Dielectric properties of NiZn ferrites prepared by the citrate precursor method

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Abstract

Dielectric properties such as dielectric constant, \( \varepsilon' \), and dielectric loss factor, tan \( \delta_e \), are reported for different compositions of NiZn ferrites prepared by the citrate precursor method and sintered in the temperature range 1100–1400°C. It is observed that \( \varepsilon' \) and tan \( \delta_e \) for samples prepared in the present work are much lower than those normally obtained for NiZn ferrites prepared by the conventional ceramic method. The low values are attributed to better compositional stoichiometry, single-phase spinel structure and uniform microstructure of the samples. The low dielectric loss makes these samples especially attractive for use at high frequencies.

Keywords: Dielectric properties; NiZn ferrites; Citrate precursor method

1. Introduction

Nickel-zinc ferrite is a versatile technological material, particularly suited for high-frequency applications. The properties of ferrite materials are known to be strongly influenced by their composition and microstructure which in turn are sensitive to the processing methods used to synthesize them. Selection of an appropriate process is, therefore, the key to obtaining good quality ferrites. In an attempt to prepare high performance ferrites with reproducible stoichiometric compositions and desired microstructures, the present work aimed at preparing NiZn ferrites using the citrate precursor method. This approach is different from the conventional ceramic or solid-solution methods which have several disadvantages particularly with respect to phase purity, control of microstructure and defect chemistry. The citrate process [1,2] is simple, easy and does not require an elaborate and expensive experimental set-up. The main advantages of this method are: (a) Its capability to yield an homogeneous mixture of the constituent ions leading to stoichiometric compositions as mixing takes place on an atomic scale in the solution state. (b) No ball-milling is required in this process and hence there is little scope of contamination of the materials. In the case of ferrites prepared by the conventional method, there is invariably some possibility of introducing iron impurities into the ferrite due to abrasion of steel balls during milling. The introduction of impurities leads to inhomogeneity in the ferrite structure which has an adverse effect on some of the dielectric properties. In addition, milling also introduces lattice stress and strains which result in distorted structures. (c) As the crystal structure evolves during the thermal decomposition of the citrate precursor it is possible to control the grain size by a suitable heat treatment giving rise to a relatively uniform microstructure. Although there are a few reports [3–7] on the preparation of NiZn ferrites by wet chemical methods, the preparation of NiZn ferrite by the citrate precursor method has not been reported. Also, there are hardly any reports on the electrical properties of NiZn ferrites prepared by the wet methods. It was therefore felt appropriate to use the citrate precursor method to prepare NiZn ferrites and study the effect of processing on their dielectric properties.
nature. This dried glassy citrate mixture was calcined at 1000°C for 1 h to obtain the spinel ferrite. The ferrite powder thus obtained was pressed at a pressure of 10 tons to obtain pellets of 1.3 cm diameter and 1.5 mm thickness. Polyvinyl alcohol (2% by weight) was used as binder. The pellets were sintered in air over a range of temperatures, 1100–1400°C, for a period of 1 h at a heating rate of 150°C h⁻¹ and were subsequently furnace-cooled. X-ray diffraction patterns of the ferrite powder as well as the sintered pellets taken on a Rigaku Geiger Flex 3 kW X-ray diffractometer revealed a single-phase spinel structure. A typical diffractogram of the NiZn ferrite powder obtained on calcination is shown in Fig. 1. The photomicrographs of the fractured surfaces of the ferrite samples were recorded on a Cambridge Stereo Scan 360 scanning electron microscope(SEM). For the dielectric measurements, silver paste was coated on polished pellets to provide electrical contact. Dielectric constants were calculated from the capacitance measurements made on a Hewlett-Packard impedance analyser 4192-A in the frequency range 30 Hz–10 MHz. The values of dielectric loss, \( \tan \delta_e \), were simultaneously recorded.

3. Results and discussion

The frequency variations of the room temperature dielectric constant \( \varepsilon' \), and dielectric loss factor, \( \tan \delta_e \), of NiZn ferrites prepared by the citrate precursor method are shown in Figs. 2–5. A decrease in the dielectric constant with frequency is observed in the range 30 Hz–10 MHz for all compositions. Dielectric constants of ferrites sintered in the temperature range 1100–1300°C are observed to be quite low, between 30 and 400, at low frequencies from 30 to about 500 Hz.
Above these frequencies, the values are much lower, approaching the intrinsic value [8] due to the polarisability of the oxygen ions. For the samples sintered at 1400°C, comparatively higher values of the dielectric constant are observed. It may be pointed out that much higher values of the dielectric constant, of the order of $10^3$–$10^4$, with pronounced dispersions at around $10^3$ Hz have been reported [9] for NiZn ferrites prepared by the conventional ceramic method.

Polarisation in ferrites has largely been attributed to the presence of Fe$^{2+}$ ions which give rise to heterogeneous spinel structure. Since Fe$^{2+}$ ions are easily polarisable, the larger the number of Fe$^{2+}$ ions the higher would be the dielectric constant. The very high values of dielectric constant obtained in the case of NiZn ferrites prepared by the conventional method, therefore, suggest the presence of more Fe$^{2+}$ ions rendering the ferrite structure highly heterogeneous. The extent of Fe$^{2+}$ ions in the ferrites largely depends upon the method of preparation. The conventional method of preparation requires the starting oxide materials to be ball-milled and subsequent heat-treatment at high temperatures of 1250–1400°C. The high temperature sintering proves deleterious as it results in Zn loss [10] from the ferrite due to volatilization and the consequent formation of Fe$^{2+}$ ions. The prolonged ball-milling of the oxides could also result in Fe$^{2+}$ being introduced into the ferrite due to abrasion of the steel balls. Thus, ferrites prepared by the conventional method are invariably likely to have more Fe$^{2+}$ and, therefore, a higher dielectric constant. Koops [9] and others [11–13] had given a similar explanation for the high values of the dielectric constant of ferrites prepared by the conventional method.

Since in the present work, no milling processes are involved, and the sintering is done at relatively lower temperatures, little deviation in stoichiometry is expected, thus giving greater structural homogeneity. Due to this, low dielectric constant values are observed. Compositional stoichiometry is an important requirement for obtaining low dielectric constants and low losses [14]. As can be observed (Figs. 2–5), the samples sintered at 1200°C exhibit low dielectric constant even at lower frequencies and it remains nearly constant over the entire frequency range studied. This suggests that Zn evaporation leading to Fe$^{2+}$ formation and consequent heterogeneity in structure becomes significant only when samples are sintered at temperatures higher than 1200°C. This is also supported by the density (calculated from the weight and bulk volume of the
samples) data (Table 1). Higher porosity results in lower dielectric constants and dielectric losses. According to these arguments, it is expected that samples sintered at 1100°C would have a still lower dielectric constant. However, the reverse has been observed in the present studies. This is due to the fact that 1100°C is not a sufficiently high temperature to result in homogeneous spinel structure free from imperfections. It thus seems that temperatures around 1200°C are appropriate for sintering the samples in order to get good ferrites.

In addition to the sintering temperature, the amount of Zn in the samples also influences the dielectric properties of the ferrites in the following two ways: (a) ferrites with a larger zinc concentration are likely to contain relatively greater amount of Fe$^{3+}$ as the probability of zinc evaporation would be more in these samples, and (b) zinc brings about perfection in the ferrite crystal structure [15]. These two effects play against each other in determining the sample properties.

SEM photographs of various samples were taken to understand the microstructure of the prepared ferrites. It is observed that the average grain size increases from about 0.6 μm for samples sintered at 1100°C to about 8.0 μm for samples sintered at 1400°C. The corresponding values for the particle size-spread are from 0.5 to 0.7 μm and from 4 to 13 μm, respectively. Since the sample with composition \( x = 0.6 \) sintered at 1200°C shows the least dielectric constant and dispersion, this sample shows good promise for use in device applications. The photomicrograph of this sample is shown in Fig. 6. As can be seen, the microstructure consists of relatively small size grains (≈ 2 μm). It is to be noted that, in general, the grain size and the size-spread for samples prepared by the present method are much smaller than those for samples prepared by the conventional method [16–18]. Small grains are preferred in ferrites [13] as oxidation advances faster in smaller grains thus leading to the acceleration of the Fe$^{2+}$ to Fe$^{3+}$ transformation. Therefore, the probability of Fe$^{2+}$ formation in smaller grains is low resulting in lower dielectric constants.

The low dielectric constant values observed in the present work suggest that the resistivity of these samples should be high [13,19]. Higher values of resistivity (\( 10^9 - 10^{11} \) Ω cm) have indeed been observed in the present work [20] as compared to those obtained (\( 10^2 - 10^4 \) Ω cm) for NiZn ferrites prepared by the conventional method [21,22].

As can be seen in Figs. 2–5, the dielectric dispersion in the samples is very small, extending up to about \( 10^3 \) Hz and is insignificant at higher frequencies. The low dielectric dispersion exhibited by the samples is due to their low dielectric constant values at low frequencies. Generally, ferrites with large dielectric constants are

![Fig. 4. Frequency variation of dielectric constant, \( \varepsilon' \), and dielectric loss factor, tan \( \delta_c \), of Ni$\text{_{1-x}}$Zn$\text{x}$Fe$\text{_{2}}$O$\text{_{4}}$ (x = 0.35) sintered at 1100, 1200, 1300 and 1400°C.](image-url)
found to exhibit pronounced dispersion in their dielectric spectra. Thus samples sintered at 1400°C which have a relatively higher dielectric constant are observed to exhibit marked dispersion. Samples sintered at 1200°C are found to exhibit the least dispersion. This behaviour is quite similar to that observed by Jankowski [23] and can be explained on the basis of the many-body interactions [24]. Owing to the disordered structure of the grain boundaries, the polarisation is due to discontinuous hopping of charges, electrons or ions, between localised states as a result of many-body interactions between its constituent parts.

It can be seen from the loss curves shown in Figs. 2–5 that: (a) the losses are frequency dependent, (b) the loss values vary with composition and sintering temperature, and (c) certain curves show the presence of loss peaks.

It is observed that the values of the loss factor for the samples are significantly lower compared to those reported [9,25] for the samples prepared by the conventional method. For instance, the loss factor for the sample of the composition \(x = 0.6\) sintered at 1200°C is around \(10^{-2}\) at frequencies around \(10^5\) Hz. The corresponding value reported in the literature [9] for the sample prepared by the conventional method is more than 2.

The dielectric loss arises due to the lag of the polarisation behind the applied alternating electric field and is caused by the impurities and imperfections in the crystal lattice. Structural defects give rise to trapping centres for the electrons, also known as correlated states [26]. As indicated above, some of the curves show loss peaks at frequencies around 200 Hz and \(10^5\) Hz. These peaks are as a result of resonance due to the matching of the time period of the applied electric field with those of the corresponding relaxation phenomena. The response time of the electrons in the trapping centres is higher than the time taken for hopping between the sites of the charged particles. It thus follows that the peak around 200 Hz is due to the relaxation in the

<table>
<thead>
<tr>
<th>Composition (\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4)</th>
<th>Density (g cm(^{-3}))</th>
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<tbody>
<tr>
<td>(x = 0.6)</td>
<td>4.11  4.62   5.12  4.92</td>
</tr>
<tr>
<td>(x = 0.5)</td>
<td>3.78  4.68   4.82  4.80</td>
</tr>
<tr>
<td>(x = 0.35)</td>
<td>3.77  4.77   5.10  5.00</td>
</tr>
<tr>
<td>(x = 0.2)</td>
<td>3.63  3.79   4.20  4.40</td>
</tr>
</tbody>
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\(^{a}\) A, B, C and D refer to sintering temperatures of 1100, 1200, 1300, and 1400°C, respectively.
correlated states and the one at the higher frequency (10^5 Hz) corresponds to the hopping of electrons. The magnitude of the loss at 200 Hz would depend on the number of correlated states which in turn depends on the extent of imperfections in the structure. The loss peak at the higher frequency is seen only in some of the samples sintered at higher temperatures of 1300 and 1400°C. As indicated earlier, the samples sintered at higher temperatures result in the creation of Fe^{2+} ions, and therefore the hopping mechanism [27] is significant in these samples. Thus, the samples sintered at lower temperatures which do not show the high frequency peak and have relatively lower losses can be considered to be structurally more perfect compared to samples sintered at higher temperatures.

On the basis of what has been said above, it follows that samples with the composition x = 0.6 and sintered at 1200°C has not only a uniformly low dielectric constant at all frequencies ranging from 100 Hz to 10 MHz, it also shows a low loss factor without any peaks. These are the desirable features in most of the devices; such devices can be successfully operated over a wide frequency range. It may also be observed, however, that the values of the dielectric constant of other samples sintered at various temperatures are also fairly low at frequencies higher than 10^5 Hz. For some of the samples, the losses are also reasonably low. For instance, samples with the composition x = 0.2 and x = 0.5 and sintered at 1200 and 1300°C show losses of the order of 10^{-3} to 10^{-4} at frequencies above 10^5 Hz, and therefore such samples can also find utility in devices operable at frequencies > 10^5 Hz.

The dielectric constant and the dielectric loss, as indicated earlier, are due to the combined effects of: (a) crystal structure perfection, (b) microstructure (porosity), (c) chemical homogeneity, and (d) the amount of Fe^{2+} in the sample. The dominance of each factor varies with the composition of the sample and the sintering temperature. The higher values of losses for x = 0.35 and x = 0.6 samples could be due to the higher density and the presence of larger amount of Fe^{2+}, respectively.

4. Conclusions

The citrate-based preparations have resulted in a dielectric constant and dielectric loss values appreciably lower than those for the samples prepared by the conventional ceramic method. This is a significant result of the present investigation and provides a convenient and economical method for the preparation of better quality ferrites which can be used over a frequency range much larger than that for which the conventionally prepared ferrites can be used.

References