Study on Preparation and Structural Characterization of Nickel Ferrites ($NiFe_2O_4$)

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Abstract

Nickel ferrite was prepared by solid state method. Starting materials of Analar (AR) grade nickel oxide and iron oxide were used to prepare the samples. The powder was weighed with desired stoichiometric compositions. The mixed powder was ground in an Agate mortar and pestle. The powder was presintered at 900˚C for 4 hr. The presintered powder was ground and sintered at 1000˚C, 1100˚C and 1200˚ C for 4 hr. X-ray Diffraction (XRD) technique was used to investigate the crystalline phase formation and to examine the lattice parameters of the samples. The average crystallite sizes were estimated by using XRD lines. The morphology was characterized by using Scanning Electron Microscope (SEM).

Keywords: $NiFe_2O_4$, Stoichiometry of composition, X-ray Diffraction, Scanning electron microscopy

Introduction

Spinel ferrites in general and magnesium ferrite in particular are technologically important materials and have widespread application in microwave devices. Ferrites are electrically non-conductive ferrimagnetic ceramic compound materials, consisting of various mixtures of iron oxides such as Hematite (Fe_2O_3) or Magnetite (Fe_3O_4) and the oxides of other metals (Agrafiotis & Zaspalis, 2004). $NiFe_2O_4$ is one of the most important binary oxides ferrite with spinel structure, which is usually used as ferrimagnets, brown pigments, and dehydrogenation catalysts. They are ferrimagnetic oxides, characterized by the arrangement of oxygen anions around metal cations in various geometric groups (Pradhan et al., 2005).

To date, literatures are available reporting the study of $NiFe_2O_4$ ferrite. The knowledge on the cation-occupation in spinel lattice, microstructural changes reflected from the sintering temperature and the related electrical and magnetic properties have not yet received sufficient study.

In the preparation of microwave ferrite materials, particular attention is given to the purity of the raw materials, stoichiometry of the composition, and porosity as well as grain characteristics of the sintered product. Several literatures describe ferrite as a very structure-sensitive material; its properties severely depend on the manufacturing process employed. Therefore, it is not easy to produce ferrites with excellent properties and high homogeneity (Kanamad et al., 2009).

This research was embarked to prepare and characterize $NiFe_2O_4$ is at different sintering temperatures by solid state method to provide an accurate understanding of the behavior of ferrite.

Experimental Details

Starting materials

The raw materials were selected by technical processing conditions and the ultimate requirements of the finished products (as spinel ferrites) are very sensitive to composition. In

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this work, high purity materials were used to prepare reproducible ferrite materials. The molecular weight and the purity of the raw materials are listed in Table (1). The molar concentrations which is listed in Table (2) was used to investigate the effect of concentration in the starting solution. The calculated weight fractions for two materials are presented in Table (3).

Table (1) Physical properties of starting materials to synthesize by solid state method

Raw Material	Purity (%)	Molecular Weight (g/mol)	Supplier
NiO	99.0	74.6928	Myanmar supply
Fe_2O_3	99.5	159.6882	Myanmar supply

Table (2) Molar ratio of the starting solutions to synthesize by solid state method

Molarity of NiO	Molarity of Fe_2O_3	Molarity of $NiFe_2O_4$
1 M	1 M	1 M

Table (3) The Calculated Weight Fraction for Molar Concentrations

Weight of NiO (g)	Weight of Fe_2O_3 (g)	Weight of $NiFe_2O_4$ (g)
1.5934	3.4066	5.0000

Samples with the general formula $NiFe_2O_4$were prepared by a solid state technique. The starting materials were analytical reagent grade oxides: ferric oxide Fe_2O_3 (99.5% purity) and nickel oxide NiO (99.0% purity). The flow chat of the synthesis procedure is shown in Fig. (1) and the process in Fig. (2).

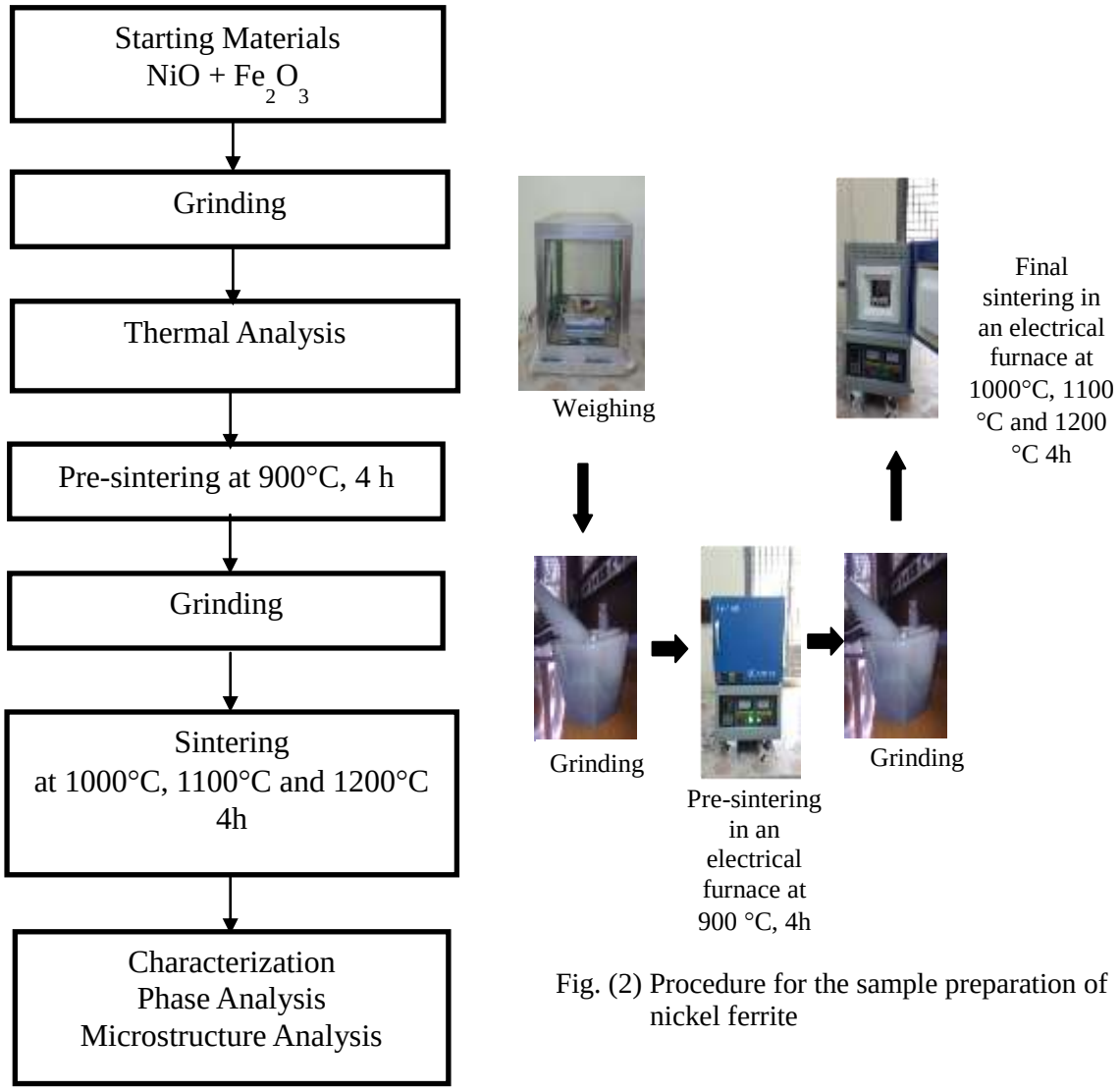


Fig. (2) Procedure for the sample preparation of nickel ferrite

Fig. (1) Flow chart of the synthesized $NiFe_2O_4$ by solid state method

These materials were mixed and ground by Agate motar and pestle for 2 h. Ethanol was used to prepare the mixture into a slurry. The slurry prepared was dried and transferred to a porcelain crucible and pre-sintered at 900^0C for 4 hr with a heating rate of 10^oC/min. The ferrite produced is usually in lump form. It was ground into powder. The samples were finally sintered at 1000˚C, 1100˚C and 1200˚C in 4hr duration. The variation of synthesis parameters on the form of $NiFe_2O_4$ was analyzed by using X-ray Diffraction technique (XRD) and Scanning Electron Microscopy (SEM).

X-ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a non-destructive technique for analyzing a wide range of materials, including fluids. Its applications include qualitative and quantitative phase analysis, crystallography, structure and relaxation determination, texture and residual stress investigations, controlled sample environment, micro-diffraction and nano-materials.

The diffraction beam from a crystal is buildup of rays scattered by all the atoms of the crystal which lie in the path of the incident beam. The diffraction of monochromatic X-rays takes place at those particular angles of incidence which satisfy Bragg's law:

$$\lambda = 2dsin\theta$$

where, λ = the wavelength of the incident X-ray beam

d = the interplanar spacing in a crystal and

2θ = the angle between the diffracted beams and transmitted beams

The angular positions of diffracted peaks give information on the properties of size and type of the unit cell while the intensities of diffracted peaks gives information on the types of atoms in the unit cell.

The lattice parameter of the cubic structure can be estimated using the following equation:

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

where a is the lattice constant (Å),

d is the interplaner spacing (Å).

In this study, XRD analysis was carried out to determine the phases of the starting materials as well as the formation of single phase spinel structure in the pre-sintered powders. The powder (about 3g) was ground and pressed into smooth and flat compacted layer in the aluminium based sample holder. The XRD patterns were scanned with step size of 0.034° (2θ) between 2θ = 10° to 70°. The obtained "fingerprint" of the spinel structure was identified by using the International Center for Diffraction Data (ICDD). For a polycrystalline powdered material, if the individual crystal is less than 100nm in size, the crystallite size can be estimated using the Scherrer equation:

$$L = \frac{\kappa\lambda}{B\cos\theta}$$

where $\boldsymbol{B}$ is peak width measured at half intensity (radians), $\boldsymbol{\lambda}$ is the wavelength (Å), $\boldsymbol{\kappa}$ is particle shape factor (for spherical particles, $\boldsymbol{\kappa}$ =0.9), and $\boldsymbol{L}$ is diameter of the crystallites (Å).

Based on the above knowledge, the crystallite size of the powder and dense pellet were calculated. The XRD spectra of the ferrite samples were obtained by using RigakuMultiflex 2KWPowder X-ray Diffractometer (XRD).

Scanning Electron Microscopy (SEM)

Morphology study was conducted using JEOL-JSM 5610LV scanning electron microscope. In SEM, high energy electrons are focused into a fine beam by electromagnetic lens through the vacuum, which is scanned across the surface of the specimen. Complex interactions of the beam electrons with the atoms of the specimen produce a wide variety of radiations products: backscattered electrons, secondary electrons, absorbed electrons, characteristic and continuum X-rays, etc. Backscattered electrons and secondary electrons are capable of carrying information about specimen composition, shape (Topography), local fine-scale surface texture, and thickness.

Before examining with SEM, the pellets were initially ground using SiC paper (grit 1000) in the first stage. The samples were then stuck to the holder by carbon tape and placed into the sample chamber of the SEM. The microstructures of the samples were obtained with different magnifications.

Results and Discussion

Phase Formation

XRD analysis was conducted to check the phase formation of the powder. The XRD patterns for the powder pre-sintered at 900˚C for 4 hr and final sintered at 1000˚C, 1100˚C and 1200˚C for 4 hr are shown in Fig. 3 (a-d) respectively.

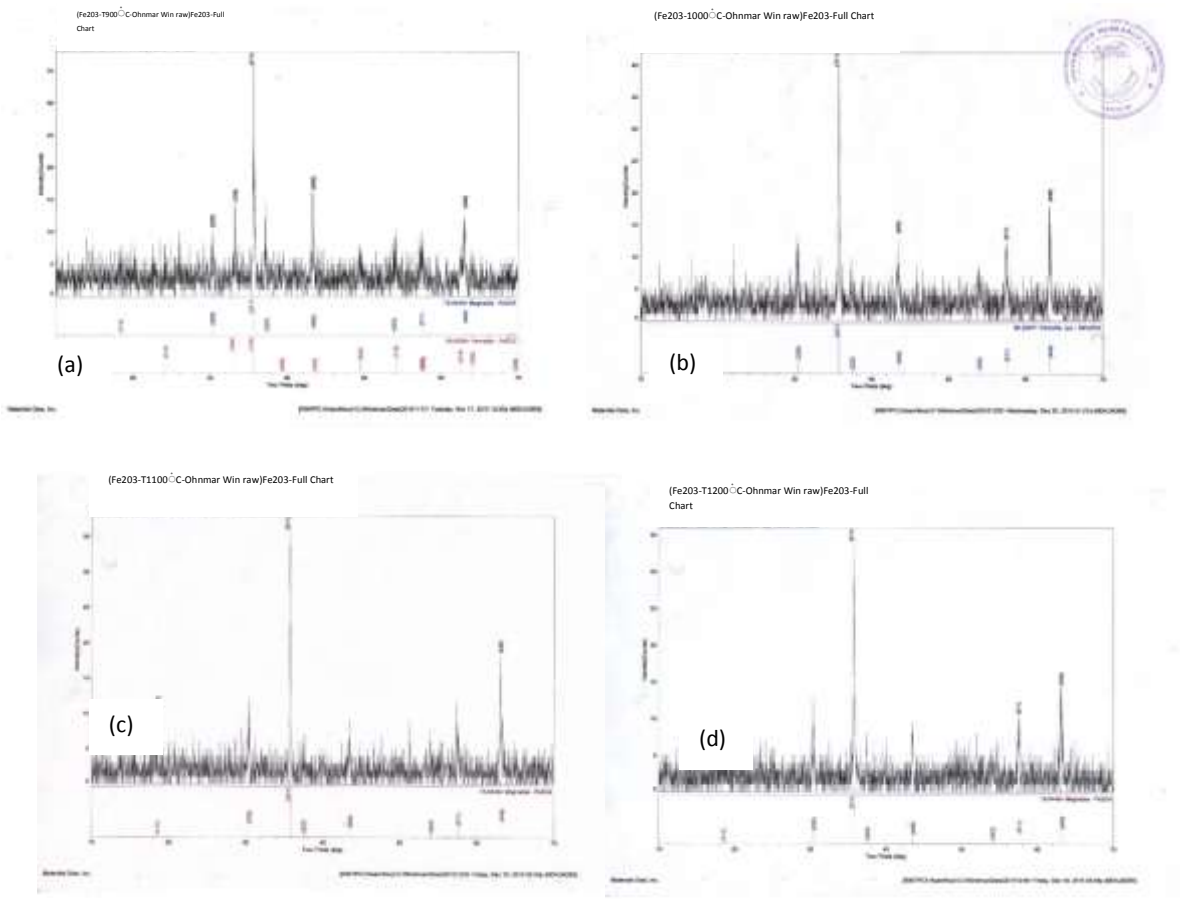


Fig. (3) The XRD patterns of the $NiFe_2O_4$ powder after final sintered at (a) 900°C, (b)1000°C, (c)1100°C, (d)1200°C

Phase Formation

XRD analysis was conducted to check the phase formation of the powder. The XRD patterns for the powder pre-sintered at 900˚C for 4 hr and final sintered at 1000˚C, 1100˚C and 1200˚C for 4 hr are shown in Fig. 4 respectively. The XRD patterns reveal that the phase formed in the samples are fcc spinel structure. There is no trace of parent materials. Therefore, it was confirmed that a single phase spinel structure was formed after pre-sintering at 900˚C for 4 hr and thermally stable until 1200˚C.

All samples were of typical cubic spinel crystal structure but have different crystallinity due to the effect of heat treatment. The lattice parameter and the crystallite size for all intense reflection peak estimated by the Scherrer equation are presented in Table 4 (a-d).

Table 4 (a) The Variation of Lattice Parameter and the Crystallite Size after Pre-sintered at 900˚C

Peak	hkl plane	2θ (deg.)	d (Å)	FWHM (degree)	Lattice constant, a (Å)	Crystallite size, L (nm)
1	220	30.285	2.9488	0.270	8.3405	29.50
2	311	35.734	2.5106	0.164	8.3267	47.81
3	400	43.400	2.0833	0.254	8.3332	31.51
4	440	63.109	1.4719	0.231	8.3263	34.66
Average					8.3317	35.87

Table 4 (b) The Variation of Lattice Parameter and the Crystallite Size after Final Sintered at 1000˚C

Peak	hkl plane	2θ (deg.)	d (Å)	FWHM (degree)	Lattice constant, a (Å)	Crystallite size, L (nm)
1	311	35.787	2.5070	0.164	8.3148	47.81
2	400	43.440	2.0814	0.156	8.3256	51.35
3	511	57.434	1.6031	0.157	8.3299	51.36
4	440	63.040	1.4734	0.217	8.3348	36.49
Average					8.3263	46.75

Table 4(c) The Variation of Lattice Parameter and the Crystallite Size after Final Sintered at 1100˚C

Peak	hkl plane	2θ (deg.)	d (Å)	FWHM (degree)	Lattice constant, a (Å)	Crystallite size, L (nm)
1	311	35.738	2.5104	0.152	8.3260	53.33
2	440	63.043	1.4733	0.137	8.3342	57.78
Average					8.3301	55.55

Table 4(d) The Variation of Lattice Parameter and the Crystallite Size after Final Sintered at 1200˚C

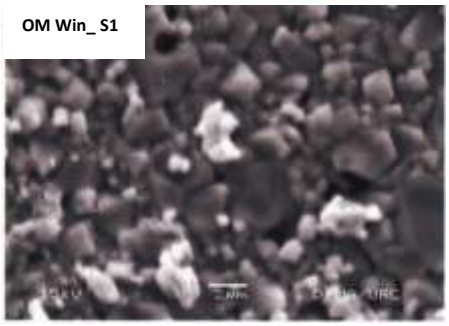
Peak	hkl plane	2θ (deg.)	d (Å)	FWHM (degree)	Lattice constant, a (Å)	Crystallite size, L (nm)
1	311	35.763	2.5087	0.196	8.3204	40.78
2	440	63.065	1.4729	0.184	8.3320	43.33
Average					8.3262	42.06

It was observed that the lattice parameter kept constant with the heat treatment showing that the sample preparation was consistent during the synthesis. It is worth to note that the crystallite size increased with the sintering temperature until 1100˚C. However, the crystallite size decreased at the sintering temperature of 1200˚C.

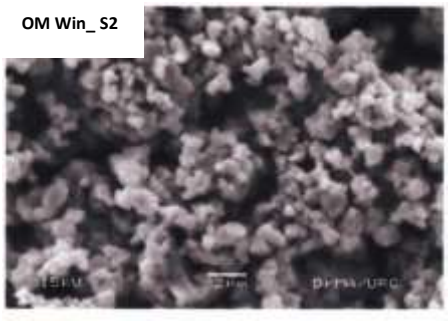
Therefore, it might be possible to do final sintering below 1200˚C in the $NiFe_2O_4$ magnetic ferrites system via solid state method.

Morphology Characterization

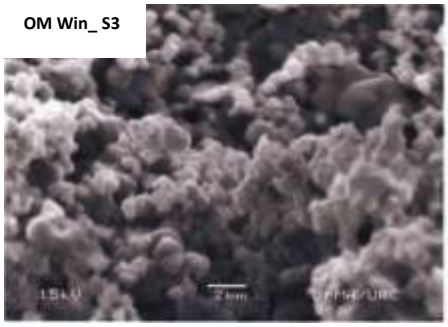
Microstructure study is essential for optimizing the properties of final product of ferrite for various applications. The SEM microstructures of $NiFe_2O_4$ final sintered at 1000˚C, 1100˚C and 1200˚C for 4 hr are shown in Figure 4(a-c) respectively.



(a)



(b)



(c)

Fig. (4) The SEM micrographs of the sintered surface$NiFe_2O_4$ powder after final sintered at (a) 1000℃, (b) 1100℃, (c) 1200 ℃

It is found that the grain size of the individual grains were 1.14μm, 0.44 μm and 0.54μm for the samples sintered at 1000˚C, 1100˚C and 1200˚C respectively. It is worth to note that the size of the grain decreased with the increased final sintered temperature of 1100˚C. However, the size of the grain again increased at the final sintered temperature of 1200˚C. Therefore it again confirmed the finding in the phase formation that the final sintering temperature should not exceed 1200˚C for $NiFe_2O_4$ prepared by solid state method.

Conclusion

The main objective of this research was to prepare $NiFe_2O_4$ in three different final sintering temperatures of 1000˚C, 1100˚C and 1200˚C by solid state method to investigate the behavior of the ferrite and the changes caused by the sintering temperature. According to the XRD characterizations, all samples have successfully formed typical cubic spinel crystal structure with different crystallinity due to the effect of heat treatment. The lattice parameter keeps constant with the heat treatment. Moreover, the crystallite size increased with the sintering temperature until 1100˚C and decreased at the sintering temperature of 1200˚C. Therefore, it is concluded that final sintering should be below 1200˚C in the $NiFe_2O_4$ magnetic ferrites system via solid state method.

According to the SEM microstructures, the size of the grain decreased with the increased final sintered temperature until 1100˚C and again increased at the final sintered temperature of 1200˚C. Therefore the final sintering temperature should not exceed 1200˚C for $NiFe_2O_4$ prepared by solid state method.

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