http://www.jourmag.org/index.php/jma

Journal of Magnetism and Its Applications

Received August 9th 2021 received in revised November 20th 2021 accepted December 25th 2021

Research article

# Effect of Ni on Dielectric Properties of MnNi-$Fe_2O_4$ Magnetic Nanoparticles

**Zulkarnain, Edi Suharyadi***

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Special Region of Yogyakarta 55281, Indonesia

**Article info**

**Keywords:**
Dielectric
Magnetic nanoparticles
Mn-$NiFe_2O_4$
Ferrites

**Abstract**

$Mn_{1-x}Ni_xFe_2O_4$ nanoparticles were successfully synthesized using co-precipitation method with various Ni concentrations. The crystal structures and dielectric properties of nanoparticles were analyzed for different Ni concentrations. The crystallite size of nanoparticles decreased from 19.7 to 3.6 nm with the increase of Ni concentration from 0.3 to 0.8. The dielectric properties were studied at frequencies of 10 – 1000 kHz. The dielectric permittivity (real and imaginary) decreased with the increase of frequency up to 200 kHz. The highest real dielectric permittivity ($\varepsilon'$) was 343.3 and the imaginary dielectric permittivity ($\varepsilon''$) was 440.5, for Ni concentration of 0.5 at frequency 10 kHz. Furthermore, the dielectric permittivity of the $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles were dependent on the frequency. This type of behavior can be explained by the Maxwell-Wagner model.

## 1. Introduction

Magnetic nanoparticles (MNPs) such as manganese ferrite have excellent magnetic and dielectric properties [1, 2]. The spinel ferrite MNPs are commonly used in recording media, microwave devices, and magnetic resonance imaging. The virtue of ferrite material has higher efficient, low cost, and the corresponding dielectric losses. The dielectric properties of ferrite spinel are generally influenced by factors of preparation method, cation distribution, grain size, etc. [3].

Ferrite with $MFe_2O_4$ formula (M = Ni, Mn, Zn) crystallizes has various structures such as a normal spinel structure, mixed or in the perfectly inverse spinel structure [4]. Manganese ferrite ($MnFe_2O_4$) has advantages over other materials due to high electrical resistivity and low eddy current loss [5], large saturation magnetization and moderate coercivity [6]. While nickel ferrite is a technologically important material, used in a wide variety of applications, including computer components, transformer cores, isolators, circulators, microwave frequencies and others [7]. Ferrite nanoparticles can be synthesized in several methods i.e., coprecipitation [8], auto-combustion [9], hydrothermal route [10], and sol gel method [11].

Yuvaraj *et al.* synthesized $Mn_{1-x}Ni_xFe_2O_4$ (with x = 0 – 0.25) with the coprecipitation method to learn the structure and properties of nonlinear optics in the samples. The result showed that the crystalline size decreased with the increase of Ni concentration [12]. Moreover, the dielectric properties of ferrite with various concentration of metal divalent and measurement frequencies are also important to be investigated. For example, the dielectric permittivity and dielectric losses of ferrites are rapidly decreasing with frequencies at the low frequency level [13]. The dielectric permittivity of manganese ferrite increased with the increase of temperature [14]. The dielectric properties of $Ni_{1-x}Mn_xFe_2O_4$ (with x = 0 – 0.5) has been investigated by Airimioaei *et. al.* [15]. Since, the crystal structure of ferrite is significantly influenced by metal divalent concentration, the dielectric properties of $Ni_{1-x}Mn_xFe_2O_4$ with wide range of metal divalent concentration is also important to be studied. Therefore, in this work, the dielectric permittivity of manganese nickel ferrite ($Mn_{1-x}Ni_xFe_2O_4$), and the impact of both with wide range of nickel concentration is investigated. The relationship between the crystal structure and the dielectric properties is also studied.

## 2. Experimental Methods

$Mn_{1-x}Ni_xFe_2O_4$ nanoparticles with various Ni concentrations (x = 0.3 – 0.8) were synthesized by the co-precipitation method. Iron chloride hexahydrate ($FeCl_3.6H_2O$) (Merck, Germany), nickel chloride hexahydrate ($NiCl_2.6H_2O$) (Merck, Germany), manganese (II) chloride ($MnCl_2.H_2O$) (Merck, Germany), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as precursor. First, $NiCl_2.6H_2O$ and $MnCl_2.H_2O$ was dissolved in 25 mL deionized water and mixed to form A solution. Afterwards, $FeCl_3.6H_2O$ also prepared in 25 mL deionized water to made B solution. The Solution A and B were mixed and stirred in 500 rpm around 3 minutes. Then, HCl (37%) about 3.37 mL was added into the mixed solution. This mixture was slowly added into a NaOH 8 M solution (dissolved in 50 mL deionized water) at 70°C at 1000 rpm for 1 hour. Then, the sample was cooled at room temperature and precipitated. The precipitation was washed in six times with deionized water. Finally, the samples were dried at 90°C for 4 h using furnace to get sample powder. The crystal structure of the samples has been studied by XRD (Merck, PanAnalytical, Cu-Kα radiation, $\lambda$ = 1.5406 Å). For dielectric analysis, the powder sample was converted into pellets with a diameter of 1.23 cm using a press force of 1000 N [16]. Dielectric properties were performed using computerized impedance spectroscopy to measure dielectric complexes, loss tangents with a frequency range from 10 kHz to 1MHz.

*Corresponding author
Email: esuharyadi@ugm.ac.id

DOI: 10.53533/JMA.v1i2.11

## 3. Results and Discussion

### 3.1 Crystal Structure

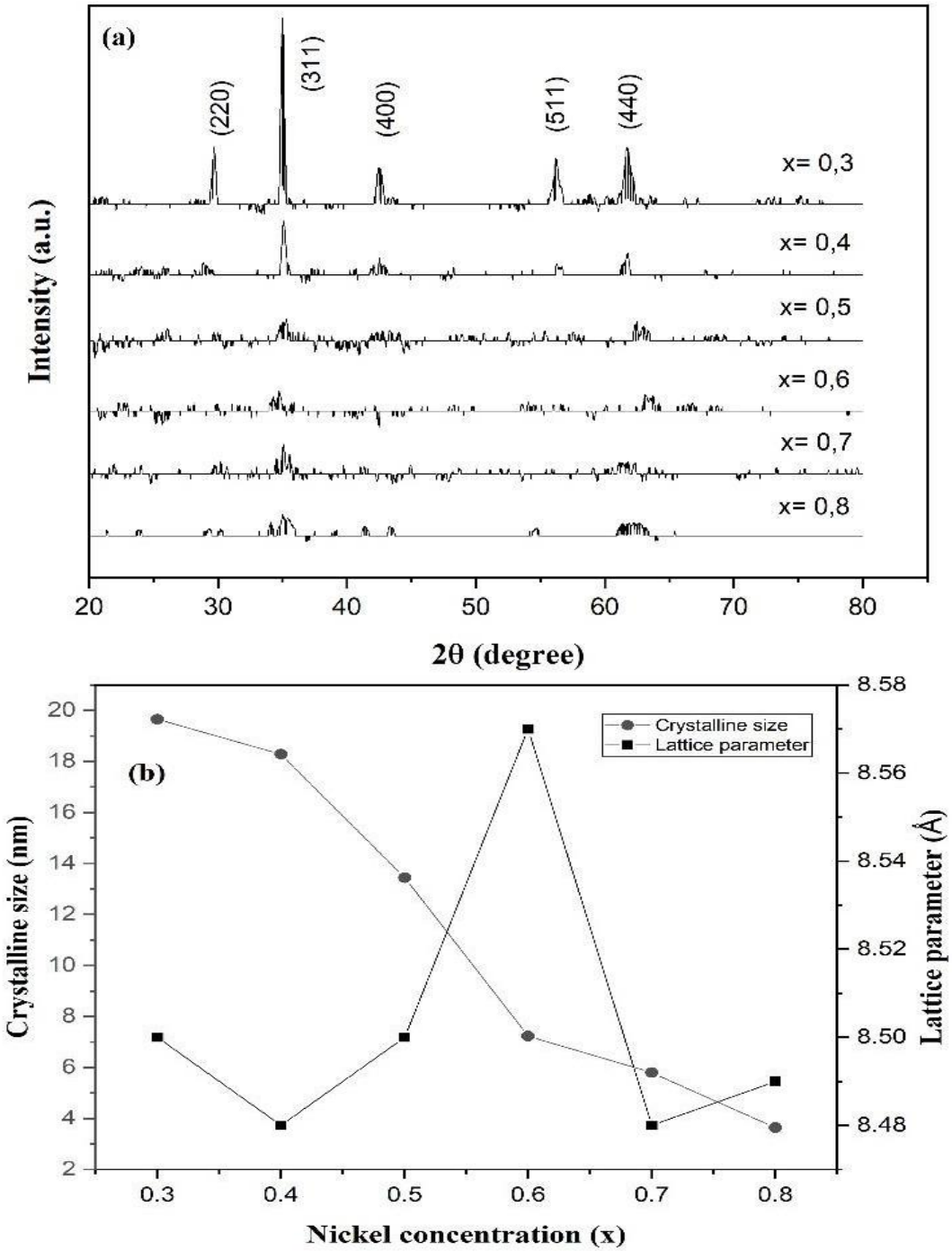



**Fig. 1.** X-ray diffraction patterns (a) and crystallite size and lattice parameter (b) of $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles.

The diffraction pattern of all samples has been matched with the standardized data diffraction (JCPDS no. 10-0325) for $NiFe_2O_4$ and (JCPDS no. 10-0319) for $MnFe_2O_4$, as shown in Fig. 1.a. There are five peaks as the fields (220), (311), (400), (511), and (440) with angles ($2\theta$) around 29°, 35°, 43°, 56°, and 63°, respectively, which is due to spinel ferrite structure of the samples.

The crystal parameters such as crystallite size was calculated by using Scherer's equation [4]:

$$t = \frac{(0.9\lambda)}{(\beta \cos\theta)} \quad (1)$$

where $t$ is the grain size, $\lambda$ is the wavelength of the Cu-K$\alpha$ radiation ($\lambda$ = 1.5406 Å), and $\beta$ is the full width at half maximum (FWHM) of the diffraction peak [3]. Lattice constant was calculated with a formula: $a^2 = d^2 (h^2+k^2+l^2)$ [17]. The crystallite size of the sample decreases from 19.7 to 3.6 nm with the increase of nickel concentration. The lattice parameter increased with the increase of Ni concentration up to x = 0.6, and then decreased, as shown in Fig. 1.b. The phenomena of the changing of the particle size at the middle level of metal divalent concentration may be caused by the exchanged of ion $Mn^{2+}$ and $Ni^{2+}$ [12].

### 3.2 Dielectric Properties

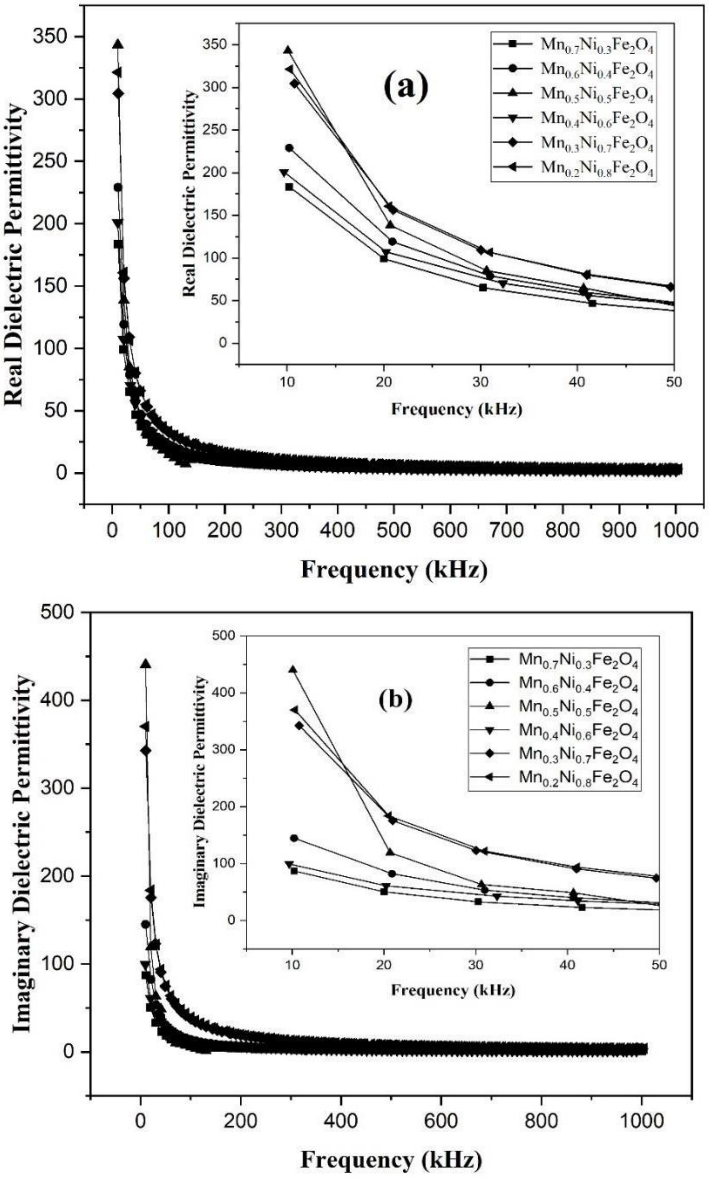



**Fig. 2.** Frequency dependences of real $\varepsilon'$ (a) and imaginary $\varepsilon''$ (b) dielectric permittivity of $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles with various Ni concentrations. Insert: at the low frequency level

The dielectric properties (the real dielectric permittivity $\varepsilon'$ and the imaginary dielectric permittivity $\varepsilon''$ were measured at the frequencies 10 - 1000 kHz and room temperature. The frequency dependence of the dielectric permittivity (real and imaginary) with various Ni concentration is shown in Figure 2. The dielectrics (real and imaginary) decreased with the increase of frequency for all samples. The dielectric permittivity (real and imaginary) decreased rapidly with the increase of frequency up to 200 kHz. The significant decrease in the value of real dielectric permittivity is shown in the low frequency range of 10 kHz to 200 kHz, then the real dielectric permittivity value begins to be constant at a higher frequency of more than 200 kHz. This also happens to the imaginary dielectric permittivity as a function of frequency, as shown in Figure 2 (b). At low frequencies, electron displacement can follow the direction of the external field given to the nanoparticles, increasing polarization which causes the value of dielectric constants to be high. Conversely, the decrease in dielectric constants with increased frequency is also caused by the inability of electrons to align their position to the given electric field so that polarization decreases and eventually results in dielectric constants decreasing and eventually tending to be constant at high frequencies. The relationship between material polarization and dielectric permittivity values (real and imaginary) is further explained using the Debye model. The value of dielectric permittivity (real and imaginary) is inversely proportional to the frequency or $\omega\tau$. Therefore, dielectric constants and electrical susceptibility are polarizing measures of a material [18]. In general, the decrease in dielectric constants along with increased frequency is a common phenomenon for ferrite materials. At low frequencies there is a phenomenon of dielectric dispersion due to Maxwell-Wegner interfacial polarization and in accordance with the theory of Koop [19]. The maximum dielectric permittivity behavior against frequency can be explained using the Rezlescu model [20]. The highest real and imaginary dielectric permittivity is 343.3 and 440.5, respectively, at Ni concentration of 0.5 at 10 kHz in frequency. The dielectric permittivity tends to increase with the increase of Ni concentration, which is due to the decrease of the crystallite size [12]. The dielectric properties were measured at the low frequency for $Mn_{1-x}Ni_xFe_2O_4$ nanoparticles. The dielectric permittivity tends to increase with the increase in nickel ions. The samples have a spinel structure in which the ions occupy two types of sites. Both of two sites are the tetrahedral sites and octahedral sites. The exchange of $Fe^{2+}$ and $Fe^{3+}$ in two type sites increased polarization [3]. The dielectric permittivity (real and imaginary) of all samples is constant at the frequencies higher than 200 kHz.

## 4. Conclusions

$Mn_{1-x}Ni_xFe_2O_4$ nanoparticles with crystallite size from 3.6 to 19.7 nm were successfully synthesized by co-precipitation method. The samples have the cubic spinel structure and crystallite size decreases with the increase of Ni concentration. The frequency dependences of the real and imaginary of dielectric permittivity is congruously represented by the Maxwell-Wagner model. The dielectric permittivity tends to increase with the increase of Ni concentration.

## Acknowledgements

This work is funded and the grant of PTUPT 2020-2022, Ministry of Education, Culture, Research & Technology, Republic of Indonesia.

## References

[1] A. Rajeshwari, I. K. Punithavthy, S. J. Jeyakumar, N. Lenin, and B. Vigneshwaran, "Dependance of lanthanum ions on structural, magnetic and electrical of manganese based spinel nanoferrites," *Ceram. Int.*, vol. 46, no. 5, pp. 6860–6870, 2020.
[2] H. Tombuloglu, G. Tombuloglu, Y. Slimani, I. Ercan, H. Sozeri, and A. Baykal, "Impact of manganese ferrite ($MnFe_2O_4$) nanoparticles on growth and magnetic character of barley (Hordeum vulgare L.)," *Environ. Pollut.*, vol. 243, pp. 872–881, 2018.
[3] Kurnia, Heriansyah, and E. Suharyadi, "Study on the influence of crystal structure and grain size on dielectric properties of manganese ferrite ($MnFeO_4$) nanoparticles," in *IOP Conference Series: Materials Science and Engineering*, 2017, vol. 202, no. 1, p. 12046.
[4] Z. Ž. Lazarević *et al.*, "Structural, electrical and dielectric properties of spinel nickel ferrite prepared by soft mechanochemical synthesis," *Mater. Res. Bull.*, vol. 48, no. 10, pp. 4368–4378, 2013.
[5] K. Akhtar, M. Gul, I. U. Haq, R. A. Khan, Z. U. Khan, and A. Hussain, "Synthesis and characterization of uniform fine particles of pure and chromium-substituted manganese ferrite with low dielectric losses," *Ceram. Int.*, vol. 42, no. 16, pp. 18064–18073, 2016.
[6] M. Zeng *et al.*, "High-frequency electromagnetic properties of the manganese ferrite nanoparticles," *J. Appl. Phys.*, vol. 117, no. 17, p. 17B527, 2015.
[7] K. Raju, C. G. Balaji, and P. V. Reddy, "Microwave properties of Al and Mn doped nickel ferrites at Ku band frequencies," *J. Magn. Magn. Mater.*, vol. 354, pp. 383–387, 2014.
[8] S. Mirzaee, Y. Azizian-Kalandaragh, and P. Rahimzadeh, "Modified co-precipitation process effects on the structural and magnetic properties of Mn-doped nickel ferrite nanoparticles," *Solid State Sci.*, vol. 99, p. 106052, 2020.
[9] R. Kesavamoorthi and C. Raja, "Studies on the Properties of Manganese Substituted Nickel Ferrite Nanoparticles.," *J. Supercond. Nov. Magn.*, vol. 29, no. 11, 2016.
[10] Y. Köseoğlu, "Structural, magnetic, electrical and dielectric properties of $Mn_xNi_{1-x}Fe_2O_4$ spinel nanoferrites prepared by PEG assisted hydrothermal method," *Ceram. Int.*, vol. 39, no. 4, pp. 4221–4230, 2013.
[11] N. Hamdaoui, Y. Azizian-Kalandaragh, M. Khlifi, and L. Beji, "Structural, magnetic and dielectric properties of $Ni_{0.6}Mg_{0.4}Fe_2O_4$ ferromagnetic ferrite prepared by sol gel method," *Ceram. Int.*, vol. 45, no. 13, pp. 16458–16465, 2019.
[12] S. Yuvaraj, N. Manikandan, and G. Vinitha, "Structural and nonlinear optical properties of nickel substituted manganese ferrite nanoparticles," *Ceram. Int.*, vol. 44, no. 18, pp. 22592–22600, 2018.
[13] R. S. Yadav *et al.*, "Structural, magnetic, dielectric, and electrical properties of $NiFe_2O_4$ spinel ferrite nanoparticles prepared by honey-mediated sol-gel combustion," *J. Phys. Chem. Solids*, vol. 107, pp. 150–161, 2017.
[14] M. M. N. Ansari, S. Khan, R. Bhargava, and N. Ahmad, "An extensive study of electrical properties of $MnFe_2O_4$ nano-ferrite," in *AIP Conference Proceedings*, 2019, vol. 2115, no. 1, p. 30076.
[15] M. Airimioaei *et al.*, "Synthesis and functional properties of the $Ni_{1-x}Mn_xFe_2O_4$ ferrites," *J. Alloys Compd.*, vol. 509, no. 31, pp. 8065–8072, 2011.
[16] Zulkarnain, "Study of Dielectric Properties and Gap Energy on $Mn_{1-x}Ni_xFe_2O_4$ Magnetic Nanoparticles," Universitas Gadjah Mada.
[17] E. R. Kumar and R. Jayaprakash, "Effect of combustion rate and annealing temperature on structural and magnetic properties of manganese substituted nickel and zinc ferrites," *J. Magn. Magn. Mater.*, vol. 348, pp. 93–100, 2013.
[18] R. Y. Hong *et al.*, "Synthesis, surface modification and photocatalytic property of ZnO nanoparticles," *Powder Technol.*, vol. 189, no. 3, pp. 426–432, 2009.
[19] J. Hassan *et al.*, "Dielectric permittivity of nickel ferrites at microwave frequencies 1 MHz to 1.8 GHz," *Ionics (Kiel).*, vol. 13, no. 4, pp. 219–222, 2007.
[20] E. R. Kumar, A. S. Kamzin, and T. Prakash, "Effect of particle size on structural, magnetic and dielectric properties of manganese substituted nickel ferrite nanoparticles," *J. Magn. Magn. Mater.*, vol. 378, pp. 389–396, 2015.