Influence of Co_2O_3 additive on electromagnetic properties of $\text{NiCuZn}/\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ composites

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In order to improve the electromagnetic properties of 80wt% NiCuZn + 20wt% $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ composites, Co_2O_3 as an additive was studied in this work. The effects of Co_2O_3 content on the electromagnetic properties were investigated, which confirmed that permeability of composites was decreased and cut-off frequency was improved with Co_2O_3 . The nonlinear fitting of permeability dispersion have revealed the relationships between domain wall resonance, spin rotation relaxation mechanisms, and local induced anisotropy, the existence of local induced anisotropy caused by ordering of Co ions could influence the initial permeability. Meanwhile, the dielectric constant was increased with the addition of Co_2O_3 , and all the samples kept a lower $\tan\delta$, which was less than 0.01 at the frequency between 10^7Hz to 10^8Hz .

Key words: electromagnetic materials, magnetic anisotropy, permeability, permittivity

1. INTRODUCTION

One material with multiple properties such as dielectric properties, piezoelectric properties, conductivity, ferromagnetic characteristics and so on have attracted great attentions in recent years^[1-3], those materials could not only make a possible to alleviate pressures from circuit dimension shrinking and high level passive integrations, but also provide the potential applications in the design of new devices. When one materials with ferromagnetic and ferroelectric simultaneously, it could generate magneto-electric^[4-5] and magneto-optic properties^[6], because the interaction between magnetization and electric polarization. Therefore, lots of magneto-dielectric composites have been designed by ferrite and ferroelectric^[7-8], now, and those composites can be divided into ceramic-based composites and polymer-based composites. it was known to all that, the permittivity and permeability of magneto-dielectric materials could obtain both inductive and capacitive properties. The higher values of inductive and capacitive of materials lead to miniaturization of relevant device, and these magneto-dielectric materials could fabricate the electrical filters, electric sensors, magneto-electric random access memory, antennas substrates^[9-10].

As our team's previous work^[11-13], $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) possess huge dielectric constant and a strong stability over a temperature range of 100 to 400K, and the NiCuZn ferrite could generate permeability, so that we fabricated $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite to obtain the magneto-dielectric properties, and this composite materials has been successfully used in LC filters with Low temperature co-firing method (LTCC). However, simple $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite have a low cut-off frequency which limited the frequency of use. In this work, we use the Co_2O_3 as the addition to improve the cut-off frequency of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$

ferrite composite, because the valence of Co ion in Co_2O_3 is the same as that of Fe ion in the ferrite, and it would enhance the permittivity of composite

2. MATERIAL AND METHODS

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{Ni}_{0.21}\text{Cu}_{0.13}\text{Zn}_{0.66}\text{Fe}_2\text{O}_4$ ferrite powders were prepared with a solid-state reaction method. The two kinds of powers were then mixed as the mass ratio of 4:1, then x% Co_2O_3 was added into the mixture and ball milled for further 10 h to obtain fine powder, and was pressed into pellet. Then, the disks were sintered at 1020 °C for 10 h, and furnace-cooled to room temperature. The phase formation was examined by an X-ray diffractometer (XRD, DX-2700, Haoyuan co.) with Cu $K\alpha$ radiation. The microstructures were observed by a scanning electron microscope (JSM-6490, JEOL, Japan). The dielectric and magnetic properties were measured by an HP4291B impedance/materials analyzer in the frequency range 1 MHz–1 GHz.

3. RESULTS AND DISCUSSION

The XRD patterns of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition were shown in Figure 1. All the samples exhibited a spinel structure (NiCuZn ferrite) and a cubic perovskite-related structure ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$), the peak intensity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was weakly for its smaller proportion in the composite. The (3 1 1) plane diffraction peak of NiCuZn ferrite shifted to lower angle with the increase of Co_2O_3 addition, One explanation is that the ionic radius of Co^{2+} (74.5pm) is bigger than that of Fe^{3+} (64.5 pm)^[14]. Figure 2 illustrated SEM micrographs of the fracture morphologies of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition sintered at 1100 °C for 10 h. As shown that, all the samples were sintered well for a uniform grain size and a relatively high density, furthermore, the grain size of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite didn't

show significant changes with Co_2O_3 contents increased.

Fig. 1 The XRD patterns of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition.

The variations of permeability of the composites with frequency are shown in Fig. 3. It can be observed that there was an slightly decreases of the real permeability μ' with the Co_2O_3 contents increased. As shown in the

Fig. 2 SEM images of the fracture morphologies of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition ((a) $x=0$, (b) $x=0.3$, (c) $x=0.4$, (d) $x=0.5$)

SEM results that there was no systematic variation of extrinsic factors such as grain size. So that, the initial permeability affected mainly by extrinsic factors can be

Fig. 3 Frequency dependence of complex permeability for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition

neglected. And the dependence of initial permeability on Co_2O_3 content must be explained by intrinsic factors such as magnetic anisotropy. For polycrystalline ferrite, the permeability spectra are described by two types of magnetizing process: spin rotation and domain wall motion :

$$\mu = \mu' - j\mu'' = 1 + \chi_{\text{spin}} + \chi_{\text{DW}} \quad (1)$$

$$\chi_{\text{spin}} = \frac{K_{\text{spin}}}{1 + i\frac{\omega}{\omega_{\text{spin}}^{\text{res}}}} \quad (2)$$

$$\chi_{\text{DW}} = \frac{K_{\text{DW}}\omega_{\text{DW}}^{\text{res}2}}{\omega_{\text{DW}}^{\text{res}2} - \omega^2 + i\beta\omega} \quad (3)$$

where ω is the magnetic field frequency, K_{spin} is the static spin susceptibility, $\omega_{\text{spin}}^{\text{res}}$ is the spin resonance frequency, K_{DW} is the static susceptibility of domain wall motion, $\omega_{\text{DW}}^{\text{res}}$ is the domain wall resonance frequency, and β is the damping factor of the domain wall motion [15-16]. The real and imaginary parts of (1) can be derived as follows:

$$\mu' = 1 + \frac{K_{\text{spin}}\omega_{\text{spin}}^{\text{res}2}}{\omega_{\text{spin}}^{\text{res}2} + \omega^2} + \frac{K_{\text{DW}}\omega_{\text{DW}}^{\text{res}2}(\omega_{\text{DW}}^{\text{res}2} - \omega^2)}{(\omega_{\text{DW}}^{\text{res}2} - \omega^2)^2 + \beta^2\omega^2} \quad (4)$$

$$\mu'' = \frac{K_{\text{spin}}\omega_{\text{spin}}^{\text{res}2}}{\omega_{\text{spin}}^{\text{res}2} + \omega^2} + \frac{K_{\text{DW}}\omega_{\text{DW}}^{\text{res}2}\beta\omega}{(\omega_{\text{DW}}^{\text{res}2} - \omega^2)^2 + \beta^2\omega^2} \quad (5)$$

The measured complex permeability data can be fitted to the formula by using five fitting parameters K_{spin} , $\omega_{\text{spin}}^{\text{res}}$, K_{DW} ,

Table 1 Permeability parameters of nonlinear least mean square fitting

x	K_{spin}	$\omega_{\text{spin}}^{\text{res}}$	K_{DW}	$\omega_{\text{DW}}^{\text{res}}$	β
0	15.844	2.59×10^8	54.03	1.313×10^8	5.03×10^8
0.3	11.87	3.23×10^8	52.4	1.86×10^8	8.38×10^8
0.4	11.36	3.44×10^8	48.307	1.94×10^8	8.395×10^8
0.5	10.665	3.8×10^8	47.002	2.042×10^8	8.735×10^8

$\omega_{\text{DW}}^{\text{res}}$, K_{DW} , β . Table 1 shows the parameter for the samples with different Co_2O_3 content. It can be seen that both spin rotation and domain wall motion are sensitive to Co_2O_3 content. Because of the insufficient oxidizing atmosphere, some Fe^{2+} would emerge in NiCuZn ferrite when sintering. And at the cooling process, those Fe^{2+} would reoxidation by Co^{3+} on account of the difference of third ionization energy which Co (33.77 eV) is higher than that of Fe (31.69 eV). In order to reduce the static magnetic energy, Co^{2+} ions will diffuse by electronic transfer ($\text{Co}^{2+} \rightarrow \text{Co}^{3+} + e$) and occupy some special octahedral site (B-site) of ferrite. When the NiCuZn ferrite composite was doped with Co ions, some Co ions would substitute on B-site and influence the local Weiss field [17], thus induce a local uniaxial anisotropy. As known that, cut-off frequency will increase as the increased anisotropy in the polycrystalline ferrite. The cut-off frequency increased as increased Co_2O_3 contents were showed in Fig. 3. Meanwhile, $\omega_{\text{DW}}^{\text{res}}$ is stand for the domain wall resonance frequency, which was related to cut-off frequency and increased with increased Co_2O_3 contents; this was corresponded to the tendency of cut-off frequency which showed in Fig. 3.

Fig. 4 showed the frequency dependence of the permittivity of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite with different Co_2O_3 addition. It can be observed that all the composite were nearly independent in the frequency ranges from 10^6 Hz to 10^9 Hz obviously, the values of dielectric constant (ϵ') increased with the increased Co_2O_3 addition in the proper range. Nowadays, internal barrier layer capacitance (IBLC) was the most acceptable theory [18], in this theory electrical properties were contributed by grains and grain boundaries (GBs), the grains possess semiconducting property and the GBs are insulating in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. According to former studies, Co ion would substitute in Ti^{4+} site of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic when Co_2O_3 doped in

Fig. 4 Frequency dependences of dielectric constant and dielectric loss for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composites with different Co_2O_3 addition

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and influenced the GBs at the same time, and Co ions doped in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ would enhance the dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic. Furthermore all the Co_2O_3 doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite showed a low dielectric loss which was less than 0.01 at the frequency between 10^7 Hz to 10^8 Hz.

4. CONCLUSION

In this paper, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite were prepared by the conventional solid-state reaction method, and the effects of different Co_2O_3 addition were investigated. Because of the insufficient oxidizing atmosphere, some Fe^{2+} would emerge in NiCuZn ferrite when sintering. And at the cooling process, Co^{2+} ions will diffuse by electronic transfer ($\text{Co}^{2+} \rightarrow \text{Co}^{3+} + e$) and occupy some special octahedral site (B-site) of ferrite, that induced a local uniaxial anisotropy and increased the cut-off frequency. Dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}/\text{NiCuZn}$ ferrite composite have been improved by Co_2O_3 additive. all the samples kept a lower $\tan\delta$, which was less than 0.01 at the frequency between 10^7 Hz to 10^8 Hz.

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