Microwave sintering of Ni–Zn ferrites: comparison with conventional sintering

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Abstract

Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ with $x = 0.0$–1.0 in steps of 0.2 have been densified to $> 95\%$ of theoretical both by conventional and microwave sintering procedures. Comparison studies were performed on these samples sintered at $1275\,^\circ\text{C}$ for 30 min. Microstructural study revealed large, but fewer pores in the microwave sintered specimens and small, but substantially more pores in the case of conventionally sintered specimens. Magnetic properties measurements showed lower coercivity and higher magnetization values for microwave sintered specimens. Lower coercivity values observed in microwave sintered specimens are attributed to larger grain size and higher magnetization values may be explained by the contribution of the ‘microwave field’ to the ‘uncoupling spin effect’. Most significantly samples sintered in a microwave field, generally, showed lower dielectric constant values compared with the samples sintered conventionally, making microwave sintering particularly suitable for high frequency applications.

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1. Introduction

Ni–Zn ferrites are one of the most versatile magnetic materials for general use, which have many applications in both low and high frequency devices and play a useful role in many technological applications such as microwave devices, power transformers in electronics, rod antennas, read/write heads for high speed digital tape, etc. because of their high resistivity, low dielectric losses, mechanical hardness, high Curie temperature and chemical stability [1–6].

The microwave sintering process has unique advantages over conventional sintering processes. The fundamental difference is in the heating mechanism. In conventional heating, heat is generated by heating elements (in resistive heating) and then transferred to sample via radiation, conduction and convection and requires long duration for sintering the materials which may cause some of the constituents to evaporate, thereby modifying the desired stoichiometry [7] and allow undesired grain growth. Unlike conventional heating, in microwave heating, the materials themselves absorb microwave energy and then transform it into heat within the sample volume and sintering can be completed in shorter times. Major advantages of microwave processing are higher energy efficiency, enhanced reaction and sintering rate and shorter cycle times and cost savings [8] and in cases such as WC–Co composites strikingly improved properties. These advantages of microwave processing for ceramics have been described in a series of papers from this laboratory [9–15].

Several researchers reported in the literature [16–26] on various properties of Ni–Zn ferrites prepared by different methods like the combustion technique, hydrothermal formation, citrate precursor method, sol–gel method, however, only limited studies have been carried out and that too on doped systems of microwave sintering of Ni–Zn ferrites [27,28]. As far as the authors are aware, no report has been published on a systematic
Investigation of microwave sintered Ni-Zn ferrites and their comparison with conventionally prepared materials.

In view of importance of these materials and advantages offered by microwave processing, a series of Ni–Zn ferrites were prepared by both conventional and microwave processes and their structural, magnetic and dielectric properties were studied and results of such an investigation presented in this paper.

2. Experimental

Ni$_1-x$Zn$_x$Fe$_2$O$_4$, where $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 were prepared using high purity NiO, ZnO and Fe$_2$O$_4$ in stoichiometric proportions. It was reported earlier that the absorptivity of Fe$_2$O$_3$ at 2.45 GHz is relatively very low as compared with Fe$_3$O$_4$ [29]. Therefore, in these experiments, Fe$_3$O$_4$ that has mixed valent Fe ions was chosen as the source of iron. The powders after thorough mixing and grinding were calcined at 1100 °C for 4 h. In order to minimize any size effects, the mass ($\approx$ 1.5 g) of the material was kept constant in all our experiments. All compositions were sintered at 1275 °C for 30 min in conventional furnace. In a parallel run, samples were fired at the same temperature and time using microwave furnace operating at a maximum input power of 2.0 kW (Amana Radarange, Model RC/20SE) with a 2.45 GHz multimode cavity. More details about this experimental set-up can be found in earlier papers [30,31].

The samples were placed at the center of the tube and to maintain the uniformity of sintering, samples were placed on a thicker SiC plate that acted as a susceptor. Ni ferrites are good microwave absorbers by themselves, therefore, undergo a rapid heating causing cracks all around the sample. In order to prevent rapid heating and cracking a gradient heat flow was developed by using SiC plates to support the pellets. Hence, a controlled heating was possible without any cracking. In addition to that SiC plates also help in concentrating the electromagnetic field around the ferrite samples [32]. Accurate input power control to the oven was possible by using a power meter in series with the variac. The temperature of the sample was monitored using an infrared pyrometer (Raytek, Marathon series) with the circular cross wire focused on the sample cross-section. We used an emissivity value of 0.75. This value was chosen based on sample color and composition. To verify the accuracy of the temperature were also simultaneously measured using an optical pyrometer (Leeds and Northrup). The infrared pyrometer was attached to a personal computer for accessing the temperature data as a function of time. Fig. 1 shows the match up values measured using IR and optical pyrometers.

All sintered samples were characterized for phase composition by X-ray diffractometer (Scintag Inc., Cupertino, USA). The microstructures of the polished

![Figure 1](image-url)  
Fig. 1. Comparison of temperatures measured using infrared and optical pyrometers. Linear fit with a slope $y = -1$, shows that they match very well.
surfaces of the samples were examined by Scanning Electron Microscopy (Hitachi Ltd., Tokyo, Japan). Six micrographs in each category, with identical magnification were taken for pore size measurements. About 500–600 pores were measured and plotted, that was used for average pore size calculations. The sintered densities were measured by the Archimedes method. The magnetic hysteresis parameters were measured using Vibrating Sample Magnetometer (Lakeshore Cryotronics Inc., USA). The sintered samples were polished and silver

Fig. 2. X-ray diffractograms of Ni-Zn ferrites sintered at 1275 °C for 30 min (a) microwave sintered, (b) conventional sintered, peak positions and peak shifts match that of reported values for corresponding compositions.
paint was coated for dielectric property measurements by using a Hewlett-Packard 4194A impedance analyzer in the frequency range from 1 kHz to 13 MHz.

3. Results and discussion

3.1. Crystal structure and microstructure

X-ray diffraction patterns of the samples sintered in microwave field and samples sintered conventionally matched with the patterns reported as shown in Fig. 2(a and b). The spinel cubic structure revealed a slight shift in the peak positions with ZnO substitutions. The shift corresponds to the crystal structure expansion due to substitution of bigger Zn ions in place of smaller Ni ions in the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ structure. As reported earlier, the Ni$^{2+}$ ions prefer octahedral sites because of their favorable alignment of charges in the octahedral site’s crystal field. Using Debye Scherrer formula, we calculated the crystallite size of the ferrites sintered in conventional furnace and microwave furnace. The results are surprising. The crystallite size versus composition ($x$) curve followed a decreasing trend with Zn$^{2+}$ ion substitution with the lowest for pure ZnFe$_2$O$_4$ spinel (see Fig. 3). Also, for a given ‘$x$’ value, the X-ray crystallite size is bigger for the microwave sintered sample than the corresponding crystallite size reported for the conventionally sintered one. This could be due to drop off in the activation energy by the surrounding electromagnetic field explained in the later part of Section 3. The densities of microwave and conventionally sintered ferrites lie almost in the same range (see Fig. 4), indirectly representing the match up of their temperatures. Under an ideal situation this X-ray crystallite size value should correspond to crystallite/grain size in the microstructure. Hence, we attempted to measure grain size from the scanning electron micrograph, which in fact was not very successful. It was hard to locate clear grain/grain boundary interface and most of the times the surface appeared plain. However, the porosity size, shape and distributions were quite different for both conventionally and microwave sintered samples, which offered a rough idea about sintering and grain size nature. The accuracy of the crystallite size determined Scherrer’s formula is not very accurate as this depends on inherent factors as crystal imperfections such as dislocations. This ‘non-ideal situation’ is probably responsible for the mismatch of the crystallite size values evaluated by XRD and SEM. Nevertheless, the decreasing trend observed in the above figure was confirmed by qualitative observation in SEM. The scanning electron micrographs of Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ are shown in Fig. 5(a and b).

One can clearly see from the micrographs that the conventionally sintered samples had tiny pores, densely distributed throughout the microstructure. The microstructure revealed bigger pores, distributed uniformly in the case of microwave-sintered sample. Pore sizes were characterized by measuring their diameter for a minimum of 500 pores in each category. The distribution is shown in Fig. 6. The average size is the size below which

![Fig. 3. Crystallite size values were calculated for all compositions by measuring FWHM value of peak (311).](image-url)
Fig. 4. Densities of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ for $x = 0.0$ to $1.0$ sintered at 1275 °C calculated using Archimedes procedure. The conventional and microwave sintered pellet densities match each other.

50% pores are distributed. The average pore size of microwave sintered Ni$_{0.9}$Zn$_{0.1}$Fe$_2$O$_4$ is 1.31 μm, which is ~2 times larger than conventionally sintered pellets. Pore size provides information like sintering, grain size etc.

Under identical experimental conditions, the porosity differences between microwave and conventionally sintered compacts are intriguing. Since the powders used in both microwave and conventional processes originate from the same batch, at time $t_0$ they have the same average particle size. After initial induction period, the grain size $Q$ can be expressed as,

$$Q = U(t - t_0)$$  \hspace{1cm} (1)

where $U$ is growth rate, $t$ is the time and $t_0$ is the induction period. The free energy difference across curved grain boundary is expressed as

$$\Delta G = \gamma V \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$  \hspace{1cm} (2)

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Fig. 5. Scanning electron micrographs of (a) conventional and (b) microwave sintered Ni$_{0.9}$Zn$_{0.1}$Fe$_2$O$_4$. Surface of microwave sintered pellets shows large pores but small in numbers whereas smaller pores and more in number for conventionally sintered composition.
Fig. 6. Variation of distribution of pores with pore size for microwave sintered and conventionally sintered Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ calculated for about 500 pores.

According to absolute rate reaction theory, the frequency of an atomic jump from position A to B is given by the equation

$$F_{A\rightarrow B} = \frac{RT}{Nh} \exp\left(\frac{-\Delta G^*}{RT}\right)$$  \hspace{1cm} (3)

Microwave field playing a crucial role in promoting the densification process by increasing the mobility of diffusing species across the grain boundary thus enhancing the growth rate. Field, therefore, reduces the activation energy for a forward jump and increases the barrier height for a reverse jump as described in Fig. 7. In that case, Eq. (3) can be represented as

$$F_{A\rightarrow B} = \frac{RT}{Nh} \exp\left(\frac{-\Delta G^* - \alpha}{RT}\right)$$  \hspace{1cm} (4)

The activation energy barrier for the reverse jump is thus increased by $1/\alpha$ and frequency for this jump is

$$F_{B\rightarrow A} = \frac{RT}{Nh} \exp\left(\frac{-\Delta G^* + \Delta G}{RT}\right)$$  \hspace{1cm} (5)

Net growth process $U = if$, where $f = \lambda(F_{A\rightarrow B} - F_{B\rightarrow A})$. Hence,

$$U = \frac{RT}{Nh} \exp\left(\frac{-\Delta G^*}{RT}\right) \left(F - \left(\frac{-\Delta G}{RT}\right)\right)$$  \hspace{1cm} (6)

where $F = \exp(-\alpha/RT)$. $\alpha = 0$ and $F = 1$ corresponds to zero field influence. Higher values favor forward jump resulting in the formation of larger grains with relatively big pores in the grain junctions. This would explain the difference in crystallite/grain sizes observed in Fig. 5(a and b).

![Graph showing variation of distribution of pores](image)

Fig. 7. Possible reduction in the activation barrier height due to the application of microwave field.

![Graph showing M-H values](image)

Fig. 8. Room temperature M. H graphs of Ni–Zn ferrites sintered using (a) microwave and (b) conventional procedures.
3.2. Magnetic properties

The room temperature M–H graphs of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ pellets sintered in microwave and conventional procedures are given in Fig. 8(a and b). All samples exhibit low coercivity values, which is typical of soft ferrites. Almost same sized and weighed samples were used for these measurements. The $M_s$ (saturation magnetization) and $H_C$ (coercivity) values were measured and plotted against the Zn concentration, shown in Fig. 9. For both conventional and microwave sintered samples, the $M_s$ value shows an increasing trend till $x = 0.4$. This trend can be explained by the formation of 'uncoupled spins' with increasing 'x' value. With more and more Zn$^{2+}$ occupying the tetrahedral sites (site of Fe$^{3+}$) the spin–spin interaction between Zn$^{2+}$ and Fe$^{3+}$ becomes increasingly uncoupled and a high magnetic field is required to align them in the direction of applied field [33,34]. The higher $M_s$ value in the case of $x = 0.4$ can be attributed to the following reasons:

i) 2.45 GHz microwave field can locally interact with charged cations resulting in alteration of Zn$^{2+}$ and Fe$^{3+}$ arrangements, that can play a crucial role in altering the dipole moments. These variations may significantly contribute to the 'uncoupling effect' [33,34] resulting in a higher value of magnetization.

ii) Simple localized temperature variations referred to as local anisothermicity, could alter the localized stoichiometry that may have contributed to the $M_s$ values.

At this point, we do not have any experimental evidence to prove these points and hence a reason other than above could also have resulted in high value of $M_s$.

The difference between the coercivity values of the microwave and conventionally sintered samples are more easily explainable. In general (except one value), for a given 'x' value, the microwave sintered sample showed a lower coercivity value compared with conventionally sintered samples. This drop in $H_C$ value is attributed to larger grains observed in microwave-sintered samples. Larger grains consist a high concentration of domain walls, and minimal energy is sufficient to move domain walls. Lowest coercivity was observed for Ni$_{0.9}$Zn$_{0.1}$Fe$_2$O$_4$ composition. The coercivity value decreases with 'x' till this composition, could be due to promotion of sintering and grain growth by ZnO.

Pure ZnFe$_2$O$_4$ is paramagnetic at room temperature with a Neel temperature, $T_N = 10$ K below which, it exhibits antiferromagnetic behavior. At elevated temperatures, volatilization of Zn$^{2+}$ ions occur in ZnFe$_2$O$_4$ causing the formation of Fe$^{2+}$ ions, thus reducing resistivity and increasing electron hopping. As a result of this process, a small magnetic moment is generated and a finite value of external field is required to align these moments in the applied field direction. This process is also believed to affect coercive field values. Besides, the $H_C$ values are also depend on the grain size values significantly. A similar result for pure ZnFe$_2$O$_4$ has been obtained by Rana et al. [33] while studying on Cu–Zn ferrites.

![Fig. 9. Variation of saturation magnetization and coercivity with Zn concentration.](image-url)
3.3. Dielectric properties

Highly conducting grains surrounded by insulating grain boundaries lead to a capacitor-like arrangement, in which domination of space-charge polarization occurs under the influence of electric field. The variation of dielectric constant with frequency for both microwave sintered and conventionally sintered pellets are shown in Fig. 10(a and b). For the conventionally sintered compositions, all the ferrite compositions showed highest value of dielectric constant at 1 kHz. A value of 5000 was obtained for pure ZnFe$_2$O$_4$. For all other compositions the dielectric constant values remain less than 1200. From 1 to 100 kHz, the dielectric constant values fall steeply whereas after 100 kHz the fall is slow and gradual. In the case of microwave-sintered samples, we obtained rather different results. In these microwave sintered, pure NiFe$_2$O$_4$ showed the highest value (about 2500). Pure ZnFe$_2$O$_4$ that showed the highest value in the case of conventionally sintering procedure, showed a value of only 308.64. Referring to Table 1, for all other compositions (except the end member) the microwave-sintered ferrites showed a much lower value compared with the conventionally sintered one of the same composition.

At higher frequencies, the electric charge carriers are unable to follow the rapid switching of the AC field and hence the dielectric constants at high frequencies are relatively low. Pure ZnFe$_2$O$_4$, sintered conventionally, has a high dielectric constant value, which is attributed to possible evaporation of Zn$^{2+}$ at 1275°C. However, use of microwaves could possibly help in retaining the Zn$^{2+}$ in the ZnFe$_2$O$_4$ structure. This explanation seems to be applicable for all Zn containing compositions. The higher dielectric constant value in the case of microwave sintered NiFe$_2$O$_4$ is possibly due to selective interaction of microwave field with Ni$^{2+}$ ions. The lower value in the case of microwave sintered mixed compositions is attributed to uniform sintering means of the microwave procedure. Though other factors such as density and porosity also have greater influence on the dielectric constant, these values for the microwave and conventionally sintered compositions lie in the same range (see Fig. 4 and Table 1).

Significant differences were observed in dielectric loss variation with frequency for microwave and conventionally sintered samples. The differences can be noticed from Fig. 11(a and b). Samples namely Ni$_{0.9}$Zn$_{0.1}$Fe$_2$O$_4$, Ni$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ and ZnFe$_2$O$_4$, prepared by microwave procedure exhibit high loss factor values at lower frequencies. However, the conventionally prepared samples have relatively lower values. Microwaves are known to interact with high loss materials due to polarized species in the specimen. On the other hand an exposure of highly absorbing species such as ferrites would result in formation of polarized species within them. This probably explains the observed differences.

4. Conclusions

Powders of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ with x varying from 0 to 1 have been synthesized using conventional ceramic procedures. Pellets made out this powder have been sintered using both microwave and conventional procedures at 1275°C for 30 min. With their densities identical, the microwave-sintered pellets contain relatively large grains compared with the corresponding conventionally sintered compositions, thus indicating an enhancement effect, possibly by the associated microwave field. The enhancement effect can be explained by introducing an enhancement factor 'z' in the conven-
Table 1. Data of conventional and microwave processed Ni-Zn ferrites

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<tr>
<th>Sample code</th>
<th>Composition</th>
<th>Density (g cm⁻³)</th>
<th>Coercivity (G)</th>
<th>Coercivity (G)</th>
<th>Loss Factor</th>
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<td>Microwave</td>
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<td>9.10</td>
<td>7.60</td>
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Fig. 11. Variation of dielectric loss values with frequency for all Ni₃₋ₓZnₓFe₂O₄ compositions sintered using (a) microwave and (b) conventional procedures.

Typical grain growth equation. Magnetic property measurements indicate that Ni₃₋ₓZnₓFe₂O₄ sintered by both conventional and microwave procedures exhibit the characteristic soft ferrite loops with high magnetization (₅) and low coercive field (₅) values for the microwave sintered ones. Low coercive fields can be due to larger grain sizes and higher magnetizations can be due to projected alteration of charge distributions inside the magnetic lattice by the surrounding electromagnetic field and their contribution to the 'uncoupling effect'. Dielectric measurements on the microwave-sintered specimens show low dielectric constant values compared with their counterparts sintered using conventional procedure, which generally are preferable for high frequency applications.
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