# Dual nonlinear dielectric resonance and strong natural resonance in Ni/ZnO nanocapsules

X. G. Liu,[a)] J. J. Jiang, D. Y. Geng, B. Q. Li, Z. Han, W. Liu, and Z. D. Zhang
*Shenyang National Laboratory for Material Science, Institute of Metal Research, and International Centre for Material Physics, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China*

(Received 4 December 2008; accepted 16 January 2009; published online 6 February 2009)

The electromagnetic characteristics of Ni/ZnO nanocapsules were studied at 2–18 GHz. The dual nonlinear dielectric resonance and strong natural resonance at 16.6 GHz contribute to excellent electromagnetic absorption. A reflection loss (RL) exceeding −20 dB was calculated in 14–18 GHz for an absorber thickness of 2.05 mm, and RL exceeds −10 dB in the whole *X*-band (10–12.4 GHz) and the whole Ku-band (12.4–18 GHz) for a thickness of 2.50 mm. The equivalent circuit model was used to explain the dual nonlinear dielectric resonance, which is ascribed to a cooperative consequence of the core/shell interfaces and the dielectric ZnO shells. *© 2009 American Institute of Physics*. [DOI: 10.1063/1.3079393]

Recently, the demand for microwave absorbers in the *X*-band (10–12.4 GHz) and Ku-band (12.4–18 GHz) increases so as to solve the electromagnetic (EM) interference problems in mobile telephone, local area network, and radar systems. Among the candidates for EM-wave absorbers, magnetic nanocapsules have attracted particular interest on account of the following facts: (1) the large saturation magnetization and high Snoek limit, (2) the suppression of the eddy current phenomenon enhancing an effective incidence to EM-wave, and (3) being composites with different kinds of EM-absorber materials.[1] As a result of good EM-wave absorption, ease of synthesis, high-temperature steady, and lower cost, the microwave absorption properties of the ZnO-based nanocomposites, such as $ZnO/SiO_2$,[2,3] ZnO/Fe,[4] and ZnO/Co,[5] have recently aroused an increasing attention.

The purpose of this study was to investigate the EM-absorption properties of Ni/ZnO nanocapsules that match the natural resonance of Ni cores and the dielectric loss of ZnO shells. The Cole–Cole semicircle approach[6] was adopted to explain dual dielectric relaxations, and the equivalent circuit model was used to explain dual nonlinear dielectric resonance of the Ni/ZnO nanocapsules. According to the skin-effect criterion, the magnetic loss in the Ni/ZnO nanocapsules is caused mainly by the natural resonance. The dual nonlinear dielectric resonance and the strong natural resonance both contribute to excellent EM-absorption properties. Reflection loss (RL) exceeding −20 dB was calculated in 14–18 GHz for an absorber thickness of 2.05 mm, while RL values exceed −10 dB in the whole Ku-band and *X*-band for 2.50 mm thickness layer. The EM properties do not change dramatically for the thicknesses of 2.40–2.60 mm for the RL exceeding −10 dB and for the thickness of 1.95–2.10 mm for the RL exceeding −20 dB.

The Ni/ZnO nanocapsules were prepared by a modified arc-discharge technique.[5] Metallic powders of Ni and Zn of 99.9% purity with the average size of 10 μm were well mixed for preparation of a target. The mixed powders with composition $Ni_{97}Zn_3$ (at. %) were compacted into a cylinder shape with diameter of 20 mm under a pressure of about 20 MPa. The compressed powders served as the anode. After the chamber was evacuated (in a vacuum of $5.0\times10^{-3}$ Pa), a mixture of argon of $1.6\times10^4$ Pa and hydrogen of $0.4\times10^4$ Pa was introduced into the chamber. The arc-discharge current was maintained at 80 A for 2 h to evaporate alloys sufficiently. Then the product in the form of powder was collected, after passivated for 8 h in argon. High-resolution transmission electron microscopy (HRTEM) images in Figs. 1(a) and 1(b) show that the nanocapsules are spherical about 5–25 nm in diameter, with well-defined core/shell structures containing Ni nanoparticles as cores and ZnO as shell. The formation of ZnO shells was explained by the fact that Zn atoms, due to lower melting point, were more easily absorbed on the Ni nanoparticles and subsequently condensed on the surface. When the products were exposed to air, Zn atoms were easily oxidized to amorphous ZnO.[7]

The specimen for measurement of EM parameters was prepared by uniformly mixing 40 wt % Ni/ZnO nanocapsules with paraffin and made into a toroidal shape ($\phi_{out}$:7.00 mm and $\phi_{in}$:3.04 mm). The paraffin was selected as the matrix of EM absorber because it is helpful for easily preparing a uniformly mixed specimen. The relative permittivity and permeability values of the specimen were measured between 2 and 18 GHz using a network analyzer (Agilent 8722ES).

The frequency dependency on the real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the complex permittivity ($\varepsilon$) for paraffin-nanocapsules composite is shown in Fig. 2(a). It can be found that there exist frequency intervals in which the permittivity presents resonant characteristics. The maximum/minimum values can be found before/after the resonant fre-

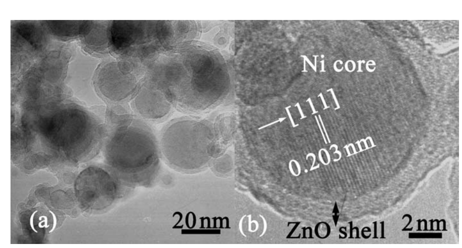


FIG. 1. (a) TEM and (b) HRTEM images of Ni/ZnO nanocapsules.

a)Electronic mail: liuxg@imr.ac.cn.

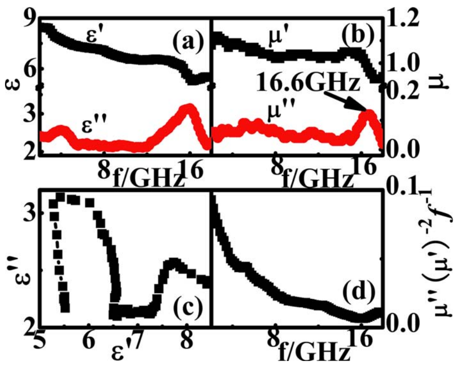


FIG. 2. (Color online) (a) Relative permittivity and (b) relative permeability as a function of frequency. (c) Typical Cole–Cole semicircles and (d) values of $\mu''(\mu')^{-2}f^{-1}$ as a function of frequency for Ni/ZnO nanocapsules-paraffin composite.

quencies on the $\varepsilon'$ curve; two peaks can also be observed near the resonant frequencies on the $\varepsilon''$ curve. These phenomena are the typical characteristics of nonlinear resonant behaviors. The resonant frequencies of $\varepsilon$ in the current frequency range are about 4 and 16.2 GHz, respectively. The dielectric loss, a ratio of $\varepsilon''$ to $\varepsilon'$, is plotted in Fig. 3. The dielectric loss exhibits two strong peaks with peak values of 0.32 and 0.59 at about 4.6 and 16.2 GHz, respectively.

Dong *et al.*[6] reported that the plot of $\varepsilon'$ versus $\varepsilon''$ would be a single semicircle, which is usually defined as the Cole–Cole semicircle. It is worthy to note that the composite presents a clear segment of two semicircles in Fig. 2(c), suggesting the existence of dual dielectric relaxation processes, while each semicircle corresponds to a Debye dipolar relaxation.[6] During the activation of an EM wave, a redistribution process of the charges occurs periodically between the Ni cores and the ZnO shells. As a result, apart from the dielectric relaxation of the ZnO shells, an additional interfacial relaxation is present because a complete core/shell interface is constructed.[8] The dual dielectric losses are therefore achieved for the Ni/ZnO nanocapsules.

When the EM wave incidents on the Ni/ZnO nanocapsules, the capacitance would be generated at the core/shell interface.[9] The $\varepsilon$ can be obtained by the relation: $\varepsilon=\varepsilon' - j\varepsilon''=1/[ifC_0Z(f)]$, where $f$ is the frequency, $Z(f)$ is the complex impedance, and $C_0$ is the capacitance of the Ni/ZnO nanocapsules. The equivalent circuit model at the interface is shown in the inset of Fig. 3, where $R$ is the resistance and $C$ is the equivalent capacitance of the Ni/ZnO nanocapsules. So the complex impedance can be obtained as $Z(f)=R+1/jfC$. Then the dielectric loss can be formulated as $\tan\delta(f) =\varepsilon''(f)/\varepsilon'(f)=fRC$. According to the free electron theory, $\varepsilon''\approx 1/2\pi\varepsilon_0 Rf$.[10] The dielectric loss can be changed as $\tan\delta(f)=C/2\pi\varepsilon_0\varepsilon''$. As well known, the capacitance is a nonlinear function of frequency. Thus, the Fourier expansion of the capacitance in the Ni/ZnO nanocapsules includes the linear and the quadratic terms of the frequency, and the corresponding value of the latter is a quarter of the former. From Fig. 3, the peak values of the dielectric loss are about 0.32 and 0.59 at 4.6 and 16.2 GHz, respectively, which just satisfy the first and the second resonances, taking values of $\varepsilon''$ into account. According to the analysis above, the dual nonlinear dielectric resonance originates mainly from the cooperative consequence of the core/shell interfaces and the dielectric ZnO shells.

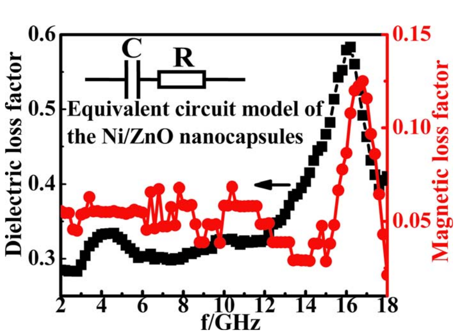


FIG. 3. (Color online) Frequency dependencies of dielectric and magnetic loss factors of Ni/ZnO nanocapsule-paraffin composite. The inset shows the equivalent circuit model of the Ni/ZnO nanocapsules.

Figure 2(b) shows the real part ($\mu'$) and imaginary part ($\mu''$) of the complex permeability ($\mu$) for which the $\mu'$ values exhibit an abrupt decrease from 1.05 to 0.93 at the 15–18 GHz range and retains almost a constant (1.05) over 2–15 GHz, due to the protection of the ZnO shell. It is noteworthy that the maximum value of the $\mu''$ appears at 16.6 GHz, which implies that the natural resonance occurs in the present Ni/ZnO nanocapsules. Compared with the bulk nickel, the natural resonance frequency of the Ni/ZnO nanocapsules remarkably shifts to the higher frequency, which is ascribed to the remarkable increase in surface anisotropic energy affected by the small size effect.[4,11] The magnetic loss, a ratio of $\mu''$ to $\mu'$, as a function of frequency, is plotted in Fig. 3. The magnetic loss exhibits a strong peak at 16.8 GHz, implying enhanced microwave absorption in the Ni/ZnO nanocapsules.

The contributors to magnetic loss, such as magnetic hysteresis, domain-wall displacement, and eddy current loss, can be excluded in the Ni/ZnO nanocapsules. The hysteresis loss is mainly caused by the time lags of the magnetization vector behind the external EM-field vector, which is negligible in a weak applied field.[1,12] Because the size of the Ni/ZnO nanocapsules is less than that of a single magnetic domain (55 nm),[1] the contribution of the domain-wall displacement that only occurs in multidomain magnetic materials can be excluded. If the magnetic loss results from eddy current loss, the values of $\mu''(\mu')^{-2}f^{-1}$ should be constant when frequency is varied.[11,13] We can call this the skin-effect criterion. As shown in Fig. 2(d), the values of $\mu''(\mu')^{-2}f^{-1}$ remarkably decrease with increasing frequency, and the change extent is bigger than 0.10. Therefore, the magnetic loss in the present nanocapsules is caused mainly by the natural resonance.

To further prove the proper match affected by the microstructure of absorbers, the RLs [RLs (dB)] were calculated (shown in Fig. 4) according to the transmit line theory.[1,3,4,11] A minimal RL of −46.9 dB was observed at 14.8 GHz, with the −20 dB bandwidth over the frequency range of 14–18 GHz for layer of 2.05 mm thickness. It is worth noting that the RL values exceeding −10 dB are obtained in the whole Ku-band (12.4–18 GHz) and the whole *X*-band (10–12.4 GHz) for 2.50 mm thickness layer. The frequency ranges for the bandwidth of −20 dB for 2.05 mm and the bandwidth of −10 dB for 2.50 mm are broader than those reported previously for a single thickness.[1–8,14] In addition, EM properties do not change dramatically for the thicknesses of 2.40–2.60 mm for the RL values exceeding −10 dB and for the thickness of 1.95–2.10 mm for the RL values exceeding −20 dB. Enhanced EM properties are ascribed to the dual nonlinear

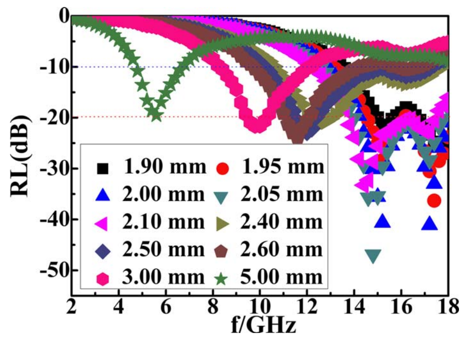


FIG. 4. (Color online) Frequency dependence of the RL of the composite containing 40 wt % Ni/ZnO nanocapsules for layers of different thicknesses.

dielectric resonance and strong natural resonance from the special core/shell structure in the Ni/ZnO nanocapsules. Two peaks for RL in Fig. 4 in the range of 14–18 GHz for the films with thickness from 1.90–2.10 mm are ascribed to different peak positions for dielectric loss factor (16.2 GHz) and magnetic loss factor (16.8 GHz), as shown in Fig. 3.

In conclusion, the Ni/ZnO nanocapsules with Ni nanoparticles as cores and ZnO as shells were prepared by arc-discharge technique. The Cole–Cole semicircle approach was adopted to explain the dual dielectric relaxations, and the equivalent circuit model was utilized to well explain the dual nonlinear dielectric resonance. The magnetic loss in the Ni/ZnO nanocapsules is mainly caused by the strong natural resonance. An optimal RL of −46.9 dB was calculated at 14.8 GHz with the −20 dB bandwidth over the frequency range of 14–18 GHz for 2.05 mm thickness layer. RL values exceeding −10 dB are obtained in the whole Ku-band and the whole *X*-band for 2.50 mm thickness layer. In addition, EM properties do not change dramatically for the thicknesses of 2.40–2.60 mm for the RL values exceeding −10 dB and for the thickness of 1.95–2.10 mm for the RL values exceeding −20 dB. The excellent EM-absorption properties are ascribed to the dual nonlinear dielectric resonance and the strong natural resonance from the special core/shell structure in the Ni/ZnO nanocapsules.

This work has been supported by the National Natural Science Foundation of China under Grant Nos. 50331030 and 50831006.

[1] X. F. Zhang, X. L. Dong, H. Huang, W. N. Wang, X. G. Zhu, B. Lv, J. P. Lei, and C. G. Lee, Appl. Phys. Lett. **89**, 053115 (2006).
[2] M. S. Cao, X. L. Shi, X. Y. Fang, H. B. Jin, W. Zhou, and Y. J. Chen, Appl. Phys. Lett. **91**, 203110 (2007).
[3] X. Y. Fang, X. L. Shi, M. S. Cao, and J. Yuan, J. Appl. Phys. **104**, 096101 (2008).
[4] X. G. Liu, D. Y. Geng, H. Meng, P. J. Shang, and Z. D. Zhang, Appl. Phys. Lett. **92**, 173117 (2008).
[5] T. Wei, C. Q. Jin, W. Zhong, and J. M. Liu, Appl. Phys. Lett. **91**, 222907 (2007).
[6] X. L. Dong, X. F. Zhang, H. Huang, and F. Zuo, Appl. Phys. Lett. **92**, 013127 (2008).
[7] X. G. Liu, D. Y. Geng, H. Meng, and Z. D. Zhang, J. Phys. D **41**, 175006 (2008).
[8] C. C. Lee and D. H. Chen, Appl. Phys. Lett. **90**, 193102 (2007).
[9] X. L. Shi, M. S. Cao, J. Yuan, Q. L. Zhao, Y. Q. Kang, X. Y. Fang, and Y. J. Chen, Appl. Phys. Lett. **93**, 183118 (2008).
[10] S. Ramo, J. R. Whinnery, and T. V. Duzer, *Fields and Waves in Communication Electronics* (Wiley, New York, 1984).
[11] X. G. Liu, D. Y. Geng, and Z. D. Zhang, Appl. Phys. Lett. **92**, 243110 (2008).
[12] M. Z. Wu, Y. D. Zhang, S. Hui, T. D. Xiao, W. A. Hines, J. I. Budnick, and G. W. Taylor, Appl. Phys. Lett. **80**, 4404 (2002).
[13] L. Qiao, F. S. Wen, J. B. Wang, and F. S. Li, J. Appl. Phys. **103**, 063903 (2008).
[14] J. R. Liu, M. Itoh, and K. I. Machida, Appl. Phys. Lett. **83**, 4017 (2003).