Microwave Absorption and Magnetic Properties of Polyaniline-Cobalt-Chromium-Zinc Ferrite Composites Postprint

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Abstract

Cobalt-chromium-zinc ferrite (Co0.7Cr0.1Zn0.2Fe2O4) and polyaniline-cobalt-chromium-zinc ferrite composite (PANI-Co0.7Cr0.1Zn0.2Fe2O4) were prepared via the polyacrylamide gel method and in-situ polymerization method, respectively, and their structures were characterized by XRD and FT-IR. The results demonstrate that the prepared Co0.7Cr0.1Zn0.2Fe2O4 ferrite crystallizes in a spinel structure, wherein a small amount of Cr3+ ions substitute Co2+ ions at the octahedral sites of the ferrite, resulting in a reduction of the lattice constant from 0.8409 nm to 0.8377 nm. The magnetic properties of the materials were measured using a vibrating sample magnetometer (VSM), revealing that the saturation magnetization (Ms), remanent magnetization (Mr), and coercivity (Hc) of the PANI-Co0.7Cr0.1Zn0.2Fe2O4 composite are 8.80 emu/g, 14 emu/g, and 37.22 kA/m, respectively, which are lower than the corresponding values of the ferrite; the microwave absorption properties of the PANICo0.7Cr0.1Zn0.2Fe2O4 composite were investigated using the waveguide method, with two maximum reflection losses observed at 14.1 GHz and 17.9 GHz in the 5-20 GHz frequency range, being -13.17 dB and -15.36 dB, respectively, which are greater than the reflection loss of the ferrite.

Full Text

Preamble

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Microwave Absorbing and Magnetic Properties of Polyaniline-Co0.7Cr0.1Zn0.2Fe2O4 Composites

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Abstract

Spinel cobalt chromium zinc ferrites (Co0.7Cr0.1Zn0.2Fe2O4) and polyaniline-Co0.7Cr0.1Zn0.2Fe2O4 composites (PANI-Co0.7Cr0.1Zn0.2Fe2O4) were prepared by polyacrylamide gel and in situ polymerization methods, respectively. The structure of the materials was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The results show that the prepared Co0.7Cr0.1Zn0.2Fe2O4 ferrite has a spinel structure. A small amount of Cr3+ ions substituted for Co2+ ions in the octahedral sites of the ferrite, causing the lattice constant to decrease from 0.8409 nm to 0.8377 nm. Magnetic properties measured by vibrating sample magnetometer (VSM) show that the saturation magnetization (Ms), remanent magnetization (Mr), and coercive force (Hc) of the PANI-Co0.7Cr0.1Zn0.2Fe2O4 composite are 8.80 emu/g, 3.14 emu/g, and 37.22 kA/m, respectively, all lower than the corresponding values of the ferrite. Microwave absorbing properties investigated by the waveguide method show that the PANI-Co0.7Cr0.1Zn0.2Fe2O4 composite exhibits two maximum reflection losses of -13.17 dB and -15.36 dB at 14.1 GHz and 17.9 GHz, respectively, in the 5-20 GHz frequency range, which are significantly greater than those of the ferrite.

Keywords: composites, ferrite, polyaniline, microwave absorbing properties, magnetic properties
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Introduction

Electromagnetic radiation and interference from various electronic devices have seriously affected people' s lives, making research on microwave absorbing materials extremely urgent. Spinel ferrites (MFe2O4, M=Fe, Co, Ni, Zn, etc.) are attractive electromagnetic shielding materials due to their good chemical stability, high absorption performance, broad absorption bandwidth, low cost, and thin coating requirements. Sun et al. prepared MnZn ferrites by solid-state reaction and studied the temperature dependence of magnetic loss. Wu Yanfei et al. prepared Me2-W type barium ferrites (BaMe2Fe16O27) by sol-gel method and investigated the electromagnetic properties with Co2+, Ni2+, and Zn2+

combinations. However, ferrite absorbers have limitations including small dielectric loss and high surface density.

Polyaniline, a dielectric absorbing material, has attracted attention due to its light weight, strong corrosion resistance, and high environmental stability, but its near-zero magnetic loss prevents its use as a single-component absorber. Polymer/ferrite composites generate synergistic effects at their interface, combining the characteristics of both components and attracting increasing interest from materials researchers. Li Yuanxun et al. coated polyaniline onto M-type barium ferrite particles by in-situ doping, achieving a reflection rate below -20 dB with a bandwidth of 15.07 GHz. Gairola et al. synthesized PANI-Mn0.2Ni0.4Zn0.4Fe2O4 composites by mechanical blending and studied coating thickness effects on electromagnetic shielding performance. Yang et al. prepared PANI-BaFe12O19 composites by in-situ polymerization, which exhibited two absorption bands in the 2.0-26.5 GHz range with maximum reflection losses of -12.5 dB at 7.8 GHz and -11.5 dB at 24.2 GHz. This work employs in-situ polymerization to prepare PANI-Co0.7Cr0.1Zn0.2Fe2O4 composites and investigates their structure, dielectric loss, reflection loss, and magnetic properties.

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1. Experimental

1.1 Sample Preparation

Co0.7Cr0.1Zn0.2Fe2O4 ferrite was prepared by the polyacrylamide gel method, and PANI-Co0.7Cr0.1Zn0.2Fe2O4 composites were synthesized via in-situ polymerization. In a typical synthesis, 1.86 g of distilled aniline monomer, 3.44 g of dodecylbenzenesulfonic acid (DBSA), 0.186 g of Co0.7Cr0.1Zn0.2Fe2O4 ferrite, and 100 mL of distilled water were added to a three-neck flask. After ultrasonic stirring for 1 h, the mixture was cooled with ice. When the temperature reached approximately 0°C, 100 mL of distilled water containing 4.56 g of ammonium persulfate (APS) was added dropwise at a constant rate using a pressure-equalizing dropping funnel over 30 min. Polymerization continued for 8 h with continuous ice addition to maintain the temperature around 0°C. The reaction mixture was then transferred to a 500 mL beaker, and 200 mL of acetone was added to break the emulsion. After standing for 24 h, the product was filtered and washed repeatedly with anhydrous ethanol and distilled water until the filtrate became colorless. The final filter cake was vacuum-dried at 60°C for 3 h to obtain the dark green PANI-Co0.7Cr0.1Zn0.2Fe2O4 composite powder.

1.2 Sample Characterization

Phase composition was analyzed using a D/max-RB X-ray diffractometer with CuKα radiation (tube voltage: 40 kV, tube current: 100 mA) in -2 step-scan mode with a step size of 0.02° and scanning rate of 7°/min. Infrared absorption peaks were examined with an AVATAR-360 Fourier transform infrared spectrometer. Magnetic parameters including saturation magnetization (Ms), remanent magnetization (Mr), and coercive force (Hc) were measured using a VSM-220 vibrating sample magnetometer under a maximum applied field of 20 kOe. Dielectric constant and reflection loss were tested by the waveguide method using an E5071C vector network analyzer.

2. Results and Discussion

2.1 XRD Analysis

[Figure 1: see original paper] shows the XRD patterns of PANI-Co0.7Cr0.1Zn0.2Fe2O4, Co0.7Cr0.1Zn0.2Fe2O4, and Co0.8Zn0.2Fe2O4. The Co0.8Zn0.2Fe2O4 pattern [Figure 1c: see original paper] exhibits characteristic diffraction peaks at 2 = 18.18°, 30.08°, 35.40°, 43.04°, 53.40°, 56.90°, and 62.42°, corresponding to the (111), (220), (311), (400), (422), (511), and (440) crystal planes of cubic spinel structure. These match well with the characteristic peaks of spinel Co0.8Zn0.2Fe2O4 (JCPDS card No. 22-1086), confirming the formation of spinel ferrite.

Compared with [Figure 1c: see original paper], all diffraction peaks in [Figure 1b: see original paper] shift slightly to higher angles without changing the crystal structure, indicating that Cr3+ successfully substituted for Co2+ in the Co0.8Zn0.2Fe2O4 lattice to form Co0.7Cr0.1Zn0.2Fe2O4. The (311) plane position shifts from 35.40° for Co0.8Zn0.2Fe2O4 to 35.54° for Co0.7Cr0.1Zn0.2Fe2O4. The lattice constant can be calculated using the formula:

$$2\sin\theta = \frac{\lambda}{2a}\sqrt{h^2 + k^2 + l^2}$$

where a is the lattice constant, λ is the X-ray wavelength (0.154178 nm), and (hkl) are the Miller indices of the strongest (311) peak. The calculated lattice constant of Co0.8Zn0.2Fe2O4 is 0.8409 nm, larger than that of Co0.7Cr0.1Zn0.2Fe2O4 (0.8377 nm). When Cr3+ ions enter the Co0.8Zn0.2Fe2O4 lattice, they replace Co2+ ions at octahedral sites. Since the effective radius of Cr3+ (0.0615 nm) is smaller than that of Co2+ (0.0745 nm), the lattice constant decreases, causing the observed rightward shift of diffraction peaks. Additionally, an impurity peak appears at 2 = 33.30° in [Figure 1b: see original paper], corresponding to Cr2O3. The PANI-Co0.7Cr0.1Zn0.2Fe2O4 pattern [Figure 1a: see original paper] shows both ferrite characteristic peaks and two broad diffraction peaks at 2 = 19.8° and 25.6°, which are characteristic of intrinsic PANI. The rigid benzene rings in polyaniline chains create periodic parallel and perpendicular arrangements with some crystallinity, producing broad diffraction patterns. This confirms the successful synthesis of PANI-Co0.7Cr0.1Zn0.2Fe2O4 composites.

2.2 FT-IR Analysis

[Figure 2: see original paper] presents the FT-IR spectra of PANI-Co0.7Cr0.1Zn0.2Fe2O4 and Co0.7Cr0.1Zn0.2Fe2O4. The spectrum of Co0.7Cr0.1Zn0.2Fe2O4 [Figure 2b: see original paper] shows a prominent absorption peak at 572 cm-1, corresponding to the metal-oxygen (M-O) stretching vibration (V1 mode) characteristic of tetrahedral sites in spinel ferrite structures. In [Figure 2a: see original paper], absorption peaks at 3446 cm-1 and 1387 cm-1 correspond to N-H stretching vibrations in polyaniline. Peaks at 1566 cm-1 and 1491 cm-1 are attributed to C=C stretching in benzene and quinone rings, while the 1237 cm-1 peak represents C-N stretching in the polyaniline backbone. The strong absorption at 1116 cm-1 arises from N=Q=N vibration (Q = quinone ring), confirming the presence of polyaniline. The characteristic M-O stretching peak at 572 cm-1 also appears in [Figure 2a: see original paper] with reduced intensity, further confirming the formation of PANI-Co0.7Cr0.1Zn0.2Fe2O4 composites, consistent with the XRD results.

2.3 Magnetic Properties

[Figure 3: see original paper] shows the hysteresis loops of PANI-Co0.7Cr0.1Zn0.2Fe2O4 and Co0.7Cr0.1Zn0.2Fe2O4. The magnetic parameters —saturation magnetization (Ms), remanent magnetization (Mr), and coercive force (Hc)—are summarized in . The PANI-Co0.7Cr0.1Zn0.2Fe2O4 composite exhibits Ms = 8.80 emu·g-1 and Mr = 3.14 emu·g-1, significantly lower than the ferrite values (Ms = 73.84 emu·g-1, Mr = 28.43 emu·g-1). The Hc value of 37.22 kA·m-1 for the composite is slightly lower than that of Co0.7Cr0.1Zn0.2Fe2O4 (38.91 kA·m-1). Co0.7Cr0.1Zn0.2Fe2O4 ferrite is a magnetic loss medium whose magnetism primarily originates from the magnetic moments of unfilled 3d electron shells of iron atoms; more unpaired d electrons yield larger magnetic moments ( ). Polyaniline is a dielectric loss medium with virtually no magnetic properties. Since the magnetism of PANI-Co0.7Cr0.1Zn0.2Fe2O4 composites mainly comes from the ferrite component, all magnetic parameters decrease after PANI incorporation.

2.4 Dielectric Loss

[Figure 4: see original paper] illustrates the frequency dependence of dielectric loss (tan = ’‘/ ’) for PANI-Co0.7Cr0.1Zn0.2Fe2O4 and Co0.7Cr0.1Zn0.2Fe2O4 over 5-20 GHz. The composite’ s tan ranges from 0.67 to 0.80, substantially higher than the ferrite’ s tan (0.10-0.36). Dielectric loss primarily depends on dipole polarization within the material. According to complex permittivity theory, when electromagnetic waves irradiate the dielectric material, interactions between ferrite particle surfaces and PANI macromolecular chains generate conduction and displacement currents, causing dielectric relaxation and space charge polarization effects. This leads to higher dielectric loss in PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ compared to pure ferrite. Additionally, ferrite is a magnetic loss absorber with negligible dielectric properties, while PANI is a dielectric loss absorber. Coating ferrite particles with PANI thus significantly enhances the composite’ s dielectric loss.

2.5 Reflection Loss

[Figure 5: see original paper] presents the reflection loss curves of PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ and $Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ as a function of frequency. Within the 5-20 GHz test range, the PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ composite shows two maximum reflection losses of -13.17 dB at 14.1 GHz and -15.36 dB at 17.9 GHz. In contrast, $Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ exhibits maximum reflection losses of only -8.2 dB and -8.1 dB. The significantly higher reflection loss of the composite facilitates bandwidth broadening and demonstrates excellent microwave absorption performance. Ferrite reflection loss originates primarily from domain wall resonance and spin resonance (with spin resonance dominating), while polyaniline’ s loss stems from strong polarization and relaxation effects caused by bound charges and electrical conductivity in the polymer. The combination of ferrite and polyaniline creates synergistic interactions, with the composite’ s electromagnetic wave absorption determined by dielectric loss from bipolarization and polarization relaxation in PANI, magnetic loss from spin resonance in ferrite, and interfacial relaxation between the polymer and magnetic particles. These combined effects result in substantially higher reflection loss for PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ composites compared to pure ferrite.

Conclusions

1. Doping Cr^{3+} ions into $Co_{0.8}Zn_{0.2}Fe_2O_4$ ferrite reduces the lattice constant from 0.8409 nm to 0.8377 nm.
2. The PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ composite exhibits $M_s = 8.80$ emu · g^{-1}, $M_r = 3.14$ emu · g^{-1}, and $H_c = 37.22$ kA · m^{-1}, all lower than the corresponding values for $Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ ferrite.
3. The PANI-$Co_{0.7}Cr_{0.1}Zn_{0.2}Fe_2O_4$ composite shows two maximum reflection losses of -13.17 dB and -15.36 dB at 14.1 GHz and 17.9 GHz, respectively, significantly higher than those of the ferrite and demonstrating superior microwave absorption performance.

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