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RADAR ABSORPTION OF $Ni_{0.7}Zn_{0.3}Fe_2O_4$ NANOPARTICLES

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NiZn-ferrite nanoparticles (9-42 nm) with the chemical formula $Ni_{0.7}Zn_{0.3}Fe_2O_4$ were synthesized by a low-temperature solid-state reaction (LTSSR) method. The powder of this ferrite was mixed with epoxy resin to be converted into a radar absorbing nanomaterial in frequencies of 8-12 GHz (X-band). X-ray techniques such as X-ray diffractometer (XRD) and also transmission electron microscope (TEM) were used to analyze the structure properties. It was found that the particle size and magnetic properties of the prepared ferrite sample showed strong dependence on the annealing temperature. The coercivity initially increased and then decreased with increasing the annealing temperature whereas the particle size and saturation magnetization continuously increased. The radar-absorbing properties were studied as a function of frequency, nanoparticle size, ferrite /epoxy resin ratio, and thickness of absorber.

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1. Introduction

Magnetic nanoparticles have some important industrial applications such as Ferro-fluids, magnetic drug delivery, high-density information storage. Fundamental understanding properties of those nanoparticles were also compared with that of bulk samples [1]. There is an increasing interest for production of new magnetic nanoparticles because of the wide applications of these materials. Since the spinel ferrites crystallize in an FCC lattice with eight formula units in the cubic unit cell, they can be distinguished as two basic types, normal and inverse spinels [2]. The composition of ferrospinels can be described by the general formula $M^{2+}[Fe^{3+}Fe^{3+}]O_4$, which has wide applications in both the technological and the catalytic fields [3].

However, unusual distribution of cations among the tetrahedral (T) and octahedral (O) sites of the coordinated oxygen is an important factor for explanation of the catalytic effectiveness. Crystal field stabilization energy, Madelung constant and cation size are three principal parameters in deciding the structure of the systems [3, 4]. Since the major influence in the activity comes from the O-ions, probably for the presence of the large exposure of these ions on the surface, it enables spinels to withstand even in extremely reducing conditions [5].

Microwave absorbers are in use since long, both in civil and military application, on account of their ability to eliminate electromagnetic wave pollution and to reduce radar signatures. Recently, the demand for microwave absorbers has increased in the frequency range of 1-20 GHz, because of their two-fold use: electromagnetic interference shielding and countermeasure to radar detection. Spinel ferrites based on Ni-Zn have been used as high-frequency ferrites for transformers core, rod antennas, radiofrequency and more recently as radar absorbing materials

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[6]. In this work we used the low-temperature solid-state reaction (LTSSR) method to synthesize nanoparticles of ferrite based on NiZn and investigated as a radar absorbing nanomaterial in a frequency range of 8-12 GHz (X-band). The nanocrystallites of these materials were characterized by structural and magnetic methods. The radar-absorbing properties were studied as a function of frequency, nanoparticle size, ferrite /epoxy resin ratio, and thickness of absorber.

2. Experimental

2.1. Synthesize of ferrite powders

The chemical reagents are ferric chloride ($FeCl_3.6H_2O$), nickel chloride ($NiCl_2.6H_2O$), zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH), which provided with high purities from Merck. To get $Ni_{0.7}Zn_{0.3}Fe_2O_4$ for example, powders of $ZnCl_2$, $NiCl_2.6H_2O$, $FeCl_3.6H_2O$ and NaOH were mixed in their stoichiometry ratios (1:1:2:8). The mixture was milled at room temperature for 30 minutes in an aqueous muller. The nanoparticles were also washed with distilled water several times. To obtain the nanoparticles with formula $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ the following reaction can be written:

$$(0.3ZnCl_2 + 0.7NiCl_2) + 2FeCl_3 + 8NaOH \rightarrow Ni_{0.7}Zn_{0.3}Fe_2O_4 + 4H_2O + 8NaCl$$

The five specimen of the Ni-Zn ferrites were synthesized as follow: $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 30 ^oC (Ni30), $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 500 ^oC for 3h (Ni500), $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 800 ^oC for 3h (Ni800), $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 1000 ^oC for 3h (Ni1000) and $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 1200 ^oC for 3h (Ni1200).

2.2. Preparation of composites

In order to explore radar-absorbing properties, magnetic nanoparticles were mixed with an epoxy resin to be converted of both materials were studied using a microwave vector network analyzer from 8 to 20 GHz. NiZn-ferrite powders were mixed with resin in the different ratio, different thickness of absorber and the reflectivity was analyzed. Then hot pressing was carried out. The mixture of ferrite powders with epoxy resin were cured at 220 _C and 5.5 MPa pressure. Curing time was for 18 min. The pressed composite was in the cylindrical form with the diameter of 40 mm.

2.3. Measurement of properties

X-ray Diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer with Cu-Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scan rate for two seconds in steps of 0.04° for 2θ. The crystalline size was calculated from X-ray line broadening analysis by the Debye-Scherer equation for the full-width at half-maximum of the strongest reflection [7]:

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

where, D is the crystalline size in nm, λ is the Cu-Kα wavelength (0.154nm), β is the half-maximum breadth, and θ is the Bragg angle of the (311) plane.

The room temperature magnetization measurements up to a maximum field of 10 KOe were carried out using AGFM [8]. TEM were used for size and size distribution.

Samples were prepared to fit in a rectangular wave-guide of X-band. The wave-guide fitted with sample was backed by a metal short for measurement of reflection loss Vector Network Analyzer (ZVK Model 10 MHz-40 GHz).

3. Results and discussion

3.1. Microstructure and magnetic properties

XRD pattern for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ (annealed at 30-1200 ^oC for 3h) is shown in Fig. 1. The average particle size for all $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders was calculated by Debye-Scherer formula [9]. It was estimated within 11 to 42 nm which is shown by detail in Table 1. The crystal phase of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ was obtained and indicated plane structure at 1000 °C. The crystal phase of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ was destroyed at 1200°C.

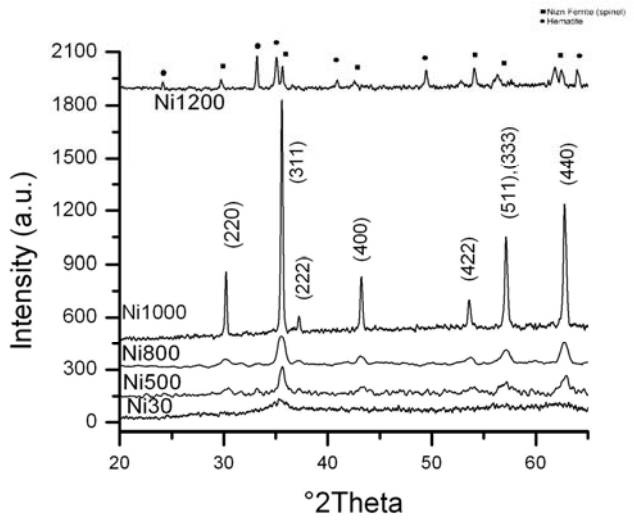

Fig 1. X-ray diffractogram of the as-prepared nanocrystalline $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at different temperature.

Fig.2 shows the TEM pattern of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite. The average particle size which estimated from the TEM pattern was found between 11 to 42 nm. In conclusion the measurements of XRD were confirmed by the results of TEM photographs.

Table 1. Magnetic properties and crystal size of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite.

specimen	M(emu/g)	Mr(emu/g)	Hc(Oe)	D (nm)
Ni30 (without heat-treatment)	3.6	0.04	7	11.7
Ni500 (annealed at 500 ^{o}c for 3h)	22	1.5	29	13.9
Ni800 (annealed at 800 ^{o}c for 3h)	35	5.4	77	16.6
Ni1000 (annealed at 1000 ^{o}c for 3h)	65	5.3	35	34.7
Ni1200 (annealed at 1200 ^{o}c for 3h)	32	2.2	22	41.6

Fig. 3 shows the results of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ AGFM measurements for different temperatures from 30 to 1200 °C. The variations of relative magnetization were traced and it was

found that the optimum temperature is 1000 °C. In this temperature the saturation may happens. Also magnetic parameters were changed as recorded in Table.1 shows the variation of saturation magnetization (M_s) and coercivity (H_c) with the annealing temperature (Figures are not shown here). The Gaussian fit to the data shows the coercivity increases with the annealing temperature higher than 800 ^oC. The changes in magnetic properties of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrites can be attributed to the modification of the particle size dependent on the annealing temperature [10]. The decrease in saturation magnetization is due to decrease in particle size and surface spin effects of small particles. The formations of surface layer in those magnetic moments, do not contribute to the magnetization of the applied field [11]. The coercivity for single domain particles decreases with particle size and becomes very small for the presence of a considerable volume fraction of superparamagnetic particles [12]. As can be seen, the samples with nanocrystallite sizes less than 10 nm have superparamagnetic behavior at room temperature.

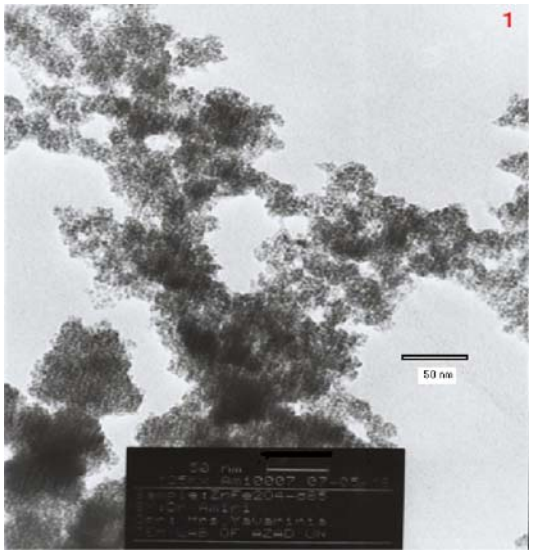

Fig 2. Transmission Electron Micrograph of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ calcined at 30℃

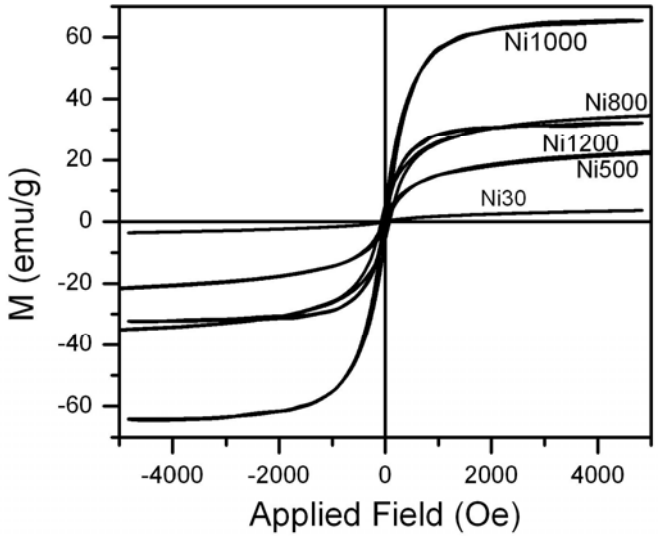

Fig 3. Plot of magnetization versus applied field for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ by AGFM

3.2. Absorption characteristics

The RL (reflection loss) is related to the normalized input impedance Z_{in} of a metal-backed microwave absorbing layer as:

$$R(dB) = 20\log\left[\frac{Z_{in}-1}{Z_{in}+1}\right] \tag{2}$$

Z_{in} is given by:

$$Z_{in} = \sqrt{\frac{\mu_r'}{\varepsilon_r'}}\tanh\left[j\frac{2\Pi}{C}\sqrt{\mu_r'\varepsilon_r'}\ fd\right] \tag{3}$$

where μ_r' and ε_r' are the complex permeability and permittivity of the composite medium, c is the velocity of light in free space, f is the frequency and d is the thickness of the absorber. The impedance matching condition is given by $Z_{in} = 1$ to represent the perfect absorbing properties.

Table 2. Effect of annealing temperature RL of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite.

specimen	Location of Max RL(GHz)	Max RL (dB) X-band	Thickness t (mm)	Bandwidth (GHz) For RL < -7dB (80% absorption)
Ni30	11.17	-7.98	2.5	0.47
Ni1000	10.66	-10.81	2.5	1.62
Ni1200	10.73	-8.38	2.5	0.36

The bandwidth of the sintered ferrite are too small (<1 GHz) for use as radar absorption materials, therefore $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite composites were prepared. Fig.4 shows the variation of RL versus frequency in NiZn-ferrite and resin for different thicknesses. It can extracted from Table 2 (The RL pattern is not shown here) that the maximum RL for Ni1000 with -10.81 dB is at the frequency of 10.66 GHz while it is reported in reference 6 that the maximum RL for NiZn-ferrite with -3.0 dB is at 11.7 GHz [6]. It is obviously appears that this composite cannot be used as a suitable wideband electromagnetic wave absorber at a thickness of 2.5 mm.

Table 3. Effect of different epoxy resin to ferrite ratios on RL of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$.

specimen	Max RL (-dB) X-band	Location of Max RL(GHz)	Max RL (-dB) Ku-band	Location of Max RL(GHz)	Thickness t (mm)
Ni1000 80/20	-7.39	10.68	-6.19	18.95	2.5
Ni1000 70/30	-6.51	10.68	-8.32	19.50	2.5
Ni1000 60/40	-10.57	10.68	-13.58	19.14	2.5

Table 3 shows the RL dependency on the frequency for the different ratios of Ferrite /epoxy resin powders. The maximum RL was improved when the ferrite/resin ratio is 60/40 wt %.

Fig.4 shows the RL patterns for the different thicknesses of powders absorber. As can be seen, the best performance of the NiZn ferrite (Ni1000) was attained at t=3.8 mm (Table 4). The maximum RL on this thickness with -31dB is at the frequency of 10.2 GHz.

This appears clearly from Fig.4 that the band which can be cover by this ferrite is about 1.97 GHz with a reflection loss higher than -20 dB (99% absorption). The maximum reflection loss of this band is -31 dB at a matching frequency of 10.20 GHz. Furthermore it can be seen that the band which can be cover by this ferrite is about 3 GHz with a reflection loss higher than -10 dB (90% absorption). The maximum reflection loss of this band is -31 dB at a matching frequency of 10.20 GHz.

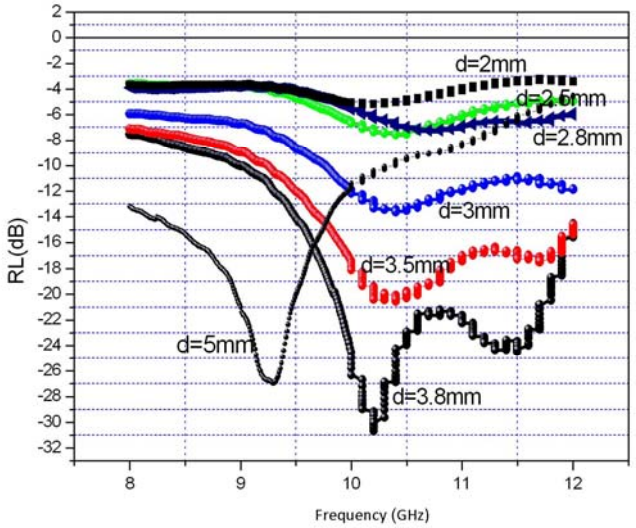

Fig.4. RL patterns for the different thicknesses of powders absorber.

Table 4. Effect of different thicknesses on RL of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite.

specimen	Max RL (dB) X-band	Location of Max R.L.(GHz)	Bandwidth (GHz) RL< -20dB (99% absorption)	Bandwidth (GHz) RL < -10dB (90% absorption)	Bandwidth (GHz) RL < -8dB (84% absorption)
Ni1000 (t=2mm)	-4.94	10.31	0	0	0
Ni1000 (t=2.5mm)	-7.23	10.31	0	0	0
Ni1000 (t=2.8mm)	-7.36	10.69	0	0	0
Ni1000 (t=3mm)	-13.34	10.35	0	2.2	2.8
Ni1000 (t=3.5mm)	-20	10.31	0	2.7	4.0
Ni1000 (t=3.8mm)	-31	10.20	1.97	3.0	4.0
Ni1000 (t=5mm)	-26	9.27	0.6	2.20	3.08

4. Conclusions

The radar-absorbing properties were studied as a function of frequency, nanoparticle size, ferrite /epoxy resin ratio, and thickness of absorber. For this reason, nanocrystallite powders of $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ were synthesized by LTSSR method. X-ray diffraction analysis confirms the formation of a spinel phase, and particle size of the ferrite samples increase with the annealing temperature. The magnetic measurements results represented that the coercivity initially increases and then decreases with increasing the annealing temperature whereas saturation magnetization continuously increases. $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ annealed at 1000 ^oC for 3h (Ni1000, t=3.8 mm) showed good absorption (99% absorption) properties in the X-band (8-12 GHz). $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ ferrite also showed a promising potential for use as the X-band radar absorbing material. In conclusion, $Ni_{0.7}$ $Zn_{0.3}Fe_2O_4$ ferrite is a promising potential for use as a material which works at high frequencies (MHz).

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