Frequency variation of initial permeability of NiZn ferrites prepared by the citrate precursor method

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Abstract

$Ni_{1-x}Zn_xFe_2O_4$ with $x = 0.2$, 0.35, 0.5 and 0.6 have been prepared by the citrate precursor method. The complex initial permeability has been studied as a function of the composition and sintering temperature. Preparation by this method has resulted in ferrites with permeability spectra comparable to those obtained by the conventional method. The main advantages of this method are the scope for preparing lower-loss ferrites and the possibility of increasing the operational frequency range.

Keywords: Ferrites; Citrate method; Initial permeability; Permeability loss; Microstructure

1. Introduction

The processing of good-quality ferrites has received a great deal of attention [1–3] during the past few years. The properties are known to be sensitive to the composition and the microstructure. The control of stoichiometry and microstructure of ferrites prepared by the conventional ceramic method is usually difficult. Some non-conventional methods have been tried, but are not commercially feasible due to some inherent disadvantages. The coprecipitation [4] and the co-spray roasting [5] processes have, however, been exploited to some extent at the commercial level. In the present work, a wet chemical method, known as the citrate precursor method [6,7], has been used for the preparation of nickel–zinc ferrites. This method mixes homogeneously, on the atomic scale, the individual metal–citrate complexes in the solution state. It has been therefore possible to control the stoichiometry in the initial stages of the preparation itself. As this method does not require any ball milling to mix the materials, there is no possibility of impurity pick-ups and hence of nonstoichiometry. The ferrite powder being formed as a result of thermal decomposition of the citrate precursor which is effected at low temperatures of a few hundred degrees only, it is possible to obtain smaller particle size. As the crystalline structure of ferrite is of decisive influence on the magnetic properties, it is imperative that the ferrites with appropriate crystal and microstructure be prepared. Whereas it is difficult to control the grain size by the conventional method which involves high heating temperatures, in the citrate method it is possible to have microstructure with the desired grain size. Also the citrate precursor method is simple, easy and does not require elaborate and expensive experimental set-up. Hardly any reports on the magnetic properties of NiZn ferrites prepared by the citrate precursor method are available. In the present work, the citrate-based preparation of NiZn ferrites and the study of their initial magnetic permeability are undertaken.

2. Experimental

$Ni_{1-x}Zn_xFe_2O_4$, with $x = 0.2, 0.35, 0.5$ and 0.6, were prepared. The dried citrate precursor mixture containing a homogeneous mixture of the constituent cations was obtained by the method described in Ref. [7]. This mixture was calcined at 1000°C for 1 h in air to obtain the ferrite. The X-ray diffraction pattern, recorded on a Rigaku Geiger Flex 3 kW X-ray diffractometer, showed distinct lines corresponding to the cubic spinel structure only. The ferrite powder obtained on calcination was mixed with 2% by weight of polyvinyl alcohol as binder and pressed into torroidal rings of 1.62 cm O.D., 0.96 cm I.D. and 0.23 cm thickness at a pressure of 5 tonnes. These torroids were sintered at different temperatures in the range 1100–1400°C for 1 h in air and were subsequently furnace cooled. The heating rate of 150°C/h was used. For measurements of initial permeability, the sintered torroids were wound with 60 turns of 30 SWG enamelled copper wire. Inductance was measured at various frequencies in the range 10 kHz–13 MHz using a Hewlett-Packard impedance analyser model 4192-A. Values of the magnetic loss factor $\tan \delta_{\mu_i}$ were also recorded. Initial permeability was calculated using the relation $\mu_i = L/L_0$, where L is the measured inductance of the sample and L_0 is the air core inductance calculated using the dimensions of the coil. The microstructures of the fractured surfaces of the samples were studied using a Cambridge Stereo Scan 360 scanning electron microscope (SEM).

3. Results and discussion

The magnetic properties of ferrites are known to be influenced by chemical composition, crystal structure, grain size and porosity. The variations of the real part μ_i' and of the imaginary part μ_i'' of complex initial permeability with frequency are studied as a function of the composition and sintering temperature. Initial permeability is an important parameter to evaluate the quality of soft ferrites. The variation in μ_i' and μ_i'' as a function of frequency for $Ni_{1-x}Zn_xFe_2O_4$ samples sintered at four different temperatures (1100, 1200, 1300 and 1400°C) showed similar behaviour. Typical variations of all the compositions sintered at 1200 and 1400°C are shown in Figs. 1 and 2, respectively. μ_i' and μ_i'' are observed to vary both with sintering temperature and zinc content.

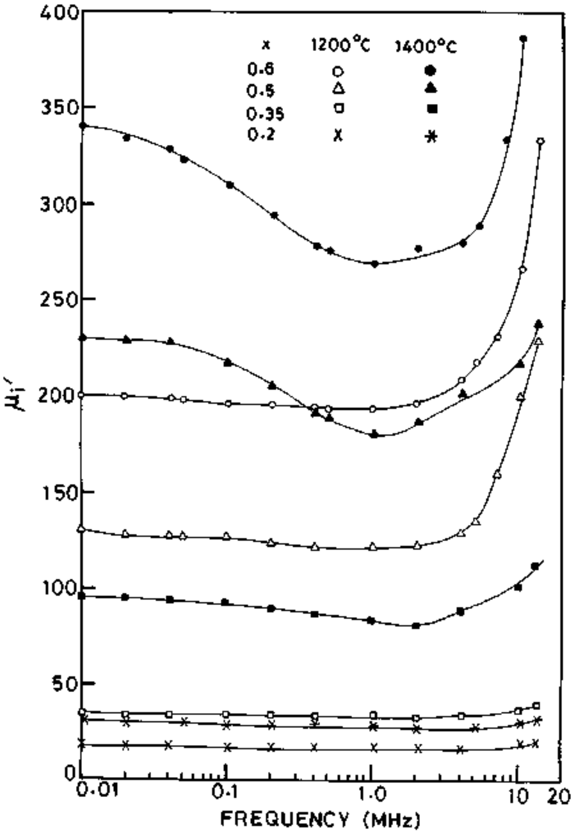

Fig. 1. Frequency variation of μ_i' of $Ni_{1-x}Zn_xFe_2O_4$ sintered at 1200 and 1400°C.

3.1. *Initial permeability, μ_i'*

The real part of the complex initial permeability, henceforth referred to as initial permeability, which

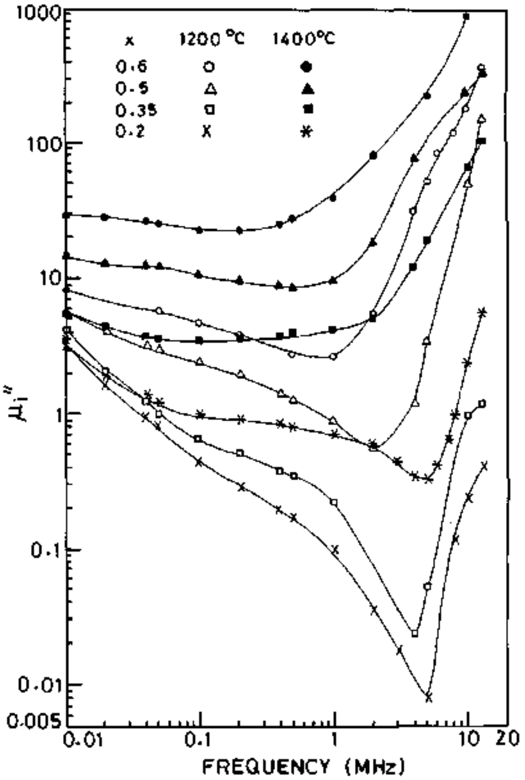

Fig. 2. Frequency variation of μ_i'' of $Ni_{1-x}Zn_xFe_2O_4$ sintered at 1200 and 1400°C.

corresponds to very low applied fields can be explained by the reversible displacement of domain walls [8,9]. The walls normally remain pinned to the grain boundary and bulge when subjected to small magnetic fields [10]. The magnetisation increases as the number of domain walls increases and the number of domain walls increases as the grain size increases. Increase in grain size was observed when the sintering temperature was raised from 1100 to 1400°C. The observed average grain sizes are 0.6, 1.9, 4.1 and 8.0 μm for the $x = 0.6$ samples sintered respectively at 1100, 1200, 1300 and 1400°C. The SEM photograph of the samples have been reported in Ref. [7]. Therefore, as observed, increase in μ_i' with increase in sintering temperature is expected. Higher sintering temperatures also result in the increase in the density of the specimen which facilitates the movement of the spins as the number of pores which impede the wall motion are reduced. The increase in the sintering temperature also results in a decrease in the magnetic anisotropy by decreasing the internal stresses and crystal anisotropy which reduce the hindrance to the movement of the domain walls resulting thereby in the increased value of μ_i' [11].

The effect of increasing zinc content in the sample is found to be similar to that of increasing the sintering temperature. It is observed that the increase in the zinc content increases the grain size [12] and density [13], and decreases the anisotropy [11] which result in an increase in the value of μ_i'.

Fig. 1 showed that μ_i' is independent of frequency for samples sintered at lower temperature and/or those having lower zinc concentration, whereas for others it decreases slightly with frequency till the onset of resonance. The decrease in μ_i' is attributed to zinc loss [14] due to evaporation which increases with increase in sintering temperature or with increasing zinc content. Zinc loss results in compositional and structural changes. The domain wall has the tendency to get pinned to the lattice imperfections thus created. At high frequencies the unpinning of the domain walls form the imperfections cannot keep pace with the rapidly changing magnetic field resulting in the decreased value of μ_i'. Sample with the highest zinc content ($x = 0.6$) shows the greatest variation in μ_i' with frequency when sintered at temperatures $\geqslant$ 1200°C while in the case of samples with $x = 0.2$ the constancy in μ_i' with frequency is observed for all samples sintered at all temperatures. Due to higher Zn content in sample with $x = 0.6$, there is a possibility of Zn evaporation even at 1200°C, whereas in the case of samples with $x = 0.2$, due to their smaller Zn concentration, the Zn loss and the variation in μ_i' is not significant even at 1400°C. The intermediate compositions show an in-between behaviour.

The rapid increase in initial permeability at higher frequencies is indicative of the onset of resonance [15]. When the frequency of the applied magnetic field equals the Larmor precession of the electron spins, resonance occurs and the energy is transferred from the field to the system in orienting the magnetic dipoles. It was not, however, possible to observe the complete resonance peaks as they seem to appear at frequencies greater than 13 MHz (the maximum frequency of the HP 4192-A impedance analyser used in the present work). The frequency of the onset of resonance varies with composition and sintering temperature; it decreases with increasing zinc content and sintering temperature and hence with increasing μ_i'. As already stated, the increase in the sintering temperature reduces the magnetic anisotropy which effectively reduces the magnitude of the local magnetic field experienced by the precessing spins. As a result, the Larmor precessional frequency decreases and the resonance is observed at lower frequencies. This observation is in agreement with those of Globus [16].

The resonance frequency represents the high-frequency limit upto which the material can be used in a device. This limit depends upon the initial permeability as per Globus' law and increases with decrease in μ_i'. Comparing the present results of samples prepared by the citrate precursor method with those reported for NiZn ferrites developed by Philips Laboratories, Eindhoven, Netherlands [17], it is found that the values of μ_i' for samples sintered at 1400°C are comparable; for instance, its value for $x = 0.5$ sample in the present work, is 230 which is very close to the value (~ 235) reported. It is further noticed that the reported resonance frequency is in the range from 4 to 40 MHz. The resonance frequencies observed in the present work in all cases are above 13 MHz. It can be concluded that although the value of μ_i' for the samples prepared by the two methods is nearly the same, the citrate precursor method is preferable as it is relatively simpler and cost-effective. Besides, since by the citrate precursor method one can obtain particle sizes much smaller than those obtained by the conventional method, it is possible to push the resonance frequency to higher values thereby increasing the operational frequency range of ferrites in applications where the requirement of high μ_i' is not rigid.

3.2. *Permeability loss, μ_i''*

The imaginary part of the complex initial permeability, henceforth referred to as permeability loss μ_i'', arises due to lag of the motion of domain walls vis-a-vis the alternating magnetic field [18]. This lag is ascribable to the imperfections in the crystal structure. As can be seen in Fig. 2, μ_i'' is observed to increase with increase in the zinc content as well as the sintering temperature. The frequency at which losses begin to increase due to the onset of resonance varies with composition and the sintering temperature. The curves obtained for samples sintered at 1400°C are similar to those reported for the conventionally prepared ferrites [17]. It is observed that samples which are sintered at lower temperatures and/or have smaller zinc content, exhibit lower loss values due to insignificant zinc loss; values of the loss factor $\tan \delta_{\mu_i}$ of about 10^{-3} to 10^{-4} at frequencies between 500 kHz and 5 MHz are observed. These values are atleast an order of magnitude lower than those normally reported ($\geqslant 10^{-2}$) [19,20] for the conventionally prepared samples. This shows that in samples sintered at lower temperature or in those having smaller zinc concentrations, defects which influence the wall movement are avoided. Another factor contributing to the low-loss values is the relatively higher purity of the samples obtained by the present method.

The present investigation shows that the ferrites prepared by the sintering at lower temperatures exhibit lower loss values, though with reduced permeabilities. The trade-off between the initial permeability and the loss factor is clearly evident. The results of the present investigations may be used to select an appropriate composition and sintering temperature to make ferrites according to the requirements of the application. Other magnetic properties such as Curie temperature, saturation magnetisation, *B–H* loop are being investigated and will be reported soon.

4. Conclusion

NiZn ferrites prepared by the citrate precursor method result in magnetic properties which are better or atleast comparable to those obtained by the conventional ceramic method. The principal advantage of the method lies in lowering the permeability losses specially for ferrites sintered at lower temperatures, and increasing the operational frequency range. The method being simple and economical, can be used to advantage on a commercial scale.

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