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A comparative study of nickel–zinc ferrites by sol–gel route and solid-state reaction

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Abstract

The properties of ferrites are affected by the microstructural problems which have become the most serious obstacles in obtaining high quality reproducible ferrites. In this study, the nickel–zinc ferrites were prepared via two different methods: the conventional classical ceramic method known as the solid-state reaction, and the newer sol–gel method. The electromagnetic and microstructural properties of both different samples were also discussed. A higher electrical resistivity and controlled initial permeability with a smaller loss were found in the sol–gel samples. Consequently, the homogenous microstructure and the advantages in terms of powder and sample preparations have been discovered by means of sol–gel technique.

Keywords: Sol–gel growth; Magnetic materials; Sintering; Microstructure

1. Introduction

The Ni–Zn ferrites have been produced by the conventional method which commercially involves both long and high temperature treatments for the oxides used in their preparation. A well-known problem in Ni–Zn ferrites made by the standard ceramic method is the loss of zinc by evaporation, caused by the required high sintering temperatures and long time, resulting in the non-stoichiometric ferrite [1]. The selection of these oxides often ends up with non-reproducible ferrites, mainly in terms of their magnetic properties [2,3]. Adding copper or other element oxides makes the ferrites fire at lower temperatures of about 1000 °C [4–6], but the impure oxides which influence many properties have usually been used. Hence, the challenge is to obtain high quality reproducible ferrites by making appropriate changes in the starting materials, and consequently in the preparation method.

The chemical methods such as co-precipitation, citrate precursor method, hydrothermal synthesis as well as the sol–gel process [7] have been selected to overcome the problem in improving the performance of the ferrites. Among these methods, the sol–gel preparation is more preferable due to its numerous advantages [8]. Some advantages which were evident in this study were its high purity, chemical homogeneity, small and uniformed particle sizes, energy saving, no reactions with containers which increase purity, and the minimized evaporation loss. However, due to the fact that the intention for the application of the sol–gel chemical method in ferrites is relatively new, the high cost involved in the use of the starting materials has become one of the disadvantages of this unconventional method. In addition, the much higher content of the organic matter associated with the metals are known to fly during the heat treatments.

In the present study, the Ni–Zn ferrites were prepared using two different methods; the sol–gel method, and the conventional method which is also known as the solid-state reaction using different starting materials. The Ni–Zn–Cu ferrite of impurity was also prepared by the solid-state reaction. The measurements were made on the initial magnetic permeability/loss factor and the Curie temperature using the copper wire-winding toroidal shapes. The electrical resistivity and density were also measured using the sintered toroidal shapes. Finally, the microstructural analyses which included both the measurements of the grain sizes and pore observation were conducted.

2. Experimental procedures

The conventional NiZn and NiZnCu ferrites were prepared according to Eqs. (1) and (2), respectively. The metal oxides of 99.99 and 99.1% purity were

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blended and homogenized in a wet ball mill for 16 h. The resultant slurry was filtered and the masses obtained were dried in an oven. The mixed powder for the NiZn ferrite was preheated at 1150 °C whereas the NiZnCu ferrite at 950 °C for 10 h. The preheated powder was milled in a Fritsch planetary micromill using ceramic balls for 5 h. Afterwards, the powder was blended with the polvinyl alcohol (1–2 wt.% PVA) and lubricated with 0.3 wt.% of zinc stearate. The granulated powder was pressed at 220 MPa in the 9.72 g toroidal shapes. Sintering was made in air, at 1300 °C for NiZn ferrite and at 1190 °C for NiZnCu ferrite, both for 10 h.

$$0.3NiO + 0.7ZnO + Fe_2O_3 \rightarrow Ni_{0.3}Zn_{0.7}Fe_2O_4 \quad (1)$$

$$0.3NiO + 0.6ZnO + 0.1CuO + Fe_2O_3 \rightarrow Ni_{0.3}Zn_{0.6}Cu_{0.1}Fe_2O_4 \quad (2)$$

$$0.3Ni(CH_3COO)_2 + 0.7Zn(CH_3COO)_2 + 2Fe(CH_3COO)_3 \rightarrow Ni_{0.3}Zn_{0.7}Fe_2(OH)_8 + 8CH_3COOH \quad (3)$$

$$Ni_{0.3}Zn_{0.7}Fe_2(OH)_8 + 8CH_3COOH \rightarrow Ni_{0.3}Zn_{0.7}Fe_2O_4 + 4H_2O + \text{volatiles} \quad (4)$$

The sol–gel-NiZn ferrite was prepared according to Eq. (3). The metal acetates were first dissolved in acetic acid and a small amount of water under a constant stirring at the room temperature. The solutions were then mixed and stirred for about 6 h. The constant stirring was kept but the room temperature was maintained at about 70 °C until the stirring bar was stopped and the gel was formed. The gel was heated at 600 °C for 4 h to form powder which was used to fabricate the 9.72 g toroids (19.4 mm o.d., 11.5 mm i.d., and 11.2 mm thick) (Fig. 1). The crystallized powder was the NiZn ferrite structure with quite a narrow particle size distribution formed according to Eq. (4) [9]. The calcined powder was mixed with the PVA and blended with 0.3 wt.% zinc stearate. The granulated powder was subsequently molded and pressed at a pressure of 220 MPa. The green toroidal shape was finally sintered at 1200 °C for 4 h in the air.

The Archimedes principle was applied to determine the density of the sintered toroids. The resistivity at the room temperature for NiZn ferrites was calculated by measuring the average electrical resistance of the sintered flat toroids coated with a silver conductive paint and connected to the HP 34401A multi-meter. The initial permeability (μ_i) and relative loss factor (RLF) were calculated by noting the inductance (L_p) and Q factor values from the HP network spectrum analyzer model 4195A in the frequency range of 10 Hz to 500 MHz on the sintered toroidal ferrite to their resonance frequency. The Curie temperature (T_c) was recorded from the temperature dependence of the inductance series (L_p) noted for 10 kHz frequency using an electric furnace and the HP LCR meter model 4284A in the frequency range of 20 Hz to 1 MHz. The SEM photomicrographs of the sintered shapes were obtained on the specimens polished with alumina and thermally etched at 100 °C below the sintering temperature and the grain size was measured by the linear intercept method.

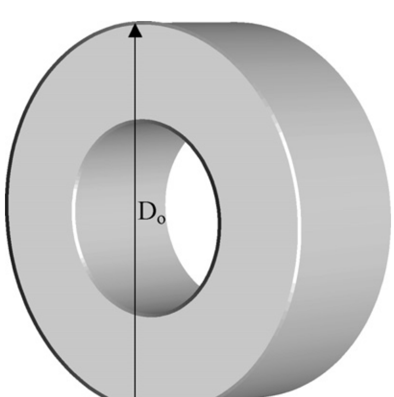

Fig. 1. Toroidal shape.

Table 1
The electromagnetic properties data

Parameter	NiZn ferrite	NiZnCu ferrite	Sol–gel-NiZn ferrite
Density (g cm^{-3})	5.04	4.99	4.12
Resistivity (Ω m)	16	–	4700
Permeability, μ_i	913	337	227
Losses, RLF (×10^{-5})	1068	384	453

3. Results and discussion

The densities of the sintered toroids are shown in Table 1. The density of the conventional ferrites was higher than those obtained in the sol–gel-NiZn ferrite. The increase in sintered density was caused by high calcination temperatures. The total pore content which was open, closed or granular was directly related to density. Therefore, the higher sintering temperature and time will remove pore contents. Nevertheless, the density of the sol–gel samples was lower due to the presence of intergranular pores, i.e., pores between the grains, as discussed in the microstructure section; however, such low density is required for the light-weight applications. A study conducted [10] on the $Ni_{0.3}Zn_{0.6}Cu_{0.1}Fe_2O_4$ composition synthesized by the sol–gel route preheated at 700 °C, and sintered at 1200 °C for 4 h showed no porosity in its final product. Thus, the change in the composition was partially responsible for the difference in densities of the ferrites which are conventionally between 4.99 and 5.1 g cm^{-3} [11,12]. This was also clearly indicated in the conventional NiZn and NiZnCu ferrites.

The resistivity of the NiZn ferrites produced by both methods used is given in Table 1. The resistivity of the grain boundaries was generally higher than the bulk resistivity. The resistivity of the samples obtained by the sol–gel method was much higher than the one derived conventionally. The ferrites have resistivity which is ranging from 0.1 Ω m to greater than 10^6 Ω m depending on their compositions and stability. The difference in the resistivity could be explained by the difference in the sintering conditions. The volatilization of zinc at higher temperatures leads to the formation of Fe^{2+} ions which increase the electron hopping and reduce the resistivity [13,14]. Thus, a higher evaporation in the zinc content and a smaller grain boundary resistivity were caused by high temperatures and duration of sintering. In this connection, the smaller resistivity was owing to the higher contact between the adjacent grains which enabled a higher electron flow at the grain boundaries. In contrast, the higher resistivity of the sol–gel samples was due to the lower or no zinc evaporation and a prominent grain boundary usually coupled with small grains.

The initial permeability, μ_i, as a function of frequency for the conventional NiZn and NiZnCu ferrites and sol–gel-NiZn ferrite are shown in Fig. 2. The initial permeability values of the conventional ferrites were higher than those of the sol–gel ferrites as depicted in Table 1, of which it was determined at 12 kHz frequency. In the conventional NiZn ferrite, the responded magnetization directions away from the easy crystalline directions occurred rapidly. Generally, the grain boundaries and local impurities and microstructural defects are relevant for the