

Effect of metal grain size on multiple microwave resonances of Fe/TiO₂ metal-semiconductor composite

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The dielectric resonance and multiple magnetic resonances which correspond to multiple microwave absorptions in the 2–18 GHz range have been studied in the composite Fe/TiO₂. The Fe grain size is found to have great impact on the dielectric resonance in this metal-semiconductor composite. The polarization mechanism is attributed to interfacial polarization. The multiple magnetic resonances can be ascribed to the natural resonance and exchange resonances, which can be explained by Aharoni's exchange resonance theory. © 2010 American Institute of Physics. [doi:10.1063/1.3496393]

Recently, much attention has been paid to microwave absorbing materials,^{1–8} especially, composites of a ferromagnetic metal and a dielectric semiconductor.^{4–7} These composites possess the combined effect of high saturation magnetization, high initial permeability, high Curie temperature of ferromagnetic metals,⁸ and the high resistivity of semiconductors, which ensures a large dielectric loss⁴ and suppresses the eddy current effect.^{5–7} In metal-semiconductor composites and other kinds of materials, magnetic resonances and dielectric resonances often appear. Although the origin of magnetic resonances has been clarified theoretically,^{1,3–11} the mechanism of dielectric resonances remains unclear. Here, we report a metal-semiconductor Fe/TiO₂ composite which exhibits a nonlinear dielectric resonance and multiple magnetic resonances. The origin of the dielectric resonance is attributed to the high resistivity resulting from the large size of Fe grains. The multiple magnetic resonances can be ascribed to natural resonance and exchange resonances that can be explained by Aharoni's exchange resonance theory.⁹ The co-occurrence of dielectric and magnetic losses ensures a reasonable basis of multiple microwave absorptions.

The Fe/TiO₂ composite was prepared by the milling and annealing method. In brief, a mixture of Fe₂O₃ and Ti powders was milled for 35 h under an argon atmosphere.⁸ The as-milled powder was denoted as sample A. Then, part of the powder was annealed at 960 °C for 30 min, which was named sample B. For comparison, another part of the powder was annealed at 350 °C for 30 min (denoted as sample C). The structures were characterized by x-ray diffraction (XRD) with Cu K_α radiation. As shown in Fig. 1(a), in sample A, TiO₂ is amorphous and the average size of Fe grains is 6.4 nm, while sample B is composed of α-Fe and TiO₂ with the average grain sizes of 50.6 nm and 51.5 nm, respectively, as estimated from the integral width of their diffraction reflections, with strain and instrumental broadening eliminated. In sample C, TiO₂ is amorphous and the Fe grain size is 17 nm. The bright-field transmission electron microscopy (TEM) and high-resolution TEM images obtained on a A-FEI Tecnai G2 F20 are presented in Figs. 1(b) and 1(c), respectively.

Toroidal specimens for microwave measurements between 2 and 18 GHz using a network analyzer Agilent 8722ES were prepared by mixing 50 wt % Fe/TiO₂ composite in a paraffin matrix.

The frequency dependence of the real part (ϵ') and imaginary part (ϵ'') of relative complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) of the paraffin-Fe/TiO₂ composite containing 50 wt % Fe/TiO₂ is shown in Fig. 2(a). For sample A, several small fluctuations are observed, which can be ascribed to the lag of electrical displacement behind the electrical field at the Fe/TiO₂ interfaces, similar to the case in Ni@C or Fe@ZnO nanocapsules.^{4,7} For sample B, maxima and minima on the ϵ' curve are found just below or above 11.2 GHz, whereas one sharp peak on the ϵ'' curve is observed at about 11.2 GHz. This feature is typical for nonlinear dielectric resonances.¹²

We have to figure out the polarization mechanism in order to further understand the origin of the dielectric resonance in sample B. Generally, there are four possible polarization mechanisms as follows: electronic, atomic or ionic,

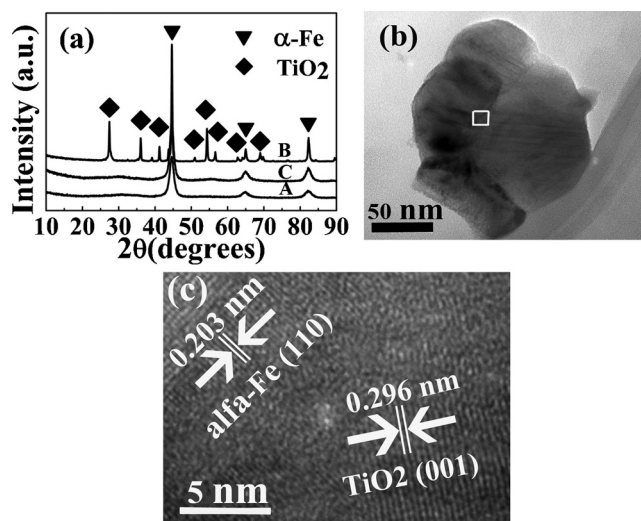


FIG. 1. (a) XRD pattern of samples A, B, and C, (b) TEM and (c) high resolution TEM micrographs of sample B.

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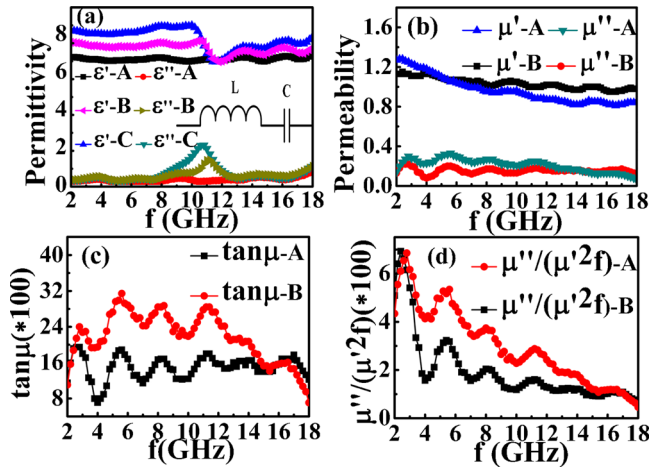


FIG. 2. (Color online) (a) Relative complex permittivity of mixtures of paraffin and the samples A, B, and C as a function of frequency and the inset shows the equivalent LC circuit model for samples B and C, (b) relative complex permeability of the mixtures of paraffin and samples A and B as a function of frequency, (c) magnetic loss tangents of the mixtures of paraffin and samples A and B as a function of frequency, and (d) $\mu''/[(\mu')^2 f]$ of samples A and B vs frequency.

orientation, and interfacial polarizations.¹³ The first two polarization processes occur in ultraviolet and infrared light ranges, respectively. The third one occurs in the microwave range but only results in dielectric relaxation instead of dielectric resonance.¹⁰ Interfacial polarization arises at very low frequency when two phases differ from each other in dielectric constant and conductivity. However, dielectric resonance due to interfacial polarization can be tuned to the microwave frequency if the electric conductivity of one phase is between 1 and 100 S/m.¹⁴ Using the method developed previously,¹⁵ the conductivity of the Fe grains in sample B was calculated to be about 10 S/m, which demonstrates that the interfacial polarization can occur around 10 GHz. Therefore, it is the interfacial polarization that dominates the polarization process in sample B.

Let us return to the dielectric resonance. The absence of dielectric resonance in sample A safely rules out the possibility that the dielectric resonance in sample B arises from high-dielectric-scattering TiO_2 dispersed in the low-dielectric-scattering paraffin.¹² By comparison, we can find the only two major differences between sample A and sample B. First, TiO_2 is crystalline in sample B but amorphous in sample A. To find out the effect of crystallinity on the dielectric resonance, sample C was prepared using the method as mentioned above. In the plot of the relative complex permittivity of sample C [Fig. 2(a)], a dielectric resonance is also found around 11.2 GHz, which means that the crystallinity of TiO_2 has no determining effect on the dielectric resonance in our samples. The second difference is that the average size of Fe grains in sample B is 50.6 nm, which is seven times larger than that of sample A (about 6.4 nm). As is well known, the size of metal grains can dramatically affect the electrical conductivity of the metal-semiconductor composites due to the fact that the critical volume fraction for percolation increases with the size of metal grains.¹⁶ Using Eq. (1), we calculated the conductivity ratios σ_B/σ_A and σ_C/σ_A to be 113 and 51, respectively. The resistivity of sample A measured at room temperature using the four-point method on a Keithley 2400 Source Meter and 2182 Nanovoltmeter

and Quantum Design superconducting quantum interference device is $8.53 \times 10^{-4} \Omega \text{ m}$, almost behaving like a conductor, but samples B and C, whose conductivities are $9.64 \times 10^{-2} \Omega \text{ m}$ and $4.35 \times 10^{-2} \Omega \text{ m}$, respectively, behave as semiconductors.

When samples B and C are exposed to microwaves, a capacitance will be generated at the interfaces of the Fe and TiO_2 grains.^{6,17,18} Meanwhile, due to interfacial polarization as mentioned above, interfacial charges accumulate and dissipate alternately at the Fe/ TiO_2 interfaces and thus a LC circuit sets in [inset of Fig. 2(a)]. Then, as well known, a dielectric resonance will happen at the frequency $f_0 = 1/(2\pi\sqrt{LC})$. However, because sample A is a conductor and thus the fine Fe grains will short-circuit the capacitances, a LC circuit cannot be completed. This is why the dielectric resonance only occurs in samples B and C and not in sample A.

The frequency dependence of the real part (μ') and the imaginary part (μ'') of relative complex permeability ($\mu_r = \mu' - j\mu''$) of the paraffin-Fe/ TiO_2 composite is given in Fig. 2(b), in which several resonance peaks can be seen in the plot. In order to determine the locations of these peaks, the magnetic tangent loss ($\tan \mu = \mu''/\mu'$) is plotted in Fig. 2(c).

In general, the microwave magnetic loss of nanoparticles can be ascribed to magnetic hysteresis, domain-wall resonance, eddy-current loss, natural resonance, and exchange resonance. The magnetic-hysteresis loss can be neglected in low fields. Domain-wall resonance usually occurs in the 1–100 MHz range.¹⁹ Thus, neither the magnetic-hysteresis loss nor the domain-wall resonance will be dominant in the microwave magnetic loss in the present composite. The eddy-current loss can be expressed by¹⁰

$$\mu'' = \frac{2}{3} \pi \mu_0 (\mu')^2 \sigma d^2 f, \quad (1)$$

where f is the applied frequency, μ_0 is the vacuum permeability, and σ is the electric conductivity of the particle. If the eddy-current loss would be the only contribution to the magnetic loss, the value of $\mu''/[(\mu')^2 f] = 2\pi\mu_0\sigma d^2/3$ should be constant when the frequency varies.¹⁰ Since the value of $\mu''/[(\mu')^2 f]$ fluctuates in the range of 2–18 GHz [Fig. 2(d)], the eddy-current loss can be excluded. Therefore, the microwave magnetic loss must be attributed to the natural resonance and the exchange resonance. Toneguzzo *et al.*¹ have suggested that the natural resonance occurs at a lower frequency than the exchange resonance. In this picture, the peak at 2.6 GHz for sample B and the one at 2.8 GHz for sample A can be attributed to the natural resonance and the other peaks result from the exchange resonance. According to the exchange-resonance theory,¹⁹ the exchange resonance frequency is given by

$$f = \gamma_0 \frac{C \mu_{kn}^2}{R^2 M_s} + f_0, \quad (2)$$

where γ_0 is the gyromagnetic ratio, C is the exchange constant, μ_{kn} are the roots of the differential spherical Bessel function, R is the grain size, M_s is the saturation magnetization, and f_0 is the natural-resonance frequency. It is noticed that μ_{kn} has a set of values, each of which corresponding to an exchange-resonance frequency. According to Aharoni⁹ and Mercier *et al.*,²⁰ ferromagnetic nanoparticles smaller than 100 nm may exhibit several exchange resonance peaks.

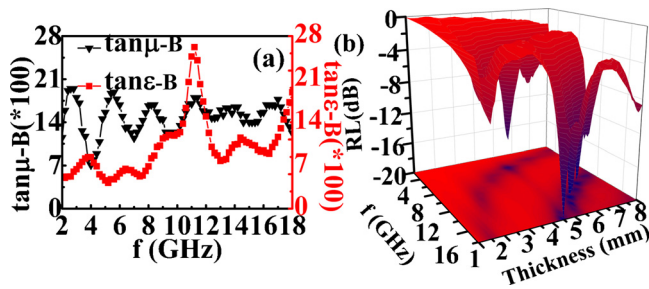


FIG. 3. (Color online) (a) Dielectric loss tangent and magnetic loss tangent of the mixture of paraffin and sample B vs frequency and (b) RL of the sample B-paraffin composite as a function of thickness and frequency.

The proper average sizes of Fe grains ensure the occurrence of the multiple exchange resonances.

As shown in Fig. 3(a), a strong magnetic loss occurs at about 2.6 GHz, which means that the Fe/TiO₂ composite can be a suitable candidate for low-frequency microwave absorber material. The reflection loss (RL) for the sample B, shown in Fig. 3(b), was derived from the relative complex permittivity and permeability data, using the transmission-line theory.²¹ Multiple microwave absorptions which correspond to the multiple dielectric and magnetic resonances shown in Fig. 3(a) are observed in the S-band (2–4 GHz), X-band (8–12 GHz), and Ku-band (12–18 GHz). Additionally, the maximum RL value shifts to lower frequency with sample thickness increasing from 1 to 8 mm. Interestingly, no strong microwave absorption occurs around 11.2 GHz where the dielectric and magnetic loss maxima coincide, which may result from an imbalance of the electromagnetic match.^{4,22}

In conclusion, both the dielectric and multiple magnetic resonances are closely related with the size of Fe grains. The average size of Fe grains has an important influence on the presence of the dielectric resonance. The magnetic resonances involve the natural resonance and exchange resonances. The latter are dependent on the ferromagnetic grain size. Thus, a proper size of the metal grains is fundamental for the dielectric resonance and multiple magnetic resonances. The co-occurrence of the dielectric loss and multiple

microwave magnetic loss in Fe/TiO₂ composite ensures a appreciable microwave absorption in the full frequency range.

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- ¹P. Toneguzzo, G. Viau, O. Acher, F. Fievet-Vincent, and F. Fievet, *Adv. Mater. (Weinheim, Ger.)* **10**, 1032 (1998).
- ²R. C. Che, L. M. Peng, X. F. Duan, Q. Chen, and X. L. Liang, *Adv. Mater. (Weinheim, Ger.)* **16**, 401 (2004).
- ³J. Ma, J. G. Li, X. Ni, X. D. Zhang, and J. J. Huang, *Appl. Phys. Lett.* **95**, 102505 (2009).
- ⁴X. F. Zhang, X. L. Dong, H. Huang, Y. Y. Liu, W. N. Wang, X. G. Zhu, B. Lv, J. P. Lei, and C. G. Lee, *Appl. Phys. Lett.* **89**, 053115 (2006).
- ⁵X. F. Zhang, X. L. Dong, H. Huang, Y. Y. Liu, B. Lv, J. P. Lei, and C. J. Choi, *J. Phys. D* **40**, 5383 (2007).
- ⁶X. G. Liu, J. J. Jiang, D. Y. Geng, B. Q. Li, Z. Han, W. Liu, and Z. D. Zhang, *Appl. Phys. Lett.* **94**, 053119 (2009).
- ⁷X. G. Liu, D. Y. Geng, H. Meng, P. J. Shang, and Z. D. Zhang, *Appl. Phys. Lett.* **92**, 173117 (2008).
- ⁸X. Ni, J. Ma, J. Li, D. Jiao, J. Huang, and X. Zhang, *J. Alloys Compd.* **468**, 386 (2009).
- ⁹A. Aharoni, *J. Appl. Phys.* **69**, 7762 (1991).
- ¹⁰S. B. Liao, *Ferromagnetic Physics* (Science, Beijing, 1992), Vol. 3, pp. 17–81.
- ¹¹G. Viau, F. Fievet-Vincent, F. Fievet, P. Toneguzzo, F. Ravel, and O. Acher, *J. Appl. Phys.* **81**, 2749 (1997).
- ¹²L. Zhen, J. T. Jiang, W. Z. Shao, and C. Y. Xu, *Appl. Phys. Lett.* **90**, 142907 (2007).
- ¹³C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill, New York, Toronto, London, 1955), pp. 52–74.
- ¹⁴N. Bowler, *IEEE Trans. Dielectr. Electr. Insul.* **13**, 703 (2006).
- ¹⁵Y. P. Mamunya, H. Zois, and L. Apekis, *Powder Technol.* **140**, 49 (2004).
- ¹⁶D. T. Zimmerman, J. D. Cardellino, K. T. Cravener, K. R. Feather, N. M. Miskovsky, and G. J. Weisel, *Appl. Phys. Lett.* **93**, 214103 (2008).
- ¹⁷X. 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).
- ¹⁸A. K. Jonscher, *Dielectric Relaxation in Solids* (Xi'an Jiaotong University Press, Xi'an, 1983), p. 64.
- ¹⁹M. Z. Wu, Y. D. Zhang, S. Hui, T. D. Xiao, S. H. Ge, W. A. Hines, J. I. Budnick, and G. W. Taylor, *Appl. Phys. Lett.* **80**, 4404 (2002).
- ²⁰D. Mercier, J. C. S. Levy, G. Viau, F. Fievet-Vincent, F. Fievet, P. Toneguzzo, and O. Acher, *Phys. Rev. B* **62**, 532 (2000).
- ²¹Y. Naito and K. Suetake, *IEEE Trans. Microwave Theory Tech.* **19**, 65 (1971).
- ²²A. Wadhawan, D. Garrett, and J. M. Perez, *Appl. Phys. Lett.* **83**, 2683 (2003).