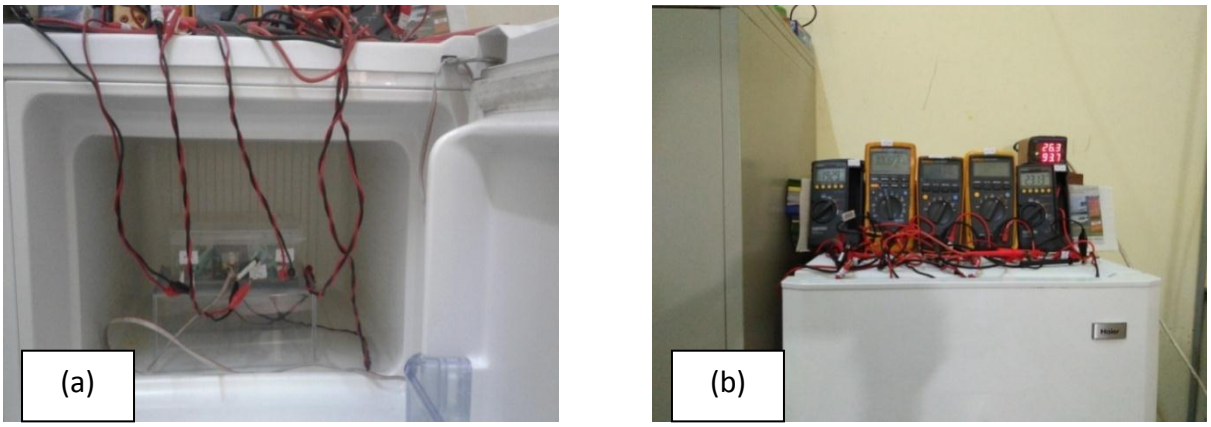

Figure 2 Photographs of the experimental setup of humidity sensitive electrical properties measurement, (a) the sample and sensor placed in the same condition and (b) the wiring connection of sample and meter

Results and Discussion

XRD Investigation

XRD patterns of Nickel ferrites, $NiFe_2O_4$, prepared by the standard solid state reaction method, co-precipitation and auto-Combustion method are shown in Figure 3. The collected diffraction lines were identified by using JCPDS data files of Cat. No. 89-4927> Trevorite, syn - $NiFe_2O_4$ for the sample prepared by standard solid state reaction method and auto-combustion method and Cat. No. 89-4927> Trevorite, syn - $NiFe_2O_4$ for the sample prepared by co-precipitation method respectively. As shown in observed XRD patterns, the collected diffraction lines were assigned with standard JCPDS data library files.

As shown in Figure 3(a), the collected peaks of the $NiFe_2O_4$ sample prepared by standard solid state reaction method are (220), (311), (222), (400), (511) and (440) respectively. In Figure 3(b), the collected peaks of the $NiFe_2O_4$ sample prepared by co-precipitation method are (220), (311), (400), (422), (511) and (440). As depicted in Figure 3(c), the collected peaks of the $NiFe_2O_4$ sample prepared by auto-combustion method are (220), (311), (400), (511) and (440). As shown in XRD patterns, the diffraction line of (311) plane is found to the strongest in intensity (I = 100%).

XRD patterns indicate the samples belong to cubic structure. In the present work, the calculated and observed lattice parameters of the samples are obtained as 8.33 Å for the $NiFe_2O_4$ sample prepared by standard solid state reaction method, 8.34 Å for the $NiFe_2O_4$ sample prepared by co-precipitation method and 8.31 Å for the $NiFe_2O_4$ sample prepared by auto-combustion method. The standard lattice parameters of the $NiFe_2O_4$ sample are $a = b = c = 8.32$ Å. Thus, the obtained lattice parameters in this work of different preparation methods are good agreement with the standard values. The crystallite sizes of the samples have been estimated by using the Scherrer formula, $D=\frac{0.9\lambda}{B\cos\theta}$, where D is he crystallite size nm, λ is the wavelength of incident X-ray (nm), θ is diffraction angle of the peak under consideration at FWHM (°) and B is observed FWHM (radian). In the present work, the average crystallite sizes were calculated and obtained as 74.11 nm for the sample prepared by solid state reaction method, 85.31 nm for the sample prepared by co-precipitation method and 49.04 nm for the sample prepared by auto-combustion method respectively. The crystallite size of the sample prepared by auto-combustion method was the smallest one among in the investigated samples using three different preparation methods. The obtained crystallite sizes showed the nanosized materials.

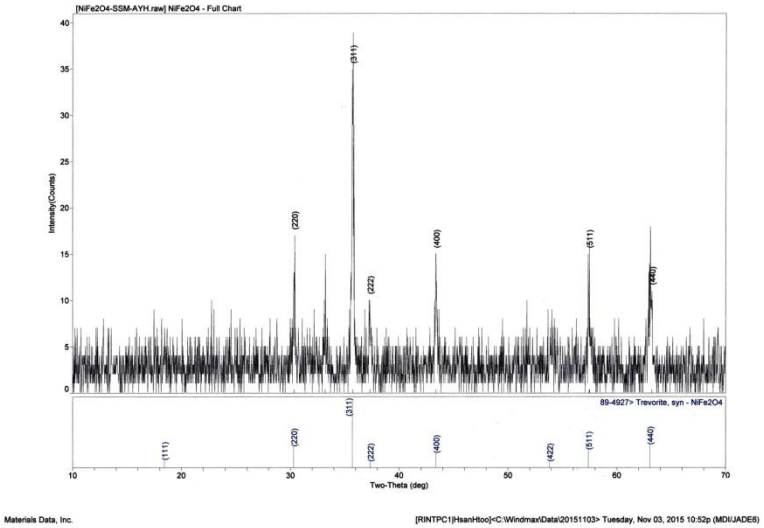

Figure 3(a) XRD pattern of $NiFe_2O_4$ prepared by solid state reaction method

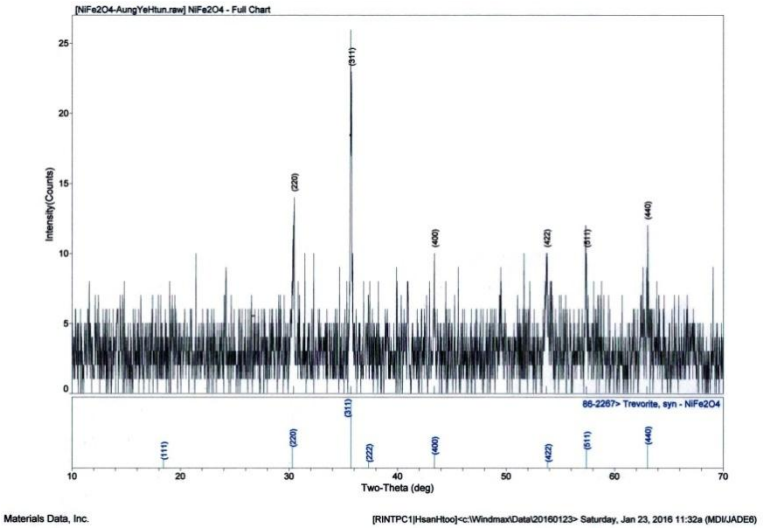

Figure 3(b) XRD pattern of $NiFe_2O_4$ prepared by co-precipitation method

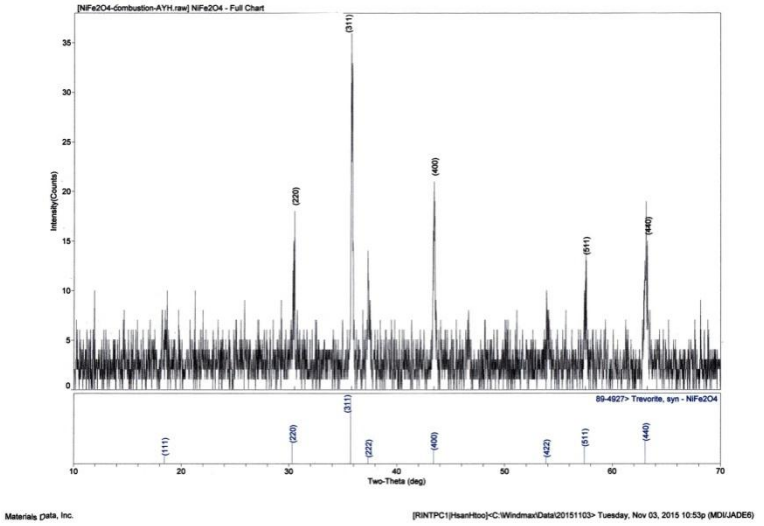

Figure 3 (c) XRD pattern of $NiFe_2O_4$ prepared by auto-combustion method

SEM Investigation

SEM images of Nickel ferrites, $NiFe_2O_4$, prepared by the standard solid-state reaction method, co-precipitation method and auto-combustion method are shown in Figure 4. As shown in figures, the grain shapes of the samples are spherical shapes and the samples from the standard solid-state reaction method and co-precipitation method are found to be similar. In Figure 4(a) and (b), the grain sizes are obtained as 0.25 – 0.40 μm and 0.15 – 0.25 μm respectively. The grains from co-precipitation method are found to be more homogeneous and smaller than that of solid state reaction method. The grain boundaries from solid state reaction method and co-precipitation method are clear than auto-combustion method. The grain shape of the sample from the auto-combustion method is the spherical with poor grain boundary. The sample composed of agglomerated particles. The obtained grain sizes are tabulated in Table 1.

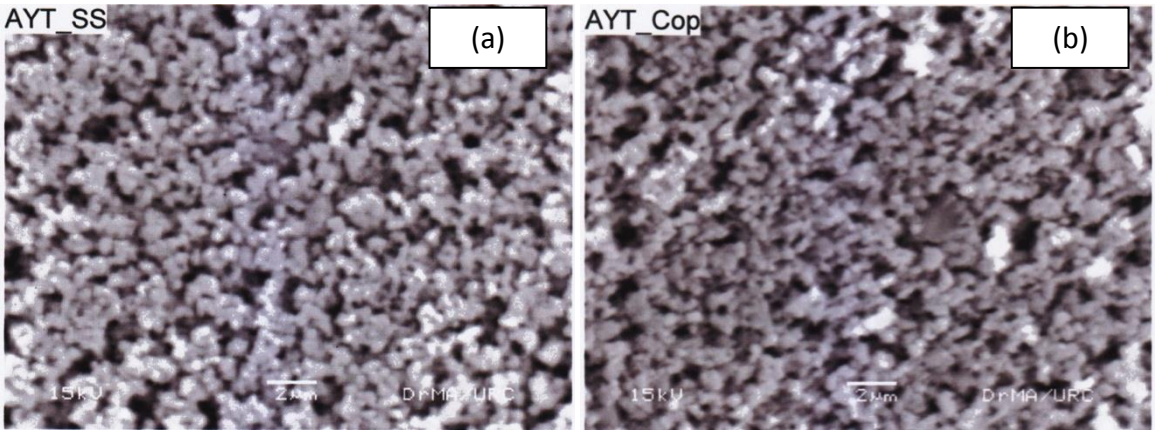

Figure 4 SEM images of $NiFe_2O_4$ prepared by (a) solid state reaction and (b) co-precipitation method

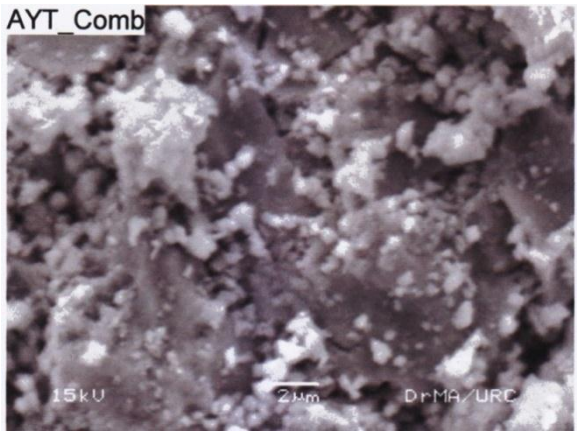

Figure 4(c) SEM image of $NiFe_2O_4$ prepared by auto-combustion method

Table 1 The grain sizes of Nickel ferrites, $NiFe_2O_4$

Method	Grain size (μm)
Solid state reaction	0.25 – 0.40
Co-precipitation	0.15 – 0.25
Auto-combustion	0.20 – 1.00

Humidity Sensitive Electrical Properties Study

The electrical resistance versus relative humidity (R vs. RH%) characteristic curves of the $NiFe_2O_4$ samples are shown in Figure 5. As shown in Figures, the electrical resistance decreased with increase in humidity because of capillary condensation of water vapours in all the pores that composed in the samples. In the observed (R vs. RH%) relationships, it is generally found that the decreasing of electrical resistances are varied with the observed corresponding humidity ranges.

The sensitivity factor "S_f" of the sample can be estimated by using the following relation; $S_f = R_{50\%}/R_{99\%}$, where $R_{50\%}$ and $R_{99\%}$ are the electrical resistances of the samples at the relative humidity 50 RH% (start point) and 99 RH% (end point) respectively. According to above relation, the sensitivity factors were calculated and obtained as follows.

For $NiFe_2O_4$ prepared by SSR method,

$S_{f\_SSR} = R_{50\%}/R_{99\%} = 60.77$

For $NiFe_2O_4$ prepared by CCP method,

$S_{f\_CCP} = R_{50\%}/R_{99\%} = 14.44$

For $NiFe_2O_4$ prepared by AC method,

$S_{f\_AC} = R_{50\%}/R_{99\%} = 18.81$

The sensitivity factor of the sample prepared by SSR method was the largest one because the 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.

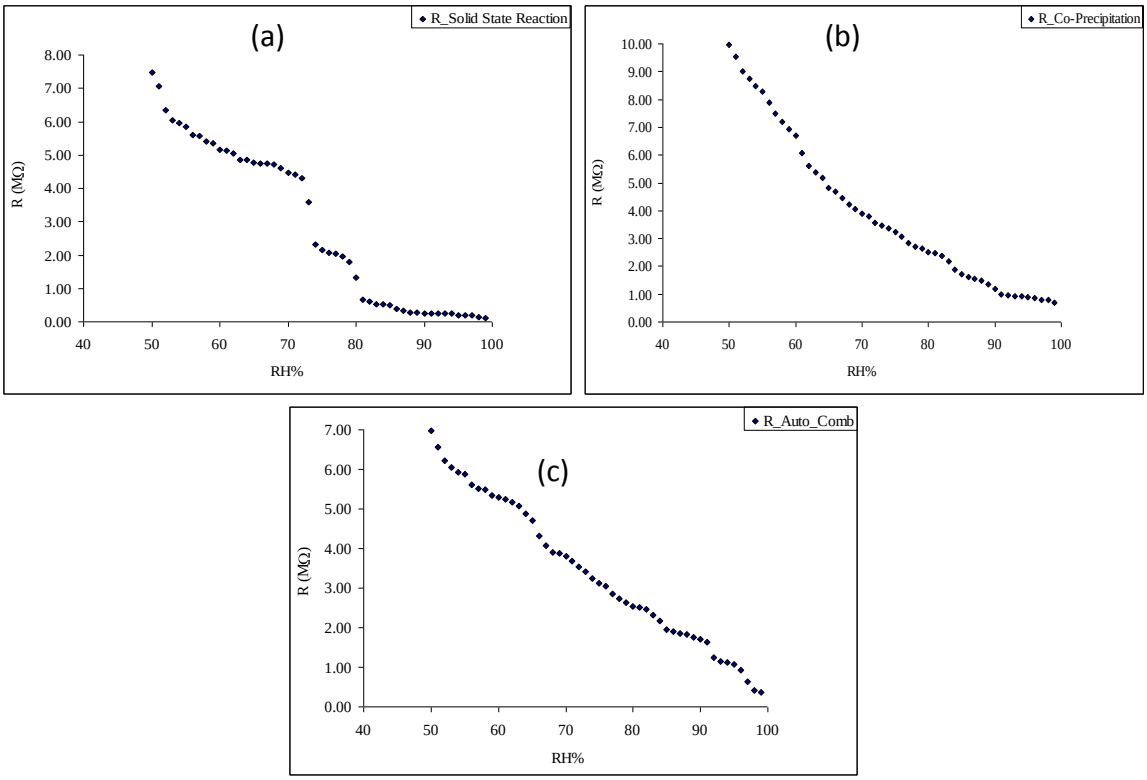

Figure 5 Electrical resistance versus relative humidity (R vs. RH%) characteristic curves of $NiFe_2O_4$ prepared by (a) SSR, (b) CCP and (c) AC method

Conclusion

Nickel ferrites, $NiFe_2O_4$ were successfully prepared by solid state reaction (SSR) method, chemical co-precipitation (CCP) method and auto-combustion (AC) method. Structural and microstructural characteristics of the samples were studied by XRD and SEM. Humidity sensitive electrical resistance was also investigated in this work. The X-ray diffraction confirmed the presence of spinel phase cubic crystalline as major phase of the as-prepared Nickel ferrite samples. The obtained lattice parameters and crystallite sizes were found to be small variation each other. It can be said that physical properties of the samples depend on the preparation techniques. From the observed SEM micrographs, the grain shapes of the samples are spherical. Due to the obtained grain sizes, the sample prepared from CCP method is the smallest and homogeneous among the investigated samples. The porosity (defect area) of the samples from SSR method and CCP method are larger than that of AC method. It indicated that the grain sizes and porosity depend on the preparation technique of the desired materials. From the humidity sensitive electrical properties measurement, the electrical resistances of the samples decreased with increase in humidity. The samples can be used as the humidity sensing materials in the relative humidity range of 50 RH% – 99 RH%. Due to the obtained sensitivity factor, the sample prepared by SSR method is the most suitable for the application of humidity sensing material among the investigated samples of different preparation methods.

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References

Ahmad, I. & Farid, M.T. (2012).Characterization of Cobalt Based Spinel Ferrites with Small Substitution of Gadolinium. *World Applied Sciences Journal*, 19, 464–469.

Attia, S.M. (2006). Study of Cation Distribution of Mn-Zn Ferrites. *Egypt Journal of Solids*, 29(2), 329–340.

Brito, V.L.O. (2010). EVALUATION OF A Ni-Zn FERRITE FOR USE IN TEMPERATURE SENSORS. *Progress in Electromagnetic Research Letters*, 13, 103–112.

Fawzi, A.Z., Sheikh, A.D. & Mathe, V.L. (2010). Structural, Dielectric Properties and AC Conductivity of $Ni_{(1-x)}Zn_xFe_2O_4$ Spinel Ferrite. *Journal of Alloys and Compounds*, 502, 231-237.

Gadkari, A.B., Shinde, T.J. & Vasambekar, P.N. (2013). Liquid petroleum gas sensor based on nanocrystallite $Mg_{0.6}Cd_{0.4}Fe_2O_4$. *Advanced Materials Letters*, 4(7), 573–576.

Patil, S.N. & Ladgaonkar, B.P. (2013). Synthesis and Implementation of $NiZnFe_2O_4$ Ferrites to Design Embedded System for Humidity Measurement. *International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering*, 19, 3813-3821.

Rezlescu, N., Rezlescu, E., Popa, P. & Tudorache, F. (2002). ON THE HUMIDITY SENSITIVITY OF A CERAMIC ELEMENT. STRUCTURE AND CHARACTERISTICS. *Journal of Institute of Technical Physics*, 8, 89-97.

Vagolu, V.K. & Samatha, K. (2013). Studies on Structural and Electrical Properties of Cobalt Substituted Nickel-Zinc Ferrites Prepared from Soft Chemical Method. *International Journal of Innovative Research and Studies*, 2(8), 99-113.