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Radio-frequency permeability and permittivity spectra of copper/yttrium iron garnet cermet prepared at low temperatures

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Abstract

Copper/yttrium iron garnet ($Cu/Y_3Fe_5O_{12}$) cermets with tailored microstructures were prepared via a facile wet chemical process. The radio-frequency permeability and permittivity spectra of the cermets were investigated in detail. A percolation phenomenon appears with increasing copper contents, and an ultra-low percolation threshold (<5.47 vol%) is obtained. For the cermets below percolation threshold, the frequency dispersion of permittivity is featured with a poly-dispersive Debye type relaxation process. For the cermets above but still near percolation threshold, plasma-like negative permittivity featured with fano-like resonances was obtained. The $Cu/Y_3Fe_5O_{12}$ cermet is a potential candidate for electromagnetic cloaking, microwave attenuation and telecommunications, etc.

Keywords: Cermet; Dielectric property; Permeability spectra; Metamaterial

1. Introduction

In recent years, ever-increasing attention has been paid to the high frequency electromagnetic properties of ceramic matrix composites due to their wide potential applications for electromagnetic absorbing, attenuation and shielding, etc.[1–7] Interestingly, recent researches show that metal/ceramic composites could exhibit negative permittivity and permeability after carefully tailoring their compositions and microstructures.[8,9] And their electromagnetic properties could be feasibly tuned by controlling their compositions and microstructures. Therefore, metacomposites with negative permittivity and negative permeability become the focus of extensive researches.[10–15]

For the realization of negative permeability, ferrites are usually chosen owing to their magneto-tunable permeability spectra.[16–20] Above all, yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG) is the most promising candidate because of its excellent negative permeability properties.[21] Generally, the negative permeability band of YIG is within radio-frequency (RF) band. Therefore, YIG matrix cermets could be potential candidates for RF metamaterials. However, in order to realize simultaneous negative permittivity and negative permeability in the same frequency band, RF negative permittivity is also required.

Up to now, RF negative permittivity is mainly obtained via periodic metallic wire arrays.[22–25] As an alternative, we propose herein a new kind of metal/YIG cermets with disordered (rather than periodic) microstructures, in which the RF negative permittivity could be provided by metallic networks. In order to avoid the unexpected deleterious reactions between metal and YIG at high sintering temperatures during the traditional ball-milling and sintering process, a facile wet chemical approach is adopted to prepare the copper/YIG cermet at low temperatures (<500 °C). The frequency dispersions of permittivity and permeability are investigated in detail. It is indicated that, magneto-tunable negative permeability could be obtained by

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applying an external magnetic field. Furthermore, plasma-like RF negative permittivity is also obtained.

2. Experimental

2.1. Preparation of the cermets

Yttrium iron garnet (YIG) powders were prepared using a typical solid state reaction method. For the preparation of porous YIG, activated carbon powder (purity ≥99.0%, 300 meshes, as pore former) and YIG powder were mixed in a mass ratio of 25:75. Then, porous YIG discs with an open porosity of ~60% were prepared by dry pressing at 80 MPa and sintering at 1250 °C for 1.5 h. The preparation process of Cu/YIG cermets is as follows: (1) Porous YIG discs were soaked in 1.5 M $Cu(NO_3)_2$ ethanol solution (prepared with copper nitrate powder with a purity ≥99.8%), vacuumized for 10 min to "press" the $Cu(NO_3)_2$ solution into porous YIG. (2) The impregnated discs were taken out and the excess $Cu(NO_3)_2$ solution on the YIG surface was rubbed off. Then, the discs were imbedded into Al_2O_3 powders, and dried in an oven at 70 °C for 2 h and 100 °C for 6 h to remove ethanol. (3) The discs were calcined at 623 K in air for 20 min to obtain the CuO/YIG precursors ($2\,Cu(NO_3)_2 = 2CuO + 4NO_2 \uparrow + O_2 \uparrow$). Finally, the CuO/YIG precursors were reduced at 400 °C in hydrogen for 3 h to get Cu/YIG cermets. The cermets with Cu mass fraction of 7 wt% (1.9 vol%), 13 wt% (3.5 vol%), 19 wt% (5.5 vol%) and 24 wt% (7.4 vol%) were prepared and referred to as Cu7, Cu13, Cu19 and Cu24, respectively.

2.2. Characterization

The morphologies of the cermets were investigated by SU-70 Field Emission Scanning Electron Microscope (FESEM). The XRD patterns were recorded at room temperature using the Rigaku D/max-rB X-ray diffractometer with CuK_α radiation. For the permittivity measurements, Cu/YIG discs with dimension of 15 mm × 15 mm × 2 mm are prepared. After the open/short compensation (to reduce the effects of the test fixture's residuals) and load compensation (to calibrate the test fixture), the disc was put between the two planar electrodes of 16453A dielectric test fixture for permittivity measurements. The impedance data (Z' and Z''") were converted to capacitance C and R for permittivity calculation ($\varepsilon' = tC/A\varepsilon_0$ and $\varepsilon'' = t/2\pi fRA\varepsilon_0$, where t is the thickness of the sample, A is the area of the electrode, ε_0 is the absolute permittivity of free space (8.85×10^{-12} F/m), C is capacitances, R is resistances, f is the frequency of the electric field. R is converted to conductivity σ by $\sigma = t/(RA)$, where t is the thickness of the sample and A is the area of the electrode. For permeability measurement, Cu/YIG cermets ring (inner diameter, outer diameter and height were 6.5 mm, 19 mm and 2 mm, respectively) was prepared. After the open/short and load compensations, the sample was put into the 16454A permeability test fixture and the inner diameter, outer diameter and height of the test composite are inputted into the computer for permeability measurements. The permeability calculation formula is $\mu^*_r = 2\pi(Z^*_m - Z^*_{sm})/[j\omega\mu_0 h \ln(c/b)] + 1$, where Z^*_m and Z^*_{sm} are the impedances of the test fixture with and without sample mounted, ω is the frequency, μ_0 is the space permeability ($4\pi \times 10^{-7}$ N/A^2), h, c and b are the height, outer diameter and inner diameter of the sample. The permittivity and permeability measurements were performed under 100 mV ac voltage at room temperature in the frequency range from 20 MHz to 1 GHz using Agilent E4991A precision impedance analyzer.

3. Results and discussions

3.1. XRD patterns and SEM results

The XRD patterns (a) and SEM images (b) of the Cu/YIG cermets are shown in Fig. 1. We can see that, the cermets consist of copper and yttrium iron garnet, without any additional phases (Fig. 1a). In traditional cermet preparation processes, the high sintering temperature (>1000 °C) may result in some unexpected reactions between metal and ceramic.[26,27] In our present work, the low processing temperature (400 °C) avoided the possible deleterious reactions between the incorporated components (copper) and the matrix (YIG) during the calcination and reduction processes. As shown in Fig. 1b, for the cermets with copper content of 7 wt%, isolated copper particles with typical size of ~50 nm are homogeneously distributed in porous YIG. Further increasing the copper content leads to the increase of the copper particle size and the contact between copper particles. In particular, closely-packed copper particles are formed in the cermets with copper contents of 19 wt% and 24 wt%.

3.2. Permeability spectra

The permeability spectra of Cu/YIG cermets with different copper contents are presented in Fig. 2a and b. For the YIG matrix, the μ'–f curve is a typical relaxation type permeability spectrum, and a sharp decrease of μ' (Fig. 2a) corresponding to a magnetic resonance loss peak (Fig. 2b) is observed. Furthermore, the frequency dispersions of permeability for YIG under different external magnetic fields were calculated using domain wall and spin resonances[28]:

$$\mu' = 1 + \frac{\omega_d^2 \chi_{d0}\left(\omega_d^2 - \omega^2\right)}{\left(\omega_d^2 - \omega^2\right)^2 + \omega^2\beta^2} + \frac{\chi_{s0}\omega_s^2\left[\left(\omega_s^2 - \omega^2\right) + \omega^2\alpha^2\right]}{\left[\omega_s^2 - \omega^2\left(1+\alpha^2\right)\right]^2 + 4\omega^2\omega_s^2\alpha^2} \quad (1)$$

$$\mu'' = \frac{\chi_{d0}\omega\beta\omega_d^2}{\left(\omega_d^2 - \omega^2\right)^2 + \omega^2\beta^2} + \frac{\chi_{s0}\omega_s\omega\alpha\left[\omega_s^2 + \omega^2\left(1+\alpha^2\right)\right]}{\left[\omega_s^2 - \omega^2\left(1+\alpha^2\right)\right]^2 + 4\omega^2\omega_s^2\alpha^2} \quad (2)$$

where μ' and μ'' are the real part and imaginary part of the permeability, χ_d and χ_s are the magnetic susceptibilities of domain wall motion and spin, $\omega_d = 2\pi f_d$ and $\omega_s = 2\pi f_s$ are the angular frequency of domain wall motion and spin, χ_{d0} and χ_{s0} are the