# Study of NiCuZn ferrite powders and films prepared by sol–gel method*

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This paper reports that a series of NiCuZn ferrite powders and films are prepared by using sol–gel method. The effects of raw material composition and the calcinate temperature on magnetic properties of them are investigated. The NiCuZn ferrite powders are prepared by the self-propagating high-temperature synthesis method and subsequently heated at 700 °C∼1000 °C. The results show that NiCuZn ferrite powders with single spinel phase can be formed after heat-treating at 750 °C. Powders obtained from $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_{1.9}O_4$ gel have better magnetic properties than those from gels with other composition. After heat-treating at 900 °C for 3 h, coercivity $H_c$ and saturation magnetization $M_s$ are 9.7 Oe (1 Oe = 80 A/m) and 72.4 emu/g, respectively. Different from the powders, NiCuZn films produced on Si (100) from the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ gel formed at room temperature possess high properties. When heat-treating condition is around 600 °C for 6 min, samples with low $H_c$ and high $M_s$ will be obtained. The minimal $H_c$ is 16.7 Oe and $M_s$ is about 300 emu/cm$^3$. In comparison with the films prepared through long-time heat treating, the films prepared through short heat-treating time exhibits better soft magnetic properties.

**Keywords:** sol–gel, NiCuZn ferrite, powder, film

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## 1. Introduction

The NiCuZn ferrites are excellent soft magnetic materials in high-frequency devices due to their low cost, high resistivity and low eddy current losses, and have been studied extensively for multilayer chip inductor applications. Compared to MnZn and NiZn ferrite materials, NiCuZn ferrite is applied in the frequency range from kHz to a few GHz, thus can realize energy conversion and impedance switching of radio frequency (RF) signal in wide band, and is widely used in the field of personal computer (PC), TV, electronic device, etc. But up to now, the applications of NiCuZn ferrite thin films in high-frequency integrated circuits have been reported scarcely. The successful growth of magnetic thin film is an important step towards their future incorporation.[1] For preparing NiCuZn films, pulsed laser deposition and RF magnetic alternative sputtering are always used, whereas sol–gel method has not been studied very much. The sol–gel method is a wet-chemical technique which is widely used in the fields of materials science and ceramic engineering since it can realize molecular level mixing. Thus it is a low temperature technique that allows for the fine control of the product's chemical composition. The precursor sol can be deposited on a substrate, or cast into a suitable container with the desired shape to form a film. In this study, sol–gel processing was used to prepare NiCuZn ferrite powders and films. Raw materials first dissolved in dimethylformamide, and then polyvinglpyrrolidone was added as a kind of surfactant. The effects of raw material composition and the calcinate temperature on magnetic properties of powders and films were investigated in order to prepare high performance NiCuZn films in the future.

## 2. Experiments

The $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $(CHCOO)_2Zn{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ (analytical grade) were used as raw materials. According to the stoichionmetric composition, the specified weights of metal salts were first dissolved in dimethlformamide

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to form a mixed solution. Stirring for 2 h at room temperature, then polyvinglpyrrolidone was added as surfactant. Acetic acid was added lastly to adjust pH value to 3.2. After stirring the solution in water bath at 70 °C for 2 h and placed for another 30 h at room temperature, stable gel was obtained. Thin films were spin coated on Si (100) substrates by spin coater with a speed of 2500 round/min for 1 min. The obtained films were dried at 120 °C for 10 min to remove the mixed solvents, and then heated at 400 °C for 30 min to pyrolyze and exclude the organic substances. Finally, thin films were heat-treated in air at different temperatures ranging from 500 °C to 800 °C. The NiCuZn ferrite powders were prepared by SHS (self-propagating high-temperature synthesis) from gel, then calcinate in air.

The phase identification of the powders was performed by using a Rigaku x-ray diffractionmeter (XRD) with Cu–K$\alpha$ radiation, and the films using Philips X pert. The structural properties of the films were characterized by an atomic force microscope (AFM, AR MFP-3D, USA). The magnetic properties of films and powders were evaluated by using vibrating sample magnetometer (VSM, Toei Kogyo VSM-5, Japan). The thicknesses of the films were measured by Surface Profiler (Dektak 8M).

# 3. Results and discussion

## 3.1. Crystalline structure of powders and films

Igniting stable gels in clean glass dishes, fluffy precursor powders were obtained. The XRD patterns (Fig. 1) show that NiCuZn ferrite with the spinel structure is formed in an intermediate phase. As heat-treating temperature plays an important role in the preparation processes of the ferrite, the precursor powders were heat-treated at 600, 700, 735, 743, 750 and 800 °C, respectively. Figure 1 gives the result of such an investigation for $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ powders. It can be seen from the XRD patterns when the temperature exceeds 750 °C, $\alpha$-$Fe_2O_3$ phase disappears and single phase of spinel NiCuZn ferrite develops. Compared to $Ni_{0.25}Cu_{0.25}Zn_{0.5}Fe_{1.96}O_{3.94}$ powders prepared by SHS method,[2] in our experiments the temperature of forming uniform spinel structure is lower (900 °C→750 °C). This result is mainly because the sol–gel method can realize molecular level mixing and polyvinglpyrrolidone can improve the activity of the reactants. The addition of Cu ions also attributes to the decrease of that temperature, since Cu ions can accelerate the reaction of ferrite in liquid phase. Whereas for films, it is apparent in Fig. 2 that for heat-treating films with same composition at 400 °C for 30 min, no spinel ferrite can be obtained. When the heat-treating temperature becomes higher, spinel ferrite emerges. The single spinel ferrite phase is achieved when the temperature is up to 600 °C, which is lower than the temperature of forming the single spinel phase of the powder samples. This result can be attributed to the larger specific surface area of films. Atoms on the surface always lack nearest neighbouring atoms, possess much damping bond and can combine with other atoms easily.[3,4] So the chemical reaction can complete at low temperature when we consider that the thickness of the films is only about 200 nm∼300 nm.

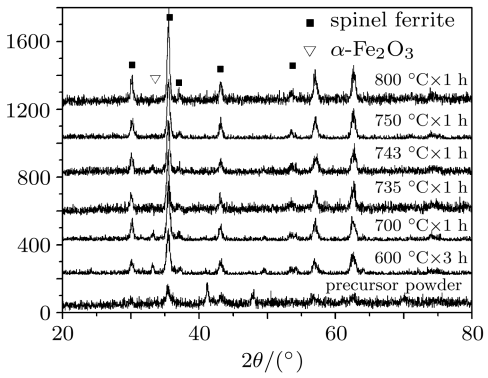



**Fig. 1.** The x-ray diffraction patterns for $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ powders with heat-treating temperature rang from 600 °C to 800 °C.

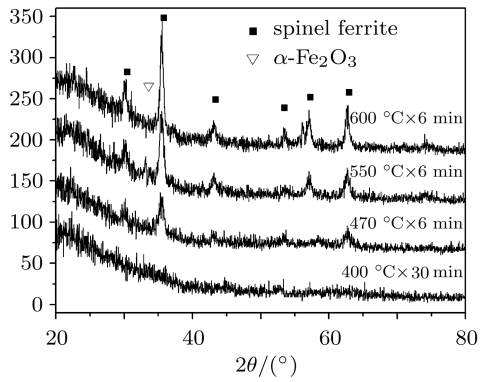



**Fig. 2.** The x-ray diffraction patterns for $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films with heat-treated for 6 min.

### 3.2. Magnetic properties of powders and films

The $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_xO_4$ ($x$ = 1.9, 2, 2.1) precursor powders were prepared by SHS, then heat-treated at 750 °C∼1000 °C for 3 h.

Figure 3 indicates that $H_c$ decreases and $M_s$ increases with the rising temperature. That may be due to the growth of the crystalline grains, which can be proved by the calculated result throught XRD patterns (Scherrer formula: $D = k\lambda/B\cos\theta$). It can be observed from Fig. 3 that at same heat-treating temperature $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_{1.9}O_4$ samples have better properties than other samples, possessing relative low $H_c$ and close $M_s$. In the producing process of multilayer inductors from ferrite powders, the powders should be sinter below 900 °C in order to avoid the problems of break, cavity, magnetic properties weakening, etc.[5] In our experiments, after sintering $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_{1.9}O_4$ precursor powder at 900 °C for 3 h in air, the $H_c$ and $M_s$ are 9.7 Oe and 72.4 emu/g, respectively. When the temperature is up to 1000 °C, the $H_c$ is 5.0 Oe and $M_s$ reaches 73.6 emu/g.

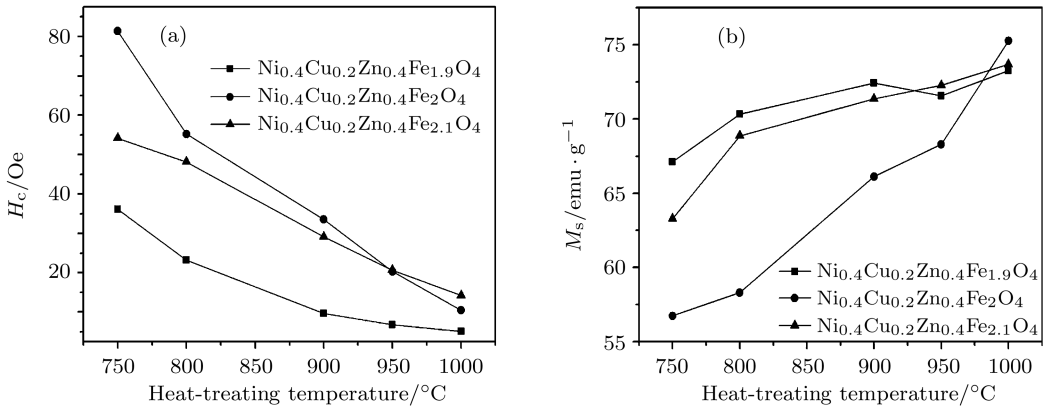



**Fig. 3.** The $H_c$ (a) and $M_s$ (b) of powders at different heat-treating temperatures (×3 h).

Wang *et al.* had prepared MnZn films on Si and $SiO_2$ substrates.[6] Their results showed that $H_c$ of films on Si substrate are smaller than those on $SiO_2$, which is mainly because the stress between ferrite films and Si substrate is smaller since the coefficient of thermal expansion of Si is bigger than that of $SiO_2$, and closer to ferrite films. In our study, $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_xO_4$ ($x$ = 1.9, 2, 2.1) films on Si (100) substrates were investigated. Ferrite films are stable and hardly peelled off from substrates.

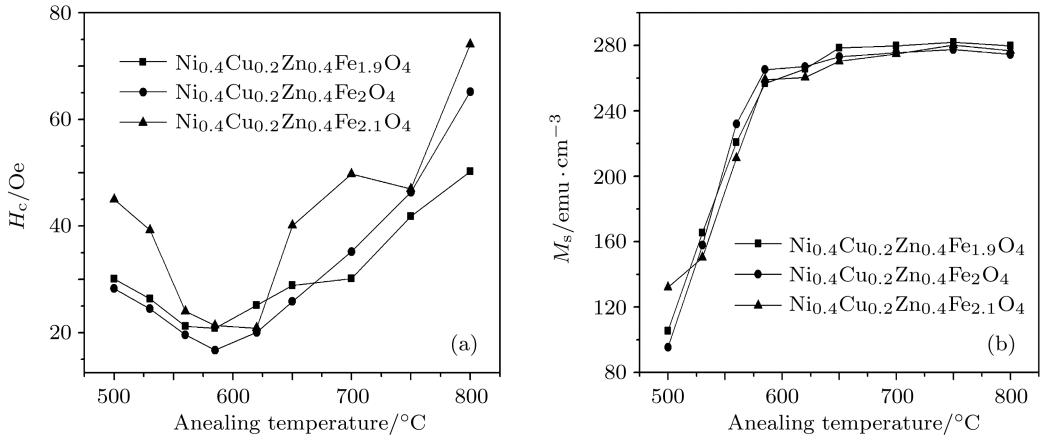



**Fig. 4.** The $H_c$ and $M_s$ of the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_xO_4$ ($x$ = 1.9, 2, 2.1) films with different anealing temperatures (×6 min).

Figure 4 is the temperature dependence of the saturation magnetization $M_s$ and coercivity $H_c$ of the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_xO_4$ ($x$ = 1.9, 2, 2.1) thin films. As it can be seen from Fig. 4, when the annealing temperature

increases to 600 °C, $H_c$ of the thin films decreases obviously, whereas $M_s$ increases drastically. These phenomena are deduced to be related to the formation of spinel structural NiCuZn ferrite as shown in XRD patterns (Fig. 2). When the annealing temperature exceeds 600 °C, $H_c$ and $M_s$ increase simultaneously. It is apparent that films and powders have different trends for $H_c$ with the annealing temperature. It is supposed to be caused by the factor as follows. Ferrite films and Si substrate have different coefficients of thermal expansion (ferrite film is $10\times10^{-6}$/°C and Si substrate is $2.6\times10^{-6}$/°C). While cooling the films down to room temperature, thermal stress will exist, that is the main factor affecting $H_c$. When the annealing temperature increases, the thermal stress increases correspondingly after cooling down, leading to the increasing $H_c$. On the other hand, the grain sizes of the samples are 10∼40 nm, so the superparamagnetic phase exists. Increasing the annealing temperature leads to grain growth, which can be seen from AFM images below (Fig. 5), thus the superparamagnetic phase reduces and $H_c$ increases.[1]

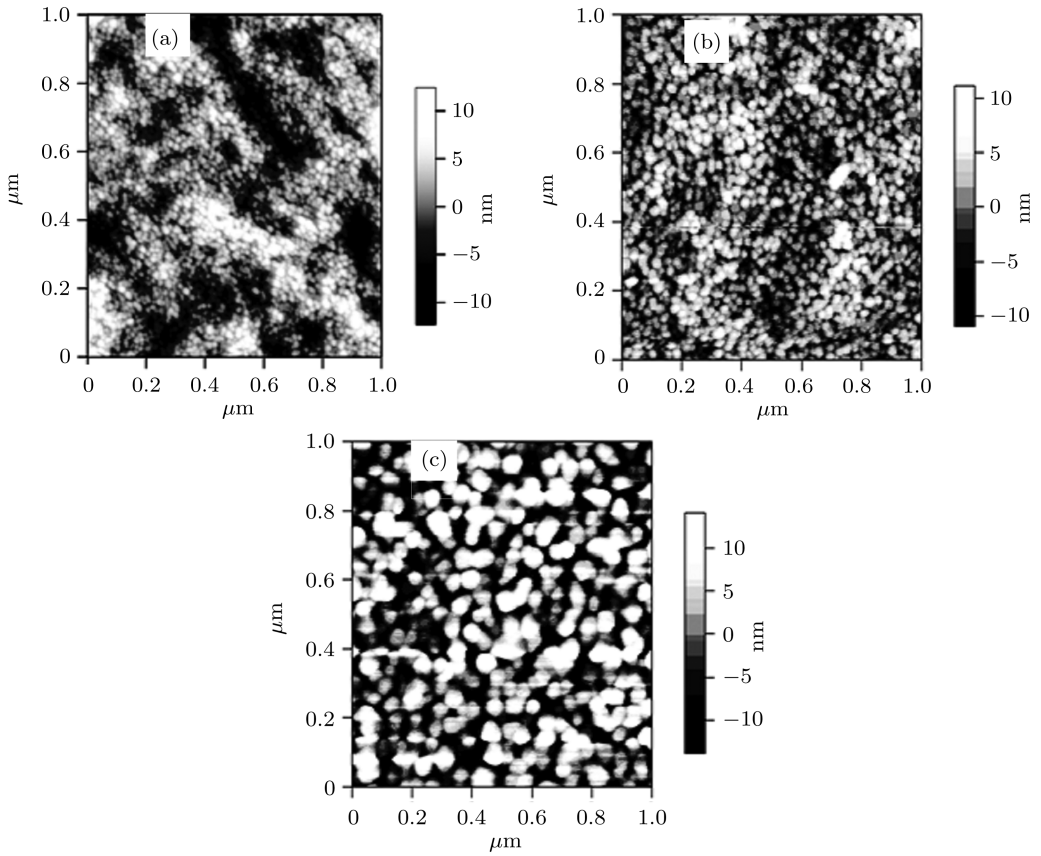



**Fig. 5.** The AFM images of $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films: (a) 585 °C×6 min; (b) 800 °C×6 min; (c) 800 °C×3 h.

Different from powder samples, among which the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_{1.9}O_4$ powders have excellent magnetic properties, figure 4 shows that $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films have higher properties than other samples at the temperature range of 500 °C∼650 °C. The reason for this result may be that powders are always heat-treated at relative high temperatures, this fact leads to the volatilization of Zn ions. Therefore, reducing Fe content can recuperate the deviation of composition to form single spinel NiCuZn ferrite.[7]

In order to obtain films with high properties, a series of $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films were heat-treated at 500 °C∼650 °C with a temperature step of 20 °C. The results are shown in Fig. 6, indicating that the minimum value 16.7 Oe of $H_c$ is achieved at 585 °C. Whereas $M_s$ increases drastically with the increasing heat-treating temperature. Heat-treating time is a very important factor in producing ferrite powders. Grains can grow larger at high temperature for a long time, then $H_c$ will decrease and $M_s$ will increase. However, this effect was not observed in film samples. Figure 7 shows that when $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films were heat-treated at temperatures from 500 °C to

800 °C for 3 h, $H_c$ increases firstly, which is relative to the stress between ferrite film and Si substrate. When the temperature exceeds 700 °C, grain growth leads to decrease of $H_c$ (Fig. 5). However, this $H_c$ is still greater than that of the films with same composition but heat-treated for 6 minutes. The reason may be that for the nano-crystalline magnetic materials, the ferromagnetic exchange coupling between grains helps decreasing $H_c$ when grain size is smaller than the exchange length.[8] The long-time heat treating leads to the increase of grain size as shown in Fig. 7, therefore $H_c$ also increases since the exchange coupling is weakened. On the other hand, at the beginning $M_s$ increases with the increase of heat-treating temperature then becomes stable. The maximum value of $M_s$ is about 300 emu/cm$^3$, which is the same as that of the film samples heat-treated for 6 minutes. So the best process for getting high performance film is heat-treating at a suitable temperature for a short time in order to restrain grain growth.

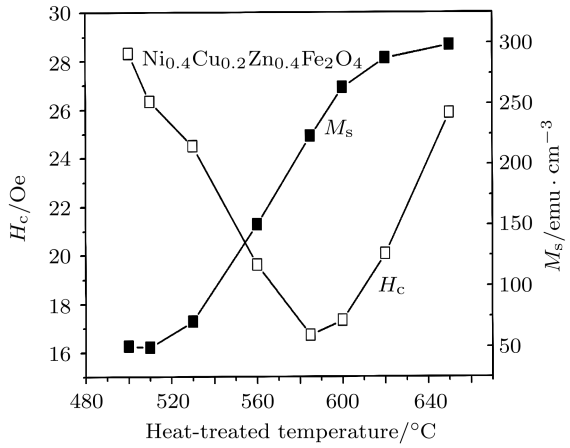



**Fig. 6.** The $H_c$ and $M_s$ of the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films versus heat-treating temperature (×6 min).

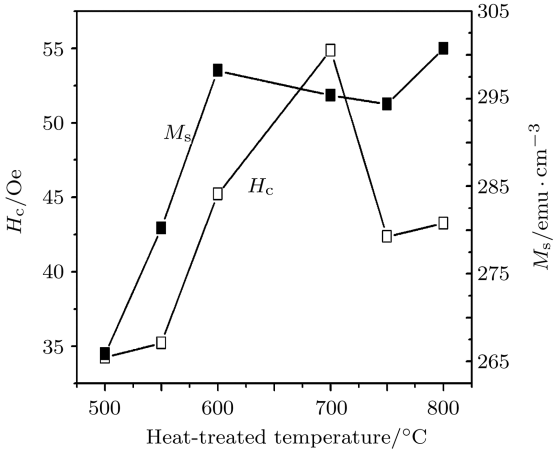



**Fig. 7.** The $H_c$ and $M_s$ of $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ films versus heat-treating temperature for 3 h.

## 4. Conclusions

Putting specified weights of $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $(CHCOO)_2Zn{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ into dimethyformamide, meanwhile adding polyvinglpyrrolidone as surfactant, and acetic acid to adjust the pH value to 3.2, we obtain stable gels. The NiCuZn ferrite powders were prepared by the SHS method and subsequent heated at 700 °C∼1000 °C. The results show that NiCuZn ferrite powders with single spinel phase can be formed after heat-treating at 750 °C for 3 h. Powders obtained from $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_{1.9}O_4$ gel have better magnetic properties than those from gels with other compositions. After heat-treating at 900 °C for 3 h, $H_c$ and $M_s$ are 9.6 Oe and 72.4 emu/g, respectively. Different from the powders, NiCuZn films produced on Si (100) from the $Ni_{0.4}Cu_{0.2}Zn_{0.4}Fe_2O_4$ gel possess high properties. When heat-treating condition is around 600 °C for 6 min, samples with low $H_c$ and high $M_s$ were obtained. The minimal $H_c$ is 16.7 Oe and $M_s$ is about 300 emu/cm$^3$. Comparing with the films prepared through long-time heat treating, we find that the films prepared through short heat-treating time exhibit better soft magnetic properties.

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