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Effects of nanocrystalline ferrite particles on densification and magnetic properties of the NiCuZn ferrites

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Abstract Effects of nanocrystalline ferrite particles addition on densification behavior and magnetic properties of the NiCuZn ferrites were investigated. It was confirmed that nanocrystalline ferrite particles enhanced densification of the samples obviously. The reason was attributed to the nanocrystalline particles, which spread around the micron-sized ferrite particles, increased contacting area and inter-diffusion of the particles. When the amount of nanocrystalline particles addition reached to 30 wt%, the samples obtained an approximate densification behavior as the 1.5 wt% Bi_2O_3 added samples. Due to relatively bigger grain size, higher sintering density and no different chemical composition sintering aids added, the sample with 30wt% nanocrystalline ferrite particles got the highest permeability and relatively high *Q*-factor when sintered at 900.

Introduction

Recently, with the development of surface mount technology (SMT) and multilayer chip devices, NiCuZn ferrites have been extensively studied and widely used to fabricate chip inductors and EMI filters, because of their relatively low sintering temperature and high resistivity with good performance at high frequencies [1–4]. In applications, the NiCuZn ferrites need to be sintered around 900 °C in order to co-fire with silver internal electrode. If the conventional mixed-oxide method was chosen, suitable amount of low melting-point sintering aids, such as Bi_2O_3, MoO_3, PbO, V_2O_5, etc. [5–9], should be introduced into NiCuZn ferrites to lower sintering temperature. However, these sintering aids easily caused discontinuous grain growth, silver diffusion into ferrites, and thus degraded the properties of ferrites and chip devices. Moreover, various wet-chemical methods, such as the sol–gel method and the co-precipitation method [10–12], had also been proposed to lower sintering temperature of the NiCuZn ferrites. In these methods, nanocrystalline ferrite particles could be obtained, which had larger surface area and larger surface free energy. Since surface free energy was considered to be a driving force in the sintering and recrystalline process, the NiCuZn ferrites could be well sintered around 900 °C without or with less sintering aids. However, the large surface free energy also made it very difficult to molding. In addition, grain size of the sintered ferrites was also small.

At present work, we combined the mixed-oxide method and the sol–gel method with considering their advantages and defects. The sol–gel method was used to prepare the nanocrystalline ferrite particles, which acted as sintering aid in the mixed-oxide method. Due to the nanocrystalline ferrite particles had the same chemical composition as the NiCuZn ferrites, high performance NiCuZn ferrites with low sintering temperature could be obtained.

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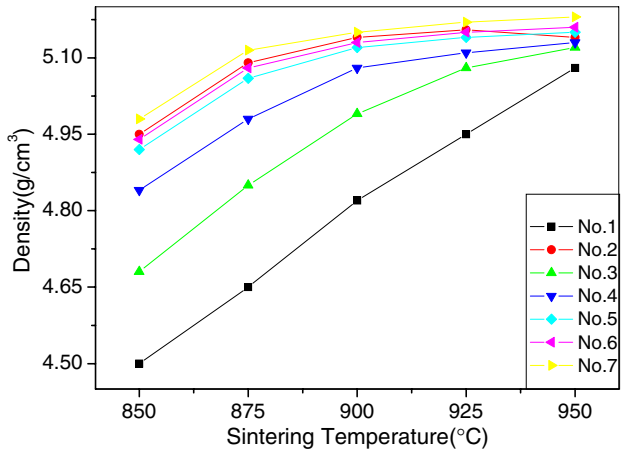

Fig. 1 Densities of the samples sintered at the temperature from 850 to 950 °C

Experimental procedure

The NiCuZn ferrites were first prepared by the conventional mixed-oxide method. The analytical grade Fe_2O_3, NiO, ZnO and CuO were weighed following the formula in Table 1 and wet-mixed in a ball mill for 6 h, using stainless steel balls as media. After drying, these powders were calcined at 750 °C for 2 h to obtain the spinel phase. The sintering aids, shown in Table 1, were then added in the obtained ferrite powders. The mixtures were wet-milled in the ball mill, respectively till the average particle size was under 1 μm. The average particle size was measured by the laser scattering particle size distribution analyzer (HORIBA LA-920). After drying, the powers were granulated with PVA and pressed in a toroidal shape under the same uniaxial pressure. The green samples were sintered at temperatures from 850 to 950 °C in 25 °C interval and held for 4 h in air, then left to cool inside the electric furnace to room temperature, with 2.5 °C/min heating and cooling rate.

The nanocrystalline ferrite particles for sintering aid were prepared by the sol–gel method. Firstly, analytical grade nickel nitrate, zinc nitrate, copper nitrate, iron nitrate and citric acid of the certain molar ratio were dissolved in distilled water, respectively. Then a small amount of ammonia was added to the solution to adjust the pH value to about 7. During this procedure, the solution was stirred using a magnetic agitator. Then, the mixed solution was poured into a dish and heated at 135 °C stirring constantly to transform it into a xerogel. When ignited, the dried gel burnt in a self-propagated combustion manner until all the gels were burnt out completely to form loose powders [10]. The crystallite size of the as-burnt powder estimated from the X-ray peak broadening of the diffraction peak using Scherrer formula was about 40–50 nm. These nanocrystalline particles were used as sintering aid in the mixed-oxide method. In addition, some of them were also granulated directly and pressed into toroidal shape samples to contrast with the samples prepared by the mixed-oxide method.

Densities of the green and sintered samples were measured by Archimedean method. Micrographs of the samples were investigated using scanning electron microscopy (SEM). The magnetic property measurements were carried out on HP4291B impedance analyzer at a frequency of 1 MHz.

Results and discussion

Densification behavior

The green densities of the samples prepared by the mixed-oxide method (No. 1–No. 6) are about 3.2 g/cm^3, and the green densities of the samples prepared by the sol–gel method (No. 7) are about 3.12 g/cm^3. The densities of the ferrite samples sintered at temperatures ranging from 850 to 950 °C are shown in Fig. 1. For the pure samples prepared by the mixed-oxide method (No. 1), sintering densities have an approximately linear relationship with the sintering temperatures, and are obviously lower than other samples. Thus, higher sintering temperature is needed

Table 1 composition, preparation methods and sintering aids of the samples

No.	Composition of the ferrites	Preparation methods	Sintering aids and their amount (wt%)	
			Bi_2O_3	Nanocrystalline ferrite particles
1	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method		
2	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method	1.5	
3	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method		10
4	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method		20
5	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method		30
6	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Mixed-oxide method		40
7	$(Ni_{0.15}Cu_{0.25}Zn_{0.6}O)_{1.02}(Fe_2O_3)_{0.98}$	Sol–gel method		

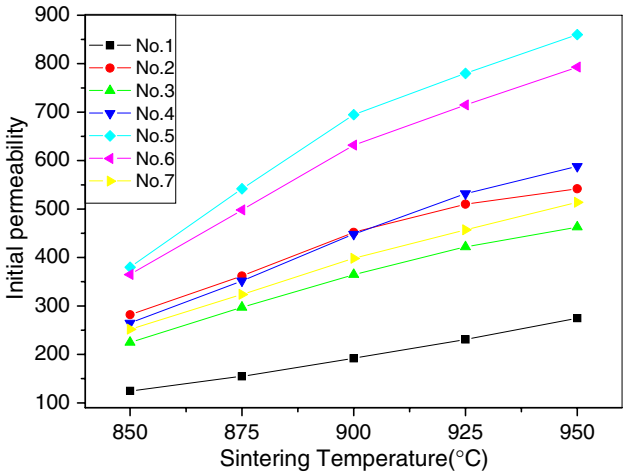

Fig. 2 Permeability of the samples sintered at temperatures from 850 to 950 °C

to densify the samples. The samples prepared by the sol–gel method (No. 7) have the highest sintering densities at all sintering temperatures, and then on sequence of the 1.5 wt% Bi_2O_3 added samples (No. 2). For the samples with nanocrystalline ferrite particles addition (No. 3–No. 6), their densification behaviors improve gradually with increasing amount of the addition. When the nanocrystalline particles' amount reaches to 30 wt%, the samples obtain an approximate densification behavior as the 1.5 wt% Bi_2O_3 added samples. Further increasing nanocrystalline particles' amount, increase of the sintering densities is inconspicuous.

Magnetic properties

Figures 2 and 3 show the permeability and Q-factor at 1 MHz of the samples sintered at different temperatures.

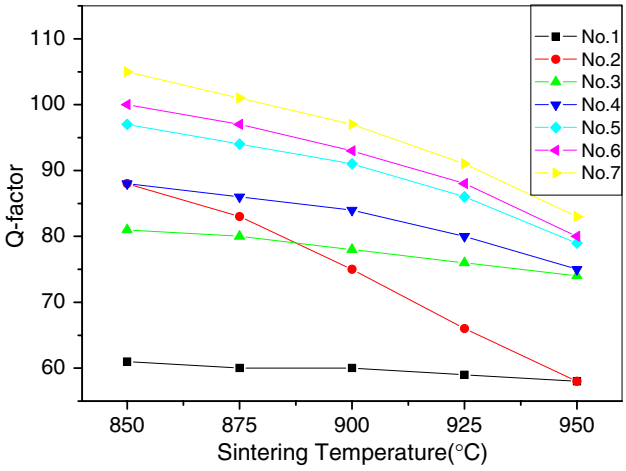

Fig. 3 Q-factor of the samples sintered at temperatures from 850 to 950 °C

The results reveal that permeability increases with the sintering temperature for all samples, which can be attributed to grain growth and increase of the sintering density. At the same sintering temperature, the samples with 30 wt% nanocrystalline particles addition (No. 5) have the highest permeability. Although the samples prepared by the sol–gel method (No. 7) or with Bi_2O_3 added (No. 2) have good densification behaviors, their performances on permeability are not prominent.

The samples prepared by the sol–gel method (No. 7) have the highest Q-factor values at all sintering points. With increasing sintering temperature, Q-factor values of all samples decrease. However, this behavior is not obvious for the pure samples prepared by the mixed-oxide method (No. 1), but marked for the samples with 1.5 wt% Bi_2O_3 added (No. 2). In addition, Q-factor values improve gradually with increasing nanocrystalline particles amount (No. 3–No. 6).

Microstructure observation

Scanning electron micrographs for samples (No. 1–No. 7) sintered at 900 °C are presented in Fig. 4. The pure sample prepared by the mixed-oxide method (No. 1) has an incomplete sintering performance, and is not very dense. The other samples reveal sintering phenomenon, and the sample with 1.5 wt% Bi_2O_3 addition (No. 2) has the biggest average grain size. However, abnormal grain growth and closed pores are also observed. The sample prepared by the sol–gel method (No. 7) has the smallest average grain size. As for the samples with nanocrystalline particles (No. 3–No. 6), grain size gradually decreases with increasing amount of the addition.

Discussion

The nanocrystalline NiCuZn ferrite particles prepared by the sol–gel method have larger surface area and larger surface free energy than the micron-sized ferrite particles prepared by the conventional mixed-oxide method. The surface free energy is a driving force in the sintering and recrystalline process [10]. So the samples prepared by the sol–gel method have a perfect densification behavior around 900 °C without any sintering aids. However, due to their high surface free energy and small particle size, these nanocrystalline ferrite particles are difficult to be pressed together during molding, so it is not easy for them to contact each other closely. As a result, the sample prepared by the sol–gel method has the smallest grain size. Densification behaviors of the samples with nanocrystalline

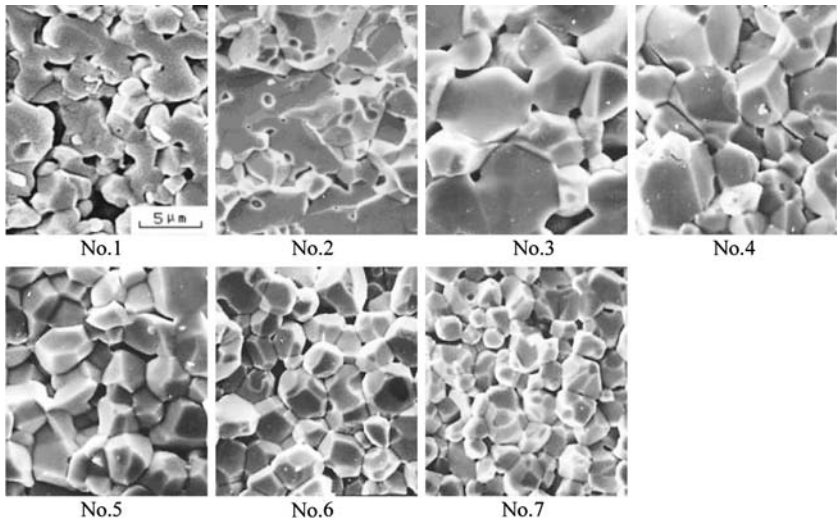

Fig. 4 SEM micrographs of the samples sintered at 900 °C

ferrite particles addition can also be attributed to the high surface free energy of the nanocrystalline particles. The nanocrystalline particles spread around the micron-sized ferrite particles and increase contacting area and inter-diffusion of the particles. Thus, densification behaviors of the samples are improved. Due to these samples are also prepared by the mixed-oxide method, existence of the micron-sized ferrite particles and wet-mill procedure ensure the close contact of the particles, accordingly, grain size grows bigger. With increasing nanocrystalline ferrite particles' amount, densification behavior becomes better, but grain size also becomes smaller. When the amount of the addition reaches to 30 wt%, densification behavior of the samples can be approximate with the 1.5 wt% Bi_2O_3 added samples.

It is very known that the magnetizing mechanism of soft ferrites results from domain rotation and domain walls motion. The domain rotation has close connection with sample's sintering density and domain walls motion is affected by the grain size and sintering density. When sintered at 900 °C, the sample with 1.5 wt% Bi_2O_3 addition has a good densification behavior and biggest average grain size, however, its permeability is not very prominent. The phenomenon is attributed to the dissolution of Bi_2O_3 into the ferrite grains, which causes a distortion of the spinel structure of ferrite, resulting in a reduction in its total magnetic moments and thus reducing magnetic permeability [9]. The fact that the sample with 30 wt% nanocrystalline ferrite particles has the highest permeability can be attributed to relatively bigger grain size, higher sintering density and no different chemical composition sintering aids added to distort the sample.

Q-factor values of the ferrite samples are mainly determined by sintering density and microstructure (including grain size, porosity, grain boundary property etc.). The sample prepared by the sol–gel method has the highest sintering density and smallest grain size, so it gets the highest *Q*-factor. The samples with more nanocrystalline ferrite particles addition can obtain a higher sintering density and smaller grain size, so *Q*-factor values enhance with increasing amount of the addition. With increasing sintering temperature, grain size of all samples increase, as a result, *Q*-factor values of all samples decrease gradually. However, this trend is very notable for the Bi_2O_3 added samples, which is attributed to abnormal grain growth and volatilization of the Bi_2O_3. As for the pure ferrite samples prepared by the mixed-oxide method, their sintering densities also increase obviously with increasing sintering temperature (as shown in Fig. 1). This fact is helpful to improve *Q*-factor and counteract the negative effects of grain growth on *Q*-factor, so in our test range, their *Q*-factor values have little connection with the sintering temperature.

Conclusion

Nanocrystalline ferrite particles addition could enhance ferrite samples' densities obviously, which was attributed to the nanocrystalline particles, which spread around the micron-sized ferrite particles, increased contacting area and inter-diffusion of the particles. Increasing nanocrystalline ferrite particles' amount, densities of the samples increased and grain size decreased gradually. With 30 wt% nanocrystalline ferrite particles addition, the sample got the highest permeability when sintered at 900 °C, which was due to relatively bigger grain size, higher sintering density and no different chemical composition sintering aids added.

Q-factor increased monotonously with increasing the nanocrystalline ferrite particles' amount, despite different sintering temperatures. The samples prepared by the sol–gel method had the highest Q-factor values.

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