Materials Chemistry and Physics 159 (2015) 173–177

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# High microwave permittivity and resonance–antiresonance electromagnetic behaviors of flake-shaped cobalt microcrystals

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## HIGHLIGHTS

- Cobalt microflakes are assemblies structure composed of cobalt nanocrystallines.
- Cobalt microflakes/wax exhibits an excellent microwave absorption in 2–16 GHz.
- Cobalt microflakes/wax composite has a relatively high permittivity in 2–16 GHz.
- Cobalt microflakes/wax composite exhibits antiresonance permeability in 2–16 GHz.

## ARTICLE INFO

*Article history:*
Received 7 April 2014
Received in revised form
10 March 2015
Accepted 29 March 2015
Available online 3 April 2015

*Keywords:*
Magnetic materials
Chemical synthesis
Electrical properties
Magnetic properties

## ABSTRACT

The high real part of permittivity (34 ~ 63), resonant permittivity and antiresonant permeability were observed simultaneously in flake-shaped cobalt microcrystal powders embedded in the wax composite in 2–16 GHz frequency range. These cobalt flakes are assembled structure composed of cobalt nanocrystalline. The estimated crystallite size of cobalt nanocrystalline is 25 nm. The scattering of complex permittivity at microwave frequency was thoroughly discussed in this paper and the antiresonant permeability behavior was explained using Mie theory and electromagnetic induction principle. The magnetic hysteresis loops of the pressed disk using cobalt powders revealed that the sample exhibited ferromagnetic characteristics with a saturation magnetization of 149 emu/g and a coercivity of 263 Oe at room temperature. The reflection loss of cobalt/wax composite with 60 wt % cobalt reaches a minimum of −12.2 dB at 11.2 GHz and the bandwidth less than −6 dB covering 9.28–13.04 GHz range with the coating thickness only 1 mm. In addition, the absorption peak sites can be adjusted easily by varying the coating thickness. The excellent microwave absorption properties in 2–16 GHz range can attribute to strong dielectric loss and relative high permeability coming from strong magnetic anisotropy.



## 1. Introduction

Cobalt flake-shaped particles have various technological applications and potential novel properties in the gigahertz (GHz) frequency range due to large magnetic anisotropy, high saturation magnetization, high microwave permeability and so on [1–3]. The excellent microwave absorption properties and relatively high permeability of the cobalt flake-shaped particles in the GHz frequency range have been intensively investigated in many literature [4,5]. However, to the best of our knowledge, the potentially high permittivities of these cobalt flake-shaped particles in the GHz frequency range have seldom been reported. In fact, these cobalt flake-shaped particles are usually layer by layer assemblies composed of cobalt nanocrystals, which maybe lead to the enhancement of grain boundary polarization and intrinsic electric dipole polarization compared to their other counterparts. Thus, the high permittivity of flake-shaped cobalt particles would be obtained.

Nowadays, simultaneous resonance of permittivity and antiresonance of permeability behaviors, different from traditional resonance spectrum were observed in some artificial or natural materials, for example, a disordered SiC/wax composite [6], Co/$SiO_2$ embedded in wax nanocomposite [7], hollow Co nanochains/wax composite [8] and so on. Their magnetic antiresonances were usually accompanied by the negative imaginary parts of permeability ($\mu''$) [9–11]. Some literature thought an attractive photons

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http://dx.doi.org/10.1016/j.matchemphys.2015.03.067
0254-0584/

potential well could also be constructed in the high permittivity scatters embedded in the low permittivity matrix in spite of their disordered structure [12,13]. The extraordinary electromagnetic properties could be explained by the Mie resonance model. The Mie resonance is highly localized and its occurrence depends mainly on the high permittivity of the scatter [6,14]. However, the argument about these phenomenons is still in process. It still needs more experimental data and theoretical analyses.

In this paper, we adopted a hydrothermal method to synthesize cobalt flake-shaped microcrystal assemblies composed of cobalt nanocrystallines. The relations between microstructure, flake size and high permittivity of cobalt flake-shaped microcrystals sample were thoroughly revealed in the 2–16 GHz range. In addition, the phenomenon of antiresonance permeability relating with resonant permittivity for the cobalt flake microcrystals powder dispersed in the wax was roughly discussed according to Mie theory and electromagnetic induction principle. Finally, the microwave absorption of cobalt/wax composite was investigated based on the measurement data of complex permittivities and complex permeabilities in the 2–16 GHz range.

## 2. Experimental

Cobalt flake-shaped microcrystals were synthesized via a hydrothermal reduction method [15,16]. The raw material of $CoCl_2 \cdot 6H_2O$ (2.5 g) and the surfactant of hexadecyl trimethyl ammonium bromide (CTAB, 2 g) were firstly dissolved in 15 ml of distilled water under magnetic stirring. 3 g sodium hydroxides (NaOH) were dissolved in 10 ml of distilled water. The NaOH solution and 10 ml of 85% hydrazine hydrate were added into the above mixed solution, which was followed by the continual vigorous stirring for 30 min. The mixed solution was then transferred to a 50 ml Teflon-lined autoclave, which was followed by the continually vigorous stirring for 30 min. The mixed solution was then transferred to a 50 ml Teflon-lined autoclave which was kept at 160 °C for 2 h and 3 h, respectively, and cooled to room temperature naturally. After thorough cleaning and drying, the purity flake-shaped cobalt microcrystals were obtained and the samples were named as Co-2h and Co-3h, respectively.

The microstructures and morphologies of these samples were characterized by X-ray powder diffraction (XRD, Japan Rigaku D/MAX–cA) using a Cu $K_a$ radiation and scanning electron microscopy (SEM, Hitachi S-4800), respectively. Magnetic hysteresis (M–H) loops were measured by a Quantum Design super-conducting quantum interference device (SQUID) MPMS system using pressed disks of cobalt powders.

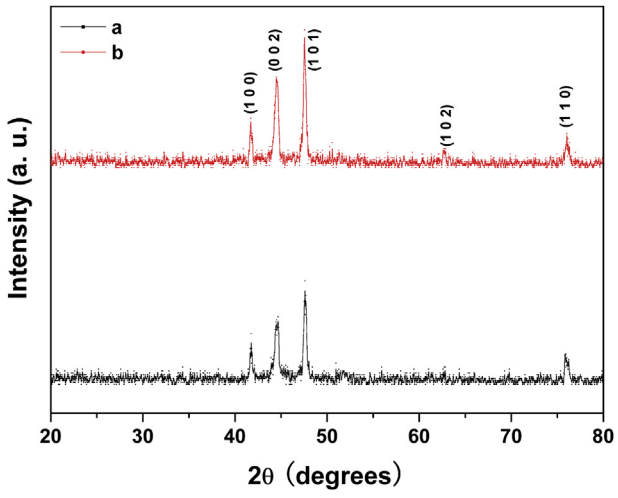


**Fig. 1.** X-ray diffraction patterns of samples obtained at different reaction time: (a) 2 h; (b) 3 h.

The as-prepared cobalt powders were dispersed into wax in the mass ratio of 3:2 and compacted into toroidal-shaped specimens with 7.0 mm outer diameter and 3.04 mm inner diameter for transmission/reflection measurements. After careful calibration of measurement setup, the complex permeability ($\mu'$, $\mu''$) and complex permittivity ($\varepsilon'$, $\varepsilon''$)for each cobalt/wax composite specimen in 2–16 GHz range were measured by using an Agilent 8510C vector network analyzer and Agilent 85071E material measurement software [4]. The cole–cole curve of $\varepsilon''$ versus $\varepsilon'$ (the $\varepsilon'$ values as horizontal axel and the $\varepsilon''$ values as vertical axel) for the same sample at each frequency point was plotted based on their measurement data in 2–16 GHz range. The reflection loss value (RL) for metal-backed the cobalt/wax coating can be calculated based on the measured complex permeability and complex permittivity at a given frequency and coating thickness according to the formula listed in the literature [16].

## 3. Results and discussion

The XRD patterns of the cobalt flake microcrystal powders are shown in Fig. 1. Both the Co-2h and Co-3h samples present the same diffraction peaks (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0), which confirms the formation of hexagonal phase (hcp) cobalt structure (JCPDS no. 05–0727) [17]. The average crystallite size (D) of the samples can be roughly calculated using the Scherrer formula $D = 0.9\lambda/(\beta\cos\theta)$, where $D$ is the crystallite size, $\lambda$ is the X-ray wavelength of 0.154 nm, $\beta$ is the half-peak width, $\theta$ is the position of the (1 0 1) peak in Fig. 1 [18]. The crystallite size (D) of the Co-2 h and Co-3 h sample is 25 nm and 28 nm, respectively.

Fig. 2 shows the typical SEM image of the as-synthesized cobalt powders. Most of the cobalt particles look like flake-shaped microcrystals with uneven sizes. It was estimated that the flakes were 4.5 μm in width, 4 ~ 8 μm in length and less than 150 nm in thickness. The amplified image of cross section for Co-2h microcrystals is given in Fig. 2(c) and it shows that these flakes are builted up by a lot of interconnected cobalt nanocrystallines. It seems that the cobalt microflakes are layer by layer assembly structure composed of cobalt nanocrystallines.

With the hydrothermal reaction time increasing to 3 h, the length and the width of the flakes do not change remarkably as shown in Fig. 2(b). In addition, compared to the Co-2 h sample, the crystallite size of cobalt nanocrystalline increases from 25 nm to 28 nm based on the Scherrer formula.

Fig. 3 shows the M–H loops recorded on the pressed disk using Co-2h powders with the field applied parallel ($H_{\parallel}$) and perpendicular ($H_{\perp}$) to the disk plane. The saturation magnetization ($M_s$) measured from the two M–H loops is 149 emu/g and 143 emu/g, respectively. The saturation magnetization of the sample is slightly lower than the corresponding value for the bulk cobalt ($M_s$ = 168 emu/g) [19]. The coercive force ($H_c$) measured from the two M–H loops is 263 $O_e$ and 265 $O_e$, respectively. The coercive force of the sample is much close to that of the cobalt nanoflakes reported by the literature [1]. It is well known that the coercive force is proportional to the magnetic anisotropy including magnetocrystalline anisotropy, shape anisotropy and surface anisotropy [15]. The much higher coercive value of the sample than that of bulk cobalt (10 $O_e$) [19] may result from the shape anisotropy of cobalt microflakes.

Fig. 4 shows the complex permittivity ($\varepsilon'$, $\varepsilon''$) and the complex permeability ($\mu'$, $\mu''$) of the compacted toroidal-shaped cobalt/wax specimen (60 wt. % cobalt). As shown in Fig. 4(a) for Co-2h sample, the $\varepsilon'$ presents a maximum value of 63 at 5.68 GHz and then decreases to 31.2 at 7.92 GHz and the other values change around 40