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Microwave absorbing materials using Ag–NiZn ferrite core–shell nanopowders as fillers

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Abstract

Silver nanoparticles coated with $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrites, forming a core–shell structure, were synthesized by utilizing hydrothermal method at different ferrite/silver ratio (ferrite/silver = 6/1, 4/1, 2/1, 1/1, 1/6) and introduced into polyurethane matrix to be a microwave absorber. The complex permittivity (ε', ε'') and permeability (μ', μ'') of absorbing composite materials consisted of ferrite/silver core–shell nanopowders and polyurethane were measured in the frequency range of 2–15 GHz. The reflection loss and matching frequency were calculated from measured data using theory of the absorbing wall for different ferrite/silver ratios. It was found that the matching frequency for reflection loss exceeded a satisfactory −25 dB at 9.0 GHz for using NiZn ferrite as a filler shifts to higher frequencies (10.9–13.7 GHz) as the ferrite/silver ratio of core–shell nano-filler decreased from 6/1 to 2/1. The present result demonstrates that microwave absorbers using ferrite/silver core-shell filler can be fabricated for the applications over 9 GHz, with reflection loss more than−25 dB for specific frequencies, by controlling the ferrite/silver ratio of the core–shell nano-fillers in the composites.
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1. Introduction

There are intensive interests in the preparation of nanomaterials because the physical properties of nanomaterials are often dramatically different from those of the bulk materials [1–2]. Microwave absorbers from ferrite-related materials used in a

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high frequency such as X band were particularly noticed [3–7]. Electronic instrument coatings with microwave absorbers avoid the interferences of electromagnetic waves, while the battle planes coating with microwave absorbers evade the detecting by radar. Usually, ferrite composites with a conducting plate as a backing material are used to achieve microwave absorption [8–11]. The absorbing characteristics of the materials depend on the frequency, layer thickness, complex permittivity ($\varepsilon' - j\varepsilon''$), and complex permeability ($\mu' - j\mu''$). The absorbing characteristics could be varied by controlling the ferrite filler volume fraction in the composite materials. The matching frequency for the reflection loss could also be changed by modifying the layer thickness of absorbing materials [12]. There were also reports on nanocrystals and core–shell structures of magnetic particles which exhibit unique magnetic properties [13–16]. However, studies of either nanoparticles or core–shell nanopowders for the applications in microwave absorbers were very limited. In the present study, the effect of ferrite/silver nanopowders with a core–shell structure on the microwave absorption behavior is reported.

2. Experimental

2.1. Core–shell nanopowders

A typical preparation procedure was as follows. Nitrates of metal Fe, Ni and Zn (99%, Arcos) were dissolved in deionized water. The mole ratio among Ni, Zn and Fe was fixed at 1:1:4 which gives a composition of $Ni_{0.5}Zn_{0.5}Fe_2O_4$. Hydroxides of Ni, Zn and Fe were co-precipitated in 1 N NH_4OH solution and the pH of the suspension was adjusted at 9−10. Then, the solution was mixed with silver nanopowder (purity 99.9%, particle size 0.5−1 μm, ALFA AESAR) and stirred for 1 h. The weight ratios of ferrite/silver powders were 6/1, 4/1, 2/1, 1/1, and 1/6. The resulting solutions containing hydroxides of metals and Ag nanopowder were poured into a tetra-fluoro-metoxil (TFM) reaction vessel. The TFM reaction vessel with the suspension was sealed and then mounted on a turnable rotor in a silicon oil bath. The temperature of the silicon oil was controlled at 180 °C and the reaction was performed for 3 h. The TFM vessel was then cooled to room temperature after the reaction. The precipitates were centrifuged at 10 k rpm for 30 min, washed with ethanol several times, and then dried in a freezing dryer for 8 h. All samples were characterized by X-ray diffraction (XRD) with Cu Kα radiation (35 kV, 25 mA, model RIGAKU) at room temperature. The morphology of the obtained powders was observed by transmission electron microscope (TEM, model TECANAI20, Phillips) at 120 kV.

2.2. Microwave absorbers

The absorbing composite materials were prepared by molding and curing the mixture of ferrite/Ag core–shell nanopowders and a thermal-plastic polyurethane (TPU) elastomer. The mixing ratio of core–shell nanopowders to TPU was 7:1 by weight. The tested specimens have a toroid-type shape, 1 mm in thickness, and outer and inner diameters of 7 and 3 mm, respectively. The permittivity (ε', ε'') and permeability (μ', μ'') of the composites were measured by using a HP8510C network analyzer in the frequency range of 2–15 GHz. For a microwave-absorbing layer terminated by a short circuit, the normalized input impedance related to the impedance in free space, Z, and reflection loss (R.L.) related to the normal incident plane wave are given by theory of the absorbing wall [8],

$$Z = \sqrt{\frac{\mu^*}{\varepsilon^*}} \tanh\left[j\frac{2\pi t}{\lambda}\sqrt{\mu^* \varepsilon^*}\right], \quad (1)$$

$$\text{R.L.} = 20 \log\left|\frac{Z-1}{Z+1}\right|, \quad (2)$$

where Z is the normalized input impedance related to the impedance in free space; ε_r^* the complex permittivity $= \varepsilon' - j\varepsilon''$; μ_r^* the complex permeability $= \mu' - j\mu''$; λ the wavelength; and t the thickness of specimen.

The impedance matching condition representing the perfect absorbing properties is given by $Z = 1$. The impedance matching condition is determined

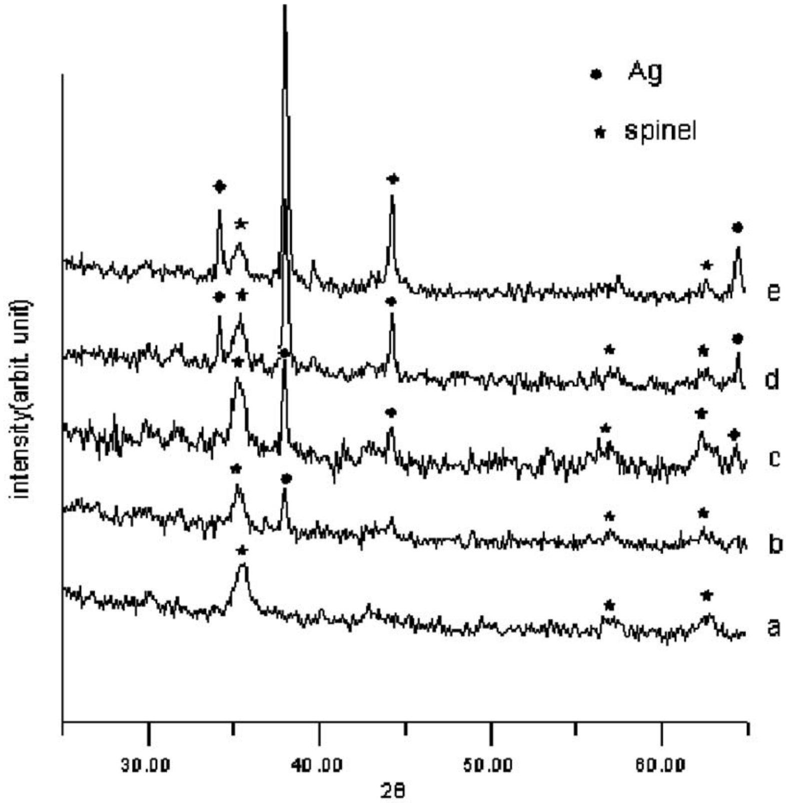

Fig. 1. X-ray of hydrothermally synthesized NiZn ferrite and core–shell ferrites at different ratio (a) NiZn ferrite, (b) ferrites/silver = 6/1, (c) 4/1, (d) 2/1, and (e) 1/1.

by the combinations of the six parameters ε', ε'', μ', μ'', λ, and t [8–10].

3. Results and discussion

3.1. Phase identification

Fig. 1 shows the crystalline phases of core–shell nanopowders, in which the peaks of silver and NiZn ferrite are evident. It confirms the co-existance of ferrite spinel phase and silver phase. For the core–shell nanopowders, the increasing of the silver content (low ferrite/silver ratio) increases the intensity of silver's peaks and the phase of spinel becomes moderate. For ferrite/Ag weight ratio 1/1 (Fig. 1, curve e), the peaks of silver are very sharp and much stronger than those of spinel. The peak intensity of spinel becomes small as its content in the ferrite/Ag core–shell particle decreases. The broad peaks of spinel also imply that the particle size of spinel phases were very fine, which was similar to our previous report [17].

3.2. TEM microstructures

Fig. 2 shows TEM micrographs of the core–shell nanopowders for different ferrite/silver ratios (a) 6/1, (b) 4/1, (c) 1/1, and (d) 1/6, respectively. For the ferrite/silver ratios are up to 4/1, the nanocrystals of NiZn ferrites agglomerate and provide a shell around silver particles as shown in Fig. 2(a) and (b). The silver particles (dark area) were deposited with numerous nanometer-sized spherical particles of NiZn ferrite, which were estimated to be in the range of 10 nm. The thickness of shell

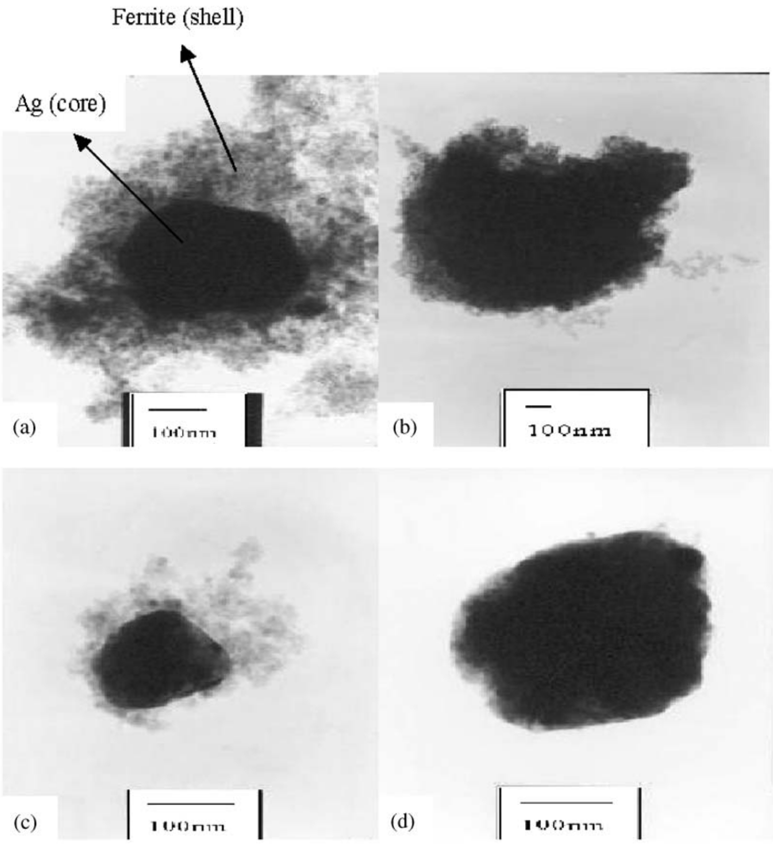

Fig. 2. TEM of synthesized core–shell nanopowders (a) ferrites/silver = 6/1, (b) 4/1, (c) 1/1, and (d) 1/6.

varies depending on the ferrite/silver ratio, which ranges as a negligible thickness (uncovered) for 1/6, 50–100 nm for 2/1, and 100–200 nm for 4/1 and 6/1, respectively. Low ferrite/silver ratio results in an uncovered surface or thin loose shell as shown in Fig. 2(c) and (d). The size of silver particles was 100–500 nm, as obtained from TEM micrographs, which was smaller than that of their initial size (500 nm–1 μm). It is thought that dissolution of silver surface might take place in the hydrothermal process. The nanocrystals of NiZn ferrites then precipitate on the surface of silver. From the observation of TEM, it is clear that hydrothermal method is applicable for the synthesis of core–shell structural nanoparticles, but may not be versatile to be able to control the uniformity of the shell thickness.

3.3. The complex permittivity and permeability spectra

Fig. 3(a)–(d) show the real and imaginary parts of permittivity (ε', ε'') and permeability (μ', μ'') spectra of pure NiZn ferrite–TPU composite and core–shell nanopowders (ferrites/silver = 6/1, 4/1, 2/1)–TPU composites. The real and imaginary parts of permittivity remained practically constant in the whole frequency range, where the ε' increased slightly for lower ferrite/silver ratio and the ε'' values were around 0.5 and independent of the ferrite/silver ratio. The fluctuation of measured data is due to the extreme sensitiveness of the equipment and should be regarded as acceptable measurement deviations. However, the low ε'' values of composites implied the

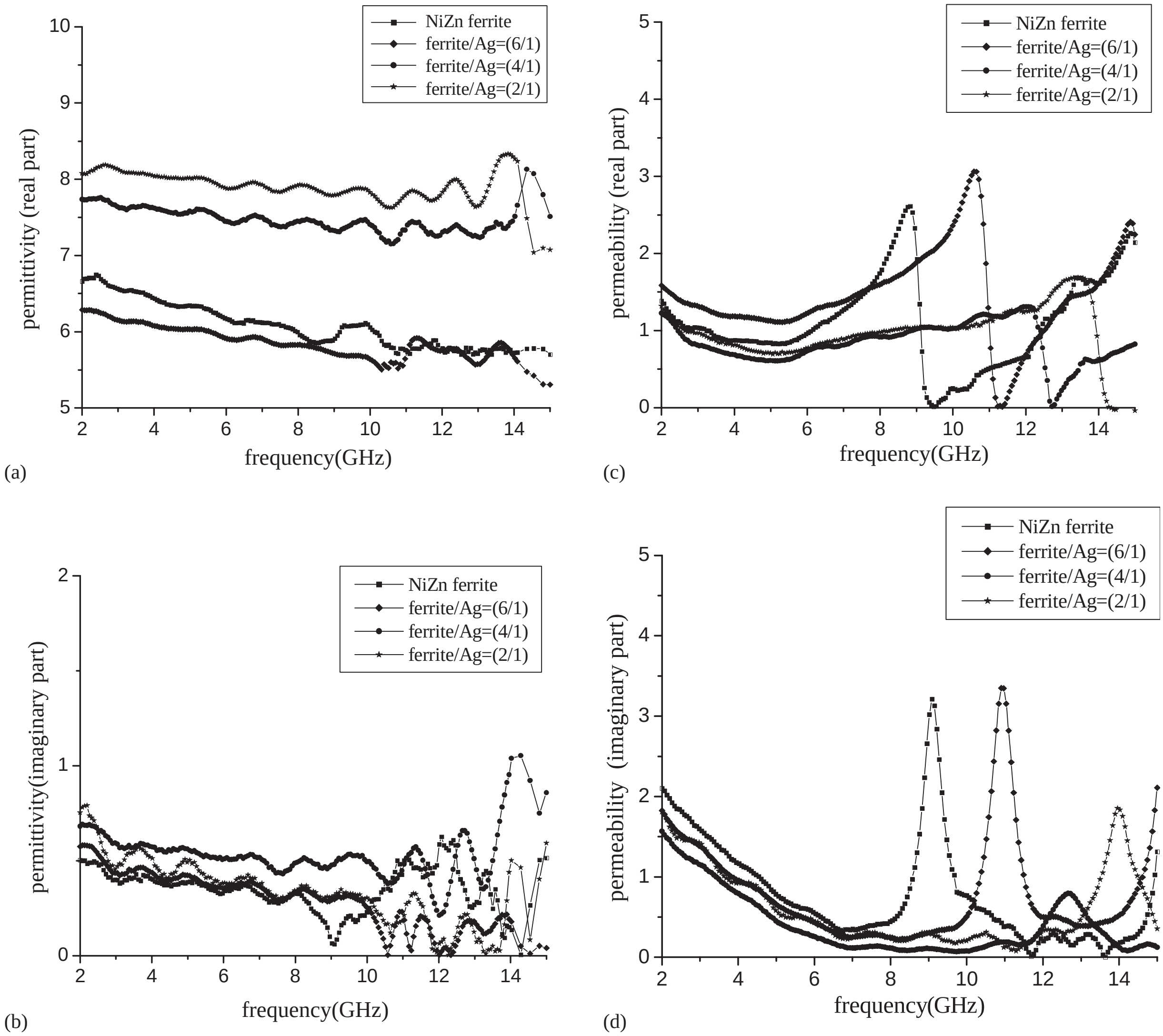

Fig. 3. The permittivity and permeability of the absorbing materials fabricated by using pure NiZn ferrite and core-shell nanopowders (NiZn ferrite/silver = 6/1, 4/1, 2/1) as fillers (a) permittivity (real part), (b) permittivity (imaginary part), (c) permeability (real part) and (d) permeability (imaginary part).

non-contacting of silver particles in the TPU matrix due to the core-shell structure. As shown in Fig. 3(c) and (d), the real part and imaginary part of the complex permeability exhibit a sharp curve at resonance frequency regions. The abrupt decrease of the real part of permeability (μ') shifts to higher frequencies, while the sharp peak of imaginary part of the permeability (μ'') also shifts to corresponding high frequencies. The effects of lower ferrite/silver ratio (higher silver content) on the real and imaginary parts of permeability for the absorbing composites are demonstrated. It is this resonance that gives the corresponding reflection loss at matching frequencies according to the theory of the absorbing wall [8–10].

3.4. The reflection loss

The reflection losses and matching frequencies for the absorbing composites fabricated from pure NiZn ferrite–TPU composite and ferrite/silver core–shell nanopowders–TPU composite, which are obtained by using Eqs. (1) and (2) are shown in Fig. 4 and Table 1. Fig. 4 indicates that the matching frequency of the pure NiZn ferrite–TPU composite was 9.020 GHz for a specimen thickness of 1.39 mm.When the ferrite/silver ratio is modified from 6/1 to 2/1, the matching frequency shifts to higher frequencies at a relatively similar thickness. However, when the ferrite/silver ratio is changed to 1/1, the value of the reflection loss is

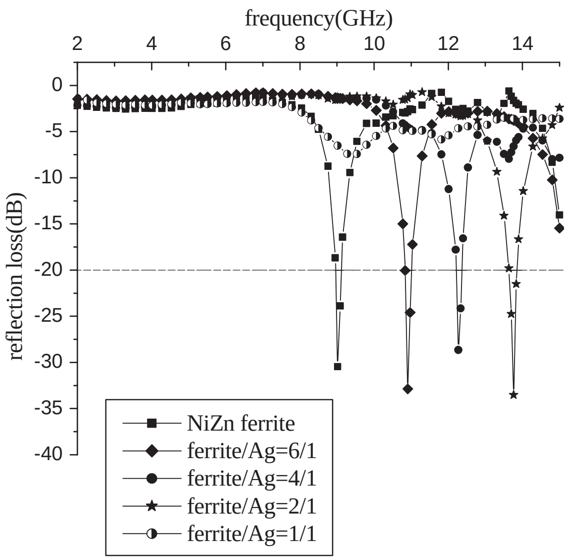

Fig. 4. The match frequencies of the absorbing materials with pure NiZn ferrite and core–shell nanopowders (NiZn ferrite, ferrites/silver =6/1, 4/1, 2/1, 1/1) as fillers.

no more satisfactory, indicating non-absorbing characteristic of the composite materials. Table 1 shows the numerical values for matching frequency, matching thickness and its reflection loss obtained from measured complex permittivities and permeabilities. It is clear that the pure NiZn ferrite–TPU composite can be considered as a microwave absorbing material at around 9 GHz, while the composites with ferrite/Ag core–shell nanopowders could be employed for frequencies higher than 9 GHz. From Figs. 3(d) and 4, it is evident that the match frequency of reflection loss curves coincides with the resonance frequency peak of imaginary part of permeability. The magnetic behavior of composite materials was clearly modified by the core–shell-structured nanopowders. Ruan et. al. [6] reported that a better microwave absorption was observed for 65 nm particle sizes than that for 5 μm of the spinel ferrite materials. Unsaturated coordination, interface polarization and multiple scatters of the nanocrystals were considered to be important factors for attenuation. In the present study, the ferrite/silver core–shell particles could be considered as a double interface (PU/ferrite/silver) relative to the single interface (PU/ferrite) of NiZn-ferrite nanoparticles alone within the polymer matrix. The electromagnetic wave would scatter and reflect repeatedly within the nanocrystals of ferrites of core–shell particles due to the complete reflection of conductive silver particles. However, these effects deserve a further study. The matching thickness for the satisfactory reflection loss at frequencies over 9 GHz was around 1–2 mm in the present study. It was easily adapted to lower frequencies by increasing the thickness of the composites.

Table 1
The reflection losses, matching thicknesses and matching frequencies for the studied absorbing materials.

Filler	Match frequency (GHz)	Thickness (mm)	Reflection loss (dB)	Band width (GHz)
NiZn ferrite	9.020	1.39	−30.457	0.195
f/Ag = 6/1	10.905	1.09	−32.871	0.260
f/Ag = 4/1	12.270	1.83	−28.648	0.195
f/Ag = 2/1	13.765	1.24	−33.532	0.260

4. Conclusion

The core-shell structural ferrite/silver nanopowders were successfully synthesized by the hydrothermal method. Ferrite/silver ratio higher than 1/1 is required to fully cover the surface of silver core. The complex permeabilities of composites were significantly modified by the incorporation of core–shell nanoparticles with different ferrite/silver ratios. With decreasing ferrite/silver ratio, the abrupt decrease of the real part of permeability, the resonance peak of imaginary part of permeability and the matching frequency of maximum reflection loss shifts to higher frequencies. Microwave absorbers for the applications over 9 GHz, and with satisfactory reflection losses, that is more than -25 dB, could be obtained at a thickness of $1-2$ mm by controlling the ferrite/silver ratio of the core–shell nano-fillers in the composites.

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