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Edi Suharyadi
Department of Physics, Universitas Gadjah Mada, Yogyakarta12850, Indonesia, suharyadi@ugm.ac.id

Dwi Indah Rahayu
Department of Physics, Universitas Gadjah Mada, Yogyakarta12850, Indonesia

Linda Armitasari
Department of Physics, Universitas Gadjah Mada, Yogyakarta12850, Indonesia

Kamsul Abraha
Department of Physics, Universitas Gadjah Mada, Yogyakarta12850, Indonesia

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Influences of Zn Concentration on Dielectric Properties of $Zn_xNi_{1-x}Fe_2O_4$ Magnetic Nanoparticles

Edi Suharyadi*, Dwi Indah Rahayu, Linda Armitasari, and Kamsul Abraha

Department of Physics, Universitas Gadjah Mada, Yogyakarta 12850, Indonesia

*E-mail: esuharyadi@ugm.ac.id

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Abstract

Dielectric properties of $Zn_xNi_{1-x}Fe_2O_4$ magnetic nanoparticles (MNPs) with various Zn concentration (x = 0.2-0.8) have been investigated over a wide frequency range 5–120 kHz. Zn-Ni ferrite MNPs have spinel cubic structure. The crystallite size of the sample for x = 0.2 was about 21.5 nm and then decreases by increasing Zn concentration. For sample with x = 0.4 at frequency 20 kHz, the real dielectric constant (ε') was 35.9, imaginary dielectric constant (ε'') was 20.4 and loss tangent ($\tan\delta$) was 0.6. Zn concentration would affect to availability of ferrous and ferric ions in the octahedral site which are preferentially occupied by Zn^{2+} ion. The dielectric constants decrease with increasing frequency. The sample with at x = 0.6 has the highest dielectric on frequency 5 kHz. The maximum AC conductivity (σ_{AC}) was 1.7 × 10^{-4} Ω^{-1} at 65 kHz observed for concentration x = 0.3. The dielectric constants and conductivity at low frequency are due to the existence of grains boundary while the dispersion in the high frequency region are due to the conducting grains.

Abstrak

Pengaruh Konsentrasi Zn pada Sifat Dielektrik Nanopartikel Magnetik $Zn_xNi_{1-x}Fe_2O_4$. Sifat dielektrik nanopartikel magnetik $Zn_xNi_{1-x}Fe_2O_4$ dengan variasi konsentrasi Zn (x = 0,2 – 0,8) telah dikaji pada rentang frekuensi (5 – 120) kHz. Nanopartikel Zn-Ni ferrite memiliki struktur kubik spinel. Ukuran kristalit nanopartikel dengan x = 0,2 adalah sekitar 21,5 nm dan berkurang seiring dengan bertambahnya konsentrasi Zn. Pada frekuensi 20 kHz, nilai konstanta dielektrik riil (ε'), konstanta dielektrik imajiner (ε'') dan rugi tangen ($\tan\delta$) dari nanopartikel dengan x = 0,4 berturut-turut adalah sebesar 35,9; 20,1 dan 0,6. Meningkatnya konsentrasi Zn berdampak pada ketersediaan ion Fe^{3+} dan Fe^{2+} dalam sub ruang oktahedral. Konstanta dielektrik berkurang seiring dengan meningkatnya frekuensi. Nilai konstanta dielektrik tertinggi terdapat pada nanopartikel dengan x = 0,6 saat frekuensi 5 kHz. Sementara itu, nilai konduktivitas AC (σ_{AC}) tertinggi terdapat pada nanopartikel dengan x = 0,3 saat frekuensi 65 kHz, yaitu 1,7 × 10-4 S/cm. Hal ini disebabkan karena polarisasi muatan terjadi pada bagian batas butir.

Keywords: Zn-Ni ferrites, magnetic nanoparticles, dielectric, coprecipitation

Introduction

Magnetic nanoparticles (MNPs) still have a great interest in fundamental science, due to their different performance compared with its bulk size. At the nanoscale, properties like electrical conductivity and mechanical strength are not the same as they are at bulk size [1]. The electronic structure of MNPs changes dramatically by the modification of particles size. Spinel ferrites MNPs are good dielectric materials and they have wide applications ranging from microwave frequency to radio frequency [2]. Zn-Ni ferrite is the most interesting one of spinel ferrites. Zn-Ni ferrite is a combination of Zn ferrite which belongs to normal spinel and Ni ferrite which belongs to inverse spinel. Based on their soft magnetic characteristics, Zn-Ni ferrite has low coercivity, high permeability, high electrical resistance and low eddy current losses [2,3]. It is found to be very useful in technological applications, such as microwave absorber which needs those characteristics. Moreover, the Zn-substitution will affect the chemical composition and different distribution of cation. Zn-substitution improves the chemical stability, corrosion resistivity, magneto-crystalline anisotropy as well magneto-optical property of Zn-Ni ferrite [3].

Dielectric properties of ferrite MNPs are depend on preparation method, grain size, cation distribution and chemical composition [4,5]. As reported by Moradmard *et al.* [4] that dielectric and electrical properties of $Ni_{1-x}Mg_xFe_2O_4$ MNPs which made by co-precipitation changed due to preparation method and chemical composition. Crystal structures show how the chemical composition and physical properties of materials are linked together. Istikhomah *et al.* [6] reported that Zn concentration could give an influence in structure and magnetic properties of $Zn_xNi_{1-x}Fe_2O_4$ MNPs which made by co-precipitation method. Atiq *et al.* [3] investigated the dielectric properties of $Ni_{1-x}Zn_xFe_2O_4$ in the frequency range from 100 Hz to 20 MHz which made by sol gel combustion method. The sol gel combustion method needs very long time and very high temperature in preparation of $Zn_xNi_{1-x}Fe_2O_4$ MNPs while the co-precipitation method is simpler, easier and only need low temperature [7]. Study of effects of Zn on dielectric properties of Mn-Zn spinel ferrite recently has been reported [8]. Many methods have been developed to synthesize $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles, such as sol-gel, solid state reaction, ceramic method, sol-gel auto combustion, and coprecipitation. Among those methods, coprecipitation is considered the most effective because it can result from a small crystallite size, high purity product, not time-consuming [9,10].

Complex dielectric constant does not decrease continuously with frequency increases due to interface polarization which is dominant at frequencies below 30 kHz [11]. In this frequency region, behavior of these materials is analogous with Debye type of relaxation process. Electronic and ionic polarization have negligible influence to the value of complex dielectric constant. That is due to the fact that those polarization only can occur in microwave region. However, the dielectric properties of Zn-Ni ferrite MNPs which made by simpler method and range measurement of frequencies which caused interface polarization have not yet been investigated in detail.

In this paper, the influence of Zn concentration on dielectric properties of $Zn_xNi_{1-x}Fe_2O_4$ MNPs prepared through co-precipitation method is investigated. The complex dielectric constant, loss tangent and AC conductivity in the frequency range from 5 to 120 kHz at room temperature are studied in detail using home-made impedance spectroscopy.

Experiment Details

$Zn_xNi_{1-x}Fe_2O_4$ MNPs (x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8) have been synthesized by using co-precipitation method with $FeCl_3.6H_2O$ (Merck, Germany), $ZnSO_4.7H_2O$ (Merck, Germany) and $NiCl_2.6H_2O$ (Merck, Germany) as precursors. Mass composition in detail is shown in Table 1. The synthesis was started by mixing 3.37 ml of HCl (37%) with $ZnSO_4.7H_2O$ and $NiCl_2.6H_2O$ for certain

Table 1. Mass Composition of Zn and Ni

x	$Zn_xNi_{1-x}Fe_2O_4$	$ZnSO_4.7H_2O$ (gram)	$NiCl_2.6H_2O$ (gram)
0.2	$Zn_{0.2}Ni_{0.8}Fe_2O_4$	0.230	0.761
0.2	$Zn_{0.3}Ni_{0.7}Fe_2O_4$	0.345	0.666
0.4	$Zn_{0.4}Ni_{0.6}Fe_2O_4$	0.460	0.570
0.5	$Zn_{0.5}Ni_{0.5}Fe_2O_4$	0.575	0.475
0.6	$Zn_{0.6}Ni_{0.4}Fe_2O_4$	0.690	0.380
0.7	$Zn_{0.7}Ni_{0.3}Fe_2O_4$	0.805	0.285
0.8	$Zn_{0.8}Ni_{0.2}Fe_2O_4$	0.920	0.190

ratio of mol which were dissolved into 20 ml of distilled water then stirred with 500 rpm for 2 minutes. The solution was dropped to NaOH 1.5 M and stirred with 1000 rpm for 60 minutes at a certain temperature. Furthermore, the solution was precipitated by external field (permanent magnet). The precipitation was washed in seven times by using distilled water to obtain a pure $Zn_xNi_{1-x}Fe_2O_4$. Samples were dried in a furnace at 90 °C for 4 hours. The crystal structure of samples were analyzed by using X-Ray Diffractometer (XRD) Shimadzu model XD-3H (Cu-Kα =1.5406 Å), and Transmission Electron Microscope (TEM) Jeol Jem-1400. The dielectric properties were measured by using computerized impedance spectroscopy on a circuit of AC in the frequency range from 5 to 120 kHz. Powder samples were firstly changed into pellets of 1.23 cm in diameter at the compressive force of 50.000 N. The dielectric properties measured such as complex dielectric, loss tangent and AC conductivity as a function of frequency.

Results and Discussion

Figure 1 shows the X-ray diffraction spectra of the samples. All of the main diffraction peaks confirmed that $Zn_xNi_{1-x}Fe_2O_4$ MNPs have spinel cubic structure with impurity phase. Diffraction peaks which indicated samples of Zn-Ni ferrite indexed to (220), (311), (400), (511), and (440) planes matched with JCPDS card No. 08-0234 [3]. The impurity phase FeO(OH) indexed to (221) plane matched with standard JCPDS card No. 220353 [6]. All diffraction peaks of MNPs shifted to lower angle by increasing Zn concentration indicated that lattice parameter were expanded. Lattice parameter increased from 8.599 Å (x=0.2) to 8.650 Å (x=0.8) due to the replacement of smaller Ni^{2+} ionic radii by larger Zn^{2+} ionic radii. Crystallite size decreased from 21.5 nm to 11.2 nm by increasing Zn concentration. This was due to the lower bond energy of Zn^{2+}-O^{2-} than Ni^{2+}-O^{2-} [12]. Figure 2 shows the dependence of crystallite size in Zn concentration.

Ring diffraction patterns from TEM characterisation are closely related to XRD analysis as shown in Fig. 3, which corresponds to the crystal plane (220), (311), (400), (511), and (440). Discontinue ring indicated the

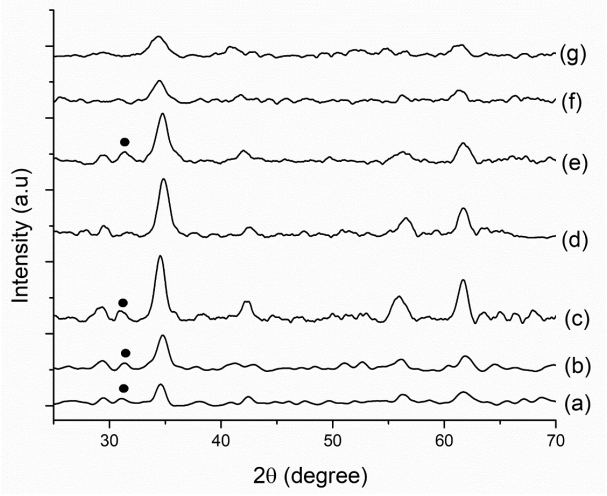

Figure 1. The X-ray Diffraction Spectra of $Zn_xNi_{1-x}Fe_2O_4$ MNPs (a) x=0.2, (b) x=0.3, (c) x=0.4, (d) x=0.5, (e) x=0.6, (f) x=0.7, and (g) x=0.8

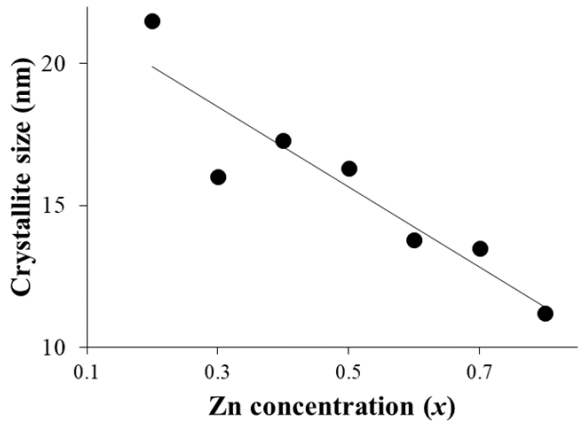

Figure 2. The Dependence of Crystallite Size of $Zn_xNi_{1-x}Fe_2O_4$ in Zn Concentration

polycrystalline structure of nanoparticles and high value of grain size. Morphology of sample with same ratio of Zn-Ni is shown in Figure 3, particles tend to agglomerate with non-uniform size. This is due to small particle size producing high surface energy and surface tension of nanoparticles. High surface energy of MNPs provide unstable surface, so agglomeration occurred to minimize their excess surface energy [13].

The dielectric properties have been measured by computerized impedance spectroscopy. Figure 4 shows the variation of dielectric constants as a function of frequency for the samples at room temperature in the frequency range from 5 to 120 kHz. For all samples, the value of real and imaginary dielectric constants is high at low frequency and then they decrease with the increases of frequency and saturated at high frequency. Those results are correspond with Maxwell-Wagner type of interfacial polarization in agreement with the Koop's phenomenological theory [14].

Based on these theories, the dielectric structure of ferrite NPs is consists of two layers: grains and grain boundaries. Grains can be considered as areas having low electrical resistance due to perfect crystalline characteristics, while on the grain boundaries are the regions having high resistance. Maxwell-Wagner interfacial polarization occurs in the grain boundaries due to the charge accumulation in these higher resistive boundaries. Furthermore, the electronic exchange between the substituted ions has an important role in the dielectric and conduction properties of the ferrites. Since the substitution is occurring at tetrahedral sites, so the phenomenon of electronic exchange due to Ni and Zn ions rise the local displacement in the direction of the external electric field. These local displacements determine the mechanism of polarization. Beyond a certain frequency of the external electric field, these local displacements cannot follow the alternating field so the dielectric constants become saturate. By increasing Zn concentration, the mobility of the charge carriers decreases which causes the local displacements of charges to decrease even further at lower frequencies [15]. Table 2 describes the value of complex dielectric constant based on Zn concentration at some frequencies.

The exchange of Fe^{2+} and Fe^{3+} ions in spinel structure will result in local displacement caused by an external electric field, so more and more sites in spinel structure can increase the polarization because of increasing the number of Fe ions. Furthermore, this composition dependent behavior of Zn-Ni ferrites can also be explained on the basis of inverse spinel structure. For the samples under study, the presence of Ni^{3+}/Ni^{2+} ions lead to the formation of p-type charge carriers (holes), while n-type charge carriers (electrons) are also present due to the presence of Fe^{3+}/Fe^{2+} ions. The local displacements of these carriers in the direction of the external field contribute to the polarization mechanism. The maximum value of dielectric constant is obtained because maximum number of Fe^{3+} ions are present at octahedral site, thus showing high hopping rates as the contribution from these n-type carriers is high as compared to p-type carriers. With the Zn substitution, Fe^{3+} ions are replaced which depletes the number of Fe ions available for the conduction process, resulting a decrease in the probability of the following exchange mechanism $Ni^{2+} + Fe^{3+} \leftrightarrow Ni^{3+} + Fe^{2+}$ [3].

Figure 5 shows the loss tangent (tan δ) and AC conductivity (σ_{AC}) as a function of frequency for the samples at room temperature in the frequency range from 5 to 120 kHz. The behavior of loss tangent can be observed from the graph that loss tangent have high values at low frequencies while decrease with the increment in frequency and becomes independent at high frequencies.

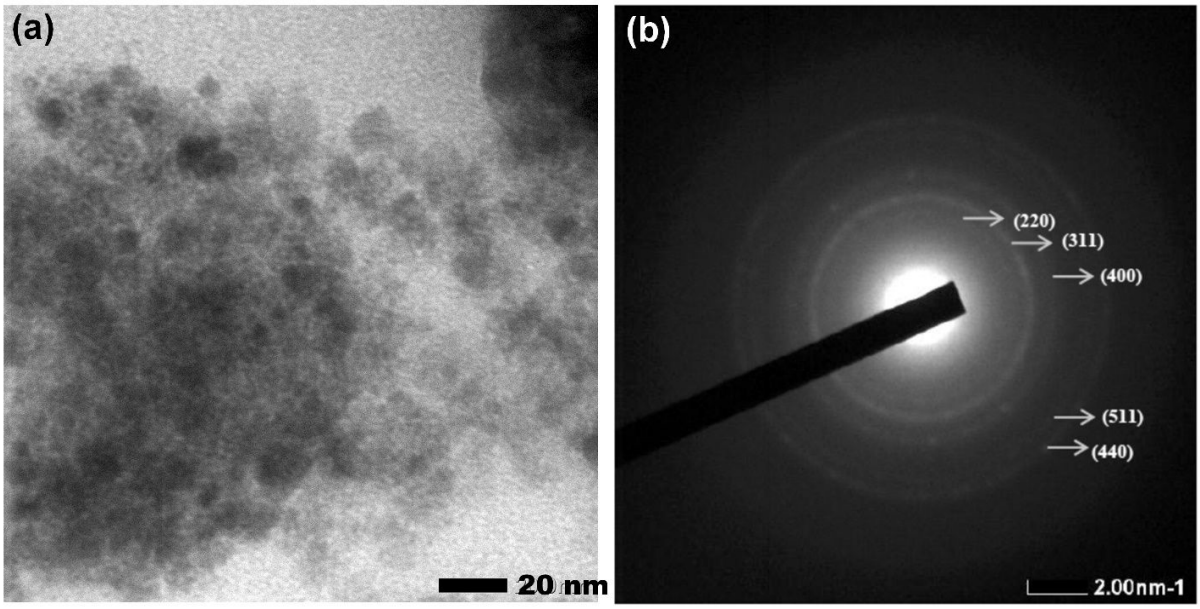

Figure 3. Morphology (a) and Diffraction Patterns (b) of of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ MNPs

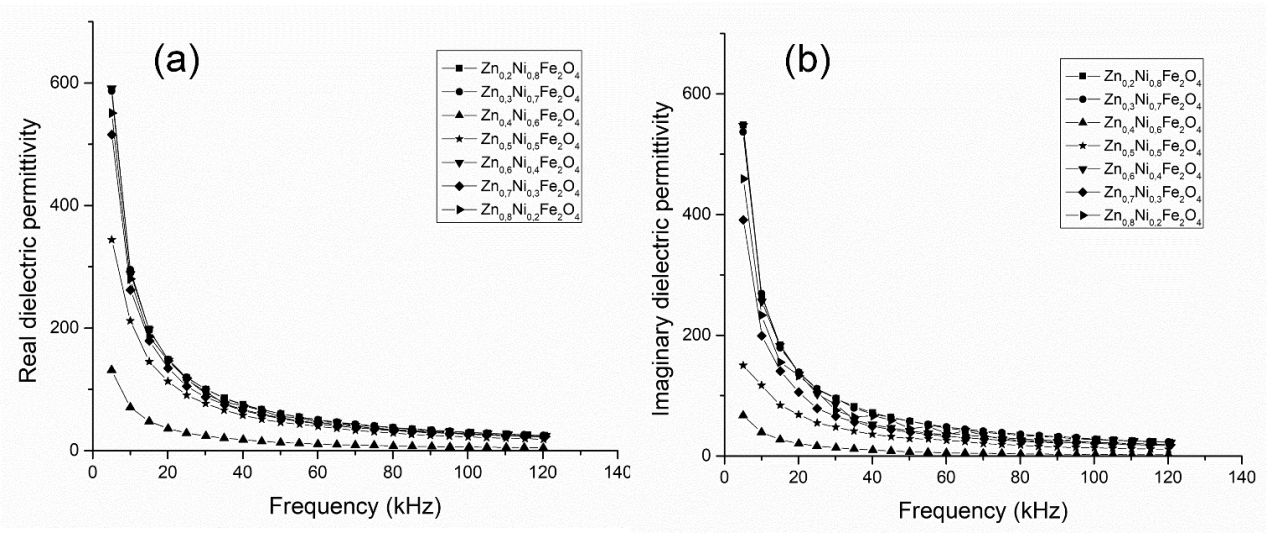

Figure 4. (a) Real and (b) Imaginary Dielectric Constants of $Zn_xNi_{1-x}Fe_2O_4$ MNPs as a Function of Frequency

Table 2. The Value of Complex Dielectric Constant of $Zn_xNi_{1-x}Fe_2O_4$ MNPs based on Zn Concentration

Zn concentration (x)	Real dielectric constant			Imaginary dielectric constant		
	20 kHz	60 kHz	100 kHz	20 kHz	60 kHz	100 kHz
0.4	36	11	6	20	5	3
0.5	113	40	22	68	26	13
0.6	147	45	29	135	35	27
0.7	135	44	27	106	33	21
0.8	146	46	28	133	38	23

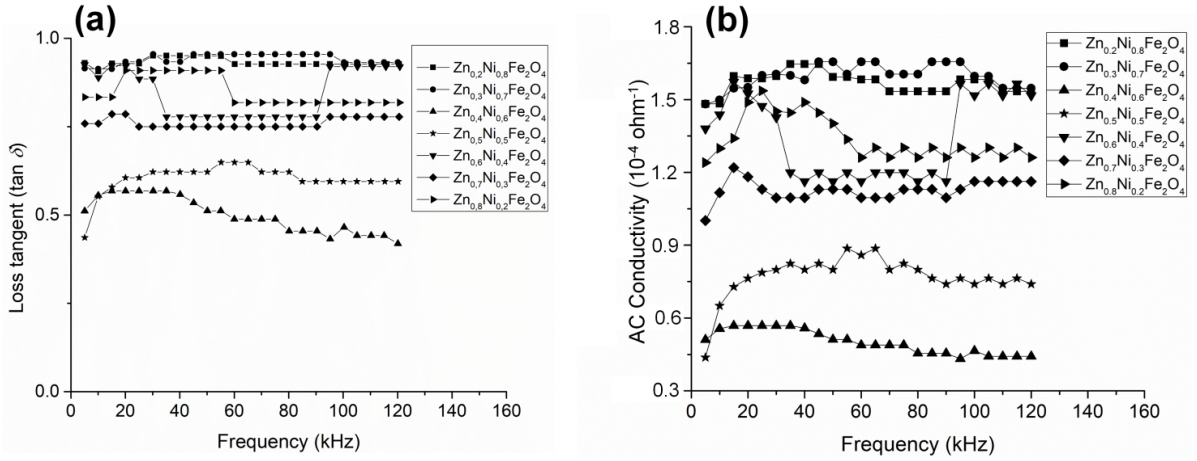

Figure 5. (a) Loss Tangent and (b) AC Conductivity of $Zn_xNi_{1-x}Fe_2O_4$ MNPs as a Function of Frequency

Loss tangent is the measure of energy absorption in the dielectric medium. These results are in accordance with the Koop's phenomenological theory and therefore, it is expected that the energy losses are high at low frequency while they are low at high frequency region. The behavior of these losses can be understood on the basis of polarization resonance with applied external field. Electrical conduction mechanism is related to the electron and polaron hopping mechanism which acts as hopping channels. An increase in frequency facilitates the conductive channels to become more active by promoting the hopping of charge carriers.

Summary

$Zn_xNi_{1-x}Fe_2O_4$ nanoparticles were successfully prepared by co-precipitation method. The increasing of Zn concentration is causing lattice parameter increases and crystallite size decreases. The crystallite size of the sample for x = 0.2 was about 21.5 nm and then decreases by increasing Zn concentration. The real and the imaginary dielectric constants and also loss tangent were increase with the increase of Zn concentration. The dielectric properties and AC conductivity were depend on frequency. Real and imaginary dielectric constants decreased with increasing frequency. The maximum AC electrical conductivity was 1.7×10^{-4} Ω^{-1} at 65 kHz observed for concentration $x = 0.3$.

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