Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1409–1412
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Sintering behavior and electromagnetic properties of Fe-deficient NiZn ferrites

Xinhua He *, Zhide Zhang, Zhiyuan Ling

Key Lab of Specially Functional Materials, Ministry of Education, Department of Electronic Materials Science & Engineering, South China University of Technology, Guangzhou, 510640, People's Republic of China

Received 9 January 2007; received in revised form 10 February 2007; accepted 26 March 2007
Available online 17 May 2007

Abstract

Sintering behavior and electromagnetic properties of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3/2x}$ ferrite (x = 0, 0.4, 0.8) by the sol–gel method are investigated. Fe deficiency in the composition enhances sintering and retards grain growth. The near fully dense Fe-deficient samples could be obtained at a sintering temperature as low as 1120 °C and the highest relative density appears in the x = 0.8 sample sintered at 1150 °C. Second phase zincite ZnO resulting from Fe deficiency plays an important role in spinel NiZn ferrites by acting as a grain growth inhibitor and the grain growth of NiZn ferrite is effectively suppressed. When the sintering temperature is above 1200 °C, extensive grain growth occurs due to the probability of serious volatilization of zinc at high temperatures. The ratio of Ni to Zn of NiZn ferrites increases with increasing Fe deficiency due to the separation of zinc from spinel lattice, which results in the decrease in initial permeability and the increase in Curie temperature and resonant frequency.

Keywords: A. Sintering; Non-stoichiometric ferrite; Sol–gel preparation; Iron deficiency

1. Introduction

NiZn ferrites are among the most widely used soft magnetic materials for high frequency applications due to their high electrical resistivity and low losses [1,2]. The small amount of iron deficiency in the composition of ferrites can increase the electrical resistivity further by reducing the amount of Fe^{2+} ions and inhibiting electron hopping between Fe^{2+} and Fe^{3+} ions at the octahedral sites of the spinel unit cell. It can also enhance the sintering and densification of NiZn ferrites [3]. Compared with stoichiometric and excess-iron ferrites, large Fe-deficient NiZn ferrites have relatively dense and uniform microstructure, fine grain size, improved temperature stability and frequency characteristics [4].

The electrical and magnetic properties of ferrites are strongly dependent on the purity of ferrite powder, the microstructure and grain boundary chemistry [5,6]. The occupation of cations in the different magnetic sublattices would be affected by the preparation technique, leading to changes in the magnetic properties [7]. The preparation technique is very important in tailoring microstructure and the properties of ceramics. The investigation on large Fe-deficient NiZn ferrites fabricated by the conventional mixed oxide method shows that NiZnO halite is formed as a second phase when the compositions in spinel deviate from stoichiometric ratio of cations to anions being 3/4 [4], whereas ZnO zincite exists in the grain boundary in annealed sol–gel powders [8].

The sol–gel process has been shown to be capable of the fabrication of NiZn ferrites and their composites with high purity, ultrafine, high chemical homogeneity [9,10]. Such wet chemical method has proved to be one of the most effective routes to decrease the sintering temperature of ferrites. However, studies on Fe-deficient NiZn ferrites are extremely scarce and iron content in composition is one of the most important factors to determine the electrical and magnetic properties of ferrite [8,11,12]. How to reduce the agglomeration in the nano-powders and the grain size in the sintered products in order to keep a high initial permeability and stable permeability variation with temperature is still a tough challenge.

The sintering behavior of nanomaterials is also a big problem because the advantages of the homogeneity and particle size have not been completely translated into improved properties in

* Corresponding author. Tel.: +86 20 87111224; fax: +86 20 87111224.
E-mail address: imxhhe@scut.edu.cn (X. He).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.03.031

sintered products, due to the difficulty in obtaining a nanocrystalline structure in the dense ceramic. In this paper, we synthesize Fe-deficient NiZn ferrite by means of a sol–gel method, and investigate the effect of Fe deficiency on sintering behavior and electromagnetic properties of NiZn ferrites.

2. Experimental procedure

The basic compositions of the ferrites were $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3/2x}$, with $x = 0$, 0.4, 0.8. Analytical grade nickel acetate ($Ni(CH_3COO)_2{\cdot}4H_2O$), zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) were dissolved in distilled water, respectively and evenly mixed. Citrate acid and ethylene glycol were added as ligands. The solution was refluxed at 75 °C for 6 h to form viscous sols and then dehydrated at 80 ± 5 °C in a vacuum oven. The dried gels were transformed into the powders after being heat-treated at 700 °C for 3 h in air.

The de-agglomerated powders were obtained by planetary ball milling in 2-propanol for 4 h with ∅1.5 mm ZrO_2 balls as grinding media. Polyvinylalcohol (2.5 wt.%) was dissolved in deionized water and mixed with the NiZn ferrite. Suitable amount of ammonium polyacrylate was added as dispersants. The powders were pressed into pellets and toroids, and were sintered in air at temperatures between 650 and 1400 °C for 3 h at same heating rate.

Densities of sintered samples were determined by the Archimedes method. The microstructures of the sintered samples were examined using scanning electron microscopy. Average grain sizes were determined by the mean linear intercept method. The values of initial permeability μ_i, Q-factor and Curie temperature were measured using a HP4194A impedance/gain analyzer. Resonant frequency was determined by a HP4291B RF impedance analyzer.

3. Results and discussion

3.1. Densification and grain growth

Initial densification behavior of the $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3/2x}$ ferrites is studied. Fig. 1 shows the linear shrinkage of NiZn ferrites as a function of temperature. All samples display similar behavior. The non-stoichiometric samples (the amount of Fe deficiency $x = 0.4$ and 0.8) exhibit slightly larger shrinkage and earlier densification temperature than the stoichiometric samples ($x = 0$). This indicates that Fe deficiency enhances initial densification process. Densification of the compacts at the initial stage of sintering can be expressed by the following equation [13]:

$$\left(\frac{\Delta L}{L_0}\right)\frac{1}{T} = A_0 \exp\left(-\frac{kQ}{RT}\right) \quad (1)$$

where $\Delta L/L_0$ is the linear shrinkage (%), T the temperature (K), Q the activation energy (kJ/mol), and R is the ideal gas constant (J/mol K). A_0 is the constant, and another constant, k, is dependent on sintering mechanism. Fig. 2 shows the curves of $\ln[(\Delta L/L_0)/(1/T)]$ versus $1/T$. The value of $\ln[(\Delta L/L_0)/(1/T)]$ varies linearly with $1/T$ when only one single mechanism is operative. As reported in Refs. [13,14], grain boundary diffusion is likely to be predominant at the initial sintering stage of such system since volume diffusion does not accompany shrinkage.

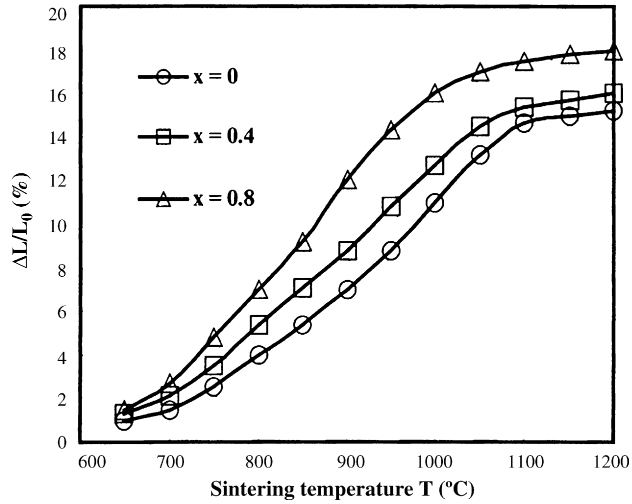

Fig. 1. Linear shrinkage $\Delta L/L_0$ (%) of sintered samples as a function of sintering temperature.

By assuming that grain boundary diffusion is predominant ($k = 1/3$), the activation energies, estimated from Fig. 2, for the amount of Fe deficiency $x = 0$, 0.4, 0.8 samples, are 203, 195, 193 kJ/mol, respectively.

The variation in relative density as a function of amount of Fe deficiency and sintering temperature is shown in Fig. 3. Fe deficiency enhances sintering and results in the improvement of densification. Relative density of NiZn ferrites increases with the increase of temperature and Fe deficiency. The highest relative density (95.5%TD) appears in the $x = 0.8$ sample sintered at 1150 °C. The densification temperature is lower for Fe-deficient ferrites. For $x = 0.4$ and 0.8 samples, the highest relative density has been approached when sintered at 1120 °C and the relative density of ferrites begins to decrease when sintering temperature is above 1200 °C.

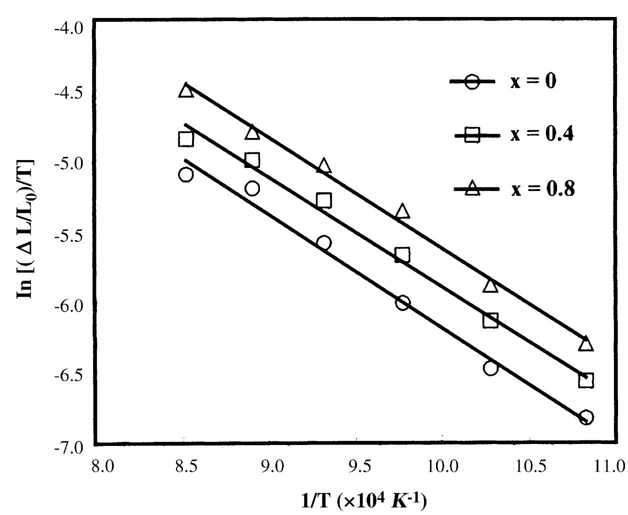

Fig. 2. Curves of $\ln[(\Delta L/L_0)/(1/T)]$ vs. $1/T$.

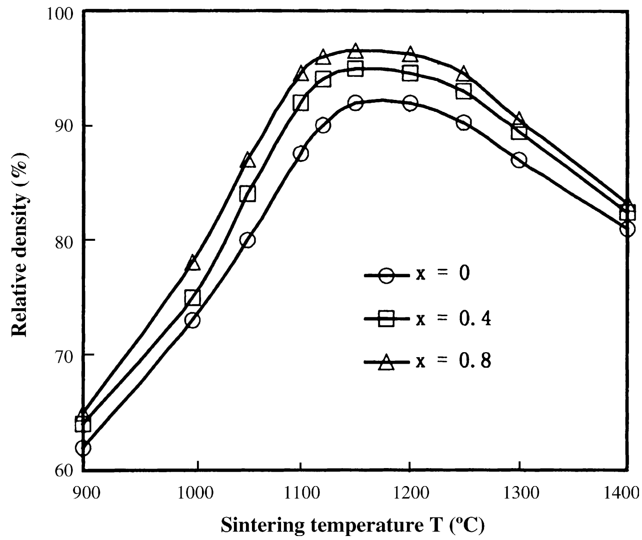

Fig. 3. The variation in relative density as a function of amount of Fe deficiency and sintering temperature.

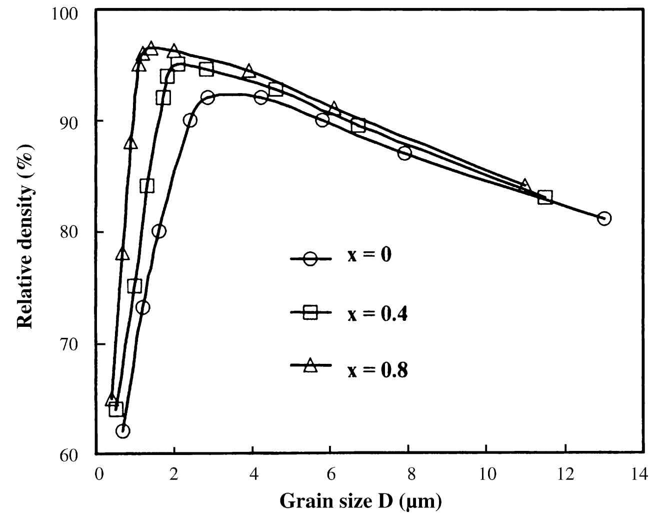

Fig. 5. Dependence of relative density as a function of grain size of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3x/2}$ ferrites.

Fig. 4 shows the variation of grain size with sintering temperature in NiZn ferrites. Grain sizes increase with increasing sintering temperature. Grain growth varies with the amount of Fe deficiency. Grain grows rapidly in the $x = 0$ sample over the whole temperature regime. In the Fe-deficient samples, the grain grows slowly when the sintering temperature is lower than 1200 °C; the grain grows considerably when the sintering temperature is higher than 1200 °C. Comparing Figs. 3 and 4, it can be seen that although the $x = 0.4$ and $x = 0.8$ samples have nearly densified when the temperature is between 1120 and 1200 °C, the grain does not grow rapidly. This result is incomparable with the accepted sintering theories in which the grain would grow quickly during the final sintering stage. One possible reason may be that second phase zincite ZnO along the grain boundary plays an important role in NiZn ferrites by acting as a grain growth inhibitor and the grain growth of NiZn ferrite is effectively suppressed [8]. When the sintering temperature is above 1200 °C, extensive grain growth occurs, which is attributed to the serious evaporation of zinc.

It can also be observed in Fig. 4 that the sample sintered at lower temperatures (<1120 °C) presents a very narrow grain size spread as a result of the fine granulation. The increase in grain size spread is observed, particularly at higher sintering temperatures (>1200 °C). Grain size spread decreases with increasing Fe deficiency, which suggests that the uniformity of grain size be improved. For nanocrystalline materials, the driving force for coarsening is high, because of the high surface area. Grain growth can be hindered by a narrow size distribution.

The relationship between relative density and grain size is shown in Fig. 5. Highest density can be obtained in the large Fe-deficient sample with fine crystalline microstructure. The rapid grain growth in high temperatures hinders the migration of the pore to the grain boundary, which contributes to the reduction of the sintered density.

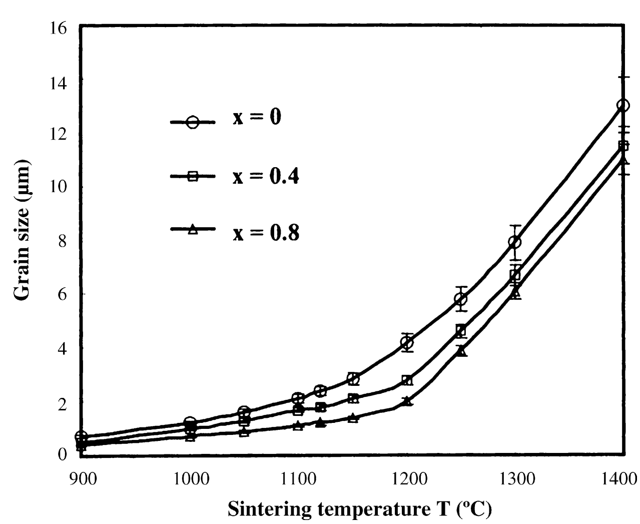

Fig. 4. Grain size and grain size spread of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3x/2}$ ferrites as a function of sintering temperature.

3.2. Electromagnetic properties

Table 1 shows the electromagnetic properties of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3x/2}$ ferrites as a function of the amount of Fe deficiency.

The initial permeability decreases drastically with increasing Fe deficiency. Q value and insulating resistivity ρ_V increase slightly. Curie temperature increases obviously from 195 to 232 °C and resonant frequency increases from 65 to 91 MHz when Fe-deficient content x in the composition varies from 0 to 0.8.

It is well known that the electric and magnetic characteristics of ferrites, such as initial permeability, Q-factor, Curie temperature, and insulating resistivity, depend on grain size, porosity, chemical composition and the second phases in grain boundary [15]. Fe content deviation from the stoichiometric composition results in the formation of zincite phase in grain boundary [8]. The occurrence of zincite crystallites suppresses

Table 1
Electromagnetic properties of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3x/2}$ ferrites as a function of the amount of Fe deficiency

The amount of Fe deficiency, x	Initial permeability at 25 °C at 1 MHz, $\mu_{i25^{\circ}C,1\ MHz}$	Q-factor at 25 °C at 1 MHz, $Q_{25^{\circ}C,1\ MHz}$	Curie temperature, T_C (°C)	Insulating resistivity, ρ_V (Ω m)	Resonant frequency, f_r (MHz)
0	141	75	195	2.2×10^7	65
0.4	122	84	217	4.5×10^7	78
0.8	105	89	232	7.3×10^7	91

the grain growth of NiZn ferrites. It is apparent that zincite plays an important role in NiZn ferrites by acting as a grain growth inhibitor. However zincite is a non-magnetic phase which will have a detrimental effect on magnetic properties by acting as a pinning point that limits domain wall motion and also by producing internal stress in its vicinity. Fine grain size and non-magnetic zincite phase result in the decrease in initial permeability. However, in this study, another main factor influencing the initial permeability and other parameters may be the variation in chemical composition of ferrites—the increase in the ratio of Ni to Zn in the NiZn ferrites due to the separation of zinc from the spinel lattice due to Fe deficiency [8], which results in the decrease in initial permeability and the increase in Curie temperature and resonant frequency.

The resistivity increases slightly with increasing amount of Fe deficiency, which may be mainly attributed to the decrease in Fe^{2+} in the ferrite. Fine grain microstructure with highly dislocated large area of grain boundary contributes to high resistivity ferrites. Low sintering temperature may be another contribution to the high resistivity too. The resistivity is at the order of 10^7 Ω m.

4. Conclusions

The effect of Fe deficiency in the composition on sintering and electromagnetic properties of $Ni_{0.5}Zn_{0.5}Fe_{2-x}O_{4-3/2x}$ ferrite ($x = 0$, 0.4, 0.8) is investigated. These powders have good sinterability and the samples can be sintered at around 1150 °C. Relative density of NiZn ferrites increases with increasing temperature and Fe deficiency. Grain size and grain size spread increase with increasing temperature. Fe deficiency results in slow grain growth and narrow grain size spread when the sintering temperature is below 1200 °C. When the sintering temperature is above 1200 °C, the grain grows rapidly due to the serious evaporation of zinc.

The amount of Fe deficiency affects the electromagnetic properties of NiZn ferrites. Fe deficiency results in the variation in chemical composition and microstructure of NiZn ferrites. The decrease in initial permeability and the increase in Curie temperature and resonant frequency with increasing Fe deficiency are due to the increase in the ratio of Ni to Zn derived from the separation of zinc from spinel lattice.

Acknowledgement

This work is supported by the Natural Science Foundation of Guangdong Province under grant number 000536.

References

[1] P.S. Anil Kumar, J.J. Shrotri, S.D. Kulkarni, C.E. Deshpande, S.K. Date, Mater. Lett. 27 (1996) 293.
[2] Y. Matsuo, M. Inagaki, T. Tomozawa, F. Nakao, IEEE Trans. Magn. 37 (2001) 2359.
[3] A. Glubus, R.V. Monjaras, IEEE Trans. Magn. 11 (1975) 1300.
[4] Z. Ling, M. Xiong, Q. Zhang, J. Magn. Magn. Mater. 219 (2000) 9.
[5] A. Verma, T.C. Goel, R.G. Mendiratta, M.I. Alam, Mater. Sci. Eng. B 60 (1999) 156.
[6] R. Hochschild, H. Fuess, J. Mater. Chem. 10 (2000) 539.
[7] C. Surig, K.A. Hempel, Ch. Sauer, J. Magn. Magn. Mater. 157/158 (1996) 268.
[8] X. He, G. Song, J. Zhu, Mater. Lett. 59 (2005) 1941.
[9] K.H. Wu, H.Y. Li, C.C. Yang, H.B. Chen, Appl. Surf. Sci. 228 (2004) 285.
[10] K.H. Wua, T.H. Tinga, M.C. Lia, W.D. Ho, J. Magn. Magn. Mater. 298 (2006) 25.
[11] K.O. Low, F.R. Sale, J. Magn. Magn. Mater. 246 (2002) 30.
[12] R.V. Mangalaraja, P. Manohar, F.D. Gnanam, J. Mater. Sci. 39 (2004) 2037.
[13] G.S.A.M. Theunissen, A.J.A. Winnubst, A.J. Burggraaf, J. Eur. Ceram. Soc. 11 (1993) 315.
[14] H. Mostaghaci, R.J. Brook, Trans. J. Br. Beram. Soc. 82 (1983) 167.
[15] D. Jiles, Introduction to Magnetism and Magnetic Materials, Chapman & Hall, London, 1995, p. 47.