Enhanced Microwave Absorption at Low Frequency of Superparamagnetic Fe_3O_4 Single Nano-crystals

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Abstract. The superparamagnetic Fe_3O_4 single nanocrystals with diameters of 10-15 nm have been synthesized via a simple method. Several characterizations such as SEM, TEM and XRD are used to obtain the morphology and crystallinity of Fe_3O_4 nanoparticles. The investigation about wave absorption property indicates that Fe_3O_4 nanocrystals is an excellent absorber, the effective frequency band (RL<-5.30 dB) of absorbers are obtained in a broad frequency range from 2.0 GHz to 15.40 GHz and the minimum reflection losses and the peak frequencies are -10.5 dB and -7.7 dB at the frequency of 10.4 GHz and 14.1 GHz, respectively.

Introduction

Fe_3O_4 has attracted extensive attention due to its metal-insulator transition around 120 K, half-metallic character, and strong spin polarization at room temperature.[1] Moreover, its magnetic properties can be tuned by changing size, shape, and dimension. Up until now, many methods have been made to synthesize this kind of nanocrystals. For example, a convenient synthesis of hydrophilic magnetite microspheres through a solovthermal method has been reported by Li and co-workers, while the resultant magnetite microspheres are ferromagnetic and are not water dispersible.[2] Recently, by using a microemulsion of oil droplets in water as confined templates, this group synthesized magnetic microspheres which can be assembled with the evaporation of low-boiling-point solvents.[3] Ge et al. [4] directly fabricated water-dispersible super-paramagnetic nano-crystal clusters with controllable diameters of 30–180 nm which is composed of small nano-crystals of 6–8 nm, by using a high-temperature reduction reaction with poly (acrylic acid) (PAA) as a stabilizer, $FeCl_3$ as a precursor, and diethylene glycol as a reductant. More recently, Zhao and coworkers synthesized highly water-dispersible magnetite nano-crystals by a modified solvothermal reaction at 200°C by reduction of $FeCl_3$ with EG in the presence of sodium acetate as an alkali source and biocompatible trisodium citrate (Na_3Cit) as an electrostatic stabilizer. [5] Recently, a simple, gram-scale, continual solution-phase processing route to prepare Fe_3O_4 nano-crystals with diameters of 10-15 nm at room temperature has been reported in our pervious studies [6].

Due to the unique absorbing microwave energy and promising applications in the stealth technology of aircraft, television image interference of high-rise buildings, and microwave darkroom and protection, much attention has been paid to microwave absorption materials. [7,8,9] Thus, extensive studies on microwave absorption properties of various materials have been investigated to look for the MAMs with high absorptive ability and wide band absorption. The most current research focuses on the electromagnetic properties in the range of 8–18 GHz [10,11,12]. Liu et al. [13] prepared the cross-shaped SiC fiber and the optimum reflection loss was - 28.47 dB at 12 GHz. Fan et al.[14] reported that the RL peak value of flaky graphite that was milled for 12 h was -25.5 dB at about 14.4 GHz. Yu et al. [15] found that the foam composite absorbers filled with carbonyl iron fiber exhibited good microwave absorbing properties in the frequency of 8–18 GHz. From the mentioned above, all the materials show excellent absorption at in a relatively narrow band; to get a material with broadband microwave absorption is still a challenge.

For magnetic material, the absorbing characteristics of the materials depend on the frequency, layer thickness, complex permittivity (ε_r), complex permeability (μ_r) and so on. Fe_3O_4 nanocrystals with the diameter about 20-50 nm, as a kind of microwave absorbers [16,17] with complex permittivity and complex permeability have been studied [18]. Fe_3O_4 is a cheap magnetic material and the dielectric permittivity is low, and can be well matched the incident wavelength, while, nanocrystals structure can improve the capability of microwave absorbing.

In this letter, we synthesized Fe_3O_4 nano-crystals with diameters of 10-15 nm and the microwave broadband absorption behavior of the Fe_3O_4 nano-crystals is also studied.

Experimental Section

Commercially available and analytical-grade reagents were used without further purification. We synthesized the Fe_3O_4 with the method as reference.

The samples were characterized by X-ray diffraction pattern (XRD), recorded on a (D/MAX 2200 PC) X-ray powder diffractometer with Cu KR radiation (λ = 0.154056 nm). The grain morphology and size was observed by sputtering with platinum for scanning electron microscope (SEM) on a FEI Siron 200 microscope and field emission scanning electron microscope (FE-SEM) on a JSM-6700F microscope.

Results and Discussion

The scanning electron microscopy (SEM) image of the product (Fig. 1a) indicates the material consists of uniformed and large quantities of uniform nano-crystals with narrow particle size distribution. Further structural characterization of the Fe_3O_4 nano-crystals is carried out using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The TEM image (shown in Fig. 1b) also confirms the products are composed of the nano-crystals with the narrow particle size distribution from 10 nm to 15 nm. HRTEM image (shown in Fig. 1c) reveals that the Fe_3O_4 nano-crystals possess a single crystal structure. Figure 1c shows that the singular spacing of the nano-crystals is 0.250 nm, which is nearly consistent with the (311) reflection plane spacing of Fe_3O_4. The XRD pattern (Fig. 1d) shows that all diffraction peaks are in good agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card No. 75-0449. No impurity peaks were observed, indicating that the sample was pure Fe_3O_4.

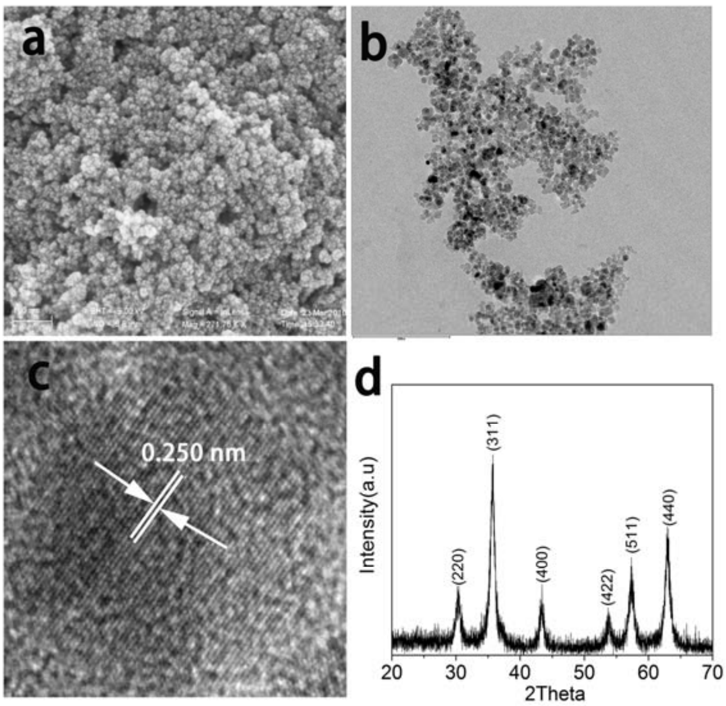

Figure 1. (a) SEM image of the product; (b) TEM image of the Fe_3O_4 nano-crystals; (c) HRTEM image; (d) XRD patterns of the product.

The specimen for microwave absorption properties measurement using coaxial wire method were prepared by uniformly mixing the Fe_3O_4 nano-crystals in a paraffin matrix which is transparent to microwave and pressing the mixture into a cylindrical shaped compact (Φ_{out} =7.00 mm and Φ_{in} =3.04 mm). The relative permittivity ε_r values were measured in the 2–18 GHz range with an Anritsu 37269D network analyzer. The frequency dependency on the relative permittivity for paraffin wax composite, including 60wt % Fe_3O_4 nanocrystals, is shown in Fig. 2. The value of slightly decreases with the frequency range 2–12 GHz and the curve presents two resonant peaks at about 10.6 and 14.6 GHz. The dielectric properties of Fe_3O_4 nanocrystals are mainly due to the interfacial polarization and orientation polarization that is attributed to the heterogeneous structure of composite comprising conducting grains separated by poorly conducting layers [19] and the dangling bonds in the surface of the particles.

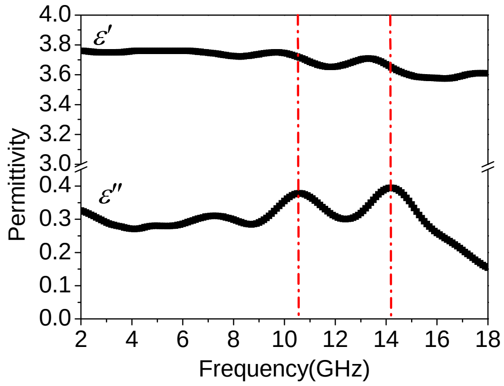

Figure 2. Frequency dependence of real part and imaginary part of permittivity

From Fig. 3, it can be seen that the value of slightly increases with the frequency range 2–12 GHz and the of Fe_3O_4 nanocrystals have the largest value of and at 2 GHz, and the complex permeability decreases smoothly with frequency, which is due to the magnetic resonance frequency. This characteristic is also in accordance with the typical permeability spectrum of ferrites in high frequencies. It can also be observed that the real part and imaginary part of permeability of Fe_3O_4 are different from the previous report about Fe_3O_4 with the diameter about 30-50nm[20], which can be explained as follows: the unique magnetic features of ferromagnetic materials of a certain size (10–15 nm) often exhibit a special form of magnetism called superparamagnetism.[21] Superparamagnetic Fe_3O_4 single nanocrystals possesses only a single magnetic domain and has a net magnetic moment that results from the sum of all uncompensated spins in the nanoparticle. Thermal excitation enables the magnetization of the single-domain particles to relax between the axes of easy magnetization, which may affect the real part and imaginary part of permeability of Fe_3O_4 nancrystals. The superparamagnetism generated by the Fe_3O_4 nancrystals of the magnetic fillers may play a very important and characteristic role on the permeability of materials [22].

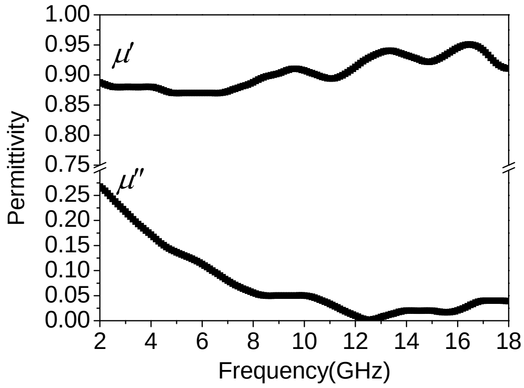

Figure 3. Frequency dependence of real part and imaginary part of permeability

The reflection loss (RL) of the electromagnetic radiation under the normal incidence of the electromagnetic field on the surface of microwave absorbing materials backed with a conductor can be calculated as: [23]

$$R = 20\log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \tag{1}$$

Here, the input impedance (Z_{in}) is given by

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}}\tanh\left[j\left(\frac{2f\pi d}{c}\right)\sqrt{\mu_r\varepsilon_r}\right] \tag{2}$$

Where ε_r and μ_r are the complex permittivity and permeability of the composite absorber, respectively; f is the frequency; d is the thickness of the absorber, and c is the velocity of light in free space.

Fig. 4a shows the calculated theoretical RL of Fe_3O_4 nancrystals with the thickness (3.5 mm) in the range of 2–18 GHz. It indicates that the minimum reflection losses and the peak frequencies are -10.5 and -7.7 dB at the frequency of 10.4 and 14.1 GHz, respectively, when the thickness is 3.5 mm. Besides, the effective microwave absorptions (RL<-5.30 dB) of absorbers are obtained in a broadband frequency range from 2 GHz to 15.40 GHz. Overall, the superparamagnetic Fe_3O_4 single nanocrystals we prepared showed the excellent absorption performances in the range of 2–18 GHz and has the potential to be the promising microwave absorbing agent.

Fig. 4b shows the calculated theoretical RL of Fe_3O_4 nancrystals with different thicknesses (2–4.5 mm) in the range of 2–18 GHz. It can be observed that the thicknesses of the absorbers have a great influence on the microwave absorbing properties and the minimum RLs corresponding to the maximum absorptions gradually shift toward the lower frequency.

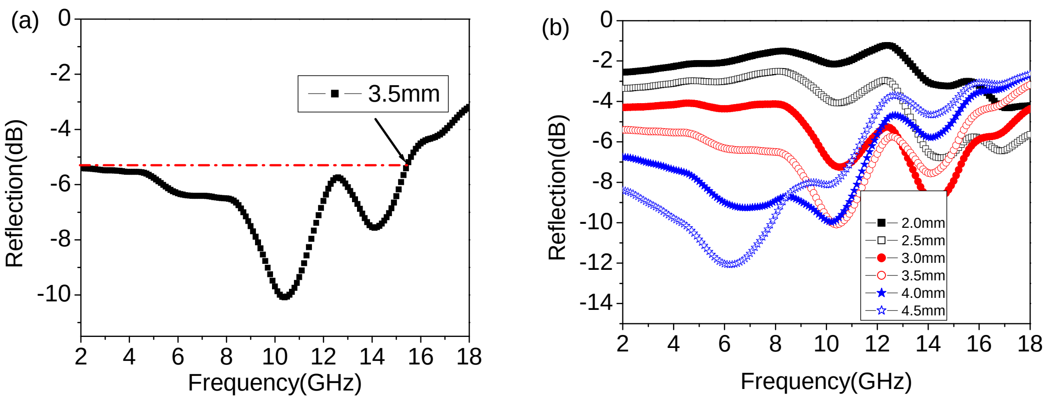

Figure 4. The calculated theoretical RL of Fe_3O_4 nancrystals (a) with a thickness of 3.5 mm and (b) with different thicknesses (2–4.5 mm) in the range of 2–18 GHz

Conclusions

The wave absorption properties of superparamagnetic Fe_3O_4 single nanocrystals nanocomposites have been studied in the frequency range of 2-18 GHz. Due to the single nanocrystals with narrow size distribution and superparamagnetism, the effective microwave absorptions (RL<-5.30 dB) of absorbers are obtained in a broadband frequency range from 2 GHz to 15.40 GHz and the minimum reflection losses and the peak frequencies are -10.5 and-7.7 dB at the frequency of 10.4 and 14.1 GHz, respectively, when the thickness is 3.5 mm. The Fe_3O_4 single nanocrystals nanocomposites show excellent wave absorption, which is a promising microwave-absorbing agent.

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References

[1] Y. J. Chen, F. Zhang, G. G. Zhao, X. Y. Fang, H. B. Jin, P. Gao, C. L. Zhu, M. S. Cao, and G. Xiao. J. Phys. Chem. C 2010, 114, 9239–9244.

[2] H. Deng, X. Li, Q. Peng, X. Wang, J. Chen, Y. D. Li, Angew. Chem. 2005, 117, 2842-2845.

[3] F. Bai, D. S. Wang, Z. Y. Huo, W. Chen, L. P. Liu, X. Liang, C. Chen, X. Wang, Q. Peng, Y. D. Li, Angew. Chem. 2007, 119, 6770-6773.

[4] J. P. Ge, Y. X. Hu, M. Biasini, W. P. Beyermann, Y. D. Yin, Angew. Chem. 2007, 119, 4420-4423.

[5] J. Liu, Z. K. Sun, Y. H. Deng, Y. Zou, C.Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li, D. Y. Zhao, Angew. Chem. Int. Ed. 2009, 48(32), 5875-5879.

[6] X. H. Guan, B. T. Zheng, M. Lu, X. Guan, G. S. Wang and L. Guo. ChemPlusChem, 2012, 77, 56-60.

[7] J.Y. Shin, J. H. Oh. IEEE Trans Magn, 1993, 29, 3437–9.

[8] P. H. Martha. J Magn Magn Mater, 2000, 215–216, 171–83.

[9] C. H. Peng, C. C. Hwang, J. Wan, J. S. Tsai, S. Y. Chen. Mater Sci Eng B, 2005, 117, 27–36.

[10] S. Jia, F. Luo, Q.C. Qing, W.C. Zhou, D.M. Zhu, Phys. B: Condens. Matter,2010, 405, 3611–3615.

[11] Y.Q. Kang, M.S. Cao, J. Yuan, L. Zhang, B. Wen, X.Y. Fang, J. Alloys Compd., 2010, 495, 254–259.

[12] X.G. Huang, J. Chen, J. Zhang, L.X. Wang, Q.T. Zhang, J. Alloys Compd., 2010, 506, 347–350.

[13] X.G. Liu, Y.D. Wang, L. Wang, J.G. Xue, X.Y. Lan, J. Inorg. Mater., 2010, 25, 441–443.

[14] Y.Z. Fan, H.B. Yang, M.H. Li, G.T. Zou, Mater. Chem. Phys., 2009, 115, 696–698.

[15] M.X. Yu, X.C. Li, R.Z. Gong, Y.F. He, H.H. He, P.X. Lu, J. Alloys Compd., 2008, 456, 452–455.

[16] Y. Yang, B.S. Zhang, W.D. Xu, Y.B. Shi, N.S. Zhou, H.X. Lu, J. Alloys Compd., 2004, 365, 300–302.

[17] A. Ghasemi, A. Morisako, J. Alloys Compd., 2008, 456, 485–491.

[18] J. Wei, J.H. Liu, S.M. Li, J. Magn. Magn. Mater., 2007, 312, 414–417.

[19] S.S. Kim, S.T. Kim, J.M. Ahn, K.H. Kim, J. Magn. Magn. Mater., 2004, 271, 39–45.

[20] X. A. Li, X. J. Han, Y. J. Tan, P. Xu., J. Alloys Compd., 2008, 464, 352–356.

[21] N. A. Frey, S. Peng, K.Cheng, S. Sun, Chem. Soc. Rev.2009, 38, 2532 – 2542.

[22] C.H. Peng, H.W. Wang, S.W. Kan, M.Z. Shen, Y.M. Wei, S.Y. Chen, J. Magn. Magn. Mater., 2004, 284, 113–119.

[23] V. Sunny, P. Kurian, P. Mohanan, P. A. Joy, M. R. Anantharaman, J. Alloys Compd. 2010, 489, 297–303.