

Effect of TiO₂ and Nb₂O₅ additives on the magnetic properties of cobalt-modified MnZn ferrites

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Abstract Cobalt-modified manganese–zinc (MnZn) power ferrites with good thermal stability were prepared by conventional ceramic technique. The influences of TiO₂ and Nb₂O₅ additives on the properties of cobalt-modified MnZn power ferrite were investigated. It was shown that moderate amount of TiO₂ and Nb₂O₅ additives could increase the permeability and reduce the power loss effectively while keeping the better thermal stability of cobalt-modified MnZn ferrite. The best magnetic properties were obtained at addition amount of 0.03 wt% TiO₂ and 0.02 wt% Nb₂O₅ with an initial permeability (μ_i) of 3200 at room temperature and power loss keeping below 400 kW/m³ from 20 to 100 °C. The related mechanisms were briefly discussed.

1 Introduction

Owing to high permeability, high saturation magnetic flux density and low power loss, MnZn ferrite are widely used as core materials for transformers in switching mode power supplies and DC–DC converters [1]. However, the power loss of most MnZn ferrites usually exhibits a minimum under a specific temperature [2]. The power loss increases quickly once the temperature deviates from the specific value, which will greatly influence the stability of the devices. Therefore, development of power ferrite materials with thermal stability is especially important.

In the past several decades, a variety of techniques have been developed to improve the electronic and magnetic

properties of MnZn ferrites. One of the most effective methods is doping small amount of additives [3–6]. Currently, the effects of single oxide (SiO₂, Bi₂O₃, TiO₂, Nb₂O₅, SnO₂, Co₂O₃, et al.) on the magnetic properties of power MnZn ferrites have been systematically studied [7–13]. Among these oxides, Co₂O₃ is considered to be an effective additive in optimizing the temperature stability of MnZn ferrites [6]. However, it was found that the initial permeability reduced and power loss increased with the increase of Co₂O₃ concentrations in most studies [7, 8]. In order to acquire the MnZn ferrites with high initial permeability, low power loss and good thermal stability simultaneously, further works still need to be done.

On the other side, researchers have identified several oxides that could effectively improve initial permeability and reduce power loss. Yu and his co-workers have revealed that moderate Nb₂O₅ could improve initial permeability and reduce power loss [3]. Nie and his partners have obtained the MnZn ferrites with low power loss by doping moderate TiO₂ [10]. Based on these results, it is reasonable to predict that low power loss, high permeability and good thermal stability could be simultaneously obtained in the MnZn ferrites by doping multiple oxides. In this paper, moderate amount of TiO₂ and Nb₂O₅ additives were doped into the cobalt-modified MnZn power ferrite. The influences of Nb₂O₅ and TiO₂ on the properties of cobalt-modified MnZn ferrite were studied.

2 Experimental

A series of MnZn power ferrite samples adopted with a basic composition (Mn_{0.673}Zn_{0.246}Fe_{2.073}Co_{0.006}O₄) were prepared by traditional ceramics process. The raw materials were weighed according to the stoichiometric ratio, with

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Fe₂O₃ (99.36 %), Mn₃O₄ (98.86 %), ZnO (99.73 %), Co₂O₃ (99.9 %) as starting materials.

The raw materials were wet mixed in deionized water via ball milling for 2 h. Then, the mixtures were dried at 100 °C and calcined at 900 °C in air for 2 h. After that, small amount of TiO₂ and Nb₂O₅ additives were doped into the mixtures (shown in Table 1) and then the mixed powders were ball milled for 4 h. After drying at 100 °C, the mixed powders were pressed (8 MPa) into the toroid specimens (22 mm outside diameter, 14 mm inner diameter, and 7 mm height) with 5–8 wt% of poly-vinyl alcohol (PVA). Finally, the specimens were sintered for 4 h at 1320 °C under controlled equilibrium oxygen partial pressure in bell-type furnace.

The mass densities of the specimens were measured by the Archimedes method and the fracture surface microstructures of the specimens were examined by scanning electron microscopy (SEM, JSM-6460). The initial permeability ($f = 1$ kHz, $B < 0.25$ mT) of samples was measured at room temperature on a HP2874 LCR meter, and the power loss(100 kHz, 200 mT) of the samples was measured by Clarke-Hess 2335 power analysis at different temperature.

3 Results and discussion

Table 2 shows the initial permeability of cobalt-modified MnZn ferrites with different amount of TiO₂ and Nb₂O₅ additives. As can be seen, all the samples with additives exhibit higher initial permeability than the one without additives. For the MnZn ferrite without any additives, the initial permeability is only about 2817(Sample T₁). The initial permeability increases to 2900 once the concentrations of TiO₂ and Nb₂O₅ additives are increased to 0.02 wt% respectively. The highest value of initial permeability (3200) is obtained at the additive amounts of 0.03 wt% TiO₂ and 0.02 wt% Nb₂O₅. However, further increasing the concentrations of additives leads to the decrease of the initial permeability.

The variation of the initial permeability is considered to be strongly related to the microstructures. Figure 1 shows the SEM micrographs of MnZn ferrites with different concentration of TiO₂ and Nb₂O₅. As can be observed, the non-uniform grains with a lot of pores appeared in the

Table 2 Effect of TiO₂ and Nb₂O₅ doped different amounts on the initial permeability and density of MnZn ferrites

Sample	T ₁	T ₂	T ₃	T ₄	T ₅
Density (g/cm ³)	4.75	4.84	4.85	4.89	4.87
Initial permeability	2817	2904	2956	3200	3102

sample without TiO₂ and Nb₂O₅ additives (Fig. 1a). Comparing with the samples without additives, the grains become more homogeneous and the porosity reduces in the sample with the concentrations of TiO₂ and Nb₂O₅ of 0.02 and 0.02 wt% respectively (Fig. 1b). When the concentrations of the TiO₂ and Nb₂O₅ are increased to 0.03 and 0.02 wt% respectively, the sample shows the lowest porosity and exhibits the most uniform microstructures (Fig. 1c). As known, the permeability is a superposition of magnetic domain twirl and domain wall displacement [7]. It has been reported that both the non-uniform grain size distribution and pores in the grain will greatly influence the twirl of magnetic domain and the displacement of domain walls, which will lead to the decrease of the initial permeability [1, 7]. Therefore, it is reasonable that moderate amount of TiO₂ and Nb₂O₅ can effectively raise the initial permeability by inducing more uniform microstructures and decreasing the porosity. Correspondingly, the decrease of the initial permeability in the sample with further increased concentrations of TiO₂ and Nb₂O₅ is acceptable as many abnormal grains with some pores appeared (Fig. 1d), which will restrict the magnetic domain twirl and domain wall displacement.

Moreover, the initial permeability (μ_i) is also closely related to the magnetic anisotropy constant K_1 [14]. The lower the $|K_1|$ is, the higher the initial permeability is. As the K_1 of MnZn ferrites is negative, moderate amount of additives with positive magnetic anisotropy constant are needed. However, the magnetic anisotropy constant K_1 of Ti⁴⁺ and Nb⁵⁺ ions equal 0, as both of them are non-magnetic ions. Therefore, the variation of the initial permeability can not be directly described to the additives of TiO₂ and Nb₂O₅. Nevertheless, it has been confirmed in the previous studies that although most of the Ti⁴⁺ and Nb⁵⁺ ions exist on grain boundaries, small amount of Ti⁴⁺ and Nb⁵⁺ ions can also dissolve into the spinel lattice and replace the Fe³⁺, inducing an amount of Fe²⁺ for keeping neutral ($Fe^{3+} + e \rightarrow Fe^{2+}$) whose magnetic anisotropy constant K_1 is positive [11, 13]. Furthermore, according to the charge neutrality, Fe²⁺ ions must be increasing with the increase of Ti⁴⁺ and Nb⁵⁺ concentrations. Therefore, TiO₂ and Nb₂O₅ additives could indirectly increase the initial permeability by inducing moderate amount of Fe²⁺ ions to compensate the negative magnetic anisotropy constant of

Table 1 Different content of additives in MnZn ferrite

Sample	T ₁	T ₂	T ₃	T ₄	T ₅
TiO ₂ (wt%)	0	0.02	0.02	0.03	0.03
Nb ₂ O ₅ (wt%)	0	0.02	0.03	0.02	0.03

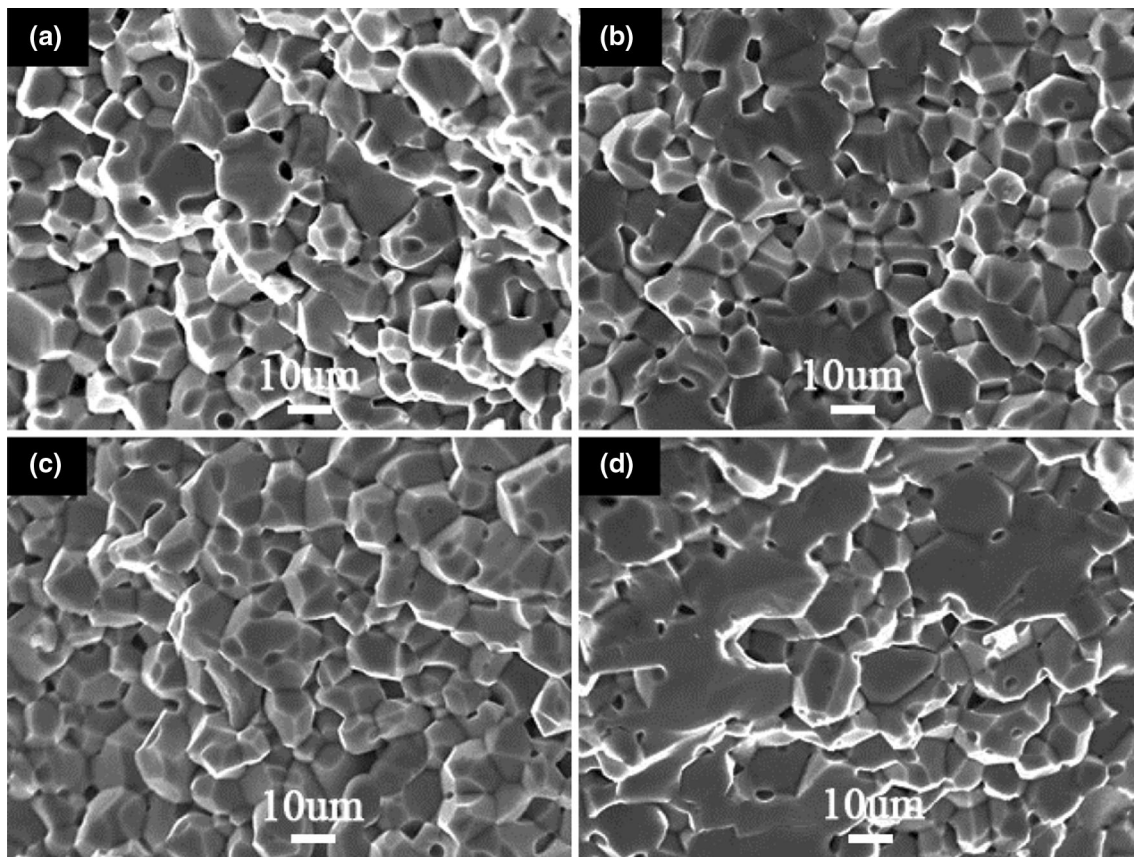


Fig. 1 SEM micrographs of MnZn ferrite with different contents of TiO_2 and Nb_2O_5 doped (a 0 wt% TiO_2 and 0 wt% Nb_2O_5 ; b 0.02 wt% TiO_2 and 0.02 wt% Nb_2O_5 ; c 0.03 wt% TiO_2 and 0.02 wt% Nb_2O_5 ; d 0.03 wt% TiO_2 and 0.03 wt% Nb_2O_5)

the MnZn ferrites. Correspondingly, further increasing of the TiO_2 and Nb_2O_5 will generate excess amount of Fe^{2+} ions, leading to the increase of $|K_1|$ of the MnZn ferrites and reducing the initial permeability.

Figure 2 shows the effect of TiO_2 and Nb_2O_5 additives on the power loss of MnZn ferrites. As shown, the power loss of all samples reduces firstly and then increases with increasing temperature, exhibiting typical power loss property of MnZn ferrite. The lowest loss point locates at the temperature between 60 and 100 °C. However, comparing with the MnZn ferrite without cobalt dopant, the power loss values of sample T₁ change more slightly in the measured temperature range [4, 17]. It suggests that the cobalt doped in the MnZn ferrites could effectively improve the thermal stability, which agrees well with previous studies [7]. The values of power loss reduce obviously with the increase of the TiO_2 and Nb_2O_5 additives. But the thermal stability does not change evidently with the increase of TiO_2 and Nb_2O_5 concentrations. The power loss of sample T₄ with 0.02 wt% Nb_2O_5 and 0.03 wt% TiO_2 reaches a minimum, which is less than the value of Ref. [11]. Further increasing the concentrations of Nb_2O_5 and TiO_2 leads to an increase of the power loss.

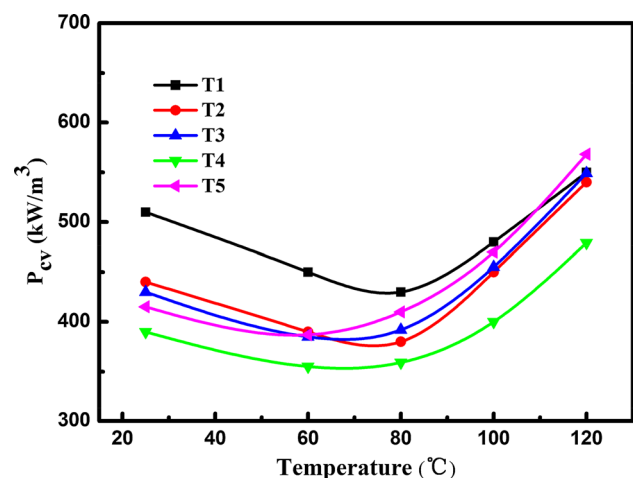


Fig. 2 The influence of TiO_2 and Nb_2O_5 doped amounts on the power loss (P_{cv}) of MnZn ferrites

As known, the total power loss (P_{cv}) of MnZn ferrites consists of three parts: magnetic hysteresis loss (P_h), eddy current loss (P_e) and residual loss (P_r). The residual loss (P_r) usually could be ignored under low frequency ($f < 500$ kHz), so the total power losses (P_{cv}) can be

expressed as $P_{cv} \approx P_h + P_e$ [15, 16]. The temperature dependence of magnetic hysteresis loss (P_h) and eddy current loss (P_e) with different concentrations of TiO_2 and Nb_2O_5 are presented in Figs. 3 and 4, respectively. It is clear that both the hysteresis loss and eddy current loss decrease with the increase of the concentrations of TiO_2 and Nb_2O_5 , and reach minima when the concentrations of TiO_2 and Nb_2O_5 are 0.03 and 0.02 wt%, then increase for higher TiO_2 and Nb_2O_5 concentrations.

The hysteresis loss (P_h) is inversely proportional to the cubic of initial permeability ($P_h \propto 1/\mu_i^3$). Similar to the initial permeability, it is considered to be closely related to the microstructure and magnetic anisotropy constant K_1 [17]. As shown in Fig. 1, the grains become more homogeneous and the porosity reduces in the sample with 0.03 wt% TiO_2 and 0.02 wt% Nb_2O_5 , which will lead to the magnetic domain swirl and domain wall displacement happen at lower magnetic field. The hysteresis loss will decrease as the reduction of the area of hysteresis loop. While for the sample with higher TiO_2 and Nb_2O_5 concentrations, the abnormal grains with pores will restrict the magnetic domain swirl and domain wall displacement and lead to the increase of the hysteresis loss [18]. On the other side, small amount of Ti^{4+} and Nb^{5+} entered the grains will lead to the increase of Fe^{2+} ions, which make positive compensation to the magnetic anisotropy constant K_1 . It also will lead to the decrease of the hysteresis loss [11, 13, 15, 16]. Similarly, the excessive TiO_2 and Nb_2O_5 will cause a higher concentration of Fe^{2+} ions, which leads to a positive K_1 value and increase the hysteresis loss. This may be the other reason for the variation of hysteresis loss.

The P_e is reported inversely proportional to the electrical resistivity and proportional to square of the average grain size ($P_e \propto D^2/\rho$) [16, 19]. As the grain size slightly increases with the increase of the TiO_2 and Nb_2O_5

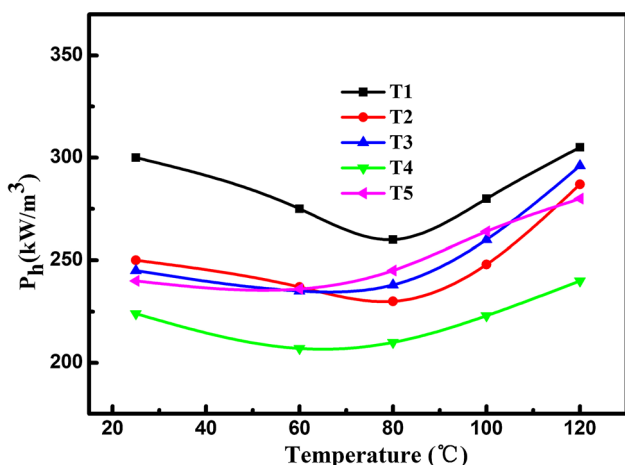


Fig. 3 The influence of TiO_2 and Nb_2O_5 doped amounts on the hysteresis loss (P_h) of MnZn ferrites

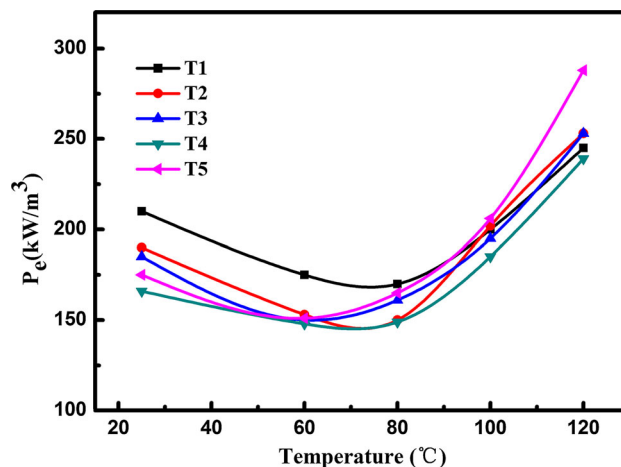


Fig. 4 The influence of TiO_2 and Nb_2O_5 doped amounts on the Eddy current loss (P_e) of MnZn ferrites

concentration (shown in Fig. 1), it is speculated that the eddy current loss is mainly dominated by the electrical resistivity. The mechanism of electrical conductivity in MnZn ferrites is mainly caused by the electron hopping between the Fe^{3+} and Fe^{2+} ions [18]. Though the Fe^{2+} ions will increase with the increase of Ti^{4+} additives according to the charge neutrality, Ti^{4+} ions have the property of localizing Fe^{2+} ions and forming stable $Ti^{4+} \sim Fe^{2+}$ pairs, which will restrict the electronic exchange between Fe^{2+} and Fe^{3+} [11]. Therefore, the grain resistivity will be improved with the increase of Ti^{4+} concentration. Meanwhile, the TiO_2 and Nb_2O_5 existed in the grain boundary will form a high resistance layer, leading to the increase of the grain boundary resistivity [4, 13, 16]. The increase of both grain and grain boundary resistivity may be responsible for the decrease of P_e when the concentration of TiO_2 and Nb_2O_5 is less than 0.03 and 0.02 wt%. However, further increasing the concentrations of TiO_2 and Nb_2O_5 might lead to the decrease of grain boundary resistivity, which may be due to the exaggerated grain growth and the decrease of the grain boundary thickness [15, 16]. Moreover, the excessive Nb^{5+} ions make the concentration of Fe^{2+} ions increase, which will improve the electronic exchange between Fe^{2+} and Fe^{3+} and result in the decrease of the grain resistivity. This may be the other reason for the increase of eddy current loss in the sample with higher TiO_2 and Nb_2O_5 concentrations.

4 Conclusions

Cobalt-modified MnZn ferrites doped with different concentrations of TiO_2 and Nb_2O_5 were prepared by conventional ceramic technique. The influence of Nb_2O_5 and TiO_2 additives on the initial permeability, microstructure, and

power loss were discussed. Moderate concentrations of TiO_2 and Nb_2O_5 additives can enhance the initial permeability of ferrites and reduce the power loss. When the concentrations of TiO_2 and Nb_2O_5 is 0.03 and 0.02 wt%, the initial permeability reaches maximum and the power loss reaches minimum. Excess Nb_2O_5 and TiO_2 will increase the power loss and reduce the initial permeability.

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