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RESEARCH ARTICLE

Magnetic and microwave absorption properties of nickel ferrite ($Ni_xFe_{3-x}O_4$) by HEM technique

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Abstract

Nickel ferrite ($Ni_xFe_{3-x}O_4$) have been synthesized using solid state reaction with composition (2x)NiO : (3-x)Fe_2O_3 (x = 0.5; 1.0; 1.5 dan 2.0) in mol in wt%. Mixing of this powder was milled with HEM (High Energy Milling) for 10 hours, and then sintered at 1000 °C for 3 h. X-ray diffraction pattern indicates that the all of samples are single phase in this stage. FTIR (Fourier transform infrared) analysis showed two absorption bands in the range of ~410 - ~600 cm^{-1} related to octahedral and tetrahedral sites. The magnetic measurement using vibrating sample magnetometer (VSM) shows that the sample exhibited a ferromagnetic behaviour with its coercivity value in the range of 164-217 Oe, and the maximum value wasshowed by x =1.5. VNA (*Vector Network Analyzer*) characterization shows the ability electromagnetic wave absorption with RL (reflection loss) value of -28 dB occurs at frequency of 10.98 GHz. It means that the $Ni_{1.5}Fe_{1.5}O_4$ sample can absorb microwave about ~96 % at 10.98 GHz.

Keywords: Nickel Ferrite, Milling, Microwave absorption, Magnetic properties.

INTRODUCTION

In recent years, the interest to develop magnetic materials for microwave absorber have been increased intensively (Chen et al. 2012). Microwave absorbing materials were used to eliminate electromagnetic wave interference and to reduce radar signatures. Due to the good magnetic and electric properties of the absorbing materials, the coating process of the target by using microwave absorbing materials could improve the absorption of the microwave energy in broadband or discrete frequencies. The application of the microwave absorbing materials is important to be used in military aircraft and vehicles to help avoiding the detection by radar (Manojit et al. 2015). Since the application of conventional microwave absorbers such as spinel ferrites is restricted in the MHz region, researches are urged to explore new types which able to absorb microwave energy in a wide frequency range. One of the good candidates as microwave absorbing materials was spinel ferrite nanoparticle due to their low dielectric and magnetic losses. Microwave absorption properties are highly dependent on processing parameters and chemical composition. These factors can greatly influence the crystal size, magnetic properties, complex magnetic permeability (μ_r) and complex permittivity (ε_r) (Chen et al. 2012 and Manojit et al. 2015).

Among various ferrites types, nanosized of nickel ferrite possesses attractive properties to studied specially applied as soft magnets, core materials in power transformers and microwave absorbing materials at high frequencies. High permeability in the radio frequency region, high electrical resistivity, high Curie temperature and low eddy current loss are important properties of nickel ferrites, which make them suitable for wide range of applications. Being a technologically important material, Ni ferrites as well as Ni-based mixed ferrites are extensively investigated by various researchers (Moradmard et al. 2015, Almásy et al. 2015 and Karakas et al. 2012). Nickel ferrite ($NiFe_2O_4$) with inverse spinel structure is an important soft magnetic material, prominently known for its high magnetic permeability, low coercive force, high saturation magnetisation, high Curie temperature and large magnetostriction constant(Gatelytė et al. 2011). These outstanding properties make $NiFe_2O_4$ attractive for a wide variety of applications, such as ferro fluids, microwave absorbing materials, super capacitor electrode materials and sensors(Gómez et al. 2013, Kishore et al. 2014 and Lazarevic et al. 2012). Until now, the research of Nickel ferrite mainly concerned to talk only about the physical properties such as magnetic properties (Kishore et al.2014) and dielectrical behaviour (Joshi et al. 2014), further research to study about the $NiFe_2O_4$ as a main compound of microwave absorbing material is rarely studied.

There are various methods that have been developed to prepare $NiFe_2O_4$ nanoparticle through chemical or physical route (Jacob et al. 2011). Among various methods of the chemical route, from previous research we were known that the single phase of $NiFe_2O_4$ nanoparticle have been successfully synthesized by using sol-gel method (Mashadi et al. 2016) otherwise among the physical route it has been

successfully synthesized through mechanical milling for 5 hours which could absorb the microwave until 95% (Rahmy 2015). The synthesis of nickel ferrite nanoparticles use this milling technique especially for the microwave absorber materials is rarely reported until now. In the present study we try to synthesize $NiFe_2O_4$ nanoparticle in the form of $Ni_xFe_{3-x}O_4$ (x = 0.5; 1.0; 1.5 and 2.0) to improve the magnetic properties (i.e. saturation magnetization and hysteresis loops) which correspond to the ability to absorb the microwave.

EXPERIMENTAL

In this study, wet milling technique by using HEM (High Energy Milling) was used to syhnthesize $Ni_xFe_{3-x}O_4$, in which the powder of Fe_2O_3 (≥99% purity) and NiO (76-77% purity) from Sigma Aldrich were used as compound materials. The mixture between Fe_2O_3 and NiO was weighed based on wt% in accordance with the stoichiometry of $Ni_xFe_{3-x}O_4$ (x = 0.5; 1.0; 1.5 and 2.0) (Rahmy 2017). Each mixture was inserted into the vial then added a solution of 50 ml ethanol and milled for 10 hours. The mixture after milling was dried at a temperature of 100 ° C (for ±2 hours) and sintered at 1000 ° C for 5 hours. Formation reaction of nickel ferrite is as follows:

$$(2x)NiO + (3-x)Fe_2O_3 \longrightarrow 2Ni_xFe_{3-x}O_4 \quad (1)$$

Samples of $Ni_xFe_{3-x}O_4$ formed were characterized by using XRD Pan Analytical to confirm the phase. FTIR brand Bruker type Tensor 27 was used to know the identification of functional groups, and VSM (Vibrating Sample Magnetometer) type Oxford VSM 1.2 H was used to know the magnetic properties of sample. Meanwhile VNA (Vector Network Analyzer) brand Advantest type R3770 300 kHz-20 GHz was used to measure the value of absorption performance and the reflection loss (dB) of the samples.

RESULTS AND DISCUSSION

Identification of the functional group of samples $Ni_xFe_{3-x}O_4$ from this research was analyzed by FTIR spectroscopy. Fig. 1 shows the FTIR absorption spectra of samples $Ni_xFe_{3-x}O_4$ in the range of 400-2000 cm^{-1}. The visible absorption peaks for sample of x = 1 ($NiFe_2O_4$) appear at wave number around 599.84 and 414.68 cm^{-1}. These two peaks are the main peak of the cluster metal ions and oxygen which associated with octahedral and tetrahedral site of spinel ferrite. In $Ni_xFe_{3-x}O_4$, all the Ni^{2+} ions are in octahedral section while Fe^{3+} is uniformly distributed in tetrahedral and octahedral site. Thus, the absorption peak appearing at wave number 414.68 cm^{-1} is owned by sub-lattice of octahedral site (vibration between atoms Ni, Fe and oxygen), whereas the absorption peak observed at wave numbers 599.84 cm^{-1} is the character of absorption cluster atoms in tetrahedral sites (vibration between Fe and oxygen) (Nejati et al. 2012). These peaks slightly shifted toward larger wave numbers with the addition of the content of Ni^{2+}. This is caused by the increased strain Ni^{2+} ions are in

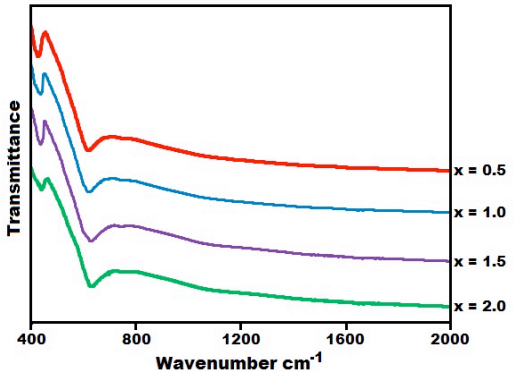

Fig. 1 Infrared spectrum of $Ni_xFe_{(3-x)}O_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h.

X-ray diffraction pattern of the sample $Ni_xFe_{3-x}O_4$ (x = 0.5; 1.0; 1.5 and 2.0) is shown in Fig. 2. X-ray diffraction patterns shows a single phase formation of spinel ferrite structure, $NiFe_2O_4$ have a cubic crystal structure with space group *Fd-3m* with lattice parameters $a = b = c = 8.3473$ Å at room temperature. The main peak appeared at 2θ around the angle of 35° with Miller index (311) as peak characteristic of the cubic spinel $NiFe_2O_4$. This analysis is supported by the emergence of other peaks are also characteristic of $NiFe_2O_4$, namely peaks (111) at an angle of around 18°, 30° (220), 37° (222), 43° (400), 53° (442), 57° (511), and 64° (440), which correspond to the MATCH database ICDD 96-100-6117.

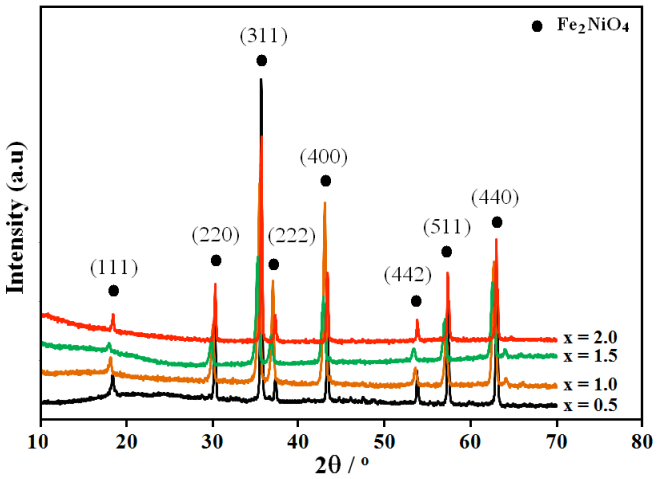

Fig. 2 X-ray diffraction pattern of $Ni_xFe_{3-x}O_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h.

The phase identification of $NiFe_2O_4$ referred to Joshi (Joshi et al. 2014). The phase composition of samples was calculated by using the GSAS software as shown in Fig. 3. Fig. 3 shows the refinement result of XRD profiles on the samples for x = 0.5; 1.0; 1.5 and 2.0.

The refinement result of XRD pattern shows that all of $Ni_xFe_{3-x}O_4$ sample with (x = 0.5; 1.0; 1.5 and 2.0) are a single phase. If (x) and (3-x) are respective y and z, so the empirical of composition is $Ni_yFe_zO_4$. This result is in accordance with the calculation results of the cationic distribution and the lattice parameters as shown in Table 1. Table 1 shows the cationic distribution and lattice parameters with varied nickel addition on the samples.

Table 1 Cationic distribution and lattice parameters of $Ni_yFe_zO_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h.

Atomic composition			Structure parameters				
x	y	z	a = b = c (Å)	V (Å^3)	ρ(gr/cm^3)	Chi (χ^2)	Rwp (%)
0.5	1.04	1.96	8.3338(1)	578.8(3)	5.600	1.024	6.10
1.0	1.23	1.77	8.2573(6)	563.0(1)	5.479	1.096	17.08
1.5	1.51	1.49	8.2775(6)	567.1(1)	5.275	1.092	14.15
2.0	1.94	1.06	8.3138(2)	574.6(5)	5.161	1.049	8.61

General formula of AB_2O_4 was crystallize in spinel structure, where A cation is transition metals with 2+ valence, and B cation is transition metals with 3+ valence. The addition of Ni^{2+} in the $Ni_xFe_{3-x}O_4$ formula will generate to form a single phase of AB_2O_4 spinnel structure. Based on Table 1 shows that A cations consist of Ni atoms while B cations consist of Fe atoms. The refinement result showed that the nickel ferrite formed a single phase empirical with compound of $Ni_{1.04}Fe_{1.96}O_4$, $Ni_{1.23}Fe_{1.77}O_4$, $Ni_{1.51}Fe_{1.49}O_4$, and $Ni_{1.94}Fe_{1.06}O_4$ are respective for x = 0.5;1.0; 1.5 and 2.0.

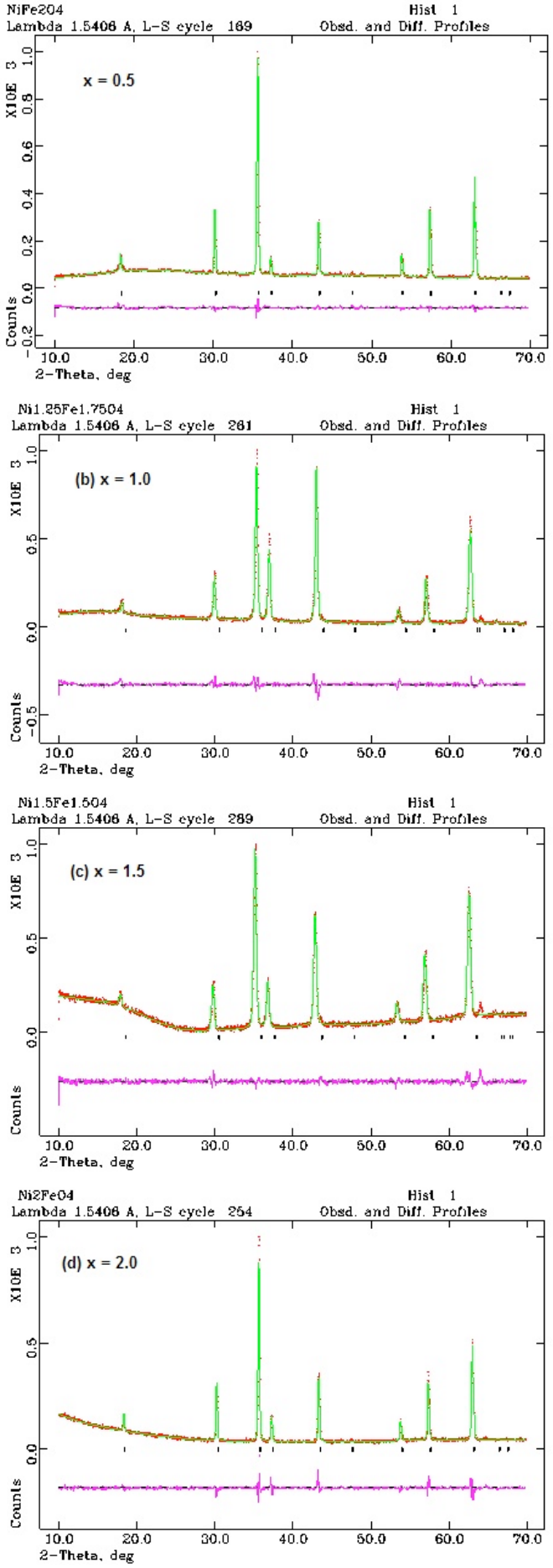

Fig. 3 The refinement of XRD pattern of the $Ni_xFe3_{-x}O_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h.

The magnetic properties of samples $Ni_xFe_{3-x}O_4$ from the synthesis by solid state reaction using milling method are described by a hysteresis curve based on measurement with the VSM in the range of -1 Tesla magnetic fields up to 1 Tesla, as shown in Fig. 4.

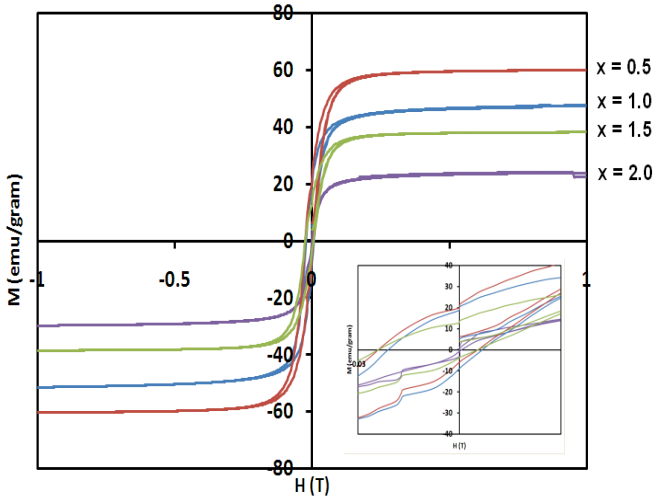

Fig. 4 Hysteresis curve of $Ni_xFe_{3-x}O_4$ sampels with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h

The hysteresis loop shows that all samples have the ferromagnetic behaviour with a relatively small of coercivity value as shown in Table 2. Based on the data in Table 2, it can be seen that the magnetization saturated (M_s) and remanence (M_r) decrease along with the increasing value of x (nickel content addition).

Table 2 Magnetic properties data of $Ni_xFe_{3-x}O_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h.

x	Magnetic parameter		
	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
0.5	45.3	20.4	164
1.0	39.5	14.2	182
1.5	32.4	13.3	217
2.0	22.1	8.8	168

Magnetization dipole moment is defined as the sum total (μ_j) atoms contained in the magnetic phase per unit volume, where μ_j expressed in Bohr magneton (μ_B) and $1\mu_B = 9.273 \times 10^{-24}$ $J.T^{-1}$. In this case, the total magnetic dipole moment of nickel is smaller than the iron so that the larger the addition of nickel then the lower the magnetization value. However, the value of coercivity increase up to x = 1.5, where the coercivity value increase up to 217 Oe, after that decrease again. Magnetic anisotropy may arise from various causes such as magnetic shape, crystal structure, the effects of stress, etc. Most ferromagnetic materials have a crystal anisotropy called magneto crystalline anisotropy in which the crystals have a preferred direction of magnetization and is called the easy directions(Nabiyouni et al. 2010). When the magnetization direction of the easy axis do this, the state of saturation can be achieved on the external magnetic field is relatively small. Conversely, when the magnetization direction of the axis of hard to do saturation state is achieved on the application magnetic field is relatively high. It is predicted for the sample $Ni_xFe_{3-x}O_4$ on the composition of x = 1.5 is thought to have microwave absorption value better than other compositions.

Fig. 5 shows the microwaves absorption of the sample $Ni_xFe_{3-x}O_4$ from synthesis by the solid state reaction using the milling method were measured by VNA in the frequency range 9.0 to 12 GHz in the form of reflection loss curves (RL). Reflection loss indicates resonance mechanism between spin magnetic of the electromagnetic wave with material causing microwave absorption.

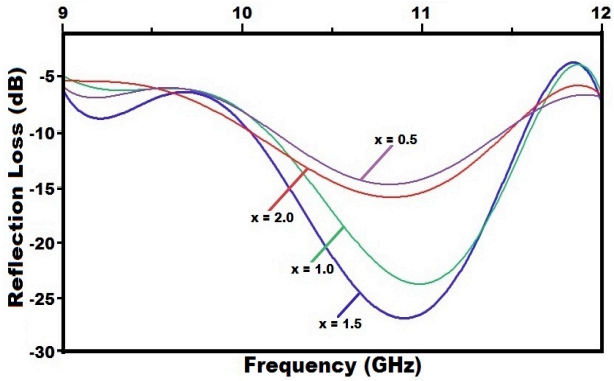

Fig. 5 Reflection loss curva of $Ni_xFe_{3-x}O_4$ with (x = 0.5; 1.0; 1.5 and 2.0) after milling for 10 h

In Fig. 5 it appears that there are a peaks lowest RL generated by the sample $Ni_xFe_{3-x}O_4$ with different peaks for each sample. Absorption of microwaves by the sample $Ni_xFe_{3-x}O_4$ increases with deficits improve the content of $Ni_{(x)}$ in the samples up to x = 1.5, while the value of x = 2.0 microwave visible decline. Increased reflection losses associated with the value of coercivity (Hc) of material. The greater the value of Hc the absorption of microwaves is also getting bigger. From the results of this study showed the maximum absorption of the sample x = 1.5 with a large uptake -28 dB at a frequency of 10.98 GHz, which means they can absorb microwaves around 96%.

CONCLUSION

From the results of this study is concluded that the samples $Ni_xFe_{3-x}O_4$ have been successfully synthesized by solid state reaction between NiO and Fe_2O_3 using milling techniques with HEM for 10 h. The XRD data shows that all of samples have a single phase with the structure of spinel ferrite particles. The visible absorption peaks for sample of $NiFe_2O_4$ appear at wave number around 599.84 and 414.68 cm^{-1}. Two of this peak is the main peak of the cluster uptake of metal ions and oxygen associated with the structure of spinel ferrite, which each associated with site octahedral and tetrahedral positions of metal ions on spinel ferrite. The hysteresis loop shows that all of samples have the ferromagnetic behaviour with a relatively small of coercivity value. The value of coercivity increase up to 217 Oe for x = 1.5, and then decrease again along with x addition. The measurement results of microwaves absorption shows that the samples with x = 1.5 gives the value RL (reflection loss) is maximum equal to -28 dB, this means that the sample x = 1.5 able to absorb microwaves up to 96% at a frequency of 10.98 GHz.

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