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Preparation of high-permeability NiCuZn ferrite[*]

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Abstract: Appropriate addition of CuO/V_2O_5 and the reduction of the granularity of the raw materials particle decrease the sintering temperature of NiZn ferrite from 1200 °C to 930 °C. Furthermore, the magnetic properties of the NiZn ferrite prepared at low temperature of 930 °C is superior to that of the NiZn ferrite prepared by sintering at high temperature of 1200 °C because the microstructure of the NiZn ferrite sintered at 930 °C is more uniform and compact than that of the NiZn ferrite sintered at 1200 °C. The high permeability of 1700 and relative loss coefficient $\tan\delta/\mu_i$ of 9.0×10^{-6} at 100 kHz was achieved in the $(Ni_{0.17}Zn_{0.63}Cu_{0.20})Fe_{1.915}O_4$ ferrite.

Key words: NiZn ferrite, Low temperature, High permeability, Low loss

INTRODUCTION

NiZn ferrite has wide application prospect in the field of radio frequency (RF) electronic device due to the high initial permeability in combination with giant resistivity (Rezlescu *et al.*, 2000; Li *et al.*, 2002; Goldman, 1990). Among all production process, the common ceramic method showed to be a good way to produce NiZn ferrite in volume. However, conventional ceramic technique requires high sintering temperature of about 1200 °C which easily leads to the abnormal growth of grains and deterioration of the magnetic properties of the NiZn ferrite (Darko and Miha, 1999). So many new techniques were tried to reduce the sintering temperature of NiZn ferrite: such as addition of CuO and some sintering aids (Hsu *et al.*, 1995; Seo and Oh, 1999; Shrotri *et al.*, 1999; Lebourgeois, 2000; Caltun *et al.*, 2002). New preparation methods, for instance sol-gel and co-precipitation methods, were also tried (Kim and Koh, 2003; Hsua *et al.*, 2004; Anil Kumar *et al.*, 1997). Moreover, the reduction of granularity of the raw materials particle

was also favorable for decreasing sintering temperature (Nakamura, 1997). Although the sintering temperature has been effectively reduced to 900 °C and is widely used to prepare the chip inductor, it is difficult to prepare the NiZn ferrite combining high initial permeability and low sintering temperature (Wang, 2001; Zhang *et al.*, 2000). Until now, there is no report of NiZn ferrite with initial permeability of more than 1500 and sintering temperature of less than 1000 °C.

EXPERIMENTS

The composition of the sample was $(Ni_{0.17}Zn_{0.63}Cu_{0.20})Fe_{1.915}O_4$. The chemical reagent-grade powders of Fe_2O_3, NiO, CuO and ZnO were mixed for six hours in a ball mill with distilled water. The average particle size of the mixture was pulverized to less than 0.8 μm. The slurry was dried and calcined at 750 °C in air for 2 h. Then the calcined powders into which was added 0.2 wt% V_2O_5 were ground in a ball mill for six hours. After the ground powders with a particle size of about 0.8 μm were dried, PVA (Polyvinyl alcohol) was added into them

for their granulation and pressing into toroidal bodies. The green bodies were sintered at 930 °C in air for 5 h. Another sample with the conventional composition of $(Ni_{0.32}Zn_{0.63}Cu_{0.05})Fe_{1.915}O_4$ having initial permeability of 1500 was prepared by conventional ceramic process i.e. sintering at 1200 °C for 2 h as previously described (Burke, 1958). The oxide reagents were same as those for low sintering temperature.

Initial permeability and loss was measured using HP4192A Impedance Analyzer at 100 kHz by a circuit loaded with a toroid shaped sample and the measurement of frequency dispersion of the ferrite was done by using HP4291B RF Impedance/Material Analyzer by a coaxial line technique in the frequency range of 1~100 MHz. The X-ray diffraction patterns of samples were obtained by a Rigaku D/max 2550PC X-ray diffractometer with scan rate of 3°/min. The SEM photomicrographs of fractured surfaces were recorded using an FEI SIRION SEM.

RESULTS AND DISCUSSION

The sintered density, initial permeability and relative loss factor of the ferrites was measured, and the results are shown in Table 1.

Due to the CuO and V_2O_5 addition and the decrease of the granularity of the raw materials particle, the sintering temperature was decreased from 1200 °C to 930 °C. High initial permeability of 1700, comparable to that of the NiZn ferrite prepared by conventional ceramic technique, was achieved in the $(Ni_{0.17}Zn_{0.63}Cu_{0.20})Fe_{1.915}O_4$ ferrite. Furthermore, the relative loss coefficient $\tan\delta/\mu_i$ was greatly reduced from 16.4×10^{-6} to 9.0×10^{-6} at 100 kHz and the density was enhanced by using low temperature sintering technique instead of the conventional technique.

X-ray diffraction patterns of the sample sintered at 930 °C are shown in Fig.1 indicating that there is no other phase than spinel phase in the patterns, which indicates that the Cu^{2+} and V^{5+} entered into the lattice.
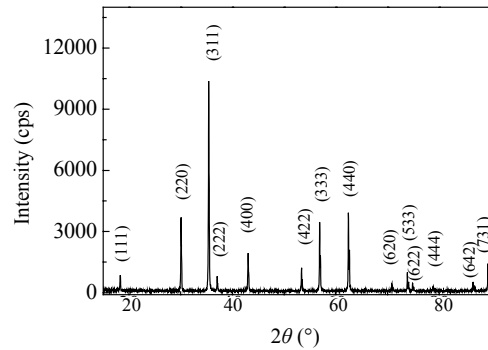

Fig.1 XRD patterns of $(Ni_{0.17}Zn_{0.63}Cu_{0.20})Fe_{1.915}O_4$ ferrite sintered at 930 °C

The morphology of the samples sintered at 930 °C and at 1200 °C is shown in Fig.2 respectively. The sample sintered at 930 °C had obviously more compact and uniform microstructure as well as bigger grain size compared to the sample sintered at 1200 °C. As known, appropriate addition of CuO and V_2O_5 can promote the diffusion of ions and accelerate the solid-reaction in the sintering process, which resulted in the growth of grains (Kim *et al.*, 2000; Caltun and Spinu, 2001). So the sample sintered at 930 °C shows more compact microstructure and bigger grain size.
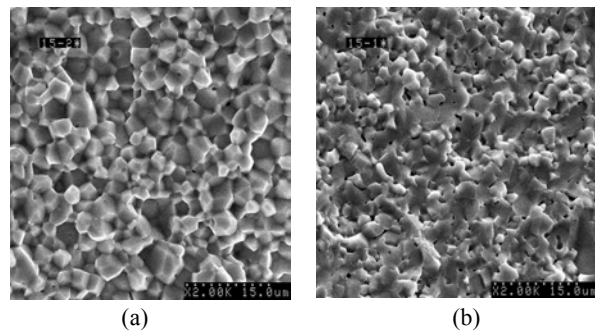

Fig.2 SEM micrograph of NiCuZn ferrites sintered at 930 °C (a) and sintered at 1200 °C (b)

Fig.3 shows the frequency dispersion of ferrites sintered at 930 °C and 1200 °C in the range of 1 MHz~100 MHz at room temperature. The two ferrites obviously showed relaxation resonance, with the real part μ' decreasing drastically at high frequency of more

Table 1 The properties of NiZn ferrite sintered at 930 °C and 1200 °C respectively

Sintering temperature (°C)	Density (kg/m³)	Initial permeability (Frequency: 10 kHz)	Relative loss factor ($\tan\delta/\mu_i$)	
			100 kHz	500 kHz
930	5.13	1700	9.0×10^{-6}	34.4×10^{-6}
1200	5.01	1684	16.4×10^{-6}	57.5×10^{-6}

than 1 MHz, because the spin rotation plays a relatively more important pole when the domain wall motion reduces. The frequency dispersion matches well with that reported in previous works (Caltun *et al.*, 2002; Nakamura, 1997). Moreover, the ferrite sintered at 930 °C possesses higher permeability at 1 MHz and lower cut-off frequency than that sintered at 1200 °C. So the ferrite sintered at 930 °C is more suitable for preparing RF elements.
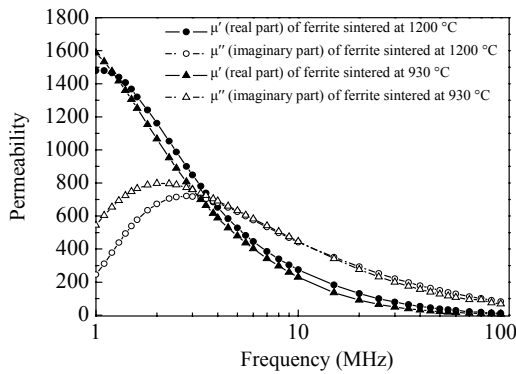

Fig.3 Permeability spectra of ferrites sintered at 930 °C and 1200 °C respectively

It is well known that the permeability of polycrystalline ferrite can be described as the superposition of two different magnetizing mechanisms: spin resonance and domain wall motion (Tsutaoka *et al.*, 1995), which can be described as follows:

$$\mu = 1 + \chi_w + \chi_{spin} \qquad (1)$$

where μ is permeability; χ_w is domain wall susceptibility; χ_{spin} is intrinsic rotational susceptibility.

χ_w and χ_{spin} may be written as $\chi_w = 3\pi M_s^2 D / 4\gamma$ and $\chi_{spin} = 2\pi M_s^2 / K_u$ with M_s saturation magnetization, K_u the total anisotropy, D the grain diameter, and γ the wall energy.

Moreover, Kondo *et al.*(2000) divided the total loss of the NiZn ferrite (P_{cv}) into loss factors that are attributed to domain wall motion (P_w) and rotation magnetization (P_{rot}).

$$P_{cv} = P_w + P_{rot} \qquad (2)$$

And P_w contains not only a loss factor due to static motion of the domain wall, which represents the motion of the domain wall originated from the quasi-static magnetic field, but also dynamic one for

NiZn ferrite, which resulted from the lag of domain wall motion to the measuring magnetic field. So it can be separated as follows (Kondo, 1999):

$$P_w = P_h + P_{wd} \qquad (3)$$

where P_w is the loss due to domain wall motion; P_h is the hysteresis loss due to static motion of the domain wall; P_{wd} is the loss factor attributed to the dynamic movement of domain wall.

Nakamura (1997) and Jankovskis (2000) indicated that the permeability was related to two different magnetizing mechanisms: the spin rotational magnetization and the domain wall motion. Furthermore, the magnetizing mechanism is mainly attributed to the domain walls motion in the frequency range less than 500 kHz. So P_w is predominant in P_{cv}. Particularly, the hysteresis P_h is much more than others in 100 kHz. Therefore, the initial permeability will increase and loss will decrease with the increase of domain motion. As known, domain walls motion can be enhanced with more uniform and bigger grain size as well as increase in the sintering density (Yamada and Ossuki, 1997; Stoppels, 1996). So higher density as well as more uniform and bigger grain favors increase in initial permeability and decrease in loss. Although more Cu^{2+} and V^{2+} entered into the lattice of the ferrite sintered at 930 °C, which diluted the M_s of ferrite and adversely affected the increase in permeability, it had higher permeability and lower loss due to the enhancement of the domain wall motion originated from the higher density as well as more uniform and bigger grain.

CONCLUSION

Ferrite with composition of $(Ni_{0.17}Zn_{0.63}Cu_{0.20})$ $Fe_{1.915}O_4$ and sintered at temperature of 930 °C had initial permeability of 1700 and relative loss coefficient $\tan\delta/\mu_i$ of 9.0×10^{-6} at 100 kHz, due to the appropriate addition of CuO/V_2O_5 and the decrease in granularity of raw materials particle.

In comparison with conventional ceramic technique, the low temperature preparation technique uses less NiO content, calcining and sintering temperature. So using the low temperature sintering method produced the novel NiZn ferrite having higher perme-

ability together with much lower sintering temperature.

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