

CHAPTER 3

EXPERIMENTAL

PROCEDURES

3.1 Selection of a Suitable Composition for MgCuZn Ferrites

The choice of composition of a soft ferrite is made to achieve one or more of the following properties ^[19]:

- a. Maximum permeability (e.g., Initial permeability)
- b. Minimum magnetic losses (e.g., Hysteresis losses, Eddy current losses and Residual losses)
- c. Temperature variation of properties between prescribed limits
- d. Adequate saturation magnetization
- e. Satisfactory behaviour over the required frequency band
- f. Minimum cost

From literature review, the importance and amount of MgO, CuO and ZnO were observed and the following criteria were obtained:

i) For **MgO**:

The composition for MgO must be high for 2 reasons ^[25]:

- a. To avoid the presence of divalent iron (Essential requirement to obtain high resistivity).
- b. To avoid the tendency of discontinuous grain growth (Essential requirement to obtain a dense ferrite).

By increasing the content of Mg²⁺ ions, domain wall mobility, initial permeability and initial susceptibility will be increased ^[23].

ii) For **ZnO**:

The addition of non-magnetic ZnO to a spinel ferrite will lead to an increase in the saturation magnetization ^[14, 19]. Increasing the ZnO content will increase the electromagnetic properties of powder, for example, increasing the zinc content in the ferrites will increase the initial permeability ^[56] and change the curie temperature ^[19].

However, increasing the ZnO content will increase the volatility, which will give disadvantages to the ferrites. Therefore, the composition for ZnO must be relatively high to produce good electromagnetic properties, but not so high as to make the ferrite powder volatile.

iii) For **CuO**:

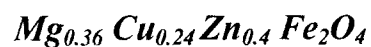
The copper content has significant influence on electromagnetic properties, such as initial permeability, quality factor, D. C. resistivity, dielectric constant, dielectric loss tangent and frequency dispersion for MgCuZn ferrites.

Copper oxide will also affect the density and sintering temperature of the ferrites. It is well known that increasing the CuO content will improve densification^[20, 22, 25] and hence reduce the sintering temperature. However, too high or too low the CuO content will affect and decrease the final density^[20, 25].

According to Murthy^[20] and Nakahata et al.^[22], the densification increases towards low sintering temperature with increasing CuO content in between 5.5 mol% to 13.5 mol%. However, Murthy^[20] shows that ferrite with 12 mol% CuO with a sintering temperature of 910°C exhibits optimum properties.

Ferrites are not suitable to be sintered at temperatures higher than 1026°C because at 1026°C, Cu²⁺ (0.70Å) react with an electron to form Cu¹⁺ (0.96Å).

Based on the findings from Murthy^[20], Nakahata et al.^[22], Rezlescu^[25] and Moulson^[19], the following stoichiometric composition was selected:



The derivation of the formula for co-precipitation process and mixed oxide route are shown in Appendix A and Appendix B, respectively.

3.2 Sample Preparation by Co-precipitation Process

MgCuZn ferrite powder was prepared through co-precipitation method. The analar grade (AR) starting materials used in this study were $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (purity of 99%, Fisher Scientific) solid, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (purity of 99%, Fisher Scientific) solid, ZnCl_2 (purity of 98.53%, Fisher Scientific) solid, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (purity of 99.77%, Fisher Scientific) solid and NaOH pellets as raw materials to prepare $\text{Mg}_{0.36} \text{Cu}_{0.24} \text{Zn}_{0.4} \text{Fe}_2\text{O}_4$ (Appendix A). Each of the starting materials was dissolved in deionised water separately to form solutions of Mg^{2+} , Cu^{2+} , Zn^{2+} and Fe^{3+} ions, individually, which were subsequently mixed together. The mixture was then slowly added into excess NaOH solution at room temperature under agitation to initiate the precipitation. During the precipitation process, the solution was continuously stirred using a magnetic agitator. The precipitate is called as precursor and is present in the slurry form. According to Huang and Egon ^[57], the pH of the suspension must be in between 12 to 13.6. Therefore, the mixtures of magnesium hydroxide, copper hydroxide, zinc hydroxide and iron hydroxide precursor were formed in suspension with pH range 12 to 13.6 and was kept for additional 1 hour with continuous stirring using a magnetic agitator. Then, the precursor or slurry was dried at a temperature between 110 – 120°C in an oven.

The precursor was washed with deionised water for a different number of washing steps for ICP (Inductively coupled plasma) analysis to determine the effectiveness of filtration and select the minimum number of washing steps required. During washing, about 10 grams of precursor powder was measured and filtered by 1000 ml deionised water until the pH in the filtrate became neutral. Washing was done in order to remove NaCl and excess NaOH that was used during mixing.

After washing, the precursor was dried at a temperature between 110 – 120°C in an oven for 2 hours and then the as-dried precursor was crushed to fine powder. The dried precursor of 1 gram was taken for TGA, SDTA and XRD analysis. The dried precursor was then divided into different batches for different calcination temperatures. After that, the dried precursor was calcined at a temperature of 400°C for 2 hours followed by the calcination temperature (600°C, 650°C, 700°C, 750°C, 800°C or 850°C) for a further 2 hours with a rate of heating of 4°C / minute in air at atmospheric pressure and cooled in the furnace. The calcined powders were ball milled for 6 hours by spinning at 350 rpm in a Planetary mill, with 10 zirconia grinding balls. Characterization was done on precipitate sample without washing, dried precursor, semi-calcined (400°C) powder and calcined (600°C, 650°C, 700°C, 750°C, 800°C and 850°C) powders by XRD analysis. A Mastersizer was used to investigate the milled size of all calcined powders.

3.3 Sample Preparation by Mixed Oxide Route

The ferrite powder was prepared using the conventional method. The analar grade (AR) powdered raw materials used in this study were MgO (purity of 98 – 100.5%, Merck Germany), CuO (purity of 99%, HmbG Chemicals), ZnO (purity of 99.5%, Fisher Scientific) and Fe₂O₃ (purity of 99%, Merck Germany) to prepare $Mg_{0.36}Cu_{0.24}Zn_{0.4}Fe_2O_4$ (Appendix B). The raw materials were mixed together and ball milled for 6 hours by spinning at 350 rpm in a Planetary mill, with 10 zirconia grinding balls for homogeneity. The mixed powder of 1 gram was taken for TGA analysis.

The mixed powders were then calcined at a temperature of 400°C for 2 hours followed by the calcination temperature (650°C, 700°C, 750°C, 800°C, 850°C or

900°C) for a further 2 hours with a rate of heating of 4°C / minute in air at atmospheric pressure and cooled in the furnace. The calcined powders were ball milled for 6 hours by spinning at 350 rpm in a Planetary mill, with 10 zirconia grinding balls. Characterization was done on powder calcined at 400°C and calcined (650°C, 700°C, 750°C, 800°C, 850°C or 900°C) powders by XRD analysis. A Mastersizer was used to investigate the milled size of all calcined powders.

3.4 The Preparation of Pellets and Toroids for Characterization, Densification and Electromagnetic Properties

After ball milling, the calcined powders were mixed with PVA 6% solution (binder) with the ratio of PVA to powder of 1:10, according to Nakahata et al. [22]. Then, 3 grams of powder were uniaxially pressed in a pellet die of 20 mm in diameter under a load of 8 tonnes for 10 minutes to form a green pellet. 3 grams of powder was uniaxially pressed in toroid die with outer diameter of 25 mm and inner diameter of 18 mm, under a load of 8 tonnes for 10 minutes to form a green toroid. The weight and height of pellets were measured before sintering for green density measurements. Both pellets and toroids were then placed into the furnace for sintering. According to Murthy [20], in order to avoid cracking, sintering must be done in two stages. Therefore, the green pellet and toroid samples were heated up to 500°C for 1 hour followed by the sintering temperature (900°C, 930°C or 950°C) for 2 hours at a heating rate of 4°C / minute in air at atmospheric pressure and cooled in the furnace. The dimensions of the sintered pellet and toroid specimens were measured at room temperature and used in the following measurements:

- a) The sintered pellet was used to measure the sintered density, DC and AC electrical resistivity with silver – paste attached on the two end – surfaces of the

sintered pellet and was also used to identify the single spinel phase and calculation of theoretical density (*TD*) from XRD data.

b) For electromagnetic properties (Initial permeability, Q – factor and Loss factor), the sintered toroid was used and wound with 50 turns of copper wire. The sintered toroid was also used to study the microstructure of the fracture surface.

3.5 Apparatus and Conditions

Thermal analysis has been carried out for determination of ferritization temperature and to investigate the possible chemical reactions by simultaneously recording of Thermogravimetry Analysis (TGA) and Simultaneously Differential Thermal Analysis (SDTA) using a Mettler Toledo TGA / SDTA 851^e. Precursor samples were heated from room temperature to 1000°C at a heating rate of 10°C / minute.

The ferrite powders and pellets were characterized by X– ray diffraction (XRD) analysis using a Phillips X' Pert MPD. XRD was used to ensure that all calcined powders and sintered specimens possessed the spinel single phase. All powders and specimens were scanned using the radiation of Cu K α with the angles (2 θ) scanned between 10 to 80°.

The microstructures of powder and fracture surface of sintered specimens were studied using a XL 40 Scanning Electron Microscopic (SEM). SEM was used to investigate the surface morphology of the dried precursor with and without washing, semi–calcined and calcined powders and fracture surface of sintered toroids.

The effectiveness of washing was determined using a Inductively coupled plasma (ICP).

The milled size was measured using a Malvern Instruments Mastersizer.

The sintered density (**SD**) was measured using an Ultrapycnometer 1000 at room temperature. The percent of porosity (**%P**) was then calculated by using the following equation:

$$(\%P) = (TD - SD) \times 100\% / TD \dots\dots\dots(3.1)$$

Where, TD is the theoretical density.

The resistance of the specimens were measured by FLUKE 45 Dual Display Multimeter at room temperature. The DC electrical resistivity, ρ was then calculated by using the following equation:

$$\rho = R (A / t) \dots\dots\dots(3.2)$$

Where, **R** is the resistance of the specimens, **A** is the surface cross – sectional area and **t** is the thickness of the specimens.

The electromagnetic properties of the toroid specimens were measured using a GW Instek LCR meter 819 with a frequency of 100 kHz and 1.275 V a.c. voltage at room temperature. The inductance quality factor and AC electrical resistivity were directly measured from the LCR meter. The initial permeability, μ_i was calculated according to the following equation [6]:

$$\mu_i = \frac{L}{0.0046 N^2 t \log \left[\frac{d_o}{d_i} \right]} \dots\dots\dots(3.3)$$

Where, **L** is inductance (μ H), **N** is number of windings, **t** is the thickness of the toroid (inch), **d_o** is outer diameter and **d_i** is inner diameter.

For the loss factor (**LF**), the following equation is used:

$$LF = 1 / (Q \mu_i) \dots\dots\dots(3.4)$$

The toroids were wound with copper wire. According to Hsu et al. ^[58], copper is the best conductor material with low cost among the rest (table 3.1).

Table 3.1: Properties of conductor materials

	Resistivity ($\times 10^{-4} \Omega \cdot \text{cm}$)	Oxidation Resistance	Cost	Melting Point ($^{\circ}\text{C}$)
Ag	1.62	good	low	961
Cu	1.72	poor	middle	1085
Au	2.4	good	high	1064
Pt	10.6	good	high	1772
Pd	10.8	good	high	1554
Ag – Pd (Pd 30 %)	25	good	middle	1150

For multilayer chip inductors, silver (Ag) is suggested as the material because of its low resistivity, resulting in components with a higher quality factor ^[17]. Additionally, Ag paste is commercially available at lower cost than Ag – Pd paste.