Effect of Calcination Temperature on Magnetic Properties of MnZn Ferrites for High Frequency Applications

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With the development of switching power supplies, miniaturization and high efficiency become hot research issues, and decreasing high-frequency losses is an effective method to achieve it. In this article, the effect of different calcination temperature on the power losses of MnZn ferrites at high frequency (500 kHz) over a broad temperature range is reported. The MnZn ferrites samples were prepared by ceramic process and the effect of calcination temperature was analyzed. The raw materials were calcined at 775 ℃, 800 ℃, 825 ℃, 850 ℃, 875 ℃, 900 ℃, 925 ℃ and 950 ℃, and the regular fluctuations of particle size (as-calcined), density (as-sintered) and magnetic properties are presented in this work. It is shown that the samples calcined at 850 ℃ exhibit optimal microstructure and magnetic properties. The newly developed MnZn ferrites are characterized by sintered density of 4.61 g/cm$^3$, initial permeability of 1223 (10 kHz/0.1 mT/25 ℃), saturation magnetic flux density of 488 mT (10 kHz/1200 A/m/25 ℃) and power losses of 68 mW/cm$^3$ (500 kHz/50 mT/100 ℃).

Keywords: calcination, pressing, MnZn ferrites, magnetic properties

1. Introduction

MnZn ferrites material ($\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$) is one of the most important soft ferrites due to its high initial permeability, high saturation magnetization, high resistivity and low power losses. Besides, the excellent performances including controllable size and structural features, easy synthesis process and tunable electromagnetic properties [1-3] cater the needs of modern electric devices. Subsequently, MnZn ferrites are applied in various applications including inductors, transformers and absorbers, electronic or telecommunication equipment, defense and the automotive [4]. Consequently, it is crucial for the advance of modern electronic device to develop MnZn ferrites. High frequency, miniaturization and high efficiency are significant characteristics for the next generation electronic devices, which require magnetic components possessing excellent high-frequency performances [5-7]. Moreover, the preparation techniques play a vital role in enhancing the magnetic properties of MnZn ferrites, however, calcination is an especially significant process. The purpose of the calcination is to form a small quantity of spinel structure and promote particle shrinkage, which is the important basis of sintering process. Furthermore, calcination is beneficial to achieve proper grain size, homogenize microstructure of as-sintered and finally improve its magnetic properties. In this work, different calcination temperatures were adopted to investigate the effect on magnetic properties and high-frequency performances.

2. Experimental details

2.1. Experimental procedure

The present work was carried out on MnZn ferrites with the chemical composition of $\text{Fe}_2\text{O}_3:\text{MnO}\cdot\text{ZnO} = 55.7:38.8:6.2$ (mol%), which was fabricated with the conventional solid state reaction process shown in Fig. 1. $\text{Fe}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$, and $\text{ZnO}$ were mixed for 1 h in deionized water and dried 16 h at 115 ℃. The mixtures were calcined in air at various temperatures for 2 h ($T_{\text{CALC}}$: 775 ℃ to 950 ℃) and then sintered at 1150 ℃ for 2 h. The as-calcined samples were further wet-pulverized in a ball mill for 1.2 h, dried and subsequently roll-oftened with the addition of a plasticizer (10 wt.% aqueous solution of polyvinyl alcohol) through spraying method. Subsequently, the granulated samples were pressed twice under axial compaction (5
MPa) to get toroidal samples (outer/inner diameter: 30 mm/17 mm/10 mm), and sintered at 1150 ℃ for 22 h using a specially constructed programmable kiln with firing schedules under equilibrium oxygen partial pressure conditions to ensure the stability of phases due to the equilibrium relation between oxygen partial pressure and temperature [8].

2.2. Characterize methods

The phases of the as-calcined and as-sintered samples were analyzed by X-ray diffraction. The XRD data were taken from 10° to 80° (0.02° step in 2θ) with Cu-Kα (λ = 1.54059 Å) radiation. Raman spectra were recorded by a laser Raman spectrophotometer (Renishaw in Via Reflex) equipped with a CCD camera with a laser of 785 nm over the range of 100-800 cm⁻¹. Furthermore, the powders (as-calcined) were characterized in terms of the distribution of particle size with laser diffraction method (Malvern Mastersizer-S). The density of as-sintered samples was measured by Archimedes' method. Polycrystalline micro-structures of cross section of as-sintered samples were characterized by Scanning Electron Microscopy (SEM-Jeol 6300). The saturation magnetic flux density and power losses were measured by Iwatsu B-H analyzer (SY8232), and initial permeability was measured by Impedance analyzer (Agilent 4294A). Lakeshore Model 7404 vibrating sample magnetometer (VSM) was used for saturation magnetization measurement.

3. Results and Discussion

Fig. 2 shows the XRD patterns of powders calcined at different temperature (775 ℃, 800 ℃, 825 ℃, 850 ℃, 875 ℃, 900 ℃, 925 ℃ and 950 ℃) and as-sintered samples. According to the analysis of the Fig. 2a, as-calcined samples mainly consist of α-Fe₂O₃ (JCPDS No.33-0664), Mn₃O₄ (JCPDS No.71-0636), and a small quantity of ZnFe₂O₄ (JCPDS No.65-3111). The valence of Zn ion is +2, thus, ZnFe₂O₄ is easily formed in air atmosphere. Obviously, there is no MnFe₂O₄ formed after calcination due to the O₂ in air. It is known that Mn₃O₄ contains two kinds of valence of +2 and +3, and the Mn²⁺ is easily
oxidized into Mn$^{3+}$ by $O_2$. Consequently, the peak of MnFe$_2$O$_4$ is not shown in XRD patterns of as-calcined samples. MnFe$_2$O$_4$ phase is formed after sintering in protection atmosphere of $N_2$ shown as spinel phase in Fig. 2b. The comparison results of as-calcined and as-sintered samples are presented in Fig. 2c, which confirms the formation of pure spinel phase.

Besides, the Raman spectra were recorded at 300 K in the frequency range from 100 to 800 cm$^{-1}$ for further confirmation of the results of XRD analysis in Fig. 3 [4, 9, 10]. Fig. 3 shows the Raman spectra of as-calcined (775 °C, 850 °C, 900 °C, and 950 °C) and as-sintered samples. The Raman spectra demonstrate that α-Fe$_2$O$_3$ peaks ($A_{1g} = 224$ cm$^{-1}$, $E_g(2) = 290$ cm$^{-1}$ and $E_g(4) = 400$ cm$^{-1}$) are detected in the as-calcined samples in Fig. 3a. In addition, three distinct characteristic peaks ($T_{2g}(2) = 325$ cm$^{-1}$, $T_{2g}(3) = 443$ cm$^{-1}$ and $A_{1g} = 622$ cm$^{-1}$) are observed in all spectra, and $E_g$ and $T_{2g}(1)$ at the range from 100 to 200 cm$^{-1}$ are ambiguous. However, it is still illustrated that pure cubic spinel structure of AB$_2$O$_4$ is formed in as-sintered samples. These results are well corroborated with XRD data.

Fig. 4 shows the distribution of particle size of as-calcined samples. The particle size increases significantly with calcination temperature ($T_{CALC}$) according to the variety of $D_v$ and SMD (Fig. 4). Meanwhile, The SEM micrographs, shown in Fig. 5, demonstrate that the microstructure of as-sintered samples is improved at proper $T_{CALC}$. It is observed that the initial increase of $T_{CALC}$ from 775 °C to 850 °C yields the gradual expansion of the grains of the as-sintered samples and remarkable reduction of intergranular pores, which also confirms that the low $T_{CALC}$ leads to low reactivity. Below 850 °C, the microstructure becomes more uniform with the increase of $T_{CALC}$, shown in Fig. 5. Consequently, the uniform microstructure leads to density improved, which exhibits an increase of respective sintered density ($D_S$) from 4.61 g/cm$^3$ to 4.69 g/cm$^3$ shown in Fig. 6. Further increase of $T_{CALC}$ (above 850 °C) favors the appearance of exaggerated grain growth leading to pores formed as shown in Fig. 5c and d. The further increase of $T_{CALC}$ trends to make the increase of concentration of Zn-rich ferrite phases formed in the as-calcined powders. Subsequently, the Zn-rich ferrite phases grow rapidly at the expense of other phases, however, Zn trends to evaporate during sintering [11]. Consequently, intergranular pores increase and $D_S$ decreases, as shown in Fig. 6. Besides, nucleation and growth would possibly release $O_2$. As the chemical equation shown [12]:

$$2F_{e}^{3+} + 3/4V_{c} + O_2 \rightarrow 2F_{e}^{2+} + 1/2O_2$$

Fe ions would combine with cation vacancies ($V_c$) in Fe-rich MnZn ferrites, which releases $O_2$ and makes

Fig. 3. (Color online) Raman spectra of MnZn ferrites, (a) as-calcined samples calcined at 775 °C, 850 °C, 900 °C and 950 °C, respectively; (b) as-sintered samples.

Fig. 4. (Color online) Particle size distribution of as-calcined samples.
porosity increased. High $T_{\text{calc}}$ makes (1) accelerated and pores are formed indirectly in bulk sample shown in Fig. 5. Therefore, optimal $T_{\text{calc}}$ is necessary for homogeneous microstructure.

Fig. 7 shows magnetization hysteresis loops of as-calcined samples ($T_{\text{calc}}$ = 775 °C, 800 °C, 825 °C, 850 °C, 875 °C, 900 °C, 925 °C and 950 °C). It is suggested that magnetization hysteresis loops are unsaturated and the coercivity ($H_c$) of as-calcined samples is large, however, MnZn ferrites are paramagnetic-like [13]. Consequently, the spinel structure is formed incompletely in as-calcined samples and $\alpha$-$\text{Fe}_2\text{O}_3$ is the main composition in as-calcined samples, which accords with XRD analysis (Fig. 2). As ref [13] reported, $\alpha$-$\text{Fe}_2\text{O}_3$ would cause magnetization hysteresis loop unsaturated. According to Fig. 7, the saturation magnetization ($M_s$) and residual magnetization ($M_r$) further increase with the
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T\textsubscript{CALC}. This is partly attributed to the increase of particle size.

Initial permeability ($\mu_i$), saturation magnetic flux density ($B_s$), and power losses ($P_{cv}$) of the prepared ferrites are measured respectively, which is the crucial parameters as a high-frequency inductive power converter. The $B_s$ of the samples measured at a magnetic field of 1200 A/m and 25 °C is shown in Fig. 8. According to the theory of ferrimagnetism, there are differences about resultant net magnetization between tetrahedral (A) and octahedral (B) sublattice in spinel ferrite [14]. Thus, due to the preserved magnetic structure and distribution of cationic in the lattice of the materials, $B_s$ should be mainly dependent on density ($D_a$). $B_s(T)$ is calculated by Eq. (2) and Eq. (3) [15]:

$$B_s(T) = B_s(0) \times (1 - T/T_C)^r \times D/D_1$$
$$B_s(0) = M_s(0) \times n \times \mu_0 \times N_a \times D_2/M$$

Here $B_s(T)$ is the magnetic flux density at T K, $B_s(0)$ is the magnetic flux density at 0 K, $\rho$ is the density of the ferrites core, $D$ is the actual density of ferrite, $D_1$ is the theoretical density of ferrite, $T_C$ is the Curie temperature (K), $r$ is a constant obtained by experiment, $M_s(0)$ is the magnetization at 0 K, $n$ is the Bohr magneton number, $N_a$ is the Advgadro’s number, $M$ is the molecular weight, and $D_2$ is the average density of ferrites. From Eq. (2), $B_s(T)$ is proportional to $D$ under certain test condition, which accords to Fig. 6. It is noticed that the samples calcined at 850 °C obtain the highest $D_a$ of 4.69 g/cm$^3$ and exhibit the highest $B_s$ of 488 mT (25 °C) and 407 mT (100 °C). The $B_s$ decreases with further increase of $T_{CALC}$, which is attributed to the decrease of density.

The initial permeability ($\mu_i$) and power losses ($P_{cv}$) of the toroids were measured under condition of 10 kHz/0.1 mT/25 °C and 500 kHz/50 mT/100 °C, respectively. The $\mu_i$ of as-sintered samples increases when $T_{CALC}$ increases from 775 °C to 850 °C, and decreases with further increase of $T_{CALC}$ (see Fig. 9). The maximum initial permeability is 1223 obtained at 850 °C due to the excellent microstructure with less pores (see Fig. 4) and high density (see Fig. 6). Since the initial permeability is proportional to the square of saturation magnetization and reversely proportional to anisotropy constant ($K$) and magnetostriction coefficient ($\lambda$), as described in Eq. (4) [16]:

$$\mu_i = M_s^2/(aK + b\lambda\sigma)$$

Where $\mu_i$ is initial permeability, $M_s$ is saturation magnetization, $K$ is magnetocrystalline anisotropy constant, $\lambda$ is magnetostricition coefficient, $\sigma$ is inner stress and $a, b$ are constants. It is concluded that the increase of the
initial permeability of as-calcined samples below 850 °C is attributed to the increase of $M_s$ and decrease of $\lambda$ and $K$ [17].

Fig. 10 shows the power losses measured at 500 kHz/50 mT/100 °C. Eddy current loss is the dominant part for core losses, is usually defined as [6]:

$$P_e = K_e f^2 B^2 / \rho \quad (5)$$

$K_e$ represents the coefficient of eddy current losses. $B$ represents the magnetic flux density, $f$ represents the frequency and $\rho$ represents the resistivity of the core. It is evident that $P_e \propto 1/\rho$. According to Verwey’s hopping mechanism [18], the electrical conduction of ferrite originates from electron hopping between the ions of the same element but of different valence states present at the octahedral (B-site). Electron hops between Fe$^{3+}$ and Fe$^{2+}$ ions ($\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+}$), which is hindered by additives to enhance the resistivity. Consequently, the minimum of $P_{cv}$ (100 °C) is obtained at 850 °C due to the homogeneous distribution of grain size and low porosity. Besides, uniform distribution of grain size is capable to make $\rho$ increased, and decrease $P_e$. These samples possess excellent high-temperature performance (low $P_{cv}$ at 100 °C), which stems from the value of magnetocrystalline anisotropy closing to zero at this temperature (100 °C) [16]. Then, the optimized power losses of 68 mW/cm$^3$ (500 kHz/50 mT/100 °C) are obtained.

4. Conclusions

In the present study, traditional ceramics technology is adopted due to its ease of operation and low cost. Subsequently, the effect of calcination temperature ($T_{\text{CALC}}$) in the range of 775 °C-950 °C on compaction and magnetic properties of MnZn ferrites ceramics is investigated. The positive correlation between the $T_{\text{CALC}}$ and the distribution of particle size is established and explained. According to our research, the samples calcined at 850 °C exhibit the optimal microstructure and best magnetic properties. The newly developed MnZn ferrites exhibit initial permeability of 1223, and power losses of 68 mW/cm$^3$ (500 kHz/50 mT/100 °C). Therefore, it is concluded that an optimal combination of compaction and magnetic properties is attained when $T_{\text{CALC}}$ is 850 °C. Consequently, it is necessary for MnZn ferrites manufacture to choose an appropriate $T_{\text{CALC}}$ because of its sensitivity of process.

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References