Room Temperature Measurements of Physical and Magnetic Characteristics of Co₀.₄Ni₀.₃Zn₀.₃Fe₂O₄ Polycrystalline Material Prepared Using Mechanically Alloyed Nanoparticles

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Abstract: Co₀.₄Ni₀.₃Zn₀.₃Fe₂O₄ ferrites material with the crystallite size in the size range 10-50 nm was prepared using mechanical alloying and sintering. The structure and morphology of samples were studied. The initial permeability (μ’) and permittivity (ε’g₀.₃₀₄) has been studied as the functions of frequency and the sintering temperatures sintering temperature using a network analyzer from 10 MHz to 1.8 GHz. X-ray diffraction confirmed the formation of spinel structure and a scanning electron micrograph was used to analyze the grain size distribution of ferrite. The permeability spectra of the resulting ferrite samples shows increasing values with the increasing sintering temperature, this is attributed to the grain growth as a result of the sintering process. Permittivity ε’ also increases with increasing average grain size, which may be ascribed to the increase in an increase in the Fe²⁺ concentration formed at elevated sintering temperature.

Key words: Mechanical alloying; Ferrite; Permeability; Permittivity; Sintering temperature.

INTRODUCTION

Nanotechnology is the creation and utilization of materials, devices and systems through the control of matter on the nanometer scale (Mathew and Juang 2007; Salerno, Landoni et al. 2008). In recent times, scientists have shown increasing interest in science and technology at the nanometre scale. This is because, at the nanoscale, properties like electrical conductivity and mechanical strength are not the same as they are too at bulk size (Huo, Chen et al.; Xiangfeng, Dongli et al. 2006). Its electronic structure also dramatically changes (Mathew and Juang 2007; Xu, Wei et al. 2009). A spinel ferrite nanoparticle belongs to the class of nanomaterials generating a lot of interest due to their technological applications. Their typical properties of having a high surface-to-volume ratio make them useful for potential applications in nanoelectronic devices, sensors, solar cells, photonics, and multiferroic materials (Xie, Li et al. 2008), catalysis (Li and Xia 2003), biomedical separation, and microwave absorbers (Hwang 2006; Nam, Joo et al. 2009), amongst host of others.

The interesting and useful magnetic and electrical properties of the spinel ferrites are governed by the choice of the cations along with Fe²⁺, Fe³⁺ ions and their distribution between tetrahedral (A) and octahedral (B) sites of the spinel lattice as well as preparation conditions (Gul and Maqsood 2008; Zhao, Xu et al. 2008). Various methods have been reportedly used for the preparation of ferrites, which includes Mechanical alloying (MA) (Jalaly, Enayati et al. 2009), Electrosprinning (Li and Xia 2003), microemulsions (Mathew and Juang 2007), hydrothermal (Xiangfeng, Dongli et al. 2006), sol–gel (Zahi, Hashim et al. 2006) and co-precipitation (Hsiang and Yao 2007). A survey of the literature (Ding, McCormick et al. 1997; Kim, Lee et al. 2001; Lee, Kim et al. 2001; Hwang 2006; Xiangfeng, Dongli et al. 2006; Gul and Maqsood 2008; Kulkarni, Lonkar et al. 2008; Xie, Li et al. 2008; Han, Ou et al. 2009; Jalaly, Enayati et al. 2009) revealed that there are no systematic studies on the permeability and permittivity of Co₀.₄Ni₀.₃Zn₀.₃Fe₂O₄ prepared via mechanical alloying, more so in the frequency range of 10 MHz to 1.8 GHz. Therefore in this paper an attempt is made to present the behavior of structural, magnetic and dielectric properties such as permeability, loss factor, permittivity (ε’) and tangent of dielectric loss (ε”) Co₀.₄Ni₀.₃Zn₀.₃Fe₂O₄ ferrite prepared using mechanical alloying and sintering. MA is chosen because it is a powerful tool for producing nanosized powders and nanocomposite materials. Such
mechanical activation effects permit the formation of equilibrium or non-equilibrium phases directly without any thermal treatments or with low-temperature annealing (Ding, McCormick et al. 1997; Cui, Wang et al. 2001; Cabrera and Sánchez 2002; Zhou, Xue et al. 2002)."

MATERIALS AND METHOD

For the synthesis of Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ material, a mixture of Fe$_2$O$_3$ (99.5% purity), Co$_3$O$_4$ (99.7%), NiO (99.0%) and ZnO (99.7%) all from Alfa Aesar were used as received without further purification. The required amounts were weighed and mixed accordingly in a vial to achieve the stoichiometry. Mechanical alloying was carried out in the hardened steel vial together with ten 12 mm steel balls for 12 h using a Spex 8000D mixer/mill. A ball to powder mass charge ratio of 10:1 was chosen. For all powder handling, milling and subsequent pressing and heat treatments were performed in air. The density and BET surface area of the as-milled powders were measured. Subsequently, the sample was made into pellets and toroidal of several batches of diameters = 20 mm and thickness of = 2 mm, with an internal diameter of = 10 mm (for toroidal sample). Each pellet/toroid was sintered at different temperature in the range 600 °C to 1000 °C at 100 °C interval. The heat treatments were carried out in air for 6 h in each case, employing a heating rate of 2 °C/m. The resulting products were used for surface, magnetic and dielectric measurements.

$$120Fe_2O_3 + 16Co_3O_4 + 36NiO + 36ZnO \rightarrow Co_{0.4}Ni_{0.3}Zn_{0.3}Fe_2O_4 + 8O_2 \uparrow$$

The crystallographic phase of the samples has been examined from the X-ray diffraction (XRD) spectrum using X-Pert PANalytical diffractometer. The spectrum of each sample was recorded at room temperature using Cu Kα radiation(λ=1.5418 Å), in the 2θ range 20 °C to 70 °C with step size 0.03° operating at 40 kV and 30mA. An Accupyl 1330 Pycnometer, using the principle of measuring the pressure change of helium in a calibrated volume was used to measure the density of the sample. The scanning electron microscope (SEM) (Cambridge Stereoscan S-250 MK-II), equipped with energy dispersive analysis of X-ray (EDX) spectrometer was employed to study the surface morphology of the samples and the elemental analysis. The magnetic permeability and dielectric permittivity were measured in the frequency range of 10 MHz to 1.8 GHz by the bridge method, using an Agilent Model 4291B Network/Spectrum analyzer. And finally, the specific saturation magnetization, coercivity and retentivity were measured at room temperature by a vibrating-sample magnetometer in a field of 10,000 Oe.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ powders are shown in Fig. 1. For the starting materials, all the major peaks of Fe$_2$O$_3$, ZnO, NiO and Co$_3$O$_4$, which can be indexed to (1 0 4), (1 0 1), (2 0 0) and (3 1 1) planes were evident. For the 12 h milled sample however, the peaks appeared as an amorphous phase, suggesting that it is a pentranary phase consisting of Co, Zn, Ni and Fe, which nucleates at interfaces and grows by interdiffusion reaction under interfacial metastable equilibrium. This is because, the ball milling facilitates such reactions by fracturing and cold-welding crystalline particles to create alternating layers with fresh interfaces, and generating a high density of defects. However, upon sintering the sample at 600 °C, the x-ray diffraction peaks became narrower, indicating an improved crystallinity. The degree of crystallinity of the sample increased with increasing sintering temperature from 600 to 1000°C, suggesting the enhancement of crystallinity due to sintering. All the peaks of the sintered samples can be clearly indexed to the seven major peaks of the spinel ferrites, which are (2 2 0), (3 1 1), (2 2 2) (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of a cubic unit cell, which correspond to cubic spinel structure. The crystallite size of the material as shown in Table 1 was determined using the well-known Scherrer’s equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength, θ the Bragg’s angle and β is the full width of the diffraction line at half the maximum intensity (FWHM). The BET surface area and the average pore volume and the density of the as-milled sample are 18.48 m$^2$/g and 17.46 nm and 5.04 g/cm$^3$ respectively. Furthermore, the density of the samples shown in Table 1 reveals an increasing density with sintering temperature, with the highest density of 5.2(8) g/cm$^3$ for the sample sintered at 1000°C. This suggested that, the MA is successful in powder compaction to achieve theoretical density (Koch and Whittenberger 1996).
Fig. 1: XRD micrographs of as-prepared samples of Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$

Table 1: Physical properties of the as-prepared Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>A (Å)</th>
<th>A=β=γ (Å)</th>
<th>2ThetaObs.</th>
<th>2ThetaCal.</th>
<th>V (Å$^3$)</th>
<th>Crystallite size (nm)</th>
<th>Density ρ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-milled</td>
<td>8.342</td>
<td>90.00</td>
<td>35.44</td>
<td>-</td>
<td>426.06</td>
<td>19.20</td>
<td>5.0(4)</td>
</tr>
<tr>
<td>600°C</td>
<td>8.371</td>
<td>90.00</td>
<td>35.54</td>
<td>35.54</td>
<td>586.59</td>
<td>33.60</td>
<td>5.2(5)</td>
</tr>
<tr>
<td>700°C</td>
<td>8.352</td>
<td>90.00</td>
<td>35.63</td>
<td>35.63</td>
<td>582.39</td>
<td>44.80</td>
<td>5.2(6)</td>
</tr>
<tr>
<td>800°C</td>
<td>8.365</td>
<td>90.00</td>
<td>35.57</td>
<td>35.57</td>
<td>585.35</td>
<td>53.70</td>
<td>5.2(6)</td>
</tr>
<tr>
<td>900°C</td>
<td>8.375</td>
<td>90.00</td>
<td>35.52</td>
<td>35.52</td>
<td>587.49</td>
<td>67.20</td>
<td>5.2(7)</td>
</tr>
<tr>
<td>1000°C</td>
<td>8.378</td>
<td>90.00</td>
<td>35.51</td>
<td>35.51</td>
<td>588.06</td>
<td>89.60</td>
<td>5.2(8)</td>
</tr>
</tbody>
</table>

The SEM micrograph of the sample sintered at 1000°C is shown in Fig 2a. From the figure, it can be seen that it is agglomerated to some extent, which can be attributed to the interaction between magnetic Nanoparticles and the relative higher annealing temperature (1000°C) (Hessien 2008). The size of the agglomerate ranges from 100 to 300 nm. From Fig. 2b, the EDX of the as-prepared sample shows clearly the presence of the constituents of Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$. The TEM photographs of the as-milled powders and the sample sintered at 1000° are shown in Fig. 3a and 3b respectively. The ferrite powders had uniform, spherical morphology. The particle sizes from TEM were determined to be 10 to 20 nm for the as-milled and 30 to 50 nm for the sintered sample. These show some consistency with the calculated values.

Fig. 2: Microstructures of the Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ samples: (a) SEM and (b) EDX, (c) of sample sintered at 1000°C.
Table 2 and Fig. 4 show the real permittivity ($\varepsilon'$) and the dielectric loss tangent ($\varepsilon''$) of the as-prepared Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ within the frequency range of 10 MHz to 1.8 GHz. The $\varepsilon'$ and $\varepsilon''$ represents the dielectric properties which symbolizes the storage capability of electric energy its dissipation (or loss) of energy within the medium respectively. From Fig. 4a, it can be seen that the samples shows a relatively constant $\varepsilon'$ up to a frequency of 400 MHz and was afterwards seen to increase with increasing frequency. The sample sintered at 1000 °C shows a higher $\varepsilon'$, suggesting that, 1000 °C sintering temperature leads to an increase in Fe$^{2+}$ concentration and is, therefore, responsible for the increase in polarization. At 1.5 GHz however, a sharp drop in the $\varepsilon'$ values was observed for all the samples. For the $\varepsilon''$ values as shown in Fig. 4b, all the samples show a high electric energy loss at higher frequency (above 1.0 GHz). Furthermore, the loss was seen to increase with increasing sintering temperature. Towards the end of the measurement range, a slight increase in the measured loss similar to those observed in the $\varepsilon'$ values. This can be attributed to the LC resonance in the measurement circuit.

Figs. 5(a) and (b) show the real permeability ($\mu'$) and the loss factor $\mu''$ respectively for the as-prepared samples sintered in the temperature range of 600 to 1000°C. As shown from Fig. 5a, the permeability increases with increasing sintering temperature, which can be attributed to the increase in the crystallite size consequent to the sintering. 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 $\mu'$ (Verma, Goel et al. 2000). For all the samples the permeability $\mu'$ and loss factor $\mu''$ were fairly constant with frequency. They however rises slightly around 900 MHz. A look at the samples sintered at 900 and 1000 shows a dispersion and absorption regions around 1.0 GHz. The observed phenomenon is attributed to the domain wall displacements, which are believed to have made a major contribution to the initial permeability. A similar phenomena was also reported in (Han, Ou et al. 2009). It is well known that the $\mu'$ characteristics depend not only on chemical composition but also on the microstructure of the sintered body. However, for a given material, the permeability is determined by in the domain wall motion and the spin rotation magnetizing mechanism (Nakamura 1997). 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 higher than 1.8 GHz (the maximum frequency of the Agilent Model 4291B Network/Spectrum analyzer used in the present work).

Table 2: Summary of the frequency and sintering temperature dependence of magnetic and dielectric properties of the as-prepared Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\mu'$ (10MHz, 1.8GHz)</th>
<th>$\mu''$ (10MHz, 1.8GHz)</th>
<th>$\varepsilon'$ (10 MHz, 1.50 GHz)</th>
<th>$\varepsilon''$ (10MHz, 1.68 GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2.52, 5.97</td>
<td>0.19, 2.34</td>
<td>6.65, 7.40</td>
<td>0.017, 0.093</td>
</tr>
<tr>
<td>700</td>
<td>3.11, 7.88</td>
<td>0.12, 5.73</td>
<td>6.39, 7.24</td>
<td>0.072, 0.14</td>
</tr>
<tr>
<td>800</td>
<td>3.14, 6.62</td>
<td>0.17, 6.35</td>
<td>6.65, 7.59</td>
<td>0.075, 0.21</td>
</tr>
<tr>
<td>900</td>
<td>4.60, 6.47</td>
<td>0.08, 10.50</td>
<td>6.31, 7.18</td>
<td>0.086, 0.25</td>
</tr>
<tr>
<td>1000</td>
<td>5.17, 7.08</td>
<td>0.03, 11.8</td>
<td>7.37, 8.66</td>
<td>0.061, 0.35</td>
</tr>
</tbody>
</table>
The permeability loss arises due to lag of the motion of domain walls vis-a-vis the alternating magnetic field (Ishino and Narumiya 1987). As can be seen in Fig. 5b, at a higher frequency (1 GHz) loss is observed to increase with increase in the sintering temperature. The frequency at which losses begin to increase due to the onset of resonance varies sintering temperature. Ferrites prepared by the sintering at lower temperatures exhibit a relatively lower loss values, though with reduced permeabilities. The relationship between $\mu'$ and the $\mu''$ is evident. Increase in the $\mu'$ values correspond to an increase in the $\mu''$. 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.
Fig. 5: Frequency dependence of (a) permeability and (b) loss factor of Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ samples sintered at various temperatures.

Co$^{2+}$ is generally known to have a high anisotropy value in Co$_{0.4}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$ ferrite. However, it is generally believed that zinc content in ferrite increases the density and decreases the anisotropy (Verma, Goel et al. 2000). The mechanism is thus, with zinc content, the Fe$^{3+}$ ions will have no magnetic neighbors and hence the spins become uncoupled which results in an increased in the value of initial permeability. This behavior is strongly reflected in the initial permeability of the material.

Fig. 6 shows the hysteresis loops at room temperature for the as-milled sample as well as the samples sintered at 600 and 1000 °C, 600, and 1000 °C. All the sintered samples exhibit some level of hysteresis loops typical of magnetic behaviors, indicating the presence of ordered magnetic structure in the spinel system. The
saturation magnetizations (M_s) of 1.6, 33.1 and 37.6 emu/g, coercivity (H_c) of 92.1, 291.4 and 92.5 G, and retentivity (M_r) of 0.13, 3.30 and 0.95 emu/g respectively. The M_s value of the as-milled sample is significantly lower than that of the sample sintered at 1000°C. This result is reasonable considering its weakly crystalline nature as revealed by XRD. The M_s value of the sample is slightly lower than those reported for the bulk samples (>40 emu/g). This can be attributed to the surface effects aroused by the distortion of the magnetic moments at the surface of nanocrystallite (Kodama, Berkowitz et al. 1996). Although particle size is increased as the sintering temperature increases from 600 to 1000 °C, the magnetic properties show little variations. This result is reasonable considering the particle size increment is small and particles are rather small, thus the influence of the surface on the magnetic properties is low.

**Fig. 6:** The VSM experimental results of the as-milled Co_{0.4}Ni_{0.3}Zn_{0.3}Fe_2O_4 and the samples sintered at 600 and 1000°C

**Conclusions:**

The cobalt ferrites with Co_{0.4}Ni_{0.3}Zn_{0.3}Fe_2O_4 were prepared using mechanically alloyed nanoparticles. The formation of a crystalline structure reaction cannot be completed by 12 h milling alone, thus requires subsequent sintering. The permeability μ' spectrum of the resulting ferrite samples shows increasing values with the increasing sintering temperature, this can be attributed to the grain-growth, consequence to sintering. The relationship between μ' and the μ" is evident. Increase in the μ' values correspond to an increase in the μ". 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. Permittivity ε' also increases with increasing average grain size, which may be ascribed to both an increase in the Fe^{2+} concentration formed at elevated sintering temperatures.

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**REFERENCES**


