CHAPTER 2

LITERATURE

REVIEW

2.1 Crystal Structure of Ferrites

The spinel structure is named after the natural mineral $MgAl_2O_4$ with its general formulae being AB_2O_4 [13, 14], where A are cations in the +2 oxidation state and B are cations in the +3 oxidation state. The spinel structure is composed of a close–packed oxygen arrangement, which consists of 32 oxygen ions to form a unit cell which is the smallest repeating unit in the crystal network (See Fig. 2.1).
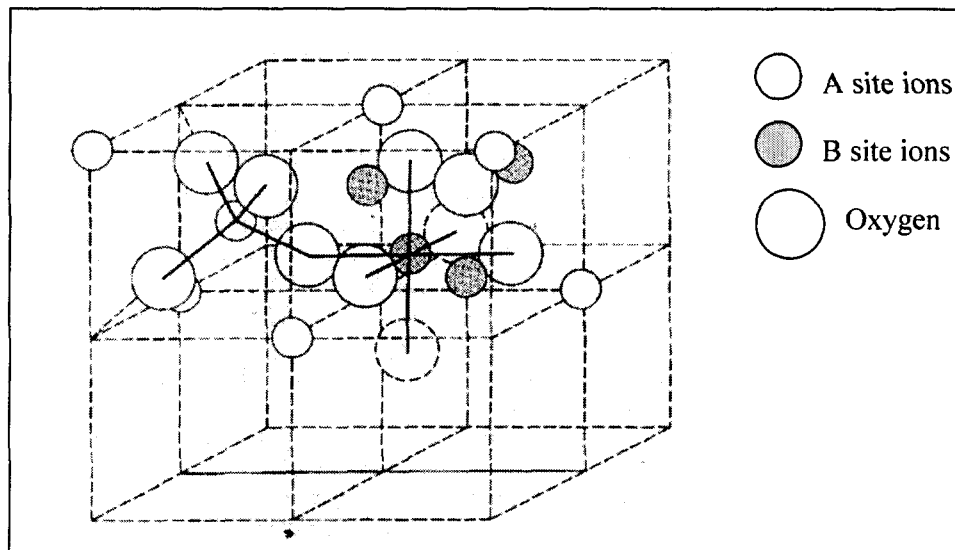

Fig. 2.1: Two subcells of a unit cell of the spinel structure [15]

The spinel structure is characterized by a FCC stacking of oxygen ions where the cations occupy 2 sites:

a) One-eighth of the tetrahedral sites (A-sites), in which metal ions are surrounded by four nearest neighboring oxygen ions, the lines connecting the centers of these oxygen ions form a tetrahedron.

b) One-half of the octahedral sites (B-sites), in which the metal ions are surrounded by six oxygen ions, the line connecting the centers of these oxygen ions form an octahedron.

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A unit cell of the spinel lattice consists of 8 cubes with 64 tetrahedral sites and 32 octahedral sites. Among these, only 8 tetrahedral and 16 octahedral sites are occupied in a full unit cell.

If the ratio of metal ions to oxygen ions is too small, vacancies can be found due to unoccupied metal sites. If the ratio is stoichiometric, the unit cell will contain 24 metal ions and 32 oxygen ions, which is 3 metal ions for every 4 oxygen ions. Therefore, the spinel unit cell will have 8 ions having the formula $MeFe_2O_4$ or (Me) O. (Fe$_2$) O$_3$, which Me refers to divalent metal ion. For example, in magnetite which has the formula FeO. Fe$_2$O$_3$, Me is Fe. Fig. 2.2 shows a summary of the number of ions occupied in A and B sites.

		Me	Fe$_2$	O$_4$
Number of ions =	A sites	-	8	32
	B sites	8	8	

Fig. 2.2: Number of ions in a unit cell of the spinel lattice. [16]

In magnetic spinels, the divalent ions can be any of these ions, i.e., Mg^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+} and Zn^{2+} ions. The presence of Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} ions can be used to provide the unpaired electron spins that cause the magnetic moment of a spinel. Other divalent ions such as Mg^{2+} and Zn^{2+} are not paramagnetic but can be used to disproportionate the Fe^{3+} ions on the crystal lattice sites to provide or increase the magnetic moment. Divalent ions are larger than trivalent ions because the larger charge will produce greater electrostatic attraction and therefore, it will pull the outer orbits to inward direction. Octahedral sites are actually larger than the

tetrahedral sites. Thus, trivalent ions (e.g., Fe^{3+}) would go into the tetrahedral sites and divalent ions would go into the octahedral sites. [33]

The preference of the individual ions in A-sites or B-sites is determined by the ionic radii of the specific ions, the size of the interstices, temperature and the orbital preference for specific coordination. However, the relative size of the ions is more important than the size of the lattice site.

2.2 MgCuZn Ferrites

Both NiCuZn Ferrites & MgCuZn Ferrites were found to be very important in multilayer chip inductors, in which silver paste was used as internal conductor.

However, NiCuZn Ferrites are comparatively sensitive to stresses and their properties are easily changed and deteriorated by stresses. Therefore, many studies and investigation were performed to reduce the stresses [17, 18]. It is suggested that MgCuZn ferrites can overcome this problem and are suitable to be used in multilayer chip inductors. MgCuZn Ferrites are candidate materials for high-frequency [19] engineering ceramics due to their high electrical resistivity, high curie temperature and low cost.

It is reported that the ions in MgCuZn Ferrites occupy the following position in spinel structure [20, 21]:

a. The Zn^{2+} ions occupy A-sites. This is caused by the electronic configuration which is favours tetrahedral coordination by the oxygen ions. Since Zn^{2+} ion is non-magnetic, the addition of Zn^{2+} ions in A-sites reduces the antiparallel coupling between magnetic moments on A and B sites because the occupancy of A sites by magnetic ions is reduced, which will lower the curie temperature [19]. However, the excess of moments on octahedral sites over

those on tetrahedral sites is increased so that the magnetization is increased. According to Moulson [19], if the Zn^{2+} content in ferrites exceeds a certain level`, the magnetization will reduce due to the reduction in antiparallel coupling between the A and B sites.

b. Mg^{2+} (stable valence, +2), Fe^{+3} and Cu^{+2} ions occupy B-sites. [22, 23]

In MgCuZn Ferrites, the following equilibrium [24] may exist during the sintering,

$$Fe^{3+} + Cu^+ \Leftrightarrow Fe^{2+} + Cu^{2+}$$

Under oxidizing conditions, some Fe^{2+} ions can be formed in ferrite to increase the probability of electron hopping. Furthermore, with increasing the sintering temperature, more Cu^+ ions are oxidized to Cu^{2+}, which results in a reduction of the resistivity. Furthermore, formation of Fe^{2+} ions can be reduced by optimizing the sintering temperature, which will minimize the material volatility and oxygen loss [23]. Rezlescu et al. [25] suggested that sintering of MgCuZn Ferrites is dominated by two diffusion mechanism, which are

a) Lattice diffusion

This may be interpreted as cation interdiffusion in the solid solution [20].

b) Grain – boundary diffusion

This diffusion will affect the grain growth during sintering, because the activation energy for lattice diffusion is higher than that for grain – boundary diffusion [26].

2.3 Ferrites Processing Method

2.3.1 Mixed Oxide Route

Conventional ceramic powder prepared by mixed oxide route is inexpensive and is adaptable to large – scale commercial production.

Multi – component oxides are made by blending together oxides, hydroxides or carbonates after the mixture are milled and calcined. The starting oxides, iron, zinc, copper and magnesium should be chosen and characterized for their purity, particle size, shape and degree of agglomeration. The starting oxides should have enough reactivity so that on mixing and calcinations, a homogeneous ferrite can be produced. In the mixed oxide route, mixing is required in order to combine raw materials into a thoroughly homogeneous mixture [27]. Mixing is usually carried out in a ceramic ball mill with ceramics balls, which can avoid concentration of one or more constituents in certain regions of the mass. During calcination process, the starting oxide particles are transformed into smaller ferrite particles with larger surface area and higher free energy, which act as the driving force for the sintering process.

Care must be taken to maintain the quantity and size distribution of the mill balls and to remove those that have become so small that they cannot be separated from the slip or powder on sieving. [19]

2.3.2 Co-Precipitation Process

Co-precipitation is one of the method to produce ferrites. Precipitation with subsequent removal of the solids by filtration is one of the most widely used techniques for the preparation of ceramic powders from solutions. This creates an inexpensive and high quality low-sintering-temperature ferrite powder. Furthermore, this process uses inexpensive raw materials and produces extremely fine powder [28].

This method will enhance homogeneity, purity, optimum particle sizes and reactivity over standard ceramic processing [29]. However, the precipitation step involves a large number of variables that can affect the process. Some variables that control this process are pH, temperature, rates of addition and degree of agitation.

The pH of an aqueous solution plays an important role in the co-precipitation process [29]. The influence of pH on the precipitation of hydroxides is obvious as the OH^- ion concentration appears in the solubility product. Thus, a suitable pH is required in the solution, so that the precipitation can be accomplished.

Other than the pH, the equilibrium of a precipitation can also be affected by solute concentrations, temperature and atmosphere. Equilibrium is seldom achieved during precipitation and a number of non – equilibrium factors should also be taken into account in the precipitation process.

The order of mixing of the solution and the precipitating agent is important. Generally, the solution of cations is added slowly with stirring to a solution containing the precipitating agent. This allows an excess of precipitating agent and the solubility products of all the cations are likely to be exceeded simultaneously [30]. If the precipitating agent is added into the cations solution, it will often cause the cations to be precipitated stepwise with the resulting inhomogeneities.

The rate of mixing is also a variable that can affect the particle size of the precipitate. Rapid mixing of cold concentrated solutions will cause the formation of finely divided precipitates. Stirring rate will affect the degree of supersaturation and the particle size. Stirring will prevent the formation of large agglomerates, which can hinder later steps of powder processing.

For some hydroxide precipitations, prolonged digestion at high pH and at temperatures near the boiling point will form an oxide phase directly that can be

filtered and used without needing a separate decomposition step. This technique is particularly useful for ferrites [31, 32].

In the co-precipitation process, the chemical species that are frequently used are the hydroxides, oxalates, carbonates and chlorides. Chlorides are chosen because of their low price and the bi product (NaCl) can be easily removed.

Co-precipitation is an economical method to produce ultrafine powders. The main advantages of co-precipitation process are greater homogeneity, greater reactivity, high purity with no grinding operation, fine particle sizes can be obtained and the elimination of a calcination process [33]. However, this method may produce coarse particles after dehydration due to agglomeration.

2.4   Ceramics Processing

2.4.1 Raw Materials

The process of selecting raw materials is governed by how critical the properties desired are, the type of equipment and processing used and economic consideration [33].

In the selection of raw materials, particle size plays an important role. During the production of ferrites, the particle size will determine the ease of mixing, compressibility, shrinkage and reactivity during sintering. The particle size requirements of the raw materials depend on the process equipment used. For example, if ball milling is used to blend the original mix, a step which coincidently reduces the particle size, therefore, a lower cost coarser raw material can be used to produced ferrites.

2.4.2 Calcination

Cacining, also called as pre – firing or pre – sintering. Calcining involves heating the blended material to an intermediate high temperature. In general, the calcining temperature will be about 100 to 300°C below the final firing temperature.

The purpose of the calcining is to start the process of forming the ferrite lattice. This process is essentially one of interdiffusing the substituent oxides into a chemically and crystallographically uniform structure [33]. The driving force for the interdiffusion is the concentration gradient. As the individual oxides interdiffuse, some ferrite is created at the interface.

In some cases, compacted powder can be sintered without prior heat treatment, but usually pre-firing or pre-sintering is required.

Calcination is important to reduce the evolution of gases in the final sintering, assist in homogenizing the materials and reduce the effects of variations in the raw materials [34].

Furthermore, calcination is an important factor to control shrinkage during sintering. The required final phases may not be completely formed but remaining chemical gradients may assist sintering. The main requirement is that calcination should yield a very consistent product.

During calcination, interdiffusion between constituent's ions occurs to partially or completely form spinel ferrites. Therefore, it reduces the extent of the diffusion that must occur during sintering in order to obtain a homogeneous body. The extent to which spinel is formed depends on the reactivity of the constituents and the oxidation during the cooling part of the cycle. [16]

2.4.3 Ball Milling

After calcining, the material that has coarsened must be broken up by ball mills or attritors. The amount of milling will determine the particle – size distribution, which in turn will influence the homogeneity of the compact going into the final firing as well as the microstructure after the sintering process [33].

Ball milling is done on a batch of powder in order to break up any agglomerates to form small and uniformly sized particles. The extent of the milling affects the forming characteristics of the powder, the sintered density and the magnetic properties [35]. Besides that, ball milling also introduces defects into the crystals, which may enhance diffusion and accelerate sintering [19].

In general, powders milled by small size grinding balls and a long milling time have a larger surface area. According to Sung et al. [36], after calcination, the surface area of ferrite powder is low. However, ball milling can effectively increase the surface area and reduce the particle size of ferrite powder. A larger surface area causes the ferrite powder to be sintered to higher density.

2.4.4 Binder

Binder is used before compaction to bind the powder particles as they move past one another in the compaction process. The choice of binder depends on the granulation process, method of forming, required strength of the formed piece before firing and exclusion of undesirable residues during sintering. Usually, binder is used in small quantity, as low as 0.5% and as much as 5%. Commonly used binders are gum arabic, ammonium alginate, acrylates and polyvinyl alcohol.

Sometimes, lubricants are used to improve powder flow during forming operation. Commonly used lubricants are waxes, wax emulsions, zinc or ammonium stearate.

2.4.5 Forming or Pressing Operation

Pressing is done to form the powder into a shape, which is as near as possible to the final desired shape. The purpose of pressing is to force the particles into close proximity, so that during sintering, they may densify and grow into a low porosity product. [16]

Before compaction takes place, a powder mass usually contains a small amount of water or binder and then the powder will be compacted into the desired shape by applying a certain amount of pressure. In order to maximize the degree of compaction, appropriate proportions of mixed coarse and fine particles should be used, so that the fraction of void space or porosity in the compacted powder can be minimized. Furthermore, plastic deformation of the particles during compaction must be avoided in order to maximize the degree of compaction.

2.4.6 Sintering

Sintering converts a compacted powder into a denser structure of crystallites joined to one another by grain boundaries [19]. During sintering, compacted powder will shrink and experience a reduction of porosity and an improvement in mechanical integrity by coalescence of the powder into a denser mass.

The purposes of the sintering process are [33]

a. To complete the interdiffusion of the component metal ions into the desired crystal lattice.

b. To establish the appropriate valencies for the multivalent ions by proper oxygen control.

c. To develop the microstructure most appropriate for the application.

The basic of sintering is the reduction of surface energy by transferring matter from the interior of grains along the grain boundaries to adjacent pores, which are eventually filled. The most mobile available entities are vacant crystal lattice sites, which move from the pores into the grain boundaries.

A close examination of the process of solid state sintering, allows three different stages to be distinguished:

Stage 1: Initial stage

Particle begins to adhere together and necks grow between these particles. At the end of this stage grain boundaries are established and grain growth begins to occur. Shrinkage is only a few percent.

Stage 2: Intermediate stage

Grain growth continues and pore channels are formed along the grain edges. At a relatively density of about 95%, the channels are pinched and close up in certain locations.

Stage 3: Final stage

Rounded, closed pores are formed at the grain boundaries and grain corners. This final stage may result in an almost completely dense material as a result of the removal of these pores or, alternatively, the pores may be trapped inside the grains when the boundaries break away from them. Pore growth may also occur as a result of vacancy migration.

Densification almost always requires shrinkage. The shrinkage takes place as a result of materials being transported by one or more of several diffusion processes. This may involve a liquid or diffusion at grain boundaries or through the volume of particles. Any vapor transport or surface diffusion will not contribute to shrinkage and densification.

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If sintering is not too rapid, residual pores and any second phase constituents are carried to the grain boundaries. If rapid sintering takes place, impurities will be trapped within the grain, which provides pinning centers for the domain walls, lowering permeability and increasing the losses in ferrites. Therefore, an appropriate rate of sintering is required.

For ferrites, excess oxygen is required during sintering operation to prevent the formation of ferrous ions. Existence of ferrous ions in ferrite will reduce the electrical resistivity and eventually increase losses and reduce the electromagnetic properties.

2.5   The Properties of Ferrites Materials

2.5.1 Domain Wall Energy

A domain wall or boundary is a region where the magnetization direction in one domain is gradually changed to the direction of the neighboring domain [33]. In this case, exchange energy is involved. Exchange energy is the energy required for the magnetization change from one direction to the neighboring direction. The exchange energy is reduced by an increase in the width of the domain wall.

However, in the presence of anisotropy energy, rotation of the magnetization from an easy direction increases the exchange energy. Therefore, domain wall energy increased as the domain width increase.

2.5.2 Permeability and Initial Permeability

Initial permeability is defined as the change in flux density (B) in the B − H hysteresis curve (H refer to applied magnetic field strength), very near to the origin and represents magnetization by reversible Bloch Wall displacements. Therefore, a major contribution to the initial permeability is Bloch Wall movements, while microstructure (grain size) has a significant influence.

Initial permeability could be resolved into two types of mechanism [37], which are:

a) Contribution from spin rotation.

b) Contribution from domain–wall motion.

The contribution from spin rotation was found to be smaller than that from domain–wall motion [38].

High magnetic anisotropy implies high–energy walls readily "pinned" by microstructure defects. Thus, in order to obtain high permeability of ferrites materials, very mobile domain walls are needed, so that a large defect–free grains together with low magnetic anisotropy are required. Furthermore, porosity will also contribute to the domain wall pinning. By increasing the amount of porosity, permeability will be decreased significantly.

Variations of initial permeability of MgCuZn ferrites are also influenced by microstructure, magnetostriction, internal stress and other factors, which can be related by the following equation [39]:

$$\mu_i \propto (M_S)^2 / (a\ K + b\ \lambda\ \sigma) \dots\dots\dots\dots\dots\dots\dots(2.1)$$

Where, μ_i = initial permeability, M_S = Saturation magnetization, σ = Inner stress;

K = Crystal magnetic anisotropy constant, λ = Magnetostriction constant.

a & b = constant

High initial permeability was attributed to the decrease of magnetostriction, high saturation magnetization and low magnetic anisotropy. High initial permeability can be obtained by carefully control of composition and microstructure.

In terms of ions, Fe^{2+} ions will affect the permeability of a material. By the presence of Fe^{2+} ions, resistivity of ferrites material will be reduced but high permeability can be obtained. The formation of Fe^{2+} ions can be minimized by proper adjustment of the sintering atmosphere during the application of the maximum temperature, so that magnetostriction can be reduced accordingly.

2.5.3 Quality Factor

Quality factor is an important parameter for inductor. A high quality factor is desirable because it implies a low magnetic loss in the ferrite and enables a better network to be made from a given number of inductors, or alternatively a given frequency characteristic to be obtained with fewer inductors.

In order to achieve a high value of effective permeability, maximum quality factor is required so that a balance between the winding and core losses can be achieved. Maximum quality factor can be obtained by using high frequencies, i.e. more than 10 kilohertz.

The quality factor can be measured by simply taking the reciprocal of the total loss tangent, $tan\ \delta_{tot}$ [16]

$$Q - Factor = 1 / tan\ \delta_{tot} \dots\dots\dots\dots\dots\dots\dots\dots (2.2)$$

The quality factor can also be interpreted as 2π times the ratio of the maximum energy stored in the system to the energy dissipated per cycle. There is a continuous exchange of energy between the magnetic field of the inductor and the electric field of the capacitor.

2.5.4 Magnetic losses

In soft magnetic materials, contribution to the dissipation is classified into three categories, which are [16]

a) Hysteresis loss, P_h

b) Eddy–current loss, P_e

c) Residual loss, P_r

Hysteresis loss is caused by the irreversible domain wall movements [40]. Hysteresis loss can be described by the following equation:

$$P_h = f \int B \, dH \dotfill (2.3)$$

Where f and B are the frequency and the magnetic flux density, respectively. From the equation, the hysteresis loss is equivalent to the area of the dc – hysteresis curve and depends linearly on the frequency.

Eddy–current loss is an extra dissipation incurred when at AC conditions, eddy currents are induced in the material. Eddy–current loss is the result from electrical currents that are induced in a magnetic material by a magnetic field that varies in magnitude and direction with time. Eddy–current loss depends on the frequency and the resistivity, ρ, which can be related by the following equation [16]:

$$P_e = C_e \, f^2 \, B^2 / \rho \dotfill (2.4)$$

Since eddy–current loss is proportional to frequency, eddy–current loss becomes an important parameter at high frequency applications, especially soft ferrites applications. Reducing eddy–current loss can be done by increasing the resistivity of a ferrite material by increasing the grain boundary resistivity, which is done by either carefully control the processing conditions [41, 42] or by adding dopants such as Nb_2O_5, ZnO_2 and Ta_2O_5 [43, 44, 45].

Sometimes, especially frequency bigger than 1MHz, extra loss under AC conditions are not attributed to eddy–current loss. In this condition, residual loss is observed. At Megahertz frequencies, the residual loss dominates the ferrite dissipation and this condition can be minimized successfully by using fine–grained ferrites [46].

Magnetic loss in a material can be measured in terms of the loss factor ($tan\ \delta_{tot}\ /\ \mu$), which can be derived as the following equation [16]:

$$tan\ \delta_{tot}\ /\ \mu = (tan\ \delta_h\ /\ \mu) + (tan\ \delta_e\ /\ \mu) + (tan\ \delta_r\ /\ \mu) \dots\dots\dots\dots\dots(2.5)$$

Where μ is the permeability, $tan\ \delta_{tot}$ is the total loss tangent, $tan\ \delta_h$ is the hysteresis loss tangent, $tan\ \delta_e$ is the eddy – current loss tangent and $tan\ \delta_r$ is the residual loss tangent. Since the total loss tangent is reciprocal to quality factor (Q), the loss – factor also can expressed as follows:

$$Loss - Factor = 1\ /\ (Q\ \mu) \dots\dots\dots\dots\dots\dots(2.6)$$

In application of ferrites, which operate at high amplitudes, for example above 10 mT, and in the typical frequency range of 15 – 100 kHz, power is dissipated mainly from hysteresis losses, although eddy current losses may also contribute significantly.

2.5.5 Electrical Resistivity

Resistivity is the material property that determines the resistance of a body according to the relation [16]:

$$\rho = R\ A\ /\ \iota \dots\dots\dots\dots\dots\dots\dots\dots\dots(2.7)$$

Where, ρ is the resistivity of the material, R is resistance of the body, A is cross sectional area and ι is thickness of the body. Resistivity is an intensive quantity, which is an intrinsic property of a material and independent of its amount or shape.

Resistivity depends on the temperature and the frequency. At higher frequencies, the crystal boundaries are more or less short-circuited by heir capacitance and the measured resistivity decreases.

Resistivity of an inductor core material is important because it determines eddy current losses, which are by electrical conductivity [16]. By increasing the electrical conductivity, the resistivity will be reduced. Since electrical conductivity is sensitive to composition, sintering conditions and microstructure, therefore, processing of ferrites need to be controlled carefully.

The rate of sintering will also affect the resistivity. If rapid sintering takes place, low resistivity and high FeO content will be obtained because at high temperatures, Fe^{2+} ion is favorable [5]. In this case, rapid cooling rates will tend to retain characteristics obtained at the high temperature and obtain a high conductivity structure. However, if sintering is followed by slow cooling, high resistivity and low FeO content will be obtained due to re-oxidation. Low FeO will restrict the opportunity for electron hopping, which will reduce the electrical conductivity.

In terms of microstructure, porosity and grain boundary play an important role. As porosity is increased, the electrical conductivity is decreased almost in proportion for a small value of porosity corresponding to the isometric uniformly distributed pores. Therefore, the pores will act as an insulator, which will increase the resistivity of a material as the porosity is increased. Grain boundaries also affect the resistivity of a material. Grain boundaries have a higher resistance than the interior of the grains. The effect of grain boundaries in polycrystalline material is related to the mean free path of the ions or electrons between collisions. This is in the order of interatomic distances for ionic conduction and is usually less than 10 to 15 nm for electronic

conductivity [47]. Thus, materials with more grain boundaries will exhibit higher resistivity.

2.5.6 Microstructure Effect on Magnetic Properties

According to Roess [48], it is impossible to have both high – permeability materials and very low losses, especially at high frequencies. Therefore, proper control of microstructure is important to obtain the desired properties of ferrite materials. From a microstructural point of view, the porosity, grain size, exaggerated grain growth and duplex grain structure play an important role on affecting the properties of ferrites materials.

In ferrites, the fewer the number of grain boundaries present, the larger the grains and the permeability will become higher. When the grain boundaries become thicker, domain walls will not be able to move across the grain boundaries easily and cause a reduction in permeability. Furthermore, lack of purity in processing will also affected the permeability. The presence of pores or inclusions or a higher chemical inhomogeneity will prevent the attainment of very high permeability. Usually, permeability will increase with grain size, but if the porosity is suppressed or located at the grain boundaries, permeability will drop, although the grain size is large.

If the grain growth is consistent or uniform, the relationship between grain size and permeability will be linear [33]. However, if some grains grew very rapid, they would trap pores, which will reduce permeability by pinning domain walls movement. This type of grain growth will include many intragranular pores and is called exaggerated or discontinuous grain growth. Distance between pores also affects the permeability. Sometimes, samples with giant grains and included porosity will have a higher

permeability than those with normally grain growth, provided the distance between pores were the same. [33]

Duplex structure occurs with some very large grains in a matrix of fine grains. It is often due to segregation of particular impurities, which produces rapid grain growth locally. According to Yoneda et al. [49], incomplete binder burnoff can cause duplex structure, which lead to reduction in permeability and increase in losses.

The movement of domain walls is limited by the presents of porosity. Pores and others imperfections will pin the domain walls, especially those within the grains, and deteriorate the magnetic properties of ferrites. Intragranular porosity is more deleterious than intergranular porosity. However, porosity is varied by control of the sintering temperature.

Grain boundaries will influence the properties of ferrites by creating a high resistivity intergranular layer, acting as a sink for impurities that serve as a sintering aid and as grain growth modifies and providing a path for oxygen diffusion, which modifies the oxidation state of cations near the boundaries. Low losses can be achieved at high frequency by increasing the crystal lattice resistivity or by addition of additives and the proper control of the microstructure to exploit the grain boundary resistivity.

2.6   Multilayer Chip inductors

Multilayer chip inductors were developed by thick film and co-firing technologies using low temperature sintering NiCuZn Ferrites [50, 51] where silver (melting point is 961°C) is used as internal electrode material due to its high conductivity and low cost. NiCuZn Ferrites are widely used in multilayer chip inductors because of their relatively low sintering temperature and high resistivity with good performance at high frequency. These characteristics are attributed to the ferrites metastable spinel

crystal system on heating. The metastable crystals dissociate on heating, when the CuO content is relatively high [52]. As compared to other materials, NiCuZn Ferrites are preferred for use in multilayer chip inductors because it has better properties at high frequencies than MnZn Ferrites and a lower densification temperature than NiZn Ferrites [53, 54].

For the multilayer design, the device is produced by co-firing ferrite layers with an internal silver conductor. Since silver has a melting point of $961^\circ C$, the co-firing temperature must be kept lower than that to prevent the silver from melting. NiCuZn Ferrites are selected in multilayer chip inductors because these ferrites can be sintered lower than $950^\circ C$. As mentioned, the low sintering temperature is attributed to its high Cu-content and the high Cu-containing ferrites are claimed to suffer thermal dissociation [52] at temperature around $900^\circ C$.

However, NiCuZn Ferrites have a large magnetostriction and their properties are sensitive against stress. Therefore, the magnetic properties of NiCuZn Ferrites are easily deteriorated or changed by the stress caused at the internal electrode during co-firing or the impact at mounting onto base substrates. In order to overcome these problems, many studies and investigations were performed to reduce the internal stress and to improve magnetostriction [17, 18]. It has been suggested that MgCuZn Ferrites are more suitable because they showed less magnetostriction, high density, high resistivity, high curie temperature and higher initial permeability than NiCuZn Ferrites. Furthermore, as compared to NiCuZn Ferrites, MgCuZn Ferrites are economical [55] and easy to synthesize.

Better electromagnetic properties, especially high initial permeability are required to reduce the number of layer of Multilayer chip inductors [39], minimizing the capacity between the layers and realizing the goals of miniaturization.