Effect of grain size on electromagnetic properties of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite

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Abstract

The electromagnetic properties of polycrystalline $Ni_{0.7}Zn_{0.3}Fe_2O_4$ with varying grain size in the range 1–12 μm, were investigated. The grain size was varied by sintering the ferrite at different temperatures/time upto 1300 °C/240 min. A rapid grain growth was observed at 1300 °C/240 min. Initial permeability was found to increase linearly with the grain size upto about 5 μm and after that the rate of increase was reduced due to the formation of more number of closed porosity. The permeability and relative loss factor were very stable upto about 10 MHz in small-grained cores. A relatively lower loss factor in the order of 10^{-5} was found in the material. Resistivity was found to decrease sharply with the grain size. The ferrite with 1250 °C/60 min firing was best for high-frequency low-loss application.

1. Introduction

The Ni–Zn ferrites are one of the most versatile, reasonable cost magnetic materials for general use in both low- and high-frequency devices because of their high resistivity, low dielectric losses, mechanical hardness, high Curie temperature and chemical stability [1–4]. The magnetic properties of Ni–Zn ferrites are strongly dependent on their chemical composition [5], porosity, grain size, etc. [6,7]. The typical Ni–Zn ferrites sinter satisfactorily only above 1250 °C, where their microstructure and properties being difficult to control because of the volatility of ZnO at such high temperatures [8]. In this context, understanding of sintering, microstructure development and co-related electromagnetic properties of the Ni–Zn ferrite is very important. Many literatures are available on these aspects of the $Ni_{1-x}Zn_xFe_2O_4$ ferrites with relatively higher Zn content (x in the

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range 0.5–0.7) [6–10]. However, the related literatures on low Zn-bearing ($x \leqslant 0.3$) ferrite are very rare. That is the reason, the present composition $Ni_{0.7}Zn_{0.3}Fe_2O_4$ has been selected for the investigation. It is known that the permeability increases with the substitution of Zn for Ni in Ni–Zn ferrite [11], but the Curie temperature and the optimum frequency range for application of it also decreases with that substitution. Generally, the composition $Ni_{1-x}Zn_xFe_2O_4$ with $x \leqslant 0.3$ is used to get a Curie temperature of $> 400\,°C$ and an application frequency range of 1–10 MHz. This paper investigates the influence of microstructure (mainly grain size) on the initial permeability, loss and resistivity of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrites.

2. Experimental

The ferrite with a nominal composition $Ni_{0.7}Zn_{0.3}Fe_2O_4$ was prepared by conventional ceramic powder processing technique, using Nickel Oxide, Zinc Oxide and Iron Oxide (all from Loba Chemie (GR-quality), India). The raw powders were mixed and ground in ball mill in wet condition. The mixed powder was calcined at $900\,°C$ for 8 h and again ground in ball mill after calcination. Milled ferrite powder was pressed at $2\,ton/cm^2$ pressure into cylindrical pellets (12 m dia, 3 mm thickness) and toroids (25×15 mm, outer:inner diameter). The samples were sintered at temperatures ranging from 1100 to $1300\,°C$ at different times from 1 to 240 min in air atmosphere. The bulk densities and porosities were measured using the Archimedes principle. Impendence analyzer (Hewlett Packard, Model 4192A, USA) was used to measure inductance and magnetic loss factor on toroids, wound with low capacitive six-turns enameled copper wire. The initial permeability was calculated as per [12] using

$$\mu_i = L/(2 \times 10^{-7}N^2H_t \ln[od/id]),$$

where L is the inductance, N is the number of turn, H_t, od and id are the toroid's thickness, outer diameter and inner diameter, respectively. Resistivity was measured on pallet samples, by applying silver electrodes on the surfaces. The grain size of polished samples were measured by the mean

linear intercept method using ZEISS "Axiotech" optical microscope equipped with Video Pro-32 Digital Image Analyzer system.

3. Results and discussion

Fig. 1 shows the variation of bulk density and true porosity with sintering time at three different sintering temperatures for the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite samples. The true porosity of the sample was calculated using X-ray density. As expected, bulk density increases and porosity decreases with temperature and time of sintering. The rate of increase in bulk density as well as the decrease in porosity during time range 1–60 min, seems to be higher than that in the range 60–240 min. The lower rate of densification above 60 min may be due to the higher amount of Zn-evaporation losses from the ceramics. In fact, all samples showed the presence of closed porosity in the range of 3–5% and the closed porosity increased with the increase in sintering time/temperature. For example; the open porosity of $1300\,°C/4$ h sample was only 0.93%, although it has 6.07% true porosity. The pores were entrapped within the grains due to the higher rate of grain growth at that temperature/time. It is difficult to remove porosity completely due to increased Zn-evaporation loss with temperature and time.
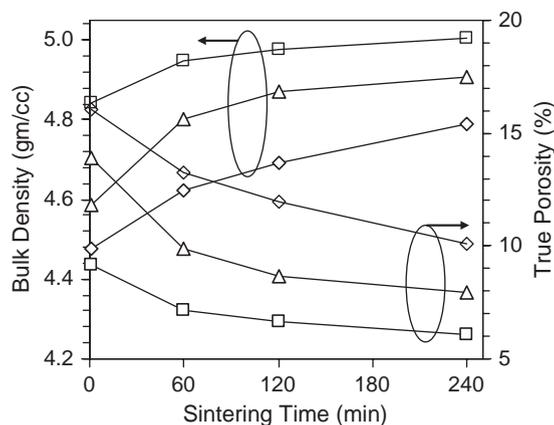

Fig. 1. Variation of bulk density and true porosity of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ with sintering time at temperatures; $\diamond = 1200\,°C$, $\triangle = 1250\,°C$; $\square = 1300\,°C$.

Fig. 2 shows the variation of permeability (μ) and grain size with sintering time at different temperatures. Before comparing magnetic properties, the experimental permeability was corrected using formula; $\mu = \mu_{\exp}/(1 - V_{pi})$, where V_{pi} is the volume fraction occupied by pores [9]. Initial permeability increases linearly with sintering temperature/time (Fig. 2). As expected, the grain size also increases with sintering temperature/time. A rapid grain growth was observed at 1300 °C due to the formation of larger amount of liquid phase in the system. The variation of permeability with grain size is also shown in Fig. 3. It shows that
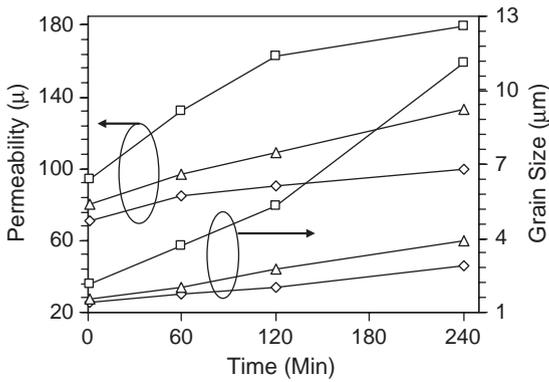

Fig. 2. Variation of permeability (μ) and grain size with sintering time at temperatures: $\diamond = 1200$ °C, $\triangle = 1250$ °C and $\square = 1300$ °C.

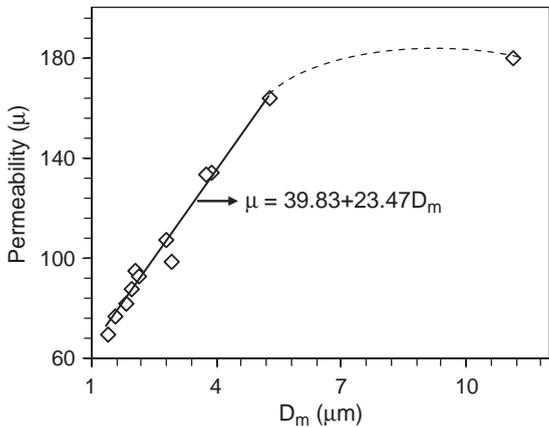Fig. 3. Effect of average grain size on initial permeability of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite.

permeability increases linearly up to $\sim 5\,\mu m$ grain size may be due to the displacement of flat 180° domain wall inside the grain. It is known that the magnetization of polycrystalline soft ferrite generally depends on both domain rotation and domain wall motions. Previous investigation [13] proposed that the critical grain size D_c, below which the single domain structure exists in Ni–Zn ferrite is only 0.08 μm. So, the magnetization in the present ferrite may be primarily controlled by domain wall motions, satisfying fully the Globus model [6]. According to Globus, μ' increases with increasing distance between pinned edges of domain wall which approximately equal to grain size. After $\sim 5\,\mu m$, the rate of permeability change decreases and the well-known [14] bend appears in the curve.

The reason may be due to the increase in closed pores (which acts as extra pinning centre) and formation of closure domain (CD) walls structure in bigger grains. It may be considered that the second pinning mechanism appears in the bigger grains due to displacement of CD walls and related strain [14]. In the linear portion of the curve (Fig. 3), the permeability may be estimated from a linear equation $\mu = 39.83 + 23.47\,D_m$. The slope (23.47) of the line, found here is lower then that (166.6) reported by Rosales et al. [7] for $Ni_{0.4}Zn_{0.6}Fe_2O_4$. That is, the slope increases with the increase in Zn-content of the ferrite, indicating, Zn helps in producing grain growth in the ferrite. The intercept of the equation (39.83), a constant value, may be the representation of spin only permeability part of total permeability as per Globus model [6], as well as the constant rotational permeability part as per non-magnetic grain-boundary model [15], when the grain size is very large than the grain boundary thickness. So, the magnetization in the present case may be satisfying both the model.

Fig. 4 shows the variation of permeability as a function of frequency. Permeability is very stable in the lower frequency range, while at higher frequencies, there is a small rise (i.e. dispersion), at least by part, in resonance phenomena [11]. The frequency dispersions are prominent for higher temperature/time fired samples and the cut-off frequency decreases with the increase in permeability. This follows Snoek's law [16] that cut-off
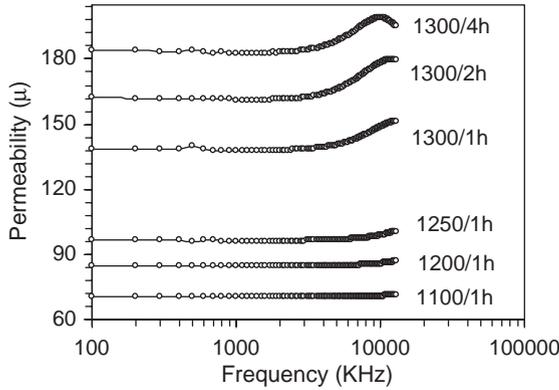
Fig. 4. Frequency dependency of permeability in $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite sintered at different temperature/time.
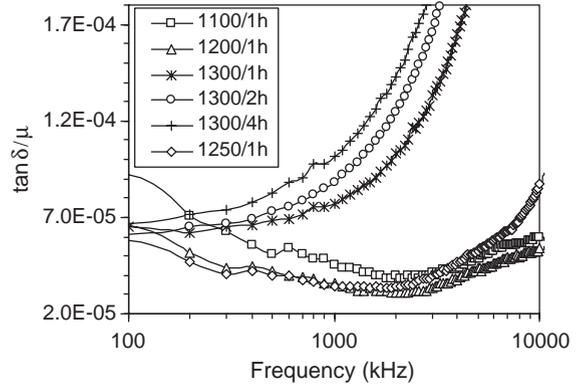

Fig. 5. Variation of relative loss factor as a function of frequency for samples sintered at different temperature/time.

frequency is inversely proportional with magnetic permeability. Those cut-off frequencies of 1300 °C/2 h and 4 h samples are 12.3 and 10.1 MHz, respectively. The cut-off frequencies of other samples are above 13 MHz, the maximum frequency limit of the instrument. It is known that the resonance frequency is determined from the complex permeability plot, the frequency at which $\mu' = \mu''$, [15]. However, the determination of that frequency was not possible in the present investigation. Because, the maxima of the μ'' vs. frequency curve was above 13 MHz, the maximum frequency limit of the instrument.

Fig. 5 shows the relative loss factor (RLF), i.e. the ratio of the magnetic loss tangent to initial permeability. High μ and low $\tan \delta$ i.e low RLF are required for high-frequency magnetic applications. The figure shows that RLF of 1100 °C/1 h core is slightly higher in lower frequency range (kHz), may be due to mainly higher hysteresis losses arising from its porous (porosity ~16%) structure. It is known that hysteresis loss increases with the increase in porosity [17]. RLF of all the cores increases in MHz frequency zone due to the resonance-relaxation losses. Only, RLF of large-grained cores (1300/1 h, 2 h, and 4 h) increase very rapidly after about 1 MHz due to their bigger grain size. It is already stated that resonance-relaxation loss frequently depends on grain size. The values of RLF found in the present ferrite are in the range 10^{-5}–10^{-4} which is about two orders of magnitude
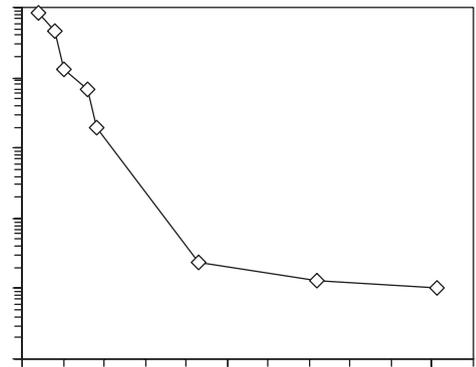

Fig. 6. AC resistivity at 100 kHz as a function of grain size for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite.

lower than those reported by others [18]. The Fig. 5 also indicates that 1250 °C/1 h-core has lowest RLF and hence the best for high-frequency applications.

The AC resistivity (ρ) was calculated using the formula $\rho = 1/(\omega \varepsilon_0 k' \tan \delta)$ [where, ε_0 is the permittivity of free space, k' is the relative dielectric constant, $\tan \delta$ is dissipation factor, ω is the angular frequency. It is observed that the AC resistivity, measured at 100 kHz, decreases with increase in grain size (Fig. 6). Also the resistivities of all the samples were found to decrease with the increase in frequency upto 13 MHz. The observed

resistivity values are in the range 10^4–10^8 ohm cm for different grain sizes. The smaller grains result in a large no of grain boundaries, which act as the scattering center for the flow of electrons and therefore increase the resistivity. The rate of resistivity decrease was low after ~5 μm grain size may be due to the formation of more and more closed porosity.

4. Conclusion

This study clearly shows that the permeability in $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite increases linearly up to ~5 μm grain size which may be due to the displacement of the flat 180° domain wall inside the grain. After ~5 μm, the rate of permeability change decreases due to the increase in closed pores and formation of closure domain walls (CD) structure. Second pinning mechanism appears in the bigger grains due to the displacement of CD walls and related strain. The relative loss factor of the ferrite fired at 1250 °C/1 h has the value in the range 10^{-5} and the ferrite is suitable for high-frequency applications. The resistivity of the ferrite is highly dependant on grain size upto ~5 μm.

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