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Adjustable microwave absorption properties of flake shaped $(Ni_{0.5}Zn_{0.5})Fe_2O_4$/Co nanocomposites with stress induced orientation

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ABSTRACT

Flake shaped $(Ni_{0.5}Zn_{0.5})Fe_2O_4$/Co nanocomposites were successfully fabricated by co-precipitating of Ni-Zn ferrite on the surface of cobalt nanoflakes. The electromagnetic characteristics of the samples were studied at the frequency of 0.1–14 GHz. The results showed that the cobalt nanoflakes in compacted nanocomposites were well orientated, and the nanocomposites were characterized with low optimal reflection loss (RL) of -33.8 dB at 11.5 GHz and broad RL bandwidth for < -20 dB in the frequency range of 7.6–12.1 GHz. At the same time, the position of the absorptive band can be adjusted by changing the mass ratio of ferrite to cobalt in the nanocomposites. It is proposed that the excellent microwave absorption properties are related to the combination of strong shape anisotropy of cobalt nanoflakes and adjustable dielectric loss.

1. Introduction

With rapid developing of electromagnetic wave shielding technology in GHz band, ferromagnetic particles were widely used due to their large saturation magnetization and thus a high Snoek' limit at high frequencies [1–4]. Among these candidates, the ferromagnetic particles with a flake shape have attracted more attention. In comparison with sphere shaped particles, flakes possess larger shape anisotropy energy which is dominant in particle system instead of magnetocrystalline anisotropy energy. The shape induced anisotropy can increase the natural resonant frequencies to the gigahertz range [5]. Moreover, the eddy current effect could be effectively suppressed in the flakes with the thickness lower than the skin depth. As a consequence, higher permeability can be obtained [6]. Kim et al. found the higher magnetic permeability and better absorbing properties in iron thin flakes dispersed in rubber matrix [7]. Similar results were observed in carbonyl-iron [8] and flake shaped FeCuNbSiB particle composites [9].

Recently, Yang et al. found that the permeability and resonance frequency of flake shaped particles can be further increased by orientation of the flakes [10]. The enhanced microwave behavior of oriented flake shaped particles can be explained by the bianisotropy picture [11]. However, the process of orientation for polycrystalline flakes is complicated which are fabricated by ball milling. In our previous report, we found that single crystal Co flakes prepared with hydrazine reduction can be naturally oriented when the flakes were compacted to ring [12]. The stress induced orientation of Co flakes is a new way to fabricate oriented microwave absorbents.

It is a serious problem that the metal magnetic nanoflakes can be easily oxidized and corroded, restricting its practical application in microwave absorption. However, a nanoshell in the surface of nanoflakes can solve the problem. Additionally, the nanoshell composed of dielectric materials contributes to microwave absorption of nanocomposite [13–16]. It's well known that the ferrites are good electromagnetic absorbents for their dielectric properties [17]. However, few attentions have been focused on the combination of ferrites and metal magnets. It's worthy to make an attempt on preparing nanocomposite of orientated cobalt nanoflakes with ferrite coatings.

In this pap1er, we fabricated cobalt flakes and deposited $(Ni_{0.5}Zn_{0.5})Fe_2O_4$ on the surface of cobalt nanoflakes. The structure and magnetic properties of the nanocomposites were investigated, the complex permittivity and permeability spectra were discussed.

2. Experimental Details

Cobalt nanoflakes were prepared in aqueous solution at 180 °C with hydrazine reduction method [18], and then the cobalt nanoflakes were coated by Ni-Zn ferrite using co-precipitation

Abbreviations: EDS, Energy Dispersive Spectrometer; GHz, gigahertz; RL, reflection loss; SAED, selected area electron diffraction; SEM, scanning electron microscope; TEM, transmission electron microscope; VSM, vibrating sample magnetometer; XRD, X-ray diffraction

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method. The 0.0028 mol as-prepared cobalt powders were dispersed in 200 ml distilled water and sonicated for 20 min. 4 ml 0.1 mol/L $NiCl_2$, 4 ml 0.1 mol/L $ZnCl_2$, 16 ml 0.1 mol/L $FeCl_2$ and 2 ml 1 M NaOH solution were added into the former suspension. The mixed solution was stirred and maintained at 95 °C with reflux for half an hour to complete the co-precipitation reaction. After washing and drying, the powers were collected. The sample was named sample A, the mass ratio of Co to Ni-Zn ferrite is 4:5. By changing the mole ratio of Co powders to Ni and Zn salt, the Co/Ni-Zn ferrite nanocomposites with different contents were prepared, and labeled as B (1:5) and C (1:10), respectively. The crystal structures of the samples were analyzed by *X*-ray diffraction (XRD) on a Philips Panalytical X'pert diffractometer with Cu Kα radiation. Photos were taken on a Hitachi S-4800 field emission scanning electron microscope (SEM) and transmission electron microscope (TEM) (JIM-2010). The samples for microwave electromagnetic properties measurement were mixed with paraffin(mass ratio of 20%), and pressed into ring shape of 7.00 mm outer diameter and 3.00 mm inner diameter with a thickness of 2 mm. The scattering parameters (S_{11}, S_{21}) were measured by a network analyzer (Agilent Technologies E8363B) in the range of 0.1–15 GHz. All of the measurements were performed at the room temperature.

3. Results and discussion

Fig. 1(a) shows that the as-prepared cobalt nanostructures are flake shape and the diameter varied from 0.5 to 10 μm, the inset picture illuminates the thickness of the nanoflake is about 84 nm. A hexagonal flake in sample A is displayed in Fig. 1(b), the inset shows the thickness of the Ni-Zn ferrite coating is about 26 nm. Fig. 1(c) shows the selected area electron diffraction (SAED) images of sample A which exhibits six fold symmetry with electron beam being along the ⟨001⟩ axis of *hcp* crystal structure. It means that the cobalt flakes are nearly single crystals and the growth of (001) plane is inhabited during the process of crystal growth. The diffraction spots corresponding to the (311) crystal plane of spinel structure are also observed. Fig. 1(d) shows the EDS pattern of sample A, and the result indicates the coexistence of Fe, Co, Ni, Zn and O elements in the sample. It can be confirmed that the cobalt nanoflakes are coated with Ni-Zn ferrite.

Fig. 2(a) shows the XRD spectra of Ni-Zn ferrite/Co nanocomposites and as-prepared Co nanoflakes. It is confirmed that the coexistence of *hcp* Co and spinel Ni-Zn ferrite phases in sample A, the result is consistent with the SAED and the EDS data. With increasing of the cobalt content, the relative intensity of the diffraction peaks for cobalt increase and ferrite become weak in the patterns of sample B and C. Single phase of *hcp* Co is observed in the pattern of as-prepared Co nanoflakes.

Fig. 2(b) shows the magnetic hysteresis loops of Ni-Zn ferrite/Co nanocomposites and as-prepared Co nanoflakes. All of the loops demonstrate typical ferromagnetism. The inset table shows the saturation magnetization (M_s), coercivity (H_c) the calculated Co mass ratio. The M_s and H_c of samples increase with Co mass ratio.

Fig. 3(a) shows the XRD patterns of compacted sample A (mixed with 20% paraffin, and pressed into ring shape) and samples A powders. The relative intensity of (002) peak in compacted sample A increase drastically, indicating the compacted nanoflakes have strong *hcp* [001] preferred orientations. The nanoflakes tend to align in a parallel direction with each other and parallel with the surface plane of the compacted ring under pressure. Fig. 3(b) shows the hysteresis loops of the compacted sample A along the directions deviating different angle θ from the out plan direction. It can be found that the easy magnetization axis is in plane direction.

Fig. 4(a) shows the real and imaginary parts of the complex relative permittivity (ε' and ε'') spectra for compacted sample A, B, C and as-prepared cobalt nanoflakes. The relationship of ε' and frequency for each sample nearly keeps a constant trend in the

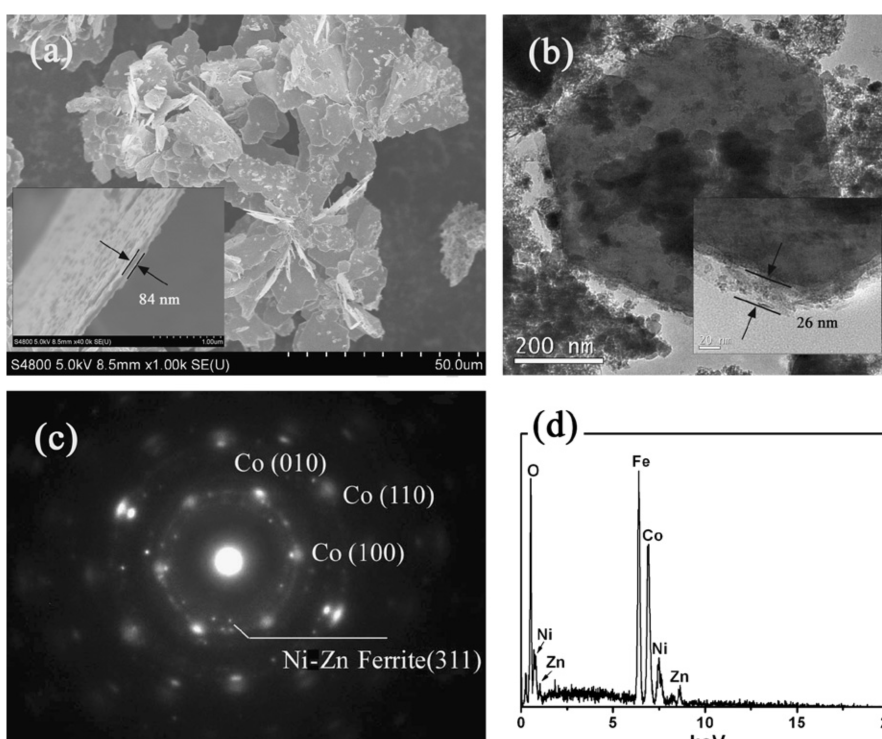

Fig. 1. SEM image of as-prepared cobalt nanoflakes (a), the inset image shows the thickness of the nanoflakes, the TEM picture of Ni-Zn ferrite coated Co nanoflakes (sample A) (b), the inset shows the thickness of the ferrite coating, the SAED pattern (c), and the EDS pattern of sample A (d).

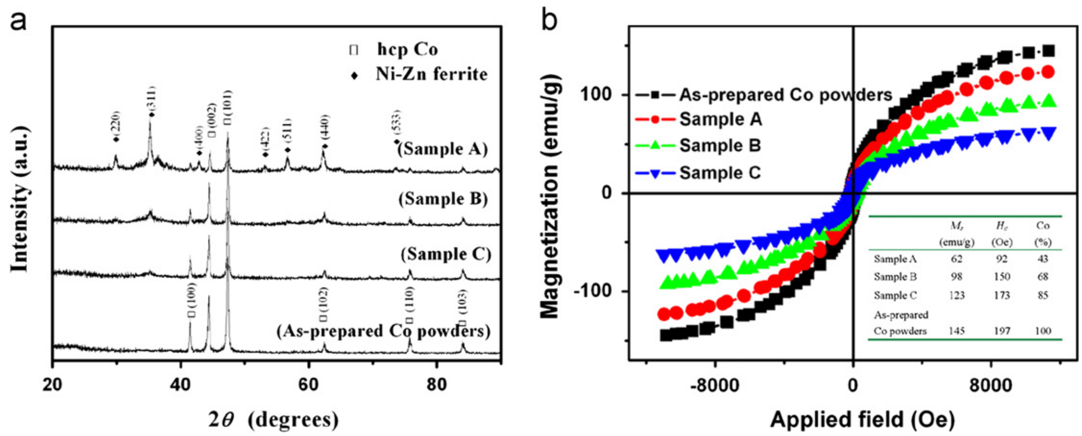

Fig. 2. XRD patterns of sample A, B, C and as-prepared cobalt nanoflakes (a), the hysteresis loops of sample A, B ,C and as-prepared cobalt nanoflakes, the inset table shows the magnetization, coercivity and calculated cobalt mass ratio for each sample (b).

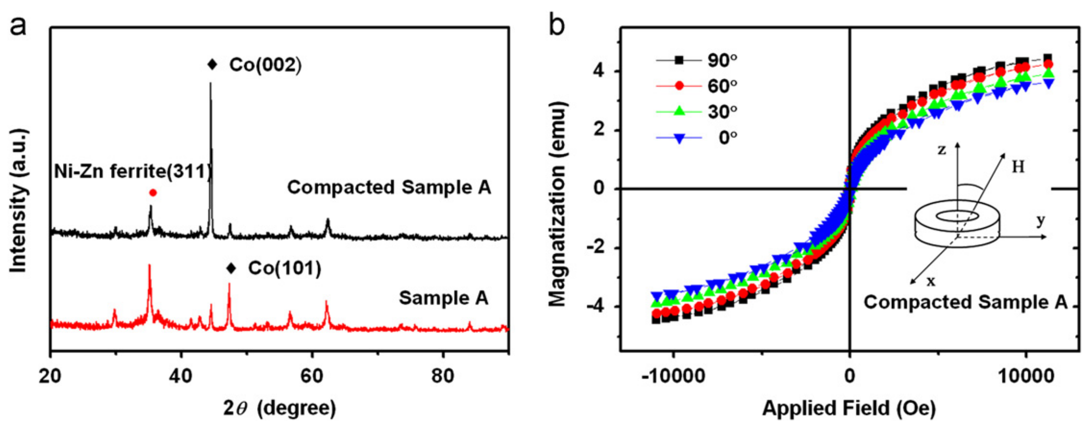

Fig. 3. XRD patterns of compacted sample A and sample A powders (a), hysteresis loops of compacted sample A along varied directions (the inset picture shows the simplified coordinate in a compacted ring) (b).

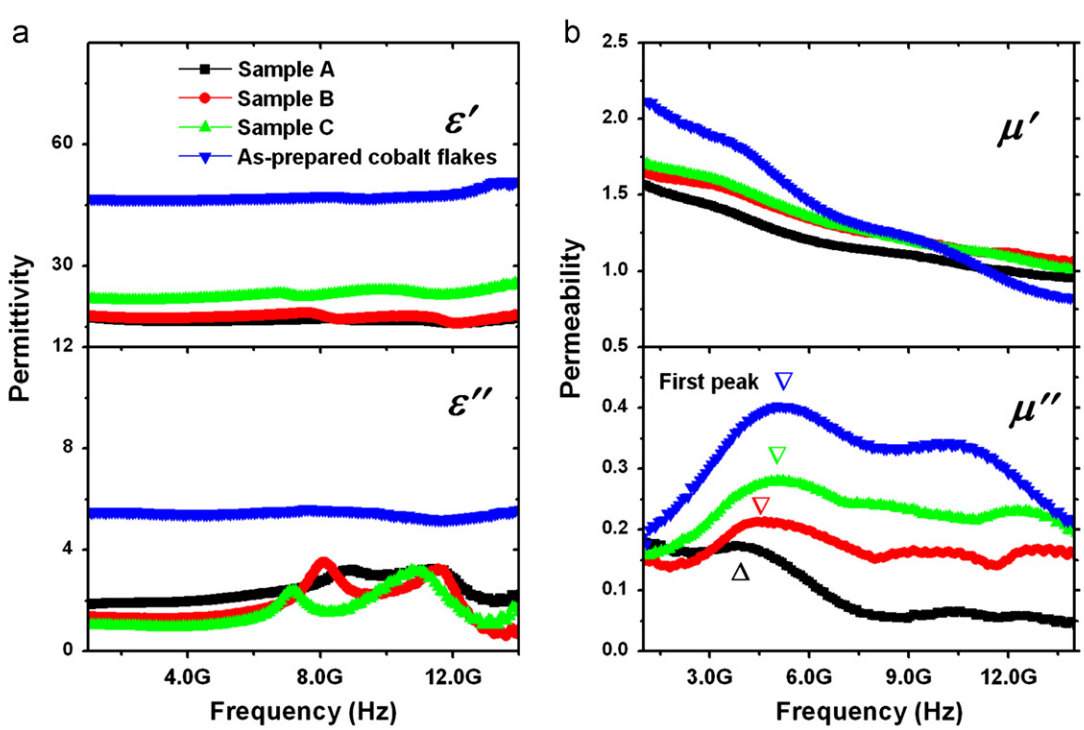

Fig. 4. Frequency dependence of the complex permittivity (a) and permeability (b) for compacted sample A, B, C and as-prepared cobalt nanoflakes.

measured range. The initial value of ε' at 1 GHz decreases from 46.8 in as-prepared cobalt flakes to 18.7 in sample A with reducing of cobalt content. The reason could be the suppression of eddy current effect for Ni-Zn ferrite. Two peaks are observed in the complex relative permittivity (ε'') spectra for sample A, B and C. The first peak is located at about 9, 8 and 7 GHz for sample A, B and C, respectively, the second one is estimated to be 11 ~ 11.5 GHz for three samples. The double peaks can be ascribed to the polarization of ferrite and the interfacial polarization on the interfaces between two phases [14,15]. A single peak appears at 5.2 GHz in ε'' spectrum for as-prepared cobalt nanoflakes, it is believed that the peak is caused by the polarization of nanoflakes. It is worthily noted that the positions of first peak shift from low frequency to high frequency band with the increment of Ni-Zn ferrite ratio.

Fig. 4(b) shows that the real and imaginary parts of the complex relative permeability (μ' and μ'') for sample A, B, C and as-prepared cobalt nanoflakes gradually decrease in whole frequency range. The initial value of μ' at 1 GHz decreases from 2.1 of as-prepared cobalt nanoflakes to 1.5 of sample C with reducing of cobalt content. There are multi-resonance peaks in

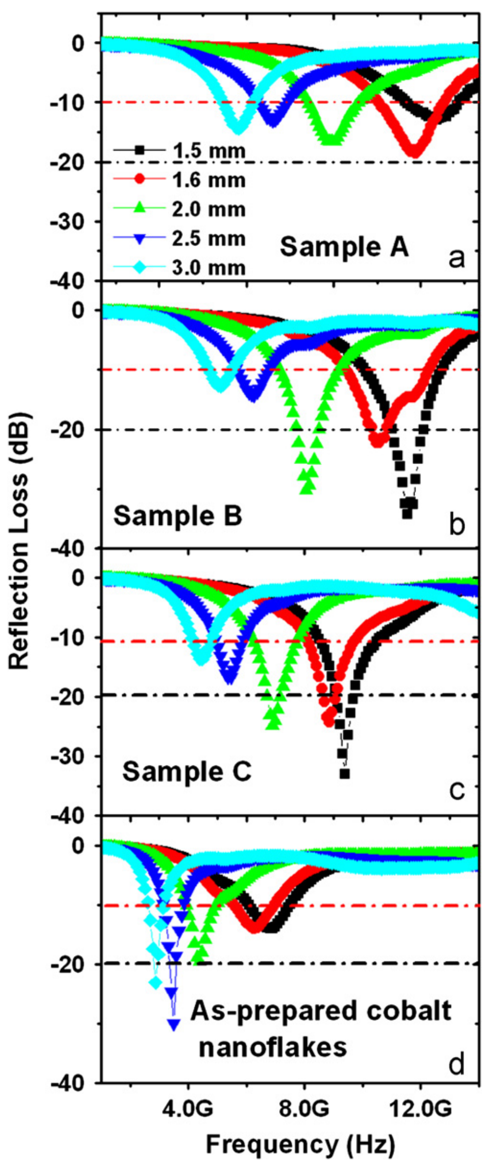

Fig. 5. Frequency dependence of calculated reflection loss for sample A (a), B (b), C (c) and as-prepared cobalt nanoflakes (d).

the μ'' spectra for each sample in the measured range. The first peak of the cobalt nanoflakes and the composites can be ascribed to the natural resonance [19], and the peak position corresponding to the natural resonance frequency (f_r) diminished from about 5 GHz in the as-prepared cobalt nanoflakes to 4 GHz in the sample A with increasing of the mass ratio of ferrite. In this study, the direction of **H** for the applied AC field is parallel to the nanoflakes which were orientated by pressure. The f_r could be simply calculated by: $f_r = (\gamma\sqrt{4\pi M_s H_e})/2\pi$ [20]. Considering the coercively is related to the effective anisotropy field (H_e), the decreasing of M_s and H_c could cause the reducing of f_r. The second and third peaks could be belonged to the exchange resonance mode [19].

According to the transmit-line theory [21], the reflection loss (RL) of sample A, B and C with varied thickness were calculated in the range of 1–14 GHz. Fig. 5(a) shows the RL of sample A for different thicknesses. The bandwidth for RL < -10 dB (note that -10 dB corresponds to about 70% microwave absorption) was obtained in the range of 5.1–13.2 GHz for a thickness from 1.5–3.0 mm, covering the whole *X*-band (9–12.4 GHz). The optimal RL is -18.1 dB at 11.7 GHz for a thickness of 1.6 mm. The RL data of sample B is shown in Fig. 5(b). The bandwidth for RL < -20 dB (corresponds to about 99% microwave absorption) is in the range of 7.6–12.1 GHz for a thickness from 1.5–2 mm, the optimal RL is -33.8 dB at 11.5 GHz for a thickness of 1.5 mm. The optimal RL of sample C was -32.5 dB at 9.4 GHz for a thickness of 1.5 mm as shown in Fig. 5(c). The optimal RL of as-prepared cobalt nanoflakes is -29.8 dB at 3.5 GHz as shown in Fig. 5(d), the bandwidth of RL < -10 dB is in 2.5–7.5 GHz for a thickness of 1.5–3.0 mm. The frequency corresponding to optimal RL and center of bandwidth (< -10 dB) shift from low frequency to high frequency band with increasing of Ni-Zn ferrite ratio, it means that the position of absorptive band can be adjusted conveniently when the thickness of absorbent is limited in application.

4. Conclusions

Orientated Ni-Zn ferrite/Co nanoflakes were successfully fabricated. The results show the nanocomposites possess adjustable and strong microwave absorptive abilities. The outstanding microwave absorption of the nanocomposites results from the combination of adjustable dielectric loss and large magnetic loss, where the coexistence of nanoshell microstructure and the orientation of nanoflakes is important. As a result, $(Ni_{0.5}Zn_{0.5})$-Fe_2O_4 coated cobalt flakes are attractive candidates for electromagnetic absorption.

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