Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Magnetism and Magnetic Materials 283 (2004) 157–163
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

High-permeability and high-Curie temperature NiCuZn ferrite

Hua Su*, Huaiwu Zhang, Xiaoli Tang, Xinyuan Xiang

Department of Micro-Electronics and Solid-Electronics, University of Electronic Science and Technology, No. 4 Sect. 2 in Jianshe North Road, Chengdu 610054, People's Republic of China

Received 26 March 2004; received in revised form 10 May 2004
Available online 15 June 2004

Abstract

High-permeability and high-Curie temperature NiCuZn ferrite was developed for use in telecommunication. In the development process, attention was focused on the amount of CuO contained in NiZn ferrite and a small additive of MoO_3 added in the NiCuZn ferrite. It was confirmed that the initial permeability of the core increased and the Curie temperature only decreased a little with 4 mol% CuO content. This was mainly attributed to the presence of Cu ions activating the sintering processes in ferrites and leading to increase in density; the decrease of magnetocrystalline anisotropy constant also does some contribution. By optimizing the MoO_3 additive, the initial permeability could get a sharp increase because of enhancement of grain size. As a result, we were able to develop the NiCuZn ferrite with a permeability of 2480 and Curie temperature of around 118 °C.

PACS: 75.50.

Keywords: Permeability; Curie temperature; CuO content; MoO_3 additive

1. Introduction

Recently, with the development of telecommunications, the Ni–Zn ferrites with high permeability and high frequency are widely used to produce all kinds of broadband elements. But till now, many compositions of these ferrites contained a high quantity of nonmagnetic Zn ferrite; it leads to decrease of Curie temperature and thermostability [1], which consumedly restricts applications of the ferrites. Therefore, it is very actual to search for a new Ni–Zn ferrite with high permeability and high Curie temperature. Gonchar and Andreev recently reported that the NiCuZn ferrite with less Zn content could obtain high Curie temperature [2]. However, in their experiments, the initial permeability of the NiCuZn ferrite only reached 2000; in addition, they did not investigate in detail the effect of different CuO contents on permeability and Curie temperature of the NiCuZn ferrite, nor

*Corresponding author. Tel.: +86-02883201440; fax: +86-02883201810.
E-mail address: uestcsh@163.com (H. Su).

0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2004.05.017

the effect of other additives on this material. Therefore, one purpose of our investigation is to further study the influence of different amounts of CuO on the ferrite magnetic properties of permeability and Curie temperature, considering that the Curie temperature of ferrites is primarily determined by the materials' main prescription and crystal structure, and has little connection with the microstructure, for example, impurity, disfigurement and grain size of the materials. However, the initial permeability of ferrites is very sensitive to the materials' microstructure. So we consider adding some special additive to improve the initial permeability, at the same time not to influence Curie temperature much. In this paper, we studied the effects of MoO_3 on the NiCuZn ferrite in order to get higher permeability.

2. Experiment procedure

NiCuZn ferrites were prepared by the solid-state reaction method. First, high-purity Fe_2O_3, NiO, ZnO and CuO powders were weighed to seven different formulations as shown in Table 1. After wet-mixing and drying, the mixtures were respectively calcinated at 980 °C in atmosphere for 2 h. In order that all samples undergo the same heat treatment, after milling, mixing PVA and pressing into toroidal shapes, all samples were sintered together in air at 1180 °C for 3 h and left to cool inside the electric furnace. The NiCuZn ferrites added MoO_3 would undergo the same procedures.

Phase purity and composition were checked by X-ray diffraction (XRD), using Cu K_α radiation. Micrographs of the samples were obtained using scanning electron microscopy (SEM). The initial permeability μ_i was measured by HP4275A impedance analyzer at a frequency of 10 kHz. Curie temperature of the cores was determined from inductance fading temperature, using HP4275A connected with an oven. Core density values were measured by the Archimedean method. Saturation magnetism (B_s) of the samples was measured by an IWATSU SY-8232 B-H analyzer at 100 Hz.

Table 1
Chemical compositions of the ferrites

	Fe_2O_3	ZnO	NiO	CuO
N0	50.5	31	18.5	0
N1	50.5	31	17.5	1
N2	50.5	31	16.5	2
N3	50.5	31	15.5	3
N4	50.5	31	14.5	4
N5	50.5	31	13.5	5
N6	50.5	31	12.5	6

3. Results and discussion

As shown in Table 1, the mixing ratios of Fe_2O_3 (50.5 mol%) and ZnO (31.0 mol%) are kept constant, while the mixing ratio of NiO is adjusted to suit the changes of CuO content. The composition of the researched ferrites can also be expressed by the formulae: $[(NiO)_{0.37-0.02x}(CuO)_{0.02x}](ZnO)_{0.62}(Fe_2O_3)_{1.01}$, where $0 \leqslant x \leqslant 6$. All of the seven core sample groups (N0)–(N6) are found to be single-phase NiZn ferrite. Fig. 1 shows the XRD patterns of samples N0, N4 and N6.

The relation between Curie temperature and CuO content is presented in Fig. 2. To roundly analyze the phenomena, the initial permeability and the bulk density of the ferrites are also examined and are presented in Fig. 3.

It is found that the Curie temperature decreases steadily with enhancement of CuO content. On the other hand, the initial permeability proves to reach its maximum with a CuO content of 4 mol% as shown in Fig. 3; at the same time the bulk density steadily enhances in our test range, but the enhancement trend becomes tardy when CuO content exceeds 4 mol%. From these results, we attribute the Curie temperature decline to a decrease in the exchange interaction between A and B sublattices. It is known that Cu^{2+} and Ni^{2+} all have strong preference for the octahedral site, but the magnetic moment of Cu^{2+} is 1.3 μ_B, less than that of Ni^{2+} which is 2.3 μ_B. So the substitution of Ni^{2+} with Cu^{2+} will decrease the net magnetic moment and the exchange interaction between A and B sublattices, which directly induces the decline of Curie temperature. The

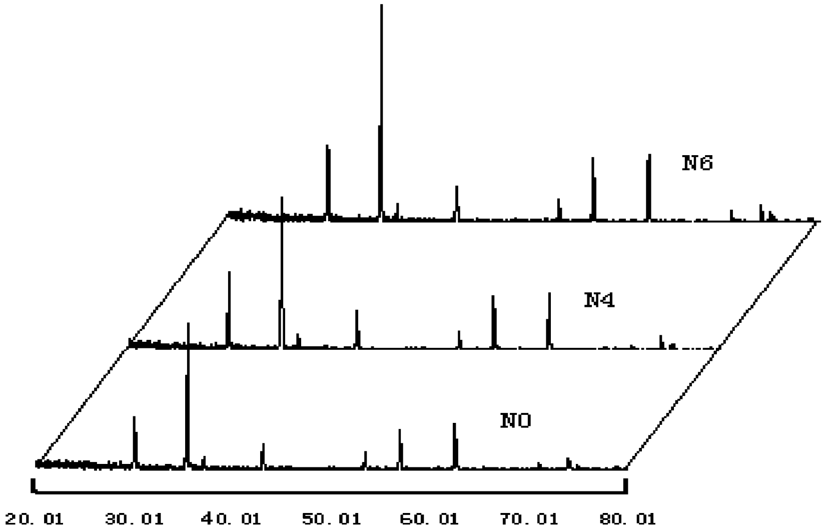

Fig. 1. X-ray diffraction patterns of N0, N4 and N6.

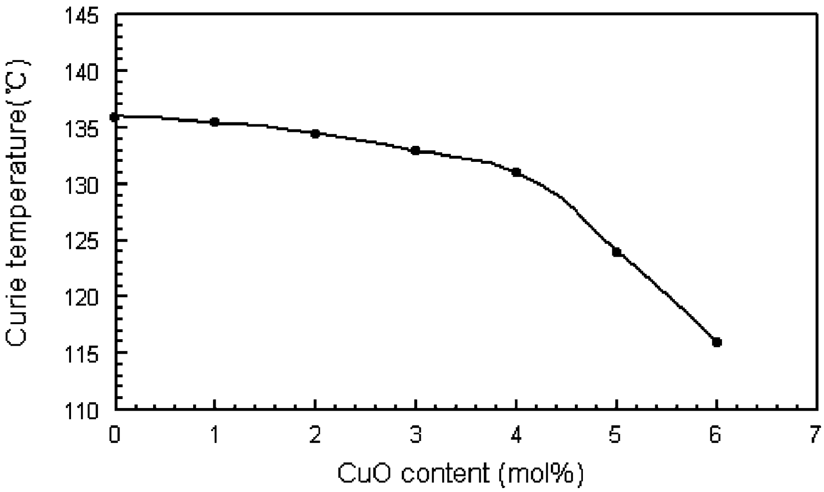

Fig. 2. Relationship between the Curie temperature and CuO content.

affection on the initial permeability is more complicated, though the net magnetic moment decreases with increase in CuO content, the bulk density also enhances as shown in Fig. 3. These two factors are mainly responsible for the change in permeability with CuO content. In one hand, the decrease in the exchange interaction reduces the permeability; on the other hand, the increase in the bulk density induced by liquid phase during sintering of CuO-added ferrite enhances the permeability. Moreover, Cu ferrite has less negative magnetocrystalline anisotropy constant (which is $-6.3 \times 10^3\,J/m^3$) compared with that of Ni ferrite (which is $-7.0 \times 10^3\,J/m^3$), and a small quantity of divalent Fe ions in ferrites has positive magnetocrystalline anisotropy constant; so the total magnetocrystalline anisotropy constant may decrease with the Cu substitution in NiCuZn ferrites,

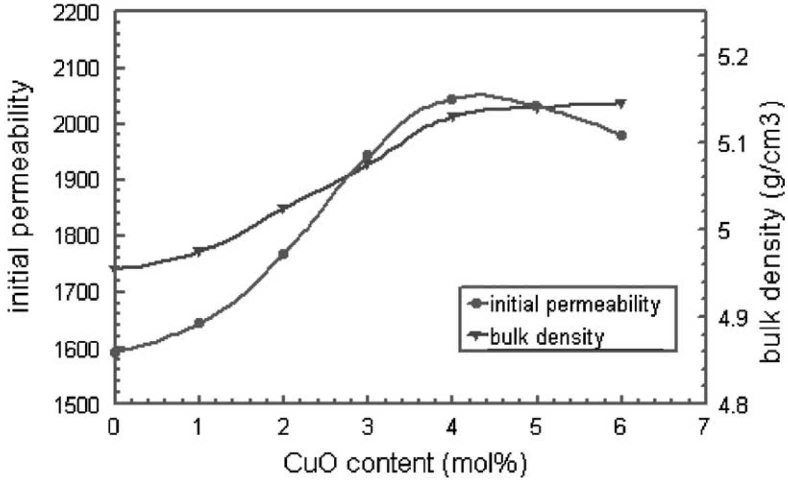

Fig. 3. Dependence of the initial permeability and bulk density on CuO content.

which also contributes to the enhancement of the initial permeability. Consequently, a maximum value of permeability occurs at CuO content 4 mol% in the present samples. Synthetically considering the initial permeability and Curie temperature, we choose the prescription with 4 mol% CuO content (N4) to investigate MoO_3 additive on magnetic properties of the ferrite in order to obtain the higher permeability and relatively higher Curie temperature of NiCuZn ferrite.

Table 2 shows the bulk density, saturation magnetism (B_s) and magnetic loss of the ferrites with different MoO_3 added.

The bulk density enhances under an increased MoO_3 additive from 0 to 0.12 wt%, and then it has seldom change with further increase in MoO_3 additive. Saturation magnetism first increases due to the added MoO_3 and reaches its peak at the MoO_3 of 0.08 and 0.12 wt%. Magnetic loss of the ferrites has little change with MoO_3 additive between 0 and 0.12 wt%, and then increases sharply with more MoO_3 added. The occurrence of maximum bulk density in our test is similar to the result reported by Seo et al. [3]. They confirmed Mo in the grain boundary by EDX analysis and predicted that the increase in bulk density is due to the liquid-phase formation of MoO_3, whose melting point is around 800°C during the sintering. However, in their report the maximum bulk density occurred at MoO_3 additive of 0.2 wt%. The difference in MoO_3 additive may be attributed to the different sintering condition and different material prescriptions, which aim at developing low sintering temperature NiCuZn ferrite for the multiplayer chip inductor.

Table 2
Sintered samples' bulk density, B_s and magnetic loss

	MoO_3 additive (wt%)	Sintering temperature (°C)	Bulk density (g/cm^3)	B_s (mT)	$\mathrm{tg}\,\delta/\mu_i \times 10^{-6}$
N4	0	1180	5.130	271	19
N41	0.04	1180	5.172	272	19
N42	0.08	1180	5.203	273	18
N43	0.12	1180	5.223	273	19
N44	0.16	1180	5.221	270	23
N45	0.20	1180	5.218	265	29

The diffraction patterns for four samples of $[(NiO)_{0.29}(CuO)_{0.08}](ZnO)_{0.62}(Fe_2O_3)_{1.01}$ ferrite (N4) without and with MoO_3 additions are shown in Fig. 4.

A single-phase spinel structure is observed for all the samples. No undesirable second phases have been detected, so we can confirm that MoO_3 addition does not affect the final crystal phase in our testing range. The dependence of the initial

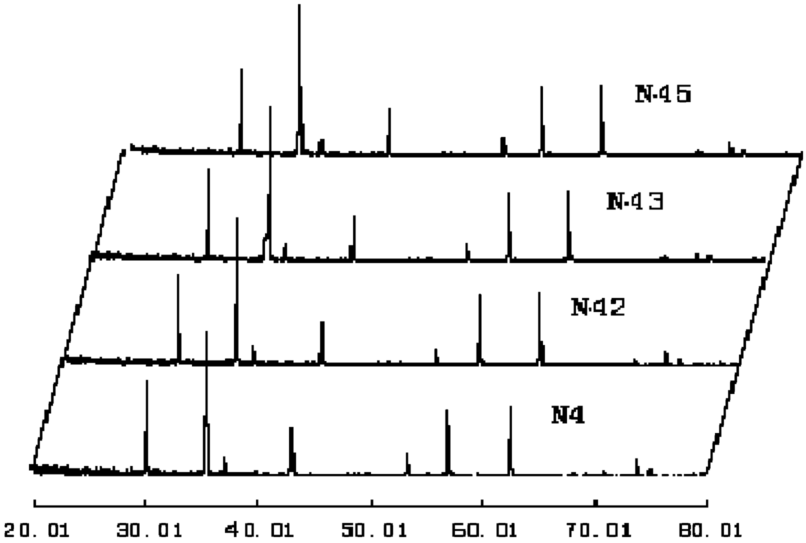

Fig. 4. X-ray diffraction patterns of N4, N42, N43 and N45.

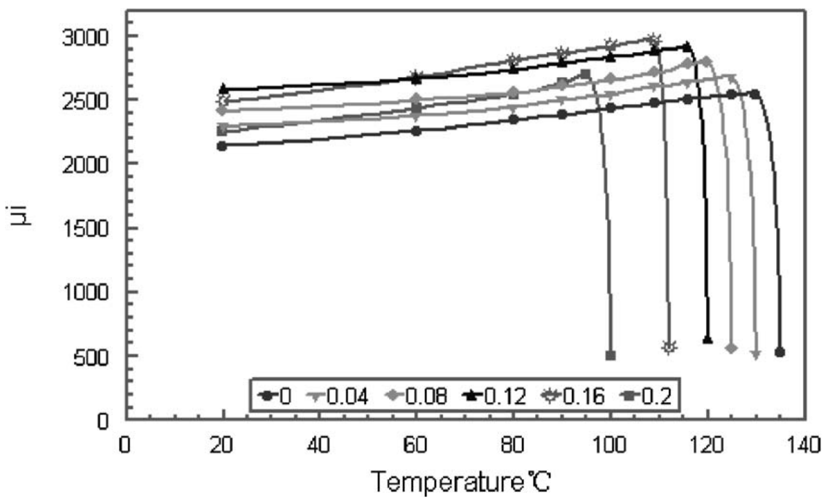

Fig. 5. Temperature dependence of initial permeability for NiCuZn ferrites with different MoO_3 added.

permeability of MoO_3-doped ferrites on temperature is shown in Fig. 5.

The decrease in the Curie temperature with increasing MoO_3 additive is observed from the figure. This suggests that a small quantity of Mo ions may be incorporated into the lattice of ferrite, resulting in the weakening in exchange interaction between A and B sublattices. The sharpness of the permeability drop at the Curie point can also show good homogeneity of the ferrites [4]. At the same time, the initial permeability increases remarkably with MoO_3 added and reaches its peak at an MoO_3 of 0.12 wt%. To determine the factors behind this phenomenon, SEM photos of NiCuZn

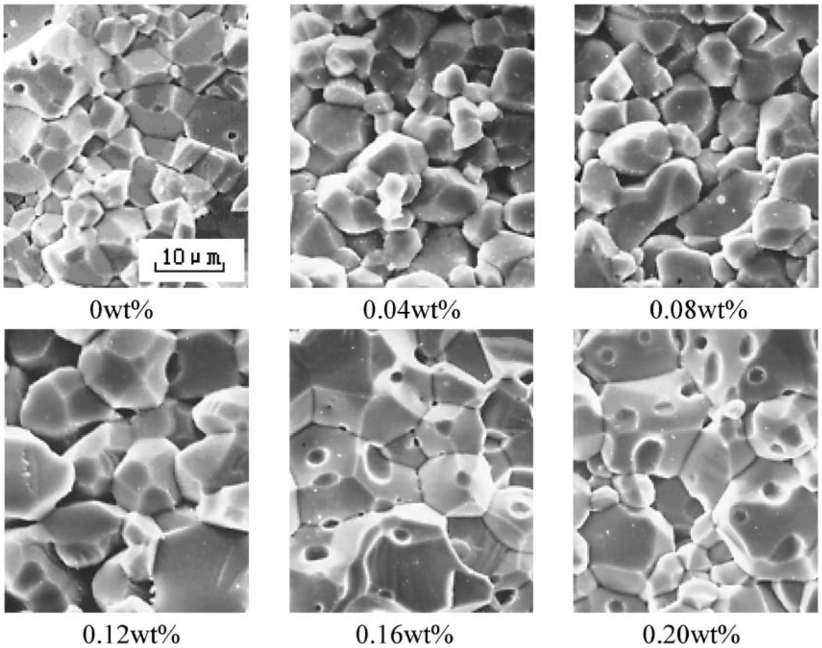

Fig. 6. SEM photos of the NiCuZn ferrite with different MoO_3 additives.

ferrites with different MoO_3 additives are shown in Fig. 6.

We can see that grain size increases obviously with addition of MoO_3. This can be explained that when there are Mo^{6+} ions in the grain boundary region, the metallic ion vacancies in the grain boundary region increase in order to balance the electric charges; as a result, the speed of the grain boundary movement increases, thereby promoting grain growth [5]. But when MoO_3 additive is about 0.12 wt%, the abnormal grain growth is observed in our tests, especially the sample with 0.2 wt% MoO_3 added. Generally, the abnormal grain growth causes formation of closed pores inside the grain, which disturbs the movement of domain wall [3], so the initial permeability decreases. The highest initial permeability of the NiCuZn ferrite (which is 2480) is obtained with an MoO_3 of 0.12 wt% addition. It is because the NiCuZn ferrite's grain size increases while abnormal grain growth and closed pores are seldom formed. The NiCuZn ferrite also has relatively higher Curie temperature, which is around 118°C.

4. Conclusions

In this experiment, the amount of CuO contained in NiZn ferrite was studied to produce high-initial-permeability and high-Curie temperature NiCuZn ferrite. Then, the effect of added MoO_3 on the sintering behaviors and magnetic properties of the NiCuZn ferrite was investigated, and the following conclusions were achieved.

1. By optimizing the CuO content, the initial permeability of the cores was increased and the Curie temperature decreased only a little. This is mainly attributed to the presence of Cu ions activating the sintering processes in ferrites and leading to increase in density; the decrease in magnetocrystalline anisotropy constant also does some contribution.
2. By optimizing the MoO_3 additive, the NiCuZn ferrite with the highest initial permeability 2480 and relatively higher Curie temperature 118 °C can be obtained. This mainly attributed to the appropriate MoO_3 having the effect of

promoting crystalline grain growth and not forming the abnormal grain growth and closed pores.

References

[1] L. Letyuk, A. Balbashov, D. Krutogin, Technology of Magnetoelectronic Materials, in: Metallurgia, Moscow, 1994, pp. 246–258 in Russian.

[2] A. Gonchar, V. Andreev, L. Letyuk, A. Shishkanov, V. Maiorov, J. Magn. Magn. Mater. 254–255 (2003) 544.

[3] S. H Seo, J.H. Oh, IEEE Trans. Magn. 35 (5) (1999) 3412.

[4] Zhenxing Yue, Ji Zhou, Zhilun Gui, Longtu Li, J. Magn. Magn. Mater. 264 (2003) 258.

[5] Y. Matsuo, K. Ono, M. Ishikura, I. Sasaki, IEEE Trans. Magn. 33 (5) (1997) 3751.