

# Structure and static magnetic properties of NiCuZn ferrite thin films

LE-ZHONG LI\*, ZHI-YONG PU, RUI WANG, LONG PENG, XIAO-QIANG TU, TAI-XING HUANG  
*College of Optoelectronic Technology, Chengdu University of Information Technology, Chengdu 610225, China*

Cu-substituted NiZn ferrite thin films,  $\text{Ni}_{0.4-x}\text{Zn}_{0.6}\text{Cu}_x\text{Fe}_2\text{O}_4$  ( $0 \leq x \leq 0.2$ ), were synthesized by sol-gel process. The crystallographic and magnetic properties of NiZn ferrite thin films have been investigated. The diffraction peak shifts towards the higher angle and the lattice parameter decreased with Cu substitution. The saturation magnetization decreases with the increasing Cu substitution, however, coercivity changed contrarily.

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*Keywords:* NiZn ferrite thin films, Sol-gel process, Cu substitution, Structure, Static magnetic property

## 1. Introduction

In recent years, multilayer chip inductors (MLCIs) have become increasingly important due to the development of surface mounted devices (SMD). SMDs are widely applied in electronic products, such as mobile phones, video cameras and notebook computers, etc. [1-3]. The Spinel ferrites are considered as the most versatile soft magnetic materials due to their excellent electromagnetic properties for high frequency applications [4-7]. NiZn ferrites exhibit favorable properties such as high resistivity, low eddy current losses, and high saturation magnetization [8-10], which can be used for thin film devices of high frequency.

The NiZn ferrite thin films have been prepared by different techniques: sol-gel [11-14], spin spray plating [15-17], magnetron sputtering [18], pulsed-laser deposition [19], etc. The sol-gel method adopted in this paper has the following advantages [20]. First, the composition of ferrites tends to be homogeneous with continuously stirred by high rotate speed magnetic stirring apparatus and films possess high quality because of the films are prepared by high rotate speed spin coater. Second, the heat treatment temperature is low, and the microstructure and microcrystallite size of thin films can be controlled by the annealing temperature. Last, the equipment is cheap and the high vacuum is not necessary.

The substituents can play an important role in determining the magnetisation and other properties of NiZn ferrite. Thus, the properties of NiZn ferrites in the bulk materials can be modified by ions substitution and adding proper additives, such as  $\text{Mn}^{2+}$  [21-23],  $\text{Cu}^{2+}$  [24,25],  $\text{Bi}^{3+}$  [26],  $\text{W}^{6+}$  [27, 28],  $\text{Nb}^{5+}$  [29] ions, etc.

Only a few works about the compositions and preparation processes have been done in the NiCuZn

ferrite thin films with Sol-Gel process [30-32]. To the best of our knowledge, no results have been reported about the effects of substitution of  $\text{Ni}^{2+}$  by  $\text{Cu}^{2+}$  on the structural and magnetic properties of NiCuZn ferrite thin films. Therefore, this paper focuses on the effects of substitution of  $\text{Ni}^{2+}$  by  $\text{Cu}^{2+}$  on the crystallographic and magnetic properties of NiZn ferrite thin films.

## 2. Experimental procedures

### 2.1. Preparation of Cu-substituted NiZn ferrite thin films

The samples of  $\text{Ni}_{0.4-x}\text{Zn}_{0.6}\text{Cu}_x\text{Fe}_2\text{O}_4$  ( $x=0, 0.05, 0.10, 0.15, 0.20$ ) ferrite thin films were synthesized by sol-gel process. Stoichiometric quantities of analytical grade  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  were first dissolved in 2-methoxyethanol to form a mixed solution. After the solution was stirred for 1 h, the acetic acid was added to adjust the concentration of the solution to 0.3mol/L. Meanwhile, polyethylene glycol was added. As a kind of surfactant, it can effectively prevent the colloidal particles of chelate from being jointed with each other. Then, the prepared solution was continuously stirred for 2 h and placed at room temperature for 36 h to form the stable sol-gel precursors used for the following processes. First, the wet films were deposited by a spin coating method on the substrate of silica glass at 4000 rpm for 30 s. Second, the wet films were dried at 200°C for 10 min to remove the mixed solvents. Third, the operation of spin coating and drying was repeated to get the required thickness of the films. Last, the dried films were heated at 400°C for 30 min to pyrolyze and exclude the organic substances and

then were annealed at 750°C for 1h in air and cooled slowly in the furnace.

## 2.2. Characterization and property measurements

The phase identification of the thin films was performed by the Philips X'Pert PRO X-ray diffractometer (XRD), with Cu  $K_\alpha$  radiation. The magnetic measurements were performed by the TOEI VSM-5S-15 vibrating sample magnetometer (VSM) at room temperature.

## 3. Results and discussion

### 3.1. Phase characterization

X-ray diffraction patterns of Cu-substituted NiZn ferrite thin films are shown in Fig. 1. The patterns match well with the characteristic reflections of cubic spinel structure and without unidentified extra peaks.

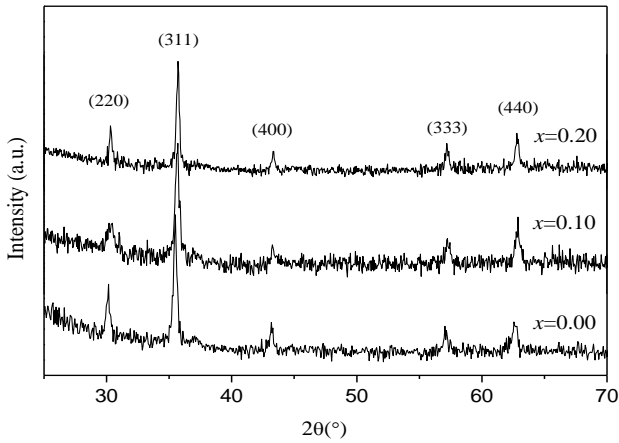


Fig. 1. X-ray diffraction patterns of Cu-substituted NiZn ferrite thin films.

The lattice parameter ( $a$ ) of Cu-substituted NiZn ferrite thin films as a function of Cu substitution ( $x$ ) is shown in Table 1. The lattice parameters of the samples are calculated by using the Bragg equation. The relation between crystal plain distance in cubic crystal lattice and lattice parameter and also Bragg equation are listed as below:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad (1)$$

$$n\lambda = 2d_{hkl} \sin\theta \quad (2)$$

In these equations  $a$  is lattice parameter,  $d$  is the distance between lattice planes,  $(h, k, l)$  is miller indices,  $n$  is an integer,  $\lambda$  is the wavelength of X-ray, and  $\theta$  is diffraction angle. From Table 1 we can see that the lattice parameters decreased from 0.8366nm to 0.8338nm with Cu substitution, which decrease trend is well in accord

with the variations of Cu-substituted bulk NiZn ferrites [25]. It is well acknowledged that the divalent  $\text{Cu}^{2+}$  ions have a strong octahedral-site (B site) preference [32]. The  $\text{Cu}^{2+}$  ion replace an equivalent number of  $\text{Ni}^{2+}$  ion from B site. The radius of the  $\text{Cu}^{2+}$  ion (0.070 nm) is smaller than that of the  $\text{Ni}^{2+}$  ion (0.078 nm) [32]. Thus,  $\text{Cu}^{2+}$  ion enters into the octahedral-site which shrinks the lattice, and then reduces the lattice parameter.

Table 1. Variations of lattice parameter ( $a$ ) and grain size ( $D$ ) of NiZn ferrite thin films with different Cu substitutions.

$\text{Ni}_{0.4-x}\text{Zn}_{0.6}\text{Cu}_x\text{Fe}_2\text{O}_4$			
$x$	$2\theta$ (°)	$a$ (nm)	$D$ (nm)
0.00	35.42	0.8366	28.3
0.10	35.62	0.8354	31.2
0.20	35.72	0.8338	36.2

Moreover, the grain sizes of Cu-substituted NiZn ferrite thin films are listed in Table 1. The grain size is determined from the diffraction peak broadening with the use of the Scherrer formula:  $D = 0.9\lambda / \beta \cos\theta$ , where  $\lambda$  is the wavelength of the target Cu  $K_\alpha$  (0.15405 nm),  $\beta$  is the line broadening at half the maximum intensity. It is observed that grain size increases with Cu substitution. A possible reason is that Cu substitution promotes the grain growth of NiZn ferrite thin films as reaction center by the increase of the bulk diffusion due to the aberration of crystal lattice, which is caused by Cu substitution. This supposition can be supported by the shrunked lattice constant (see Table 1).

### 3.2. Magnetic properties

The hysteresis loops of  $\text{Ni}_{0.4-x}\text{Zn}_{0.6}\text{Cu}_x\text{Fe}_2\text{O}_4$  ( $0 \leq x \leq 0.2$ ) ferrite thin films are shown in Fig. 2. Fig. 3 shows the saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) of thin films as a function of Cu substitution ( $x$ ).  $M_s$  decreases and  $H_c$  increases with the increasing Cu substitution. The results indicate that the maximum value of  $M_s$  (302.2 emu/cm<sup>3</sup>) and minimum value of  $H_c$  (200.6 Oe) have been obtained when  $x=0$ . And compared the results of NiCuZn ferrite thin films with reference 32, the present work obtained the higher values of  $M_s$  and  $H_c$ .

It is well known that the ferrites  $\text{MFe}_2\text{O}_4$  with the spinel structure are based on a face-center cubic lattice of the oxygen ions. Each spinel unit cell contains eight formula units. In each unit cell, there are 64 tetrahedral sites (A sites) and 32 octahedral sites (B sites). Therefore, the chemical, structural, and magnetic properties of ferrite are strongly influenced by their composition and microstructure, which are sensitive to the preparation methodologies [33]. They show various magnetic

properties depending on the cation distribution. Various cations can be placed in the structure of  $AB_2O_4$  in A site and B site can result in the interesting physical and chemical properties in spinel ferrites [34]. The decrease in  $M_s$  here may be explained by more lattice defects, bigger internal stress and weaker A-O-B superexchange interaction, where A is tetrahedral-site and B is octahedral-site.

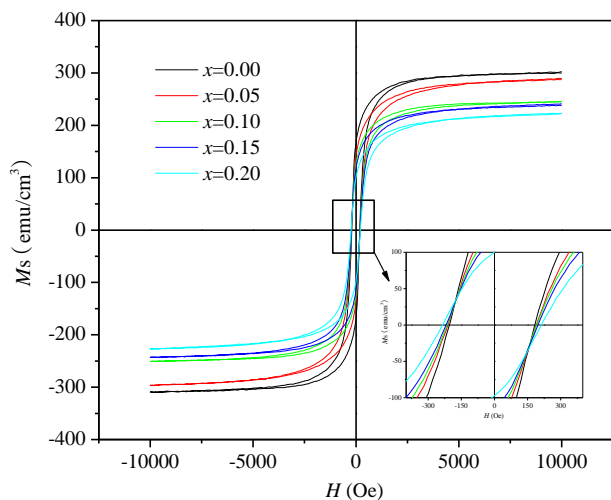
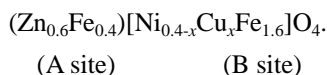


Fig. 2. Hysteresis loop of  $Ni_{0.4-x}Zn_{0.6}Cu_xFe_2O_4$  ferrite thin films with different  $x$ .

According to Miller's site preference energies of ions [35], the cations distribution of films can be written as follows:



According to Néel model, the magnetic moment in Bohr magneton of  $Ni_{0.4-x}Zn_{0.6}Cu_xFe_2O_4$  ferrite thin films is calculated by the following equation:

$$M = |M_B - M_A| = |8.8 - x|\mu_B. \quad (3)$$

Where  $M_A$  and  $M_B$  are the magnetic moments in the A and B sites, and the magnetic moments of  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Fe^{3+}$  ions are 0, 2, 1, and 5  $\mu_B$ , respectively [34]. Simultaneously, the term of saturation magnetization ( $M_s$ ) is defined as the vector sum of magnetic moment per unit cell, and is written as the following equation:

$$M_s = \frac{8M}{a^3} \quad (4)$$

Therefore, the substitution of Ni by Cu and its effect on A-B and B-B interactions leads to the decrease of

magnetization. The magnetization of the tetrahedral lattice is smaller, due to the presence of diamagnetic zinc ions (0  $\mu_B$ ) than the octahedral lattice, although the  $Fe^{3+}$  ions have the largest moment (5 $\mu_B$ ). The magnetization of the A sublattice is expected to be constant due to unchanged Zn content in these ferrite system whereas, the magnetization of B sublattice will be decreased with increase of lower magnetic moment of Cu. This will make a net decrease in the magnetization of the  $NiZnCu$  ferrite thin films. So,  $M_s$  reduces as a function of Cu substitution due to a little change in lattice parameter ( $a$ ), and a large decrease in magnetic moment ( $M$ ).

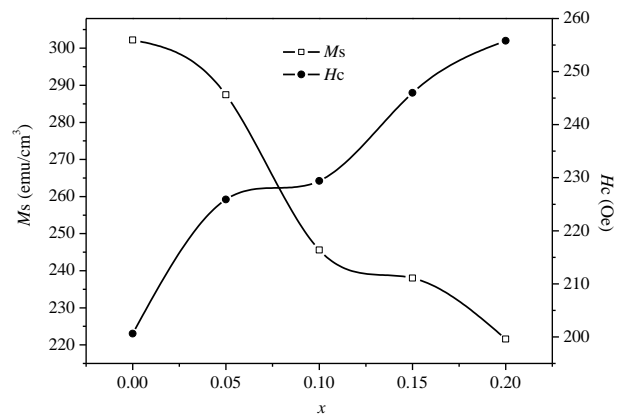


Fig. 3. Variations of  $M_s$  and  $H_c$  of  $Ni_{0.4-x}Zn_{0.6}Cu_xFe_2O_4$  ferrite thin films with different  $x$ .

The coercivity ( $H_c$ ) of ferrite thin films as a function of Cu substitution ( $x$ ) is shown in Fig. 3. According to Stoner-Wohlfarth single domain theory [36],  $H_c$  increased with the increase of grain size when the grain is single domain structure. And the critical grain size of  $NiZn$  ferrite thin films synthesized by sol-gel process is about 50 nm between single domain and multi-domain structure [37]. Thus, the increase of  $H_c$  is due to the grain is single domain structure and the average grain size increases with the increase of Cu substitution. On other hand,  $H_c$  is related to the internal stress and saturation magnetization by the relation:

$$H_c \propto \frac{\lambda_s \sigma}{M_s} \quad (5)$$

Where  $\lambda_s$  is the saturation magnetostriction coefficient,  $\sigma$  is the inner stress and  $M_s$  is the saturation magnetization. According to this relation,  $H_c$  would increase with an increase in internal stress and a decrease in  $M_s$ . From the previous analysis in lattice parameters of samples, it can be deduced that internal stress increase with Cu substitution due to distortion of lattice. Therefore, the increase of internal stress and the decrease of saturation magnetization is another reason that result in  $H_c$  increase.

#### 4. Conclusions

Cu-substituted NiZn ferrite thin films,  $\text{Ni}_{0.4-x}\text{Zn}_{0.6}\text{Cu}_x\text{Fe}_2\text{O}_4$  ( $0 \leq x \leq 0.2$ ), have been synthesized by a sol-gel method. The crystallographic and magnetic properties of thin films have been investigated and the following results have been obtained:

(1) The lattice parameter decreased and the grain size increased with Cu substitution.

(2) The saturation magnetization ( $M_s$ ) decreases and the coercivity ( $H_c$ ) increases with the increasing Cu substitution.

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