Thermal Property and Structural Characteristics of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ Ferrite Material

Mulugetta Duressa Kassa[1]

[1]*Department of Physics, College of Natural Science, Arba Minch University, Arba Minch, Ethiopia*

Abstract - *In this study, spinel $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite material was synthesized by solid state reaction method. The thermal property and the structure of this material were investigated by thermogravimetric and differential thermal analysis (TGA-DTA), x-ray powder diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy. TGA/DTA analysis confirmed that 800 oC is the appropriate temperature for synthesizing. From the TGA/DTA study, the weight loss regions and the stable phase formation of the synthesized ferrite were identified. The XRD analysis revealed that the synthesized ferrite material is has cubic spinel structure with Fd-3m space group. From obtained XRD data, different structural parameters such as the lattice constant, unite cell volume and crystal size of Ni0.9Cu0.1Fe2O4 ferrite were also suggested. From the FT-IR study of the material, two distinct strong absorption peaks were identified at wavenumbers 391.5 cm-1 and 577.5 cm-1. These formation of bands confirmed the formation of spinel ferrite phase.*

Key words: Ferrite material, Solid state reaction method, Structure, Structural parameter, Thermal property.

1. INTRODUCTION

Ferrites are magnetic compounds which are composed of metallic oxides and iron oxide as their main components. Most of ferrites have spinel structure with a formulae AB_2O_4, where "A" are divalent ions such as Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, etc. and "B" are the trivalent ions such as Fe^{3+} Cr^{4+} and Al^{3+} [1]. In recent years, spinel ferrites have been investigated because of their great useful electrical and magnetic properties as well as their wide applications, such as microwave devices, magnetic switches, electromagnetic circuits, magnetic cores, medical diagnostics, information storage etc. [2]. These properties of ferrites depend on several factors, such as synthesis method, the distribution of cations along the tetrahedral and octahedral cites, calcination as well as sintering conditions, chemical composition, crystal size and cation distribution in the two sub-lattices [2,3]. Moreover, these properties of spinel ferrite can be controlled by chemical composition, substitution, method of synthesis and the particle size. Therefore, serious studies have been carried out to improve the magnetic and electrical properties of ferrites. Nickel ferrite ($NiFe_2O_4$) is a cubic ferrite having normal spinel structure at bulk level with Ni^{2+} in tetrahedral and Fe^{3+} octahedral sites and inverse spinel structure at nano crystal level with Ni^{2+} in octahedral site and Fe^{3+} equally distributed among octahedral and tetrahedral sites [4]. The cubic unit cell of $NiFe_2O_4$ ferrite contains 8 formula units and containing 32 octahedral and 64 tetrahedral sites [5]. $NiFe_2O_4$ is also the most widely used soft magnetic material because of it excellent chemical stability, good mechanical hardness and low eddy current loss at higher frequencies. In this research work, Cu^{2+} substituted $Ni_{0.1}Cu_{0.1}Fe_2O_4$ ferrite material was synthesized by solid state reaction method. The thermal, structural and magnetic properties of this material was investigated using different characterization techniques.

2. MATERIALS AND METHODS

2.1. Synthesis Procedures

$Ni_{0.1}Cu_{0.1}Fe_2O_4$ ferrite material was synthesized by solid state reaction method with precursors $NiCO_3$, CuO and Fe_2O_3. Initially, a stoichiometric amount of $NiCO_3$, CuO and Fe_2O_3 raw materials was ground in agate mortar for two hours. Further 40 ml of methanol was added in the mixture and grounded again for one hour. And then, the mixed powder was calcined at 800 ^oC for 12 hours in air with a heating and cooling rate of 5 ^oC/min. Finally, the calcined powder was ground in a gate mortar for about one hour to obtain the fine powder material.

2.2. Material Characterizations

The thermal analysis of $Ni_{0.1}Cu_{0.1}Fe_2O_4$ sample was performed using DTG-60H instrument by heating the precursors from room temperature to 1000^oC with a heating and cooling rate of 10°C per minute in nitrogen atmosphere. The structure of $Ni_{0.1}Cu_{0.1}Fe_2O_4$ ferrite material was characterized by powder X-ray diffraction using a Phillips XPERT-PRO diffractometer fitted with Cu Kα radiation of wave length λ = 1.54060 Å between 2θ = 15^o and 80^o. The FT-IR spectroscopy characterization

technique was employed in the transmittance method with potassium Bromide (KBr) as IR window in the wave number region of 400 - 1,500 cm^{-1} using ALFA-T instrument.

3. ESULTS AND DISCUSSION

3.1. Thermal Analysis

TGA/DTA is an instrument that used to study the materials characteristics related to either mass loss or gain due to decomposition or oxidation. Figure 4.1 shows the TGA/DTG curves for $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite precursor. From the TGA curve of $Ni_{0.9}Cu_{0.1}Fe_2O_4$, three weight loss regions were identified. Initial weight loss 1.02 mg or 6.9 % between room temperature to 227 ^{0}C, as indicated by the first DTA peak centered at 107.7 ^{0}C, is attributed to evaporation of the residual water absorbed by the precursors during storage and methanol used during a grinding. The second weight loss 1.5 mg or 10.3% between 227 ^{0}C and 538.9 ^{0}C temperature corresponds to the decomposition of nickel carbonate ($NiCO_3$) and iron oxide (Fe_2O_3) precursors. This effect was also identified by a sharp endodermic peak at 297 ^{0}C. The third weight loss 1.23 mg or 11.7% between 538.9 ^{0}C and 650 ^{0}C temperature corresponds to the decomposition of the remaining precursors to form a pure crystalline $Ni_{0.9}Cu_{0.1}Fe_2O_4$. This effect was also identified by a sharp endodermic peak at 511 ^{0}C. Finally, at higher temperature, the TGA curve became more flattened, indicating stable phase formation of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ compound.

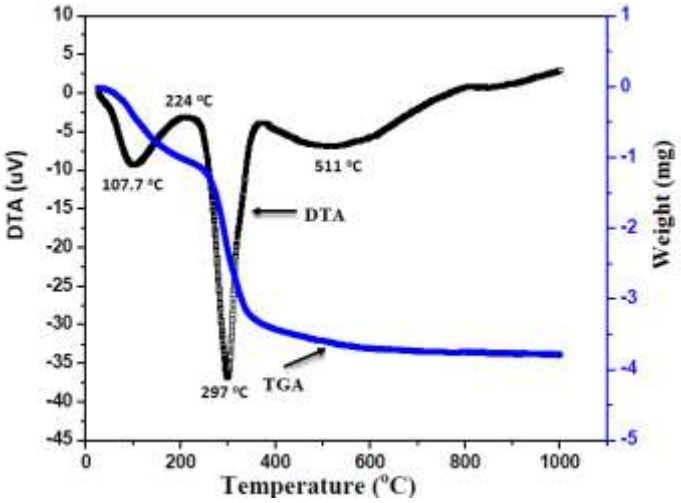

Figure-1: TGA/DTA curves of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite material.

3.2. XRD Analysis

The XRD analysis study was conducted to investigate the structural analysis of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite material synthesized by solid state reaction method at calcination temperature of 1000 ^{o}C for 10 hours in air. The characterization techniques were conducted between the Bragg angles 10° and 80° as shown in Figure 4.2. It was found that well-defined sharp diffraction peaks were identified. This indicates that the synthesized samples possessed higher degree of crystallinity. The strong diffraction peaks with miller indices (111), (220), (311), (222), (400), (422), (511), (400), (622) and (444) confirmed a single-phase cubic spinel with Fd3m space group formation in $Ni_{0.9}Cu_{0.1}Fe_2O_4$ sample [6]. No other phases or impurities are identified, which indicates the formation of single phase spinel $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite. Further, the XRD patterns also showed broad diffraction peaks, which represents the nano scale crystallite size of the synthesized sample.

In order to investigate the structural parameters of the synthesized $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite, the lattice constant (a), unit cell volume (V) and the crystal size (L) were calculated using the equations;

$$a = d\sqrt{h^2 + k^2 + l^2}$$

$$L = \frac{0.9\lambda}{\beta \cos\theta}$$

$$V = a^3$$

where d is the inter-planar spacing, hkl are Miller indices, ƛ is the wavelength of x-ray, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Braggs' angle. The obtained results are summarized in Table 1. The lattice parameter, the unite cell volume and the crystal size of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ were found to be 8.538 Å, 58.23 nm and 583.19 $(Å)^3$, respectively. The average crystallite size calculated using Debye–Scherer equation confirms the nano crystalline nature of the $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite material. The calculated lattice parameter of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ sample is slightly higher when compared with the pure $NiFe_2O_4$ (8.337 Å) [7]. This is due to the ionic volume differences of Cu^{2+} (0.7240 Å) and Ni^{2+} (0.69 Å) [7].

3.3. X-ray density, bulk density, surface area and porosity studies

The structural parameters, such as the x-ray density, the bulk densities, surface area and porosity play important role in controlling the structural properties of ferrite materials. The x-ray density ρ_{ex} and bulk density ρ_B of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite compound was calculated using the relation [8,9];

$$\rho_{ex} = \frac{nM}{N\,a^3} \quad \text{and} \quad \rho_B = \frac{M}{A\,t}$$

where M is the molecular weight, N is the Avogadro's number (6.022×10^{23} mol^{-1}), 'a' is the lattice parameter of the synthesized ferrite, n is the number of formula units per unit cell, A is the area of the pellet and t is the thickness of the pellet of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ compound.

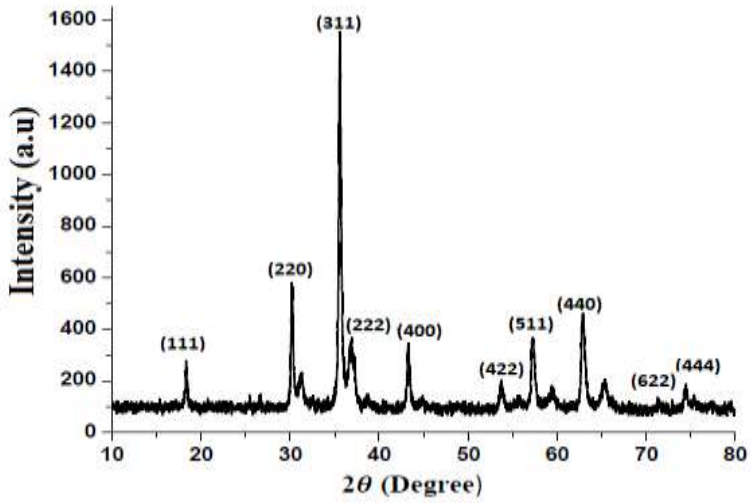

Figure-3: XRD analysis of $Ni_{0.9}Cu_{0.1}Fe_2O_4$.

Table-1: 2θ values, d-spacing, lattice constants, cell volumes and crystal sizes of the synthesized samples.

Sample	2θ value for (400) (degree)	d-spacing for (400) (Å)	Lattice Constant *L* a (Å)	Unite Cell Volu me V $(Å)^3$	Crystal Size from (311) (nm)
$Ni_{0.9}Cu_{0.1}Fe_2O_4$	43.2826	2.0887	8.3548	583.19	33.2

The surface area (S) and porosity (P) of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite compound was calculated using the relations [8,9];

$$S = \frac{6}{L\,\rho_{ex}} \quad \text{and} \quad P = \frac{\rho_{ex} - \rho_b}{\rho_{ex}}$$

Where L is the crystal size of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ compound.

The x-ray density as well as the bulk density of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite are found to be 5.35 g/cm^3 and 3.7 g/cm^3, respectively. This shows that the bulk density of the give sample is larger its bulk density. This is may be related to existence of pores in the samples, which depend on sintering temperature. Similar results have been reported by Nusrat J. *et al.* [10]. The surface area

and the porosity of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite are found to be 33.8 m^2/g and 30.8%, respectively. This is the common feature in spinel ferrite oxide.

3.4. FT-IR study

Fourier transform infrared spectroscopy is an important characterization technique to identify the chemical and structural changes occurring in materials through the presence of different vibrational modes in the crystal lattice. Figure 3 shows the FT-IR spectra of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite recorded at room temperature in the range of 350 cm^{-1} to 1500 cm^{-1}. As it can be seen from the figure, two prominent absorption bands are identified. The first absorption band observed at around 391.5 cm^{-1} is associated with the stretching vibration modes between

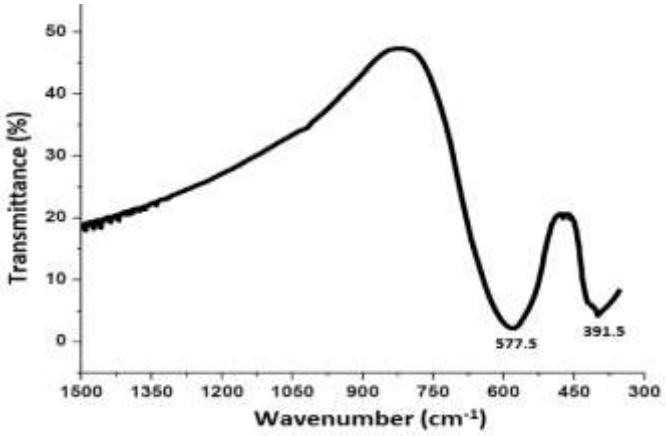

Figure-3: FT-IR spectra of $Ni_{0.9}Cu_{0.1}Fe_2O_4$.

metal cations and oxygen bonds at the tetrahedral sites in $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite [11]. The second absorption band formed at around 577.5 cm^{-1} corresponds to the stretching vibration modes between metal cations and oxygen bonds at the octahedral sites in $Ni_{0.9}Cu_{0.1}Fe_2O_4$ ferrite [11]. These formation of bands confirm the formation of spinel ferrite phase. The difference in the bond length of oxygen-metal ions in the tetrahedral and octahedral sites is responsible for the different positions of the frequency bands.

4. CONCLUSION

The crystalline $Ni_{0.9}Cu_{0.1}Fe_2O_4$ spinel ferrite sample was successfully synthesized via solid state reaction method using $NiCO_3$, CuO and Fe_2O_3 raw materials. The TGA/DTA showed the formation of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ compound through a direct reaction between $NiCO_3$, CuO and Fe_2O_3 precursors. The lattice parameter was found to be 8.538 Å. The unite cell volume and the crystal size of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ sample were 583.19 $(Å)^3$ and 58.23 nm, respectively. The XRD pattern of $Ni_{0.9}Cu_{0.1}Fe_2O_4$ powder sample has a good agreement with the standard reported XRD results of $NiFe_2O_4$. From FT-IR spectroscopy characterization, the obtained absorption bands revealed the formation of the cubic spinel structure, which is in agreement with XRD results of the samples.

ACKNOWLEDGEMENT

The author is thankful to Dr. k. Vijaya babu and Materials Science Engineering Department, ASTU for caring out the characterization measurement of this work.. Author is also thankful to Dr. Paulos Taddesse and Department of chemistry for assisting and providing some facilities to conduct the experimental work.

REFERENCES

[1]. S.S. Ata-Allah, M. Kaiser , Conductivity and dielectric studies of copper–aluminate substituted spinel nickel ferrite, Journal of Alloys and Compounds, vv. 471, 2009, pp. 303–309.

[2]. V. Dinesh and V. Kavita, Substitutional effect on structural and dielectric properties of $Ni_{1-x}A_xFe_2O_4$ (A = Mg, Zn) mixed spinel ferrites, Materials Chemistry and Physics, vol. 140, 2013, pp. 412-418.

[3]. A.M. Gabal and Y.M. Angari, Effect of diamagnetic substitution on the structural, magnetic and electrical properties of $NiFe_2O_4$, Materials Chemistry and Physics, vv. 115, 2009, pp. 578–584.

[4]. M.H. Khedr, Isothermal reduction kinetics at 900–1100°C of NiFe2O4 sintered at 1000–1200°C Journal of Analytical and Applied Pyrolysis, vv. 73, 2005, pp.123–129.

[5]. Sr. Hucn, C. O'NerLrand A. NevnorsKy, Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution, American Mineralogist, Vol. 68, , 1983, pages 181-I94.

[6]. K.Maaz, S.Karem, A. Mashiatullah, J.Liu, M.D Hou, Y.M.
Sun, J.L. Duan, H.J you, D. Mo, Y.F. Cheng, Phyisca B: Condensed Matter, vv. 40, 2009, pp. 3947-3951.

[7]. Hoque M.S., Choudhury A. and Islam F. Characterization of Ni–Cu mixed spinel ferrite. Journal of Magnetism and Magnetic Materials, vol. 251, 2002, pp. 292–303. Structural and

[8]. K. Vijaya Babu , G. Satyanarayana, B. Sailaja, G.V. Santosh Kumar, K. Jalaiah , M. Ravi, J. Results Phys. 9 (2018) 55–62.

[9]. S. Raghuvanshi, F. Mazaleyrat, S. N. Kane, AIP Advances, 8 (2018) 1-11.

[10]. N. Jahan, F.Z. Chowdhury and A.K.M. Zakaria, Electrical properties of chromium substituted nickel ferrite by conventional ceramic method, Materials Science-Poland, vv. 34, 2016, pp. 185-191.

[11]. D. Baraliya, H. H. Joshi, Spectroscopic and thermographic study of Ni–Zn ferrites, J Therm Anal Calorim (2015) 119:85–90.