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The influence of Mn dopant on the electromagnetic properties of NiCuZn ferrite

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Abstract

In this paper, a citrate precursor method was used to prepare nano-sized NiCuZn ferrite powders with a composition of $(Ni_{0.15}Cu_{0.2}Zn_{0.65}O)(Fe_{2-x}Mn_xO_{3+0.5x})_{0.99}$, ($x$ = 0–0.04). Because of excellent sintering activity, the nanocrystals can be sintered below 900 °C without the addition of sintering aids. The effect of Mn dopant on the microstructures and the initial permeability was investigated. The results show that the introduction of Mn into NiCuZn ferrite has a great influence on its electromagnetic properties. The initial permeability of NiCuZn ferrite increases greatly with a small amount of Mn addition firstly, and then further increase of Mn content leads to a decrease in the initial permeability. By changing the content of Mn addition, the useful frequency dependence of initial permeability could be adjusted in a range of frequency from several hundreds of kilohertzs to several megahertzs.

Keywords: D. Ferrite; NiCuZn; Electromagnetic properties; Mn doping

1. Introduction

In the past 10 years, with the development of surface mounting technology, great progresses have been made in the miniaturization of electromagnetic components. As one of the most important media materials, Ni–Cu–Zn ferrite has been commercially used to manufacture multiplayer chip inductor in high frequency region. In order to be cofired with the inner electrode (usually Ag is the most suitable internal contact material with a melting point of 961 °C), Ni–Cu–Zn ferrite must be sintered below 900 °C. The normal way to lower the sintering temperature is using sintering aids such as Bi_2O_3, V_2O_5 etc, which usually does great harm to the magnetic property of the ceramics acquired [1–4]. Ultrafine Ni–Cu–Zn ferrite with uniform composition, small grain size, and narrow size distribution is expected to realize low-temperature sintering and attain ideal magnetic property at the same time [5].

In this paper, a citrate precursor method [6] was used to prepare nano-sized NiCuZn ferrite powders with a composition of $(Ni_{0.15}Cu_{0.2}Zn_{0.65}O)(Fe_{2-x}Mn_xO_{3+0.5x})_{0.99}$, ($x$ = 0–0.04). Samples made of nano-sized powders could be sintered at a low temperature of 890 °C without any sintering aids. The effect of Mn content on densitification and microstructures as well as the electromagnetic properties of the ferrite ceramics was investigated.

2. Experimental procedure

The starting materials were iron nitrate, nickel acetate, copper acetate, and citric acid. Firstly, iron nitrate was dissolved in distilled water before being precipitated by a ammonia solution to form $Fe(OH)_3$. Filtered, washed, the fresh $Fe(OH)_3$ precipitate was dissolved into hot citric acid solution at 60–80 °C in the ratio of 1:1 of Fe:citric acid, and a transparent solution was obtained. Then, nickel and copper acetate were added in stoichiometric quantities in the above solution to give the required composition $(Ni_{0.15}Cu_{0.2}Zn_{0.65}O)(Fe_{2-x}Mn_xO_{3+0.5x})_{0.99}$ (where x = 0.005, 0.01, 0.015, 0.025, 0.03, 0.035, and 0.04, named as M005, M010, ... and M040, respectively). After that appropriate ammonia was drop into the above sol until it was neutral or slightly alkaline (pH 6–8). After heating at 125 °C, dried gel was obtained. Finally, the gel was heat-treated at 700 °C for 4 h, resulting Mn-doped Ni–Cu–Zn

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nanocrystals with grain size of about 50 nm determined by TEM.

The nanocrystalline powders were pre-milled and pressed into disks (10 mm in diameter and 1.0 mm thickness) and toroidal samples (20 mm outside diameter, 10 mm inside diameter, and 3 mm thickness) with the addition of 5 wt.% PVA as lubricant. The ceramic samples sintered at 890 °C were used for magnetic property measurements.

The crystalline structures were determined by a Rigaku powder X-ray diffractometer (XRD) using Cu Kα radiation. The morphology and grain size of the nanocrystalline powders were observed using a JEM-200CX transmission electron microscopy (TEM). The magnetic properties of the ceramics were measured using an HP 4291A RF impedance analyzer. The dc resistivity of the ceramic was determined using an HP 4040B micro-amperemeter. The microstructures of the ceramics were investigated using a Zeiss CSM-950 scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows XRD patterns of $(Ni_{0.15}Cu_{0.2}Zn_{0.65}O)(Fe_{2-x}Mn_xO_{3+0.5x})_{0.99}$ nanocrystalline powders calcined at 700 °C. It is obvious that a single-phase NiCuZn ferrite with spinel crystal structure was formed for all the powders. Mn substitution does not affect the final crystal phase.

The microstructures of the ceramics sintered at 890 °C with various Mn content were observed using SEM. Fig. 2 shows the SEM images for the specimens with $x = 0$, 0.015, 0.025, and 0.03, respectively. The ceramic grain size decreases with increasing Mn content from 1.4 μm for undoped sample, to 0.5 μm for the composition with $x = 0.03$. It indicates the doping of Mn ion could suppress the grain growth of NiCuZn ferrite.

The Mn-substiution has a significant effect on the sintering behavior of NiCuZn ferrite, as shown in Fig. 3, the little Mn doping could enhance the densification, but further more Mn addition leads to a decrease in the density on the contrary. The density of the Mn-doped NiCuZn ferrite sintered at 890 °C reaches its maximum value (97.5%) at $x = 0.015$.

Fig. 4 gives the frequency-dependent permeability curves of ceramic samples with different Mn content. It is found that the initial permeability does not change linearly with the Mn substitution and it goes up firstly from 400 to 510 as Mn concentration increases from 0 to 0.015, then drops to 300 for the composition with $x = 0.03$. As well known, the electromagnetic properties of the NiCuZn ferrite as a soft

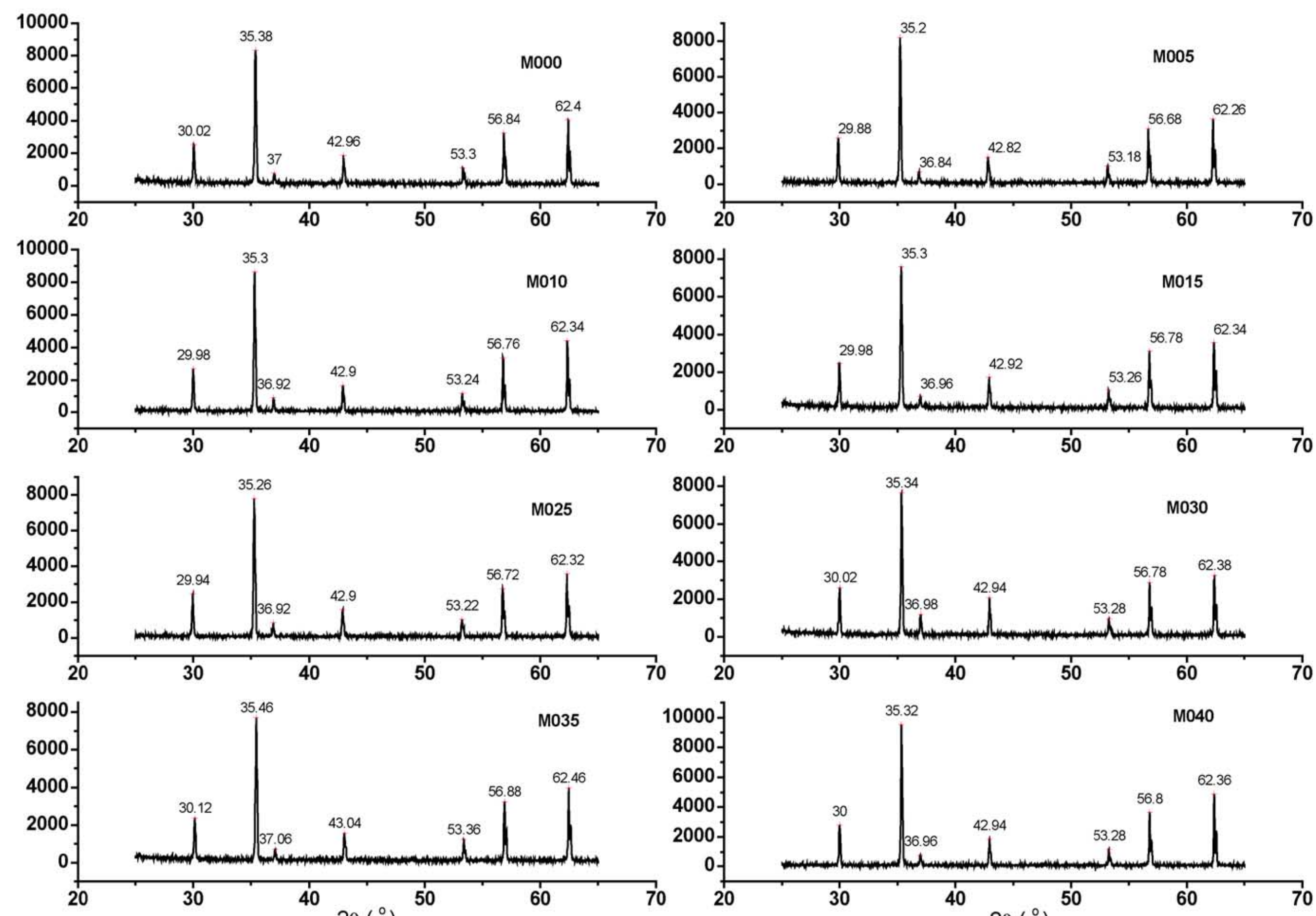
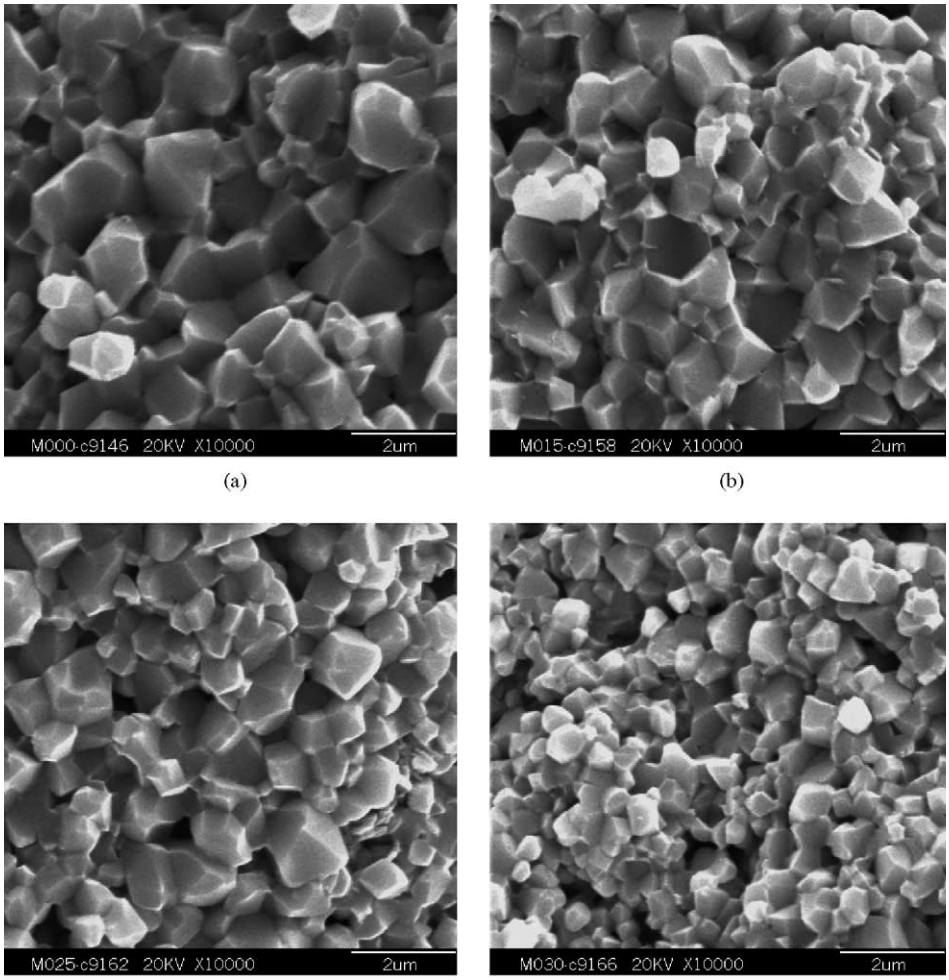


Fig. 1. XRD patterns of $(Ni_{0.15}Cu_{0.2}Zn_{0.65}O)(Fe_{2-x}Mn_xO_{3+0.5x})_{0.99}$ nanocrystalline powders.



(a) (b) (c) (d)

Fig. 2. SEM images of the fractures of ceramic samples with Mn content of (a) 0; (b) 0.015; (c) 0.025; and (d) 0.030.

magnetic material may be affected by many factors such as the composition, the microstructure, additives, density, and the grain size etc. In fact, the initial permeability of ferrite is usually expressed as the following equation

$$\mu_i = \frac{M_s^2}{(aK + b\lambda\sigma)} \quad (1)$$

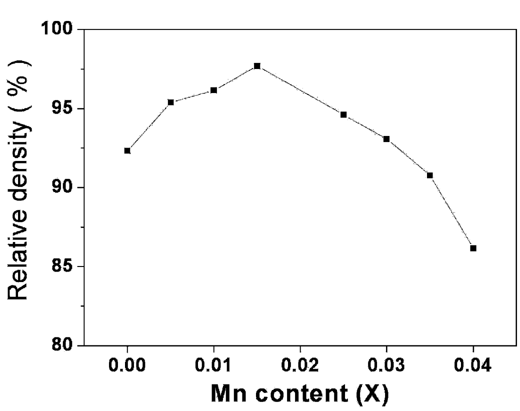


Fig. 3. Density for the ceramic samples with various Mn content.

where μ_i is the initial permeability, M_s the saturation magnetization, K the crystal magnetic anisotropy, λ the magnetostriction constant, σ the inner stress, and a and b are constants. Therefore, in our case, the significant increase in the initial permeability within the range $0 \le x \le 0.15$ is

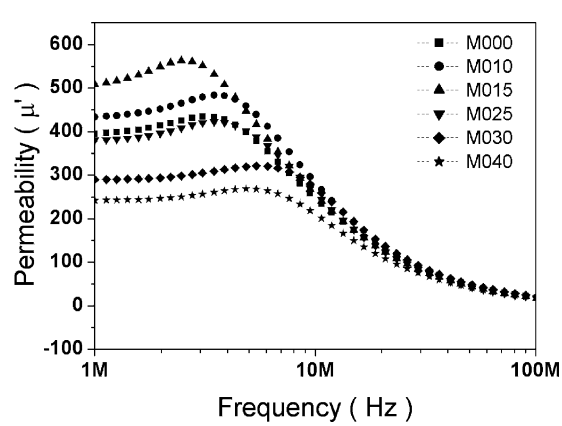


Fig. 4. Frequency dependence of initial permeability for the samples with various Mn content.

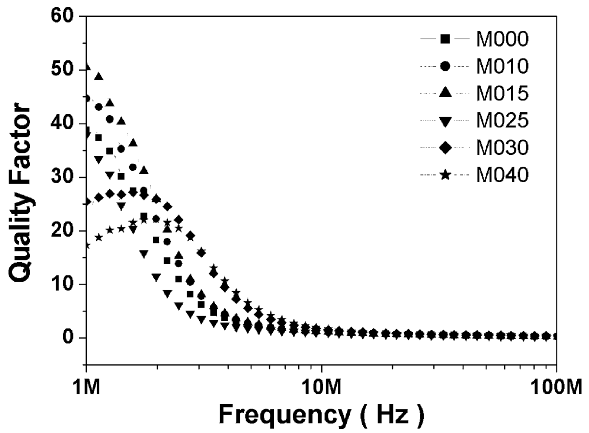


Fig. 5. Quality factor vs. frequency for the ferrite samples with various Mn content.

attributed to the decrease of magnetostriction constant induced by Mn substitution as reported by Nam et al. [7]. On the other hand, the magnetic properties may be also affected by the grain size and the density, and enhanced by the increase of the grain size [8]. When x is above 0.025, the density and the grain size are decreased obviously by Mn substitution as shown in Figs. 2 and 3. These may be the reasons for the drop of the initial permeability of the ferrite with excess Mn addition. The results indicate that an optimum microstructure must be taken into account to obtain Mn-doped NiCuZn ferrites with high performance. The most important result is that the initial permeability of the sample with $x = 0.015$ sintered at 890 °C was above 500, which is really hard to be achieved using conventional ceramic method with such fine-grained microstructure.

Fig. 5 shows the quality factor versus frequency of Mn substituted NiCuZn ferrites. Similar to the relationship between the initial permeability and Mn content, the quality factor value (at 1 MHz) increases firstly and then drops. This is consistent with the variation of the density with Mn concentration.

Furthermore, an adequate dc resistivity of the ferrite is also required in manufacturing of MLCI so as to avoid "creeping" while electroplating, which may do great harm to the quality of components. In our case, the ceramics sintered from the nanocrystals show high dc resistivity of 10^9–10^{10} Ω cm, which is much more preferable for practical production and for the reliability of the components.

4. Conclusions

Mn substituted NiCuZn ferrite nanocrystals were successfully synthesized via a citrate precursor method and could be sintered at a low temperature below 900 °C without any sintering aids. The introduction of Mn ion into NiCuZn ferrite has a great influence on its microstructures and electromagnetic properties. The initial permeability and quality factor of NiCuZn ferrite are enhanced obviously with a small amount of Mn addition firstly, and then excess Mn content leads to a decrease in the initial permeability as well as quality factor. By changing the content of Mn addition, the useful frequency dependence of initial permeability could be adjusted in a range of frequency from several hundreds of kilohertzs to several megahertzs. The obtained NiCuZn ferrite with optimum Mn substitution of 0.015, possesses fine-grained microstructure, showing high initial permeability above 500 and high quality factor over 50 at 1 MHz, which is an excellent material for high frequency MLCIs application.

Acknowledgements

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